Tamás Matolcsi

ORDINARY THERMODYNAMICS

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Preface

1. Undoubtedly, a branch of theoretical physics formalized in a more exact mathematical way is more reliable. Mathematization means that we have to use mathematically exact notions, ruling out **tacit assumptions** which are 'natural', 'evident' notions, properties, facts 'not to be explained'. Such tacit assumptions cause, in general, troubles and misunderstandings in a theory. Namely, in different situations the same 'evidence' is interpreted differently, and it happens frequently that 'natural properties' contradict each other. For instance, the notion of set in earlier mathematics was a tacit assumption and the set of all sets was an evidence; moreover, the following two facts were considered trivial: 1. if there is a one-to-one correspondence between the elements of two sets, then the two sets contain the same amount of elements, 2. a proper subset of a set contains less elements than the set itself. Nowadays, having the precise logical setup of set theory, we know that the set of all sets does not exist and assertions 1 and 2 cannot hold simultaneously (point 1 is accepted in set theory). Of course, not all tacit assumptions are misleading, but we can have confidence only in a theory not appealing to tacit assumptions.

Classical mechanics, quantum mechanics, classical electromagnetism are mathematically developed branches of physics which work well though they are not free of tacit assumptions. In a sharp contradistinction, thermodynamics is essentially characterized by a contradictory and confused system of tacit assumptions which is well illustrated as follows.

2. In usual thermodynamics *equilibrium* is a fundamental concept, and it is always underlined that all other notions – such as temperature – have a meaning only in equilibrium. Equilibrium is an 'evident' notion, 'everybody knows what it is'. However, observing more thoroughly, we find that equilibrium is used in several different senses. For instance, one speaks about 'the equilibrium of a body' and one says, too, that 'two bodies are in equilibrium with each other'. Perhaps the reader does not notice the trouble, but changing the words body and equilibrium, we can see that something is not right: 'the illness of a man' and 'two men are in illness with each other'.

Equilibrium has the tacitly accepted property that it is unvaried, constant in time. Furthermore, on the basis of some simple everyday experience, a fundamental property of equilibrium is formalized as the zeroth law of thermodynamics: *an intensive state function corresponds to every interaction in such a way that their equal value on the bodies is a necessary and sufficient condition of equilibrium.* Then it is deduced – because this must hold for any two parts of a body, too – that *the homogeneity of the intensive quantities is the necessary and sufficient* *condition of the equilibrium of a body.* However, this **is not true** as shown by the following examples.

It is a simple fact that the pressure of a gas (liquid) in a container resting on the Earth is not homogeneous, growing downwards because of the gravity. Thus homogeneity in equilibrium does not hold necessarily in the presence of exterior volume force (which is proportional to the density).

The pressure of a gas consisting of electrically charged particles in equilibrium in a spherical container is not homogeneous, growing radially from the centre towards the container wall (gravity neglected). Thus homogeneity in equilibrium does not hold necessarily in the presence of interior volume force.

Let us take an elastic ball resting in the atmosphere, and let us neglect gravity. The three bodies in equilibrium, the air in the ball, the elastic hull and the atmosphere, have different pressures. The pressure of the air inside is larger than that of the atmosphere, and the pressure of the hull is not homogeneous (it is larger on the internal surface than on the external surface), though no volume force acts on the hull. Thus homogeneity in equilibrium does not hold necessarily even in the absence of volume force.

In the previous examples we have made explicit that the bodies in question are at rest with respect to the Earth considered inertial. It is not hard to see that equilibrium is a relative notion, i.e. it depends on observers (reference systems). The pressure of a neutral gas in equilibrium in a container resting on a rotating disk is not homogeneous, growing radially from the rotation axis outwards (gravity neglected). Thus homogeneity in equilibrium with respect to a non-inertial observer does not hold necessarily.

Finally, let us note that according to the mentioned zeroth law, a body whose temperature and pressure are homogeneous at every instant but change in time would be in equilibrium but this contradicts the other tacitly accepted property that no change occurs in equilibrium.

3. Simple examples have demonstrated that the zeroth law of thermodynamics is not fulfilled, in general, which undermines our confidence: are the first and second laws correct? Our mistrust increases if we observe that the formulation of the first and second laws concerns state changes though usual thermodynamics admits only equilibrium as meaningful. To overcome this difficulty, one introduces the notion of *quasi-static process*: a process in which the body is always in equilibrium; a quasi-static process is a sequence of equilibria. Though it is emphasized that such a process is an idealization, a limiting case of real processes when the change is very slow, we can doubt that such an idealization is correct. Namely, let us take a mechanical analogue: a body is in equilibrium if it does not change position and has zero velocity (e.g. rests on a horizontal plane). We can carry the body in another equilibrium very slowly (in such a way that it be approximately in equilibrium at every instant), and even more and more slowly, but in the quasi-static limit – when its velocity is always zero – there is no process. Is not a quasi-static process an absurdity?

The first law, we shall see, is essentially correct in its usual form. On the other hand, the diverse and hardly conceivable forms of the second law make us suspicious that at this point the theory suffers from tacit assumptions. It is worth citing some formulations of the second law.

Original, earlier formulations:

Kelvin–Planck:

It is impossible to construct a periodically operating device which produces no effect, except the raising of a weight and the cooling of a heat reservoir.[1]

It is impossible to devise an engine which, working in a cycle, shall produce no effect other than the extraction of a heat from reservoir and the performance of an equal amount of mechanical work.[2]

No process is possible whose sole result is the complete conversion of heat into work.[3]

Clausius:

Heat cannot pass by itself from a colder to a warmer body.

It is impossible to devise an engine which, working in a cycle, shall produce no effect other than the transfer of heat from a colder to a hotter body.

No process is possible whose sole result is the transfer of heat from a colder to a hotter body.

Sometimes one 'demonstrates' that the Kalvin-Planck formulation and the Clausius formulation are equivalent; we point out the error of such a 'proof' in 13.16 and in 12.16 we show that the two types of assertions are not equivalent at all.

Some recent formulations are based on the zeroth law which, as we have seen, is not correct:

In an isolated system, the macroscopic processes induced by the inhomogeneities (spontaneous processes) always decrease the inhomogeneities. As a consequence, the system approaches an equilibrium. This trend of being homogeneous is the second law of thermodynamics.[4]

The following law determines the direction of processes: the inhomogeneities of the intensive quantities try to vanish, compelling the extensive quantities to flow in a direction which helps the inhomogeneities to disappear.[5]

Carnot's formulation[6]:

1. Every thermodynamical system has a state function (called entropy) S in such a way that $\delta Q \leq TdS$ for the heat absorbed in any infinitesimal quasi-static process and equality holds only for reversible processes.

2. The entropy of a closed system can never decrease; it increases in an irreversible process and remains constant in a reversible one.

On the basis of Carnot's formulation, the second law is stated nowadays mostly with the aid of entropy:

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[1] D.Haar–H.Wergeland: *Elements of Thermodynamics*, Addison–Wesley,1960

[2] A.B.Pillard:*Elements of Classical Thermodynamics*, Cambridge Univ. 1966

[3] C.J.Adkins: *Equilibrium Thermodynamics*, Cambridge University Press, 1983, 3rd edition

[4] A. Harmatha: *Termodinamika műszakiaknak*, Műszaki Kiadó, Budapest, 1982, p. 61

[5] I.Fényes: *Termosztatika és termodinamika*, Műszaki Könyvkiadó, Budapest, 1968, p. 203

[6] K. Denbigh: *The Principles of Chemical Equilibrium*, Cambridge Univ. Press, 1966; pp. 36-38

When the stable equilibrium has been reached in an isolated system, the entropy has a maximum.

The spontaneous processes in an isolated system have such a direction which forces the entropy to increase. [7]

It has been considered for a long time that the entropy maximum in equilibrium and the increase of entropy in non-equilibrium processes are equivalent. Nowadays this is known to be false which will be clearly shown in our treatment, too (cf. 12.11.1 and 13.15.1).

We can immediately see why the quoted formulations are not sufficient: the *isolated* or *closed system*, the *spontaneous process*, the *direction of a process* are all **tacit assumptions**, so the forms of the second law concerning them are completely **inconceivable**. Moreover, the entropy maximum in equilibrium is meaningful only if the entropy of equilibrium is compared with the entropy of non-equilibrium states not defined in the theory; similarly, the law of entropy increase involves non-equilibrium processes, not defined in the theory. This mentioned flaw of entropy maximum is ruled out formally by introducing 'equilibria with inside constraints' and requiring the maximum for the equilibrium without constraint but then it is taken as evidence that with the constraints removed, a process starts in which the entropy increases.[8]

Last but not least we mention that the quoted formulations of the second law are unnaturally one sided: they concern only closed (isolated) systems; we expect a more general law on the direction of processes.

4. The second law – no matter, in what formulation – is regarded as a law of irreversibility. It is worth citing some usual assertions in this respect, too.

The direction of change of state functions is not determined in a reversible process, so the process can run equally in every direction.

In an irreversible process the change of state functions is restricted, the process can run spontaneously only in one direction.

If the state of a thermodynamic system changes in such a way that there is a possible process running through the same states but in reversed order then the process is reversible, otherwise it is irreversible.

These statements (assertions? definitions?) are inconceivable, too: the *possible processes*, the *spontaneous processes*, the *running of a process*, etc. are all **tacit assumptions**.

Reversibility is often identified with the invariance under time reversal, and it is stated that "a purely mechanical process is always reversible", because the Newtonian equation is invariant under time reversal. We have to make two comments in this respect.

The first concerns the relation between the above 'definition' of reversibility and the time reversal. Let us consider, for instance, the Earth revolving around the Sun: we see the ellipse and the Earth moving on it. Reversing this motion in time, we see the same ellipse and the Earth moving on it in the opposite direction. However, the mechanical state is not only the position, but the position and the momentum together: the process runs in the phase space. If the position

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[7] A. Harmatha, loc. cit. pp. 69-72

[8] H.B.Callen: *Thermodynamics*, Wiley and Sons, NY. 1985, p. 39.

of the reversed motion coincides with some position of the original motion, the momentum of the reversed motion is opposed (not equal) to the momentum of the original motion. The reversed motion does not run through the same states as the original one: time reversal invariance does not correspond to the desired notion of reversibility.

Our second remark is that it is doubtful whether reversibility and time reversal have something in common at all. We do not know what reversibility is, we have only some vague idea of it, but we can be convinced that it cannot depend on observers. On the other hand, we have an exact definition of time reversal, and we also know that it depends on observers. Without expounding precisely, we illustrate this by the previous example. If A rests with respect to the Sun and observes the Earth, he sees it running on an ellipse. Reversing this motion, he sees that the Earth runs backward on the same ellipse. If B moves uniformly with respect to the Sun and observes the Earth, he sees it running on a right-handed spiral. Reversing this motion, he sees that the Earth runs backward on the same spiral. However, if B observes the motion reversed by A, he sees that the Earth runs forward on a left-handed spiral.

5. There are, of course, mathematically exact formulation of the second law in diverse axiomatic frameworks. There is a lot of axiomatic frameworks, so there is a lot of second laws [9]. The main trouble is not the diversity of the second laws but the fact that though all those have highly abstract forms, they refer to a rather restricted family of phenomena (processes); e.g. mostly they are formulated only for cycles, furthermore they do not concern processes of bodies with varying particle number (diffusion, phase transition, chemical reaction) as well as processes with electromagnetic phenomena.

These axiomatic frameworks – though contributed significantly to the development of thermodynamics – do not provide well working theories for the description of natural phenomena.

6. In well-working branches of theoretical physics – classical mechanics, quantum mechanics, classical electromagnetism – the **process** is the fundamental notion which is defined as a solution of differential equations: Newtonian equation, Schrödinger equation, Maxwell equations. Equilibria are special processes which do not vary in time. Thus processes, in particular equilibria, are well-defined objects.

Real processes, varying in time appear in thermodynamics, too, 'near to equilibrium' which are treated by Onsager's theory. Nonequilibria are not meaningful in usual thermodynamics, thus the insufficiency of the Onsager theory is well demonstrated by the following questions: which non-meaningful objects are near to equilibrium and in what sense are they near to it?

Thermodynamics will be a well-established theory if we build it up in such a way that its fundamental notion is the process governed by some differential equation. To do this, first of all we must abandon the old belief that quantities – such as temperature – have meaning only in equilibrium. In all branches of physics, the measuring instructions of quantities require slow changes ('approximate equilibrium'). Consider, for instance, an electric field: taking a charge, we

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[9] *New Perspectives in Thermodynamics*, ed. J. Serrin, Springer, 1986

have to measure the force acting on it. In such a way we are not able to measure the electric field in a light beam, but this does not prevent us from accepting the electric field as a meaningful, existing quantity in a light beam. Similarly, we can accept that temperature, too, is an existing and meaningful quantity in a large class of nonequilibrium processes.

The diverse theories of continuum physics (irreversible thermodynamics) are theories similar to the mentioned well-working ones: the quantities are considered to be varying in time and space, thus processes are functions defined in spacetime which are governed by partial differential equations. These theories only have a technical flaw: they are rather complicated from a mathematical point of view.

Neglecting thermodynamical phenomena in continuum physics, we arrive at continuum mechanics. This theory describes every mechanical phenomena. In some special cases, however – if deformation is negligible – the continuum description is unnecessarily complicated, and it can be replaced with a simpler one in which the bodies are considered as rigid, and so, instead of partial differential equations, we can deal with ordinary differential equations. We know, of course, that in reality a body is never rigid, it is deformed under the action of a force, and a sufficiently large force causes a significant deformation, but we take into account only such processes in which deformations are negligible.

7. A correct formulation of usual thermodynamics – which we call **ordinary thermodynamics** – can be achieved in analogy of the above facts. If we can neglect the mechanical aspects of the phenomena and we can consider the bodies **homogeneous** (i.e. every quantity characterizing the body has the same value at all points of the body), then the continuum thermodynamical description can be replaced by a theory in which the processes are determined by ordinary differential equations.

We have seen that in usual thermodynamics equilibrium is identified with the homogeneity of quantities (which is not right) and a quasi-static process is such that the body is in equilibrium at every instant. Changing the word equilibrium to homogeneity, we give a right meaning to a quasi-static process: a nonequilibrium process in which all quantities are homogeneous at every instant. In what follows we prefer to say homogeneous process instead of quasi-static process. In a homogeneous process the properties of a body vary only in time, while they are constant in space.

Thus ordinary thermodynamics is based on the assumption that the quantities are homogeneous in the processes. We have seen, however, that this does not hold necessarily even in equilibrium. Nevertheless, this does not mean that such a theory is useless and worthless. We have to bear in mind only that – as every theory – it is applicable only for a restricted class of phenomena. A theory itself does not answer the question, under what circumstances it gives a good description: classical mechanics does not specify when a body can be considered as rigid or point-like, and ordinary thermodynamics does not reveal us when the bodies can be considered homogeneous.

Introduction

1. It is well known that our common objects consist of several times 10^{23} molecules which chase, attract and repulse each other, emit and absorb electromagnetic radiation. This chaotic inner life mostly appears outwards as relatively uniform, still because of the large number of microscopic phenomena, it results in a macroscopic average quiet. Continuum physics describes this average phenomena. To understand ordinary thermodynamics, we have to survey continuum physics.

2. Let us consider a body consisting of equal, neutral molecules. Of course, the neutral molecules consist of charged particles which emit and absorb electromagnetic radiation, so electromagnetism plays a significant role in this case, too.

The average velocity of molecules is a characteristic of the state of the body. Let us imagine that the body (a glass of water) is at rest with respect to us. Then we observe that every point of the body is at rest with respect to us: the average velocity is zero at every point of the body. Our experience regarding the Brown motion tells us that indeed only the average velocity is zero. Let us stir the water: it will flow and, of course, the Brown motion remains in the flowing water, too. Accordingly, we distinguish between the macroscopic motion (flow) of the body and the microscopic motion inside the body. The flow of the body (continuum) is characterized by the average velocity of molecules which is described by assinging velocity values to space and time points. Regarding a solid body, the word ‘flow’ seems strange but the oscillation of a solid body is really a flow. By the way, quiet and flow are relative notions (a quiet with respect to us is a flow with respect to another observer). After all, we can state that the history of a continuum is described by a **velocity field** which is a function assigning (absolute) velocity values to spacetime points.

Another characteristic of the body is its **density**, i.e. the mass contained in a unit volume element. The density, in general, is different at different points and varies in time; thus the density, too, is a function defined in spacetime.

Mass, momentum and energy flow from one place to another in the body. We distinguish between two types of such flows: the convective currents and the conductive currents. The convective current is related to the macroscopic motion, so to the velocity field, the conductive current is related to the microscopic motion. It is evident that if a part of a body flows from one place to another, then mass, momentum and energy flow as well. Momentum and energy can flow without macroscopic motion: the molecules hustle each other, emit and absorb electromagnetic radiation.

A current describes the quantity flowing through a unit surface in a spacepoint in a unit time interval (this can be made more precise from a mathematical point of view); thus a current, too, is a function defined in spacetime and having values in an appropriate set. The density of a quantity multiplied by the velocity field yields the corresponding convective current.

The mass density is already mentioned. The momentum density equals the product of the mass density and the velocity field because the resultant momentum of microscopic motion is zero.

The energy density consists of two components. The macroscopic kinetic energy density equals the half of the product of mass density and the square of the velocity field. The **internal energy density** of a body comes from the kinetic energy due to the microscopic motion, the interaction energy and the chemical energy of molecules. The internal energy density is a characteristic of the body.

Furthermore, the conductive currents, too, are characteristic of the body. It is evident that mass has no conductive current. The conductive current of momentum is just the **stress tensor**: the momentum flowing through a unit surface in a unit time interval equals the force acting on the unit surface. The conductive current of internal energy is called **heat flow** because the usual heat conduction is just the flow of internal energy. Namely, let us accept roughly that the temperature is proportional to the microscopic kinetic energy. Let two bodies with different temperature be in contact with each other. On the contact surface the molecules of the bodies interact (collide), the faster molecules give kinetic energy to the slower ones. internal energy flows from one body to another which, from a macroscopic point of view, appears as a heat flow.

The conservation of mass, moment and energy is expressed by balance equations.

3. Instead of mass density, it will be convenient to use its reciprocal, the **specific volume**, the volume of a unit mass. At the same time, instead of internal energy density, we use **specific internal energy**, the energy of a unit mass; it equals the quotient of internal energy density by mass density.

Let e, $\boldsymbol{u}$, v, $\boldsymbol{k}$ and $\boldsymbol{P}$ denote the specific internal energy, the velocity field, the specific volume, the heat flow and the stress tensor, respectively; recall that all these are functions defined in spacetime, and now it is underlined that we consider a nonrelativistic theory. If the total mass of the body is constant and there is no exterior force acting on the body, then the balance of energy, momentum and mass yields the equations

$$\begin{aligned}\mathtt{D}_{\boldsymbol{u}}e &= -\,v(\nabla\cdot\boldsymbol{k}+\boldsymbol{P}:\nabla\boldsymbol{u}),\\ \mathtt{D}_{\boldsymbol{u}}\boldsymbol{u} &= -\,v\nabla\cdot\boldsymbol{P},\\ \mathtt{D}_{\boldsymbol{u}}v &= v\nabla\cdot\boldsymbol{u}\end{aligned}$$

where $\mathtt{D}_{\boldsymbol{u}}$ is the differentiation with respect to the velocity field $\boldsymbol{u}$, usually called the *substantial derivation*, ∇ is the spacelike differentiation, while the dot and the colon denote the scalar product of two vectors and two tensors, respectively. We do not go into more detail because we shall use all this only for heuristic considerations.

We see that there are more unknowns than equations: we need further relations. Let us accept now that a process of the continuum is uniquely determined by the quantities on the left-hand side, i.e. by $(e, \boldsymbol{u}, v)$. Then $\boldsymbol{P}$ and $\boldsymbol{k}$ are to be given as functions of $(e, \boldsymbol{u}, v)$; in this case we have just as many unknowns as equations (which gives only a hope to have a unique solution).

4. Besides the fact that the conductive current of internal energy is called heat flow, up to this point there has been no indication, how the previous considerations concern heat phenomena, because all the quantities in question are mechanical ones. We explained the term heat flow by supposing a relation between internal energy and temperature. Indeed, heat phenomena enter the equations at this point. More closely: the internal energy, though it has a clear meaning, cannot be measured directly. Instead of it we have the temperature T as a simply available quantity. The temperature appears in usual formulae for the conductive currents, too. For instance, the static pressure P (deriving from the stress tensor) of an ideal gas has the form $Pmv = kT$ where m is the mass of a molecule and k is the Boltzmann constant. Similarly, our rough experience that "heat flows from a hotter place to a colder one" is expressed by Fourier's law, $\boldsymbol{k} = -\lambda \nabla T$ where λ is a positive constant.

Thus the equations refer to $(e, \boldsymbol{u}, v)$ but the conductive currents are naturally given as functions of $(T, \boldsymbol{u}, v)$. As a consequence, we must have a relation between e and T; more precisely, we have to give e as a function of $(T, \boldsymbol{u}, v)$.

5. The zeroth and second law of thermodynamics, as we have seen in the Preface, are doubtful. On the contrary, the first law is essentially right in its usual form. We can recognize the first law in the above balance of internal energy: the internal energy changes due to the heat conduction $-v\nabla \cdot \boldsymbol{k}$ and the mechanical working $-v\boldsymbol{P} : \nabla \boldsymbol{u}$. Supposing $\boldsymbol{P} = P\boldsymbol{I}$, where P is the usual elastic pressure of a gas or a liquid and $\boldsymbol{I}$ is the identity tensor, we get the more familiar form $-v\boldsymbol{P} : \nabla \boldsymbol{u} = -vP\nabla \cdot \boldsymbol{u} = -P\mathtt{D}_{\boldsymbol{u}} v$.

The balance equations describe the changes only inside the body; the changes connected with the surface of the body are taken into account by boundary conditions. If we consider the body as a whole, i.e. we do not look for how the energy is distributed in the body and are interested only in its total energy, then integrating the balance equation and taking into account the boundary conditions, we get that the difference between the energy $E(t_2)$ and $E(t_1)$ at the instants t_2 and t_1, respectively, equals the sum of the energy (heat) $Q(t_1, t_2)$ conducted to the body during the time interval $[t_1, t_2]$, the work $W(t_1, t_2)$ done on the body and the energy $L(t_1, t_2)$ conveyed by mass transport to the body:

$$E(t_2) - E(t_1) = Q(t_1, t_2) + W(t_1, t_2) + L(t_1, t_2).$$

This is the first law of thermodynamics. Mostly one considers the case when the mass of the body is constant; then the third term is missing. Furthermore, we have to mention that the above form is valid only for a body consisting of equal, neutral molecules. If, for instance, electric phenomena can take place, too, then an additional term appears referring to energy change due to electricity. In general, there are as many terms on the right-hand side as many interactions.

Such a form of the first law of thermodynamics is valid for any processes, it is not restricted to 'quasi-static' ones.

The energy values on the left hand side contain both the the kinetic energy and the internal energy: $E = E_{kin} + E_{in}$. Thermodynamics is concerned with the case when the kinetic energy of the body is zero at the instants in question, i.e. the points of the body are at rest with respect to an inertial observer in both instants t_1 and t_2; in other words, $E_{kin}(t_2) = E_{kin}(t_1) = 0$, so $E(t_2)$ and $E(t_1)$ are purely internal energy values. It is important that when E is replaced by E_{in}, the equality above does not hold for arbitrary instants, only for those when the kinetic energy is zero.

6. As mentioned in the Preface, we should like to obtain ordinary thermodynamics from continuum thermodynamics in such a way that we take into account only homogeneous processes. Then the ∇ operator applied to every quantity yields zero; however, this implies that the time derivatives are zero as well: there is no change in time, everything is constant. There is no nontrivial homogeneous process. Nevertheless, this does not prevent us from constructing a good model for homogeneous processes, in the same way, as we treat rigid bodies in mechanics, though we know that in reality rigid bodies do not exist.

To establish ordinary thermodynamics, we accept that the velocity field is constant (zero with respect to an inertial observer) but we consider specific internal energy and specific volume changing in time. Thus ordinary thermodynamics involves implicitly an inertial observer with respect to which the bodies are at rest. Then substantial time derivative becomes ordinary time derivative, denoted as usual by a dot.

Hence the specific internal energy and the specific volume vary in time; accordingly, the first law of thermodynamics, on the analogy of the first balance equation, is written in the form $\dot{e} = q + w$ where q is the specific **heating**, w is the specific **working**. Note that q and w are quantities referring to a unit time interval, so they are of power type.

There is no counterpart of the second balance in ordinary thermodynamics, because we consider the velocity as constant. The divergence of the velocity field stands on the right-hand side of the third balance equation, and the velocity field is determined by the stress tensor according to the second balance equation. Thus the right-hand side of the third balance equation is obtained indirectly from the stress tensor which must be given as a function of the process. As a consequence, the third balance equation suggests us $\dot{v} = f$ where the **springing** f – and, of course, q and w, too – are to be known as functions of the process.

7. The stress tensor in continuum physics is decomposed in the form $\boldsymbol{P} = \boldsymbol{R} + \boldsymbol{V}$, where $\boldsymbol{R}$ is the elastic part and $\boldsymbol{V}$ is the viscous part. The **energy dissipation** – the fact that only a part of the internal energy can be converted into other energy while other energies can be converted into internal energy completely – is formulated by the Clausius–Duhem inequality

$$-\frac{\boldsymbol{k}\cdot\nabla T}{T} - \boldsymbol{V} : \nabla\boldsymbol{u} \geq 0$$

which restricts how the heat flow and the viscous tensor can depend on the process $(e, v, \boldsymbol{u})$.

The energy dissipation in ordinary thermodynamics will occur on the analogy of the above inequality.

8. Let us resume the results of our previous heuristics.

In continuum theory a process is $(e, \boldsymbol{u}, v)$ defined in spacetime and determined by the balance equations in Paragraph 3; the quantities $\boldsymbol{P}$ and $\boldsymbol{k}$ on the right-hand side of the balance equations are to be given as functions of the process $(e, \boldsymbol{u}, v)$ in such a way that the Clausius–Duhem inequality fulfils.

In ordinary thermodynamics a process is (e, v), a function of time determined by the dynamical equations

$$\begin{aligned} \dot{e} =& q + w, \\ \dot{v} =& f, \end{aligned}$$

where the dynamical quantities q, w and f are given functions of the process (e, v) and they fulfil a convenient dissipation inequality (treated later).

The heat phenomena appear in ordinary thermodynamics in the same way as in continuum physics: the quantities on the right-hand side of the equations can be given in a natural way depending on the temperature T instead of internal energy e.

Ordinary thermodynamics fixes exactly what brings forth the processes of a homogeneous body (the dynamical quantities), how they do it (the dynamical equations) and in what direction processes can run (dissipation inequality).

We have to mention that the first law treated in Paragraph 5 is stronger than the first law appearing in the dynamical equations because this latter concerns processes in which kinetic energy is missing.

9. The previous heuristics concerns bodies which have constant mass and consist of equal, neutral particles. Now we do not touch the bodies whose particles can be different or electrically charged, etc. (such bodies will be thoroughly treated in the book) because we only wanted to depict the tasks and the methods of ordinary thermodynamics. However, it is worth describing the dynamical equations for bodies with varying mass which occur in diffusion processes.

If g denotes the mass density change in unit time, $\boldsymbol{u}_g$ and e_g the velocity and the specific energy of the mass coming to the body, then

$$\begin{aligned} \mathtt{D}_{\boldsymbol{u}} e =& -v\left(\nabla\cdot\boldsymbol{k} + \boldsymbol{P} : \nabla\boldsymbol{u} - \frac{1}{2} g |\boldsymbol{u}_g - \boldsymbol{u}|^2 - g e_g\right), \\ \mathtt{D}_{\boldsymbol{u}} \boldsymbol{u} =& -v\big(\nabla\cdot\boldsymbol{P} - g(\boldsymbol{u}_g - \boldsymbol{u})\big), \\ \mathtt{D}_{\boldsymbol{u}} v =& \, v(\nabla\cdot\boldsymbol{u} - v g). \end{aligned}$$

10. Finally, we say a few words about the structure of treatment, the mathematical tools and the notations.

Concerning the treatment, the topics will be first introduced heuristically, their physical meaning will be enlightened in a mathematically loose way, then we come to the exact mathematical definitions and propositions.

The thermodynamical quantities as variables of functions are denoted by the usual simple letters e, v, T, P, etc. If one of them is expressed as a function of some others, then we use special types. More closely, T and v being the variables, the functions are denoted by script letters: $\mathfrak{e}$, $\mathcal{P}$, etc.; e and v being the variables, the functions are denoted by boldface letters: $\mathbf{T}$, $\mathbf{P}$, etc. Our formulae take into account the physical dimension of the quantities in the SI system. For more detail see App. 2.

Besides the fundamental notions of analysis – open set, the closure of a set, continuity, differentiability – we often apply the inverse function theorem and the implicit function theorem and the notion of submanifolds which can be found in App. 3 and App. 5, respectively.

Beside the well-known existence and uniqueness theorem of differential equations, the notions and theorems of stability theory are applied throughout the book, because one of the main tasks of ordinary thermodynamics is to investigate the trend to equilibrium which is based on Liapunov's stability theory. The necessary knowledge in this area is summarized in App. 7 and certain questions regarding definiteness, important from the point of view of stability, are given in App. 1.

I SIMPLE MATERIALS

1 Constitutive functions

1.1 The fundamental thermodynamical quantities

According to our experience, the fundamental characteristics of a material consisting of equal, electrically neutral molecules are the following: the **specific internal energy** e, the **specific volume** v, the **temperature** T, the **pressure** P and the **chemical potential** μ. In classical thermodynamics, contrary to continuum mechanics, instead of the quantities per unit mass, one uses the quantities per molecule; we, too, accept that specific means **per molecule**. A simple relation holds between quantities per unit mass and quantities per molecule if the material consists of equal particles. If $\hat{v}$ is the volume per unit mass and m is the mass of a molecule, then $v = m\hat{v}$. Thus, it does not matter which quantity is used for materials of equal molecules. The relation between $\hat{v}$ and v is more complicated if the material is the mixture of different molecules; in this case the treatment is simpler if we take quantities per molecule. We mention that sometimes one considers molar quantities. If $\hat{V}$ is the molar volume, then $\hat{V} = Lv$, where L is the Avogadro number (Loschmidt number) which approximately equals $6 \cdot 10^{23}$.

We sall use the SI measuring units of the quantities listed above, which are J, m^3, K, Pa and J, respectively. The specific internal energy, the specific volume and the temperature always have positive values. App. 2 contains the notions and notations concerning measure lines.

A significant part of a number of books on classical thermodynamics is dedicated to the definition and measurement of absolute temperature. This is indeed an important question, like the definition and measurement of mass in mechanics. However, treatments of theoretical mechanics start with the knowledge of mass; similarly, we take now the scale of absolute temperature as known.

The first four ‘everyday’ quantities from the above-listed ones have been referred to in the Introduction, too. The physical meaning of chemical potential will be clarified later; now we mention only that it plays a fundamental role in diffusion and phase transition processes and it expresses the entire internal energy change due to the change of the particle number.

The listed five quantities are not independent: their relations characterize the material. Measuring the simultaneously possible values of these quantities, we can establish their relations at least in principle. The particle number, the volume – consequently, the specific volume –, the pressure and the temperature can be measured directly.

It is worth emphasizing this assertion because one frequently expresses scruples regarding the temperature, saying that it can be measured only in equilibrium and it is doubtful, how very low and very high temperature is measured where our devices do not work. As mentioned in Paragraph 6 of the Preface, the measuring prescription of almost all physical quantities refers to 'near equilibrium' when the quantities do not change too rapidly. Moreover, measuring very small and vary large values is problematic for all quantities; how to measure, e.g. such a huge pressure which breaks down every device? How to measure the mass of a house? Thus, we can neglect those scruples.

Let us return to what we have said: knowing the mass of a molecule and measuring the mass of a body, we can determine the particle number. Thus the specific volume, the pressure and the temperature are directly measurable quantities, in contradistinction to the internal energy and the chemical potential.

Chemical potential is related to the change of particle number end expresses the internal energy change, thus we can suppose without worry that internal energy does not depend on chemical potential if the particle number is constant. Then the first law gives a possibility for measuring the internal energy. We take a thermally insulated body (a given amount) of the material in question, then starting from a 'ground state' with determined specific volume v_0, temperature T_0 and pressure P_0 (and unknown specific internal energy e_0), we do diverse amounts of work on it; then we measure its volume, temperature and pressure. According to the first law – because now the heating is zero –, the internal energy of the final states differs from that of the ground state in the amount of works done. Thus internal energy – at least in principle – can be brought into relation with specific volume, temperature and pressure (apart from an additive constant).

Knowing how the specific internal energy of a material is related to specific volume, temperature and pressure, we can use this material for measuring heating, according to the first law: if the particle number is constant, heating is the difference between the time rate of internal energy and working.

Then we give the following prescription for measuring chemical potential: let a body in a state determined by specific volume v, temperature T and pressure P be connected with an environment (a body having a huge number of particles) of the same material and having the same state in such a way that diffusion may occur between the body and the environment. Let us conduct a 'little amount' ΔQ of heat to the body in such a way that its specific volume, temperature and pressure remains v, T and P, respectively. Then ΔN particle diffuses into the environment (the change of particle number can be measured by the mass change of the body). Then the equality $\Delta Q = (e + Pv - \mu)\Delta N$ – where e is the specific internal energy corresponding to v, T and P – reveals to us how the chemical potential is connected with specific volume, temperature and pressure.

In this way we can determine for a material the set Σ of simultaneously possible values of e, v, T, P and μ, which characterizes the material from the thermodynamical point of view, which suggests us the following mathematical definition.

Definition *A non-void subset* Σ *of* $(\mathrm{J})^+ \times (\mathrm{m}^3)^+ \times (\mathrm{K})^+ \times (\mathrm{Pa}) \times (\mathrm{J})$ *is called a* **general simple material**. *The elements of* Σ *are the* **states** *of the material.*

The adjective simple now has the physical meaning “consisting of equal, electrically neutral molecules" and the adjective general refers to the fact that this is the most general possibility.

1.2 Other thermodynamical quantities

A state of a material is denoted by (e, v, T, P, μ) and we agree that the same symbols, e, etc. denote the maps $\Sigma \to (\mathrm{J})^+$, $(e, v, T, P, \mu) \mapsto e$, etc., too. Using these symbols, we introduce several functions regarding the material which will be important later.

Definition *Let* Σ *be a general simple material. Then*

- $s := \dfrac{e + Pv - \mu}{T} : \Sigma \to (\mathrm{J/K})$ *is the* **specific entropy** *of the material,*
- $h := e + Pv = \mu - Ts : \Sigma \to (\mathrm{J})$ *is the* **specific enthalpy** *of the material,*
- $f := e - Ts = \mu - Pv : \Sigma \to (\mathrm{J})$ *is the* **specific free energy** *of the material.*

1.3 Rules for the relations among the thermodynamical quantities

According to our simple and direct experience, the thermodynamical quantities obey some general rules valid for all materials, such as: “if a material absorbs heat (gets internal energy), then its temperature grows", “if the material is compressed, then its pressure grows". More precisely,

- for fixed volume, more internal energy correspond to higher temperature,
- for fixed temperature, larger pressure correspond to smaller volume.

However, a deeper examination shows that the second rule is not valid necessarily: at boiling temperature, the same pressure corresponds to the smaller specific volume of liquid water and the larger specific volume of vapour. It seems, this rule only holds locally, i.e. for volume values near to each other.

According to another, seemingly general experience “for fixed volume, larger pressure corresponds to higher temperature", but this does not hold for water in the interval between 0^oC and 4^oC.

All that warns us to be careful, not to generalize too hastily our experience. **In addition, accepting something as a general rule, we do not assert that it necessarily holds in reality; doing so we only restrict the area of our investigations, determine precisely the validity domain of the theory in question**.

1.4 Formalization of the basic rules

Let us suppose that specific internal energy and pressure can be given as a function of specific volume and temperature in the forms $(v, T) \mapsto \mathfrak{e}(v, T)$ and $(v, T) \mapsto \mathcal{P}(v, T)$, respectively (this will be detailed in the next paragraph). Then we can state

- for fixed v, the assignment $T \mapsto \mathfrak{e}(v, T)$ is strictly monotone increasing,
- for fixed T, the assignment $v \mapsto \mathcal{P}(v, T)$ is locally strictly monotone decreasing.

To avoid misunderstanding, we give the precise meaning of the last notion: if $(v_0, T) \in \mathrm{Dom}\mathcal{P}$, then v_0 has a neighbourhood in which for all v_1 and v_2 such that $(v_1, T), (v_2, T) \in \mathrm{Dom}\mathcal{P}$, the relation $v_1 < v_2$ holds if and only if $\mathcal{P}(v_1, T) > \mathcal{P}(v_2, T)$.

If $\mathcal{P}$ is continuous, then $\mathcal{P}(\cdot, T)$ is strictly monotone decreasing on every interval in its domain.

Let us recall that the required properties are fulfilled where the functions are continuously differentiable and

$$\frac{\partial \mathfrak{e}}{\partial T} > 0, \qquad \frac{\partial \mathcal{P}}{\partial v} < 0$$

hold.

These inequalities play a fundamental role in the sequel: the 'really good' materials exhibit them on a 'sufficiently large set'.

1.5 Simple materials

The properties listed in the previous paragraph are summarized in the following mathematical definition.

Definition *The general simple material* Σ *is called* **simple material** *if there are*

(i) $D \subset (\mathrm{m}^3)^+ \times (\mathrm{K})^+$*, the* **constitutive domain***,*

(ii) $\mathfrak{e} : D \to (\mathrm{J})^+, \quad \mathcal{P} : D \to (\mathrm{Pa}), \quad \boldsymbol{\mu} : D \to (\mathrm{J})$

continuous functions, the **constitutive functions***, whose graph equals* Σ *i.e.*

$$\Sigma = \Big\{ \big(\mathfrak{e}(v,T), v, T, \mathcal{P}(v,T), \boldsymbol{\mu}(v,T)\big) \mid (v,T) \in D \Big\};$$

furthermore, the function $T \mapsto \mathfrak{e}(v,T)$ *is strictly monotone increasing for all possible* v*, and the function* $v \mapsto \mathcal{P}(v,T)$ *is locally strictly monotone decreasing for all possible* T*,*

(iii) the subset R *of* D*,* **the regular domain***, on which the constitutive functions are continuously differentiable and satisfy* **the intrinsic stability conditions**

$$\frac{\partial \mathfrak{e}}{\partial T} > 0, \qquad \frac{\partial \mathcal{P}}{\partial v} < 0$$

is an open subset dense in D *(i.e. the closure of* R *contains* D*).*

In the case of simple materials the elements of D are called **states**; this little abuse does not cause misunderstanding because D and Σ determine each other uniquely. We can interpret also that 'the state (v,T)' is an abbreviation for 'the state determined by (v,T)'.

Later on a simple material will referred to by the symbol

$$(D, \mathfrak{e}, \mathcal{P}, \boldsymbol{\mu}, R).$$

The quantities introduced in 1.2 which are functions defined on Σ, can be given as functions of specific volume and temperature:

- $\mathfrak{s}(v,T) := \dfrac{\mathfrak{e}(v,T) + \mathcal{P}(v,T)v - \mu(v,T)}{T}$,
- $\mathfrak{h}(v,T) := \mathfrak{e}(v,T) + \mathcal{P}(v,T)v$,
- $\mathfrak{f}(v,T) := \mathfrak{e}(v,T) - T\mathfrak{s}(v,T)$,

where (v,T) runs over the set D.

1.6 Entropic property

Thermodynamical investigations indicate that the constitutive functions are not independent, even, there are strong relations among them which can be given with the aid of specific entropy. We accept these relations as particular, restrictive properties rather than generally valid rules.

Definition *A simple material* $(D, \mathfrak{e}, \mathcal{P}, \mu, R)$ *is* **entropic** *or has the* **entropic property** *if*

$$T\frac{\partial \mathfrak{s}}{\partial T} = \frac{\partial \mathfrak{e}}{\partial T}, \qquad T\frac{\partial \mathfrak{s}}{\partial v} = \frac{\partial \mathfrak{e}}{\partial v} + \mathcal{P}$$

is fulfilled on the regular domain.

If the specific entropy is twice differentiable, then

$$T\frac{\partial \mathcal{P}}{\partial T} = \frac{\partial \mathfrak{e}}{\partial v} + \mathcal{P}$$

holds which can be deduced easily from the equality $\frac{\partial^2 \mathfrak{s}}{\partial v \partial T} = \frac{\partial^2 \mathfrak{s}}{\partial T \partial v}$. This relation and the definition of the entropic property yield that

$$\frac{\partial \mathfrak{s}}{\partial v} = \frac{\partial \mathcal{P}}{\partial T}.$$

Thus the two equalities above are necessary for the entropic property (in case of twice differentiability); if the regular domain is simply connected, they are sufficient as well.

It follows immediately from the definition of simple materials:

Proposition *The simple material* $(D, \mathfrak{e}, \mathcal{P}, \mu, R)$ *has the entropic property if and only if*

$$\frac{\partial \mu}{\partial v} = v\frac{\partial \mathcal{P}}{\partial v}, \qquad \frac{\partial \mu}{\partial T} = -\mathfrak{s} + v\frac{\partial \mathcal{P}}{\partial T} \tag{$*$}$$

holds on the regular domain.

The relations $(*)$ are called **Gibbs–Duhem relations**.

1.7 A special kind of material with entropic property

In usual textbooks on thermodynamics one deals tacitly – without precise definition – with simple materials and mostly considers only the constitutive function of pressure, though this is not enough for the thermodynamical characterization of the material. However, it will be ‘almost sufficient’ if continuous differentiability and entropic property are required.

Namely, let us suppose that we have the continuously differentiable function $(v,T) \mapsto \mathcal{P}(v,T)$ on the non-void open set $R_0 \subset (\mathrm{m}^3)^+ \times (\mathrm{K})^+$ such that $\frac{\partial \mathcal{P}}{\partial v} < 0$ everywhere. If entropic property holds, then the function $\mathfrak{e}$ satisfies

$$\frac{\partial \mathfrak{e}}{\partial v} = T\frac{\partial \mathcal{P}}{\partial T} - \mathcal{P}$$

according to 1.6, from which we deduce that

$$\mathfrak{e}(v,T) = \varepsilon(T) + \mathfrak{r}(v,T) \qquad \big((v,T) \in R_0\big),$$

where $\mathfrak{r}$ is the primitive function with respect to v of the function on the right-hand side of the previous equality and $\varepsilon : (\mathrm{K})^+ \rightarrowtail (\mathrm{J})^+$ is a function which will be supposed to be continuously differentiable. Let R_1 be the largest possible subset of R_0 on which the function $\mathfrak{e}(v,\cdot)$ is strictly monotone increasing for all v. For all T the function $v \mapsto \mathfrak{r}(v,T)$ is continuously differentiable but this does not imply that $\mathfrak{r}$ itself is continuously differentiable (in both variables). Let us suppose that the interior R of the set

$$\left\{(v,T) \in R_1 \mid \mathfrak{r} \text{ is continuously differentiable }, \ \varepsilon'(T) + \frac{\partial \mathfrak{r}(v,T)}{\partial T} > 0\right\}$$

is not void.

Let $\mathcal{P}$ and $\mathfrak{e}$ be later on the restrictions of those functions onto R. Then specific entropy as a function of (v,T) on R is determined by the relations

$$\frac{\partial \mathfrak{s}}{\partial T} = \frac{1}{T}\frac{\partial \mathfrak{e}}{\partial T}, \qquad\qquad \frac{\partial \mathfrak{s}}{\partial v} = \frac{\partial \mathcal{P}}{\partial T}$$

which come from the formula of 1.6.

Finally, on the basis of the definition of specific entropy, we obtain the chemical potential as a function of (v,T) on R.

R will be the regular domain of the material and the constitutive domain D can be an arbitrary set containing R and contained in the closure of R in such a way that all the constitutive functions can be continuously extended to D (for instance $D = R$).

Note that this procedure determines both the specific internal energy and the specific entropy only up to an additive constant.

It is worth mentioning that we can choose another way to construct the constitutive functions. Namely, on the basis of exercise 2 in 1.9, the specific free energy is of the form

$$\mathfrak{f}(v,T) = \mathcal{R}(v,T) + \varphi(T)$$

where $\mathcal{R}$ is the primitive function of $\mathcal{P}$ with respcet to v and φ is an arbitrary constinuously differentiable function. Then the specific entropy is obtained by exercise 2 in 1.9, so we can derive all the constitutive functions.

1.8 The Nernst property

The first and second laws, mentioned in the Preface and the Introduction, concern processes. The third law – called also the Nernst law – refers to the properties of constitutive functions near to absolute zero temperature. Thus the third law precedes the first and second ones from a logical point of view. The third law, too, has several different formulations. Most frequently it is stated that entropy tends to zero when temperature tends to zero. We give a precise formulation as a restricting property instead of a generally valid 'law'.

Definition *A simple material* $(D, \mathfrak{e}, \mathcal{P}, \boldsymbol{\mu}, R)$ *has the* **Nernst property** *if*

– *it is entropic,*

– $O_D := \overline{D} \cap \big((\mathrm{m}^3)^+ \times \{0\}\big) \neq \emptyset$,

– $\mathfrak{s}$ *and* $\mathrm{D}\mathfrak{s}$ *continuously extendable to* O_D *in such a way that the extensions are constant on* O_D.

In other words:

– there is a $v_0 \in (\mathrm{m}^3)^+$ such that $(v_0, 0)$ is the accumulation point of D,

– specific entropy $\mathfrak{s}$, $\frac{\partial \mathfrak{s}}{\partial v}$ and $\frac{\partial \mathfrak{s}}{\partial T}$ have limits in all accumulation points $(v_0, 0)$ of D and the limits do not depend on v_0.

Thus for a Nernst material the limit

$$\lim_{(v,T)\to(v_0,0)} \mathfrak{s}(v,T) =: s_0,$$

exists for all accumulation points $(v_0, 0)$ of D and s_0 is the same for all v_0. The specific entropy is determined up to an additive constant, thus we can choose $s_0 = 0$ for a Nernst material (the entropy is zero at zero temperature).

We call attention to the fact that $(v_0, 0)$ can be an accumulation point of D in such a way that $(v_0, T) \notin D$ for any T in the neighbourhood of zero, thus the limit of $\mathfrak{s}$ in $(v_0, 0)$ cannot be obtained as $\lim\limits_{T\to 0} \mathfrak{s}(v_0, T)$ (a good example is the point $(b, 0)$ for van der Waals materials treated in 2.2).

For fixed v the function $T \mapsto \mathfrak{e}(v, T)$ is strictly monotone decreasing and bounded below, thus if $(v_0, 0)$ is an accumulation point of R such that $(v_0, T) \in D$ for (positive) T-s in a neighbourhood of zero, then $\lim\limits_{T\to 0} \mathfrak{e}(v_0, T)$ exists (for all materials) but this limit can depend on v_0. If, moreover, the material has the Nernst property, then the specific free energy has (because of its definition) a limit in $(v_0, 0)$, too, and

$$\lim_{T\to 0} \mathfrak{f}(v_0, T) = \lim_{T\to 0} \mathfrak{e}(v_0, T).$$

On the basis of the entropic property in 1.6, we deduce for Nernst materials that the limits of $\frac{\partial \mathfrak{e}}{\partial T}$ and $\frac{\partial \mathfrak{e}}{\partial v} + \mathcal{P}$ in the points of O_D are zero.

1.9 Exercises

1. Deduce the necessary conditions given in 1.6 for the entropic property.
2. Prove that the entropic property is equivalent to

$$\frac{\partial \mathfrak{f}}{\partial v} = -\mathcal{P}, \qquad \frac{\partial \mathfrak{f}}{\partial T} = -\mathfrak{s}.$$

3. Construct the constitutive functions by the method described in 1.7 starting from the following pressure functions.

a) Given the positive constants a and b (having convenient physical dimension) and the temperature T_0,

$$R_0 := \{(v,T) \mid a\,(T - T_0 \log(T/T_0)) - bv > 0\}\,,$$

$$\mathcal{P}(v,T) := a\,(T - T_0 \log(T/T_0)) - bv.$$

b) Given the positive constants a, b and c (having convenient physical dimension),

$$R_0 := \left\{(v,T) \mid 2a(v - bT) - \frac{c}{v^2} < 0\right\},$$

$$\mathcal{P}(v,T) := a(v - bT)^2 + \frac{c}{v}.$$

c) Given the positive constants a, b and c (having convenient physical dimension),

$$R_0 := \{(v,T) \mid aT(b - v) + \frac{c}{v^2} > 0\},$$

$$\mathcal{P}(v,T) := aT(b - v) + \frac{c}{v}.$$

4. Give R for the previous exercises and the largest possible D.

5. The Nernst law ('postulate') is often formulated in such a way that the limit of specific entropy exists at zero temperature and one tacitly accepts that this limit is independent of specific volume values.

Then considering the equality $\mathfrak{s} = \frac{\mathfrak{e}-\mathfrak{f}}{T}$, one states that $\mathfrak{e}$ and $\mathfrak{f}$ have the same limit at zero temperature. But this is true only if at least one of them has a limit, which does not hold necessarily (except the case when the limit can be obtained in the form $\lim\limits_{T\to 0}$.)

Then referring to the L'Hospital rule, one states that the limit of $\frac{\partial\mathfrak{e}}{\partial T} - \frac{\partial\mathfrak{f}}{\partial T}$ at zero temperature equals the limit of $\mathfrak{s}$, i.e. zero. Then according to the relations of exercise 2, one concludes that the limit of $\frac{\partial\mathfrak{e}}{\partial T}$ at zero temperature is zero.

The L'Hospital rule, however, says that if

$$\frac{\frac{\partial\mathfrak{e}}{\partial T} - \frac{\partial\mathfrak{f}}{\partial T}}{1} \tag{$*$}$$

has a limit as T tends to 0, then

$$\frac{\mathfrak{e} - \mathfrak{f}}{T} = \mathfrak{s} \tag{$**$}$$

has a limit, too, and the limits are equal. Conversely is not true: the existence of the limit of $(**)$ does not imply the existence of the limit of $(*)$.

Consequently, if only the existence of the limit of $\mathfrak{s}$ at zero temperature is supposed, we cannot deduce the existence of the limit of $\frac{\partial\mathfrak{e}}{\partial T}$ (neither in the case when the limit of $\mathfrak{s}$ is obtained in the form $\lim\limits_{T\to 0}$).

Further, with a different reasoning, but essentially deriving from the fact that the limit of entropy at zero temperature is independent of specific volume, one deduces that the limit of $\frac{\partial\mathfrak{s}}{\partial v}$ is zero, too, which is 'trivial' from

$$0 = \lim_{T\to 0} \frac{\partial\mathfrak{s}(v,T)}{\partial v} = \lim_{T\to 0} \lim_{v'\to v} \frac{\mathfrak{s}(v',T) - \mathfrak{s}(v,T)}{v' - v}$$

if the limit can be obtained in the form $T \to 0$ and the order of the two limits can be interchanged; but these are not fulfilled, in general.

Now we ask the reader to examine in what conditions the equality

$$\lim_{T\to 0} \frac{\partial \mathcal{P}(v,T)}{\partial T} = 0$$

holds.

2 Some special simple materials

Here and later on k is the Boltzmann constant:

$$k = 1,38... \cdot 10^{-23} \mathrm{J/K}.$$

Now we suppose that all materials to be treated have the entropic property, that the constitutive functions are continuously differentiable, and we construct the constitutive functions according to 1.7. We give only the results, the details are left to the reader.

2.1 Ideal gases

$$R_0 := (\mathrm{m}^3)^+ \times (\mathrm{K})^+, \qquad \mathcal{P}(v,T) := \frac{kT}{v}.$$

Then

$$\mathfrak{e}(v,T) = \varepsilon(T),$$

where $\varepsilon : (\mathrm{K})^+ \rightarrowtail (\mathrm{J})^+$ is a continuously differentiable function, supposed to be defined on an interval, and having everywhere positive derivative. The intrinsic stability condition regarding pressure is fulfilled everywhere, thus

$$R = (\mathrm{m}^3)^+ \times \mathrm{Dom}\varepsilon.$$

Put $\mathfrak{c} := \varepsilon'$.

Fixing a temperature T_0 and introducing the function

$$\eta(T,T_0) := \exp\left(\int\limits_{T_0}^{T} \frac{\mathfrak{c}(\tau)}{\mathfrak{c}(T_0)\tau}\, d\tau \right),$$

we get that

$$\mathfrak{s}(v,T) = \mathfrak{c}(T_0) \log \eta(T,T_0) + k \log \frac{v}{v_0} \qquad \big((v,T) \in R\big)$$

where v_0 is a fixed specific volume.

The properties of logarithm suggest us to reduce the right-hand side, but we must be careful not to make an error: e.g. $\mathfrak{c}(T_0)$ cannot be put as an exponent under the logarithm because it is not a real number (an element of (J/K)). A right formula is

$$\mathfrak{s}(v,T) = k\log\left(\eta(T,T_0)^{\frac{\mathfrak{c}(T_0)}{k}}\frac{v}{v_0}\right).$$

Finally, for the chemical potential we obtain

$$\mu(v,T) = \varepsilon(T) + kT - T\mathfrak{s}(v,T) \qquad \big((v,T) \in R\big).$$

It is worth examining the special case when $\mathfrak{c}$ is constant,

$$\varepsilon(T) = \lambda kT + e_0 \qquad (T \in (\mathrm{K})^+)\ ,$$

where λ and e_0 are positive constants. Then $R = (\mathrm{m}^3)^+ \times (\mathrm{K})^+$ and $\eta(T,T_0) = \frac{T}{T_0}$, consequently,

$$\mathfrak{s}(v,T) = k\log\left(\left(\frac{T}{T_0}\right)^{\lambda}\frac{v}{v_0}\right),$$

and

$$\mu(v,T) = kT\left(\lambda + 1 - \log\left(\left(\frac{T}{T_0}\right)^{\lambda}\frac{v}{v_0}\right)\right) + e_0.$$

We mention that one often takes the constant e_0 to be zero. Then the internal energy would be zero at zero temperature. If the internal energy meant only the kinetic energy (and the interaction energy of molecules which is zero for an ideal gas), this would be correct. However, as mentioned, the thermodynamical treatment of chemical reactions requires that the energy of chemical bonds be a part of internal energy; e_0 gives account of this part of internal energy.

The constitutive functions of ideal gases are well applicable to describe real gases at high temperature and large specific volume. To get better descriptions of real gases, several other constitutive functions were suggested by diverse assumptions on the interaction of gas molecules. Some of them will be given in the next paragraphs.

2.2 van der Waals materials

Given the non-negative constants a and b (of convenient physical dimension),

$$R_0 := \left\{(v,T)\ \middle|\ v > b, \quad -\frac{kT}{(v-b)^2} + \frac{2a}{v^3} < 0\right\},$$

$$\mathcal{P}(v,T) = \frac{kT}{v-b} - \frac{a}{v^2}.$$

Note that the second inequality in the definition of R_0 determines just the set on which the formula of the function $\mathcal{P}$ has negative partial derivative with respect to v. Then

$$\mathfrak{e}(v,T) = \varepsilon(T) - \frac{a}{v},$$

where $\varepsilon : (\mathrm{K})^+ \rightarrowtail (\mathrm{J})^+$ is a continuously differentiable function, supposed to be defined on an interval, and having positive derivative everywhere. Then

$$R := \{(v,T) \in R_0 \mid T \in \mathrm{Dom}\varepsilon\}.$$

Now, with the functions $\mathfrak{c}$ and η introduced in the previous paragraph,

$$\mathfrak{s}(v,T) = \mathfrak{c}(T_0)\log \eta(T,T_0) + k \log \frac{v-b}{v_0-b} \qquad \big((v,T) \in R\big).$$

Again, the special case

$$\varepsilon(T) = \lambda k T + e_0 \qquad (T \in (\mathrm{K})^+)$$

is worth mentioning where λ and e_0 are positive constants; then $\eta(T,T_0) = \frac{T}{T_0}$, so

$$\mathfrak{s}(v,T) = k \log \left(\left(\frac{T}{T_0}\right)^{\lambda} \frac{v-b}{v_0-b} \right)$$

and

$$\boldsymbol{\mu}(v,T) = kT \left(\lambda + \frac{v}{v-b} - \log \left(\left(\frac{T}{T_0}\right)^{\lambda} \frac{v}{v_0} \right) \right) + e_0.$$

If $b = 0$ and $a = 0$, we regain the constitutive functions of the ideal gases. Further, we see that if $v \gg b$ and $kT \gg \frac{a(v-b)}{v^2}$ and $\varepsilon(T) \gg \frac{a}{v}$, the present functions are well approximated by the functions of the ideal gases.

Perhaps it is not superfluous to emphasize that it is not right to say that the ideal gas functions well approximate the van der Waals ones if $b \approx 0$ and $a \approx 0$ because such approximate equalities make no sense. Similarly, we cannot impose the condition $v \gg a$ (which formally seems good) for the approximation, because a and v cannot be compared: they have different physical dimensions, namely $a \in (\mathrm{Jm}^3)$ and $v \in (\mathrm{m}^3)$.

2.3 The Clausius materials

Given the non-negative constants a, b and c,

$$R_0 := \left\{ (v,T) \;\middle|\; v > b, \quad \frac{kT^2}{a} > \frac{(v-b)^2}{(v+c)^2} \right\},$$

$$\mathcal{P}(v,T) = \frac{kT}{v-b} - \frac{a}{T(v+c)}.$$

Then

$$\mathfrak{e}(v,T) = \varepsilon(T) + \frac{2a}{T} \log \frac{v+c}{v_0+c},$$

where v_0 is a specific volume value and $\varepsilon : (\mathrm{K})^+ \rightarrowtail (\mathrm{J})^+$ is a continuously differentiable function, supposed to be defined on an interval, and

$$R := \left\{ (v,T) \in R_0 \;\middle|\; \varepsilon'(T) > \frac{2a}{T^2} \log \frac{v+c}{v_0+c} \right\} \neq \emptyset.$$

With the aid of the functions $\mathfrak{c}$ and η introduced for ideal gases now we have

$$\mathfrak{s}(v,T) = \mathfrak{c}(T_0)\log\eta(T,T_0) + k\log\frac{v-b}{v_0-b} + \frac{a}{T^2}\log\frac{v+c}{v_0+c} \qquad \big((v,T)\in R\big).$$

If $b=0$ and $a=0$ – for arbitrary c and v_0 – we regain the constitutive functions of ideal gases. Further, we see that if $v \gg b$ and $kT^2 \gg \frac{a(v-b)}{v+c}$ and $\varepsilon(T) \gg \frac{2a}{T}\left|\log\frac{v+c}{v_0+c}\right|$, the present functions are well approximated by the functions of the ideal gases.

2.4 The Berthelot materials

Given the non-negative constants a and b,

$$R_0 := \{(v,T) \mid v > bT, \quad kT^2v^2 > a(v-bT)^2\},$$

$$\mathcal{P}(v,T) = \frac{kT}{v-bT} - \frac{a}{Tv}.$$

Then

$$\mathfrak{e}(v,T) = \varepsilon(T) + \frac{2a}{T}\log\frac{v}{v_0} - \frac{bkT^2}{v-bT},$$

where v_0 is a specific volume value and $\varepsilon : (\mathrm{K})^+ \rightarrowtail (\mathrm{J})^+$ is a continuously differentiable function, supposed to be defined on an interval, and

$$R := \left\{(v,T)\;\middle|\; \varepsilon'(T) - \frac{2a}{T^2}\log\frac{v}{v_0} - \frac{2bkT}{v-bT} - \frac{b^2kT^2}{(v-bT)^2} > 0\right\} \neq \emptyset.$$

With the aid of the functions $\mathfrak{c}$ and η introduced for ideal gases now we have

$$\mathfrak{s}(v,T) = c(T_0)\log\eta(T,T_0) + k\log\frac{v-bT}{v_0-bT_0} - \frac{bkT}{v-bT} + \frac{a}{T^2}\log\frac{v}{v_0} \qquad \big((v,T)\in R\big).$$

If $a=0$ and $b=0$, we regain the constitutive functions of ideal gases. Further, we see that if $v \gg bT$, $kT^2 \gg \frac{a(v-bT)}{v}$ and $\varepsilon(T) \gg \frac{2a}{T}\left|\log\frac{v}{v_0} - \frac{bkT^2}{v-bT}\right|$ the present functions are well approximated by the functions of the ideal gases.

2.5 The Kammerlingh Onnes materials

We start with the pressure function

$$\mathcal{P}(v,T) = \frac{kT}{v}\left(1 + \sum_{n=1}^{\infty}\frac{c_n(T)}{v^n}\right)$$

where $c_n : (\mathrm{K})^+ \to ((1/\mathrm{m}^3)^n)^+$ are differentiable functions, called **virial coefficients**.

R_0 is the largest open subset consisting of the pairs (v,T) for which the series

$$\sum_{n=1}^{\infty}\frac{c_n(T)}{v^n} \qquad \text{and} \qquad \sum_{n=1}^{\infty} n\frac{c_n(T)}{v^n}$$

are absolute and uniformly convergent and for which

$$-1-\sum_{n=1}^{\infty}(n+1)\frac{c_n(T)}{v^n}<0.$$

If we require that also the series

$$\sum_{n=1}^{\infty}\frac{c_n'(T)}{v^n}$$

be absolute and uniformly convergent, then

$$\mathfrak{e}(v,T)=\varepsilon(T)-kT^2\sum_{n=1}^{\infty}\frac{c_n'(T)}{nv^n},$$

where ε is the function known from the previous examples and, of course, it is required that the set is not void where the partial derivative of $\mathfrak{e}$ with respect to T is positive.

Now, with the usual notations we have

$$\mathfrak{s}(v,T)=\mathfrak{c}(T_0)\log\eta(T,T_0)+k\log\frac{v}{v_0}-k\sum_{n=1}^{\infty}\frac{c_n(T)+Tc_n'(T)}{nv^n}.$$

2.6 Concluding remarks

The cited constitutive functions were introduced for the description of thermodynamical properties of some materials. They are well applicable for gases in some domain of the variables. Thus these functions model some materials under rather restricted circumstances. A real material is too complicated to be described by analytic functions. The everywhere differentiability of the constitutive functions is a too strong requirement; we shall see that some phases of the materials are separated by the break of these functions.

The constitutive functions in the exercises of the previous section do not correspond to real materials; being rather simple, they serve only for training.

2.7 Exercises

1. Describe the **Callendar materials** with the non-negative constants a and b, starting from the pressure function

$$\mathcal{P}(v,T)=\frac{kT}{v-b+\frac{a}{T}}$$

which is defined on the pairs (v,T) where the nominator is positive and the partial derivative with respect to v is negative.

2. Give the van der Waals materials in Kammarlingh Onnes form using the series expansion

$$\frac{1}{v-b}=\frac{1}{v}\frac{1}{1-b/v}=\frac{1}{v}\left(1+\sum_{n=1}^{\infty}\left(\frac{b}{v}\right)^n\right)$$

which is valid for $v > b$.

Give also the Clausius, Berthelot and Callendar materials in Kammerlingh Onnes form.

3. Derive the constitutive functions of the materials treated above using the specific free energy (see the end of Section 1.7). For van der Waals materials,

$$\mathfrak{f}(v, T) = kT \log \frac{v - b}{v_0 - b} + \frac{a}{v} + \varphi(T).$$

4. An ideal gas cannot have the Nernst property: because of the form of R according to 2.1, there are only two possibilities:

(i) R has no accumulation point of form $(v, 0)$,

(ii) $(v, 0)$ is an accumulation point of R for all v.

In the latter case, as it is obvious from the expression in 2.1, the limit of the entropy in $(v, 0)$, if exists, depends on v.

R has at most one accumulation point for van der Waals, Clausius and Berthelot materials; can these materials have the Nernst property?

What can we say about the Callendar materials?

5. Let

$$\mathfrak{c}(T) := \lambda k \exp\left(-\frac{T_0}{T}\right)$$

where $\lambda > 0$ (e.g. $\lambda = 3/2$), and T_0 is a given temperature value. The well-known properties of the exponential function imply

$$\lim_{T \to \infty} \mathfrak{c}(T) = \lambda k, \qquad \lim_{T \to 0} \frac{\mathfrak{c}(T)}{T^n} = 0$$

for all non-negative real number n. In particular, for $n = 1$, $T \mapsto \frac{c(T)}{T}$ is a continuous function, whose limit at zero is zero.

Using this function, examine the properties of $\eta(T, T_0)$ defined in 2.1.

6. Describe the specific enthalpy and the specific free energy of ideal gases as functions of (v, T) in the case $\mathfrak{c} = \lambda k$.

3 Change coefficients

3.1 Convention about notations

In this section we treat some formal properties of processes of simple materials, without specifying, how such processes can be induced (can they be induced at all?). Our investigations yield information on important measurable properties of materials such as specific heat, thermal expansion coefficient, etc.

A process of a general simple material means that the state of the material varies in time, which is described by functions $t \mapsto e(t)$, $t \mapsto v(t)$, $t \mapsto T(t)$, $t \mapsto P(t)$ and $t \mapsto \mu(t)$ defined on a time interval. In the case of a simple material, $t \mapsto v(t)$ and $t \mapsto T(t)$ determine the others: $e(t) = \mathfrak{e}(v(t), T(t))$, $P(t) = \mathcal{P}(v(t), T(t))$, $\mu(t) = \mathfrak{u}(v(t), T(t))$. Now we shall consider exclusively processes which run in the regular domain and are continuously differentiable.

This is the first point where we meet the ambiguity that the same latter denotes two different – but strongly related – objects. For instance, T denotes a temperature value, i.e. an element of $(\mathrm{K})^+$ and T denotes a function defined on a time interval and having values in $(\mathrm{K})^+$. Accordingly, if φ is a function of specific volume and temperature, then φ denotes the function $(v, T) \mapsto \varphi(v, T)$ as well as the function $t \mapsto \varphi(v(t), T(t))$. This ambiguity makes the formulas easy to survey and therefore offers much more benefit than the danger of misunderstanding.

3.2 Processes of special type

Some special processes having particular importance are the following:

- **isochoric** processes when the volume is constant,
- **isothermal** processes when the temperature is constant,
- **isobaric** processes when the pressure is constant,
- **isentropic** processes when the entropy is constant.

Now we shall refer to the first law of thermodynamics mentioned in Paragraph 6 of the Introduction, considering ideal working, i.e.

$$\dot{e} = q - P\dot{v}.$$

The processes are supposed to run in the regular domain, therefore we can rewrite this equation for time derivative of the specific volume and the temperature:

$$\left(\frac{\partial \mathfrak{e}}{\partial v} + P\right)\dot{v} + \frac{\partial \mathfrak{e}}{\partial T}\dot{T} = q.$$

A process is called **adiabatic** if the heating is zero (i.e. in the case of heat insulation); then $\dot{e} = -P\dot{v}$.

If the material is entropic, then the function $t \mapsto s(t) := \mathfrak{s}(v(t), T(t))$ satisfies $T\dot{s} = \dot{e} + P\dot{v}$, consequently the adiabatic processes equal the isentropic ones.

3.3 Other processes with constraints

The processes listed above correspond to some ‘constraint’, the specific volume or the temperature does not change (isochoric and isothermal processes), or their changes are not independent (isobaric, isentropic and adiabatic processes), more closely the time derivatives of specific volume and temperature are submitted to the following relations:

$$\frac{\partial \mathcal{P}}{\partial v}\dot{v} + \frac{\partial \mathcal{P}}{\partial T}\dot{T} = 0,$$

$$\frac{\partial \mathfrak{s}}{\partial v}\dot{v} + \frac{\partial \mathfrak{s}}{\partial T}\dot{T} = 0,$$

$$\left(\frac{\partial \mathfrak{e}}{\partial v} + P\right)\dot{v} + \frac{\partial \mathfrak{e}}{\partial T}\dot{T} = 0$$

where, according to our convention about notations, the symbols before the time derivatives mean the functions $t \mapsto \frac{\partial \mathcal{P}}{\partial v}\big(v(t), T(t)\big)$, etc.

As a generalization, we shall consider processes in which the changes of volume and temperature are submitted to a constraint, given by continuous functions $\mathfrak{a} : (\mathrm{m}^3)^+ \times (\mathrm{K})^+ \rightarrowtail (\mathrm{u}/\mathrm{m}^3)$ and $\mathfrak{b} : (\mathrm{m}^3)^+ \times (\mathrm{K})^+ \rightarrowtail (\mathrm{u}/\mathrm{K})$ (where u is an arbitrary measure unit) in such a way that

$$\mathfrak{a}\dot{v} + \mathfrak{b}\dot{T} = 0.$$

Of course, we applied again our convention about the notations: the symbols before the time derivatives mean the functions $t \mapsto \mathfrak{a}(v(t), T(t))$ and $t \mapsto \mathfrak{b}(v(t), T(t))$. Such processes are the ones (but not only those) in which a continuously differentiable quantity $\mathcal{M} : (\mathrm{m}^3)^+ \times (\mathrm{K})^+ \rightarrowtail (\mathrm{u})$ is constant:

$$\dot{M} = \frac{\partial \mathcal{M}}{\partial v}\dot{v} + \frac{\partial \mathcal{M}}{\partial T}\dot{T} = 0.$$

Such a process – if it has no special name (like isobaric) – will be called an $\mathfrak{a}$-$\mathfrak{b}$ process. Note that

$$\dot{v} \supset -\frac{\mathfrak{b}}{\mathfrak{a}}\dot{T}, \qquad \dot{T} \supset -\frac{\mathfrak{a}}{\mathfrak{b}}\dot{v} \tag{$*$}$$

where the symbol $\supset$ shows that the left-hand side can be defined on a larger set than the right hand-side which is meaningful only where the denominator is not zero.

3.4 Thermal expansion coefficients

Dividing the previous relation $(*)$ by v, we get the relative change of the volume on the left-hand side, and the right-hand side is proportional to the temperature change. Therefore, the proportionality coefficient (the function 'deprived of the time change')

$$-\frac{1}{v}\frac{\mathfrak{b}}{\mathfrak{a}} : (\mathrm{m}^3)^+ \times (\mathrm{K})^+ \rightarrowtail (1/\mathrm{K})$$

is called the $\mathfrak{a}-\mathfrak{b}$**-thermal coefficient** (of course, if the $\mathfrak{a}$-$\mathfrak{b}$ process has a particular name – e.g. isobaric – then the thermal expansion coefficient is named similarly).

A simple special case is the isobaric thermal expansion coefficient ($\mathfrak{a}$ and $\mathfrak{b}$ are the partial derivatives of $\mathcal{P}$),

$$\alpha := \frac{1}{v}\left(\frac{\frac{\partial \mathcal{P}}{\partial T}}{-\frac{\partial \mathcal{P}}{\partial v}}\right),$$

which is defined on the whole regular domain.

Another simple case is the adiabatic thermal expansion coefficient, when $\mathfrak{b} = \frac{\partial \mathfrak{e}}{\partial T}$, $\mathfrak{a} = \frac{\partial \mathfrak{e}}{\partial v} + \mathcal{P}$, defined in the subset where $\mathfrak{a}$ is not zero.

3.5 Compressibility factors

The equality

$$\dot{P} = \frac{\partial \mathcal{P}}{\partial v}\dot{v} + \frac{\partial \mathcal{P}}{\partial T}\dot{T}$$

and the second relation of $(*)$ in 3.3 yield

$$\dot{P} \supset v\left(\frac{\partial \mathcal{P}}{\partial v} - \frac{\partial \mathcal{P}}{\partial T}\frac{\mathfrak{a}}{\mathfrak{b}}\right)\left(\frac{\dot{v}}{v}\right).$$

The change of pressure is proportional to the relative change of volume; the negative reciprocal of the proportionality coefficient, i.e. the function

$$\frac{1}{v\left(-\frac{\partial \mathcal{P}}{\partial v} + \frac{\partial \mathcal{P}}{\partial T}\frac{\mathfrak{a}}{\mathfrak{b}}\right)} : (\mathrm{m}^3)^+ \times (\mathrm{K})^+ \rightarrowtail (\mathrm{Pa})$$

is called the **$\mathfrak{a}$–$\mathfrak{b}$-compressibility factor**.

A simple special case is the isothermal compressibility factor ($\mathfrak{a}$ and $\mathfrak{b}$ are the partial derivative of temperature, i.e. $\mathfrak{a} = 0$, $\mathfrak{b} = 1$),

$$\kappa := \frac{1}{v}\frac{1}{\left(-\frac{\partial \mathcal{P}}{\partial v}\right)}.$$

Another simple special case is the adiabatic compressibility factor.

3.6 Strain coefficients

The first relation of $(*)$ in 3.3 and the equality written for the pressure in the previous paragraph yield

$$\frac{\dot{P}}{P} \supset \frac{1}{P}\left(-\frac{\partial \mathcal{P}}{\partial v}\frac{\mathfrak{b}}{\mathfrak{a}} + \frac{\partial \mathcal{P}}{\partial T}\right)\dot{T}.$$

The relative change of pressure is proportional to the temperature; the proportionality coefficient, the function

$$\frac{1}{\mathcal{P}}\left(-\frac{\partial \mathcal{P}}{\partial v}\frac{\mathfrak{b}}{\mathfrak{a}} + \frac{\partial \mathcal{P}}{\partial T}\right) : (\mathrm{m}^3)^+ \times (\mathrm{K})^+ \rightarrowtail (1/\mathrm{K})$$

is called the **$\mathfrak{a}$–$\mathfrak{b}$-strain coefficient**.

A simple special case is the isochoric strain coefficient ($\mathfrak{a}$ and $\mathfrak{b}$ are the partial derivatives of specific volume, i.e. $\mathfrak{a} = 1$, $\mathfrak{b} = 0$),

$$\beta := \frac{1}{\mathcal{P}}\frac{\partial \mathcal{P}}{\partial T}.$$

Another simple special case is the adiabatic strain coefficient.

3.7 Specific heats

The first law for an $\mathfrak{a}$-$\mathfrak{b}$ process and the first relation of $(*)$ in 3.3 yield

$$\left(\frac{\partial \mathfrak{e}}{\partial T} - \frac{\mathfrak{b}}{\mathfrak{a}}\left(\frac{\partial \mathfrak{e}}{\partial v} + P\right)\right)\dot{T} \subset q.$$

Heating is proportional to the change of temperature; the proportionality coefficient, the function

$$\frac{\partial\mathfrak{e}}{\partial T} - \frac{\mathfrak{b}}{\mathfrak{a}}\left(\frac{\partial\mathfrak{e}}{\partial v} + \mathcal{P}\right) : (\mathrm{m}^3)^+ \times (\mathrm{K})^+ \rightarrowtail (\mathrm{J/K})$$

is called the $\mathfrak{a}$-$\mathfrak{b}$ **specific heat** or the $\mathfrak{a}$-$\mathfrak{b}$ **heat capacity**.

An important special case is the isochoric specific heat (specific heat at constant volume) ($\mathfrak{a} = 1$, $\mathfrak{b} = 0$),

$$\mathfrak{c}_v := \frac{\partial\mathfrak{e}}{\partial T},$$

and the isobaric specific heat (specific heat at constant pressure) ($\mathfrak{a}$ and $\mathfrak{b}$ are the partial derivatives of $\mathcal{P}$),

$$\mathfrak{c}_p := \frac{\partial\mathfrak{e}}{\partial T} + \left(\frac{\frac{\partial\mathcal{P}}{\partial T}}{-\frac{\partial\mathcal{P}}{\partial v}}\right)\left(\frac{\partial\mathfrak{e}}{\partial v} + \mathcal{P}\right),$$

which are defined on the whole regular domain.

We recall that here the specific heat refers to one molecule. The specific heat used in practice is 'heat per unit mass' which is the quotient of the present one by the mass of a molecule.

The third law ('Nernst postulate') is often stated in the form that the absolute zero temperature cannot be reached which is a consequence of the fact that perfect heat insulation does not exist and near to the absolute zero a small heat produces a large temperature change. The exact formulation of the latter assertion is the following: according to what has been said at the end of 1.8, if $\frac{\mathfrak{a}}{\mathfrak{b}}$ is bounded near to the zero temperature, then the $\mathfrak{a}-\mathfrak{b}$ specific heat of a Nernst material has zero limit at zero temperature.

3.8 Latent heats

The first law for isothermal processes yields

$$\left(\frac{\partial\mathfrak{e}}{\partial v} + P\right)\dot v = q.$$

Heating is proportional to the volume change; the proportionality coefficient, i.e. the function

$$\mathfrak{l}_v := \frac{\partial\mathfrak{e}}{\partial v} + \mathcal{P} : (\mathrm{m}^3)^+ \times (\mathrm{K})^+ \rightarrowtail (\mathrm{Pa})$$

is called the **expansion heat**.

Let us consider now the change of a quantity $\mathcal{M}$ in an isothermal process; then $\dot M = \frac{\partial\mathcal{M}}{\partial v}\dot v$, and consequently

$$\left(\frac{\partial\mathfrak{e}}{\partial v} + P\right)\frac{1}{\frac{\partial\mathcal{M}}{\partial v}}\dot M \subset q.$$

Heating is proportional to the change of $\mathcal{M}$; the proportionality coefficient, i.e. the function

$$\mathfrak{l}_{\mathcal{M}} := \frac{\mathfrak{l}_v}{\frac{\partial\mathcal{M}}{\partial v}}$$

is called the **$\mathcal{M}$-latent heat**.

3.9 Normal dilation

Our simple experience indicates that the expansion heat is positive: if a body absorbs heat and its temperature remains constant then it expands. This is not true, however, for water in the interval between 0^oC and 4^oC. Recall that water was a counterexample in 1.3 also from another point of view: in the interval in question, the pressure increases with decreasing temperature and constant volume. These two ‘abnormal’ properties balance each other, corresponding to the following important definition.

Definition *The simple material* $(D, \mathfrak{e}, \mathcal{P}, \boldsymbol{\mu}, R)$ *is of* **normal dilation** *if*

$$\left(\frac{\partial \mathfrak{e}}{\partial v} + \mathcal{P}\right) \frac{\partial \mathcal{P}}{\partial T} \geq 0$$

on the regular domain.

If the material is entropic and the entropy is twice differentiable, then according to 1.6, the material is of normal dilation.

3.10 Practical importance of the change coefficients

It is irrelevant for the coefficients introduced previously how the processes advance in time; only the quality and the quantity of the state change is important. Applying the usual ‘delta symbol’ for the changes of the constitutive variables, we can write e.g. that in isobaric processes

$$\frac{\Delta v}{v} \approx \alpha(v, T)\Delta T.$$

Most of the change coefficients in question can be measured easily (the internal energy change does not appear in the formulae), and provide some information on the constitutive functions, because e.g.

$$\frac{\alpha}{\beta\kappa} = \mathcal{P}, \qquad\qquad \frac{\alpha}{\kappa} = \frac{\partial \mathcal{P}}{\partial T}$$

(more precisely, only the relation $\subset$ holds instead of equality).

The constitutive function of pressure and the isochoric specific heat determine the constitutive function of the specific internal energy, at least locally, and for entropic materials the specific entropy, too, at least locally. Indeed, according to 1.7,

$$\mathfrak{e}(v, T) = e(v_0, T_0) + \int\limits_{T_0}^{T} \mathfrak{c}_v(v,\tau) d\tau + \int\limits_{v_0}^{v} \left(T \frac{\partial \mathcal{P}(\nu, T)}{\partial T} - \mathcal{P}(\nu, T) \right) d\nu,$$

for (v, T) in the neighbourhood of an arbitrarily given $(v_0, T_0) \in R$, and for entropic material

$$\mathfrak{s}(v, T) = s(v_0, T_0) + \int\limits_{T_0}^{T} \frac{\mathfrak{c}_v(v,\tau)}{\tau} d\tau + \int\limits_{v_0}^{v} \frac{\partial \mathcal{P}(\nu, T)}{\partial T} d\nu.$$

3.11 Change coefficients of ideal gases

We easily deduce for ideal gases that

$$\frac{1}{\alpha(v,T)} = \frac{1}{\beta(v,T)} = T, \qquad \frac{1}{\kappa(v,T)} = \mathfrak{l}_v(v,T) = \frac{kT}{v},$$

moreover $\mathfrak{c}_v$ and $\mathfrak{c}_p$ do not depend on specific volume and

$$\mathfrak{c}_p - \mathfrak{c}_v = k.$$

Experience and theoretical considerations (in statistical mechanics) show that for not too low temperature and for small density (large specific volume) the isochoric specific heat for one-atomic gases is approximately $\frac{3}{2}k$, for two-atomic gases it is approximately $\frac{5}{2}k$. That is why it is generally accepted that the isochoric specific heat of ideal gases is independent of temperatureand (the constants denoted by simple letters)

- $c_v = \frac{3}{2}k$ for the one-atomic gas,
- $c_v = \frac{5}{2}k$ for the two-atomic gas.

Correspondingly,

- $c_p = \frac{5}{2}k$ for the one-atomic gas,
- $c_p = \frac{7}{2}k$ for the two-atomic gas.

3.12 Transition heat

So far we have considered processes in which phase transition does not occur. Phase transitions will be treated later but some of their aspects belong logically to this section; therefore we ask the reader to skip this paragraph and to return after having studied Section 6 whose notions and notations are used here.

Let us take two bodies whose states are in different phases of the same material; let the phases have a first-order connection. The number of particles in the bodies change in a phase transition, thus the first law for the two bodies reads

$$\begin{aligned} \dot{E}_1 &= Q_1 - P_1\dot{V}_1 + \mu_1\dot{N}_1, \\ \dot{E}_2 &= Q_2 - P_2\dot{V}_2 + \mu_2\dot{N}_2. \end{aligned}$$

As a matter of fact, we consider processes in which the total number of the bodies is constant: $\dot{N}_1 + \dot{N}_2 = 0$.

We examine the (idealized) case when the phase transition happens at temperature T and pressure P on the phase line Γ. (As an example imagine a glass of water in an atmosphere with sufficiently low temperature. The water cools, reaches the freezing point, starts to freeze; then, during freezing, both the water and the ice have approximately the same constant pressure and temperature.) Then the specific internal energy and specific volume, too, are constant in both phases and the first law has the form

$$\begin{aligned} e_1\dot{N}_1 &= Q_1 - Pv_1\dot{N}_1 + \mu_1\dot{N}_1, \\ -e_2\dot{N}_1 &= Q_2 + Pv_2\dot{N}_1 - \mu_2\dot{N}_1 \end{aligned}$$

where, of course, $v_1 = \boldsymbol{v}_1(T, P)$ etc. Then it follows

$$Q_1 + Q_2 = T(\boldsymbol{s}_1(T, P) - \boldsymbol{s}_2(T, P))\dot{N}_1.$$

The sum of heatings is proportional to the change of particle number, the proportionality coefficient,

$$\Gamma \to (\mathrm{J}), \quad (T, P) \mapsto T\big(\boldsymbol{s}_1(T, P) - \boldsymbol{s}_2(T, P)\big)$$

is called the **transition heat** from the second phase into the first one.

Note that the chemical potentials of the phases coincide on Γ, consequently the transformation heat can also be written in the form $\boldsymbol{h}_1(T, P) - \boldsymbol{h}_2(T, P)$, where $\boldsymbol{h}$ is the specific enthalpy as a function of temperature and pressure.

We recall that here the transformation heat refers to one molecule. The transformation heat used in practice is 'heat per unit mass' which is the quotient of the present one by the mass of a molecule.

3.13 Exercises

1. Show that

$$\mathfrak{c}_p = \mathfrak{c}_v + \alpha \mathfrak{l}_v v.$$

Moreover, the normal dilation property is equivalent to $\alpha \mathfrak{l}_v \geq 0$. If the material has this property, then $\mathfrak{c}_p \geq \mathfrak{c}_v$.

2. Prove that for entropic material

$$\mathfrak{l}_v \kappa = \alpha T,$$

which implies

$$\mathfrak{c}_p - \mathfrak{c}_v = \frac{vT\alpha^2}{\kappa}.$$

3. Demonstrate that for entropic material

$$\mathfrak{c}_v = -T\frac{\partial^2 \mathfrak{f}}{\partial T^2}.$$

4. Give the form of the adiabatic thermal expansion coefficient $\hat{\alpha}$, the adiabatic compressibility factor and demonstrate that

$$\frac{\kappa}{\hat{\kappa}} = \frac{\mathfrak{c}_p}{\mathfrak{c}_v}.$$

5. The partial derivative with respect to the specific volume of the continuously differentiable function $\mathcal{P}$ on the regular domain is negative; as a consequence of the inverse function theorem, the assignment $v \mapsto \mathcal{P}(v, T)$ is locally injective for all T, i.e. it has a local inverse: specific volume can be given locally as a function of temperature and pressure. Let $(T, P) \mapsto \boldsymbol{v}(T, P)$ be such a function. Prove that

$$\alpha(\boldsymbol{v}(T, P), T) = \frac{1}{\boldsymbol{v}(T, P)}\frac{\partial \boldsymbol{v}(T, P)}{\partial T}, \qquad \kappa(\boldsymbol{v}(T, P), T) = -\frac{1}{\boldsymbol{v}(T, P)}\frac{\partial \boldsymbol{v}(T, P)}{\partial P}.$$

6. Use the notations of the previous exercise. Specific internal energy, too, can be locally given as a function of temperature and pressure: $(T,P)\mapsto \boldsymbol{e}(T,P)$. Then the specific enthalpy has the form $(T,P)\mapsto \boldsymbol{h}(T,P) := \boldsymbol{e}(T,P) + P\boldsymbol{v}(T,P)$. Demonstrate that

$$\mathfrak{c}_p(\boldsymbol{v}(T,P),T) = \frac{\partial \boldsymbol{h}(T,P)}{\partial T}.$$

7. Prove that for van der Waals materials

$$\frac{1}{\alpha(v,T)} = T\frac{v}{v-b} - \frac{2a(v-b)}{kv^2}, \qquad \frac{1}{\beta(v,T)} = T - \frac{a(v-b)}{kv},$$

$$\frac{1}{\kappa(v,T)} = \frac{kTv}{(v-b)^2} - \frac{2a}{v^2},$$

consequently,

$$\frac{\alpha(v,T)}{\beta(v,T)} = \frac{k}{v-b}, \qquad \mathfrak{l}_v(v,T) = \frac{kT}{v-b}.$$

8. Deduce for Clausius and Berthelot materials the change coefficients treated in this section.

9. What conditions imply the validity of the following equalities

$$\lim_{T\to 0}\mathfrak{c}_p(v,T)=0, \qquad \lim_{T\to 0}\alpha(v,T)=0, \qquad \lim_{T\to 0}\beta(v,T)=0, \qquad \lim_{T\to 0}\kappa(v,T)=0$$

which are often stated in connection with the Nernst property (third law) in usual treatments of thermodynamics.

4 State curves

4.1 Introductory remarks

According to the previous section, the processes of a material are functions $t \mapsto \big(v(t),T(t)\big)$, which are supposed now to run in the regular domain and to be continuously differentiable. The process determines the function $t \mapsto \big(e(t),v(t),T(t),P(t),\mu(t)\big)$, whose range is called a **state curve**. The state curves will be studied through their projections onto convenient planes. Because internal energy and chemical potential are not directly measurable, only the projections onto the v–T, v–P and T–P planes are of practical importance.

According to the names introduced in 3.2, we speak, among others, about isochors, isobars, isotherms and adiabats.

The projection of isotherms onto the v–T plane are 'horizontal' lines, onto the T–P plane are 'vertical' lines; therefore only their projection onto the v–P plane are interesting; they are, for fixed temperature T, the sets $\{(v,P) \mid \mathcal{P}(v,T) = P\}$, in other words, the graph of the function $v \mapsto \mathcal{P}(v,T)$.

The isobars have non-trivial projections only onto the v–T plane; they are sets of form $\{(v,T) \mid \mathcal{P}(v,T) = \text{const}\}$.

4.2 Adiabats

The adiabatic processes are characterized by the relation

$$\mathfrak{l}_v \dot{v} + \mathfrak{c}_v \dot{T} = 0, \tag{$*$}$$

where the notations of the previous section are used. It is known from the theory of differential equations that the range of such processes in the v–T plane is described by the differential equation

$$\frac{dT}{dv} = -\frac{\mathfrak{l}_v(v,T)}{\mathfrak{c}_v(v,T)}.$$

Making $\dot{v}$ explicit from $\dot{P} = \frac{\partial \mathcal{P}}{\partial v}\dot{v} + \frac{\partial \mathcal{P}}{\partial T}\dot{T}$, and putting it into equality $(*)$, we get for an adiabatic process

$$\mathfrak{l}_p \dot{P} + \mathfrak{c}_p \dot{T} = 0;$$

similarly, with $\dot{T}$, we obtain

$$\frac{\partial \mathcal{P}}{\partial v}\mathfrak{c}_p \dot{v} - \mathfrak{c}_v \dot{P} = 0.$$

Consequently, the projections of adiabats onto the T–P and v–P planes are described by the differential equations

$$\frac{dT}{dP} = -\frac{\mathfrak{l}_p}{\mathfrak{c}_p},$$

$$\frac{dP}{dv} = \frac{\partial \mathcal{P}}{\partial v}\frac{\mathfrak{c}_p}{\mathfrak{c}_v},$$

respectively (except the points where $\mathfrak{c}_p$ and $\mathfrak{c}_v$ have zero value).

If the material is entropic and its specific entropy is known, then the projection of adiabats onto the v–T plane can be given in the form $\{(v,T) \mid \mathfrak{s}(v,T) = \text{const}\}$, too.

4.3 State curves of ideal gases

We take an ideal gas whose specific internal energy is defined for all temperatures (see 2.1).

4.3.1 Isotherms

The isotherm, with given temperature T, of the ideal gas on the v–P plane is the set

$$\{(v,P) \mid Pv = kT = \text{const.}\},$$

which is a branch of hyperbole. A 'higher' hyperbole corresponds to a higher temperature (Figure 4.1). This helps us to imagine the graph of the function $\mathcal{P}$ (called sometimes the thermal state surface): we translate the isotherms behind the plane of the page in a distance corresponding to their temperature, and so we draw the surface shown in Figure 4.2.

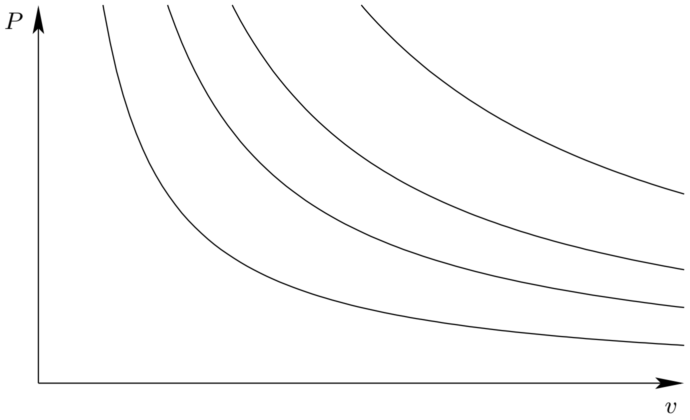

Figure 4.1

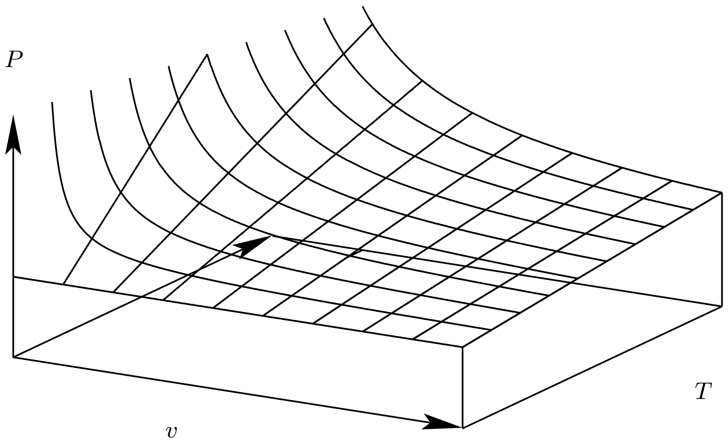

Figure 4.2

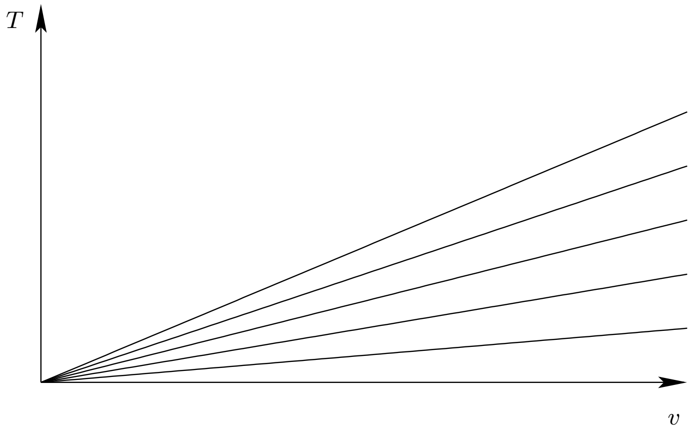

Figure 4.3

4.3.2 Isobars and isochors

The isobar, with given pressure P, of the ideal gas on the v–T plane is the set

$$\left\{(v,T) \mid T = \left(\frac{P}{k}\right) v\right\},$$

which is half line starting from the origin. A line with larger slope corresponds to a higher pressure (Figure 4.3).

Similar straight lines are the isochors on the T–P plane.

4.3.3 Adiabats

The ideal gas is entropic, so its adiabats are just the isentropic curves; according to the expression in 2.1, they are

$$\{(v,T) \mid \eta(T,T_0)^{c(T_0)/k} v = \text{const.}\}.$$

If $c_v = \lambda k$ (where λ is a positive number, e.g. 3/2 or 5/2), then the adiabats in the v–T plane are

$$\{(v,T) \mid T^\lambda v = \text{const.}\},$$

or

$$\{(v,T) \mid T v^{\gamma-1} = \text{const.}\},$$

with the usual notation

$$\gamma := \frac{c_p}{c_v} = 1 + \frac{1}{\lambda}.$$

The adiabats on the other two planes have the form

$$\{(v,P) \mid P v^\gamma = \text{const.}\},$$

and

$$\{(T,P) \mid T^\gamma P^{1-\gamma} = \text{const.}\},$$

respectively.

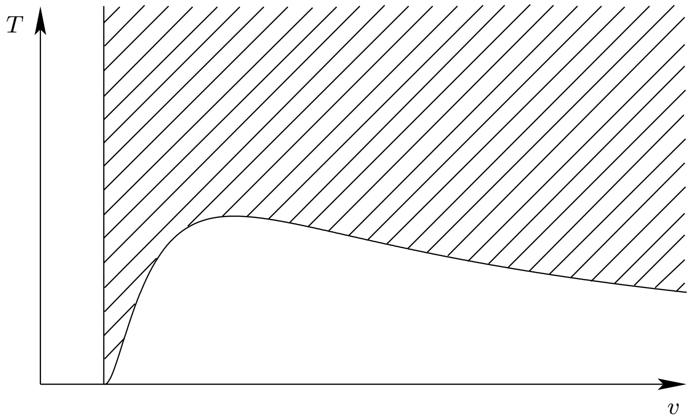

Figure 4.4

4.4 State curves of van der Waals materials

4.4.1 The regular domain

The regular domain of the van der Waals material given in 2.2 is the part of

$$R_0 := \left\{ (v,T) \;\middle|\; v > b, \quad -\frac{kT}{(v-b)^2} + \frac{2a}{v^3} < 0 \right\}$$

determined by the restriction imposed on specific internal energy . This restriction does not influence our considerations, therefore we can disregard it.

R_0 is an open set whose boundary

$$\{(v,T) \mid v = b\} \cup \left\{ (v,T) \;\middle|\; -\frac{kT}{(v-b)^2} + \frac{2a}{v^3} = 0 \right\}$$

can be made evident. The first condition gives a 'vertical line', the second one, being equivalent to

$$\left\{ (v,T) \mid T = \frac{2a}{k} \frac{(v-b)^2}{v^3} \right\},$$

gives the graph of the function $v \mapsto \frac{2a}{k}\frac{(v-b)^2}{v^3}$ which can be studied with the aid of the differential calculus. We get that it has a maximum at $3b$ with value $8a/27kb$ (Figure 4.4). The area under the graph does not belong to the constitutive domain, so R_0 is the marked part.

4.4.2 Isotherms

The isotherm, with given temperature T, of the van der Waals material on the v–P plane is the subset of the graph of the function

$$v \mapsto \frac{kT}{(v-b)} - \frac{a}{v^2} \qquad\qquad (v > b),$$

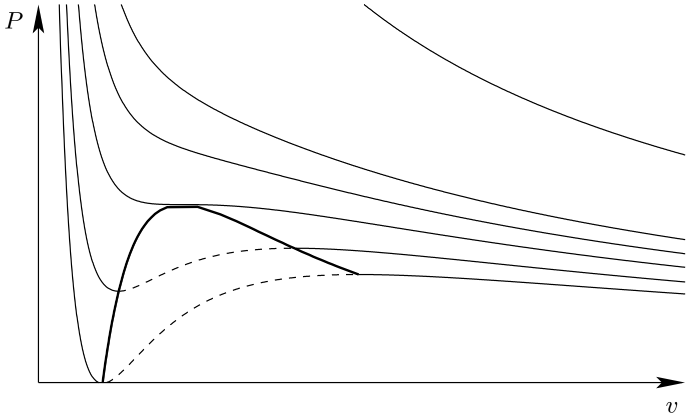

Figure 4.5

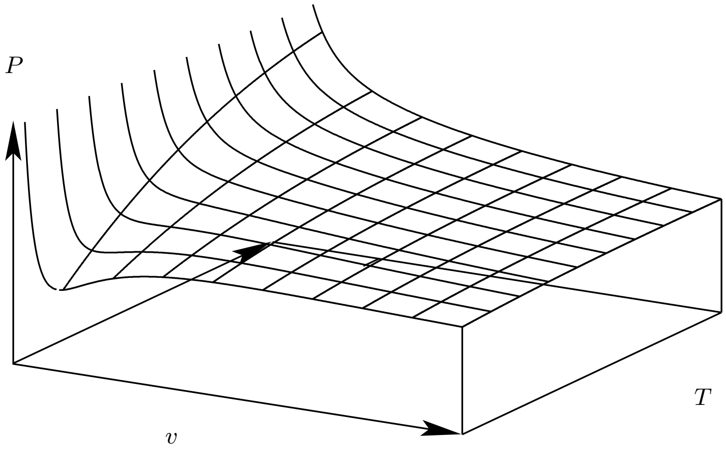

Figure 4.6

where its derivative is negative.

Let us introduce the **critical values**

$$v_c := 3b, \qquad T_c := \frac{8a}{27kb}, \qquad P_c := \frac{a}{27b^2}.$$

Then, according to the previous paragraph, if

– $T > T_c$, then the derivative is everywhere negative,

– $T = T_c$, then the derivative is everywhere negative, except the point v_c,

– $T < T_c$, then the derivative is zero at certain points v_1 and v_2, such that $v_1 < v_c < v_2$, and it is positive on the interval $]v_1, v_2[$, it is negative for values smaller than v_1 and for ones larger than v_2.

The isotherms on the v–P plane are illustrated in Figure 4.5. They are drawn by dashed lines outside the constitutive domain according to the formula of $\mathcal{P}$. The bold curves passing through the minima and maxima of the formal isotherms

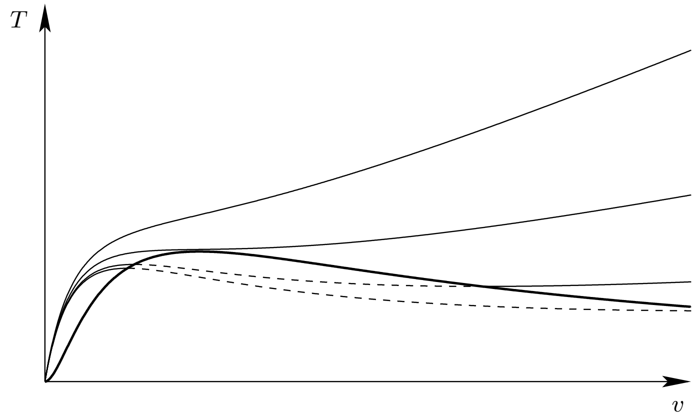

Figure 4.7

correspond to the boundary of the constitutive domain; they are usually called **spinodal curves**.

This helps us imagine the graph of the function $\mathcal{P}$ (called sometimes the thermal state surface): we translate the isotherms behind the plane of the page in a distance corresponding to their temperature, and so we draw the surface shown in Figure 4.6.

4.4.3 Isobars

The isobar, with given pressure P, of the van der Waals material on the v–T plane is the set

$$\left\{(v,T)\;\middle|\; v>b,\quad T>\frac{2a}{k}\frac{(v-b)^2}{v^3},\quad T=\frac{1}{k}\left(P+\frac{a}{v^2}\right)(v-b)\right\},$$

which is the graph of the expression on the right-hand side as a function of v which can be studied with the aid of the differential calculus. Figure 4.7 shows some isobars.

4.4.4 Adiabats

The van der Waals material is entropic, thus its adiabats are the isentropic curves which can be given in the form

$$\{(v,T)\mid \eta(T,T_0)^{c(T_0)/k}(v-b)=\text{const.}\},$$

according to 2.2. If $c_v=\lambda k$, then they are

$$\{(v,T)\mid T^{\lambda}(v-b)=\text{const.}\}.$$

4.5 Exercises

1. Deduce the form of the adiabats of the ideal gas without the entropy from the differential equation given in 4.2.

2. Describe the adiabats of the van der Waals material on the v–P and the T–P planes.

3. For arbitrary van der Waals material (for arbitrary a and b), introducing the dimensionless quantities

$$\nu := \frac{v}{v_c}, \qquad \tau := \frac{T}{T_c}, \qquad \pi := \frac{P}{P_c},$$

we can represent the thermal state surface in the form

$$\pi = \frac{8\tau}{3v - 1} - \frac{3}{v^2}.$$

Outline the constitutive domain, the critical points, the isotherms and the isobars in these variables.

4. Prove that for van der Waals materials

$$\mathfrak{c}_p(v_c, T) - \mathfrak{c}_v(v_c, T) = \frac{kT}{T - T_c},$$

$$\kappa(v_c, T) = \frac{3k}{4b}\frac{1}{T - T_c},$$

where, of course, $T > T_c$.

5. Demonstrate that for van der Waals materials

$$\frac{\partial \mathcal{P}}{\partial v}(v_c, T_c) = \frac{\partial^2 \mathcal{P}}{\partial v^2}(v_c, T_c) = 0.$$

6. Examine the isotherms, isobars and adiabats of the materials given in Exercise 3 of 1.9.

7. Examine the isotherms, isobars and adiabats of the Clausius and Berthelot materials.

8. A *piezotropic point* of a material is a point (v, T) of the constitutive domain where $\frac{\partial \mathcal{P}(v,T)}{\partial T} = 0$; the set of piezotropic points is the *piezotrope*.

Find the piezotropes of the ideal gas, the van der Waals materials, the Clausius and Berthelot materials and the materials given in Exercise 3 of 1.9.

5 Canonical variables

5.1 Fundamental relations

A fundamental property of simple materials is that the specific internal energy is a strictly monotone increasing function of temperature; consequently, the temperature can be given as a function of specific internal energy and specific volume, called the **canonical variables**. This means that we have the function $\mathbf{T}$ on the set

$$\mathrm{D} := \{(\mathfrak{e}(v, T), v) \mid (v, T) \in D\}$$

in such a way that

$$\mathbf{T}(\mathfrak{e}(v, T), v) = T \qquad \big((v, T) \in D\big)$$

and

$$\mathfrak{e}(v, \mathbf{T}(e, v)) = e \qquad\qquad \big((e, v) \in \mathrm{D}\big).$$

Then the pressure, too, can be given as a function of the canonical variables, for which

$$\mathbf{P}(e, v) := \mathcal{P}(v, \mathbf{T}(e, v)) \qquad\qquad \big((e, v) \in \mathrm{D}\big)$$

and

$$\mathcal{P}(v, T) = \mathbf{P}(\mathfrak{e}(v, T), v) \qquad\qquad \big((v, T) \in D\big)$$

hold from which we deduce for the partial derivatives

$$\frac{\partial \mathbf{T}}{\partial e} = \frac{1}{\frac{\partial \mathfrak{e}}{\partial T}}\bullet, \qquad \frac{\partial \mathbf{T}}{\partial v} = -\frac{\frac{\partial \mathfrak{e}}{\partial v}}{\frac{\partial \mathfrak{e}}{\partial T}}\bullet,$$

$$\frac{\partial \mathbf{P}}{\partial e} = \frac{\frac{\partial \mathcal{P}}{\partial T}}{\frac{\partial \mathfrak{e}}{\partial T}}\bullet, \qquad \frac{\partial \mathbf{P}}{\partial v} = \left(\frac{\partial \mathcal{P}}{\partial v} - \frac{\partial \mathcal{P}}{\partial T}\frac{\frac{\partial \mathfrak{e}}{\partial v}}{\frac{\partial \mathfrak{e}}{\partial T}}\right)\bullet,$$

$$\frac{\partial \mathfrak{e}}{\partial T} = \frac{1}{\frac{\partial \mathbf{T}}{\partial e}}\bullet, \qquad \frac{\partial \mathfrak{e}}{\partial v} = -\frac{\frac{\partial \mathbf{T}}{\partial v}}{\frac{\partial \mathbf{T}}{\partial e}}\bullet,$$

$$\frac{\partial \mathcal{P}}{\partial T} = \frac{\frac{\partial \mathbf{P}}{\partial e}}{\frac{\partial \mathbf{T}}{\partial e}}\bullet, \qquad \frac{\partial \mathcal{P}}{\partial v} = \left(\frac{\partial \mathbf{P}}{\partial v} - \frac{\partial \mathbf{P}}{\partial e}\frac{\frac{\partial \mathbf{T}}{\partial v}}{\frac{\partial \mathbf{T}}{\partial e}}\right)\bullet$$

which, of course, are valid where the functions are differentiable. As to the notations, we refer to App. 3.

It can be seen that

$$\mathrm{R} := \big\{\big(\mathfrak{e}(v, T), v\big) \mid (v, T) \in R\big\}$$

is the set where the function $(\mathbf{T}, \mathbf{P})$ is continuously differentiable and the inequalities

$$\frac{\partial \mathbf{T}}{\partial e} > 0, \tag{$*$}$$

$$\frac{\partial \mathbf{P}}{\partial v}\frac{\partial \mathbf{T}}{\partial e} - \frac{\partial \mathbf{P}}{\partial e}\frac{\partial \mathbf{T}}{\partial v} < 0 \tag{$**$}$$

hold.

Note that the right-hand side of the second inequality is the determinant of the derivative of the function $(\mathbf{T}, \mathbf{P})$, i.e. of the matrix

$$\begin{pmatrix} \frac{\partial \mathbf{T}}{\partial e} & \frac{\partial \mathbf{T}}{\partial v} \\ \\ \frac{\partial \mathbf{P}}{\partial e} & \frac{\partial \mathbf{P}}{\partial v} \end{pmatrix}.$$

Of course, all other quantities, such as chemical potential, specific entropy, specific enthalpy and specific free energy can be given as functions of the variables (e, v):

– $\boldsymbol{\mu}(e, v) := \mu(v, \mathbf{T}(e, v))$,

- $\mathbf{s}(e,v) := \mathfrak{s}(v, \mathbf{T}(e,v))$,
- $\mathbf{h}(e,v) := \mathfrak{h}(v, \mathbf{T}(e,v))$,
- $\mathbf{f}(e,v) := \mathfrak{f}(v, \mathbf{T}(e,v))$.

The variables v and T are the natural variables from a practical (experimental) point of view, but the canonical variables e and v are more suitable for theoretical investigations. A technical difficulty of thermodynamics is that the function $\mathbf{T}$ cannot be explicitly given even for a relatively simple $\mathfrak{e}$.

5.2 Canonical form of simple materials

According to the previous considerations, a simple material can also be given by the canonical variables (e,v) as a quintet

$$(\mathrm{D}, \mathbf{T}, \mathbf{P}, \boldsymbol{\mu}, \mathrm{R}),$$

where

(i) $\mathrm{D} \subset (\mathrm{J})^+ \times (\mathrm{m}^3)^+$, is the **canonical constitutive domain**,

(ii) $\mathbf{T} : \mathrm{D} \to (\mathrm{K})^+, \quad \mathbf{P} : \mathrm{D} \to (\mathrm{Pa}), \quad \boldsymbol{\mu} : \mathrm{D} \to (\mathrm{J})$
the **canonical constitutive functions** are continuous,

(iii) the **canonical regular domain** R is the nonvoid open subset of D in which the constitutive functions are continuously differentiable and the **intrinsic stability conditions** $(*)$ and $(**)$ of the previous paragraph hold.

In this case, too, the pairs (e,v) in the canonical constitutive domain are called states (see 1.5).

In the sequel we omit the attribute canonical regarding constitutive domain, constitutive functions, etc. if it does not cause misunderstanding.

5.3 Entropic property in the canonical variables

The condition of entropic property becomes simpler in the canonical variables. Namely, if the material is entropic, then the equalities in 5.1 imply for the partial derivatives of the entropy function

$$\mathbf{s}(e,v) := \mathfrak{s}(v, \mathbf{T}(e,v)) \qquad \big((e,v) \in \mathrm{D}\big)$$

that

$$\frac{\partial \mathbf{s}}{\partial e} = \frac{1}{\mathbf{T}}, \qquad \frac{\partial \mathbf{s}}{\partial v} = \frac{\mathbf{P}}{\mathbf{T}}, \qquad \text{in other words} \qquad \mathtt{D}\mathbf{s} = \left(\frac{1}{\mathbf{T}}, \frac{\mathbf{P}}{\mathbf{T}}\right)$$

on the canonical regular domain.

If specific entropy is twice continuously differentiable, then the necessary condition for the entropic property – because of the equality of second partial derivatives in different order – is that

$$\frac{\partial \mathbf{T}}{\partial v} = \mathbf{P}\frac{\partial \mathbf{T}}{\partial e} - \mathbf{T}\frac{\partial \mathbf{P}}{\partial e}$$

be fulfilled. If the canonical regular domain is simply connected and $(\mathbf{T}, \mathbf{P})$ is continuously differentiable, then this is sufficient, too.

The specific entropy of an entropic material is twice differentiable and has the second derivative

$$\mathtt{D}^2\mathbf{s} = -\frac{1}{\mathbf{T}^2}\begin{pmatrix} \frac{\partial \mathbf{T}}{\partial e} & \frac{\partial \mathbf{T}}{\partial v} \\ \mathbf{P}\frac{\partial \mathbf{T}}{\partial e} - \mathbf{T}\frac{\partial \mathbf{P}}{\partial e} & \mathbf{P}\frac{\partial \mathbf{T}}{\partial v} - \mathbf{T}\frac{\partial \mathbf{P}}{\partial v} \end{pmatrix}.$$

The matrix in parentheses is symmetric (because of the necessary condition mentioned in the previous paragraph) and has the determinant

$$\mathbf{T}\left(-\frac{\partial \mathbf{T}}{\partial e}\frac{\partial \mathbf{P}}{\partial v} + \frac{\partial \mathbf{T}}{\partial v}\frac{\partial \mathbf{P}}{\partial e}\right).$$

According to the intrinsic stability conditions, the first matrix entry and the determinant of the matrix are positive; equivalently, the matrix is positive definite. Because of the negative multiplier before the matrix, we can state:

Proposition *The second derivative of the specific entropy of an entropic material as a function of the canonical variables* (e, v) *is negative definite on the regular domain.*

We call attention to the fact that the above assertion for the second derivative of the specific entropy is true only in the variables (e, v), it does not hold for the second derivative of $(v, T) \mapsto \mathfrak{s}(v, T)$.

5.4 Canonical form of ideal gases and van der Waals materials

If the ideal gas has constant specific heat, then $\mathfrak{e}(v, T) = cT + e_0$, thus temperature can be given explicitly as a function of specific internal energy :

$$\mathrm{D} = \{(e, v) \mid e > e_0,\ v > 0\}, \qquad \mathbf{T}(e, v) = \frac{e - e_0}{c}.$$

If the van der Waals material has constant specific heat, temperature can be given explicitly as a function of specific internal energy and specific volume:

$$\mathrm{D} = \left\{(e, v) \;\middle|\; e > e_0 - \frac{a}{v}, v > b\right\}, \qquad \mathbf{T}(e, v) = \frac{e - e_0 + \frac{a}{v}}{c}.$$

5.5 Exercises

1. Which examples of Exercise 3 in 1.9 allow us to give explicitly temperature as a function of specific internal energy and specific volume?

2. Show that for an entropic material

$$\frac{\partial \boldsymbol{\mu}}{\partial e} = v\frac{\partial \mathbf{P}}{\partial e} - \mathbf{s}\frac{\partial \mathbf{T}}{\partial e}, \qquad \frac{\partial \boldsymbol{\mu}}{\partial v} = v\frac{\partial \mathbf{P}}{\partial v} - \mathbf{s}\frac{\partial \mathbf{T}}{\partial v},$$

hold on the regular canonical domain; the above relations can be written in the form

$$\begin{pmatrix} \frac{\partial \boldsymbol{\mu}}{\partial e} \\ \frac{\partial \boldsymbol{\mu}}{\partial v} \end{pmatrix} = (-\mathbf{s}, v)\begin{pmatrix} \frac{\partial \mathbf{T}}{\partial e} & \frac{\partial \mathbf{T}}{\partial v} \\ \frac{\partial \mathbf{P}}{\partial e} & \frac{\partial \mathbf{P}}{\partial v} \end{pmatrix},$$

or

$$\mathtt{D}\boldsymbol{\mu} = (-\mathbf{s}, v)\mathtt{D}(\mathbf{T}, \mathbf{P}).$$

3. If the material is entropic, then $\frac{\partial \mathbf{s}}{\partial e} = \frac{1}{\mathbf{T}} > 0$, consequently, specific internal energy can be given, at least locally, as a function of specific entropy and specific volume. Let $\hat{e}$ be such a function. Then, of course, all the other quantities can be given as functions of s and v, which will be denoted by a 'hat' over the usual symbols. Demonstrate that

$$\frac{\partial \hat{e}}{\partial s} = \hat{T}, \qquad \frac{\partial \hat{e}}{\partial v} = -\hat{P}.$$

4. Examine the state curves on the e–v plane. Prove that the adiabats are determined by the differential equation $\dfrac{de}{dv} = -\mathbf{P}(e, v)$.

6 Phases

6.1 Introductory remarks

A phase of a material is a characteristic form in which the material appears. Everyday phases are the solid, the liquid and the gaseous ones, but a material can have other phases, such as different crystalline phases. The solid–liquid and liquid–gaseous phase transitions, in general, are well observable, spectacular processes in which specific volume abruptly increases or decreases, internal energy (heat) is emitted or absorbed. Other phase transitions manifest themselves only in the abrupt or 'irregular' change of other (nonconstitutive) quantities, e.g. specific heat becomes 'infinitely large'.

It is known that water is solid at certain temperatures and pressures and liquid or gaseous at some other temperatures and pressures. The different crystalline phases of a material, too, are characterized by the temperature and pressure values in which they can exist. Experience shows that the phases of a material can be determined by temperature and pressure. The phase diagrams in the T–P plane are well known: they illustrate the phase lines which separate the different phases (Figure6.1).

Here we are confronted with the well-known but rarely emphasized fact that the line separating the liquid and gaseous phases ends at a critical point. Over this point the liquid and gaseous phases are fused, they cannot be distinguished.

The chemical potential is supposed to play a fundamental role in determining the phase lines which are usually deduced from the fact that the chemical potentials – as functions of T and P – corresponding to the adjoining phases have equal values: if μ_1 and μ_2 denote the chemical potential of two phases, then the phase line between them would be the set

$$\{(T, P) \mid \mu_1(T, P) = \mu_2(T, P)\}.$$

This is, however, doubtful because of the mentioned fusion of the liquid and gaseous phases.

The above facts point out that the usual notion of phases is not clear and give us hints how we proceed:

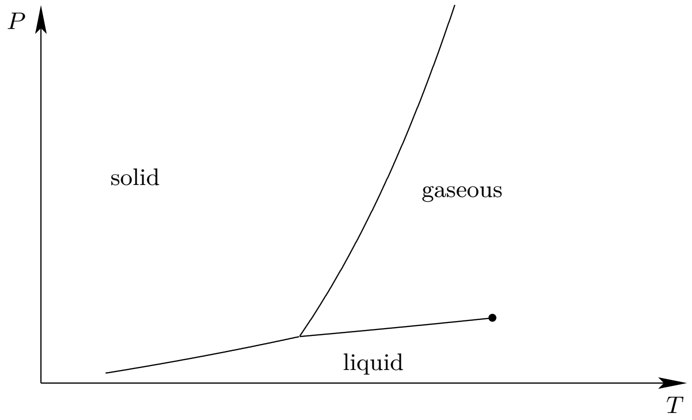

Figure 6.1

1. we have to define the exact notion of phases of simple materials which reflects that

   (i) phases can be characterized by temperature and pressure,

   (ii) the processes in a single phase are 'smooth enough',

2. we have to describe the connections of phases (which replace the phase lines).

6.2 Definition of phases

We find convenient now to introduce the notation

$$\mathcal{T} : D \to (\mathrm{K})^+, \qquad (v, T) \mapsto T.$$

According to the previous statement 1. (ii), a phase is a subset of the regular domain. We know that for fixed T the function $v \mapsto \mathcal{P}(v, T)$ is locally injective (strictly monotone decreasing), that is why

$$(\mathcal{T}, \mathcal{P}) : D \to (\mathrm{K})^+ \times (\mathrm{Pa}), \quad (v, T) \mapsto \big(T, \mathcal{P}(v, T)\big)$$

is locally injective, too. Where it is injective, its inverse gives v as a function of (T, P); in other words, there the state of the material can be characterized by temperature and pressure. This suggests us the following:

Definition *A* **phase** *of the simple material* $(D, \mathfrak{e}, \mathcal{P}, \mathfrak{u}, R)$ *is a connected open subset* Z *of* R *on which* $(\mathcal{T}, \mathcal{P})$ *is injective, and* Z *is maximal with this properties, i.e. if* N *is a connected open subset of* R *on which* $(\mathcal{T}, \mathcal{P})$ *is injective and* $Z \subset N$*, then* $Z = N$*.*

Proposition *Every element of* R *is contained in a phase.*

Proof Let $(v, T) \in R$. The point (v, T) has a neighbourhood on which $(\mathcal{T}, \mathcal{P})$ is injective, thus the family of connected open subsets, which contain (v, T) and on which $(\mathcal{T}, \mathcal{P})$ is injective is not void. Let us take a chain in this family; it is

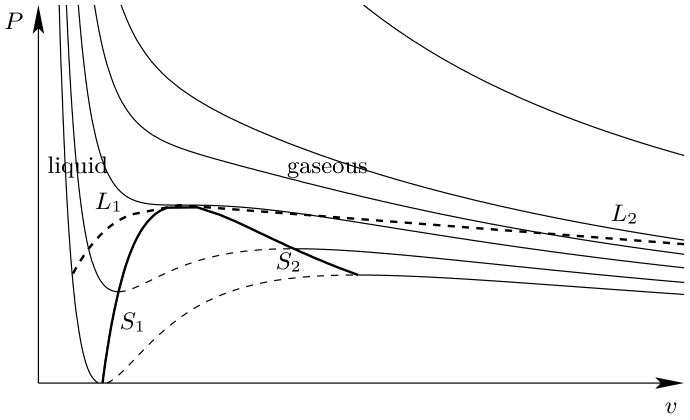

Figure 6.2

evident that the union of subsets in the chain belongs to the family in question and this union is an upper bound of the chain. Then Zorn's lemma implies that there is a maximal element in this family. ☐

Note that it is not excluded that a state belongs to more phases (this corresponds to the fact that the liquid and gaseous phases are fused over the critical point).

6.3 Phases of the van der Waals material

The van der Waals materials exhibit well the fusion of two phases (Figure 6.2).

Let us draw the isotherms according to Figure 4.5 and lay down an imaginary horizontal line through the maximum of every isotherm, marking the point where this horizontal line meets the same isotherm. The points give a curve L_1. A similar procedure with the minima gives the line L_2. The domain over the curves L_1 and S_2 corresponds to the gaseous phase, the domain over the curves S_1 and L_2 coresponds to the liquid phase. The common part of the two phases is represented by the domain over the curves L_1 and L_2. The domain between the curves S_1 and L_1 is the purely liquid phase and the domain between the curves S_2 and L_2 is the purely gaseous phase (Figure 6.2).

6.4 Phases in the canonical variables

We can also use the canonical variables for describing phases. A phase of the simple material $(\mathrm{D}, \mathbf{T}, \mathbf{P}, \boldsymbol{\mu}, \mathrm{R})$ in the canonical variables is a connected open subset Z of R on which the function $(\mathbf{T}, \mathbf{P})$ is injective, and Z is maximal with these properties.

Indeed, if Z is a phase in the variables (v, T) (as defined in 6.2), then

$$\mathrm{Z} := \left\{ \big(\mathfrak{e}(v,T), v\big) \mid (v,T) \in Z \right\}$$

has all the properties listed above; conversely, if Z is a subset with the above properties, then

$$Z := \{(v, \mathbf{T}(e,v)) \mid (e,v) \in \mathrm{Z}\}$$

is a phase in the sense of Definition 6.2. All that follows from the fact that the function $(e, v) \mapsto (v, \mathbf{T}(e, v))$ is continuously differentiable on Z, maps Z onto Z, moreover, $(\mathcal{T}, \mathcal{P})|_Z$ composed by this functions results in $(\mathbf{T}, \mathbf{P})|_{\mathrm{Z}}$, which is therefore a continuously differentiable injection on Z.

6.5 Characterization of phases by temperature and pressure

Let us consider a phase Z of the material $(D, \mathfrak{e}, \mathcal{P}, \mathfrak{\mu}, R)$. The function $(\mathcal{T}, \mathcal{P})$ is a continuously differentiable injection on Z, its derivative

$$\begin{pmatrix} 0 & \frac{\partial \mathcal{P}}{\partial v} \\ 1 & \frac{\partial \mathcal{P}}{\partial T} \end{pmatrix}$$

has non-zero determinant, thus the function

$$((\mathcal{T}, \mathcal{P})|_Z)^{-1} : (\mathrm{K})^+ \times (\mathrm{Pa}) \rightarrowtail (\mathrm{K})^+ \times (\mathrm{m}^3)^+$$

is defined on a connected open subset and is continuously differentiable. The second component of this function, denoted by $\boldsymbol{v}_Z$, give the specific volume as a function of temperature and pressure. Then $\boldsymbol{e}_Z(T, P) := \mathfrak{e}(\boldsymbol{v}_Z(T, P), T)$ is specific internal energy as a function of temperature and pressure in the given phase.

It is quite easy to see that

$$(\boldsymbol{e}_Z, \boldsymbol{v}_Z) = ((\mathbf{T}, \mathbf{P})|_{\mathrm{Z}})^{-1}.$$

The **chemical potential of the phase** as a function of temperature and pressure,

$$(T, P) \mapsto \mu_Z(T, P) := \mathfrak{\mu}(\boldsymbol{v}_Z(T, P), T) = \boldsymbol{\mu}(\boldsymbol{e}_Z(T, P), \boldsymbol{v}_Z(T, P))$$

will play a fundamental role in the sequel.

The Gibbs–Duhem relations (see 1.6) for an entropic material give

$$\frac{\partial \mu_Z}{\partial T} = -\boldsymbol{s}_Z, \qquad \frac{\partial \mu_Z}{\partial P} = \boldsymbol{v}_Z, \tag{$*$}$$

where $\boldsymbol{s}_Z(T, P) = \mathfrak{s}(\boldsymbol{v}_Z(T, P), T))$.

For convenient v, T and P we have

$$\boldsymbol{e}_Z(T, \mathcal{P}(v, T)) = \mathfrak{e}(v, T), \qquad \boldsymbol{v}_Z(T, \mathcal{P}(v, T)) = v,$$

or

$$\mathfrak{e}(\boldsymbol{v}_Z(T, P), T) = \boldsymbol{e}_Z(T, P), \qquad \mathcal{P}(\boldsymbol{v}_Z(T, P), T) = P$$

from which we infer that

$$\frac{\partial \boldsymbol{v}_Z}{\partial P} = \frac{1}{\frac{\partial \mathcal{P}}{\partial v}}\bullet, \qquad \frac{\partial \boldsymbol{v}_Z}{\partial T} = -\frac{\frac{\partial \mathcal{P}}{\partial T}}{\frac{\partial \mathcal{P}}{\partial v}}\bullet,$$

$$\frac{\partial \boldsymbol{e}_Z}{\partial P} = \frac{\frac{\partial \mathfrak{e}}{\partial v}}{\frac{\partial \mathcal{P}}{\partial v}}\bullet, \qquad \frac{\partial \boldsymbol{e}_Z}{\partial T} = \left(\frac{\partial \mathfrak{e}}{\partial T} - \frac{\partial \mathfrak{e}}{\partial v}\frac{\frac{\partial \mathcal{P}}{\partial T}}{\frac{\partial \mathcal{P}}{\partial v}}\right)\bullet,$$

$$\frac{\partial \mathcal{P}}{\partial v} = \frac{1}{\frac{\partial v_Z}{\partial P}}\bullet, \qquad \frac{\partial \mathcal{P}}{\partial T} = -\frac{\frac{\partial v_Z}{\partial T}}{\frac{\partial v_Z}{\partial P}}\bullet,$$

$$\frac{\partial \mathfrak{e}}{\partial v} = \frac{\frac{\partial e_Z}{\partial P}}{\frac{\partial v_Z}{\partial P}}\bullet, \qquad \frac{\partial \mathfrak{e}}{\partial T} = \left(\frac{\partial e_Z}{\partial T} - \frac{\partial e_Z}{\partial P}\frac{\frac{\partial v_Z}{\partial T}}{\frac{\partial v_Z}{\partial P}}\right)\bullet .$$

6.6 Change of variables

According to the previous considerations, **dealing only with a single phase**, we can choose at will the variables (v, T) or (e, v) or (T, P) (or (s, v) or (s, P), etc.) for describing the states of a material and we can use the known relations regarding the partial derivatives of constitutive functions.

We emphasize that such a change of variables is not correct on the whole regular domain.

6.7 A useful formalism

If $(D, \mathfrak{e}, \mathcal{P}, \mathfrak{y}, R)$ is a simple material, then

$$\{\mathfrak{e}(v,T), v, T, \mathcal{P}(v,T), \mathfrak{y}(v,T) \mid (v,T) \in R\} = \\ = \{e, v, \mathbf{T}(e,v), \mathbf{P}(e,v), \boldsymbol{\mu}(e,v) \mid (e,v) \in \mathrm{R}\}$$

is a two-dimensional submanifold in (J) × (m^3) × (K) × (Pa) × (J) (the graph of the continuously differentiable function $(\mathfrak{e}, \mathcal{P}, \mathfrak{y})|_R$ or $(\mathbf{T}, \mathbf{P}, \boldsymbol{\mu})|_\mathrm{R}$) whose closure contains the set Σ defined in 1.1.

Now we shall use some simple and well-known notions of the theory of manifolds allowing us to deduce useful formulae which can be well applied without any knowledge of manifolds.

The restriction of the functions e, etc. (see 1.2) onto the above manifold is continuously differentiable. Using the same symbols e, etc. for these restrictions, the equality

$$Ts = e + Pv - \mu$$

yields

$$s\mathtt{d}T + T\mathtt{d}s = \mathtt{d}e + v\mathtt{d}P + P\mathtt{d}v - \mathtt{d}\mu$$

for the differential of the functions.

The entropic property reads now

$$T\mathtt{d}s = \mathtt{d}e + P\mathtt{d}v,$$

or, equivalently (the Gibbs–Duhem relations),

$$\mathtt{d}\mu = -s\mathtt{d}T + v\mathtt{d}P.$$

Further, for the specific enthalpy $h = e + Pv$

$$\mathtt{d}h \ (= \mathtt{d}e + v\mathtt{d}P + P\mathtt{d}v) = T\mathtt{d}s + v\mathtt{d}P,$$

and for the specific free energy $f = e - Ts$

$$\mathtt{d}f \ (= \mathtt{d}e - s\mathtt{d}T - T\mathtt{d}s) = -P\mathtt{d}v - s\mathtt{d}T.$$

Leaving the theory of manifolds, we can conceive these easy available equalities as formal rules which summarize the relations among the partial derivatives of the functions in question with respect to diverse variables in such a way that $\mathtt{d}$ symbolize the derivative in arbitrary variables.

If the variables (v, T) are used, then

$$\mathtt{d}v = \left(\frac{\partial v}{\partial v}, \frac{\partial v}{\partial T}\right) = (1, 0), \qquad \mathtt{d}T = \left(\frac{\partial T}{\partial v}, \frac{\partial T}{\partial T}\right) = (0, 1),$$

$$\mathtt{d}e = \left(\frac{\partial \mathfrak{e}}{\partial v}, \frac{\partial \mathfrak{e}}{\partial T}\right), \qquad \text{etc.}$$

If the variables (e, v) are used, then

$$\mathtt{d}e = (1, 0), \qquad \mathtt{d}v = (0, 1), \qquad \mathtt{d}T = \left(\frac{\partial \mathbf{T}}{\partial e}, \frac{\partial \mathbf{T}}{\partial v}\right), \qquad \text{etc.}$$

If the variables (T, P) are used (which is always possible regarding a single phase Z), then

$$\mathtt{d}T = (1, 0), \qquad \mathtt{d}P = (0, 1), \qquad \mathtt{d}\mu_Z = \left(\frac{\partial \mu_Z}{\partial T}, \frac{\partial \mu_Z}{\partial P}\right), \qquad \text{etc.}$$

For instance, the condition

$$T\mathtt{d}s = \mathtt{d}e + P\mathtt{d}v$$

of the entropic property directly gives the formulae of 5.3 in the variables (e, v) but it yields – in the variables (T, P) for a given phase Z – also the relations

$$T\frac{\partial \boldsymbol{s}_Z}{\partial T} = \frac{\partial \boldsymbol{e}_Z}{\partial T} + P\frac{\partial \boldsymbol{v}_Z}{\partial T},$$

$$T\frac{\partial \boldsymbol{s}_Z}{\partial P} = \frac{\partial \boldsymbol{e}_Z}{\partial P} + P\frac{\partial \boldsymbol{v}_Z}{\partial P}.$$

6.8 Exercises

1. Give relations among the partial derivatives of $\mathbf{T}$ and $\mathbf{P}$, and the partial derivatives of $\boldsymbol{e}_Z$ and $\boldsymbol{v}_Z$.

2. Let Z be a phase of a material and $\boldsymbol{h}_Z := \boldsymbol{e}_Z + P\boldsymbol{v}_Z$, i.e. $\boldsymbol{h}_Z$ is the specific enthalpy of the material as a function of temperature and pressure. ($\boldsymbol{h}_Z(T, P) = \mathfrak{h}(\boldsymbol{v}_Z(T, P), T)$). Prove for entropic material that

$$\frac{\partial \boldsymbol{h}_Z}{\partial T} = \boldsymbol{c}_p, \qquad \frac{\partial \boldsymbol{h}_Z}{\partial P} = \boldsymbol{v}_Z - T\frac{\partial \boldsymbol{v}_Z}{\partial T},$$

where $\boldsymbol{c}_p$ is the specific heat at constant pressure as a function of (T, P).

3. Demonstrate $\frac{\partial s_Z}{\partial T} > 0$ for an entropic material.

4. Deduce the formulae of Exercises 2 and 3 of 5.5 2. and 3. from the formalism given in 6.7.

5. An ideal gas has only one phase. Suppose the specific heat of the ideal gas is λk (where $\lambda > 0$) and give the specific internal energy and specific volume as a function of temperature and pressure. Show that the chemical potential has the form

$$\mu(T,P) = kT\left((\lambda+1) - \log\left(\left(\frac{T}{T_0}\right)^{\lambda+1}\frac{P_0}{P}\right)\right) + e_0.$$

7 Phase connections

7.1 Introductory remarks

Now we examine what relations can have different phases of a material. The relation between two phases can be classified roughly as follows: the two phases

- overlap,
- are bordering,
- do not contact.

According to this classification – to be refined later – and keeping the historical names partly, we speak about zeroth-order, second-order and first-order phase connections, respectively.

We retained the historical names regarding the order, but in usual terminology one says phase transition instead of phase connection. The name phase transition in this respect, is, however, somewhat misleading because transition in everyday language means a process, thus phase transition should mean the process of phase change. The classifications of Ehrenfest and Tisza, the Clausius–Clapeyron equation, etc. characterize the phase lines and phase surfaces that appear on the well-known phase diagrams and do not refer to any processes. Using our terminology, we say that a phase transition can occur between two phases being in a phase connection.

The following considerations refer to a given simple material $(D, \mathfrak{e}, \mathcal{P}, \mathfrak{u}, R)$.

7.2 Zeroth-order phase connections

Definition *The* **zeroth-order connection** *of the phases* Z_1 *and* Z_2 *of the simple material is the set* $\overline{Z_1} \cap \overline{Z_2} \cap R$. *We say that the two phases have a zeroth-order connection if their zeroth-order connection is not void.*

Applying the usual notation for the boundary of sets ($\partial Z := \overline{Z} \setminus Z$, thus $\overline{Z} = Z \cup \partial Z$) and some trivial set-theoretical identities, taking into account that the phases are subsets of R, we can write the zeroth-order connection of the phases in the form

$$(Z_1 \cap Z_2) \cup (Z_1 \cap \partial Z_2) \cup (\partial Z_1 \cap Z_2) \cup (\partial Z_1 \cap \partial Z_2 \cap R).$$

The zeroth connection of two overlapping phases (like the liquid and gaseous phases) is not void but disjoint phases, too, can have a zeroth-order connection.

7.3 Second-order phase connections

Definition *The* **second-order connection** *of the phases Z_1 and Z_2 of the simple material is the set $\overline{Z_1} \cap \overline{Z_2} \cap (D \setminus R)$. We say that the two phases have a second-order connection if their second-order connection is not zero.*

Applying the previous simple set-theoretical identities and taking into account that the phases are disjoint from $(D \setminus R)$, we can describe the second-order phase connection in the form

$$\partial Z_1 \cap \partial Z_2 \cap (D \setminus R).$$

Thus the second-order connection contains only boundary points of the phases.

It is evident that a point cannot belong to both the zeroth-order connection and the second-order connection. It may happen, however, that two phases can have both zeroth-order connection and second-order connection. For instance, the second-order connection of the liquid and gaseous phases of a van der Waals material is the critical point as it is obvious from the formulae of 6.3.

The second-order phase connection contains boundary points of R; consequently, in such points $(\mathfrak{e}, \mathcal{P}, \boldsymbol{\mu})$

– is not continuously differentiable, or

– does not satisfy at least one of the conditions of intrinsic stability.

The points of the second-order phase connection in the canonical variables can be characterized similarly: there $(\mathbf{T}, \mathbf{P}, \boldsymbol{\mu})$

– is not continuously differentiable, or

– does not satisfy at least one of the conditions of intrinsic stability, i.e. the derivative of $(\mathbf{T}, \mathbf{P})$ is not positive definite.

7.4 λ transitions

It is typical that in some points of the second-order phase connection the specific heat becomes ‘infinite’, i.e. $\frac{\partial \mathfrak{e}}{\partial T}$ is not defined in such a point (v_m, T_m) and its reciprocal tends to zero at (v_m, T_m).

This can be illustrated by a simple diagram in such a way that the horizontal axis represents the states, one of the phases stands on the left of the point (v_m, T_m), the other on the right, and the specific heat values are represented on the vertical axis (Figure 7.1).

If a process passes through the phase connection (e.g. it runs in the diagram from the right to the left), then the specific heat becomes ‘infinite’: such processes are called λ **transitions** because of the form of this curve.

Experience shows λ transitions in which specific heat increases infinitely only on one side, and transitions in which specific heat has a finite jump (Figure 7.2).

It is worth examining the λ transitions in canonical variables, too. If specific heat becomes infinite in both sides, then $(\mathbf{T}, \mathbf{P})$ is continuously differentiable but $\frac{\partial \mathbf{T}}{\partial e}$ becomes zero in the transition point: the first condition of intrinsic stability is not satisfied (the derivative of $(\mathbf{T}, \mathbf{P})$ is negative semidefinite there). If the λ transition is infinite only on one side, then $(\mathbf{T}, \mathbf{P})$ is not differentiable in the transition point.

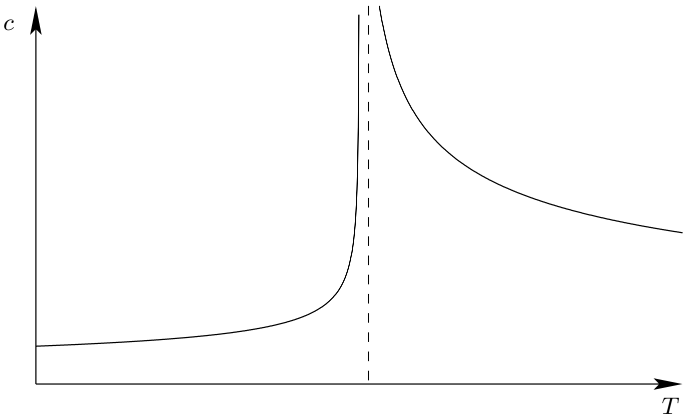

Figure 7.1

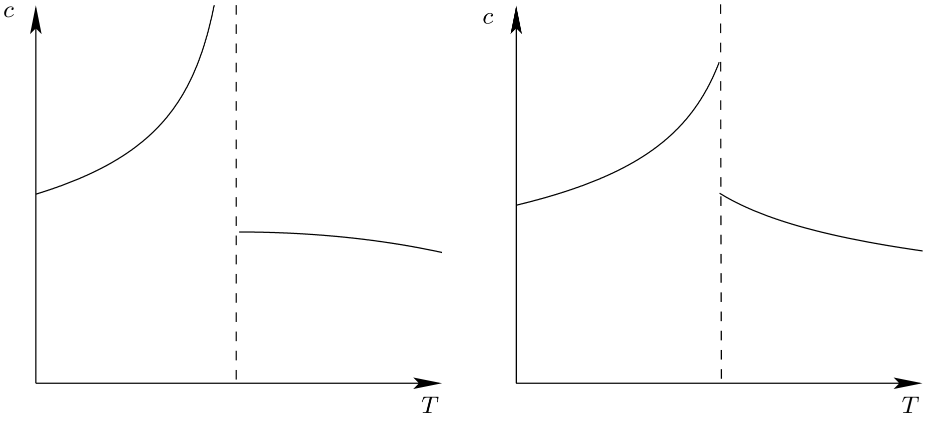

Figure 7.2

7.5 On the classification of second-order phase connections

The considerations in the previous paragraph are only illustrations; a thorough treatment of second-order phase connections requires the clarification of the notion of one-sided derivatives which is not easy because the functions in question – contrary to the illustrative diagrams – have two variables.

Lastly we mention that in the usual literature only the transitions with two-sided infinity (called transitions of Tisza type) and transitions with finite jumps (called transitions of Ehrenfest type) are treated.[1]

7.6 First-order phase connections

The first-order phase connections (‘transitions’) are usually defined by the equal values of the chemical potentials of the phases (see 6.5).

This involves two problems. First, in this way the usual phase lines mentioned in 6.1 would be obtained in the T–P plane but we want to get the phase connection as a subset in the v–T plane (or in canonical variables, in the e–v plane). Second, the chemical potentials can be equal on a too large set, e.g. on the whole intersection of the liquid and gaseous phases.

The second problem can be ruled out by excluding the intersection of the phases from the definition (equivalently, by excluding the zeroth-order connections and the second-order connections, which is a natural requirement).

Definition 1 *Let* Z_1 *and* Z_2 *be two phases of a simple material. We say that* $(v_1, T) \in Z_1 \setminus \overline{Z_2}$ *and* $(v_2, T) \in Z_2 \setminus \overline{Z_1}$ *are in* **first-order connection with each other** *if* $\mathcal{P}(v_1, T) = \mathcal{P}(v_2, T)$ *and* $\boldsymbol{\mu}(v_1, T) = \boldsymbol{\mu}(v_2, T)$.

Definition 2 *Let* C_1 *be the subset of states in* $Z_1 \setminus \overline{Z_2}$ *which are in first-order connection with some states in* $Z_2 \setminus \overline{Z_1}$ *and let* C_2 *be the similar set* $Z_2 \setminus \overline{Z_1}$. *The* **first-order connection** *of the phases* Z_1 *and* Z_2 *is the pair* (C_1, C_2). *The phases are in first-order connection if the sets* C_1 *and* C_2 *are not void.*

For fixed T the function $v \mapsto \mathcal{P}(v, T)$ is injective on the phases, therefore every state in C_1 is in first-order connection with exactly one state in C_2, and vice versa; thus ‘being in first-order connection’ is a bijection between C_1 and C_2.

The van der Waals material helps us grasp the essence of first-order phase connections (see 7.9).

7.7 Clausius–Clapeyron equation

Let (C_1, C_2) be the first-order connection of the phases Z_1 and Z_2. Then we have

$$(\mathcal{T}, \mathcal{P})[C_1] = (\mathcal{T}, \mathcal{P})[C_2] =: \Gamma$$

and $\mu_1(T, P) = \mu_2(T, P)$ if $(T, P) \in \Gamma$ where μ_1 and μ_2 are the chemical potentials of the phases Z_1 and Z_2 as defined in 6.5. The converse of the latter assertion is true also:

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[1] A general study of second-order phase connections is given in the paper by T. Matolcsi: Classification of Phase Transitions, *ZAMP* 47(1996)837–857

Proposition 1

$$\Omega := (\mathcal{T},\mathcal{P})[Z_1 \setminus \overline{Z_2}] \cap (\mathcal{T},\mathcal{P})[Z_2 \setminus \overline{Z_1}] \subset (\mathrm{K})^+ \times (\mathrm{Pa})$$

is an open subset and

$$\Gamma = \{(T,P) \in \Omega \mid \mu_1(T,P) = \mu_2(T,P)\}.$$

Proof $(\mathcal{T},\mathcal{P})$ is continuously differentiable and injective on the phases and this is true for its inverses, too, so it maps open subsets of the phases onto open subsets. Consequently, Ω is open. Further, the definition of first-order connections implies trivially that $\mu_1(T,P) \neq \mu_2(T,P)$ if $(T,P) \in \Omega \setminus \Gamma$.

Proposition 2 *If the simple material is entropic, then C_1 and C_2 are curves in $Z_1 \setminus \overline{Z_2}$ and $Z_2 \setminus \overline{Z_1}$, respectively. Γ is a curve in Ω which is determined by the Clausius–Clapeyron differential equation (see below).*

Proof If $(T,P) \in \Gamma$, then $\big(\boldsymbol{v}_1(T,P),T\big) \in C_1$ and $\big(\boldsymbol{v}_2(T,P),T\big) \in C_2$, therefore these elements cannot be equal, $\boldsymbol{v}_1(T,P) - \boldsymbol{v}_2(T,P) \neq 0$. The Gibbs–Duhem relations (see 6.5 $(*)$) and the implicit function theorem imply that every element (T_0,P_0) of Γ – the set where $\mu_1 - \mu_2$ takes zero values – has a neighbourhood Δ such that $\Gamma \cap \Delta$ is the graph of a continuously differentiable function $(\mathrm{K})^+ \rightarrowtail (\mathrm{Pa})$ which is the solution of the differential equation

$$\frac{dP}{dT} = \frac{\boldsymbol{s}_1(T,P) - \boldsymbol{s}_2(T,P)}{\boldsymbol{v}_1(T,P) - \boldsymbol{v}_2(T,P)} \tag{$*$}$$

with initial value $P(T_0) = P_0$. As a consequence, Γ is a one-dimensional submanifold, i.e. a curve.

Then it is evident that C_1 and C_2 are curves, as images of Γ by the continuously differentiable inverses of the functions $(\mathcal{T},\mathcal{P})|_{Z_1}$ and $(\mathcal{T},\mathcal{P})|_{Z_2}$, respectively. ☐

The differential equation $(*)$ is called the Clausius–Clapeyron equation.

Using the **transformation heat**

$$q_{12}(T,P) := T\boldsymbol{s}_1(T,P) - T\boldsymbol{s}_2(T,P) \qquad ((T,P) \in \Gamma)$$

we can write the Clausius–Clapeyron equation in the form

$$\frac{dP}{dT} = \frac{q_{12}(T,P)}{T\big(\boldsymbol{v}_1(T,P) - \boldsymbol{v}_2(T,P)\big)}$$

which is suitable because it refers to directly measurable quantities.

Now the reader is asked to revert to 3.12.

7.8 Critical points

Definition *Let (C_1,C_2) be the first-order connection of the phases Z_1 and Z_2. The points of the set $\overline{C}_1 \cap \overline{C}_2 \cap D$ are called the* **critical points** *of the two phases.*

Proposition *The critical points of two phases belong to the second-order connection of the phase.*

Proof It is evident that the critical points are in the set $\overline{Z_1} \cap \overline{Z_2} \cap D$, thus we have only to show that they are not in R. Let (v_c, T_c) be a critical point and suppose it is in R. Then it has a neighbourhood in which $(\mathcal{T}, \mathcal{P})$ is injective and its inverse is continuously differentiable. Consequently, – because (v_c, T_c) is an element of the closures of C_1 and C_2 – $(T_c, P_c) := \big(T_c, \mathcal{P}(v_c, T_c)\big)$ is in the closure of Γ. If U is an arbitrary neighbourhood of (v_c, T_c), then $(\mathcal{T}, \mathcal{P})[U]$ is a neighbourhood of (T_c, P_c), thus $\Gamma \cap (\mathcal{T}, \mathcal{P})[U] \neq \emptyset$. This means that there are (v_1, T_1) in $C_1 \cap U$ and (v_2, T_2) in $C_2 \cap U$ such that $T_1 = T_2$ and $\mathcal{P}(v_1, T_1) = \mathcal{P}(v_2, T_2)$. We arrived at the contradiction that $(\mathcal{T}, \mathcal{P})$ is not injective in any neighbourhood of (v_c, T_c); as a consequence, (v_c, T_c) cannot be in R.

7.9 First-order phase connections of the van der Waals material

Let us recall the purely liquid phase and the purely gaseous phase (see Figure 6.2) which correspond to $Z_1 \setminus \overline{Z}_2$ and $Z_2 \setminus \overline{Z}_1$ in the previous paragraph. The curves C_1 and C_2 lay in these sets; temperature, pressure and chemical potential take the same values in the corresponding points of C_1 and C_2. A horizontal line intersects an isotherm below the critical temperature (Figure 7.3) in points where temperature and pressure have the same values. We have to determine which of the horizontal lines intersects the isotherm in points where also the chemical potential has the same value.

Let us accept that the constitutive functions are valid in the form given in 2.2 outside the constitutive domain, too, i.e. in the part of the v–T plane where $\frac{\partial \mathcal{P}}{\partial v} > 0$ (which is the part below the spinodal lines). In this part, as in a phase, the function $v \mapsto \mathcal{P}(v, T)$ is injective, thus in this part, too, specific volume can be given as a continuously differentiable function of temperature and pressure; let $\boldsymbol{v}_0$ be this function. Then the chemical potential can also be given there as a continuously differentiable function of temperature and pressure and the Gibbs–Duhem relations (see 6.5 (∗)) hold for this function μ_0. The continuity of the function $\boldsymbol{\mu}$ formally extended outside the constitutive domain implies that μ_1 and μ_0 can be continuously extended to the spinodal line S_1 where their extensions coincide; similar can be said about μ_2, μ_0 and S_2.

Let us fix a temperature T below the critical value and let $P_{min}(T)$ and $P_{max}(T)$ be the pressure values where the isotherm with temperature T has minimum and maximum, respectively. According to the previous considerations, we have $\mu_1(T, P_{min}(T)) = \mu_0(T, P_{min}(T))$ and $\mu_0(T, P_{max}(T)) = \mu_2(T, P_{max}(T))$.

Because

$$\mu_1(T, P) - \mu_2(T, P) = \big[\mu_1(T, P) - \mu_1(T, P_{min}(T))\big] + \\ + \big[\mu_0(T, P_{min}(T)) - \mu_0(T, P_{max}(T))\big] + \big[\mu_2(T, P_{max}(T)) - \mu_2(T, P)\big]$$

holds for an arbitrary pressure P, the Gibbs–Duhem relation regarding the partial

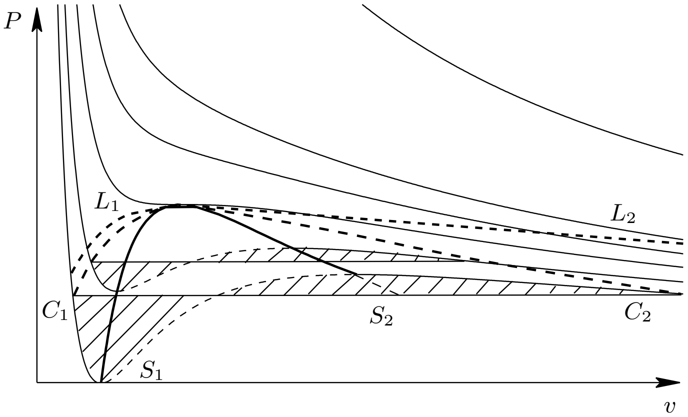

Figure 7.3

derivative of the chemical potential yields

$$\mu_2(T,P) - \mu_1(T,P) =$$
$$= \int\limits_{P}^{P_{min}(T)} \boldsymbol{v}_1(T,\pi)d\pi + \int\limits_{P_{min}(T)}^{P_{max}(T)} \boldsymbol{v}_0(T,\pi)d\pi + \int\limits_{P_{max}(T)}^{P} \boldsymbol{v}_2(T,\pi)d\pi.$$

The points $\boldsymbol{v}_1(T,P)$ and $\boldsymbol{v}_2(T,P)$ on the isotherm with temperature T which correspond to the curves C_1 and C_2, respectively are determined by the pressure P for which the sum of the three integrals is zero. This means that the marked areas on Figure 7.3 are equal which is called the Maxwell rule. We point out that the equality of areas is the consequence of a formal calculation, it has no physical meaning.

Now we can easily draw the image of C_1 and C_2 on the v–P plane (denoted by the same letters C_1 and C_2 in Figure 7.3), called usually the **binodal lines**. It is evident that the critical point according to definition 7.8 is just the critical point of the van der Waals material defined in 4.4.2.

7.10 Exercises

Treat the first-order phase connections according to the following scheme.

1. Let Z_1 and Z_2 be two phases of a simple material in the canonical variables. $(e_1, v_1) \in \mathrm{Z}_1 \setminus \overline{\mathrm{Z}_2}$ and $(e_2, v_2) \in \mathrm{Z}_2 \setminus \overline{\mathrm{Z}_1}$ are in first-order connection with each other if $(\mathbf{T}, \mathbf{P}, \boldsymbol{\mu})(e_1, v_1) = (\mathbf{T}, \mathbf{P}, \boldsymbol{\mu})(e_2, v_2)$.

2. The first-order conection of the two phases is the pair $(\mathrm{C}_1, \mathrm{C}_2)$ where C_1 consists of the states in $\mathrm{Z}_1 \setminus \overline{\mathrm{Z}_2}$ which are in first-order connection with some state in $\mathrm{Z}_2 \setminus \overline{\mathrm{Z}_1}$ and C_2 has a similar meaning.

3. ‘To be in first-order connection’ is a bijection between C_1 and C_2.

4. $\Gamma = (\mathbf{T}, \mathbf{P})[\mathrm{C}_1] = (\mathbf{T}, \mathbf{P})[\mathrm{C}_2]$.

8 Bodies

8.1 The notion of a body

A body is just a certain amount of a material: a glass of water, a piece of ice, a tube of air, etc. The number of particles in the body can change: the water evaporates, the ice is melting, the air escapes, etc. A state of a body is characterized by the state of its material and the **particle number** of the body. The values of the particle number are actually positive integers but we consider them being arbitrary positive real numbers, in other words, particle number is supposed to be a 'continuous variable'. This little deception corresponds to the everyday practice that mass of a material is considered to be continuously distributed. Moreover, we allow the zero value of the particle number, too, for the possibility of treating processes in which the body disappears (e.g. the ice melted completely).

Definition *A* **body** *consisting of a general simple material* Σ *is the set* $\Sigma \times \mathbb{R}_0^+$.

This definition is the most general one; in the sequel, however, we shall use it only for bodies consisting of simple materials. A body consisting of a material $(D, \mathfrak{e}, \mathcal{P}, \mu, R)$ will be denoted by

$$(D \times \mathbb{R}_0^+, \mathfrak{e}, \mathcal{P}, \mu, R), \quad \text{and} \quad (\mathrm{D} \times \mathbb{R}_0^+, \mathbf{T}, \mathbf{P}, \boldsymbol{\mu}, \mathrm{R}),$$

according to which variables are used.

The body is called **entropic** if its material is entropic.

At first sight we are inclined to call states the elements of $D \times \mathbb{R}_0^+$ but we must be aware that only one state corresponds to the zero value of particle number, therefore, $(v_1, T_1, 0)$ and $(v_2, T_2, 0)$ are the same state for all (v_1, T_1) and (v_2, T_2) in D. That is why we accept that the elements of $D \times \mathbb{R}^+$ as well as the set $D \times \{0\}$ are the **states** of the body.

If we examine processes of a body in which the particle number is constant, then the zero value of particle number is uninteresting (nothing happens) and in the case of non-zero value of particle number we can disregard the particle number and we can regard the pair (v, T) – or (e, v) – as the state of the body.

8.2 The entire quantities

Treating bodies and denoting by N the particle number, we find it suitable to use the **entire volume** $V := Nv$ as a variable instead of specific volume which means exactly the following. The infinitely differentiable function

$$(\mathrm{m}^3)^+ \times (\mathrm{K})^+ \times \mathbb{R}_0^+ \to (\mathrm{m}^3)_0^+ \times (\mathrm{K})^+ \times \mathbb{R}_0^+,$$
$$(v, T, N) \mapsto (Nv, T, N) =: (V, T, N)$$

maps the set $D \times \{0\}$ (the state with zero value of particle number) into a subset of $0 \times (\mathrm{K})^+ \times 0$ and establishes a bijection between $(\mathrm{m}^3)^+ \times (\mathrm{K})^+ \times \mathbb{R}^+$ and $(\mathrm{m}^3)^+ \times (\mathrm{K})^+ \times \mathbb{R}^+$, and here it has the infinitely differentiable inverse

$$(V, T, N) \mapsto (V/N, T, N).$$

On the set

$$\{(V, T, N) \mid N \neq 0,\ (V/N, T) \in D\}$$

we introduce the function

$$\hat{\mathcal{P}}(V, T, N) := \mathcal{P}(V/N, T)$$

and similarly the function $\hat{\mu}$. For the sake of brevity and perspicuity, we accept the usual ambiguous notation that we write $\mathcal{P}$ and μ instead of $\hat{\mathcal{P}}$ and $\hat{\mu}$, respectively, i.e. two different functions will be denoted by the same symbol. Then we easily derive:

$$\frac{\partial \mathcal{P}}{\partial V} = \frac{1}{N}\frac{\partial \mathcal{P}}{\partial v}, \qquad \frac{\partial \mathcal{P}}{\partial N} = -\frac{v}{N}\frac{\partial \mathcal{P}}{\partial v},$$

where, of course, the variables are (V, T, N) on the left-hand side, and $(v, T) = (V/N, T)$ on the right-hand side.

Furthermore, the entire quantities are used instead of the specific ones:
$\mathcal{E}(V, T, N) := N\mathfrak{e}(V/N, T)$ is the (entire) internal energy,
$\mathcal{S}(V, T, N) := N\mathfrak{s}(V/N, T)$ is the (entire) entropy,
$\mathcal{H}(V, T, N) := N\mathfrak{h}(V/N, T)$ is the (entire) enthalpy,
$\mathcal{F}(V, T, N) := N\mathfrak{f}(V/N, T)$ is the (entire) free energy.

Then

$$\frac{\partial \mathcal{E}}{\partial V} = \frac{\partial \mathfrak{e}}{\partial v}, \qquad \frac{\partial \mathcal{E}}{\partial T} = N\frac{\partial \mathfrak{e}}{\partial T}, \qquad \frac{\partial \mathcal{E}}{\partial N} = \mathfrak{e} - v\frac{\partial \mathfrak{e}}{\partial v},$$

and similar relations hold for $\mathcal{S}$, $\mathcal{H}$ and $\mathcal{F}$.

As a consequence, the partial derivatives of the entire quantities satisfy the same relations as the derivatives of the specific quantities; e.g. for an entropic body

$$T\frac{\partial \mathcal{S}}{\partial V} = \frac{\partial \mathcal{E}}{\partial V} + \mathcal{P}, \qquad T\frac{\partial \mathcal{S}}{\partial T} = \frac{\partial \mathcal{E}}{\partial T},$$

$$\frac{\partial \mathcal{F}}{\partial V} = -\mathcal{P}, \qquad \frac{\partial \mathcal{F}}{\partial T} = -\mathcal{S},$$

moreover, we have

$$T\frac{\partial \mathcal{S}}{\partial N} = \frac{\partial \mathcal{E}}{\partial N} - \mu, \qquad \frac{\partial \mathcal{F}}{\partial N} = \mu.$$

8.3 Entire canonical variables

It is often convenient to use the **(entire) internal energy** E and the **(entire) volume** V instead of specific internal energy e and specific volume v, respectively. The infinitely differentiable function

$$\begin{aligned}(\mathrm{J})^+ \times (\mathrm{m}^3)^+ \times \mathbb{R}_0^+ &\to (\mathrm{J})_0^+ \times (\mathrm{m}^3)_0^+ \times \mathbb{R}_0^+,\\ (e, v, N) &\mapsto (Ne, Nv, N) =: (E, V, N)\end{aligned}$$

maps the set $D \times \{0\}$ (the state with zero value of particle number) into the single element $(0, 0, 0)$ and establishes a bijection between $(\mathrm{J})^+ \times (\mathrm{m}^3)^+ \times \mathbb{R}^+$ and $(\mathrm{J})^+ \times (\mathrm{m}^3)^+ \times \mathbb{R}^+$ and here it has the infinitely differentiable inverse

$$(E, V, N) \mapsto (E/N, V/N, N).$$

For an arbitrary subset H of $(\mathrm{J})^+ \times (\mathrm{m}^3)^+$ we introduce the notation

$$\mathrm{H} * \mathbb{R}^+ := \{(Ne, Nv, N) \mid (e, v) \in \mathrm{H}, N \in \mathbb{R}^+\}.$$

In the sequel we shall identify the sets $\mathrm{D} \times \mathbb{R}^+$ and $\mathrm{D} * \mathbb{R}^+$, i.e. in the case $N \neq 0$, instead of the state (e, v, N) we shall use the corresponding (E, V, N), called also state. Besides such states, $(0, 0, 0) \in (\mathrm{J})^+_0 \times (\mathrm{m}^3)^+_0 \times \mathbb{R}^+_0$ is a state of the body.

The quantities (E, V, N) are called the entire canonical variables. The use of the entire canonical variables has the advantage that the state with zero value of particle number is represented by a single element.

In what follows we always consider $N \neq 0$.

Using the variables (E, V, N), we introduce the function

$$\hat{\mathbf{T}}(E, V, N) := \mathbf{T}(E/N, V/N)$$

and similarly the functions $\hat{\mathbf{P}}$ and $\hat{\boldsymbol{\mu}}$ which are continuously differentiable on the set $\mathrm{R} * \mathbb{R}^+$.

For the sake of brevity and perspicuity, we accept the usual ambiguous notation that we write $\mathbf{T}$ instead of $\hat{\mathbf{T}}$, i.e. two different functions will be denoted by the same symbol. Then we easily derive:

$$\frac{\partial \mathbf{T}}{\partial E} = \frac{1}{N}\frac{\partial \mathbf{T}}{\partial e}, \qquad \frac{\partial \mathbf{T}}{\partial V} = \frac{1}{N}\frac{\partial \mathbf{T}}{\partial v},$$

where, of course, the variables are (E, V, N) on the left-hand side and $(e, v) = (E/N, V/N)$ on the right-hand side.

Furthermore,

$$\frac{\partial \mathbf{T}}{\partial N} = \frac{1}{N}\left(-e\frac{\partial \mathbf{T}}{\partial e} - v\frac{\partial \mathbf{T}}{\partial v}\right), \tag{$*$}$$

or, equivalently,

$$E\frac{\partial \mathbf{T}}{\partial E} + V\frac{\partial \mathbf{T}}{\partial V} + N\frac{\partial \mathbf{T}}{\partial N} = 0,$$

and similar formulae hold for $\mathbf{P}$ and $\boldsymbol{\mu}$, too.

For the functions
- $\mathbf{S}(E, V, N) := N\mathbf{s}(E/N, V/N)$,
- $\mathbf{H}(E, V, N) := N\mathbf{h}(E/N, V/N)$,
- $\mathbf{F}(E, V, N) := N\mathbf{f}(E/N, V/N)$

(using the ambiguous notations) we easily obtain

$$\frac{\partial \mathbf{S}}{\partial E} = \frac{\partial \mathbf{s}}{\partial e}, \qquad \frac{\partial \mathbf{S}}{\partial V} = \frac{\partial \mathbf{s}}{\partial v}$$

and

$$\frac{\partial \mathbf{S}}{\partial N} = \mathbf{s} - e\frac{\partial \mathbf{s}}{\partial e} - v\frac{\partial \mathbf{s}}{\partial v}$$

and similar formulae for $\mathbf{H}$ and $\mathbf{F}$, too.

8.4 Entropic property in the entire canonical variables

If the body is entropic, we have for the entire entropy in the entire canonical variables

$$\frac{\partial \mathbf{S}}{\partial E} = \frac{1}{\mathbf{T}}, \quad \frac{\partial \mathbf{S}}{\partial V} = \frac{\mathbf{P}}{\mathbf{T}}, \quad \frac{\partial \mathbf{S}}{\partial N} = -\frac{\boldsymbol{\mu}}{\mathbf{T}},$$

in other words,

$$\mathtt{D}\mathbf{S} = \left(\frac{1}{\mathbf{T}}, \frac{\mathbf{P}}{\mathbf{T}}, -\frac{\boldsymbol{\mu}}{\mathbf{T}}\right).$$

The second derivative of the entropy is

$$\mathtt{D}^2\mathbf{S} = -\frac{1}{\mathbf{T}^2}\begin{pmatrix} \frac{\partial \mathbf{T}}{\partial E} & \frac{\partial \mathbf{T}}{\partial V} & \frac{\partial \mathbf{T}}{\partial N} \\ \mathbf{P}\frac{\partial \mathbf{T}}{\partial E} - \mathbf{T}\frac{\partial \mathbf{P}}{\partial E} & \mathbf{P}\frac{\partial \mathbf{T}}{\partial V} - \mathbf{T}\frac{\partial \mathbf{P}}{\partial V} & \mathbf{P}\frac{\partial \mathbf{T}}{\partial N} - \mathbf{T}\frac{\partial \mathbf{P}}{\partial N} \\ -\boldsymbol{\mu}\frac{\partial \mathbf{T}}{\partial E} + \mathbf{T}\frac{\partial \boldsymbol{\mu}}{\partial E} & -\boldsymbol{\mu}\frac{\partial \mathbf{T}}{\partial V} + \mathbf{T}\frac{\partial \boldsymbol{\mu}}{\partial V} & -\boldsymbol{\mu}\frac{\partial \mathbf{T}}{\partial N} + \mathbf{T}\frac{\partial \boldsymbol{\mu}}{\partial N} \end{pmatrix}.$$

It is symmetric, thus some relations hold among certain partial derivatives. We see immediately from the equality 8.3 $(*)$ and the similar equality for $\mathbf{P}$ and $\boldsymbol{\mu}$ that the last row of the matrix is a linear combination of the first ones, therefore, the matrix has zero determinant. Furthermore, it is trivial that the inequalities expressing the negative definiteness of specific entropy remain valid for the entire entropy:

$$\frac{\partial \mathbf{T}}{\partial E} > 0, \qquad \frac{\partial \mathbf{T}}{\partial E}\frac{\partial \mathbf{P}}{\partial V} - \frac{\partial \mathbf{T}}{\partial V}\frac{\partial \mathbf{P}}{\partial E} < 0.$$

All these yield the following important result.

Proposition $\mathtt{D}^2\mathbf{S}(E,V,N)$ *is negative semidefinite for all* $(E,V,N) \in \mathrm{R} * \mathbb{R}^+$*; its kernel is one-dimensional, spanned by* (E,V,N).

In usual treatments of thermodynamics one often requires that the second derivative of the entire entropy be negative definite[2], which is impossible.

It is worth noting here that the sum of two negative semidefinite forms is negative semidefinite, too; if the intersection of their kernels is zero, then their sum is negative definite. As a consequence, $\mathtt{D}^2\mathbf{S}(E_1,V_1,N_1) + \mathtt{D}^2\mathbf{S}(E_2,V_2,N_2)$ is negative definite if and only if (E_1,V_1,N_1) and (E_2,V_2,N_2) are not parallel, or equivalently, $(E_1/N_1, V_1/N_1) \neq (E_2/N_2, V_2/N_2)$.

8.5 A useful formalism

Corresponding to paragraph 6.7,

$$\begin{aligned}\{\mathcal{E}(V,T,N), V, T, \mathcal{P}(V,T,N), \mu(V,T,N) \mid (V,T,N) \in R \times \mathbb{R}^+\} &= \\ = \{E, V, \mathbf{T}(E,V,N), \mathbf{P}(E,V,N), \boldsymbol{\mu}(E,V,N) \mid (E,V,N) \in \mathrm{R} \times \mathbb{R}^+\}&\end{aligned}$$

is a three-dimensional submanifold in (J) × (m^3) × (K) × (Pa) × (J) × $\mathbb{R}$.

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[2] H.B.Callen: *Thermodynamics*, Wiley and Sons, N.Y. 1985, p. 38

The entire quantities can be considered as defined on this manifold, and applying the usual symbols, we can write

$$TS = E + PV - \mu N,$$

which yields

$$S\mathtt{d}T + T\mathtt{d}S = \mathtt{d}E + V\mathtt{d}P + P\mathtt{d}V - N\mathtt{d}\mu - \mu\mathtt{d}N.$$

for the differential of the functions.

The entropic property reads now

$$T\mathtt{d}S = \mathtt{d}E + P\mathtt{d}V - \mu\mathtt{d}N,$$

or, equivalently (the Gibbs–Duhem relations),

$$N\mathtt{d}\mu = -S\mathtt{d}T + V\mathtt{d}P.$$

Further, for the entire enthalpy $H = E + PV$

$$\mathtt{d}H (= \mathtt{d}E + V\mathtt{d}P + P\mathtt{d}V) = T\mathtt{d}S + V\mathtt{d}P + \mu\mathtt{d}N,$$

and for the entire free energy $F = E - TS$

$$\mathtt{d}F (= \mathtt{d}E - S\mathtt{d}T - T\mathtt{d}S) = -P\mathtt{d}V - S\mathtt{d}T + \mu\mathtt{d}N.$$

Leaving the theory of manifolds, we can conceive these easily available equalities as formal rules which summarize the relations among the partial derivatives of the functions in question with respect to diverse variables in such a way that $\mathtt{d}$ symbolize the derivative in arbitrary variables.

8.6 Legendre transforms

Our considerations in this paragraph concern the regular domain.

For an entropic body, the partial derivatives of the entire entropy in the canonical variables are simple combinations of the constitutive functions. Therefore the 'natural variables' of the entropy are (E, V, N).

The Legendre transform (see App. 4) of the entropy with respect to E is $S - \frac{E}{T}$, having $\left(\frac{1}{T}, V, N\right)$ as natural variables. Multiplying it by $-T$, we get the free energy, having (T, V, N) as natural variables (or, in our usual order (V, T, N).

We can argue in another way. Entropy is a (locally) strictly monotone function of the energy, thus E can be expressed as a function of (S, V, N) which are the 'natural variables' of energy, because, as it is easily seen from the previous paragraph, the partial derivatives of energy are T, $-P$ and μ as functions of (S, V, N). The Legendre transform of the energy with respect to the entropy is the free energy having (V, T, N) as natural variables; the partial derivatives of the free energy then are $-P$, $-S$ and μ.

The free energy and the Legendre transform of the energy with respect to the entropy and the particle number play a fundamental role in statistical physics. The latter one is

$$J := E - TS - \mu N,$$

having (V, T, μ) as natural variables:

$$\mathtt{d}J = -P\mathtt{d}V - S\mathtt{d}T - N\mathtt{d}\mu,$$

where P, S and N are functions of (V, T, μ).

8.7 Exercises

1. Deduce relations for the partial derivatives of the entire free energy in the canonical variables.

2. Give the pressure as a function of (V, T, N) and then as a function of (E, V, N) for a body consisting of an ideal gas and a body consisting of a van der Waals material, if the specific heat is constant.

II SYSTEM OF SIMPLE BODIES: A SURVEY

9 Dynamics of processes

9.1 Introductory remarks

In the previous chapter the kinematics (formal properties) of processes were treated; in the present chapter we examine the dynamics of processes.

Systems of bodies, dynamics of their processes, dynamical quantities, etc. appear in this chapter heuristically; the exact definitions will be given in Chapter IV.

The state of a body is the joint of its volume, temperature and particle number, or its internal energy, volume and particle number; according to what has been said earlier, the state – except the one with zero particle number – can be described by (v, T, N) or (e, v, N) or (V, T, N) or (E, V, N).

The total canonical variables (E, V, N) are the most convenient for general considerations; of course, everything can be formulated in other variables, too, and in some special cases other variables can be used more efficiently.

A **process** of a simple body is the time change of its state: a function $t \mapsto \big(E(t), V(t), N(t)\big)$ defined on a time interval. For the notations see 3.1.

The internal energy of a body can change in three ways: by conduction, by doing work and by gaining (or losing) particles.

We shall follow the usual way of speaking, originating from the early period of thermodynamics, which suggests as if there were a ‘heat quantity’, but we emphasize that this is not true. The word ‘heat’ always refers to some special change of internal energy. For instance, one speaks about ‘the heat given to a body’ which means in a right setting ‘the internal energy given to the body by conduction’. A further usual notion is the freezing heat which means in reality the difference of internal energy in a liquid state and in a solid state and this amount of internal energy is conducted to the environment when freezing.

9.2 The dynamical equation

As said in the Introduction, our basic concept is that the dynamics of processes is described by differential equations: a process $t \mapsto \big(E(t), V(t), N(t)\big)$ governed by the following **dynamical equation**:

$$\dot{E} = Q + W + L, \qquad \dot{V} = F, \qquad \dot{N} = G.$$

The **dynamical quantities** on the right-hand side are the following:

– the **heating** Q is the internal energy conducted to the body in unit time,

– the **working** W is the work done on the body in unit time,

– the **transferring** L is the internal energy conveyed by particles to the body in a unit time,

– the **springing** F is volume change in unit time,

– the **converting** G is the particle number change in unit time,

which are functions defined on $\mathrm{D} * \mathbb{R}^+$ (e.g. $Q = \mathbf{Q}(E, V, N)$) but this is not written for the sake of brevity.

The first member of the dynamical equation is the **first law of thermodynamics**. We emphasize that it is only one member of the dynamical equation, which is not sufficient for determining processes.

Let us note that

1. the first law here concerns only homogeneous processes, thus it is less general than that mentioned in Paragraph 5 of the Introduction,

2. the quantities Q, W and L refer to unit time, contrary to the quantities denoted by the same letters in Paragraph 5 of the Introduction.

9.3 About working and transferring

Working always contains a part due to the extension (contraction) of the body. The force the body exerts on a surface element equals the product of the pressure and the surface element, and the work performed on the surface element equals the product of force and displacement. Consequently, the expansion work performed in unit time is $-P\dot{V}$ (the negative sign appears because working in the first law is positive if it increases the internal energy of the body). Working can contain other parts, too; for instance, during expansion the body works against viscous friction.

Working is called **ideal** if

$$W = -PF.$$

As mentioned, the chemical potential expresses the internal energy change due to the arrival of a particle at the body. This means that if the transferring is **ideal** then

$$L = \mu G.$$

Nonideal transferring occurs e.g. if the average kinetic energy of the arriving particles differs from that of the particles in the body.

We suppose that the nonideal parts of working and transferring are proportional to the square of springing and converting, respectively; thus the working and transferring have the form

$$W = -PF + \pi F^2, \qquad L = \mu G + \xi G^2$$

where $\pi \geq 0$, the **mechanical lost coefficient** and $\xi \geq$ the **material lost coefficient** are ‘small near to equilibrium’; the exact notion of the expression in quotations marks will be given in 10.7.

9.4 A few words about the first law

In usual treatments one writes the first law in the form

$$\mathtt{d}E = \delta Q + \delta W \tag{1}$$

considering tacitly bodies with constant particle number. This correspond to our

$$\dot{E} = Q + W, \quad \text{more precisely} \quad \dot{E} = \mathbf{Q}(E, V) + \mathbf{W}(E, V). \tag{1'}$$

One says that $\mathtt{d}E$ is a total differential while the 'infinitesimal heat' δQ and the 'infinitesimal work' δW are not total differentials. This means in our framework that there is no function $(E, V) \mapsto \Phi(E, V)$ such that $\mathbf{Q}(E(t), V(t)) = \frac{d}{dt}\Phi(E(t), V(t))$.

Furthermore one says that in a quasi-static reversible process $\delta Q = T\mathtt{d}S$ and $\delta W = -P\mathtt{d}V$, thus

$$\mathtt{d}E = T\mathtt{d}S - P\mathtt{d}V. \tag{2}$$

Since then one considers only quasi-static reversible processes, the above equality is identified with the first law; (1) and (2) are considered equivalent for quasi-static reversible processes.

Equality (2), in our framework, is the expression of entropic property (for constant particle number) (see Paragraph 8.5). In other words, if the body is entropic, then the formulae of Paragraph 8.4 result in

$$\dot{E} = T\dot{S} - P\dot{V}, \quad \text{i.e.} \quad \dot{E} = \mathbf{T}(E, V)\mathbf{S}(E, V)^{\cdot} - \mathbf{P}(E, V)\dot{V}. \tag{2'}$$

Note that relations (1') and (2') are far from being equivalent in any circumstances. Namely, (1') is a **differential equation** for E where Q and W are given functions of (E, V), whereas (2') is a simple **equality** regarding constitutive functions. Of course, if working is ideal, we get $T\dot{S} = Q$, i.e. $\mathbf{T}(E, V)\mathbf{S}(E, V)^{\cdot} = \mathbf{Q}(E, V)$ but this does not give any information about heating (about the function $\mathbf{Q}$): this is just an alternative expression of the differential equation (1').

Thus, in usual terms, (1) and (2) are not equivalent for any processes: (1) is an **equation** while (2) is an **equality** (see the Appendix).

9.5 The specific dynamical quantities

We can use specific internal energy and specific volume to describe processes. Then, according to Paragraph 9 of the Introduction, the dynamical law becomes

$$\dot{e} = q + w + g\alpha, \qquad \dot{v} = f + g\beta, \qquad \dot{N} = gN,$$

where q is the **specific heating**, w is the **specific working**, f is the **specific springing**, g is the **specific converting**, α and β are quantities, 'small near to equilibrium'. For processes 'near to equilibrium' and with ideal working and ideal transferring we have

$$\dot{e} = q - Pf, \qquad \dot{v} = f, \qquad \dot{N} = G.$$

Then

$$\dot{E} = Q - PF + \mu G, \qquad \dot{V} = F, \qquad \dot{N} = G,$$

moreover $\dot{V} = \dot{N}v + N\dot{v}$ and $\dot{E} = \dot{N}e + N\dot{e}$, thus we infer that

$$Nf = F - Gv, \qquad Nq = Q - G(Ts).$$

The formula for the springing is transparent: the change of specific volume consists of two parts: one is due to the change of total volume and the other is due to the change of particle number.

Similarly, the formula for heating is transparent: the specific heating consists of two parts: one corresponds to the total heating, the other to the internal energy change due to the change of particle number.

9.6 System of bodies

If several bodies interact with each other, then a process of the system is the joint of the processes of the bodies, and the process of the system is governed by the joint of differential equations concerning the processes of the bodies.

If one of the bodies is very large compared to the others, then its state will be approximately independent of the state of the other bodies (the temperature of the room does not change while a glass of tea is cooling). Thus, in this case we consider that the large body, called the **environment** acts on the other bodies which do not act on the environment. The states (processes) of the environment are independent of the processes of the bodies connected to the environment.

The environment is described as a material $(\mathrm{D}_a, \mathbf{T}_a, \mathbf{P}_a, \boldsymbol{\mu}_a, \mathrm{R}_a)$ with a **given process** $t \mapsto (e_a(t), v_a(t)) \in \mathrm{D}_a$ (the particle number of the environment is considered to be 'very large' and constant).

Thus, the process of $n \geq 1$ interacting bodies in a given environment is $\big((E_i, V_i, N_i) \mid i = 1, \dots, n\big)$, governed by the dynamical equation

$$\dot{E}_i = Q_i + W_i + L_i, \qquad \dot{V}_i = F_i \qquad \dot{N}_i = G_i$$

$$(i = 1, \dots, n).$$

The heating Q_i of the i-th body is the internal energy conducted to the body in unit time; evidently, it consists of the heatings due to the other bodies and of the heating due to a **heat source** in the body:

$$Q_i = Q_{i,s} + \sum_{k=a,1}^{n} Q_{ik},$$

where Q_{ik} is the heating due to the k-th body (environment for $k = a$) and $Q_{i,s}$ is the heating due to the heat source.

Similarly, the converting G_i of the i-th body consists of the convertings due to the other bodies and the converting due a **particle source** in the body:

$$G_i = G_{i,s} + \sum_{k=a,1}^{n} G_{ik};$$

furthermore,

$$F_i = \sum_{k=a,1}^{n} F_{ik}, \qquad W_i = \sum_{k=a,1}^{n} W_{ik}.$$

The quantities Q_{ik}, etc. are called **dynamical quantities** of the system.

It will be convenient to introduce the notations

$$A_{ik} := Q_{ik} + W_{ik} + L_{ik}, \qquad A_i := \sum_{k=a,1}^{n} A_{ik}.$$

9.7 Independence of interactions

We accept – as in mechanics – that the interaction of two bodies is independent of other interactions of the bodies in question. This means that the dynamical quantities with subscript ik depends only on the states of the i-th and k-th bodies.

10 Properties of dynamical quantities

10.1 Convention about notations

As a consequence of the independence of interactions, it suffices to take into account two bodies for the investigation of the properties of the dynamical quantities. In the sequel we denote the quantities of a chosen body in the usual way, and we write a subscript $_*$ for the quantities of another body. Thus (E, V, N) is a state of the chosen body, and (E_*, V_*, N_*) is a state of the other body, $\mathbf{T}$ and $\mathbf{T}_*$ are the corresponding temperatures, etc.

The values of the functions $\mathbf{T}$, $\mathbf{P}$ and $\boldsymbol{\mu}$ will be denoted by T, P and μ, respectively, and similar notation will be applied for the quantities with subscript $_*$.

The dynamical quantities as functions will be denoted by the letters $\mathbf{Q}$, $\mathbf{F}$, etc., Q, F, etc. standing for their values.

It will often be convenient to write the values of the functions in some formulae instead of the functions if this does not cause misunderstanding. We have to be cautious only in one situation, namely $\mathbf{Q} = 0$ and $Q = 0$ have different meaning: the first says that the function $\mathbf{Q}$ is 'identically zero', i.e. it has only zero values, the second says that the value in question of $\mathbf{Q}$ is zero. We shall sharply distinguish between these two cases (of course, between $\mathbf{F} = 0$ and $F = 0$, etc., too).

10.2 Exact form of the dynamical quantities

According to what has been said, we are given functions

$$(E, V, N, E_*, V_*, N_*) \mapsto \begin{cases} \mathbf{Q}(E, V, N, E_*, V_*, N_*), \\ \mathbf{F}(E, V, N, E_*, V_*, N_*), \\ \mathbf{G}(E, V, N, E_*, V_*, N_*), \\ \boldsymbol{\pi}(E, V, N, E_*, V_*, N_*), \\ \boldsymbol{\xi}(E, V, N, E_*, V_*, N_*) \end{cases}$$

defined on the set $(\mathrm{D}*\mathbb{R}_0^+)\times(\mathrm{D}_* * \mathbb{R}_0^+)$. These dynamical quantities are supposed to be continuous, moreover continuously differentiable on the interior of their domain. The assumption of continuity excludes some interactions (e.g. the converting in the case of a valve is not continuous; but also the assumption of homogeneity is doubtful for a valve).

Let us introduce the notations

$$\mathbf{W} := -\mathbf{P}\mathbf{F} + \boldsymbol{\pi}\mathbf{F}^2, \qquad \mathbf{L} := \boldsymbol{\mu}\mathbf{G} + \boldsymbol{\xi}\mathbf{G}^2,$$

$$\mathbf{A} := \mathbf{Q} + \mathbf{W} + \mathbf{L}$$

(which make sense in such a way that $\mathbf{P}$ and $\boldsymbol{\mu}$ are considered as functions of (E, V, N, E_*, V_*, N_*) not depending on (E_*, V_*, N_*)).

Of course, we are given the functions $\mathbf{Q}_*$, etc. on the set $(\mathrm{D}_* * \mathbb{R}_0^+) \times (\mathrm{D} * \mathbb{R}_a^+)$, for which similar properties and notations are accepted as above.

10.3 Mutuality

The number of particles passing from one body to the other is evidently equal to the negative of the number of particles passing from the second body to the first. The same is true for the volume change and for the internal energy change. Therefore we accept the 'law of action-reaction', called here **mutuality**

$$\mathbf{A}(E, V, N, E_*, V_*, N_*) = -\mathbf{A}_*(E_*, V_*, N_*, E, V, N),$$

$$\mathbf{F}(E, V, N, E_*, V_*, N_*) = -\mathbf{F}_*(E_*, V_*, N_*, E, V, N),$$

$$\mathbf{G}(E, V, N, E_*, V_*, N_*) = -\mathbf{G}_*(E_*, V_*, N_*, E, V, N).$$

Note that such a mutuality does not necessarily hold for heating, working and transferring as explained in the next paragraph.

10.4 Indirect heat conduction

Heating is the conducted internal energy – the transport of internal energy due to the collision of the molecules – in unit time. Then it seems natural to expect that mutuality holds for heatings, too. Mutuality for internal energies and that for heatings, however, exclude each other.

For a clear explanation, let us consider two bodies which interact only with each other (the two bodies are isolated together). Then mutuality for internal energies gives for any processes that

$$\dot{E} + \dot{E}_* = 0.$$

The bodies in ordinary thermodynamics are considered homogeneous; so this theory can be well applied only to phenomena in which inhomogeneity is negligible. In reality every nontrivial process is inhomogeneous. Because of the assumption of homogeneity, only internal energy appears in the description, kinetic energy is neglected, though kinetic energy is present in real processes: a body expands, its points are moving. Thus, having the above equality, i.e. $E + E_* = \text{const.}$, we do not formulate energy conservation quite correctly because we do not (cannot) into account kinetic energy.

Retaining energy conservation expressed by mutuality for internal energies, we modify our idea on heating. A body expanding, pushes the molecules of another body near the contact surface, so gives them kinetic energy which, as a consequence of viscosity, becomes later internal energy. This procedure can be considered as a heating in two steps: a part of the internal energy of a body turns into kinetic energy of the other body which then dissipates into internal energy. Then we can conceive that heating consists of two parts: the **direct heating** due to the (microscopic) collision of the molecules and the **indirect heating** due to the (macroscopic) pushing of the molecules; mutuality occurs for direct heatings but it does not for indirect ones.

A similar situation occurs in particle transport. The particles passing from a hotter body to a colder one have larger average kinetic energy, the excess energy dissipates into internal energy because of viscosity. Again we can conceive either that the transferring is not ideal or that heating consists of a direct part and an indirect one.

10.5 Convention about the dynamical quantities

The previous consideration is quite reasonable but in practice we cannot describe the direct heating and the indirect one separately: heating as a dynamical quantity given in Paragraph 10.2 contains both the direct part and the indirect part.

Our reasoning have shown that indirect heating and non-ideal working are closely related. In fact, we could always consider ideal working and transferring, the non-ideal parts conceived as indirect heatings. This is not always convenient, however.

Namely, heat insulation means that direct heating is missing (but indirect one is not necessarily!). Thus if we want to express heat insulation by $\mathbf{Q} = 0$ (we have no other possibility), then, in general, we cannot consider ideal working and transferring.

Recapitulating: we can suppose that

– if $\mathbf{Q} \neq 0$, then $\boldsymbol{\pi} = 0$ and $\boldsymbol{\xi} = 0$,

– if $\mathbf{Q} = 0$, then $\boldsymbol{\pi} = 0$ and $\boldsymbol{\xi} = 0$ if these equalities do not lead to a contradiction.

10.6 Forbidden interactions

A non-permeable wall between two bodies blocks particle transport, a rigid wall makes volume change impossible, there is no energy conduction through a heat-insulated wall. It seems, we would say that

- particle transport is forbidden if and only if $\mathbf{G} = 0$,
- volume change is forbidden if and only if $\mathbf{F} = 0$,
- energy conduction is forbidden if and only if $\mathbf{Q} = 0$.

These are, however, too strong requirements; namely, the blocking, in general, is realized only in some circumstances. Let us consider a seed: it has a hull through which water cannot pass under a given temperature (to hinder sprouting). Similarly, a body can have a wall which is absolutely rigid below a given temperature but is elastic above it. Thus a right setting of an impossible interaction requires only that the corresponding dynamical quantity should be zero on a convenient domain, as follows.

Transferring is impossible in the state (E, V, N) of the body if it has a (mathematical) neighbourhood such that for all (E', V', N') in that neighbourhood and for all states (E_*, V_*, N_*) of the other body

$$\mathbf{G}(E', V', N', E_*, V_*, N_*) = 0$$

holds. This property will be denoted by

$$\mathbf{G}||_{(E,V,N)} = 0.$$

Of course, the notations

$$\mathbf{F}||_{(E,V,N)} = 0, \qquad \mathbf{Q}||_{(E,V,N)} = 0.$$

have the same meaning for springing and for heating.

Then it is evident what $\mathbf{G}||_{(E,V,N)} \geq 0$ means. Lastly, $\mathbf{G}||_{(E,V,N)} \neq 0$ denotes that transferring is possible in the state (E, V, N). This means that to every (mathematical) neighbourhood of (E, V, N) there are an (E', V', N') in that neighbourhood and a state (E_*, V_*, N_*) of the other body in such a way that $\mathbf{G}(E', V', N', E_*, V_*, N_*) \neq 0$.

Note that this does not exclude that $\mathbf{G}(E, V, N, E_*, V_*, N_*) = 0$ for the given (E, V, N) and for some – possibly for all – (E_*, V_*, N_*).

In what follows, for the sake of simplicity, forbidden interactions will be expressed by $\mathbf{G} = 0$, $\mathbf{F} = 0$, $\mathbf{Q} = 0$ which can be replaced with the above weaker requirements if necessary.

10.7 Equilibrium properties

Constant processes of body systems (processes not varying in time) are called **standstill**. It is evident – with the notations of 9.6 – that $Q_i + W_i + L_i = 0$, $F_i = 0$ and $G_i = 0$ for all i in a standstill. If every dynamical quantity is zero, not only their sums, i.e. $Q_{ik} = 0$, $W_{ik} = 0$, $L_{ik} = 0$, $F_{ik} = 0$ and $G_{ik} = 0$ for all i and k, then the standstill is an **equilibrium**; a non-equilibrium standstill is called a **stationary state**.

It was pointed out in the Preface that the zeroth law is not valid in general. This does not mean, however, that it must be discarded; we have also seen that in reality homogeneous processes do not exist, nevertheless we retained the notion of homogeneous processes as a suitable approximation for certain phenomena.

We accept the zeroth law as a restriction instead of a general truth: we shall deal only with phenomena in which “the equal values of the corresponding intensive quantities of the possible interactions are the necessary and sufficient condition for equilibrium".

The exact meaning of the phrase between quotation marks is expressed by the **equilibrium properties** of the dynamical quantitities which will be precisely formulated in Section 14.1; some of them is illustrated below where $T := \mathbf{T}(E, V, N)$, $P := \mathbf{P}(E, V, N)$, $T_* := \mathbf{T}_*(E_*, V_*, N_*)$, etc.

1. Let us suppose that converting is forbidden, i.e. $\mathbf{G} = 0$.

1a) If springing is also forbidden, $\mathbf{F} = 0$ (and, of course, $\mathbf{Q} \neq 0$ in order to have a nontrivial case), then there is no indirect heating, so we can suppose that $\mathbf{Q}(E, V, N, E_*, V_*, N_*) = 0$ if and only if $T = T_*$.

1b) If heating is also forbidden, $\mathbf{Q} = 0$ (and, of course, $\mathbf{F} \neq 0$), then purely mechanical interaction occurs, so we can suppose that $\mathbf{F}(E, V, N, E_*, V_*, N_*) = 0$ if and only if $P = P_*$.

1c) If neither heating nor springing is forbidden, then it seems right to accept the sufficient condition: if $T = T_*$ and $P = P_*$, then $\mathbf{Q}(E, V, N, E_*, V_*, N_*) = 0$ and $\mathbf{F}(E, V, N, E_*, V_*, N_*) = 0$. A necessary condition can be the following: mechanics suggests that equilibrium cannot exist if the pressures differ (regardless of temperature), so we accept that $\mathbf{F}(E, V, N, E_*, V_*, N_*) = 0$ implies $P = P_*$. Now indirect heating is not excluded but it disappears when volume does not change; in turn, direct heating disappears only when the temperatures are equal. Thus we accept that if $\mathbf{Q}(E, V, N, E_*, V_*, N_*) = 0$ and $P = P_*$, then $T = T_*$.

2. If converting is not forbidden, i.e. $\mathbf{G} \neq 0$, then it seems right to accept that for zero values of $\mathbf{G}$, heating and springing satisfy the same relations as above.

A further fundamental assumption is that if particle transport is not influenced by a semipermeable wall ($\mathbf{G}$ can have both positive and negative values), then $\mathbf{G}(E, V, N, E_*, V_*, N_*) = 0$ implies that $\mu = \mu_*$.

If there is a semipermeable wall between the bodies, e.g. $\mathbf{G} \leq 0$ then $\mathbf{G}(E, V, N, E_*, V_*, N_*) = 0$ implies that $\mu \geq \mu_*$.

Finally, we mention the equilibrium properties of the lost coefficients (‘small near equilibrium’): if $P = P_*$, then $\boldsymbol{\pi}(E, V, V, E_*, V_*, N_*) = 0$ and if $\mu = \mu_*$, then $\boldsymbol{\xi}(E, V, V, E_*, V_*, N_*) = 0$.

10.8 The dissipation inequality

A fundamental experimental fact is that the processes in Nature are irreversible. Another fact is, however, that at present there is no exact general definition of irreversibility in physics. One tries to express irreversibility by the second law in thermodynamics but we have seen in the Introduction that the usual formulations are not precise and their meaning is doubtful.

We can summarize our everyday experience about irreversibility by saying that the ‘direction of processes is not arbitrary’: ‘heat flows a hotter place to a colder one’, ‘matter flows from a place with higher pressure to a place with lower pressure’. All these are strongly related to the fact that energy dissipates in processes, i.e. in every process a positive amount of internal energy is produced from other forms of energy; as a consequence, internal energy cannot be transformed completely into other (mechanical, electric, etc.) energy.

Processes are determined by the dynamical equation. Some properties of the dynamical quantitities must reflect that “the direction of processes is not arbitrary". In continuum theory energy dissipation is expressed by the Clausius–

Duhem inequality (see Paragraph 7 of Introduction) whose counterpart is looked for ordinary thermodynamics. The difference here corresponds to the gradient there, thus the term regarding heat conduction suggests us to accept $-\frac{Q}{T}(T-T_*)$; accordingly, the term regarding working is accepted to be $-\frac{W}{P}(P-P_*)$, and a similar formula is used for transferring, too: the **dissipation inequality** of dynamical quantitities is suggested to be

$$-\frac{Q}{T}(T-T_*)+F(P-P_*)-G(\mu-\mu_*)\geq$$
$$(\pi+\pi_*)F^2+(\xi+\xi_*)G^2\geq 0 \quad (*)$$

supplemented by the requirement that equality holds if and only if $Q=0$, $F=0$ and $G=0$ (implying $W=0$ and $L=0$, too).

The content of this inequality is evident. If we consider the special case when all the three terms are positive, then

– if $T>T_*$, then $Q<0$: heat flows from a hotter body to colder one;

– if $P>P_*$ and $P>0$, then $W<0$: a body with higher pressure works on the body with lower pressure, i.e. the body with higher pressure expands;

– if $\mu>\mu_*$ and $\mu>0$, then $L<0$: particles transfer energy from a body with higher chemical potential to a body with lower chemical potential.

We emphasize, however, that only the sum of the three terms must be positive, the terms separately need not be positive, in general.

$A=Q+W+L$ yields

$$Q=A+PF-\mu G-\pi F^2-\xi G^2$$

which allows us to transform the dissipation inequalityinto

$$A\left(\frac{1}{T}-\frac{1}{T_*}\right)+F\left(\frac{P}{T}-\frac{P_*}{T_*}\right)+G\left(-\frac{\mu}{T}+\frac{\mu_*}{T_*}\right)\geq$$
$$\left(\frac{\pi}{T}+\frac{\pi_*}{T_*}\right)F^2+\left(\frac{\xi}{T}+\frac{\xi_*}{T_*}\right)\geq 0, \quad (**)$$

This form of the dissipation inequality plays a fundamental role for entropic bodies.

10.9 Other two inequalities

We have from the previous equality that

$$Q\leq A+PF-\mu G;$$

if F and G are not zero, equality holds only when the lost coefficients are zero, in other words, in the ideal case.

The same equality gives

$$\frac{Q}{T}=\frac{A+PF-\mu G-\pi F^2-\xi G^2}{T}$$

and

$$\frac{Q_*}{T_*}=\frac{A_*+P_*F_*-\mu_*G_*-\pi_*F_*^2-\xi_*G_*^2}{T}.$$

Summing up these equalities, using the mutuality properties and the dissipation inequality, we get

$$\frac{Q}{T} + \frac{Q_*}{T_*} \geq 0. \tag{+}$$

Now let us suppose that the bodies in question are entropic (see Paragraph 9.4), and let us consider a process; then $A = \dot{E}$, $F = \dot{V}$ and $G = \dot{N}$. Consequently, the first inequality results in

$$Q \leq T\dot{S},$$

and the other inequalities give

$$(S + S_*)^{\cdot} \geq 0. \tag{++}$$

10.10 A few words about the second law

Let us recall Carnot's formulation of the second law (see the Preface):

1. Every thermodynamical system has a state function (called entropy) S in such a way that $\delta Q \leq TdS$ for the heat absorbed in any infinitesimal quasi-static process and equality holds only for reversible processes.

2. The entropy of a closed system can never decrease; it increases in an irreversible process and remains constant in a reversible one.

Now we can see the precise meaning of these assertions.

The first assertion corresponds to inequality (+) which folows only from the non-negativity of the lost coefficients.

The second assertion corresponds to inequality (++) which follows from the dissipation inequality.

As cited in the Preface, several authors says that the second law is the entropy increase in non-equiligrium processes. This icrease is the consequence of the dissipation inequality.

Others says the second law is that the entropy of a closed system is maximal in equlibrium. Later we shall see that this is the consequence of the intrinsic stability conditions.

Moreover it is often asserted that the second law implies the trend to equilibrium. Later we shall see that the trend to equilibrium i.e. asymptotic stability of equilibrium is a consequence of

– both the intrinsic stability conditions
– and the dissipation inequality.

We apply these precisely defined notions and do not formulate a second law.

11 Thermodynamical forces

11.1 Introductory remarks

Internal energy, volume and particle number are called **extensive quantities**, temperature, pressure and chemical potential are called **intensive quantities**. The extensive quantities are characterized by the following property: if a body is cut in two halves, then the energy, etc. of each half becomes the half of the original energy, etc. (this allows us to use specific quantities). The intensive quantities are characterized by the following property: if a body is cut in two halves, then the temperature, etc. of each half remains the original temperature.

The dynamical equation describes the change of extensive quantities, the dynamical quantitities are considered as given functions of the extensive quantities but their equilibrium property is formulated by the intensive quantities (see 10.7).

11.2 The notion of thermodynamical forces

We said that if particle interchange is forbidden (the converting is the zero function) then $T - T_* = 0$ and $P - P_* = 0$ imply that $Q = 0$; if particle interchange is not forbidden, then $\mu - \mu_* = 0$ is a third sufficient condition for the zero value of heating. Similar can be said about springing and converting: if the difference of the corresponding intensive quantities of the bodies take zero value, then the dynamical quantitities do the same.

The collection of the difference of the corresponding intensive quantities of two bodies is called the **thermodynamical force** between the bodies. More closely,

$$\big(-(T - T_*), P - P_*, -(\mu - \mu_*)\big)$$

is the thermodynamical force acting on the chosen body from the side of the other body (denoted by $*$).

Because the dynamical equation concerns the extensive quantities, investigations in most cases are simpler if we use the canonical variables. Then the 'everyday' intensive quantities T, P and μ are replaced with the **canonical intensive quantities** $\frac{1}{T}$, $\frac{P}{T}$ and $-\frac{\mu}{T}$ which are the partial derivatives of the total entropy for an entropic body:

$$\frac{\partial \mathbf{S}}{\partial E} = \frac{1}{\mathbf{T}}, \qquad \frac{\partial \mathbf{S}}{\partial V} = \frac{\mathbf{P}}{\mathbf{T}}, \qquad \frac{\partial \mathbf{S}}{\partial N} = -\frac{\boldsymbol{\mu}}{\mathbf{T}}.$$

Correspondingly, a pairing is made among the extensive and intensive quantities: $\frac{1}{T}$ is coupled to E, $\frac{P}{T}$ to V and $-\frac{\mu}{T}$ to N.

Of course, the intensive quantities and the canonical intensive quantities determine each other uniquely.

The collection of the difference of the corresponding canonical intensive quantities of two bodies is called the **canonical thermodynamical force**. More closely,

$$\left(\frac{1}{T} - \frac{1}{T_*}, \frac{P}{T} - \frac{P_*}{T_*}, -\left(\frac{\mu}{T} - \frac{\mu_*}{T_*}\right)\right)$$

is the canonical thermodynamical force acting on the chosen body from the side of the other body (denoted by $*$).

The thermodynamical force and the canonical thermodynamical force determine each other uniquely by the following formulae:

$$-(T - T_*) = TT_*\left(\frac{1}{T} - \frac{1}{T_*}\right),$$

$$\begin{aligned} P - P_* &= -\,PT_* \left(\frac{1}{T} - \frac{1}{T_*}\right) + T_* \left(\frac{P}{T} - \frac{P_*}{T_*}\right) = \\ &= -\,P_* T \left(\frac{1}{T} - \frac{1}{T_*}\right) + T \left(\frac{P}{T} - \frac{P_*}{T_*}\right), \end{aligned}$$

and the same relation holds for $\mu - \mu_*$, too.

It is suitable to write the above formulae in a matrix form:

$$\begin{aligned} \begin{pmatrix} -(T - T_*) \\ P - P_* \\ -(\mu - \mu_*) \end{pmatrix} &= T_* \begin{pmatrix} T & 0 & 0 \\ -P & 1 & 0 \\ \mu & 0 & 1 \end{pmatrix} \begin{pmatrix} \frac{1}{T} - \frac{1}{T_*} \\ \frac{P}{T} - \frac{P_*}{T_*} \\ -\left(\frac{\mu}{T} - \frac{\mu_*}{T_*}\right) \end{pmatrix} = \\ &= T \begin{pmatrix} T_* & 0 & 0 \\ -P_* & 1 & 0 \\ \mu_* & 0 & 1 \end{pmatrix} \begin{pmatrix} \frac{1}{T} - \frac{1}{T_*} \\ \frac{P}{T} - \frac{P_*}{T_*} \\ -\left(\frac{\mu}{T} - \frac{\mu_*}{T_*}\right) \end{pmatrix}, \end{aligned}$$

$$\begin{aligned} \begin{pmatrix} \frac{1}{T} - \frac{1}{T_*} \\ \frac{P}{T} - \frac{P_*}{T_*} \\ -\left(\frac{\mu}{T} - \frac{\mu_*}{T_*}\right) \end{pmatrix} &= \frac{1}{TT_*} \begin{pmatrix} 1 & 0 & 0 \\ P & T & 0 \\ -\mu & 0 & T \end{pmatrix} \begin{pmatrix} -(T - T_*) \\ P - P_* \\ -(\mu - \mu_*) \end{pmatrix} = \\ &= \frac{1}{TT_*} \begin{pmatrix} 1 & 0 & 0 \\ P_* & T_* & 0 \\ -\mu_* & 0 & TT_* \end{pmatrix} \begin{pmatrix} -(T - T_*) \\ P - P_* \\ -(\mu - \mu_*) \end{pmatrix}. \end{aligned}$$

Lastly, we mention that, according to our earlier convention, we omit the attribute canonical if there is no risk of confusion.

11.3 Pseudolinear dynamical quantitities

We say that the dynamical quantitities are **pseudolinear functions of the thermodynamical force** or briefly **pseudolinear** if they can be represented as linear combinations of the components of the thermodynamical force or the canonical thermodynamical force in which the coefficients are functions of the states, i.e.

$$\begin{aligned} Q &= -\lambda_Q(T - T_*) + \beta_Q(P - P_*) - \vartheta_Q(\mu - \mu_*) = \\ &= \lambda_Q^c \left(\frac{1}{T} - \frac{1}{T_*}\right) + \beta_Q^c \left(\frac{P}{T} - \frac{P_*}{T_*}\right) - \vartheta_Q^c \left(\frac{\mu}{T} - \frac{\mu_*}{T_*}\right), \end{aligned}$$

$$\begin{aligned} F &= -\lambda_F(T - T_*) + \beta_F(P - P_*) - \vartheta_F(\mu - \mu_*) = \\ &= \lambda_F^c \left(\frac{1}{T} - \frac{1}{T_*}\right) + \beta_F^c \left(\frac{P}{T} - \frac{P_*}{T_*}\right) - \vartheta_F^c \left(\frac{\mu}{T} - \frac{\mu_*}{T_*}\right), \end{aligned}$$

$$
\begin{aligned}
G = -\lambda_G(T - T_*) + \beta_G(P - P_*) - \vartheta_G(\mu - \mu_*) = \\
= \lambda^c_G \left(\frac{1}{T} - \frac{1}{T_*}\right) + \beta^c_G \left(\frac{P}{T} - \frac{P_*}{T_*}\right) - \vartheta^c_G \left(\frac{\mu}{T} - \frac{\mu_*}{T_*}\right),
\end{aligned}
$$

where the coefficients λ_Q, λ^c_Q, etc. are continuous functions of (E, V, N, E_*, V_*, N_*).

It is evident that pseudolinear dynamical quantitities take zero value for the zero value of the thermodynamical force.

According to our experience, the main driving force of material, mechanical and thermal interaction is the difference of chemical potentials, the difference of pressures and the difference of temperatures, respectively. The terms in the pseudolinear form of dynamical quantitities which are not proportional to the corresponding main driving force are consequences of **cross effects**. Indirect heating is such a cross effect.

The above formulae can be written in a matrix form:

$$
\begin{pmatrix} Q \\ F \\ G \end{pmatrix} = \begin{pmatrix} \lambda_Q & \beta_Q & \vartheta_Q \\ \lambda_F & \beta_F & \vartheta_F \\ \lambda_G & \beta_G & \vartheta_G \end{pmatrix} \begin{pmatrix} -(T - T_*) \\ P - P_* \\ -(\mu - \mu_*) \end{pmatrix} = \begin{pmatrix} \lambda^c_Q & \beta^c_Q & \vartheta^c_Q \\ \lambda^c_F & \beta^c_F & \vartheta^c_F \\ \lambda^c_G & \beta^c_G & \vartheta^c_G \end{pmatrix} \begin{pmatrix} \frac{1}{T} - \frac{1}{T_*} \\ \frac{P}{T} - \frac{P_*}{T_*} \\ -\left(\frac{\mu}{T} - \frac{\mu_*}{T_*}\right) \end{pmatrix}.
$$

The matrices above are called the (**canonical**) **dynamical matrices** for which we deduce

$$
\begin{aligned}
\begin{pmatrix} \lambda^c_Q & \beta^c_Q & \vartheta^c_Q \\ \lambda^c_F & \beta^c_F & \vartheta^c_F \\ \lambda^c_G & \beta^c_G & \vartheta^c_G \end{pmatrix} &= \begin{pmatrix} \lambda_Q & \beta_Q & \vartheta_Q \\ \lambda_F & \beta_F & \vartheta_F \\ \lambda_G & \beta_G & \vartheta_G \end{pmatrix} \begin{pmatrix} T & 0 & 0 \\ -P & 1 & 0 \\ \mu & 0 & 1 \end{pmatrix} T_* = \\
&= \begin{pmatrix} \lambda_Q & \beta_Q & \vartheta_Q \\ \lambda_F & \beta_F & \vartheta_F \\ \lambda_G & \beta_G & \vartheta_G \end{pmatrix} \begin{pmatrix} T_* & 0 & 0 \\ -P_* & 1 & 0 \\ \mu_* & 0 & 1 \end{pmatrix} T,
\end{aligned}
$$

$$
\begin{aligned}
\begin{pmatrix} \lambda_Q & \beta_Q & \vartheta_Q \\ \lambda_F & \beta_F & \vartheta_F \\ \lambda_G & \beta_G & \vartheta_G \end{pmatrix} &= \begin{pmatrix} \lambda^c_Q & \beta^c_Q & \vartheta^c_Q \\ \lambda^c_F & \beta^c_F & \vartheta^c_F \\ \lambda^c_G & \beta^c_G & \vartheta^c_G \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ P & T & 0 \\ -\mu & 0 & T \end{pmatrix} \frac{1}{TT_*} = \\
&= \begin{pmatrix} \lambda^c_Q & \beta^c_Q & \vartheta^c_Q \\ \lambda^c_F & \beta^c_F & \vartheta^c_F \\ \lambda^c_G & \beta^c_G & \vartheta^c_G \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ P_* & T_* & 0 \\ -\mu_* & 0 & T_* \end{pmatrix} \frac{1}{TT_*}.
\end{aligned}
$$

11.4 The pair conductance matrices

We have already introduced the quantity $A := Q + W + L$ which appears in the dynamical equation and in the dissipation inequality. Then

$$
\begin{pmatrix} A \\ F \\ G \end{pmatrix} = \begin{pmatrix} \lambda^c_A) & \beta^c_A & \vartheta^c_A \\ \lambda^c_F & \beta^c_F & \vartheta^c_F \\ \lambda^c_G & \beta^c_G & \vartheta^c_G \end{pmatrix} \begin{pmatrix} \frac{1}{T} - \frac{1}{T_*} \\ \frac{P}{T} - \frac{P_*}{T_*} \\ -\left(\frac{\mu}{T} - \frac{\mu_*}{T_*}\right) \end{pmatrix}.
$$

Definition *The matrix above is called the* **canonical pair conductance matrix**, *respectively.*

The world pair refers to the interaction of two bodies. Later we introduce the conductance matrix for a system consisting of more bodies.

It is not hard to show that the dynamical matrices and the pair conductance matrix determine determine each other uniquely.

11.5 Mechanically strong springing

Our experience indicates that a higher pressure overcomes a lower one for arbitrary (possibly non-equal) temperatures of the bodies, the body with higher pressure expands at the cost of the body with lower pressure.

We say that in the case of zero converting springing is **mechanically strong**, if $\mathbf{P}(E,V,N) > \mathbf{P}_*(E_*,V_*,N_*)$, and $\mathbf{P}(E,V,N) < \mathbf{P}_*(E_*,V_*,N_*)$ imply that $\mathbf{F}(E,V,N,E_*,V_*,N_*) > 0$, and $\mathbf{F}(E,V,N,E_*,V_*,N_*) < 0$, respectively. Then $\mathbf{P}(E,V,N) = \mathbf{P}_*(E_*,V_*,N_*)$ implies that $\mathbf{F}(E,V,N,E_*,V_*,N_*) = 0$. According to 1c) in 10.7, for mechanically strong springing $\mathbf{F}(E,V,N,E_*,V_*,N_*) = 0$ if and only if $\mathbf{P}(E,V,N) = \mathbf{P}_*(E_*,V_*,N_*)$.

This is expressed in the pseudolinear case that $\lambda_F = 0$ (though it may be otherwise because of the non-uniqueness); thus if converting is zero and springing is mechanically strong, then

$$\begin{pmatrix} Q \\ F \end{pmatrix} = \begin{pmatrix} \lambda_Q & \beta_Q \\ 0 & \beta_F \end{pmatrix} \begin{pmatrix} -(T-T_*) \\ P-P_* \end{pmatrix}.$$

11.6 The dissipation inequality in the pseudolinear case

If the dynamical quantitities have the form given in 11.3 and working and transferring are ideal, then the dissipation inequality reads

$$\begin{pmatrix} -(T-T_*) & P-P_* & -(\mu-\mu_*) \end{pmatrix} \begin{pmatrix} \frac{\lambda_Q}{T} & \frac{\beta_Q}{T} & \frac{\vartheta_Q}{T} \\ \lambda_F & \beta_F & \vartheta_F \\ \lambda_G & \beta_G & \vartheta_G \end{pmatrix} \begin{pmatrix} -(T-T_*) \\ P-P_* \\ -(\mu-\mu_*) \end{pmatrix} \geq 0,$$

or

$$\begin{pmatrix} \frac{1}{T}-\frac{1}{T_*} & \frac{P}{T}-\frac{P_*}{T_*} & -\left(\frac{\mu}{T}-\frac{\mu_*}{T_*}\right) \end{pmatrix} \begin{pmatrix} \hat{\lambda}^c_A & \hat{\beta}^c_A & \hat{\vartheta}^c_A \\ \lambda^c_F & \beta^c_F & \vartheta^c_F \\ \lambda^c_G & \beta^c_G & \vartheta^c_G \end{pmatrix} \begin{pmatrix} \frac{1}{T}-\frac{1}{T_*} \\ \frac{P}{T}-\frac{P_*}{T_*} \\ -\left(\frac{\mu}{T}-\frac{\mu_*}{T_*}\right) \end{pmatrix} \geq 0,$$

where

$$\hat{\lambda}^c_A := \lambda^c_Q - P\lambda^c_F + \mu\lambda^c_G, \quad \hat{\beta}^c_A := \beta^c_Q - P\beta^c_F + \mu\beta^c_G, \quad \hat{\vartheta}^c_A := \vartheta^c_Q - P\vartheta^c_F + \mu\vartheta^c_G.$$

This tempts us to believe that the conductance matrix is positive semidefinite which is not necessarily true because the matrix and the vectors are functions.

11.7 Symmetry properties of the canonical conductance matrix

Conductance matrices are used in continuum physics, and in Onsager's theory, too. According to Onsager, the conductance matrix – at least in equilibrium – is symmetric. We should point out that such a statement can be right only for the canonical conductance matrix, the symmetry of the conductance matrix makes no sense. Namely, the symmetry of the conductance matrix would require that $\beta_Q + (\lambda)$ be equal to λ_F which is impossible because these coefficients have the physical dimension J/sPa and m^3/Ks, respectively.

According to our habit, instead of requiring that the canonical pair conductance matrix be symmetric, we define symmetricity as a special property. Remember that the canonical conductance matrix is a matrix-valued function.

Definition *The canonical pair conductance matrix given in 11.4 is*
(i) **strongly Onsagerian** *if it is constant and symmetric,*
(ii) **Onsagerian** *if it is symmetric (i.e. its every value is symmetric),*
(iii) **weakly Onsagerian** *if the zero value of the canonical thermodynamical force implies that its corresponding value is symmetric.*

Thus the conductance matrix in 11.4 is weakly Onsagerian if $\mathbf{T}(E,V,N) = \mathbf{T}_*(E_*,V_*,N_*)$, $\mathbf{P}(E,V,N) = \mathbf{P}_*(E_*,V_*,N_*)$ and $\boldsymbol{\mu}(E,V,N) = \boldsymbol{\mu}_*(E_*,V_*,N_*)$ imply that $\lambda_F^c(E,V,N,E_*,V_*,N_*) = (\beta_Q^c + (\beta))(E,V,N,E_*,V_*,N_*)$, etc.

11.8 Concluding remarks

The simple relation between the thermodynamical force and the canonical thermodynamical force can evoke the feeling that they are equivalent, i.e. it does not matter which of them is used. This is not so. Usually one characterizes equilibrium by the zero value of the thermodynamical force. If there is no constraint, this is right for both forces, because e.g.

$$T - T_* = 0, \quad P - P_* = 0$$

if and only if

$$\frac{1}{T} - \frac{1}{T_*} = 0, \qquad \frac{P}{T} - \frac{T_*}{P_*} = 0.$$

However, if the temperature difference is not a driving force (when the bodies are heat insulated), then $T - T_* = 0$ is not necessary for equilibrium, and $P - P_* = 0$ is not equivalent to $P/T - P_*/T_* = 0$. $P - P_*$, whose zero value is necessary for equilibrium, is a combination of two components of the canonical thermodynamical force.

This will be clearly explained in Paragraph 15.3.2 by the precise definition of constraints.

11.9 Exercises

1. Suppose that the heating has the form
(i) $(aP^2T_* - bP_*T^2)$,

(ii) $(bPT_*^2 - aP_*^2T)$,
where a and b are functions depending only on the particle number N.

Give the coefficients λ, λ^c etc. according to 11.3.

2. Let us call two (canonical) dynamical matrices equivalent if they result in the same dynamical quantitities. Show that this is really an equivalence relation.

III SIMPLE SYSTEMS WITHOUT PARTICLE CHANGE

We treat special systems in this chapter. The dynamical quantitities, their fundamental properties and the dynamical equation will be formulated according to Chapter II.

The existence and stability of equilibria will be the main questions in each system. Trend to equilibrium is expressed mathematically by the asymptotic stability of a locally unique equilibrium and by the strict asymptotic stability of the set of other equilibria for which the knowledge summarized in App. 7 is indispensable.

The study of these special systems helps the reader master the principles and methods of the dynamical description of systems, understand the importance of the properties of the dynamical quantitities, to be prepared for the general treatment in the next chapter.

12 One body in a given environment

12.1 Introductory remarks

We investigate a system consisting of a body and an environment, supposing that there is no particle source in the body, the body and the environment cannot interchange particles (converting is zero), thus the particle number of the body is constant.

Because the particle number of the body is constant (particle number is not an explicit variable), we can use the specific extensive quantities for describing a state of the body. Accordingly, the specific dynamical quantitities enter the dynamical equation.

12.2 General formulae

12.2.1 General framework of the description

Based on Chapter II, the description of a system now will be the following:

1. There are a body of material $(\mathrm{D}, \mathbf{T}, \mathbf{P}, \boldsymbol{\mu}, \mathrm{R})$ and an environment of material $(\mathrm{D}_a, \mathbf{T}_a, \mathbf{P}_a, \boldsymbol{\mu}_a, \mathrm{R}_a)$.

2. There are the specific heating $\mathbf{q}$, the specific springing $\mathbf{f}$, the lost coefficient $\boldsymbol{\pi}$, defined on the set $\mathrm{D} \times \mathrm{D}_a$; furthermore, $\mathbf{w} := -(\mathbf{P} + \boldsymbol{\pi})\mathbf{f}$ is the specific working.

These dynamical quantitities satisfy

– the equilibrium properties:

0) $\boldsymbol{\pi}(e,v,e_a,v_a)=0$ if $\mathbf{P}(e,v)=\mathbf{P}_a(e_a,v_a)$,

1)(a) if $\mathbf{f}=0$, $\mathbf{q}\neq 0$, then $\mathbf{q}(e,v,e_a,v_a)=0$ if and only if $\mathbf{T}(e,v)=\mathbf{T}_a(e_a,v_a)$,

1)(b) if $\mathbf{q}=0$, $\mathbf{f}\neq 0$, then $\mathbf{f}(e,v,e_a,v_a)=0$ if and only if $\mathbf{P}(e,v)=\mathbf{P}_a(e_a,v_a)$,

1)(c) if $\mathbf{f}\neq 0$ and $\mathbf{q}\neq 0$, then

$*$ if $\mathbf{f}(e,v,e_a,v_a)=0$, then $\mathbf{P}(e,v)=\mathbf{P}_a(e_a,v_a)$,

$*$ if $\mathbf{q}(e,v,e_a,v_a)=0$ and $\mathbf{P}(e,v)=\mathbf{P}_a(e_a,v_a)$, then $\mathbf{T}(e,v)=\mathbf{T}_a(e_a,v_a)$,

$**$ if $\mathbf{T}(e,v)=\mathbf{T}_a(e_a,v_a)$ and $\mathbf{P}(e,v)=\mathbf{P}_a(e_a,v_a)$, then $\mathbf{q}(e,v,e_a,v_a)=0$ and $\mathbf{f}(e,v,e_a,v_a)=0$,

– the dissipation inequality:

$$-\frac{\mathbf{q}}{\mathbf{T}}(\mathbf{T}-\mathbf{T}_a)-\frac{\mathbf{w}}{\mathbf{P}}(\mathbf{P}-\mathbf{P}_a)\geq 0,$$

where equality holds if and only if $\mathbf{q}(e,v,e_a,v_a)=$ and $\mathbf{f}(e,v,e_a,v_a)=0$. If working is ideal, then

$$(\mathbf{q}-\mathbf{P}\mathbf{f})\left(\frac{1}{\mathbf{T}}-\frac{1}{\mathbf{T}_a}\right)+\mathbf{f}\left(\frac{\mathbf{P}}{\mathbf{T}}-\frac{\mathbf{P}_a}{\mathbf{T}_a}\right)\geq 0.$$

3. There is a given process $t\mapsto(e_a(t),v_a(t))\in \mathrm{D}_a$ of the environment which is a continuous function defined on a time interval.

4. There is the given specific heat source $t\mapsto q_s(t)$ which is a continuous function defined on a time interval.

5. The process $t\mapsto\big(e(t),v(t)\big)$ of the body is determined by the dynamical equation

$$\begin{aligned}\dot{e}&=q_s+\mathbf{q}(e,v,e_a,v_a)+\mathbf{w}(e,v,e_a,v_a),\\ \dot{v}&=\mathbf{f}(e,v,e_a,v_a).\end{aligned}$$

Remark The symbol $*$ in item 3 refers to a property saying how the equal values of intensive quantities follow from the zero value of the dynamical quantitities; the symbol $**$ refers to the joint inversion of the former relations: how the equal values of intensive quantities imply the zero value of the dynamical quantitities.

12.2.2 Other variables

The body and the environment do not interchange particles, thus the material of the environment is not important from the point of view of processes. In practice environmentcan be well characterized by its temperature and pressure, therefore in the sequel the variables (e_a,v_a) will be replaced with (T_a,P_a) (but the same letter will stand for the dynamical quantitities, so we write, e.g. $\mathbf{q}(e,v,T_a,P_a)$ and the process of the environment is considered in the form $t\mapsto\big(T_a(t),P_a(t)\big)$.

Sometimes it will be convenient to use the variables (v,T) instead of (e,v). Then with the notations

$$\mathfrak{q}(v,T,T_a,P_a):=\mathbf{q}(\mathfrak{e}(v,T),v,T_a,P_a),$$

$$\mathfrak{f}(v,T,T_a,P_a):=\mathbf{f}(\mathfrak{e}(v,T),v,T_a,P_a),$$

and

$$\mathfrak{c}_v(v,T) := \frac{\partial \mathfrak{e}(v,T)}{\partial T},$$

$$\mathfrak{n}(v,T,T_a,P_a) := \frac{\partial \mathfrak{e}(v,T)}{\partial v} + \mathcal{P}(v,T) + \boldsymbol{\pi}(\mathfrak{e}(v,T),v,T_a,P_a)$$

the dynamical equation becomes

$$\begin{aligned} \mathfrak{c}_v(v,T)\dot{T} &= q_s + \mathfrak{q}(v,T,T_a,P_a) - \mathfrak{n}(v,T,T_a,P_a)\mathfrak{f}(v,T,T_a,P_a), \\ \dot{v} &= \mathfrak{f}(v,T,T_a,P_a). \end{aligned}$$

We mention that the symbol $\mathfrak{f}$ has been previously used for the specific free energy in the variables (v,T); unfortunately, there are more quantities than letters, so we are forced sometimes to apply the same symbol for different objects. Now this will not cause confusion because we shall not involve free energy in the investigations.

12.2.3 Equilibrium

According to 10.7, a standstill is a time-independent process (a constant solution of the dynamical equation). There is no standstill if the heat source and the process of the environment are not constant. In the sequel (except Paragraph 12.8 and the exercises) we take a zero heat source and a constant environment process:

$$q_s = 0, \qquad T_a = \text{const.}, \qquad P_a = \text{const.}$$

Then every standstill is evidently an equilibrium (when every dynamical quantity takes zero value). The state (e_o, v_o) is an equilibrium if and only if

$$\mathbf{q}(e_o,v_o,T_a,P_a) = 0, \qquad \mathbf{f}(e_o,v_o,T_a,P_a) = 0,$$

or, equivalently, the state (v_o, T_o) is an equilibrium if and only if

$$\mathfrak{q}(v_o,T_o,T_a,P_a) = 0, \qquad \mathfrak{f}(v_o,T_o,T_a,P_a) = 0.$$

12.2.4 Entropic body

If the body is entropic, the function (written in the usual symbolic form)

$$L := s - \frac{e + P_a v}{T_a} \tag{$*$}$$

will play an important role; this function, up to an additive and multiplicative constant, is the **total specific entropy of the body and the environment-together**.

The specific entropy of the environment is

$$s_a = \frac{e_a + P_a v_a - \mu_a}{T_a}.$$

The body and the environment constitute a closed system, i.e. their total energy and total volume are constant. If N and N_a are the particle numbers of the body and the environment, respectively, then

$$Ne + N_a e_a =: E_s = \text{const.}, \qquad Nv + N_a v_a =: V_s = \text{const.}.$$

Then the entropy of the environment is

$$N_a s_a = -N\frac{e + P_a v}{T_a} + \frac{E_s + P_a V_s - N_a \mu_a}{T_a}.$$

Temperature, pressure, chemical potential are constant in the given process of the environment (and, of course, the particle number of the environment is constant, too), so so the sum of the entropies $Ns + N_a s_a$ is a multiple of the function $(*)$ plus a constant.

The symbolic function $(*)$ will be actually given both in the variables (e, v) and in the variables (v, T):

$$(e, v) \mapsto \mathbf{L}(e, v) := \mathbf{s}(e, v) - \frac{e + P_a v}{T_a},$$

and

$$(v, T) \mapsto \mathcal{L}(v, T) := \mathfrak{s}(v, T) - \frac{\mathfrak{e}(v, T) + P_a v}{T_a}.$$

These functions are continuously differentiable on the regular domain R and R, respectively, and if the body is entropic, then

$$\frac{\partial \mathbf{L}}{\partial e} = \frac{1}{\mathbf{T}} - \frac{1}{T_a}, \qquad \frac{\partial \mathbf{L}}{\partial v} = \frac{\mathbf{P}}{\mathbf{T}} - \frac{P_a}{T_a},$$

$$\frac{\partial \mathcal{L}}{\partial v} = \left(\frac{1}{T} - \frac{1}{T_a}\right)\frac{\partial \mathfrak{e}}{\partial v} + \frac{\mathcal{P}}{T} - \frac{P_a}{T_a}, \qquad \frac{\partial \mathcal{L}}{\partial T} = \left(\frac{1}{T} - \frac{1}{T_a}\right)\frac{\partial \mathfrak{e}}{\partial T}.$$

12.3 Processes without constraint

12.3.1 Properties of the dynamical quantitities

The body and the environmentare coupled both mechanically and thermally, $\mathfrak{q} \neq 0$ and $\mathfrak{f} \neq 0$, thus the equilibrium properties are the following:

– $\mathcal{P}(v, T) = P_a$ implies $\boldsymbol{\pi}(v, T, T_a, P_a) = 0$,

$*$ $\mathfrak{f}(v, T, T_a, P_a) = 0$ implies $\mathcal{P}(v, T) = P_a$,

$*$ $\mathfrak{q}(v, T, T_a, P_a) = 0$ and $\mathcal{P}(v, T) = P_a$ imply $T = T_a$,

$**$ $T{=}T_a$, and $\mathcal{P}(v, T){=}P_a$ imply $\mathfrak{q}(v, T, T_a, P_a){=}0$ and $\mathfrak{f}(v, T, T_a, P_a){=}0$.

As a consequence, equality holds in the dissipation inequality if and only if $T = T_a$ and $\mathcal{P}(v, T) = P_a$.

12.3.2 Uniqueness of equilibrium

The equilibrium properties imply that (v_o, T_o) in the constitutive domain is an equilibrium if and only if

$$T_o = T_a, \qquad \mathcal{P}(v_o, T_a) = P_a.$$

Evidently, equilibrium can exist only if T_a and P_a are possible temperature and pressure of the body. The equilibrium, in general, is not unique: the same pressure value can correspond to different values of specific volume (e.g. in the case of a van der Waals material the same temperature and pressure value can correspond to a pure liquid state and to a pure gas state, too).

Because $v \mapsto \mathcal{P}(v, T_a)$ is injective on a phase, we have:

Proposition *The equilibrium (if exists) is unique in every phase.*

12.3.3 Stability of equilibrium

Let us suppose that the dynamical quantitities are pseudolinear (and let us apply now the notations of 11.3 for the specific quantities):

$$q = -\lambda_q(T - T_a) + \beta_q(P - P_a),$$
$$f = -\lambda_f(T - T_a) + \beta_f(P - P_a),$$

where $(v, T, T_a, P_a) \mapsto \lambda_q(v, T, T_a, P_a)$, etc. are continuous functions.

Then the dynamical equation in 12.2.2 becomes

$$\begin{pmatrix} \mathfrak{c}(v,T)_v \dot{T} \\ \dot{v} \end{pmatrix} = \begin{pmatrix} -\lambda_q + n\lambda_f & \beta_q - n\beta_f \\ -\lambda_f & \beta_f \end{pmatrix} \begin{pmatrix} T - T_a \\ \mathcal{P}(v,T) - P_a \end{pmatrix},$$

where, of course, $\lambda_q = \lambda_q(v, T, T_a, P_a)$ etc. and $n = \mathfrak{n}(v, T, T_a, P_a)$.

It seems reasonable to assume that the cross effects are negligible near to equilibrium, i.e. heating is not affected significantly by the pressure difference and springing is not affected significantly by the temperature difference near equilibrium (the latter is trivially true for mechanically strong springing).

Proposition *If*

$$\beta_q(v_o, T_a, T_a, P_a) = 0, \qquad \lambda_f(v_o, T_a, T_a, P_a) = 0,$$

$$\lambda_a := \lambda_q(v_o, T_a, T_a, P_a) > 0, \qquad \beta_a := \beta_f(v_o, T_a, T_a, P_a) > 0,$$

and the body is of normal dilation (see 3.9), then the equilibrium $(v_o, T_a) \in R$ is asymptotically stable.

Proof Let us divide the first equation by $\mathfrak{c}_v$. The right-hand side of the dynamical equation is a differentiable function of the variables (v, T) at the equilibrium (λ_q etc. are continuous, $(v, T) \mapsto T - T_a$ and $(v, T) \mapsto \mathcal{P}(v, T) - P_a$ are differentiable and have zero value at the equilibrium). Putting

$$c_a := \mathfrak{c}_v(v_o, T_a),$$

$$\nu_a := P_a + \frac{\partial \mathfrak{e}}{\partial v}(v_o, T_a), \qquad \xi_a := \frac{\partial \mathcal{P}}{\partial T}(v_o, T_a), \qquad \rho_a := -\frac{\partial \mathcal{P}}{\partial v}(v_o, T_a)$$

and taking into account our assumptions and $\boldsymbol{\pi}(v_o, T_a) = 0$, we get the derivative in the equilibrium of the right-hand side of the dynamical equation:

$$\begin{pmatrix} -\frac{\lambda_a + \nu_a \beta_a \xi_a}{c_a} & \frac{\nu_a \beta_a \rho_a}{c_a} \\ \\ \beta_a \xi_a & -\beta_a \rho_a \end{pmatrix}.$$

This matrix has the characteristic polynomial

$$x \mapsto x^2 + \left(\beta_a \rho_a + \frac{\lambda_a + \nu_a \xi_a \beta_a}{c_a} \right) x + \beta_a \rho_a \frac{\lambda_a}{c_a};$$

our conditions imply that all the coefficients are positive, thus the eigenvalues of the matrix have a negative real part.

According to the linearization method of the stability theory, the equilibrium is asymptotically stable.

12.3.4 Stability of equilibrium of an entropic body

Our previous result requires, among others, the normal dilation property which is satisfied if the body is entropic. Note that according to our convention in 10.5, we can take ideal working.

Proposition *If the body is entropic and working is ideal, then every equilibrium in the regular domain is asymptotically stable.*

Proof Now we use the canonical variables. Let $(e_o, v_o) \in \mathrm{R}$ be an equilibrium which is equivalent to

$$\mathbf{T}(e_o, v_o) = T_a, \qquad \mathbf{P}(e_o, v_o) = P_a.$$

The first derivative of the function $\mathbf{L}$ given in Paragraph 12.2.4 is zero in equilibrium, its second derivative equals the second derivative of the specific entropy which is negative definite (see 5.3); as a consequence, $\mathbf{L}$ has a strict local maximum at (e_o, v_o).

The derivative of $\mathbf{L}$ along the dynamical equation, the function

$$\overset{\bullet}{\mathbf{L}}(e, v) := \left(\frac{1}{\mathbf{T}(e, v)} - \frac{1}{T_a} \right) \big(\mathbf{q}(e, v, T_a, P_a) - \mathbf{P}(e, v) \mathbf{f}(e, v, T_a, P_a) \big) + \\ + \left(\frac{\mathbf{P}(e, v)}{\mathbf{T}(e, v)} - \frac{P_a}{T_a} \right) \mathbf{f}(e, v, T_a, P_a)$$

takes zero value only in equilibrium and everywhere else it is positive (because of the dissipation inequality); in other words, $\overset{\bullet}{\mathbf{L}}$ has a strict local minimum at (e_o, v_o).

Therefore, $\mathbf{L}$ is a Liapunov function for asymptotic stability of equilibria.

12.4 Isochoric processes

12.4.1 Properties of the dynamical quantitities

We examine a system in which the volume of the body is constant, i.e. the body and the environment are coupled only thermally. Then $\mathfrak{f} = 0$ and $\boldsymbol{\pi}$ does not matter. The equilibrium property of heating reads (see 12.2.1):

$*$ $\mathfrak{q}(v, T, T_a, P_a) = 0$ if and only if $T = T_a$.

The dissipation inequality is

$$-q(T - T_a) \geq 0 \qquad \text{or} \qquad q\left(\frac{1}{T} - \frac{1}{T_a}\right) \geq 0$$

where equality holds if and only if $T = T_a$.

12.4.2 Uniqueness of equilibrium

For all $v_\mathrm{o} \in (\mathrm{m}^3)^+$

$$U(v_\mathrm{o}) := \{(v_\mathrm{o}, T) \in D \mid T \in (\mathrm{K})^+\}$$

is an invariant set of the dynamical equation

$$\mathfrak{c}_v(v, T)\dot{T} = \mathfrak{q}(v, T, T_a, P_a), \qquad \dot{v} = 0.$$

$U(v_\mathrm{o})$ is the isochoric curve in the v–T plane (a ‘vertical line’ in the constitutive domain). Its part in the regular domain is a one-dimensional submanifold,

With a given a v_o, $(v_\mathrm{o}, T_\mathrm{o})$ is an equilibrium if and only if

$$T_\mathrm{o} = T_a;$$

the set of equilibrium is the part of the isotherm corresponding to T_a (a ‘horizontal line’ in the constitutive domain). Then it is trivially true:

Proposition *Equilibrium on every isochoric curve (if exists) is unique.*

12.4.3 Stability of equilibrium

Proposition *For all v_o the equilibrium $(v_\mathrm{o}, T_a) \in U(v_\mathrm{o}) \cap R$ is asymptotically stable in $U(v_\mathrm{o})$.*

Proof Let us parameterize the invariant submanifold near the equilibrium by temperature. Then the reduced dynamical equation becomes:

$$\mathfrak{c}_v(v_\mathrm{o}, T)\dot{T} = \mathfrak{q}(v_\mathrm{o}, T, T_a, P_a).$$

The function $T \mapsto \Lambda(T) := -(T - T_a)^2$ is continuously differentiable and has a strict maximum at T_a.

The derivative of Λ along the reduced dynamical equation, the function

$$T \mapsto \overset{\bullet}{\Lambda}(T) = -2(T - T_a)\frac{\mathfrak{q}(v_\mathrm{o}, T, T_a, P_a)}{\mathfrak{c}_v(v_\mathrm{o}, T)};$$

has a strict local minimum at T_a by the uniqueness of the equilibrium, the dissipation inequality and the positivity of specific heat.

12.4.4 Stability of equilibrium of an entropic body

Though the previous result is most general, it is worth considering an entropic body.

Let us use the canonical variables; then parameterizing $U(v_o)$ by internal energy, we find the reduced dynamical equation

$$\dot{e} = \mathbf{q}(e, v_o, T_a, P_a).$$

The equilibrium e_o is determined by $\mathbf{T}(e_o, v_o) = T_a$. We can easily show that

$$e \mapsto \Lambda(e) := \mathbf{L}(e, v_o) = \mathbf{s}(e, v_o) - \frac{e + P_a v_o}{T_a}$$

is a Liapunov function for asymptotic stability of equilibrium.

Indeed, it is continuously differentiable in a neighbourhood of equilibrium and

$$\Lambda'(e) = \frac{1}{\mathbf{T}(e, v_o)} - \frac{1}{T_a}.$$

Thus the first derivative of Λ at e_o is zero, its second derivative

$$\Lambda''(e) = -\frac{1}{\mathbf{T}(e, v_o)^2}\frac{\partial \mathbf{T}(e, v_o)}{\partial e} < 0,$$

consequently Λ has a strict local maximum at e_o.

The derivative of Λ along the reduced dynamical equation, the function

$$e \mapsto \overset{\bullet}{\Lambda}(e) := \left(\frac{1}{\mathbf{T}(e, v_o)} - \frac{1}{T_a}\right)\mathbf{q}(e, v_o, T_a, P_a)$$

takes zero value only in equilibrium, everywhere else it is positive according to the dissipation property, in other words, it has a strict minimum at e_o.

12.5 Adiabatic processes

12.5.1 Properties of the dynamical quantitities

Let us suppose that the body is heat insulated from the environment, i.e. the body and the environment are coupled only mechanically: $\mathfrak{q} = 0$. Let us recall (see Paragraph 10.5) that in this case we can suppose ideal working only if it does not lead to a contradiction. Now we take non-ideal working though it is not necessary.

The equilibrium properties of the dynamical quantitities (see 12.2.1) are the following:

– $\boldsymbol{\pi}(v, T, T_a, P_a) = 0$ if $\mathcal{P}(v, T) = P_a$,

∗ $\mathfrak{f}(v, T, T_a, P_a) = 0$ if and only if $\mathcal{P}(v, T) = P_a$,

The dissipation inequality is

$$-\frac{w}{P}(P - P_a) \geq 0,$$

where equality holds if and only if $P = P_a$. Let us note that $-\frac{w}{P} = \left(1 + \frac{\pi}{P}\right) f$ and π has zero value if $P = P_a$; thus

$$\mathfrak{f}(v, T, T_a, P_a)(\mathcal{P}(v, T) - P_a) \geq 0 \tag{$*$}$$

in a neighbourhood of the isobaric curve corresponding to P_a and equality holds if and only if (v, T) is on that curve, i.e. $\mathcal{P}(v, T) = P_a$.

12.5.2 Uniqueness of equilibrium

The dynamical equation in the variables (v, T) now has the form

$$\mathfrak{c}_v(v, T)\dot{T} = -\mathfrak{n}(v, T, P_a)\dot{v}, \qquad \dot{v} = \mathfrak{f}(v, T, P_a). \tag{$*$}$$

Because of the special form of the dynamical equation, the volume and the temperature do not change independently. Namely, the range of a process is a **generalized adiabat**, the graph of a solution of the differential equation

$$\frac{d\tau}{dv} = -\frac{\mathfrak{n}(v, \tau, P_a)}{\mathfrak{c}_v(v, \tau)}$$

(we say generalized adiabat because adiabat means the corresponding curve in the case of ideal working (see Section 3)).

In other words, generalized adiabats are invariant sets of the dynamical equation ($*$).

(v_o, T_o) is an equilibrium if and only if

$$\mathcal{P}(v_o, T_o) = P_a;$$

in other words, the set of equilibria is the isobaric curve L corresponding to P_a.

Thusn equilibria on a generalized adiabat C are the intersection points of C and the isobaric curve L.

If $(v_o, T_o) \in C \cap L$ is in the regular domain, then both C and L are one-dimensional submanifolds in a neighbourhood of (v_o, T_o); their tangent vectors at (v_o, T_o) are

$$\left(-\frac{\partial \mathcal{P}}{\partial v}, \frac{\partial \mathcal{P}}{\partial T}\right)\Bigg|_{(v_o, T_o)}, \qquad \text{and} \qquad (\mathfrak{c}_v(v_o, T_o), -\mathfrak{n}(v_o, T_o, P_a)),$$

respectively. $\boldsymbol{\pi}$ takes zero value in equilibrium, thus

$$\mathfrak{n}(v_o, T_o, P_a) = P_a + \frac{\partial \mathfrak{e}}{\partial v}(v_o, T_o).$$

It is a simple fact that if the body is of normal dilation (see 3.9), then the two tangent vectors are not parallel, thus C and L have no other intersection point in a neighbourhood of (v_o, T_o); as a consequence, we have:

Proposition *If the body is of normal dilation, then the equilibrium in every generalized adiabat (if exists) is locally unique in the regular domain.*

12.5.3 Stability of equilibrium

Proposition *Let C be a generalized adiabat. If the normal dilation property is satisfied, then every equilibrium $(v_o, T_o) \in C \cap R$ is asymptotically stable in C.*

Proof The submanifold C is parameterized by the function $v \mapsto \big(v, \tau(v)\big)$. Then the reduced dynamical equation becomes

$$\dot{v} = \mathfrak{f}(v, \tau(v), T_a, P_a).$$

The conditions of intrinsic stability and the normal dilation property imply that

$$\frac{d}{dv}\mathcal{P}(v, \tau(v))\bigg|_{v=v_o} = \left(\frac{\partial \mathcal{P}}{\partial v} - \frac{\partial \mathcal{P}}{\partial T}\frac{\mathcal{P} + \frac{\partial \mathfrak{e}}{\partial v}}{\mathfrak{c}_v}\right)(v_o, T_o) < 0,$$

thus, the derivative of the function $v \mapsto \mathcal{P}(v, \tau(v))$ (which is continuous) is negative in a neighbourhood of v_o.

The function

$$v \mapsto \Lambda(v) := -\big(\mathcal{P}(v, \tau(v)) - P_a\big)^2$$

is continuously differentiable in a neighbourhood of v_o and has a strict local maximum at v_o (because of the local uniqueness of equilibrium in C).

The derivative of Λ along the reduced dynamical equation, the function

$$v \mapsto \overset{\bullet}{\Lambda}(v) = -2(\mathcal{P}(v, \tau(v)) - P_a)\left(\frac{d}{dv}\mathcal{P}(v, \tau(v))\right)\mathfrak{f}(v, \tau(v), T_a, P_a)$$

has a strict local minimum in v_o because of $\frac{d}{dv}\mathcal{P}(v, \tau(v)) < 0$, the local uniqueness of equilibrium and the dissipation inequality $(*)$.

12.5.4 Stability of equilibrium of an entropic body

Let us examine adiabatic processes of an entropic body if working is ideal. Then adiabatic processes are isentropic, and

$$\mathfrak{c}_v(v, \tau(v))\frac{d\tau(v)}{dv} = -\left(\mathcal{P}(v, \tau(v)) + \frac{\partial \mathfrak{e}}{\partial v}(v, \tau(v))\right) = -\tau(v)\frac{\partial \mathcal{P}}{\partial T}(v, \tau(v)).$$

The previous proposition is valid in this case, too, but it is worth noting that now

$$v \mapsto \Lambda(v) := \mathcal{L}(v, \tau(v)) = \mathfrak{s}(v_o, T_o) - \frac{\mathfrak{e}(v, \tau(v)) + P_a v}{T_a}$$

is another Liapunov function for asymptotic stability. It is defined and continuously differentiable in a neighbourhood of v_o and

$$T_a \Lambda'(v) = -\left(\frac{\partial \mathfrak{e}}{\partial v}(v, \tau(v)) + \frac{\partial \mathfrak{e}}{\partial T}(v, \tau(v))\frac{d\tau(v)}{dv} + P_a\right) = \mathcal{P}(v, \tau(v)) - P_a.$$

Consequently, the first derivative of Λ at v_o is zero; furthermore,

$$\begin{aligned} T_a\Lambda''(v) &= \frac{\partial \mathcal{P}}{\partial v}(v,\tau(v)) - \frac{\partial \mathcal{P}}{\partial T}(v,\tau(v))\frac{d\tau(v)}{dv} = \\ &= \frac{\partial \mathcal{P}}{\partial v}(v,\tau(v)) - \frac{\tau(v)}{\mathfrak{c}_v(v,\tau(v))}\left(\frac{\partial \mathcal{P}}{\partial T}(v,\tau(v))\right)^2 < 0, \end{aligned}$$

thus Λ has a strict local maximum at v_o.

The derivative of Λ along the reduced dynamical equation, the function

$$v \mapsto \overset{\bullet}{\Lambda}(v) = \frac{\mathcal{P}(v,\tau(v)) - P_a}{T_a}\mathfrak{f}(v,\tau(v),T_a,P_a)$$

takes zero value only at v_o and is positive in a neighbourhood of v_o because of the dissipation inequality and the local uniqueness of equilibrium; in other words, it has a strict minimum at v_o.

12.6 Isothermal processes

12.6.1 Properties of the dynamical quantitities

Let us examine processes in which the body has constant temperature T_o. The previous constraints – constant volume, heat insulation – were described by an evident manner by the dynamical quantitities. The constraint of constant temperature is reflected in the dynamical quantitities, too, but in a more involved way: heating and working are not independent. This seems natural: we experience that a body becomes warmer when being compressed; in order that the body does not become warmer (isothermal process) in spite of compressing, we must cool it, i.e. extract heat from it. The faster the compression, the larger the heat extraction per unit time.

The relation between heating and working can be obtained most easily in the variables (v,T); then a process has the form $t \mapsto \big(v(t),T_\mathrm{o}\big)$, and the dynamical equation becomes

$$\begin{aligned} 0 &= \mathfrak{q}(v,T_\mathrm{o},,T_a,P_a) - \mathfrak{n}(v,T_\mathrm{o},T_a,P_a)\mathfrak{f}(v,T_\mathrm{o},T_a,P_a), \\ \dot{v} &= \mathfrak{f}(v,T_\mathrm{o},T_a,P_a). \end{aligned}$$

We see that heating is proportional to springing:

$$\mathfrak{q} = \mathfrak{n}\,\mathfrak{f}.$$

As a consequence, $(v_\mathrm{o},T_\mathrm{o})$ is an equilibrium if and only if $\mathfrak{f}(v_\mathrm{o},T_\mathrm{o},T_a,P_a) = 0$; then $\mathfrak{q}(v_\mathrm{o},T_\mathrm{o},T_a,P_a) = 0$, too, so by the equilibrium properties of the dynamical quantitities (see 12.2.1) we have $\mathcal{P}(v,T) = P_a$ and $T_\mathrm{o} = T_a$. Thus if $T_\mathrm{o} \neq T_a$, then $\mathfrak{f}(v,T_\mathrm{o},T_a,P_a) \neq 0$: there is no equilibrium. This is understandable from a physical point of view: if, e.g. $T_\mathrm{o} > T_a$, then the body heats the environment, and we have to compress the body permanently in order to keep its temperature constant.

Thus (v_o, T_a) is an equilibrium if and only if $\mathcal{P}(v_o, T_a) = P_a$ or, equivalently, $* \ \mathfrak{f}(v_o, T_a, T_a, P_a) = 0$ if and only if $\mathcal{P}(v_o, T_a) = P_a$,

The dissipation inequality gives – as in the previous paragraph – that

$$\mathfrak{f}(v, T_a, T_a, P_a)(\mathcal{P}(v, T_a) - P_a) \geq 0$$

for all (v, T_a) in a neighbourhood of (v_o, T_a) and equality holds if and only if $v = v_o$.

12.6.2 Uniqueness of equilibrium

$U(T_o) := \{(v, T_o) \mid v \in (\mathrm{m}^3)^+\}$, the isotherm with temperature T_o is an invariant set of the dynamical equation. We have seen that if $T_o \neq T_a$, then there is no equilibrium, and (v_o, T_a) is an equilibrium if and only if

$$\mathcal{P}(v_o, T_a) = P_a.$$

Because the function $v \mapsto \mathcal{P}(v, T_a)$ is injective in every phase, we have:

Proposition *The equilibrium on the isotherm $U(T_a)$ (if exists) is unique in every phase.*

12.6.3 Stability of equilibrium

Proposition *Every equilibrium (v_o, T_a) in the regular domain is asymptotically stable in $U(T_a)$.*

Proof The reduced dynamical equation is

$$\dot{v} = \mathfrak{f}(v, T_a, T_a, P_a).$$

The function $v \mapsto \mathcal{P}(v, T_a)$ is continuously differentiable and strictly monotone decreasing in a neighbourhood of v_o. Consequently, the function

$$v \mapsto \Lambda(v) := -\big(\mathcal{P}(v, T_a) - P_a\big)^2$$

has a strict local maximum at v_o. The derivative of Λ along the reduced dynamical equation, the function

$$v \mapsto \overset{\bullet}{\Lambda}(v) = -2(\mathcal{P}(v, T_a) - P_a)\frac{\partial \mathcal{P}(v, T_a)}{\partial v}\mathfrak{f}(v, T_a, T_a, P_a)$$

has a strict local minimum at v_o because of the local uniqueness of the equilibrium, the dissipation inequality and the intrinsic stability condition $\frac{\partial \mathcal{P}(v, T_a)}{\partial v} < 0$.

12.6.4 Stability of equilibrium of an entropic body

Though the previous result is most general, it is worth considering an entropic body.

Then

$$v \mapsto \Lambda(v) := \mathcal{L}(v, T_a) = \mathfrak{s}(v, T_a) - \frac{\mathfrak{e}(v, T_a) + P_a v}{T_a}$$

is another Liapunov function for asymptotic stability: continuously differentiable in a neighbourhood of v_o and

$$\Lambda'(v) = \frac{\mathcal{P}(v, T_a) - P_a}{T_a},$$

thus the first derivative of Λ is zero at v_o. Furthermore,

$$T_a \Lambda''(v) = \frac{\partial \mathcal{P}(v, T_a)}{\partial v} < 0,$$

so Λ has a strict local maximum at v_o.

The derivative of Λ along the reduced dynamical equation, the function

$$v \mapsto \overset{\bullet}{\Lambda}(v) := \frac{\mathcal{P}(v, T_a) - P_a}{T_a} \mathfrak{f}(v, T_a, T_a, P_a)$$

has a strict local minimum at v_o because of the local uniqueness of the equilibrium and the dissipation inequality.

12.7 Isobaric processes

12.7.1 Properties of the dynamical quantitities

Let us examine processes in which the body has constant pressure P_o. The constraint of constant pressure establishes a relation between working and heating. This seems natural: we experience that by heating a body, the pressure of the body increases; in order to keep the body pressure constant in spite of heating, the body has to expand. The stronger the heating, the faster the expansion.

To obtain the relation between heating and working, let us use again the variables (v, T). v and T do not change independently:

$$\mathcal{P}(v, T) = P_\mathrm{o} \tag{$*$}$$

must hold implying

$$\frac{\partial \mathcal{P}}{\partial v} \dot{v} + \frac{\partial \mathcal{P}}{\partial T} \dot{T} = 0.$$

This relation and the dynamical equation allows us to deduce

$$\left(\mathfrak{c}_v + \mathfrak{n} \frac{\frac{\partial \mathcal{P}}{\partial T}}{-\frac{\partial \mathcal{P}}{\partial v}} \right) \mathfrak{f} = \frac{\frac{\partial \mathcal{P}}{\partial T}}{-\frac{\partial \mathcal{P}}{\partial v}} \mathfrak{q}.$$

If $\mathfrak{q}(v_\mathrm{o}, T_\mathrm{o}, T_a, P_a) = 0$ – implying that $\mathfrak{f}(v_\mathrm{o}, T_\mathrm{o}, T_a, P_a) = 0$, too – then the equilibrium properties of the dynamical quantitities (see 12.2.1) give $T_\mathrm{o} = T_a$ and $\mathcal{P}(v_\mathrm{o}, T_a) = P_a$. We consider processes satisfying equality $(*)$; thus if $P_\mathrm{o} \neq P_a$, then $\mathfrak{q}(v_\mathrm{o}, T_\mathrm{o}, T_a, P_a) \neq 0$: there is no equilibrium. This is understandable from a physical point of view: if, e.g. $P_\mathrm{o} > P_a$, then the body expands, is not in equilibrium; we can hinder expansion by extracting heat from the body but this is not an equilibrium either.

Thus we shall consider (v, T)-s for which

$$\mathcal{P}(v, T) = P_a \tag{$**$}$$

holds. As a consequence – the pressure of the body equals the pressure of the environment – the lost coefficient takes zero values in such processes, so the relation between springing and heating can be written if the form

$$\mathfrak{c}_p \mathfrak{f} = \frac{\frac{\partial \mathcal{P}}{\partial T}}{-\frac{\partial \mathcal{P}}{\partial v}} \mathfrak{q},$$

where $\mathfrak{c}_p$ is the specific heat at constant pressure (see 3.7).

Moreover, (v_o, T_o) is an equilibrium if and only if $T_o = T_a$ or, equivalently, $*$ $\mathfrak{q}(v_o, T_o, T_a, P_a) = 0$ if and only if $T_o = T_a$.

The dissipation inequality gives

$$-\mathfrak{q}(v, T, T_a, P_a)(T - T_a) \geq 0$$

for all (v, T) satisfying $(**)$ and equality holds if and only if $T = T_a$.

12.7.2 Uniqueness of equilibrium

We infer from the relation between heating and springing that

$$U(P_o) := \{(v, T) \mid \mathcal{P}(v, T) = P_o\},$$

the isobaric curve corresponding to P_o is an invariant set of the dynamical equation 12.2.2. We have seen that if $P_o \neq P_a$, then there is no equilibrium, and (v_o, T_o) is an equilibrium if and only if $T_o = T_a$ and $\mathcal{P}(v_o, T_a) = P_a$. We can argue as previously, to prove:

Proposition *On the isobaric curve with pressure P_a, the equilibrium (if exists) is unique in every phase.*

12.7.3 Stability of equilibrium

Proposition *If the specific heat at constant pressure is positive, then every equilibrium $(v_o, T_a) \in U(P_a)$ in the regular domain is asymptotically stable in $U(P_a)$.*

Proof Let us express volume as a function of temperature in a neighbourhood of (v_o, T_a) from the implicit relation $\mathcal{P}(v, T) = P_a$; let ν be this function. Then the reduced dynamical equation becomes (on the basis of the relation between springing and heating)

$$\mathfrak{c}_p(\nu(T), T)\dot{T} = \mathfrak{q}(\nu(T), T, T_a, P_a).$$

The function

$$T \mapsto \Lambda(T) := -(T - T_a)^2$$

has a strict local maximum at T_a and its derivative along the reduced dynamical equation, the function

$$T \mapsto \overset{\bullet}{\Lambda}(T) = -2(T - T_a)\frac{\mathfrak{q}(\nu(T), T, T_a, P_a)}{\mathfrak{c}_p(\nu(T), T)}$$

has a strict local minimum at T_a because of the dissipation inequality. ☐

The condition imposed on the specific heat at constant pressure may seem curious, because “it is well known" that c_p is positive; but this is not necessarily valid in our framework. It holds if the body has the normal dilation property which follows if the body is entropic.

12.7.4 Stability of equilibrium of an entropic body

It is worth noting that for an entropic body

$$T \mapsto \Lambda(T) := \mathcal{L}(\nu(t), T) = \mathfrak{s}(\nu(T), T) - \frac{\mathfrak{e}(\nu(T), T) + P_a\nu(T)}{T_a}$$

is another Liapunov function for asymptotic stability. It is continuously differentiable in a neighbourhood of T_a and because of

$$\frac{d\nu(T)}{dT} = -\frac{\frac{\partial \mathcal{P}}{\partial T}}{\frac{\partial \mathcal{P}}{\partial v}}(\nu(T), T)$$

we have

$$\Lambda'(T) = \left(\frac{1}{T} - \frac{1}{T_a}\right)\mathfrak{c}_p(\nu(T), T),$$

i.e. its first derivative is zero at T_a.

For an entropic body the specific heat at constant pressure is positive, thus

$$\Lambda''(T_a) = -\frac{1}{T_a^2}\mathfrak{c}_p(\nu(T), T) < 0,$$

therefore, Λ has a strict local maximum at T_a.

The derivative of Λ along the reduced dynamical equation, the function

$$T \mapsto \overset{\bullet}{\Lambda}(T) := \left(\frac{1}{T} - \frac{1}{T_a}\right)\mathfrak{q}(\nu(T), T, T_a, P_a)$$

has a strict local minimum at T_a because of the dissipation inequality.

12.8 Non-zero heat source

Let a heat source $q_s \neq 0$ be in the body. Then (with the usual loose notations)

$$\dot{e} = q_s + q + w, \qquad \dot{v} = f.$$

In a standstill $\dot{e} = 0$ and $\dot{v} = 0$; the latter implies $w = 0$, thus $q = -q_s$: a standstill is a stationary process. Furthermore, if the body is heat insulated, ($\mathfrak{q} = 0$, adiabatic process), then there is no standstill.

We can say less about the stability of stationary states.

Let us suppose that the heat source q_s, the temperature T_a and the pressure P_a of the environment are constant, furthermore, the dynamical quantitities are pseudolinear:

$$q = -\lambda_q(T - T_a) + \beta_q(P - P_a),$$
$$f = -\beta_f(P - P_a) + \beta_f(P - P_a),$$

where $\lambda_q > 0$ is constant. Let us use the variables (v, T). We easily find that (v_o, T_o) is a stationary state if and only if $\mathcal{P}(v_o, T_o) = P_a$ and $T_o = T_a + \frac{q_s}{\lambda}$. Putting $q_s = \lambda(T_o - T_a)$ into the dynamical equation, we get the same form as in Paragraph 12.3, T_a replaced by T_o. Therefore the linearization method allows us to deduce the same result on asymptotic stability, too.

It is not evident, however, how we could use entropy for assuring asymptotic stability; can we use it at all?

12.9 Elastic hull

Now we treat a system which is theoretically different from, but practically similar to, the previous ones. Let us imagine a gas in an elastic hull (ball, tyre) put in the atmosphere. The pressure (strain) of the elastic hull is considered to be homogeneous (but it is not, as said in Paragraph 2 of the Preface) and to depend on the enclosed volume: the larger the volume, the larger the pressure.

Besides the customary data (body and environment), we suppose to have a continuously differentiable function $\mathbf{p} : (\mathrm{m}^3)^+ \to (\mathrm{Pa})$ (the pressure of the hull as a function of volume) whose derivative is positive everywhere (the pressure is strictly monotone increasing). Then we accept that

– the dynamical equation has the usual form,

– the dynamical quantitities satisfy the usual conditions (equilibrium property, dissipation inequality) in such a way that the pressure P_a of the environment is replaced by $P_a + \mathbf{p}$.

As a consequence, $(e_o, v_o) \in \mathrm{R}$ is an equilibrium if and only if

$$\mathbf{T}(e_o, v_o) = T_a, \qquad \mathbf{P}(e_o, v_o) = P_a + \mathbf{p}(v_o).$$

Proposition *If the body is entropic and working is ideal and there is no constraint, then every equilibrium in the regular domain is asymptotically stable.*

Proof Let $\mathbf{r}$ be a primitive function of $\mathbf{p}$. Then the function

$$(e, v) \mapsto \Lambda(e, v) := \mathbf{s}(e, v) - \frac{e + P_a v + \mathbf{r}(v)}{T_a}$$

is twice differentiable on the regular domain; its derivative

$$\frac{\partial \Lambda}{\partial e} = \frac{1}{\mathbf{T}} - \frac{1}{T_a}, \qquad \frac{\partial \Lambda}{\partial v} = \frac{\mathbf{P}}{\mathbf{T}} - \frac{P_a + \mathbf{p}}{T_a}$$

is zero in equilibrium. Its second derivative

$$\mathtt{D}^2\Lambda = \mathtt{D}^2\mathbf{s} + \begin{pmatrix} 0 & 0 \\ 0 & -\frac{\mathbf{p}'}{T_a} \end{pmatrix},$$

is negative definite (the sum of a negative definite and a negative semi-definite matrix). Thus Λ has a strict local maximum in equilibrium.

The derivative of Λ along the dynamical law, the function

$$\overset{\bullet}{\Lambda}(e,v) = \\ = \left(\frac{1}{\mathbf{T}(e,v)} - \frac{1}{T_a}\right)\Big(\mathbf{q}(e,v,T_a,P_a+\mathbf{p}(v)) - \mathbf{P}(e,v)\mathbf{f}(e,v,T_a,P_a+\mathbf{p}(v))\Big) + \\ + \left(\frac{\mathbf{P}(e,v)}{\mathbf{T}(e,v)} - \frac{P_a+\mathbf{p}(v)}{T_a}\right)\mathbf{f}(e,v,T_a,P_a+\mathbf{p}(v)).$$

has a strict local minimum in equilibrium because of the local uniqueness of equilibrium and the dissipation inequality.

12.10 Zeroth-order and second-order phase transitions

The particle number is not a dynamical variable in zeroth-order and second-order phase transitions, the whole body passes from one phase into another. Hence, such phase transitions are described corresponding to the previous scheme. As an illustration, let us consider the simplest system: a body in a given environment. Then we apply 12.2.1 and we are interested in processes 'connecting' two phases in zeroth-order or second-order phase connection. We explain the expression in quotation mark for a second-order phase transition; the reader is asked to do it for the zeroth-order one.

Let the phases Z_1 and Z_2 of a material have a second-order phase connection, i.e. $\mathrm{C} := \overline{\mathrm{Z}_1} \cap \overline{\mathrm{Z}_2} \cap (\mathrm{D} \setminus \mathrm{R}) \neq \emptyset$. A second-order phase transition occurs in a process $t \mapsto \big(e(t), v(t)\big)$ if there are instants t_1, t_C, t_2 such that

$$(e(t_1), v(t_1)) \in \mathrm{Z}_1, \quad (e(t_C), v(t_C)) \in \mathrm{C}, \quad (e(t_2), v(t_2)) \in \mathrm{Z}_2.$$

We are mostly interested in the stability of equilibria. In Section 12 we considered equilibria in a phase, we could prove asymptotic stability of equilibria in the regular domain. Therefore, a zeroth-order phase transition is of no importance from this point of view. Equilibria on a second-order phase connection are a different matter. It can be shown that an equilibrium on a second-order phase connection of Ehrenfest type is asymptotically stable, on a second-order phase connection of Tisza type can be asymptotically stable, stable and unstable. Having not treated precisely the classification of second-order phase connections, we do not deal with such equilibria.

First-order phase transitions will be treated in Section 20.

12.11 Extremum properties

12.11.1 Conditions of stability

Note that asymptotic stability (of an equilibrium in the regular domain) is assured essentially by two types of condition: the **intrinsic stability conditions** (a property of materials expressed by the constitutive functions) and the **dissipation inequalities** (a property of interactions expressed by the dynamical quantitities).

12.11.2 The role of entropy

It is best seen in the case of entropic bodies that the intrinsic stability conditions imply the maximum of the Liapunov function whereas the dissipation inequalities imply the minimum of the derivative of the Liapunov function along the dynamical equation. The intrinsic stability conditions alone are not sufficient.

The Liapunov function – except the case of the elastic hull – is the total entropy of the bodies and the environment.

Thus, the total entropy has a strict maximum in equilibrium. Its derivative along the dynamical equation, the **entropy production** has a strict minimum in equilibrium where it takes zero value: the entropy is strictly monotone increasing in non-equilibrium processes.

Now we clearly see that the maximum of the total entropy and the positive entropy production are independent (Paragraph 3 of the Preface).

It is worth mentioning that the entropy maximum in equilibrium and positive entropy production in non-equilibrium processes does not hold for the case of elastic hull where the Liapunov function is not the total entropy of the body and the environment. We could think that if we described the hull in a more realistic way as a separate body, then the total entropy of the body, the hull and the environment would be the Liapunov function. This cannot be done, however, in the framework of ordinary thermodynamics: the hull described as a separate body cannot have homogeneous pressure. This indicates that the entropy maximum and the entropy production are doubtful in continuum physics.

12.11.3 Warning

In usual treatments of thermodynamics, equilibrium in different systems is identified with the extremum of different functions. Those assertions are based on formal calculations and obscure the important fact that **always the total entropy has a maximum in equilibrium**.

For instance, one says that for isothermal processes the total free energy has a minimum in equilibrium. This is true because the isothermal total free energy is the negative of the total entropy, up to an additive and multiplicative constant:

$$N(e - Ts) + N_a(e_a - T_a s_a) = -T_a(Ns + N_a s_a) + (Ne + N_a e_a).$$

Furthermore, one says that for isobaric processes, the total enthalpy has a minimum in equilibrium. This is true but vacant because the isobaric total enthalpy is constant:

$$N(e + P_a v) + N_a(e_a + P_a v_a) = (Ne + N_a e_a) + P_a(Nv + N_a v_a).$$

We could think on the basis of the usual formulations that instead of the total free energy or the total enthalpy, the free energy of the body or the enthalpy of the body have a minimum at equilibrium. This, however, makes no sense because the environment can be chosen arbitrarily, so an arbitrary state of the body can be equilibrium.

12.12 Remarks on the intensive constraints

12.12.1 'Infinitely' slow, 'infinitely' fast

Fixed volume and heat insulation (isochoric processes and adiabatic processes) are constraints easily realizable in practice (at least approximately). On the contrary, it is almost impossible to fix temperature or pressure. In usual treatments one takes it for granted that the processes of a body in thermal contact with a 'heat bath' (an environment with given constant temperature) are isothermal (the temperature of the body equals the temperature of the heat bath). This is not so because, e.g. a hot body cools in a colder environment. Let us try to make it better: the processes of a body in thermal contact with a heat bath are isothermal if the initial temperature of the body equals the temperature of the heat bath. Unfortunately, this is not true either. It is an everyday experience that bodies become warmer when being compressed even in a heat bath (the atmosphere). More cautious authors say that the processes of a body in thermal contact with a heat bath are isothermal if the volume change of the body is 'infinitely slow' or the heat conduction between the body and the heat bath is 'infinitely fast'. Let us examine whether we can precisely explain such statements.

Let us take the system in Paragraph 12.3 described by the variables (v, T), let the body be ideal gas with constant specific heat c and

$$\mathfrak{q}(v, T, T_a, P_a) := -\lambda(T - T_a), \qquad \mathfrak{f}(v, T, T_a, P_a) := \beta(\mathcal{P}(v, T) - P_a),$$

where λ and β are positive constants.

Then the dynamical equation is

$$\begin{aligned} c\dot{T} &= -\lambda(T - T_a) - \beta\mathcal{P}(v, T)(\mathcal{P}(v, T) - P_a), \\ \dot{v} &= \beta(\mathcal{P}(v, T) - P_a). \end{aligned}$$

Note that if the temperature is constant, $T = T_a$, then $\dot{T} = 0$, consequently $\mathcal{P}(v, T) - P_a = 0$, thus $\dot{v} = 0$, too: the process is a constant; in other words, a process with constant temperature is necessarily an equilibrium, non-equilibrium process cannot be isothermal (in accordance with our experience).

Let us suppose that the volume change is 'infinitely slow', i.e. β is 'infinitely small'. If $\beta = 0$, then the first law – because of the initial condition $T(t_0) = T_a$ – gives $T(t) = T_a$ for all instants t. But then the second member of the dynamical equation is $\dot{v} = 0$: the volume, too, is constant. An 'infinitely slow' volume change cannot produce a non-equilibrium isothermal process.

Let us suppose now that heat conduction is 'infinitely fast', i.e. λ is 'infinitely large'. Dividing the first law by λ we get

$$\frac{c\dot{T}}{\lambda} = -(T - T_a) - \frac{\beta}{\lambda}\mathcal{P}(v, T)(\mathcal{P}(v, T) - P_a) \qquad (*)$$

and letting λ tend to infinity, we obtain formally $T = T_a$. The second member of the dynamical equation is then modified only slightly: we have to replace T with T_a, but it remains a good equation for the volume change. 'Infinitely fast' heat conduction is a meaningful notion, it gives non-equilibrium isothermal processes.

We have to be careful, however, because the limit $\lambda \to \infty$ is not so simple as it seems at first sight. Let $t \mapsto \big(v_\lambda(t), T_\lambda(t)\big)$ be the solution of the dynamical equation with initial condition $v_\lambda(t_0) = v_0$, $T_\lambda(t_0) = T_a$. It may happen that $\dot{T}_\lambda(t)$ tends to infinity for some t as λ tends to infinity, so $\frac{\dot{T}_\lambda(t)}{\lambda}$ does not tend to zero. Fortunately this is not case; we can apply App. 6. The partial derivative of the right-hand side of $(*)$ with respect to T is negative for sufficiently large λ-s; consequently, if $t \mapsto v(t)$ is the solution of the initial value problem

$$\dot{v} = \beta(\mathcal{P}(v, T_a) - P_a), \qquad v(t_0) = v_0,$$

then

$$\lim_{\lambda\to\infty} v_\lambda(t) = v(t), \qquad \lim_{\lambda\to\infty} T_\lambda(t) = T_a$$

for all $t > t_0$.

Thus we can conceive that the process will be isothermal if the heat conduction is ‘infinitely fast’ between the body and the heat bath. More precisely: the faster the heat conduction, the closer the process to an isothermal one. Another formulation: because the quotient $\frac{\beta}{\lambda}$ appears in the equation, we can say: the process is nearly isothermal *if heat is conducted much faster than volume changes.* The form of the equation clearly shows that the phrase in italics is not equivalent to *if volume changes much slower than heat is conducted.* That is why ‘infinitely fast’ heat conduction is a meaningful notion but ‘infinitely slow’ volume change is not.

We can see similarly that ‘infinitely fast’ volume change is a meaningful notion for isobaric processes.

12.12.2 Practically isothermal processes

We can approximately realize isothermal processes even if heat conduction is not fast by adequately varying the temperature and the pressure of the environment: if we compress a body in such a way that the pressure applied is always a little larger than the pressure of the body, then the volume changes slowly and the body has time to conduct heat to the environment.

Let us consider processes without constraint that run in a single phase; they can be described by temperature and pressure. A process $t \mapsto \big(T(t), P(t)\big)$ is **practically isothermal** if there is a temperature value T_a (the temperature of the environment) and an $\epsilon > 0$ real number (‘small enough’) such that

$$|T(t) - T_a| < \epsilon\mathrm{K} \quad (t > t_0), \qquad \lim_{t\to\infty} T(t) = T_a \tag{$*$}$$

where K is the temperature unit and t_0 is the initial instant.

We shall show that a practically isothermal process can be produced by varying the pressure of the environment adequately in such a way that the final pressure be a prescribed P_∞, i.e.

$$\lim_{t\to\infty} P(t) = P_\infty.$$

If the pressure of the environment is constant $P_s \in [P(t_0), P_\infty]$ and $\pi > 0$ is an arbitrary real number, then – because the equilibrium (T_a, P_s) is asymptotically stable – there are real numbers $\beta(P_s) > 0$ and $\xi(P_s) > 0$ such that if

$$|T(t_s) - T_a| < \beta(P_s)\mathrm{K} \qquad \text{and} \qquad |P(t_s) - P_s| < \xi(P_s)\mathrm{Pa}$$

(where Pa is the pressure unit) for some $t_s \geq t_0$, then

$$|T(t) - T_a| < \epsilon \mathrm{K}, \qquad \text{and} \qquad |P(t) - P_s| < \pi \mathrm{Pa} \tag{1}$$

for all $t > t_s$, moreover

$$\lim_{t\to\infty} T(t) = T_a \qquad \text{and} \qquad \lim_{t\to\infty} P(t) = P_s. \tag{2}$$

We assume that

$$\beta := \inf\{\beta(P_s) \mid P_s \in [P(t_0), P_\infty]\} > 0,$$

$$\xi := \inf\{\xi(P_s) \mid P_s \in [P(t_0), P_\infty]\} > 0.$$

Then we choose

$$P_0 := \min\left\{P(t_0) + \frac{\xi}{2}\mathrm{Pa}, P_\infty\right\}$$

for the initial pressure of the environment. Let us solve the dynamical equation on the interval $[t_0, \infty[$ with the initial values $(T_a, P(t_0))$, putting (T_a, P_0) for the environment. The process satisfies conditions (1) and (2) for $s = 0$. Thus if $P_0 = P_\infty$, then equality $(*)$ holds. If $P_0 < P_\infty$, then we choose an instant $t_1 > t_0$ such that $|T(t_1) - T_a| < \beta\mathrm{K}$ and $|P(t_1) - P_0| < \frac{\xi}{4}\mathrm{Pa}$ (such a t_1 exists because of (2)).

Let then

$$P_1 := \min\left\{P_0 + \frac{\xi}{2}\mathrm{Pa}, P_\infty\right\}.$$

Evidently, $|P(t_1) - P_1| < \xi\mathrm{Pa}$. Let us solve the dynamical equation on the interval $[t_1, \infty[$ with the initial values $\big(T(t_1), P(t_1)\big)$ putting (T_a, P_1) for the environment. The process satisfies conditions (1) and (2) for $s = 1$. Thus if $P_1 = P_\infty$, then equality $(*)$ holds. If $P_1 < P_\infty$, then we choose an instant $t_2 > t_1$ such that $|T(t_2) - T_a| < \beta\mathrm{K}$ and $|P(t_2) - P_1| < \frac{\xi}{4}\mathrm{Pa}$.

There is a positive integer n such that $n\frac{\xi}{2}\mathrm{Pa} > P_\infty - P(t_0)$; consequently, we find instants $t_0 < t_1 < \cdots < t_n$ and pressure values $P_0 < P_1 < \cdots < P_n = P_\infty$ such that if P_i is the pressure of the environmentin the time interval $[t_i, t_{i+1}[$ $(i = 0, \dots, n;\ n + 1 := \infty)$, the process of the body has the required properties.

We emphasize that the practically isothermal process is realized by constant temperature and varying pressure of the environment.

Practically isobaric processes can be realized in a similar manner.

12.13 Control instead of constraint

12.13.1 The notion of control

Fixed volume, constant temperature etc. are described by constraints which correspond to 'infinitely rigid' wall, 'infinitely fast' heat conduction etc. We can produce such processes by controls instead of constraint. Control means a conveniently prescribed varying environment. We met a similar situation in the previous paragraph but now we wish to achieve exactly isochoric, isothermal, etc. processes. More closely, we look for a process $t \mapsto \big(T_a(t), P_a(t)\big)$ of the environment assuring that the process of the body be isochoric, isothermal, etc.

12.13.2 Control for isochoric processes

We wish to assure that $v(t) = v_o$ for all $t > t_0$; then we look for a function $t \mapsto \big(T_a(t), P_a(t)\big)$ such that

$$\mathfrak{c}_v(v_o, T)\dot{T} = \mathfrak{q}(v_o, T, T_a, P_a), \qquad \mathfrak{f}(v_o, T, T_a, P_a) = 0$$

holds for some function $t \mapsto T(t)$ with given initial $T(t_0)$.

This is an interesting mathematical problem. Its solution – if exists – is not unique, in general. Indeed, let us take

$$\mathfrak{f}(v, T, T_a, P_a) = \beta(\mathcal{P}(v, T) - P_a)$$

where $\beta > 0$ is constant. Then

$$P_a(t) = \mathcal{P}(v_o, T(t)), \tag{$*$}$$

and the first law becomes

$$\mathfrak{c}_v(v_o, T)\dot{T} = \mathfrak{q}(v_o, T, T_a, \mathcal{P}(v_o, T))$$

which is an ordinary differential equation if T_a (the control temperature) is an arbitrary continuous function, thus it has a solution $t \mapsto T(t)$ with the given initial value. The solution put in $(*)$ gives the control pressure, too.

12.13.3 Control for isothermal processes

We wish to assure $T(t) = T_o$ for all $t > t_0$; then we look for a function $t \mapsto (T_a(t), P_a(t))$ such that

$$\mathfrak{q}(v, T_o, T_a, P_a) = \mathfrak{n}(v, T_o, T_a, P_a)\mathfrak{f}(v, T_o, T_a, P_a), \qquad \dot{v} = \mathfrak{f}(v, T_o, T_a, P_a)$$

holds for some function $t \mapsto v(t)$ with initial value $v(t_0)$.

Let us take again

$$\mathfrak{f}(v, T, T_a, P_a) = \beta(\mathcal{P}(v, T) - P_a),$$

where $\beta > 0$ is a constant. Then

$$P_a(t) = \mathcal{P}(v(t), T_o) - \frac{\dot{v}(t)}{\beta}, \tag{$*$}$$

and the first law becomes

$$\mathfrak{q}(v, T_o, T, T_a, \mathcal{P}(v, T_o - \dot{v}/\beta)) = \mathfrak{n}(v, T_o, T_a, \mathcal{P}(v, T_o - \dot{v}/\beta))\dot{v}$$

which is an implicit ordinary differential equation if T_a (the control temperature) is an arbitrary continuous function, thus it has a solution $t \mapsto v(t)$ with the given initial value. The solution put in $(*)$ gives the control pressure, too.

12.14 Heat engines

12.14.1 A model of a heat engine

Heat engines are machines that perform mechanical work utilizing heat flow or apply mechanical work to produce a heat flow. Though in reality such machines are complicated and use phase transitions, chemical reactions, electromagnetic phenomena, etc., the simple processes treated up to now allow us to draw a rough picture about their operation [1].

We model the engine as a body with constant particle number N which is in contact with a convenient environment in such a way that the process $t \mapsto \big(v(t), T(t)\big)$ of the body is **periodic**. Let us introduce the notations

$$Q(t){:=}N\mathfrak{q}\big(v(t),T(t),T_a(t),P_a(t)\big), \quad W(t){:=}N\mathfrak{w}\big(v(t),T(t),T_a(t),P_a(t)\big).$$

Let us fix a time interval $[t_1, t_2]$ in which a period, the **cycle** is realized and let

$$\tau^+ := \{t \in [t_1,t_2] \mid Q(t) > 0\}, \qquad \tau^- := \{t \in [t_1,t_2] \mid Q(t) < 0\},$$

$$Q_c^+ := \int\limits_{\tau^+} Q(t)\,dt, \qquad Q_c^- := -\int\limits_{\tau^-} Q(t)\,dt, \qquad Q_c := \int_{t_1}^{t_2} Q(t)\,dt,$$

$$W_c := \int_{t_1}^{t_2} W(t)\,dt.$$

The function $t \mapsto Q(t)$ is continuous, thus $\tau^\pm$ is an open subset; as a consequence, it has zero measure (Lebesgue measure) if and only if it is void. $Q_c^\pm \ge 0$ and is zero if and only if $\tau^\pm$ is void.

Q_c^+ and Q_c^- are the heat absorbed and emitted, respectively, by the engine in the cycle, W_c is the work performed on the engine, thus $-W_c$ is the work performed by the machine. Evidently, $Q_c = Q_c^+ - Q_c^-$.

The state of the machine at the beginning and at the end of the cycle is the same; consequently, we infer from the first law that

$$0 = Q_c + W_c.$$

12.14.2 Characterization of the heat flows

The entire entropy of the body in the process is $t \mapsto S(t) := Ns\big(e(t), v(t)\big)$. Let us suppose that working is ideal and the body is entropic. Then the equalities in Paragraph 5.3 yield

$$\dot{S} = \frac{Q}{T};$$

the process is periodic, thus $S(t_1) = S(t_2)$ and consequently

$$0 = \int_{t_1}^{t_2} \frac{Q(t)}{T(t)}\,dt = \int\limits_{\tau^+} \frac{Q(t)}{T(t)}\,dt + \int\limits_{\tau^-} \frac{Q(t)}{T(t)}\,dt,$$

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[1] This subsection is based on the book C.Truesdell–S.Bharatha: *Classical Thermodynamics as a Theory of Heat Engines*, Springer, 1977

in other words,

$$\int\limits_{\tau^+} \frac{Q(t)}{T(t)}\,dt = \int\limits_{\tau^-} \frac{-Q(t)}{T(t)}\,dt.$$

Introducing the notations

$$T^{+\uparrow} := \sup\{T(t) \mid t \in \tau^+\}, \qquad T^{+\downarrow} := \inf\{T(t) \mid t \in \tau^+\},$$

$$T^{-\uparrow} := \sup\{T(t) \mid t \in \tau^-\}, \qquad T^{-\downarrow} := \inf\{T(t) \mid t \in \tau^-\},$$

we obtain

$$\frac{Q_c^+}{T^{+\uparrow}} \le \frac{Q_c^-}{T^{-\downarrow}}, \qquad \frac{Q_c^+}{T^{+\downarrow}} \ge \frac{Q_c^-}{T^{-\uparrow}}. \tag{$*$}$$

We see that either both Q_c^+ and Q_c^- are zero or none of them is zero; if the work performed is not zero, then the engine both absorbs and emits heat: **the engine cannot perform work only by absorbing heat**.

12.14.3 The thermal efficiency

The thermal efficiency of the engine is the quotient of the work performed by the heat absorbed in a cycle:

$$\eta_c := \frac{-W_c}{Q_c^+} = \frac{Q_c^+ - Q_c^-}{Q_c^+}.$$

The previous estimates give us (if the working is ideal and the body is entropic) that

$$\eta_c \le 1 - \frac{T^{-\downarrow}}{T^{+\uparrow}}.$$

12.14.4 The Carnot cycle

If the temperature is constant on both τ^+ and τ^-, i.e.

$$T^{+\downarrow} = T^{+\uparrow} =: T^+, \qquad T^{-\downarrow} = T^{-\uparrow} =: T^-,$$

then equality holds in the estimates $(*)$:

$$\frac{Q_c^+}{T^+} = \frac{Q_c^-}{T^-}. \tag{$**$}$$

If the engine works in the cycle, i.e. $-W_c > 0$, then $Q_c^+ > Q_c^-$ which imply by $(**)$ that $T^+ > T^-$: the temperature of the body is higher when heat is absorbed than the temperature of the body when heat is emitted. Then the thermal efficiency is

$$\eta_c = 1 - \frac{T^-}{T^+}.$$

We can suppose without restricting generality that τ^+ is at the beginning of the cycle. The temperature is a continuous function, thus there is an interval after both τ^+ and τ^- in which heat does not flow. This is the **Carnot cycle** consisting of four steps:

1. The body expands at constant temperature T^+ (absorbs heat and works);
2. The body is heat insulated, expands and cools to the temperature T^- (works adiabatically);
3. The body is compressed at constant temperature T^- (emits heat and work is performed on it);
4. The body is heat insulated, is compressed and warms to the temperature T^+ (work is performed on it adiabatically).

12.14.5 The efficiency

It is worth noting that the real efficiency is the quotient of the work done by the absorbed energy. This is less than the thermal efficiency because the absorbed energy is more than the absorbed heat which is well seen in the case of a Carnot cycle: we waste energy

– to make a contact between the body and a heat bath,
– to make a heat insulation and later to remove it,
– to make a contact between the body and another heat bath,
– to make a heat insulation and later to remove it.

12.15 Thermal efficiency with maximal power

Let us take a body undergoing a Carnot cycle. Let us suppose that the body on the isothermal parts T^+ and T^- is in contact with heat baths having constant temperature $T_a^+ > T^+$ and $T_a^- < T^-$, respectively, and the heatings are

$$Q^+ = -\lambda^+(T^+ - T_a^+), \qquad Q^- = -\lambda^-(T_a^- - T^-).$$

Then

$$Q_c^+ = Q^+\tau^+, \qquad Q_c^- = Q^-\tau^-$$

and relation $(**)$ in Paragraph 12.14.4 $(**)$ yields

$$\frac{\tau^+}{\tau^-} = \frac{Q^-T^+}{Q^+T^-}.$$

Let γ denote the proportion of the time period and the time of the isothermal parts. Then the average power of the engine in a cycle is

$$\frac{Q_c^+ - Q_c^-}{t_2 - t_1} = \frac{Q^+\tau^+ - Q^-\tau^-}{\gamma(\tau^+ + \tau^-)} = \frac{Q^+Q^-(T^+ - T^-)}{\gamma(Q^-T^+ + Q^+T^-)}.$$

We wish to choose the temperature of the engine on the isothermal parts in such a way that the engine have maximal power [2]. A necessary condition is that the

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[2] This paragraph is based on the paper Curzon F. L. – Ahlborn B.: Efficiency of a Carnot Engine at Maximum Power Output, *American Journal of Physics* 43(1975) 22-24

partial derivatives of the average power with respect to the working temperatures are zero:

$$-\lambda^+(T^+ - T^-) + Q^+ - \frac{Q^+(T^+ - T^-)}{Q^-T^+ + Q^+T^-}(Q^- - \lambda^+T^-) = 0,$$

$$\lambda^-(T^+ - T^-) - Q^- - \frac{Q^-(T^+ - T^-)}{Q^-T^+ + Q^+T^-}(\lambda^-T^+ + Q^+) = 0$$

from which we obtain

$$T^- - T_a^- = \sqrt{\frac{\lambda^+T^-}{\lambda^-T^+}}(T_a^+ - T^+).$$

Putting this into the first equation, we get for $1 - T_a^+/T^+$ a second-order equation having the solution (necessarily less than 1)

$$1 - \frac{T_a^+}{T^+} = \frac{1 - \sqrt{T^-/T^+}}{1 + \sqrt{\lambda^+/\lambda^-}};$$

this equality and the previous one gives

$$1 - \frac{T_a^-}{T^-} = \frac{\sqrt{T^+/T^-} - 1}{1 + \sqrt{\lambda^-/\lambda^+}}.$$

Finally, we get easily

$$\frac{T^-}{T^+} = \sqrt{\frac{T_a^-}{T_a^+}},$$

thus

$$\eta_c = 1 - \sqrt{\frac{T_a^-}{T_a^+}}$$

is the thermal efficiency with maximal power.

Furthermore, we deduce that

$$\frac{\tau^+}{\tau^-} = \sqrt{\frac{\lambda^-}{\lambda^+}},$$

and introducing the notation

$$\xi := \frac{\sqrt{\lambda^-T_a^+} + \sqrt{\lambda^+T_a^-}}{\sqrt{\lambda^+} + \sqrt{\lambda^-}},$$

we obtain the temperatures corresponding to the maximal power:

$$T^+ = \xi\sqrt{T_a^+}, \qquad T^- = \xi\sqrt{T_a^-}.$$

The theory of *finite-time thermodynamics*[3] is developed on the basis of the above considerations; finite-time thermodynamics deals with optimalization of

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[3] Bery R. S. – Kazakov V. – Sienutycz S.– Szwast J. – Tsirlin A. H. : *Thermodynamic Optimization of Finite-Time Processes*, John Wiley and Sons NY, 1999

thermodynamical processes and its name refers to the conception that more realistic processes are considered than the earlier ‘infinitely slow’ so ‘infinitely long’ lasting quasi-static processes.

It is worth mentioning that the above method is applicable only for heatings of special form and that isothermal processes can be controlled by the pressure of the environment.

12.16 Remarks on the second law

Paragraph 12.11.2 clearly shows that the formulations of the second law such as “the entropy is maximal in an equilibrium of a closed system" and “entropy increases in non-equilibrium processes" are independent. We return to it in Paragraph 13.15.1

Clausius’ formulation that “heat cannot pass by itself from a colder to a warmer body" is expressed by dissipation inequalities.

The Kelvin–Planck formulation “it is impossible to devise an engine which, working in a cycle, shall produce no effect other than the extraction of a heat from reservoir and the performance of an equal amount of mechanical work" has nothing to do with Clausius’ formulation because, as it is seen from our result in Paragraph 12.14.2, it is based only on the entropic property and on ideal working, it does not refer to dissipation inequalities.

It is worth examining more thoroughly this surprising fact. Let us suppose for the sake of simplicity that the heat engine absorbs and emits heat isothermally (Carnot cycle). We have seen that the temperature of the body is higher when heat is absorbed than the temperature of the body when heat is emitted. Then one usually concludes that heat has flown from a hotter place to a colder one. But this is not right. Heat flows into the engine from something and heat flows from the engine to something. The formulae contain only the **temperatures of the engine** and there is no hint at all what temperature has the something from which the engine absorbs heat (why cannot it be lower than that of the engine?) and what temperature has the something to which the engine emits heat (why cannot it be higher than that of the engine?)

The empirical fact that – in simple cases – the environment cannot have lower temperature than the engine has when heat is absorbed and cannot have higher temperature than the engine has when heat is emitted and the Carnot cycle as a classical example resulted in the tacit assumption that the engine and the environment have equal temperature in the isothermal part of the cycle. And this tacit assumption is responsible for the false assertion that the Kelvin–Planck formulation of the second law implies the Clausius formulation.

Let us summarize what can be said about the forms a to d of the second law cited in Paragraph 3 of the Preface.

c. Entropy maximum is a consequence of the conditions of inner stability.

d. Entropy increase is a consequence of the dissipation inequalities.

b. Clausius’ formulation is reflected by the dissipation inequalities.

a. The Kelvin–Planck formulation follows from the entropic property (and ideal working).

Therefore, a and b instead of being equivalent, are independent. Similarly, c and d are independent; b and d are related (it would be difficult to prove that they are equivalent). a is independent from all the others.

12.17 Exercises

1. Show that the canonical conductance matrix corresponding to Paragraph 12.3 has symmetric value in equilibrium, thus it is weakly Onsagerian.

2. Treat the constraint-free processes, the isochoric processes, the adiabatic processes, the isothermal processes and the isobaric processes using the (e, v) variables.

3. The dynamical equation describing processes is, in general, too complicated for having explicit analytic solutions. Now we list some simple cases in which the solutions can be obtained in a relatively simple way.

(i) Let us take a body having a constant specific heat c; let us suppose, moreover, that the heating between the body and the environment has the form $\mathfrak{q}(v, T, T_a, P_a) = -\lambda(T - T_a)$ where $\lambda > 0$ is constant. Then for the isochoric processes of a body we obtain Newton's classical equation for cooling (warming):

$$c\dot{T} = -\lambda(T - T_a)$$

which has solutions

$$T(t) = T_a + \exp\left(-\frac{\lambda}{c}(t - t_0)\right)(T(t_0) - T_a).$$

(ii) Let us consider isothermal processes of an ideal gas if $\mathfrak{f}(v, T, T_a, P_a) = \beta(\mathcal{P}(v, T) - P_a)$ where $\beta > 0$ is constant. Then

$$\dot{v} = \beta\left(\frac{kT_a}{v} - P_a\right),$$

$$b\big(v(t) - v(t_0)\big) + \log\frac{bv(t) - 1}{bv(t_0) - 1} = -ab(t - t_0),$$

where $a := \beta P_a$, $b := \dfrac{P_a}{kT_a}$.

(iii) Let us consider isobaric processes of an ideal gas with constant specific heat c, supposing that $\mathfrak{q}(v, T, T_a, P_a) = -\lambda(T - T_a)$, where $\lambda > 0$ is constant. Then

$$(c + k)\,\dot{T} = -\lambda(T - T_a),$$

which is the same equation as in, with $c + k$ (specific heat at constant pressure) instead of c (specific heat at constant volume).

4. Solve Exercise 3 (i) if the temperature of the environment is a function of time, $T_a(t) = \beta(t - t_0)^r$ where $\beta \neq 0$ and $r = 1, 2$.

5. Treat the isochoric, isothermal and isobaric processes with non-zero heat source and in a constant environment. How can the isothermal (isobaric) processes be realized?

6. Can a stationary state exist if neither the heat source nor the environment is constant?

7. Treat the isochoric, adiabatic, isothermal and isobaric processes for a gas in an elastic hull.

8. Describe the realization of practically isobaric processes in analogy with Paragraph 12.12.2.

9. Give the control of isochoric and isobaric processes if $q = -\lambda(T - T_a)$ where $\lambda > 0$ is constant.

10. Treat the control of isobaric processes.

11. A body can be in contact with two environments (e.g. a window-glass with the atmospheres inside and outside). The ordinary thermodynamics can provide a good model only if the pressures of the environments are equal or the body is rigid and fixed (otherwise the body would not be at rest with respect to the environments).

If the body is heat insulated, the number of environments (of course having the same pressure) is irrelevant. If the body is not heat insulated, we can treat the constraint-free case, the isochoric processes and the isobaric processes.

Let the environments have the same pressure P_a and temperature T_a and T_b, respectively. Let us suppose that the heating is

$$-\lambda_a(T - T_a) - \lambda_b(T - T_b),$$

where $\lambda_a > 0$ and $\lambda_b > 0$ are constant.

Let us use the variables (v, T). Then (v_o, T_o) is a stationary state if and only if

$$\mathcal{P}(v_o, T_o) = P_a \quad \text{and} \quad T_o = \frac{\lambda_a T_a + \lambda_b T_b}{\lambda_a + \lambda_b}.$$

Using the linearization method, verify that – under some (known) conditions – a stationary state in the regular domain is asymptotically stable in all the three mentioned cases. Give the isochor processes in an explicit form.

13 Two bodies in a given environment

13.1 Introductory remarks

We shall examine processes of a system consisting of an environment and two bodies whose particle number is constant and there is no particle source. The treatise can be easily generalized for more bodies.

Contrary to the previous section, though the particle numbers are constant, the entire energy and volume of the bodies will be the convenient variables. The constant particle numbers will be omitted from the notations, thus we write, e.g. $\mathcal{P}(V, T)$ and $\mathbf{T}(E, V)$ instead of $\mathcal{P}(V, T, N)$ and $\mathbf{T}(E, V, N)$. Furthermore, for the sake of simplicity, we shall refer to constitutive domains (regular domains) by the entire quantities; we write, e.g. $(V, T) \in D$ and $(E, V) \in \mathrm{D}$ instead of $(V/N, T) \in D$ and $(E/N, V/N) \in \mathrm{D}$.

13.2 General formulae

13.2.1 General framework of description

Based on Chapter II, a system will be described as follows.

1. There are two given bodies having materials $(\mathrm{D}_1, \mathbf{T}_1, \mathbf{P}_1, \boldsymbol{\mu}_1, \mathrm{R}_1)$ and $(\mathrm{D}_2, \mathbf{T}_2, \mathbf{P}_2, \boldsymbol{\mu}_2, \mathrm{R}_2)$, respectively, and having constant non-zero particle numbers N_1 and N_2, respectively, and there is a given environment of material $(\mathrm{D}_a, \mathbf{T}_a, \mathbf{P}_a, \boldsymbol{\mu}_a, \mathrm{R}_a)$.

2. There are given dynamical quantitities
– $\mathbf{Q}_{12}$, $\mathbf{F}_{12}$, $\boldsymbol{\pi}_{12}$ defined on $\mathrm{D}_1 \times \mathrm{D}_2$,
– $\mathbf{Q}_{21}$, $\mathbf{F}_{21}$, $\boldsymbol{\pi}_{21}$ defined on $\mathrm{D}_2 \times \mathrm{D}_1$,
– $\mathbf{Q}_{1a}$, $\mathbf{F}_{1a}$, $\boldsymbol{\pi}_{1a}$ defined on $\mathrm{D}_1 \times \mathrm{D}_a$,
– $\mathbf{Q}_{2a}$, $\mathbf{F}_{2a}$, $\boldsymbol{\pi}_{2a}$ defined on $\mathrm{D}_2 \times \mathrm{D}_a$,
continuous functions, continuously differentiable on the interior of their domain. The dynamical quantitities, with the notations

$$\mathbf{W}_{12} := -(\mathbf{P}_1 + \boldsymbol{\pi}_{12})\mathbf{F}_{12}, \qquad \text{etc.}$$

$$Q_{12} := \mathbf{Q}_{12}(E_1, V_1, E_2, V_2), \qquad T_1 := \mathbf{T}_1(E_1, V_1), \qquad \text{etc.}$$

satisfy
– mutuality:

$$Q_{12} + W_{12} = -(Q_{21} + W_{21}), \qquad F_{12} = -F_{21},$$

– the equilibrium properties for $i = 1, 2$ and $k = a, 1, 2$:
0) $\pi_{ik} = 0$ if $P_i = P_k$,

1)(a) if $\mathbf{F}_{ik} = 0$, $\mathbf{Q}_{ik} \neq 0$, then $Q_{ik} = 0$ if and only if $T_i = T_k$,
1)(b) if $\mathbf{Q}_{ik} = 0$, $\mathbf{F}_{ik} \neq 0$, then $F_{ik} = 0$ if and only if $P_i = P_k$,
1)(c) if $\mathbf{F}_{ik} \neq 0$, $\mathbf{Q}_{ik} \neq 0$, then
∗ if $F_{ik} = 0$, then $P_i = P_k$,
∗ if $Q_{ik} = 0$ and $P_i = P_k$, then $T_i = T_k$,
(implying that if $Q_{ik} = 0$ and $F_{ik} = 0$, then $P_i = P_k$ and $T_i = T_k$)
∗ ∗ if $T_i = T_k$ and $P_i = P_k$, then $Q_{ik} = 0$ and $F_{ik} = 0$,
– the dissipation inequalities:

$$-\frac{Q_{12}}{T_1}(T_1 - T_2) - \frac{W_{12}}{P_1}(P_1 - P_2) \geq 0,$$

$$-\frac{Q_{21}}{T_2}(T_2 - T_1) - \frac{W_{21}}{P_2}(P_2 - P_1) \geq 0,$$

$$-\frac{Q_{1a}}{T_1}(T_1 - T_a) - \frac{W_{1a}}{P_1}(P_1 - P_a) \geq 0,$$

$$-\frac{Q_{2a}}{T_2}(T_2 - T_a) - \frac{W_{2a}}{P_2}(P_2 - P_a) \geq 0,$$

where equality holds if and only if the corresponding dynamical quantitities have zero value (e.g. $Q_{12} = 0$ and $F_{12} = 0$); if the workings are ideal, then

$$\big(Q_{12} - P_1F_{12}\big)\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + F_{12}\left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right) \geq 0,$$

$$\big(Q_{21} - P_2F_{21}\big)\left(\frac{1}{T_2} - \frac{1}{T_1}\right) + F_{21}\left(\frac{P_2}{T_2} - \frac{P_1}{T_1}\right) \geq 0,$$

$$\big(Q_{1a} - P_1F_{1a}\big)\left(\frac{1}{T_1} - \frac{1}{T_a}\right) + F_{1a}\left(\frac{P_1}{T_1} - \frac{P_a}{T_a}\right) \geq 0,$$

$$\big(Q_{2a} - P_2F_{2a}\big)\left(\frac{1}{T_2} - \frac{1}{T_a}\right) + F_{2a}\left(\frac{P_2}{T_2} - \frac{P_a}{T_a}\right) \geq 0$$

(note that the first and the second inequalities coincide because of mutuality).

3. There is a given process $t \mapsto \big(E_a(t), V_a(t)\big) \in \mathrm{D}_a$ of the environment, a continuous function defined on a time interval.

4. There are the given heat sources $t \mapsto Q_{1,s}(t)$ and $t \mapsto Q_{2,s}(t)$, continuous functions defined on a time interval.

5. The processes $t \mapsto \big(E_1(t), V_1(t), E_2(t), V_2(t)\big)$ of the bodies are governed by the dynamical equation

$$\begin{aligned}
\dot{E}_1 &= Q_{1,s} + Q_{1a} + Q_{12} + W_{1a} + W_{12},\\
\dot{V}_1 &= F_{1a} + F_{12},\\
\dot{E}_2 &= Q_{2,s} + Q_{2a} + Q_{21} + W_{2a} + W_{21},\\
\dot{V}_2 &= F_{2a} + F_{21},
\end{aligned}$$

where $Q_{1a} := \mathbf{Q}_{1a}(E_1, V_1, E_a, V_a)$, etc.

13.2.2 Other variables

Sometimes temperature is used instead of internal energy as an independent variable. Then we write $\mathcal{Q}_{12}(V_1, T_1, V_2, T_2)$, etc. and a process of the bodies is $t \mapsto \big(V_1(t), T_1(t), V_2(t), T_2(t)\big)$, so $\dot{E}_1$ and $\dot{E}_2$ in the dynamical equation are to be replaced with $\mathcal{E}_1(V_1, T_1)^{\cdot}$ and $\mathcal{E}_2(V_2, T_2)^{\cdot}$, respectively.

We suppose that the given process of the environment runs in a single phase, thus it can be given by temperature and pressure (as common in practice). Therefore instead of the variables (E_a, V_a), we shall use the variables (T_a, P_a), retaining the symbols of the functions, e.g. we shall write $\mathbf{Q}_{1a}(E_1, V_1, T_a, P_a)$ and $\mathcal{Q}_{1a}(V_1, T_1, T_a, P_a)$; furthermore, the given process of the environment will appear in the form $t \mapsto \big(T_a(t), P_a(t)\big)$.

13.2.3 Equilibrium

In the sequel (except the exercises) we take zero heat sources and constant process of the environment:

$$Q_{1,s} = Q_{2,s} = 0, \qquad T_a = \text{const}, \qquad P_a = \text{const}.$$

Then $(E_{1o}, V_{1o}, E_{2o}, V_{2o}) \in \mathrm{D}_1 \times \mathrm{D}_2$ is an equilibrium if and only if

$$\mathbf{Q}_{12}(E_{1\mathrm{o}},V_{1\mathrm{o}},E_{2\mathrm{o}},V_{2\mathrm{o}})=0,\qquad \mathbf{F}_{12}(E_{1\mathrm{o}},V_{1\mathrm{o}},E_{2\mathrm{o}},V_{2\mathrm{o}})=0,$$

$$\mathbf{Q}_{21}(E_{2\mathrm{o}},V_{2\mathrm{o}},E_{1\mathrm{o}},V_{1\mathrm{o}})=0,\qquad \mathbf{F}_{21}(E_{2\mathrm{o}},V_{2\mathrm{o}},E_{1\mathrm{o}},V_{1\mathrm{o}})=0,$$

$$\mathbf{Q}_{1a}(E_{1\mathrm{o}},V_{1\mathrm{o}},T_a,P_a)=0,\qquad \mathbf{F}_{1a}(E_{1\mathrm{o}},V_{1\mathrm{o}},T_a,P_a)=0,$$

$$\mathbf{Q}_{2a}(E_{2\mathrm{o}},V_{2\mathrm{o}},T_a,P_a)=0,\qquad \mathbf{F}_{2a}(E_{2\mathrm{o}},V_{2\mathrm{o}},T_a,P_a)=0.$$

Similarly, if temperature is used as a variable, $(V_{1\mathrm{o}},T_{1\mathrm{o}},V_{2\mathrm{o}},T_{2\mathrm{o}})\in D_1\times D_2$ is an equilibrium if and only if $\mathcal{Q}_{12}(V_{1\mathrm{o}},T_{1\mathrm{o}},V_{2\mathrm{o}},T_{2\mathrm{o}})=0$, etc.

13.2.4 Entropic bodies

The function (given in the customary symbolic form)

$$L := S_1+S_2-\frac{E_1+E_2+P_a(V_1+V_2)}{T_a} \tag{$*$}$$

will play an important role; this is the **total entropy** of the bodies and the environment together, up to an additive constant. Indeed,

$$S_a=\frac{E_a+P_aV_a-\mu_aN_a}{T_a}$$

is the entropy of the environment. The bodies and the environment together form a closed system, i.e the total internal energy and the total volume are constant,

$$E_1+E_2+E_a=:E_s=\text{const},\qquad V_1+V_2+V_a=:V_s=\text{const},$$

thus

$$S_a=-\frac{E_1+E_2+P_a(V_1+V_2)}{T_a}+\frac{E_s+P_aV_s-\mu_aN_a}{T_a}.$$

Since the process of the environment is constant, the sum of the entropies of the bodies and the entropy of the environment, $S_1+S_2+S_a$ equals $(*)$ plus a constant.

The function $(*)$ will be actually given in the variables (E_1,V_1,E_2,V_2):

$$(E_1,V_1,E_2,V_2)\mapsto \mathbf{L}(E_1,V_1,E_2,V_2):=$$
$$:=\mathbf{S}_1(E_1,V_1)+\mathbf{S}_2(E_2,V_2)-\frac{E_1+E_2+P_a(V_1+V_2)}{T_a},$$

and in the variables (V_1,T_1,V_2,T_2):

$$(V_1,T_1,V_2,T_2)\mapsto \mathcal{L}(V_1,T_1,V_2,T_2):=$$
$$:=\mathcal{S}_1(V_1,T_1)+\mathcal{S}(V_2,T_2)-\frac{\mathcal{E}(V_1,T_1)+\mathcal{E}(V_2,T_2)+P_a(V_1+V_2)}{T_a}.$$

These functions are continuously differentiable on the regular domains $\mathrm{R}_1 \times \mathrm{R}_2$ and $R_1 \times R_2$, respectively, and for entropic bodies

$$\frac{\partial \mathbf{L}}{\partial E_i} = \frac{1}{\mathbf{T}_i} - \frac{1}{T_a}, \qquad \frac{\partial \mathbf{L}}{\partial V_i} = \frac{\mathbf{P}_i}{\mathbf{T}_i} - \frac{P_a}{T_a},$$

$$\frac{\partial \mathcal{L}}{\partial V_i} = \left(\frac{1}{T_i} - \frac{1}{T_a}\right)\frac{\partial \mathcal{E}_i}{\partial V_i} + \frac{\mathcal{P}_i}{T_i} - \frac{P_a}{T_a}, \qquad \frac{\partial \mathcal{L}}{\partial T_i} = \left(\frac{1}{T_i} - \frac{1}{T_a}\right)\frac{\partial \mathcal{E}_i}{\partial T_i},$$

$$(i = 1, 2).$$

13.3 System without constraint

13.3.1 Properties of the dynamical quantitities

There is no restriction on the interaction of the bodies and the environment: no dynamical quantity is identically zero. Therefore, we have the equilibrium properties (taking into account the mutuality $F_{21} = -F_{12}$)

$*$ if $F_{12} = 0$ (and so $F_{21} = 0$), then $P_1 = P_2$,

$*$ if $Q_{12} = 0$ or $Q_{21} = 0$ and $P_1 = P_2$, then $T_1 = T_2$,

(implying that if $Q_{12} = 0$ or $Q_{21} = 0$ and $F_{21} = 0$, then $P_1 = P_2$ and $T_1 = T_2$)

$**$ if $T_1 = T_2$ and $P_1 = P_2$, then $Q_{12} = 0$, $Q_{21} = 0$ and $F_{12} = 0$,

furthermore, for $i = 1, 2$

$*$ if $F_{ia} = 0$, then $P_i = P_a$,

$*$ if $Q_{ia} = 0$ and $P_i = P_a$, then $T_i = T_a$,

(implying that if $Q_{ia} = 0$ and $F_{ia} = 0$, then $P_i = P_a$ and $T_i = T_a$)

$**$ if $T_i = T_a$ and $P_i = P_a$, then $Q_{ia} = 0$ and $F_{ia} = 0$.

Note that as a consequence of the equilibrium properties, equality holds in the dissipation inequalities given in 13.2.1 if and only if $T_1 = T_2 = T_a$ and $P_1 = P_2 = P_a$.

13.3.2 Uniqueness of equilibrium

According to the equilibrium properties of dynamical quantitities and Paragraph 13.2.3, $(E_{1o}, V_{1o}, E_{2o}, V_{2o})$ is an equilibrium if and only if

$$\mathbf{T}_1(E_{1o}, V_{1o}) = \mathbf{T}_2(E_{2o}, V_{2o}) = T_a, \qquad \mathbf{P}_1(E_{1o}, V_{1o}) = \mathbf{P}_2(E_{2o}, V_{2o}) = P_a.$$

It is evident that equilibrium can exist only if (T_a, P_a) is in the range of both $(\mathbf{T}_1, \mathbf{P}_1)$ and $(\mathbf{T}_2, \mathbf{P}_2)$. The temperature–pressure function is injective in a phase, thus we have:

Proposition *For every phase* Z_1 *of the first body and for every phase* Z_2 *of the second body, the equilibrium in* $\mathrm{Z}_1 \times \mathrm{Z}_2$ *(if exists) is unique.*

13.3.3 Stability of equilibrium

Proposition *If the bodies are entropic and the workings are ideal, then every equilibrium in* $\mathrm{R}_1 \times \mathrm{R}_2$ *is asymptotically stable.*

Proof Let $(E_{1o}, V_{1o}, E_{2o}, V_{2o}) \in \mathrm{R}_1 \times \mathrm{R}_2$ be an equilibrium. The first derivative of the function $\mathbf{L}$ in Paragraph 13.2.4 is zero in equilibrium. Its second derivative

$$\mathtt{D}^2\mathbf{L}(E_1, V_1, E_2, V_2) = \begin{pmatrix} \mathtt{D}^2\mathbf{S}_1(E_1, V_1) & 0 \\ 0 & \mathtt{D}^2\mathbf{S}_2(E_2, V_2) \end{pmatrix}$$

is negative definite. Thus, $\mathbf{L}$ has a strict local maximum at $(E_{1o}, V_{1o}, E_{2o}, V_{2o})$.

The derivative of $\mathbf{L}$ along the dynamical equation, $\overset{\bullet}{\mathbf{L}}$ equals

$$\left(\frac{1}{T_1} - \frac{1}{T_a}\right)(Q_{1a} + Q_{12} + W_{1a} + W_{12}) + \left(\frac{P_1}{T_1} - \frac{P_a}{T_a}\right)(F_{1a} + F_{12}) +$$
$$\left(\frac{1}{T_2} - \frac{1}{T_a}\right)(Q_{2a} + Q_{21} + W_{2a} + W_{21}) + \left(\frac{P_2}{T_2} - \frac{P_a}{T_a}\right)(F_{2a} + F_{21}),$$

where the customary loose notations are applied. We have $W_{1a} + W_{12} = -P_1(F_{1a} + F_{12})$ and a similar relation for the second body, thus using mutuality $Q_{21} - P_2F_{21} = -(Q_{12} - P_1F_{12})$ and $F_{21} = -F_{12}$, we get

$$\left(\frac{1}{T_1} - \frac{1}{T_a}\right)(Q_{1a} - P_1F_{1a}) + \left(\frac{P_1}{T_1} - \frac{P_a}{T_a}\right)F_{1a} +$$
$$\left(\frac{1}{T_2} - \frac{1}{T_a}\right)(Q_{2a} - P_2F_{2a}) + \left(\frac{P_2}{T_2} - \frac{P_a}{T_a}\right)F_{2a} +$$
$$\left(\frac{1}{T_1} - \frac{1}{T_2}\right)(Q_{12} - P_1F_{12}) + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right)F_{12}.$$

This expression – of course, as a function of (E_1, V_1, E_2, V_2) – has zero value only in equilibrium, everywhere else in a neighbourhood of equilibrium is positive because of the local uniqueness of equilibrium and the dissipation inequalities; thus $\overset{\bullet}{\mathbf{L}}$ has a strict local minimum at $(E_{1o}, V_{1o}, E_{2o}, V_{2o})$.

Therefore, $\mathbf{L}$ is a Liapunov function for asymptotic stability.

13.4 Fixed total volume

13.4.1 Properties of the dynamical quantitities

The bodies are only in thermal contact with the environment:

$$\mathbf{F}_{1a} = \mathbf{F}_{2a} = 0.$$

The equilibrium properties of the dynamical quantitities are

$*$ if $F_{12} = 0$, then $P_1 = P_2$,

$*$ if $Q_{12} = 0$ or $Q_{21} = 0$, and $P_1 = P_2$, then $T_1 = T_2$,

(implying that if $Q_{12} = 0$ or $Q_{21} = 0$ and $F_{12} = 0$, then $P_1 = P_2$ and $T_1 = T_2$),

$**$ if $T_1 = T_2$ and $P_1 = P_2$, then $Q_{12} = 0$, $Q_{21} = 0$ and $F_{12} = 0$,

$*$ $Q_{1a} = 0$ if and only if $T_1 = T_a$ and $Q_{2a} = 0$ if and only if $T_2 = T_a$.

As a consequence, equality holds in the dissipation inequalities if and only if $P_1 = P_2$ and $T_1 = T_2 = T_a$.

13.4.2 Uniqueness of equilibrium

The dynamical equation given in 13.2.1 becomes

$$\dot{E}_1 = Q_{1a} + Q_{12} + W_{12}, \qquad \dot{E}_2 = Q_{2a} + Q_{21} + W_{21},$$
$$\dot{V}_1 = F_{12}, \qquad \dot{V}_2 = F_{21};$$

the mutuality $F_{21} = -F_{12}$ yields that the total volume of the bodies is constant:

$$\dot{V}_1 + \dot{V}_2 = 0.$$

For all $V_\mathrm{s} \in (\mathrm{m}^3)^+$

$$U(V_\mathrm{s}) := \{(E_1, V_1, E_2, V_2) \mid V_1 + V_2 = V_\mathrm{s}\}$$

is an invariant set of the dynamical equation.

$(E_{1\mathrm{o}}, V_{1\mathrm{o}}, E_{2\mathrm{o}}, V_\mathrm{s} - V_{1\mathrm{o}})$ is an equilibrium if and only if

$$\mathbf{T}_1(E_{1\mathrm{o}}, V_{1\mathrm{o}}) = \mathbf{T}_2(E_{2\mathrm{o}}, V_\mathrm{s} - V_{1\mathrm{o}}) = T_a, \qquad \mathbf{P}_1(E_{1\mathrm{o}}, V_{1\mathrm{o}}) = \mathbf{P}_2(E_{2\mathrm{o}}, V_\mathrm{s} - V_{1\mathrm{o}}).$$

Proposition *For all phases* Z_1 *and* Z_2 *of the bodies, the equilibrium in* $U(V_\mathrm{s}) \cap (\mathrm{Z}_1 \times \mathrm{Z}_2)$ *(if exists) is unique.*

Proof The equilibrium volume is determined by

$$\mathcal{P}_1(V_{1\mathrm{o}}, T_a) = \mathcal{P}_2(V_\mathrm{s} - V_{1\mathrm{o}}, T_a).$$

The function

$$V_1 \mapsto \mathcal{P}_1(V_1, T_a) \qquad \big((V_1, T_a) \in Z_1\big)$$

is strictly monotone decreasing, the function

$$V_1 \mapsto \mathcal{P}_2(V_\mathrm{s} - V_1, T_a) \qquad \big((V_\mathrm{s} - V_1, T_a) \in Z_2\big)$$

is strictly monotone increasing, therefore they can have equal values at least at one point, i.e. $V_{1\mathrm{o}}$ is uniquely defined. Temperature is a strictly monotone increasing function of internal energy, thus $\mathbf{T}_1(E_{1\mathrm{o}}, V_{1\mathrm{o}}) = T_a$ and $\mathbf{T}_2(E_{2\mathrm{o}}, V_\mathrm{s} - V_{1\mathrm{o}}) = T_a$ for a given $V_{1\mathrm{o}}$ determine uniquely the internal energy values in equilibrium.

13.4.3 Stability of equilibrium

Proposition *If the bodies are entropic and the workings are ideal, then for all* V_s *the equilibrium*

$$(E_{1\mathrm{o}}, V_{1\mathrm{o}}, E_{2\mathrm{o}}, V_\mathrm{s} - V_{1\mathrm{o}}) \in \mathrm{R}_1 \times \mathrm{R}_2$$

is asymptotically stable in $U(V_\mathrm{s})$*.*

Proof Parameterizing $U(V_\mathrm{s})$ by (E_1, V_1, E_2), we get the reduced dynamical equation

$$\dot{E}_1 = Q_{1a} + Q_{12} - P_1 F_{12}, \qquad \dot{E}_2 = Q_{2a} + Q_{21} - P_2 F_{21},$$
$$\dot{V}_1 = F_{12},$$

where, of course, in the dynamical quantitities V_2 is replaced with $V_\mathrm{s} - V_1$, i.e.

$$Q_{12} = \mathbf{Q}_{12}(E_1, V_1, E_2, V_\mathrm{s} - V_1), \quad \text{etc.}$$

The function

$$\begin{aligned}(E_1, V_1, E_2) \mapsto \Lambda(E_1, V_1, E_2) := \mathbf{L}(E_1, V_1, E_2, V_\mathrm{s} - V_1) = \\ = \mathbf{S}_1(E_1, V_1) + \mathbf{S}_2(E_2, V_\mathrm{s} - V_1) - \frac{E_1 + E_2}{T_a} + \text{const}\end{aligned}$$

is continuously differentiable in a neighbourhood of equilibrium and

$$\frac{\partial\Lambda(E_1, V_1, E_2)}{\partial E_1} = \frac{1}{\mathbf{T}_1(E_1, V_1)} - \frac{1}{T_a}, \qquad \frac{\partial\Lambda(E_1, V_1, E_2)}{\partial E_2} = \frac{1}{\mathbf{T}_2(E_2, V_\mathrm{s} - V_1)} - \frac{1}{T_a},$$

$$\frac{\partial\Lambda(E_1, V_1, E_2)}{\partial V_1} = \frac{\mathbf{P}_1(E_1, V_1)}{\mathbf{T}_1(E_1, V_1)} - \frac{\mathbf{P}_2(E_2, V_\mathrm{s} - V_1)}{\mathbf{T}_2(E_2, V_\mathrm{s} - V_1)}.$$

We see that the first derivative of Λ has zero value in equilibrium.

For the second derivative we easily get

$$\mathtt{D}^2\Lambda(E_1, V_1, E_2) = \begin{pmatrix} \mathtt{D}^2\mathbf{S}_1(E_1, V_1) & 0 \\ 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ 0 & C^*\mathtt{D}^2\mathbf{S}_2(E_2, V_\mathrm{s} - V_1)C \end{pmatrix}$$

where

$$C := \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$$

and * denotes the transpose of a matrix. The second derivative is the sum of two negative semidefinite matrices; their kernels are spanned by the vectors $(0, 0, 1)$ and $(1, 0, 0)$, respectively; thus the sum is negative definite. Therefore $\mathbf{L}$ has a strict local maximum in equilibrium.

The derivative of Λ along the reduced dynamical equation, $\overset{\bullet}{\Lambda}$ equals

$$\left(\frac{1}{T_1} - \frac{1}{T_a}\right)(Q_{1a} + Q_{12} - P_1F_{12}) + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right)F_{12} + \left(\frac{1}{T_2} - \frac{1}{T_a}\right)(Q_{2a} + Q_{21} + P_2F_{12}),$$

where the customary loose notations are applied. Using mutuality $Q_{21} - P_2F_{21} = -(Q_{12} - P_1F_{12})$, and $F_{21} = -F_{21}$, we get

$$\left(\frac{1}{T_1} - \frac{1}{T_a}\right)Q_{1a} + \left(\frac{1}{T_2} - \frac{1}{T_a}\right)Q_{a0} + \left(\frac{1}{T_1} - \frac{1}{T_2}\right)(Q_{12} + W_{12}) + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right)F_{12}.$$

This expression – of course, as a function of (E_1, V_1, E_2) – has zero value only in equilibrium, everywhere else in a neighbourhood of equilibrium it is positive because of the local uniqueness of equilibrium and the dissipation inequalities; thus $\overset{\bullet}{\mathbf{L}}$ has a strict local minimum at $(E_{1\mathrm{o}}, V_{1\mathrm{o}}, E_{2\mathrm{o}})$.

Therefore, Λ is a Liapunov function for asymptotic stability.

13.5 Fixed total volume and joint heat insulation

13.5.1 Properties of the dynamical quantitities

The bodies are completely insulated from the environment:

$$\mathbf{F}_{1a} = \mathbf{F}_{2a} = 0, \qquad\qquad \mathbf{Q}_{1a} = \mathbf{Q}_{2a} = 0.$$

The equilibrium properties of the dynamical quantitities are
$*$ if $F_{12} = 0$, then $P_1 = P_2$,
$*$ if $Q_{12} = 0$ or $Q_{21} = 0$, and $P_1 = P_2$, then $T_1 = T_2$,
(implying that if $Q_{12} = 0$ or $Q_{21} = 0$ and $F_{12} = 0$, then $P_1 = P_2$ and $T_1 = T_2$),
$**$ if $T_1 = T_2$ and $P_1 = P_2$, then $Q_{12} = 0$, $Q_{21} = 0$ and $F_{12} = 0$.

As a consequence, equality holds in the dissipation inequalities if and only if $P_1 = P_2$ and $T_1 = T_2$.

13.5.2 Uniqueness of equilibrium

Now the dynamical equation is

$$\begin{aligned} \dot{E}_1 &= Q_{12} + W_{12}, & \dot{E}_2 &= Q_{21} + W_{21}, \\ \dot{V}_1 &= F_{12}, & \dot{V}_2 &= F_{21}; \end{aligned}$$

the mutuality $Q_{21} + W_{21} = -(Q_{12} + W_{12})$ and $F_{21} = -F_{12}$ yield

$$\dot{E}_1 + \dot{E}_2 = 0 \qquad \text{and} \qquad \dot{V}_1 + \dot{V}_2 = 0;$$

the total internal energy and the total volume of the bodies are constants.

For all $E_\mathrm{s} \in (\mathrm{J})^+$ and $V_\mathrm{s} \in (\mathrm{m}^3)^+$

$$U(E_\mathrm{s}, V_\mathrm{s}) := \{(E_1, V_1, E_2, V_2) \mid E_1 + E_2 = E_\mathrm{s},\ V_1 + V_2 = V_\mathrm{s}\}$$

is an invariant set of the dynamical equation.

$(E_{1\mathrm{o}}, V_{1\mathrm{o}}, E_\mathrm{s} - E_{1\mathrm{o}}, V_\mathrm{s} - V_{1\mathrm{o}})$ is an equilibrium in $U(E_\mathrm{s}, V_\mathrm{s})$ if and only if

$$\mathbf{T}_1(E_{1\mathrm{o}}, V_{1\mathrm{o}}) = \mathbf{T}_2(E_\mathrm{s} - E_{1\mathrm{o}}, V_\mathrm{s} - V_{1\mathrm{o}}) \qquad \mathbf{P}_1(E_{1\mathrm{o}}, V_{1\mathrm{o}}) = \mathbf{P}_2(E_\mathrm{s} - E_{1\mathrm{o}}, V_\mathrm{s} - V_{1\mathrm{o}}).$$

The local uniqueness of equilibrium in $U(E_\mathrm{s}, V_\mathrm{s})$ is given implicitly by the following result on asymptotic stability.

13.5.3 Stability of equilibrium

Proposition *If the bodies are entropic and the workings are ideal, then for all* $(E_\mathrm{s}, V_\mathrm{s})$ *the equilibrium*

$$(E_{1\mathrm{o}}, V_{1\mathrm{o}}, E_\mathrm{s} - E_{1\mathrm{o}}, V_\mathrm{s} - V_{1\mathrm{o}}) \in \mathrm{R}_1 \times \mathrm{R}_2$$

(if exists) is asymptotically stable in $U(E_\mathrm{s}, V_\mathrm{s})$.

Proof Parameterizing $U(E_\mathrm{s}, V_\mathrm{s})$ by (E_1, V_1), we get the reduced dynamical equation

$$\begin{aligned}\dot{E}_1 &= Q_{12} - P_1 F_{12},\\ \dot{V}_1 &= F_{12},\end{aligned}$$

where, of course, in the dynamical quantitities E_2 and V_2 are replaced with $E_\mathrm{s} - E_1$ and $V_\mathrm{s} - V_1$, respectively, i.e.

$$Q_{12} = \mathbf{Q}_{12}(E_1, V_1, E_\mathrm{s} - E_1, V_\mathrm{s} - V_1), \quad \text{etc.}$$

The function

$$\begin{aligned}(E_1, V_1) \mapsto \Lambda(E_1, V_1) := \mathbf{L}(E_1, V_1, E_\mathrm{s} - E_1, V_\mathrm{s} - V_1) = \\ = \mathbf{S}_1(E_1, V_1) + \mathbf{S}_2(E_\mathrm{s} - E_1, V_\mathrm{s} - V_1) + \text{const.}\end{aligned}$$

is continuously differentiable in a neighbourhood of equilibrium and its first derivative

$$\mathtt{D}\mathbf{S}_1(E_1, V_1) - \mathtt{D}\mathbf{S}_2(E_\mathrm{s} - E_1, V_\mathrm{s} - V_2) =$$

$$\left(\frac{1}{\mathbf{T}_1(E_1, V_1)} - \frac{1}{\mathbf{T}_1(E_\mathrm{s} - E_1, V_\mathrm{s} - V_1)}, \frac{\mathbf{P}_1(E_1, V_1)}{\mathbf{T}_1(E_1, V_1)} - \frac{\mathbf{P}_1(E_\mathrm{s} - E_1, V_\mathrm{s} - V_1)}{\mathbf{T}_1(E_\mathrm{s} - E_1, V_\mathrm{s} - V_1)}\right)$$

has zero value in equilibrium.

Its second derivative

$$\mathtt{D}^2\mathbf{S}_1(E_1, V_1) + \mathtt{D}^2\mathbf{S}_2(E_\mathrm{s} - E_1, V_\mathrm{s} - V_1),$$

is negative definite as a sum of two negative definite matrices. Therefore, $\mathbf{L}$ has a strict local maximum in equilibrium; as a consequence, the equilibrium is locally unique.

The derivative of Λ along the reduced dynamical equation, $\overset{\bullet}{\Lambda}$ equals

$$\left(\frac{1}{T_1} - \frac{1}{T_2}\right)(Q_{12} - P_1 F_{12}) + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right) F_{12},$$

where the customary loose notations are applied.

This expression – of course, as a function of (E_1, V_1) – has zero value only in equilibrium, everywhere else in a neighbourhood of equilibrium it is positive because of the local uniqueness of equilibrium and the dissipation inequalities; thus $\overset{\bullet}{\mathbf{L}}$ has a strict local minimum at $(E_{1\mathrm{o}}, V_{1\mathrm{o}})$.

Therefore, Λ is a Liapunov function for asymptotic stability.

13.6 Fixed total volume and individual heat insulations

13.6.1 Properties of the dynamical quantitities

The bodies are completely insulated from the environment and are heat insulated from each other:

$$\mathbf{F}_{1a} = \mathbf{F}_{2a} = 0, \qquad \mathbf{Q}_{1a} = \mathbf{Q}_{2a} = \mathbf{Q}_{12} = \mathbf{Q}_{21} = 0.$$

Now we cannot take ideal working. The equilibrium properties of the dynamical quantitities are

– if $P_1 = P_2$, then $\pi_{12} = 0$,

$*$ $F_{12} = 0$ if and only if $P_1 = P_2$.

Note that the dissipation inequalities are reduced to

$$-\frac{W_{12}}{P_1}(P_1 - P_2) \geq 0$$

where, as a consequence of the equilibrium properties, equality holds if and only if $P_1 = P_2$. We have $-\frac{W_{12}}{P_1} = F_{12}\left(1 + \frac{\pi_{12}}{P_1}\right)$ and π_{12} is zero if $P_1 = P_2$. Thus

$$\mathbf{F}_{12}(\mathbf{P}_1 - \mathbf{P}_2) \geq 0$$

in a neighbourhood of $\{(E_1, V_1, E_2, V_2) \mid \mathbf{P}_1(E_1, V_1) = \mathbf{P}_2(E_2, V_2)\}$ and equality holds if and only if $\mathbf{P}_1(E_1, V_1) = \mathbf{P}_2(E_2, V_2)$.

13.6.2 Uniqueness of equilibrium

Now the dynamical equation is

$$\dot{E}_1 = W_{12}, \qquad \dot{E}_2 = W_{21},$$
$$\dot{V}_1 = F_{12}, \qquad \dot{V}_2 = F_{21},$$

and mutuality yields that

$$\dot{E}_1 + \dot{E}_2 = 0 \qquad \text{and} \qquad \dot{V}_1 + \dot{V}_2 = 0.$$

Furthermore, we have

$$\dot{E}_1 = -(P_1 + \pi_{12})\dot{V}_1 \tag{$*$}$$

(and a similar relation for the second body, too). Then

$$E_1 + E_2 = E_\mathrm{s} = \text{const.} \qquad V_1 + V_2 = V_\mathrm{s} = \text{const.},$$

moreover, internal energy can be given as a function of volume by the solution of the differential equation

$$\frac{dE_1}{dV_1} = -\mathbf{P}_1(E_1, V_1) - \boldsymbol{\pi}_{12}(E_1, V_1, E_\mathrm{s} - E_1, V_\mathrm{s} - V_1). \tag{$**$}$$

Let C be the integral curve of this differential equation passing through the point $(E_\mathrm{s}, V_\mathrm{s})$. Then

$$U(E_\mathrm{s}, V_\mathrm{s}, C) :=$$
$$:= \{(E_1, V_1, E_2, V_2) \mid E_1 + E_2 = E_\mathrm{s}, V_1 + V_2 = V_\mathrm{s}, (E_1, V_1) \in C\}$$

is an invariant set of the dynamical equation.

$(E_{1\mathrm{o}}, V_{1\mathrm{o}}, E_{2\mathrm{o}}, V_{2\mathrm{o}})$ is an equilibrium in $U(E_\mathrm{s}, V_\mathrm{s}, C)$ if and only if

$$\mathbf{P}_1(E_{1\mathrm{o}}, V_{1\mathrm{o}}) = \mathbf{P}_2(E_{2\mathrm{o}}, V_{2\mathrm{o}}).$$

The local uniqueness of equilibrium in $U(E_\mathrm{s}, V_\mathrm{s}, C)$ is given implicitly by the following result on asymptotic stability.

13.6.3 Stability of equilibrium

Proposition *If the bodies have the normal dilation property, then for all* $E_{\mathrm{s}} \in (\mathrm{J})^{+}$ *and* $V_{\mathrm{s}} \in (\mathrm{m}^3)^{+})$ *the equilibrium*

$$(E_{1\mathrm{o}}, V_{1\mathrm{o}}, E_{2\mathrm{o}}, V_{2\mathrm{o}}) \in U(E_{\mathrm{s}}, V_{\mathrm{s}}, C) \cap (\mathrm{R}_1 \times \mathrm{R}_2)$$

(if exists) is asymptotically stable in $U(E_{\mathrm{s}}, V_{\mathrm{s}}, C)$*.*

Proof Parameterizing $U(E_{\mathrm{s}}, V_{\mathrm{s}}, C)$ by V_1, we get the reduced dynamical equation

$$\dot{V}_1 = \mathbf{F}_{12}\big(\mathtt{E}_1(V_1), V_1, E_{\mathrm{s}} - \mathtt{E}_1(V_1), V_{\mathrm{s}} - V_1\big)$$

where $\mathtt{E}_1$ is the solution of the differential equation $(**)$ whose graph is C.

It is easy to see that the function

$$V_1 \mapsto \Lambda(V_1) := \Big(\mathbf{P}_1(\mathtt{E}_1(V_1), V_1) - \mathbf{P}_2(E_{\mathrm{s}} - \mathtt{E}_1(V_1), V_{\mathrm{s}} - V_1)\Big)^2$$

has a strict minimum in equilibrium and continuously differentiable in a neighbourhood of equilibrium. Its first derivative equals

$$\frac{\partial \mathbf{P}_1}{\partial V_1}([1]) + \frac{\partial \mathbf{P}_2}{\partial V_2}([2]) - \left(\frac{\partial \mathbf{P}_1}{\partial E_1}([1]) + \frac{\partial \mathbf{P}_2}{\partial E_2}([2])\right)\big(\mathbf{P}_1([1]) + \boldsymbol{\pi}_{12}([1],[2])\big) \qquad (*)$$

multiplied by $2(\mathbf{P}_1([1]) - \mathbf{P}_2([2]))$, where $[1] := (\mathtt{E}_1(V_1), V_1)$, $[2] := (E_{\mathrm{s}} - \mathtt{E}_1(V_1), V_{\mathrm{s}} - V_1)$.

Relations in Paragraph 5.1, the conditions of intrinsic stability and the normal dilation property imply

$$\frac{\partial \mathbf{P}}{\partial V} - \frac{\partial \mathbf{P}}{\partial E}\mathbf{P} = \left(\frac{\partial \mathcal{P}}{\partial V} - \frac{\frac{\partial \mathcal{P}}{\partial T}}{\frac{\partial \mathcal{E}}{\partial T}}\left(\frac{\partial \mathfrak{e}}{\partial v} + \mathcal{P}\right)\right) \bullet < 0.$$

$\boldsymbol{\pi}_{12}$ has zero value in equilibrium, thus expression $(*)$ is negative in equilibrium, so by continuity, it is negative in a neighbourhood of equilibrium. Thus the derivative of Λ multiplied by the right-hand side of the dynamical equation is negative in a neighbourhood of equilibrium and zero in equilibrium because of the dissipation inequality: the derivative of Λ along the reduced dynamical equation has a strict local maximum in equilibrium.

Therefore, Λ is a Liapunov function for asymptotic stability.

13.7 Fixed individual volumes

13.7.1 Properties of the dynamical quantitities

The bodies are only in thermal contact with each other and with the environment:

$$\mathbf{F}_{1a} = \mathbf{F}_{2a} = \mathbf{F}_{12} = \mathbf{F}_{21} = 0.$$

The springings are zero, so mutuality implies

$$Q_{12} = -Q_{21}.$$

The equilibrium properties of the dynamical quantitities are:
$*$ $Q_{12} = 0$ (and so $Q_{21} = 0$) if and only if $T_1 = T_2$,
$*$ $Q_{1a} = 0$ if and only if $T_1 = T_a$ and $Q_{2a} = 0$ if and only if $T_2 = T_a$.
The dissipation inequalities become

$$Q_{12}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \geq 0,$$

$$Q_{1a}\left(\frac{1}{T_1} - \frac{1}{T_a}\right) \geq 0, \qquad Q_{2a}\left(\frac{1}{T_2} - \frac{1}{T_a}\right) \geq 0,$$

where equality holds if and only if $T_1 = T_2$, $T_1 = T_a$ and $T_2 = T_a$, respectively.

13.7.2 Uniqueness of equilibrium

Now the dynamical equation is

$$\begin{aligned} \dot{E}_1 &= Q_{1a} + Q_{12}, & \dot{E}_2 &= Q_{2a} + Q_{21}, \\ \dot{V}_1 &= 0, & \dot{V}_2 &= 0. \end{aligned}$$

For all $V_{1\mathrm{o}}, V_{2\mathrm{o}} \in (\mathrm{m}^3)^+$

$$U(V_{1\mathrm{o}}, V_{2\mathrm{o}}) := \{(E_1, V_1, E_2, V_2) \mid V_1 = V_{1\mathrm{o}},\ V_2 = V_{2\mathrm{o}}\}$$

is an invariant set of the dynamical equation.

$(E_{1\mathrm{o}}, V_{1\mathrm{o}}, E_{2\mathrm{o}}, V_{2\mathrm{o}})$ is an equilibrium in $U(V_{1\mathrm{o}}, V_{2\mathrm{o}})$ if

$$\mathbf{T}_1(E_{1\mathrm{o}}, V_{1\mathrm{o}}) = \mathbf{T}_2(E_{2\mathrm{o}}, V_{2\mathrm{o}}) = T_a.$$

The functions $E_i \mapsto \mathbf{T}_i(E_i, V_{1\mathrm{o}})$ $(i = 1, 2)$ are injective, so the following proposition is evident:

Proposition *The equilibrium in $U(V_{1\mathrm{o}}, V_{2\mathrm{o}})$ (if exists) is unique.*

13.7.3 Stability of equilibrium

Proposition *If the bodies are entropic, then for all $V_{1\mathrm{o}}$ and $V_{2\mathrm{o}}$ the equilibrium*

$$(E_{1\mathrm{o}}, V_{1\mathrm{o}}, E_{2\mathrm{o}}, V_{2\mathrm{o}}) \in U(V_{1\mathrm{o}}, V_{2\mathrm{o}}) \cap (\mathrm{R}_1 \times \mathrm{R}_2)$$

is asymptotically stable in $U(V_{1\mathrm{o}}, V_{2\mathrm{o}})$.

Proof Parameterizing $U(V_{1\mathrm{o}}, V_{2\mathrm{o}})$ by (E_1, E_2), we get the reduced dynamical equation

$$\dot{E}_1 = Q_{1a} + Q_{12}, \qquad \dot{E}_2 = Q_{2a} + Q_{21},$$

where, of course, in the dynamical quantitities V_1 and V_2 are replaced with $V_{1\mathrm{o}}$ and $V_{2\mathrm{o}}$, respectively, i.e.

$$Q_{12} = \mathbf{Q}_{12}(E_1, V_{1\mathrm{o}}, E_2, V_{2\mathrm{o}}), \quad \text{etc.}$$

The function

$$(E_1, E_2) \mapsto \Lambda(E_1, E_2) := \mathbf{L}(E_1, E_2, V_{1o}, V_{2o}) =$$
$$= \mathbf{S}_1(E_1, V_{1o}) + \mathbf{S}_2(E_2, V_{2o}) - \frac{E_1 + E_2}{T_a} + \text{const.}$$

is continuously differentiable in a neighborhood of equilibrium and

$$\frac{\partial \Lambda(E_1, E_2)}{\partial E_i} = \frac{1}{\mathbf{T}_i(E_i, V_{io})} - \frac{1}{T_a} \qquad (i = 1, 2).$$

The first derivative of Λ has zero value in equilibrium.

Its second derivative

$$\mathtt{D}^2\Lambda(E_1, E_2) = \begin{pmatrix} -\left(\frac{1}{\mathbf{T}_1^2}\frac{\partial \mathbf{T}_1}{\partial E_1}\right)(E_1, V_{1o}) & 0 \\ 0 & -\left(\frac{1}{\mathbf{T}_2^2}\frac{\partial \mathbf{T}_2}{\partial E_2}\right)(E_2, V_{2o}) \end{pmatrix},$$

is evidently negative definite. Therefore, Λ has a strict local maximum in equilibrium.

The derivative of Λ along the reduced dynamical equation, $\overset{\bullet}{\Lambda}$ equals

$$\left(\frac{1}{T_1} - \frac{1}{T_a}\right)(Q_{1a} + Q_{12}) + \left(\frac{1}{T_2} - \frac{1}{T_a}\right)(Q_{2a} + Q_{21}).$$

Using the mutuality $Q_{21} = -Q_{12}$, we get

$$\left(\frac{1}{T_1} - \frac{1}{T_a}\right)Q_{1a} + \left(\frac{1}{T_2} - \frac{1}{T_a}\right)Q_{2a} + \left(\frac{1}{T_1} - \frac{1}{T_2}\right)Q_{12}.$$

This expression – of course as a function of (E_1, E_2) – has zero value only in equilibrium, everywhere else in a neighbourhood of equilibrium it is positive because of the local uniqueness of equilibrium and the dissipation inequalities; thus $\overset{\bullet}{\mathbf{L}}$ has a strict local minimum at (E_{1o}, E_{2o}).

Therefore, Λ is a Liapunov function for asymptotic stability.

13.8 Fixed individual volumes and joint heat insulation

13.8.1 Properties of the dynamical quantitities

The bodies are completely insulated from the environment and they are only in thermal contact with each other:

$$\mathbf{F}_{1a} = \mathbf{F}_{2a} = \mathbf{F}_{12} = \mathbf{F}_{21} = 0, \qquad \mathbf{Q}_{1a} = \mathbf{Q}_{2a} = 0.$$

The springings are zero, so mutuality implies that

$$Q_{12} = -Q_{21}.$$

The equilibrium properties of the dynamical quantitities are

$*$ $Q_{12} = 0$ (and so $Q_{21} = 0$) if and only $T_1 = T_2$.

The dissipation inequality becomes

$$Q_{12}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \geq 0,$$

where equality holds if and only if $T_1 = T_2$.

13.8.2 Uniqueness of equilibrium

Now the dynamical equation is

$$\begin{aligned} \dot{E}_1 &= Q_{12}, & \dot{E}_2 &= Q_{21}, \\ \dot{V}_1 &= 0, & \dot{V}_2 &= 0; \end{aligned}$$

mutuality yields that $\dot{E}_1 + \dot{E}_2 =$. Thus for all $E_s \in (J)^+$ and $V_{1o}, V_{2o} \in (m^3)^+$

$$U(E_s, V_{1o}, V_{2o}) := \{(E_1, V_1, E_2, V_2) \mid E_1 + E_2 = E_s,\ V_1 = V_{1o},\ V_2 = V_{2o}\}$$

is an invariant set of the dynamical equation.

$(E_{1o}, V_{1o}, E_s - E_{1o}, V_{2o})$ is an equilibrium in $U(E_s, V_{1o}, V_{2o})$ if and only if

$$\mathbf{T}_1(E_{1o}, V_{1o}) = \mathbf{T}_2(E_s - E_{1o}, V_{2o}) = T_a.$$

We can prove as previously:

Proposition *The equilibrium in $U(E_s, V_{1o}, V_{2o})$ (if exist) is unique.*

13.8.3 Stability of equilibrium

Proposition *For all E_s, V_{1o} and V_{2o} the equilibrium*

$$(E_{1o}, V_{1o}, E_s - E_{1o}, V_{2o}) \in R_1 \times R_2$$

is asymptotically stable in $U(E_s, V_{1o}, V_{2o})$.

Proof Parameterizing $U(E_s, V_{1o}, V_{2o})$ by E_1, we get the reduced dynamical equation

$$\dot{E}_1 = \mathbf{Q}_{12}(E_1, V_{1o}, E_s - E_1, V_{2o}).$$

The reader is asked to verify that

$$E_1 \mapsto := -\big(\mathbf{T}_1(E_1, V_{1o}) - \mathbf{T}_2(E_s - E_1, V_{2o})\big)^2$$

is a Liapunov function for asymptotic stability.

It is worth mentioning that now the entropic property is not required; but if the bodies are entropic, then

$$E_1 \mapsto \Lambda(E_1) := \mathbf{L}(E_1, V_{1o}, E_s - E_1, V_{2o}) = \mathbf{S}_1(E_1, V_{1o}) + \mathbf{S}_2(E_s - E_1, V_{2o}) + \text{const.}$$

is a Liapunov function, too, for asymptotic stability.

13.9 Individual heat insulations

13.9.1 Properties of the dynamical equation

The bodies are only in mechanical contact with each other and with the environment:

$$\mathbf{Q}_{1a} = \mathbf{Q}_{2a} = \mathbf{Q}_{12} = \mathbf{Q}_{21} = 0.$$

Though all the heatings are zero, we can take ideal workings without contradiction.

The equilibrium properties of the dynamical equation are
$*$ $F_{12} = 0$ (and so $F_{21} = 0$) if and only if $P_1 = P_2$,
$*$ $F_{1a} = 0$ if and only if $P_1 = P_a$ and $F_{2a} = 0$ if and only if $P_2 = P_a$.

The dissipation inequalities (with ideal workings) become

$$F_{12}(P_1 - P_2) \geq 0,$$

$$F_{1a}(P_1 - P_a) \geq 0, \qquad F_{2a}(P_2 - P_a) \geq 0,$$

where equality holds if and if $P_1 = P_2$, $P_1 = P_a$ and $P_2 = P_a$, respectively.

13.9.2 Uniqueness of equilibrium

Now the dynamical equation is

$$\begin{aligned} \dot{E}_1 &= -P_1(F_{1a} + F_{12}), & \dot{E}_2 &= -P_2(F_{2a} + F_{21}), \\ \dot{V}_1 &= F_{1a} + F_{12}, & \dot{V}_2 &= F_{2a} + F_{21} \end{aligned}$$

from which we infer

$$\dot{E}_1 + P_1\dot{V}_1 = 0, \qquad \dot{E}_2 + P_2\dot{V}_2 = 0.$$

Consequently, in such processes internal energy can be given as a function of volume for both bodies (cf. 13.6). Namely, let C_i be an integral curve of the differential equations

$$\frac{dE_i}{dV_i} = -\mathbf{P}_i(E_i, V_i) \qquad (i = 1, 2). \tag{$*$}$$

Then

$$U(C_1, C_2) := C_1 \times C_2 = \{(E_1, V_1, E_2, V_2) \mid (E_1, V_1) \in C_1, (E_2, V_2) \in C_2\}$$

is an invariant set of the dynamical equation.

$(E_{1\mathrm{o}}, V_{1\mathrm{o}}, E_{2\mathrm{o}}, V_{2\mathrm{o}})$ is an equilibrium in $U(C_1, C_2)$ if and only if

$$\mathbf{P}_1(E_{1\mathrm{o}}, V_{1\mathrm{o}}) = \mathbf{P}_2(E_{2\mathrm{o}}, V_{2\mathrm{o}}) = P_a.$$

The local uniqueness of equilibrium in $U(C_1, C_2)$ is given implicitly by the following result on asymptotic stability.

13.9.3 Stability of equilibrium

Proposition *If the bodies are entropic (and the workings are ideal), then for all C_1 and C_2 the equilibrium*

$$(E_{1\mathrm{o}}, V_{1\mathrm{o}}, E_{2\mathrm{o}}, V_{2\mathrm{o}}) \in U(C_1, C_2) \cap (\mathrm{R}_1 \times \mathrm{R}_2)$$

(if exists) is asymptotically stable in $U(C_1, C_2)$.

Proof Parameterizing $U(C_1, C_2)$ by (V_1, V_2), we get the reduced dynamical equation

$$\dot{V}_1 = F_{1a} + F_{12}, \qquad\qquad \dot{V}_2 = F_{2a} + F_{21},$$

where, of course, in the dynamical quantitities E_1 and E_2 are replaced with $\mathtt{E}_1(V_1)$ and $\mathtt{E}_2(V_2)$, respectively ($\mathtt{E}_i$ is the solution of $(*)$ whose graph is C_i), i.e.

$$F_{12} = \mathbf{F}_{12}(\mathtt{E}_1(V_1), V_1, \mathtt{E}_2(V_2), V_2), \qquad \text{etc.}$$

The reader is asked to prove that

$$(V_1, V_2) \mapsto \Lambda(V_1, V_2) := \mathbf{L}(\mathtt{E}_1(V_1), V_1, \mathtt{E}_2(V_2), V_2) = \\ = \text{const.} - \frac{\mathtt{E}_1(V_1) + \mathtt{E}_2(V_2) + P_a(V_1 + V_2)}{T_a}$$

is a Liapunov function for asymptotic stability.

13.10 Joint heat insulation

13.10.1 Properties of the dynamical quantitities

The bodies are not in thermal contact with the environment:

$$\mathbf{Q}_{1a} = \mathbf{Q}_{2a} = 0.$$

The equilibrium properties of the dynamical quantitities are

$*$ if $F_{12} = 0$ (and so $F_{21} =)$), then $P_1 = P_2$,

$*$ if $Q_{12} = 0$ or $Q_{21} = 0$ and $P_1 = P_2$, then $T_1 = T_2$,

(implying that if $Q_{12} = 0$ or $Q_{21} = 0$ and $F_{12} = 0$, then $T_1 = T_2$ and $P_1 = P_2$),

$**$ if $T_1 = T_2$ and $P_1 = P_2$, then $Q_{12} = 0$, $Q_{21} = 0$ and $F_{12} = 0$,

$*$ $F_{1a} = 0$ if and only if $P_1 = P_a$ and $F_{2a} = 0$ if and only if $P_2 = P_a$.

13.10.2 Unsolved problem

$(E_{1o}, V_{1o}, E_{2o}, V_{2o})$ is an equilibrium if and only if

$$\mathbf{T}_1(E_{1o}, V_{1o}) = \mathbf{T}_2(E_{2o}, V_{2o}) \qquad \mathbf{P}_1(E_{1o}, V_{1o}) = \mathbf{P}_2(E_{2o}, V_{2o}) = P_a.$$

We have three equations for four unknowns: equilibrium is not unique even locally. We should like to find invariant sets that the equilibrium is locally unique in. Unfortunately, we cannot find such subsets even in the simple case of ideal workings (which are allowed in spite of zero heatings).

The question of stability of equilibria is not yet solved.

13.11 Constant temperature

13.11.1 Properties of the dynamical quantitities

The bodies have equal constant temperature. As in Paragraph 12.6, we can show that equilibrium can exist only if the temperature of the bodies is equal to that of the environment.

It will be convenient to use temperature as a variable instead of internal energy.

Springings and heatings are not independent; we have, as in Paragraph 12.6 that

$$\mathcal{Q}_{ik} := -\mathcal{N}_{ik}\mathcal{F}_{ik},$$

where

$$\mathcal{N}_{ik}(V_i, T_i, V_k, T_k) := \mathcal{P}_i(V_i, T_i) + \frac{\partial \mathcal{E}_i}{\partial V_i}(V_i, T_i) + \boldsymbol{\pi}_{ik}(V_i, T_i, V_k, T_k).$$

The equilibrium properties of the dynamical quantitities are
$*$ $\mathcal{F}_{12}(V_1, T_a, V_2, T_a) = 0$ if and only if $\mathcal{P}_1(V_1, T_a) = \mathcal{P}_2(V_2, T_a)$,
$*$ $\mathcal{F}_{ia}(V_i, T_a, T_a, P_a) = 0$ if and only if $\mathcal{P}_i(V_i, T_a) = P_a \quad (i = 1, 2)$.
The dissipation inequalities become

$$\mathcal{F}_{12}(V_1, T_a, V_2, T_a)(\mathcal{P}_1(V_1, T_a) - \mathcal{P}_2(V_2, T_a)) \geq 0,$$

$$\mathcal{F}_{1a}(V_1, T_a, T_a, P_a)(\mathcal{P}_1(V_1, T_a) - P_a) \geq 0,$$

$$\mathcal{F}_{2a}(V_2, T_a, T_a, P_a)(\mathcal{P}_2(V_2, T_a) - P_a) \geq 0,$$

where equality holds if and only if $\mathcal{P}_1(V_1, T_a) = \mathcal{P}_2(V_2, T_a)$, $\mathcal{P}_1(V_1, T_a) = P_a$ and $\mathcal{P}_2(V_2, T_a) = P_a$, respectively.

13.11.2 Uniqueness of equilibrium

$$U(T_a) := \{(V_1, T_a, V_2, T_a) \mid V_1, V_2 \in (\mathrm{m}^3)^+\}$$

is an invariant set of the dynamical equation.

$(V_{1\mathrm{o}}, T_a, V_{2\mathrm{o}}, T_a)$ is an equilibrium if and only if

$$\mathcal{P}_1(V_{1\mathrm{o}}, T_a) = \mathcal{P}_2(V_{2\mathrm{o}}, T_a) = P_a.$$

Pressure is a strictly monotone decreasing function of volume in a phase, thus we have:

Proposition *For all phases Z_1 and Z_2 of the bodies, the equilibrium in $U(T_a) \cap (Z_1 \times Z_2)$ (if exists) is unique.*

13.11.3 Stability of equilibrium

Proposition *If the bodies are entropic, then for all T_a the equilibrium*

$$(V_{1\mathrm{o}}, T_a, V_{2\mathrm{o}}, T_a) \in R_1 \times R_2$$

is asymptotically stable in $U(T_a)$.

Proof Parameterizing $U(T_a)$ by (V_1, V_2), we get the reduced dynamical equation

$$\dot{V}_1 = \mathcal{F}_{1a}(V_1, T_a, T_a, P_a) + \mathcal{F}_{12}(V_1, T_a, V_2, T_a),$$
$$\dot{V}_2 = \mathcal{F}_{2a}(V_2, T_a, T_a, P_a) + \mathcal{F}_{21}(V_2, T_a, V_1, T_a).$$

The reader is asked to verify that

$$(V_1, V_2) \mapsto \mathcal{L}(V_1, T_a, V_2, T_a) =$$
$$= \mathcal{S}_1(V_1, T_a) + \mathcal{S}_2(V_2, T_a) - \frac{\mathcal{E}_1(V_1, T_a) + \mathcal{E}_2(V_1, T_a) + P_a(V_1 + V_2)}{T_a}$$

is a Liapunov function for asymptotic stability.

13.12 Constant temperature and fixed total volume

13.12.1 Properties of the dynamical quantitities

Besides the properties listed in the previous paragraph, we have

$$\mathbf{F}_{1a} = \mathbf{F}_{12} = 0.$$

13.12.2 Uniqueness of equilibrium

If temperature is used as a variable instead of internal energy, then for all $V_\mathrm{s} \in (\mathrm{m}^3)^+$

$$U(T_a, V_\mathrm{s}) := \{(V_1, T_a, V_2, T_a) \mid V_1 + V_2 = V_\mathrm{s}\}$$

is an invariant set of the dynamical equation.

$(V_{1\mathrm{o}}, T_a, V_\mathrm{s} - V_{1\mathrm{o}}, T_a)$ is an equilibrium if and only if

$$\mathcal{P}_1(V_{1\mathrm{o}}, T_a) = \mathcal{P}_2(V_\mathrm{s} - V_{1\mathrm{o}}, T_a).$$

As in Paragraph 13.4, we have:

Proposition *For all phases Z_1 and Z_2 of the bodies, the equilibrium in $U(T_a, V_\mathrm{s}) \cap (Z_1 \times Z_2)$ (if exists) is unique.*

13.12.3 Stability of equilibrium

Proposition *For all T_a and V_s*

$$(V_{1\mathrm{o}}, T_a, V_\mathrm{s} - V_{1\mathrm{o}}, T_a) \in R_1 \times R_2$$

is asymptotically stable in $U(T_a, V_\mathrm{s})$.

Proof Parameterizing $U(T_a, V_\mathrm{s})$ by V_1, we get the reduced dynamical equation

$$\dot{V}_1 = \mathcal{F}_{12}(V_1, T_a, V_\mathrm{s} - V_1, T_a).$$

The reader is asked to verify that

$$V_1 \mapsto \big(\mathcal{P}_1(V_1, T_a) - \mathcal{P}_2(V_\mathrm{s} - V_1, T_a)\big)^2$$

is a Liapunov function for asymptotic stability.

It is worth mentioning that entropic property is not required; but if the bodies are entropic, then

$$V_1 \mapsto \mathcal{L}(V_1, T_a, V_s - V_1, T_a) = \\ = \mathcal{S}_1(V_1, T_a) + \mathcal{S}_2(V_s - V_1, T_a) - \frac{\mathcal{E}_1(V_1, T_a) + \mathcal{E}_2(V_s - V_1, T_a)}{T_a} + \text{const.}$$

is a Liapunov function, too, for asymptotic stability.

13.13 Constant pressure

13.13.1 Properties of the dynamical quantitities

The bodies have equal constant pressure. As in Paragraph 12.7, we can show that equilibrium can exist only if the pressure of the bodies is equal to that of the environment. Because of the equality of pressures, the lost coefficients take zero value in every process.

Springings and heatings are not independent; we have, as in Paragraph 12.7 that

$$\mathcal{F}_{12}(V_1, T_1, V_2, T_2) + \mathcal{F}_{1a}(V_1, T_1, T_a, P_a) = \\ = \mathcal{K}_1(V_1, T_1)\big(\mathcal{Q}_{12}(V_1, T_1, V_2, T_2) + \mathbf{Q}_{1a}(V_1, T_1, T_a, P_a)\big),$$

where

$$\mathcal{K}_1(V_1, T_1) := -\frac{1}{\mathfrak{c}_{p,1}(V_1, T_1)} \frac{\frac{\partial \mathcal{P}_1(V_1, T_1)}{\partial T_1}}{\frac{\partial \mathcal{P}_1(V_1, T_1)}{\partial V_1}},$$

and the same relation holds by interchanging the subscripts 1 and 2.

The equilibrium properties of heatings are (because now $P_1 = P_2 = Pa$)
* $Q_{12} = 0$ if and only if $T_1 = T_2$,
$Q_{1a} = 0$ if and only if $T_1 = T_a$, $Q_{2a} = 0$ if and only if $T_2 = T_a$.

Th dissipation inequalities are

$$-Q_{12}(T_1 - T_2) \geq 0, \quad \text{or} \quad Q_{12}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \geq 0,$$

$$Q_{1a}\left(\frac{1}{T_1} - \frac{1}{T_a}\right) \geq 0, \qquad Q_{2a}\left(\frac{1}{T_2} - \frac{1}{T_a}\right) \geq 0.$$

13.13.2 Uniqueness of equilibrium

It is evident that

$$U(P_a) := \{(V_1, T_1, V_2, T_2) \mid \mathcal{P}_1(V_1, T_1) = \mathcal{P}_2(V_2, T_2) = P_a\}$$

is an invariant set of the dynamical equation.

$(V_{1o}, T_{1o}, V_{2o}, T_{2o})$ is an equilibrium if and only if $T_{1o} = T_{2o} = T_a$ and $\mathcal{P}_1(V_{1o}, T_a) = \mathcal{P}_2(V_{2o}, T_a) = P_a$.

Proposition *For all phases* Z_1 *and* Z_2 *the equilibrium in* $U(P_a) \cap (Z_1 \times Z_2)$ *(if exists) is unique.*

13.13.3 Stability of equilibrium

Proposition *If the bodies are entropic, then for all P_a the equilibrium*

$$(V_{1\mathrm{o}}, T_a, V_{2\mathrm{o}}, T_a) \in U(P_a) \cap (R_1 \times R_2)$$

is asymptotically stable in $U(P_a)$.

Proof Let us express volumes as functions of temperature near $(V_{1\mathrm{o}}, T_a)$ and $(V_{2\mathrm{o}}, T_a)$ from the implicit relations $\mathcal{P}_1(V_1, T_1) = P_a$ and $\mathcal{P}_2(V_2, T_2) = P_a$, respectively; let $\nu_i \quad (i = 1, 2)$ denote these functions. Then $U(P_a)$ can be parameterized by (T_1, T_2) and the reduced dynamical equation becomes

$$\begin{aligned}\mathfrak{c}_{p,1}(\nu_1(T_1), T_1)\dot{T}_1 &= \mathcal{Q}_{1a}(\nu_1(T_1), T_1, T_a, P_a) + \mathcal{Q}_{12}(\nu_1(T_1), T_1, \nu_2(T_2), T_2),\\ \mathfrak{c}_{p,2}(\nu_2(T_2), T_2)\dot{T}_2 &= \mathcal{Q}_{2a}(\nu_2(T_2), T_2, T_a, P_a) + \mathcal{Q}_{21}(\nu_2(T_2), T_2, \nu_1(T_1), T_1).\end{aligned}$$

The reader is asked to prove as in Paragraph 12.7

$$\begin{aligned}(T_1, T_2) \mapsto \mathcal{L}(\nu_1(T_1), T_1, \nu_2(T_2), T_2) &= \\ &= \mathcal{S}_1(\nu_1(T_1), T_1) + \mathcal{S}_2(\nu_2(T_2), T_2) - \\ &- \frac{\mathcal{E}_1(\nu_1(T_1), T_1) + \mathcal{E}_2(\nu_2(T_2), T_2) + P_a(\nu_1(T_1) + \nu_2(T_2))}{T_a}\end{aligned}$$

is a Liapunov function for asymptotic stability.

13.14 Constant pressure and joint heat insulation

13.14.1 Properties of the dynamical quantitities

The bodies are heat insulated from the environment, thus besides the properties listed in the previous paragraph, we have

$$\mathbf{Q}_{1a} = \mathbf{Q}_{2a} = 0.$$

13.14.2 Uniqueness of equilibrium

Mutuality and equality of pressures give now $Q_{12} + Q_{21} = 0$ from which we infer

$$\dot{E}_1 + P_a\dot{V}_1 + \dot{E}_2 + P_a\dot{V}_2 = 0.$$

As a consequence, for all $H_\mathrm{s} \in (\mathrm{J})$

$$\begin{aligned}U(P_a, H_\mathrm{s}) := \{(V_1, T_1, V_2, T_2)\ |\mathcal{P}_1(V_1, T_1) = \mathcal{P}_2(V_2, T_2) = P_a,\\ \mathcal{E}_1(V_1, T_1) + \mathcal{E}_2(V_2, T_2) + P_a(V_1 + V_2) = H_\mathrm{s}\}\end{aligned}$$

is an invariant set of the dynamical equation (H_s is the total enthalpy of the bodies).

$(V_{1\mathrm{o}}, T_{1\mathrm{o}}, V_{2\mathrm{o}}, T_{2\mathrm{o}}) \in U(P_a, H_\mathrm{s})$ is an equilibrium if and only if

$$T_{1\mathrm{o}} = T_{2\mathrm{o}} =: T_\mathrm{o}, \qquad \mathcal{P}_1(V_{1\mathrm{o}}, T_\mathrm{o}) = \mathcal{P}_2(V_{2\mathrm{o}}, T_\mathrm{o}) = P_a,$$

$$\mathcal{E}_1(V_{1\mathrm{o}}, T_\mathrm{o}) + \mathcal{E}_2(V_{2\mathrm{o}}, T_\mathrm{o}) + P_a(V_{1\mathrm{o}} + V_{2\mathrm{o}}) = H_\mathrm{s}.$$

The local uniqueness of equilibrium in $U(P_a, H_\mathrm{s})$ is given implicitly by the following result on asymptotic stability.

13.14.3 Stability of equilibrium

Proposition *If the bodies are entropic, then for all P_a and H_s the equilibrium*

$$(V_{1\mathrm{o}}, T_{1\mathrm{o}}, V_{2\mathrm{o}}, T_{2\mathrm{o}}) \in U(P_a, H_\mathrm{s}) \cap (R_1 \times R_2)$$

(if exists) is asymptotically stable in $U(P_a, H_\mathrm{s})$.

Proof Let us take the functions ν_1 and ν_2 of the previous paragraph.

The function $T_2 \mapsto \mathcal{E}_2(\nu_2(T_2), T_2) + P_a\nu_2(T_2)$ is continuously differentiable, its derivative $\mathfrak{c}_{p,2}(\nu_2(T_2), T_2)$ is nowhere zero, thus the relation $\mathcal{E}_1(\nu_1(T_1), T_1) + \mathcal{E}_2(\nu_2(T_2), T_2) + P_a(\nu_1(T_1) + \nu_2(T_2)) = H_\mathrm{s}$ allows us to express T_2 as a function of T_1 at least locally; let τ_2 be this function. Then $U(P_a, H_\mathrm{s})$ can be parameterized by T_1 and the reduced dynamical equation becomes

$$\mathfrak{c}_{p,1}(\nu_1(T_1), T_1)\dot{T}_1 = \mathbf{Q}_{12}\big(\nu_1(T_1), T_1, \nu_2(\tau_2(T_1)), \tau_2(T_1)\big).$$

The reader is asked to prove that

$$\begin{aligned} T_1 \mapsto \mathcal{L}(\nu_1(T_1), T_1, \nu_2(\tau_2(T_1)), \tau_2(T_1)) &= \\ &= \mathcal{S}_1(\nu_1(T_1), T_1) + \mathcal{S}_2(\nu_2(\tau_2(T_1)), \tau_2(T_1)) + \text{const.} \end{aligned}$$

is a Liapunov function for asymptotic stability.

13.15 Extremum properties

13.15.1 Conditions of stability

As in Paragraph 12.11.1, we emphasize that asymptotic stability was proven for equilibria in the regular domain on the basis of **two different types of conditions**: the conditions of intrinsic stability (properties of the materials reflected in the constitutive functions) and the dissipation inequalities (properties of the interactions reflected in the dynamical quantitities). The former assure the maximum of the Liapunov function, the latter assure the minimum of the derivative of the Liapunov function along the dynamical equation.

13.15.2 The role of entropy

In one-body systems, except the system without constraint, asymptotic stability can be proved very generally without entropy. In two-body systems, except a few ones, asymptotic stability can only be proved with the aid of entropy; the exceptional systems are submitted to the most constraints.

It seems, the more the 'degree of freedom', the more the role of entropy. Moreover, we mention that when working cannot be ideal (fixed total volume and individual heat insulations), then the entropy is useless.

In the treated systems (except the one mentioned above and the one in Paragraph 13.10 which represents an unsolved problem) if the bodies are entropic and the workings are ideal, then the total entropy of the bodies and the environment is a Liapunov function for asymptotic stability.

Therefore, the total entropy has a strict maximum in equilibrium. The derivative of the total entropy along the dynamical equation, the **entropy production** is the sum of quantities appearing in the dissipation inequalities, thus it has a strict minimum in equilibrium; in other words, total entropy increases strictly monotonically in non-equilibrium processes.

It is again evident that the maximum of the total entropy and the positivity of entropy production are independent of each other.

13.15.3 Warning

We emphasize that always the **total entropy has a maximum in equilibrium**. As said in Paragraph 12.11.3, in usual treatments equilibrium is identified with the extremum of diverse functions.

We have seen the fundamental fact:

– the total entropy of the bodies and the environment has a maximum in equilibrium.

Moreover, we know that

– the total energy of the bodies and the environment is constant.

Then we can deduce that

– if the temperature of the bodies is constant, then the total free energy of the bodies and the environment has a minimum in equilibrium,

– if the pressure of the bodies is constant, then the total enthalpy of the bodies and the environment is constant.

Now, contrary to the one-body systems, it is meaningful to examine the extremum of the total quantities (entropy, internal energy, free energy, enthalpy) of the two bodies.

Our result makes it clear that

– **if the total volume V_s and the total internal energy E_s of the bodies are fixed, then the total entropy of the bodies has a maximum in equilibrium** because the expression ($*$) in Paragraph 13.2.4 becomes

$$S_1 + S_2 - \frac{E_\mathrm{s} + P_a V_\mathrm{s}}{T_a},$$

which, up to an additive constant, is the total entropy of the bodies;

– **if the total volume V_s and the total entropy S_s of the bodies are fixed, then the total internal energy of the bodies has a minimum in equilibrium** because the expression in Paragraph 13.2.4 ($*$), multiplied by T_a, becomes

$$T_a S_\mathrm{s} - E_1 - E_2 - P_a V_\mathrm{s},$$

which, up to an additive constant, is the negative of the total internal energy of the bodies;

– **if the total volume V_s is fixed and the temperature of the bodies is constant T_a, then the total free energy of the bodies has a minimum in equilibrium** because the expression in Paragraph 13.2.4 ($*$), multiplied by T_a, becomes

$$T_a S_1 + T_a S_2 - E_1 - E_2 - P_a V_\mathrm{s}$$

which, up to an additive constant, is the negative of the total free energy of the bodies;

– **if the total entropy S_s is fixed and the pressure of the bodies is constant P_a, then the total enthalpy of the bodies has a minimum in equilibrium** because the expression in Paragraph 13.2.4 (∗), multiplied by T_a, becomes

$$T_a S_s - E_1 - E_2 - P_a(V_1 + V_2)$$

which, up to an additive constant, is the negative of the total enthalpy of the bodies.

The above four extrema appear in usual treatments of thermodynamics. The second and fourth can only be of theoretical importance because it is practically impossible to fix the value of the total entropy of the bodies. On the other hand, there is a number of other interesting cases (we have seen them) which are not mentioned at all.

It is not reasonable to pick out only four cases and to formulate their equilibrium as extrema of different functions. It is important to see that **equilibrium in all cases is characterized by the maximum of the total entropy of the bodies and the environment**.

13.16 On the second law again

13.16.1 On the formulations of Clausius and Planck

The Kelvin–Planck formulation

“No process is possible whose sole result is the complete conversion of heat into work",

and the Clausius formulation

“No process is possible whose sole result is the transfer of heat from a colder to a hotter body"

are frequently claimed to be equivalent; now we study a ‘proof’ of this equivalence. [4]

Let us take two heat baths of temperature T_a and T_b, respectively, with $T_a < T_b$. Let us take two bodies which are only in mechanical contact with each other and in mechanical and thermal contact with the heat baths. Then

$$\dot{E}_1 = Q_{1a} + Q_{1b} + W_{1a} + W_{1b} + W_{12},$$

$$\dot{E}_2 = Q_{2a} + Q_{2b} + W_{2a} + W_{2b} + W_{21}.$$

The expression ‘sole result’ means that we the final state (internal energy and volume) of each body equals the initial state. The duration of the process does not appear in the formulations, so we can choose an arbitrarily short interval, i.e. we can take $\dot{E}_1 = \dot{E}_2 = 0$.

Let us suppose that the Kelvin–Planck formulation is not true. Then there is a body (‘engine’), let it be the first one, so that $Q_{1a} = 0$, $W_{1a} = W_{1b} = 0$ and

$$0 = Q_{1b} + W_{12}, \quad \text{and} \quad Q_{1b} > 0.$$

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[4] C. J. Adkins: *Equilibrium Thermodynamics*, Cambridge University Press, 1983, 3rd edition

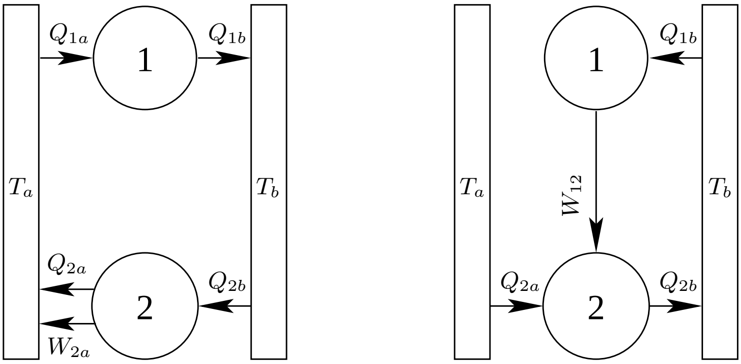

Figure 13.1

Let the second body be coupled to the first one in such a way that $W_{21} = -W_{12}$, furthermore, let $W_{2a} = W_{2b} = 0$ and

$$0 = Q_{2a} + Q_{2b} - W_{12}, \quad \text{and} \quad Q_{2a} > 0$$

(Figure 13.1). The sum of the two equalities above yields

$$0 = Q_{2a} + \big(Q_{1b} + Q_{2b}\big) \quad \text{and} \quad Q_{2a} > 0.$$

If the two bodies together are considered as a single system, then the system absorbs heat Q_{2a} from the heat bath T_a and emits the same amount of heat to the heat bath T_b: heat flows from a colder place to a hotter one, and the Clausius formulation is not true.

Let us suppose that the Clausius formulation is not true. Then there is a body, let it be the first one, so that $W_{1a} = W_{1b} = W_{12} = 0$ and

$$0 = Q_{1a} + Q_{1b}, \quad \text{and} \quad Q_{1b} < 0.$$

Let the second body be independent of the first one, i.e. $W_{12} = W_{21} = 0$, furthermore, let $W_{2b} = 0$ and

$$0 = Q_{2a} + Q_{2b} + W_{2a}, \quad \text{and} \quad Q_{2b} = -Q_{1b} > 0, \quad Q_{2a} < 0, \quad W_{2a} < 0$$

(Figure 13.1). The sum of the two equalities above yields

$$0 = \big(Q_{1a} + Q_{2a}\big) + W_{2a}.$$

If the two bodies together are regarded as a single system, then the system absorbs heat $Q_{1a} + Q_{2a}$ which is converted completely to work: the Kelvin–Planck formulation is not true.

We have seen in Paragraph 12.16 that the two formulations are really independent, thus the ‘proof’ must be incorrect. It is not evident, however, where the error is. But it is remarkable that the inequality $T_a < T_b$ is not referred to anywhere. Now, in order to detect error, one should take the reversed inequality $T_a > T_b$ and run through the ‘proof’. Then he/she observes that the second part does not go: if $Q_{2a} < 0$ and $Q_{2b} > 0$, then the engine works absorbing heat from a colder heat bath and emitting heat to a hotter one, and this is impossible. Is this impossible? Why? Where is it formulated in the theory that this is impossible? Nowhere. Thus the ‘proof’ involves the following tacit assumption which is as strong as any of the formulations to be proved:

“There is an engine which works absorbing heat from a hotter place and emitting heat to a colder place but there is no engine which works absorbing heat from a colder place and emitting heat to a hotter place".

13.17 Exercises

1. What can be said about the constraint-free system with the method of linearization (cf 12.3)?

2. Why cannot the local uniqueness of equilibrium in $U(E_\mathrm{s}, V_\mathrm{s})$ be proven without assuming the entropic property (see Paragraph 13.5)? Examine the other systems, too, where the local uniqueness of equilibrium is not stated explicitly.

3. Why is $(E_1, E_2) \mapsto (\mathbf{T}_1(E_1, V_{1\mathrm{o}}) - T_a)^2 + (\mathbf{T}_2(E_2, V_{2\mathrm{o}}) - T_a)^2$ not a Liapunov function for asymptotic stability in the case of fixed individual volumes?

4. Why is $(V_1, V_2) \mapsto (\mathbf{P}_1(\mathtt{E}(V_1), V_1) - P_a)^2 + (\mathbf{P}_2(\mathtt{E}(V_2), V_2) - P_a)^2$ not a Liapunov function for asymptotic stability in the case of individual heat insulations?

5. Show that if the specific heats are constant, then a convenient modification of the previous functions is a good Liapunov function.

6. Demonstrate that there is no isothermal equilibrium if the temperature of the bodies does not equal that of the environment and the bodies are not heat insulated from the environment.

7. Examine the system in which the bodies are heat insulated from the environment and the temperature of the bodies is constant. How can this system be realized?

8. Treat the systems in which
   - the bodies are heat insulated from each other,
   - the bodies are heat insulated from each other and the total volume is fixed,
   - the bodies are heat insulated from each other and the individual volumes are fixed,
   - the volume of one of the bodies is fixed,
   - one of the bodies is heat insulated,
   - one of the bodies is heat insulated from the environment.

9. Let the bodies be heat insulated from the environment and let the volume of each body be fixed. Suppose that the internal energy of each body depends only on temperature, and the specific heat is constant, i.e. $\mathcal{E}_i(V_i, T_i, N_i) = N_i c_i T_i$ $(i = 1, 2)$. Take $Q_{12} = -\lambda(T_1 - T_2)$ where $\lambda > 0$ is constant. Then the total internal energy E_s of the bodies is constant,

$$N_1 c_1 T_1 + N_2 c_2 T_2 = E_\mathrm{s},$$

and the dynamical equation yields

$$N_1 c_1 \dot{T}_1 = -\lambda(T_1 - T_2).$$

Then the equilibrium temperature is

$$T_{\mathrm{o}} = \frac{E_{\mathrm{s}}}{N_1c_1 + N_2c_2}$$

and we get the solution of the dynamical equation in the form

$$T_1(t) = \exp\left(-\lambda\frac{N_1c_1 + N_2c_2}{N_1N_2c_1c_2}(t - t_0)\right)\big(T_1(t_0) - T_{\mathrm{o}}\big).$$

10. Give explicitly the solution of the dynamical equation if the volume of both bodies is fixed and the formulae of the previous exercise are valid, moreover the heating between the bodies and the environmentis $Q_{ia} = -\lambda_i(T_i - T_a)$ where $\lambda_i \geq 0$ is constant $(i = 1, 2)$.

11. Take the bodies as in the previous exercise and suppose constant heat sources Q_{1s} and Q_{2s} are in the bodies. If $\lambda\lambda_1 + \lambda\lambda_2 + \lambda_1\lambda_2 \neq 0$ (i.e. at least one of the bodies is in thermal contact with the environment), then there exists a stationary state given by

$$T_{1\mathrm{o}} = T_a + \frac{(\lambda + \lambda_2)Q_{1s} + \lambda Q_{2s}}{\lambda\lambda_1 + \lambda\lambda_2 + \lambda_1\lambda_2},$$

$$T_{2\mathrm{o}} = T_a + \frac{(\lambda + \lambda_1)Q_{2s} + \lambda Q_{1s}}{\lambda\lambda_1 + \lambda\lambda_2 + \lambda_1\lambda_2}.$$

Give explicitly the solution of the dynamical equation.

IV SYSTEM OF SIMPLE BODIES; GENERAL TREATMENT

14 Description of systems

14.1 Exact definition of systems

Based on Chapter II, particular systems were treated in Chapter III which, hopefully, will make the mathematical definition of the systems of bodies comprehensible. First of all, we call attention to an important fact: bodies that can interchange particles must have the same material, otherwise they do not continue to be simple (i.e. consisting of equal molecules).

For the sake of perspicuity, we shall use the logical symbols $\Longleftrightarrow$ and $\Longrightarrow$ (avoided elsewhere) in the following definition. As concerns the symbols $*$, $**$ and $***$, we refer to the remark in 12.2.1.

Definition *A system consisting of*

– *given bodies,*
– *a given environment,*
– *given sources*

is the following:

1. *A positive integer* n *and simple materials* $(\mathrm{D}_i\mathbf{T}_i, \mathbf{P}_i, \boldsymbol{\mu}_i, \mathrm{R}_i)$ $(i = a, 1 \ldots, n)$*; the* a*-th material is called the* **environment***, the body corresponding to the* $a \neq i$*-th material is called the* i*-th* **body of the system**.

2. *For all* $i, k = a, 1, \ldots, n$*, the* **dynamical quantities**

$$\begin{aligned}
\mathbf{Q}_{ik} &: (\mathrm{D}_i * \mathbb{R}_0^+) \times (\mathrm{D}_k * \mathbb{R}_0^+) \to (\mathrm{J/s}),\\
\mathbf{F}_{ik} &: (\mathrm{D}_i * \mathbb{R}_0^+) \times (\mathrm{D}_k * \mathbb{R}_0^+) \to (\mathrm{m}^3/\mathrm{s}),\\
\mathbf{G}_{ik} &: (\mathrm{D}_i * \mathbb{R}_0^+) \times (\mathrm{D}_k * \mathbb{R}_0^+) \to (1/\mathrm{s}),\\
\boldsymbol{\pi}_{ik} &: (\mathrm{D}_i * \mathbb{R}_0^+) \times (\mathrm{D}_k * \mathbb{R}_0^+) \to (\mathrm{Pa}),\\
\boldsymbol{\xi}_{ik} &: (\mathrm{D}_i * \mathbb{R}_0^+) \times (\mathrm{D}_k * \mathbb{R}_0^+) \to (\mathrm{J})
\end{aligned}$$

which are continuous, moreover continuously differentiable on the interior of their domain. If the material of the i*-th and the* k*-th body is different, then* $\mathbf{G}_{ik} = 0$.

Let us introduce the quantities

$$\mathbf{W}_{ik} := -\big(\mathbf{P}_i\mathbf{F}_{ik} + \boldsymbol{\pi}_{ik}\mathbf{F}_{ik}^2\big), \qquad \mathbf{L}_{ik} := \boldsymbol{\mu}_i\mathbf{G}_{ik} + \boldsymbol{\xi}_{ik})\mathbf{G}_{ik}^2,$$

$$\mathbf{A}_{ik} := \mathbf{Q}_{ik} + \mathbf{W}_{ik} + \mathbf{L}_{ik}$$

and the simplified notations

$$Q_{ik} := \mathbf{Q}_{ik}(E_i, V_i, N_i, E_k, V_k, N_k), \quad F_{ik} := \mathbf{F}_{ik}(E_i, V_i, N_i, E_k, V_k, N_k),$$
$$G_{ik} := \mathbf{G}_{ik}(E_i, V_i, N_i, E_k, V_k, N_k),$$

$$A_{ik} := \mathbf{A}_{ik}(E_i, V_i, N_i, E_k, V_k, N_k), \quad W_{ik} := \mathbf{W}_{ik}(E_i, V_i, N_i, E_k, V_k, N_k),$$
$$L_{ik} := \mathbf{L}_{ik}(E_i, V_i, N_i, E_k, V_k, N_k)$$

$$\pi_{ik} := \boldsymbol{\pi}_{ik}(E_i, V_i, N_i, E_k, V_k, N_k), \quad \xi_{ik} := \boldsymbol{\xi}_{ik}(E_i, V_i, N_i, E_k, V_k, N_k),$$

$$T_i := \mathbf{T}_i(E_i, V_i, N_i), \quad P_i := \mathbf{P}_i(E_i, V_i, N_i), \quad \mu_i := \boldsymbol{\mu}_i(E_i, V_i, N_i).$$

Then the dynamical quantities satisfy

– **mutuality**:

$$A_{ik} = -A_{ki}, \quad F_{ik} = -F_{ki}, \quad G_{ik} = -G_{ki},$$

– *the* **equilibrium properties**:

(I) if $N_i N_k = 0$ *then* $Q_{ik} = 0$, $F_{ik} = 0$, $G_{ik} = 0$, $\pi_{ik} = 0$ *and* $\xi_{ik} = 0$,
(II) for $N_i N_k \neq 0$
0) $P_i = P_k \implies \pi_{ik} = 0$,
$\mu_i = \mu_k \implies \xi_{ik} = 0$.
1) if $\mathbf{G}_{ik} = 0$,
(a) and $\mathbf{F}_{ik} = 0$, $\mathbf{Q}_{ik} \neq 0$, *then*
$* \; Q_{ik} = 0 \iff T_i = T_k$,
(b) and $\mathbf{Q}_{ik} = 0$, $\mathbf{F}_{ik} \neq 0$, *then*
$* \; F_{ik} = 0 \iff P_i = P_k$,
(c) if $\mathbf{F}_{ik} \neq 0$, $\mathbf{Q}_{ik} \neq 0$, *then*
$* \; F_{ik} = 0 \implies P_i = P_k$,
$* \; Q_{ik} = 0$ *and* $P_i = P_k \implies T_i = T_k$,
$** \; T_i = T_k$ *and* $P_i = P_k \implies Q_{ik} = 0$ *and* $F_{ik} = 0$;
2) if $\mathbf{G}_{ik} \neq 0$ *and can have both positive and negative values*
(a) and $\mathbf{F}_{ik} = 0$, $\mathbf{Q}_{ik} = 0$, *then*
$* \; G_{ik} = 0 \iff \mu_i = \mu_k$;

(b) and $\mathbf{F}_{ik} = 0$, $\mathbf{Q}_{ik} \neq 0$, *then*

$* \; G_{ik} = 0 \implies \mu_i = \mu_k$,

$* \; \mu_i = \mu_k$ *and* $Q_{ik} = 0 \implies T_i = T_k$

(which imply that if $G_{ik} = 0$ *and* $Q_{ik} = 0$, *then* $\mu_i = \mu_k$ *and* $T_i = T_k$*),*

$* * \; \mu_i = \mu_k$ *and* $T_i = T_k \implies G_{ik} = 0$ *and* $Q_{ik} = 0$*;*

(c) and $\mathbf{F}_{ik} \neq 0$, $\mathbf{Q}_{ik} = 0$, *then*

$* \; G_{ik} = 0 \implies \mu_i = \mu_k$,

$* \; \mu_i = \mu_k$ *and* $F_{ik} = 0 \implies P_i = P_k$

(which imply that if $G_{ik} = 0$ *and* $F_{ik} = 0$, *then* $\mu_i = \mu_k$ *and* $P_i = P_k$*),*

$* * \; \mu_i = \mu_k$ *and* $P_i = P_k \implies G_{ik} = 0$ *and* $F_{ik} = 0$*;*

(d) and $\mathbf{F}_{ik} \neq 0$, $\mathbf{Q}_{ik} \neq 0$, *then*

$* \; G_{ik} = 0 \implies \mu_i = \mu_k$,

$* \; \mu_i = \mu_k$ *and* $F_{ik} = 0 \implies P_i = P_k$,

$* \; \mu_i = \mu_k$, $P_i = P_k$ *and* $Q_{ik} = 0 \implies T_i = T_k$

(which imply that if $G_{ik} = 0$, $F_{ik} = 0$ *and* $Q_{ik} = 0$, *then* $\mu_i = \mu_k$, $P_i = P_k$ *and* $T_i = T_k$*),*

$* * * \; \mu_i = \mu_k$, $P_i = P_k$ *and* $T_i = T_k \implies G_{ik} = 0$, $F_{ik} = 0$ *and* $Q_{ik} = 0$*;*

3) if $\mathbf{G}_{ik} \neq 0$ *and* $\mathbf{G}_{ik} \geq 0$ *(or* $\mathbf{G}_{ik} \leq 0$*), then the previous relations (a) to (d) are satisfied in such a way that* $\mu_i \geq \mu_k$ *(or* $\mu_i \leq \mu_k$*) appears everywhere instead of* $\mu_i = \mu_k$.

– *the* **dissipation inequalities***:*

$$-\frac{Q_{ik}}{T_i}(T_i - T_k) + F_{ik}(P_i - P_k) - G_{ik}(\mu_i - \mu_k) \geq \\ (\pi_{ik} + \pi_{ki})\mathbf{F}_{ik}^2 + (\xi_{ik} + \xi_{ki})\mathbf{G}_{ik}^2 \geq 0,$$

where equality holds if and only if $Q_{ik} = 0$, $F_{ik} = 0$, *and* $G_{ik} = 0$ *(implying that* $W_{ik} = 0$ *and* $L_{ik} = 0$, *too); this is equivalent to*

$$A_{ik}\left(\frac{1}{T_i} - \frac{1}{T_k}\right) + F_{ik}\left(\frac{P_i}{T_i} - \frac{P_k}{T_k}\right) - G_{ik}\left(\frac{\mu_i}{T_i} - \frac{\mu_k}{T_k}\right) \geq \\ \left(\frac{\pi ik}{T_i} + \frac{\pi_{ki}}{T_k}\right)\mathbf{F}_{ik}^2 + \left(\frac{\xi_{ik}}{T_i} + \frac{\xi_{ki}}{T_k}\right)\mathbf{G}_{ik}^2 \geq 0. \quad \text{(IV1)}$$

3. *A* **process of the environment***, a continuous function* $t \mapsto \big(E_a(t), V_a(t), N_a\big) \in \mathrm{D}_a * \mathbb{R}^+$ *defined on a time interval.*

4. *For all* $i = 1, \dots, n$ *the* **sources***, continuous functions* $t \mapsto Q_{i,s}(t) \in (\mathrm{J/s})$ *and* $t \mapsto G_{i,s}(t) \in (1/\mathrm{s})$ *defined on a time interval.*

5. *The* **dynamical equation**

$$\dot{E}_i = Q_i + W_i + L_i \qquad \dot{V}_i = F_i, \qquad \dot{N}_i = G_i$$

$$(i = 1, \dots, n),$$

where

$$Q_i := Q_{i,s} + \sum_{k=a,1}^{n} Q_{ik}, \quad F_i := \sum_{k=a,1}^{n} F_{ik}, \quad G_i := G_{i,s} + \sum_{k=a,1}^{n} G_{ik},$$

$$W_i := \sum_{k=a,1}^{n} W_{ik}, \qquad L_i := L_{i,s} + \sum_{k=a,1}^{n} L_{ik}.$$

Remarks (i) We use the names according to the previous chapter: $\mathbf{Q}_{ik}$ is the **heating** of the i-th body due to the k-th body, etc. The solutions of the dynamical equation are the **processes** of the system.

(ii) Some of the equilibrium properties follow from the dissipation inequalities; e.g. $T_i = T_k$, $P_i = P_k$ and $\mu_i = \mu_k$ imply equality in the dissipation inequality, thus, according to the requirement, $Q_{ik} = 0$, $F_{ik} = 0$ and $G_{ik} = 0$ must hold.

(iii) As a consequence of mutuality, the dynamical quantities with two equal subscripts are zero, except the lost coefficients; those are, however, are multiplied by zero in the dynamical equation, thus they can be taken to be zero.

(iv) The dynamical quantities with subscripts ak (which would determine the processes of the environment) do not appear in the dynamical equation (the process of the environment is given independently of the bodies), they are listed only for the sake of formal simplicity. Given the quantities with subscripts ka, the quantities $\mathbf{Q}_{ak}(E_a, V_a, N_a, E_k, V_k, N_k) := -\mathbf{Q}_{ka}(E_k, V_k, N_k, E_a, V_a, N_a)$, etc. satisfy formally all the requirements.

(v) The environment is conceived to be 'infinitely large', its particle number has the constant value N_a in the given process, so it plays no role in the dynamical equation. The particle number of the environment is a dummy variable in the dynamical quantities which appears only for the sake of uniform formulation.

14.2 Consequences of the equilibrium properties and the dissipation inequalities

As we mentioned, the equilibrium properties and the dissipation inequalities are not independent. Moreover, they allow us to deduce further properties. We shall consider ideal workings and transferrings. Some of the following relations remain valid for the non-ideal case, too.

Let us apply the notations in item 2 of Definition 14.1. In the ideal case the dissipation inequalities can be rewritten in the form

$$-\frac{Q_{ik}}{T_i}(T_i - T_k) + F_{ik}(P_i - P_k) - G_{ik}(\mu_i - \mu_k) \geq 0.$$

Proposition *Let the workings and transferrings be ideal and let* $N_i N_k \neq 0$.

1) *If* $\mathbf{G}_{ik} = 0$,

(a) *and* $\mathbf{F}_{ik} = 0$, $\mathbf{Q}_{ik} \neq 0$, *then* $Q_{ik} > 0$ *if and only if* $T_i - T_k < 0$,

(b) *and* $\mathbf{Q}_{ik} = 0$, $\mathbf{F}_{ik} \neq 0$, *then* $F_{ik} > 0$ *if and only if* $P_i - P_k > 0$,

(c) *and* $\mathbf{F}_{ik} \neq 0$, $\mathbf{Q}_{ik} \neq 0$, *then*

$*$ if $P_i - P_k > 0$ and $T_i - T_k = 0$, then $(E_i, V_i, N_i, E_k, V_k, N_k)$ has a neighbourhood in which for all $(E'_i, V'_i, N'_i, E'_k, V'_k, N'_k)$ the strict inequality $\mathbf{F}_{ik}(E'_i, V'_i, N'_i, E'_k, V'_k, N'_k) > 0$ holds,

$*$ if $T_i - T_k < 0$ and $P_i - P_k = 0$, then $(E_i, V_i, N_i, E_k, V_k, N_k)$ has a neighbourhood in which for all $(E'_i, V'_i, N'_i, E'_k, V'_k, N'_k)$ the strict inequality $\mathbf{Q}_{ik}(E'_i, V'_i, N'_i, E'_k, V'_k, N'_k) > 0$ holds.

2) If $\mathbf{G}_{ik} \neq 0$ and can have both positive and negative values,

(a) and $\mathbf{F}_{ik} = 0$, $\mathbf{Q}_{ik} = 0$, then $G_{ik} > 0$ if and only if $\mu_i - \mu_k < 0$,

(b) and $\mathbf{F}_{ik} = 0$, $\mathbf{Q}_{ik} \neq 0$, then if $\mu_i - \mu_k < 0$ and $T_i = T_k$, then $(E_i, V_i, N_i, E_k, V_k, N_k)$ has a neighbourhood in which for all $(E'_i, V'_i, N'_i, E'_k, V'_k, N'_k)$ the strict inequality $\mathbf{G}_{ik}(E'_i, V'_i, N'_i, E'_k, V'_k, N'_k) > 0$ holds,

(c) and $\mathbf{F}_{ik} \neq 0$, $\mathbf{Q}_{ik} = 0$, then if $\mu_i - \mu_k < 0$ and $P_i - P_k = 0$, then $(E_i, V_i, N_i, E_k, V_k, N_k)$ has a neighbourhood in which for all $(E'_i, V'_i, N'_i, E'_k, V'_k, N'_k)$ the strict inequality $\mathbf{G}_{ik}(E'_i, V'_i, N'_i, E'_k, V'_k, N'_k) > 0$ holds,

(d) and $\mathbf{F}_{ik} \neq 0$, $\mathbf{Q}_{ik} \neq 0$, then if $\mu_i - \mu_k < 0$ and $T_i - T_k = 0$, $P_i - P_k = 0$, then $(E_i, V_i, N_i, E_k, V_k, N_k)$ has a neighborhood in which for all $(E'_i, V'_i, N'_i, E'_k, V'_k, N'_k)$ the strict inequality $\mathbf{G}_{ik}(E'_i, V'_i, N'_i, E'_k, V'_k, N'_k) > 0$ holds,

and the same assertions are true with reversed inequalities.

Proof 1)(a) and 1)(b) are evident from the equilibrium properties and the dissipation inequalities. We shall show the first relation in 1)(c), the others can be proved similarly.

Let $P_i > P_k$. Then the equilibrium property implies that F_{ik} cannot be zero. If $T_i - T_k = 0$, then – because $\mathbf{G}_{ik} = 0$ – the dissipation inequality implies $F_{ik} > 0$. The function $\mathbf{F}_{ik}$ is continuous, thus its values are greater than zero in a neighbourhood of the point in question.

14.3 Equilibrium

Definition *A* **standstill** *(***stationary process***) of the system is a constant process.* **Equilibrium** *is a standstill in which every dynamical quantity has zero value.*

It is evident that equilibrium can occur in a system only if all the sources are zero. The state of the system $\big((E_{io}, V_{io}, N_{io}) \mid i = 1, \dots, n\big)$ as a constant function is a standstil if and only if the right sides of the dynamical equation – the sums of the corresponding dynamical quantities – are zero at that state.

Let us take a standstill of a system. If this standstill were not an equilibrium, then heat or volume or particle would pass among the bodies in such a way that the absorbed and emitted quantities are equal for all bodies. Let us consider e.g. three bodies; then the same amount of heat would pass from the first body to the second body, from the second to the third and from the third to the first. Our experience shows that such a process does not exist; this is supported by the following result.

Proposition *Without sources every standstill is an equilibrium.*

Proof Let us use the notations introduced in item 2 of Definition 14.1. We have to show that if

$$A_i := \sum_{k=a,1}^{n} A_{ik} = 0, \qquad F_i := \sum_{k=a,1}^{n} F_{ik} = 0, \qquad G_i := \sum_{k=a,1}^{n} G_{ik} = 0, \qquad (*)$$

for all $i = 1, \dots, n$, then

$$A_{ik} = 0, \qquad F_{ik} = 0, \qquad G_{ik} = 0 \qquad (**)$$

for all $i = 1, \dots, n$ and $k = a, 1, \dots, n$ (with the formal dynamical quantities with subscripts ak we shall consider that i can take the value a, too).

The dissipation inequalities yield that

$$\sum_{i,k=a,1}^{n} \left[A_{ik}\left(\frac{1}{T_i} - \frac{1}{T_k}\right) + F_{ik}\left(\frac{P_i}{T_i} - \frac{P_k}{T_k}\right) - G_{ik}\left(\frac{\mu_i}{T_i} - \frac{\mu_k}{T_k}\right)\right] \geq 0,$$

where equality holds if and only if $(**)$ is satisfied. Let us execute the following simple transformations:

$$\sum_{i,k=a,1}^{n} A_{ik}\left(\frac{1}{T_i} - \frac{1}{T_k}\right) = \sum_{i,k=a,1}^{n} A_{ik}\left(\left(\frac{1}{T_i} - \frac{1}{T_a}\right) - \left(\frac{1}{T_k} - \frac{1}{T_a}\right)\right) =$$

$$= \sum_{i,k=a,1}^{n} A_{ik}\left(\frac{1}{T_i} - \frac{1}{T_a}\right) + \sum_{i,k=a,1}^{n} A_{ki}\left(\frac{1}{T_k} - \frac{1}{T_a}\right) =$$

$$= 2\sum_{i,k=a,1}^{n} A_{ik}\left(\frac{1}{T_i} - \frac{1}{T_a}\right) = 2\sum_{i=a,1}^{n} A_i\left(\frac{1}{T_i} - \frac{1}{T_a}\right).$$

The second equality is obtained by mutuality. A similar result can be deduced for springings and convertings, too. Then we get

$$\sum_{i=1}^{n} \left[A_i\left(\frac{1}{T_i} - \frac{1}{T_a}\right) + F_i\left(\frac{P_i}{T_i} - \frac{P_a}{T_a}\right) - G_i\left(\frac{\mu_i}{T_i} - \frac{\mu_a}{T_a}\right)\right] \geq 0,$$

where equality holds if and only if $(**)$ is satisfied. Here the sum would start from zero but the zeroth member is zero because of the multipliers $1/T_a - 1/T_a$, etc.

It is evident, that $(*)$ implies the equality in the above relation which, in turn, implies $(**)$.

14.4 Exercises

1. Demonstrate that if $\mathbf{G}_{ik} = 0$ and the workings are ideal, then the two terms in the dissipation inequality are zero for (E_i, V_i, N_i) and (E_k, V_k, N_k) which are 'sufficiently near to each other' .

2. Deduce relations similar to those in 14.2 when $\mathbf{G}_{ik} \geq 0$.

3. Verify that Proposition 14.2 and the previous two exercises remain true if $\mathbf{G}_{ik} = 0$ etc. is replaced by $\mathbf{G}_{ik}||_{(E_i,V_i,N_i)} = 0$,m etc. (see 10.6).

4. What can be said instead of 1)(c) in 14.2 for mechanically strong springings?

15 Summarizing formulae

15.1 General notations

The description of systems can be put in an abstract framework which exhibits well the essence of the mathematical structure and allows us to introduce further notions and to deduce some general results.

For the sake of simplicity, we suppose that the sources are zero; besides the results concerning the equilibria, everything can be repeated for non-zero sources, too.

We examine a system consisting of n bodies and an environment with a given process.

Let us put

$$x_i := \left((E_i, V_i, N_i) \;\middle|\; i = a, 1, \dots, n \right).$$

Then the given process of the environment is $t \mapsto x_a(t)$ (contrary to the treatment of particular systems, here we do not leave this process (E_a, V_a, N_a) for (T_a, P_a)). A state of the system is

$$x := (x_i \mid i = 1, \dots, n),$$

an element of

$$\mathop{\times}_{i=1}^{n} (\mathrm{D}_i * \mathbb{R}_0^+),$$

which is a subset of the vector space

$$X := \Big((\mathrm{J}) \times (\mathrm{m}^3) \times \mathbb{R} \Big)^n .$$

We allowed that the particle number of bodies takes the zero value, because it can happen that a body becomes empty in a process.

If the particle number of a body is zero, then its energy and volume are zero as well; such a state is a special boundary point of the states with non-zero particle number and it has qualitatively different properties. In the sequel we shall consider processes running in the set

$$X_D := \mathop{\times}_{i=1}^{n} (\mathrm{D}_i * \mathbb{R}^+),$$

i.e. each body has non-zero particle number.

It will be suitable to replace temperature T with kT where k is the Boltzmann constant; kT has energy dimension, i.e. $kT \in (\mathrm{J})$. Then the values of canonical intensive quantities of are

$$\left(\frac{1}{kT_i}, \frac{P_i}{kT_i}, -\frac{\mu_i}{kT_i} \right) \qquad (i = a, 1, \dots, n),$$

thus, the canoncial intensive quantities are functions

$$\mathbf{y}_i : \mathrm{D}_i * \mathbb{R}^+ \to \left(\frac{1}{\mathrm{J}} \right) \times \left(\frac{1}{\mathrm{m}^3} \right) \times \mathbb{R} \qquad (i = a, 1, \dots, n).$$

The dual of a one-dimensional vector space is its 'reciprocal', i.e. the dual of (J) is (1/J) etc.

As a consequence, the Cartesian product of the canonical intensive quantities of the bodies,

$$\mathbf{y} := \mathop{\times}_{i=1}^{n} \mathbf{y}_i := \mathop{\times}_{i=1}^{n} \left(\frac{1}{k\mathbf{T}_i}, \frac{\mathbf{P}_i}{k\mathbf{T}_i}, -\frac{\boldsymbol{\mu}_i}{k\mathbf{T}_i} \right) : X_D \to X^*$$

is a continuous function, continuously differentiable on

$$X_R := \mathop{\times}_{i=1}^{N} (\mathrm{R}_i * \mathbb{R}^+).$$

The Cartesian product of the thermodynamical forces between the bodies and the environment plays an important role in the sequel.

Definition *The function* $\mathbf{F} : X_D \times (\mathrm{D}_a * \mathbb{R}^+) \to X^*$ *defined by*

$$\mathbf{F}(x, x_a) := (\mathbf{y}_i(x_i) - \mathbf{y}_a(x_a) \mid i = 1, \ldots, n)$$

is called the **nominal thermodynamical force***.*

15.2 The dynamical equation

The dynamical equations

$$\dot{E}_i = \sum_{k=a,1}^{n} (Q_{ik} + W_{ik} + L_{ik}),$$

$$\dot{V}_i = \sum_{k=a,1}^{n} F_{ik} \qquad \dot{N}_i = \sum_{k=a,1}^{n} G_{ik}$$

$$(i = 1, \ldots, n)$$

with the notation

$$\mathbf{R}_{ik} := (\mathbf{Q}_{ik} + \mathbf{W}_{ik} + \mathbf{L}_{ik}, \mathbf{F}_{ik}, \mathbf{G}_{ik}) : \\ (\mathrm{D}_i * \mathbb{R}^+) \times (\mathrm{D}_k * \mathbb{R}^+) \to \big((\mathrm{J/s}) \times (\mathrm{m}^3/\mathrm{s}) \times (1/\mathrm{s})\big)$$

for $(i, k = a, 1, \ldots, n)$ can be written in the form

$$\dot{x}_i = \sum_{k=a,1}^{n} \mathbf{R}_{ik}(x_i, x_k) \qquad (i = 1, \ldots, n)$$

or with the more concise notation

$$\mathbf{R}(x, x_a) := \left(\sum_{k=a,1}^{n} \mathbf{R}_{ik}(x_i, x_k) \;\middle|\; i = 1, \ldots, n \right)$$

$$(x \in X_D, x_a \in \mathrm{D}_a * \mathbb{R}^+)$$

in the form

$$(x : I \to X_D)? \qquad \dot{x} = \mathbf{R}(x, x_a).$$

If $\mathbf{R}(x, x_a)$ depends on x_a, then a standstill can exist only if x_a is constant. It was shown in 14.3 that in the case of ideal workings and transferrings x is an equilibrium if and only if $\mathbf{R}(x, x_a) = 0$ (in other words, every standstill is an equilibrium).

15.3 Constraints

15.3.1 Introductory remarks

To make clear the exact notion of constraints, we recall the systems treated in 12.5, 12.7, 13.5 and 13.4:

1. a body with constant particle number and thermally insulated from the environment,

2. a body with constant particle numberand constant pressure in a given environment,

3. two bodies with constant particle number completely insulated from the environment,

4. two bodies with constant particle number and fixed total volume.

The constraints are expressed in these cases as follows:

$$\dot{E} + \mathbf{P}(E, V)\dot{V} = 0, \qquad \dot{N} = 0,$$

$$\frac{\partial \mathbf{P}(E, V)}{\partial E}\dot{E} + \frac{\partial \mathbf{P}(E, V)}{\partial V}\dot{V} = 0, \qquad \dot{N} = 0,$$

$$\dot{E}_1 + \dot{E}_2 = 0, \qquad \dot{V}_1 + \dot{V}_2 = 0, \qquad \dot{N}_1 = 0, \qquad \dot{N}_2 = 0,$$

$$\dot{V}_1 + \dot{V}_2 = 0, \qquad \dot{N}_1 = 0, \qquad \dot{N}_2 = 0.$$

The constraints can be described in a similar way for the other systems treated in Sections 12 and 13, too. If the bodies can interchange particles (diffusions and phase transitions), then the constraints can be more general. Namely, the constraints here are of equality type but there can be constraints of inequality type, too: the semipermeable walls mean that the convertings have non-negative or non-positive values. Now we exclude such constraints; a particular one will be treated in 18.7.

Note that the zero on the right-hand side of the equalities above is in diverse one-dimensional vector spaces; multiplying by convenient constants and so achieving that always the zero real number appears, we can unify the formulae. We find that a constraint means that the process velocities are not independent, more closely: some linear combinations of the process velocities are zero. The equalities hold for all processes, so they must be satisfied if the velocities are replaced by the corresponding dynamical quantities.

Consequently, the first property of a constraint is formulated as follows.

We are given a subset Γ of the continuous functions $X_D \to X^*$ such that $\{\gamma(x) \mid \gamma \in \Gamma\}$ is linearly independent for all $x \in X_D$ and

$$\gamma(x)\mathbf{R}(x, x_a) = 0 \qquad (\gamma \in \Gamma, x \in X_D, x_a \in \mathrm{D}_a * \mathbb{R}^+), \tag{$*$}$$

or, with the notation

$$K(x) := \bigcap_{\gamma \in \Gamma} \mathrm{Ker}\gamma(x),$$

$$\mathbf{R}(x, x_a) \in K(x) \qquad (x \in X_D, x_a \in \mathrm{D}_a * \mathbb{R}^+).$$

(We allow ourselves a little loose notation, for the sake of simplicity, because in fact $\mathbf{R}(x, x_a)$ has values in $K(x)/s$ where s is the time unit (second).)

$K(x)$ is called the **constraint subspace** corresponding to x. Evidently, every constraint subspace has $2n - |\Gamma|$ dimensions, where $|\Gamma|$ is the cardinality of Γ.

It is not difficult to see that $(*)$ is equivalent to $(\gamma \circ x)\dot{x} = 0$ for all processes $x : I \to X_D$ of the system (with arbitrary given process x_a of the environment) and for all elements γ of Γ.

15.3.2 The effective thermodynamical force

Γ is not enough for the description of a constraint because for a given x (and for arbitrary x_a) we can pick up a number of subspaces $K(x)$ containing $\mathbf{R}(x, x_a)$.

Further properties of constraints are formulated by thermodynamical forces and equilibria, as it will be shown by the chosen examples.

1. In the adiabatic processes of a body with constant particle number, the (one-dimensional) constraint subspaces are spanned by elements of the form $(-P, 1, 0)$. Applying the nominal thermodynamical force

$$\left(\frac{1}{kT} - \frac{1}{kT_a}, \frac{P}{kT} - \frac{P_a}{kT_a}, -\frac{\mu}{kT} + \frac{\mu_a}{kT_a}\right)$$

(as an element of the dual of $(\mathrm{J}) \times (\mathrm{m}^3) \times \mathbb{R}$) to those elements, we get the real thermodynamical force

$$\left(\frac{1}{kT} - \frac{1}{kT_a}\right)(-P) + \left(\frac{P}{kT} - \frac{P_a}{kT_a}\right) = \frac{1}{kT_a}(P - P_a)$$

(recall 11.8: in the case of heat insulation the quantity $P - P_a$ – or a quantity, proportional to that one – is the real driving force whose zero value characterizes the equilibrium).

2. If a body with constant particle number is constrained to isobaric processes with pressure P_o in a given environment, then the springing is proportional to heating, $F = \alpha Q$, thus the dynamical equation becomes

$$\dot{E} = (1 - P_o\alpha)Q, \qquad \dot{V} = \alpha Q, \qquad \dot{N} = 0.$$

This means that in a state (E, V, N) for which $\mathbf{P}(E, V, N) = P_o$ holds, the (one-dimensional) constraint subspace is spanned by $(1 - P_o\alpha(E, V, N), \alpha(E, V, N), 0)$.

Applying the nominal thermodynamical force (described in the previous example) to this element, we get the real thermodynamical force

$$\left(\frac{1}{kT} - \frac{1}{kT_a}\right)(1 - P_\mathrm{o}\alpha) + \left(\frac{P_\mathrm{o}}{kT} - \frac{P_a}{kT_a}\right)\alpha = \frac{1}{kT} - \frac{1}{kT_a} + \frac{\alpha}{kT_a}(P_\mathrm{o} - P_a),$$

whose zero value characterizes the equilibrium: it has zero value if the pressure P_a of the environment is constant and equals P_o and does not have zero value (there is no equilibrium) if $P_\mathrm{o} \neq P_a$ (see Exercise 3 in 15.10).

3. If two bodies with constant particle number are completely insulated from the environment, then the (two-dimensional) constraint subspaces are spanned by the vectors $(1, 0, 0, -1, 0, 0)$ and $(0, 1, 0, 0, -1, 0)$. Applying the nominal thermodynamical force

$$\left(\frac{1}{kT_1} - \frac{1}{kT_a}, \frac{P_1}{kT_1} - \frac{P_a}{kT_a}, -\frac{\mu_1}{kT_1} + \frac{\mu_a}{kT_a}, \frac{1}{kT_2} - \frac{1}{kT_a}, \frac{P_2}{kT_2} - \frac{P_a}{kT_a}, -\frac{\mu_2}{kT_2} + \frac{\mu_a}{kT_a}\right)$$

to those vectors, we get the members of the real thermodynamical forces:

$$\left(\frac{1}{kT_1} - \frac{1}{kT_2}\right) \qquad \text{and} \qquad \left(\frac{P_1}{kT_1} - \frac{P_2}{kT_2}\right).$$

4. If two bodies with constant particle number have a fixed total volume, the (three-dimensional) constraint subspaces are spanned by the vectors $(1, 0, 0, 0, 0, 0)$, $(0, 0, 0, 1, 0, 0)$ and $(0, 1, 0, 0, -1, 0)$. Applying to them the previous nominal thermodynamical force, we get the members of the real thermodynamical forces:

$$\left(\frac{1}{kT_1} - \frac{1}{kT_a}\right), \qquad \left(\frac{1}{kT_2} - \frac{1}{kT_a}\right), \qquad \left(\frac{P_1}{kT_1} - \frac{P_2}{kT_2}\right).$$

Note that we would expect also $\left(\frac{1}{kT_1} - \frac{1}{kT_2}\right)$ as a member of the real thermodynamical force but this can be obtained from the above independent members.

All these indicate that, in general, the restriction of the nominal thermodynamical force to the constraint subspaces,

$$\mathbf{F}(x, x_a)|_{K(x)} \in K(x)^*$$

gives the real thermodynamical force corresponding to the constraint.

Definition *Let* Γ *be given according to 15.3.1. The function*

$$(x, x_a) \mapsto \mathbf{F}_\Gamma(x, x_a) := \mathbf{F}(x, x_a)|_{K(x)} \in K(x)^* \qquad (x \in X_D, x_a \in \mathrm{D}_a * \mathbb{R}^+)$$

is called the **effective thermodynamical force** *corresponding to* Γ*.*

We mention that the target set of this function is, in general, different for different x-s; that is why it is rightly defined as a section of the vector bundle $\bigcup\limits_{x \in X_D} \{x\} \times K(x)$.

We require as a further main property of constraints that the standstills (equilibria or stationary states) be characterized by the zero value of the effective thermodynamical force: $\mathbf{R}(x, x_a) = 0$ if and only if $\mathbf{F}_\Gamma(x, x_a) = 0$.

15.3.3 Exact definition

Definition *Let us use the summarizing notations of 15.1 and 15.2 regarding the system consisting of n bodies. We say that the system is subjected to the constraint* Γ *if* Γ *is a subset of continuous functions* $X_D \to X^*$ *so that*

(i) $\{\gamma(x) \mid \gamma \in \Gamma\}$ *is linearly independent for all* $x \in X_D$*,*

(ii) $\mathbf{R}(x, x_a) \in K(x)$ *for all* $x \in X_D$ *and* $x_a \in \mathrm{D}_a * \mathbb{R}^+$*, where* $K(x) := \bigcap_{\gamma\in\Gamma} \mathrm{Ker}\gamma(x)$ *is the* **constraint subspace** *corresponding to x,*

(iii) $\mathbf{R}(x, x_a) = 0$ *if and only if* $\mathbf{F}(x, x_a)|_{K(x)} = 0$ $(x \in X_D, x_a \in \mathrm{D}_a * \mathbb{R}^+)$.

The system is free of constraints if $\Gamma = \emptyset$, in other words, $K(x) = X$ for all $x \in X_D$. Then the effective thermodynamical force equals the nominal thermodynamical force.

The constraint is called differentiable, continuously differentiable, twice differentiable, etc. if all $\gamma \in \Gamma$ is the restriction of a differentiable, etc. function.

15.3.4 Classification of constraints

The constraint Γ is called **holonomic** if for every $\gamma \in \Gamma$ there is a continuously differentiable function $\varphi_\gamma : X \rightarrowtail \mathbb{R}$ defined on a subset containing X_D and $\gamma = \mathtt{D}\varphi_\gamma|_{X_D}$; otherwise the constraint is **anholonomic**.

It is a well-known necessary condition for a continuously differentiable constraint to be holonomic that $\mathtt{D}\gamma(x)$ – the derivative of γ at x, a bilinear mapping $X \times X \to \mathbb{R}$ – be symmetric for all x.

The void constraint is holonomic.

15.3.5 Constraint submanifolds

Let the constraint be holonomic and let $\varphi_\gamma : X \rightarrowtail \mathbb{R}$ be as previously. Then for arbitrary process $x : I \to X_D$ and for all $\gamma \in \Gamma$ we have $\mathtt{D}\varphi_\gamma(x)\dot{x} = 0$, i.e. $\varphi_\gamma \circ x = \text{const}$. Thus if $c_\gamma \in \mathrm{Ran}\varphi_\gamma$ and $c := (c_\gamma \mid \gamma \in \Gamma)$, then

$$U(c) := \bigcap_{\gamma\in\Gamma} \overset{-1}{\varphi_\gamma}(\{c_\gamma\})$$

is an invariant set of the dynamical equation. Because $\{\mathtt{D}\varphi_\gamma(x) \mid \gamma \in \Gamma\}$ is linearly independent for all $x \in U(c)$, $U(c)$ is a submanifold of X having $2n-|\Gamma|$ dimensions.

It is evident that $U(c)$-s are different for different c-s, and their union contains X_D.

It is known that $K(x) = \bigcap_{\gamma\in\Gamma} \mathrm{Ker}(\mathtt{D}\varphi_\gamma(x)) = T_x(U_c)$, where the last symbol stands for the tangent space of U_c at x.

In general, not only for holonomic constraints, a submanifold $U \subset X$ is called a **constraint submanifold** if

$$T_x(U) = K(x) \qquad (x \in U \cap X_D). \tag{$*$}$$

If U is a constraint submanifold, then

$$\mathbf{R}(x, x_a) \in T_x(U) = K(x) \qquad (x \in U \cap X_D).$$

A constraint is called a **fibration** if for every point of X_D there is a constraint submanifold containing the point.

All the holonomic constraints are fibrations but also an anholonomic constraint can be a fibration.

The constraints of the introductory examples 1, 3 and 4 are holonomic, the constraint of example 2, though being anholonomic, is a fibration.

15.4 The pseudolinear case

15.4.1 The nominal conductance matrix

Let us suppose that the dynamical quantities are pseudolinear and let $\mathbf{C}_{ik}$ denote the conductance matrix between the i-th and k-th bodies ($i, k = a, 1, \dots, n$) (see Section 11.4); then

$$\mathbf{R}_{ik}(x_i, x_k) = \mathbf{C}_{ik}(x_i, x_k)\big(\mathbf{y}_i(x_i) - \mathbf{y}_k(x_k)\big).$$

It can be obtained easily that

$$\sum_{k=a,1}^{n} \mathbf{C}_{ik}(x_i, x_k)\big(\mathbf{y}_i(x_i) - \mathbf{y}_k(x_k)\big) = \sum_{k=1}^{n} \mathbf{B}_{ik}(x, x_a)\big(\mathbf{y}_k(x_k) - \mathbf{y}_a(x_a)\big),$$

where

$$\mathbf{B}_{ik}(x, x_a) := \begin{cases} -\mathbf{C}_{ik}(x_i, x_k) & \text{if } i \neq k, \\ \sum\limits_{j=a,1}^{n} \mathbf{C}_{ij}(x_i, x_j) & \text{if } i = k. \end{cases}$$

Hence, with the notation

$$\mathbf{B}(x, x_a) := \big(\mathbf{B}_{ik}(x, x_a) \mid i, k = 1, \dots n\big) \qquad (x \in X_D,\ x_a \in \mathrm{D}_a * \mathbb{R}^+) \qquad (*)$$

and with the nominal thermodynamical force we have

$$\mathbf{R}(x, x_a) = \mathbf{B}(x, x_a)\mathbf{F}(x, x_a),$$

in other words, the dynamical equation has the form

$$(x : I \to X_D)? \qquad \dot{x} = \mathbf{B}(x, x_a)\mathbf{F}(x, x_a).$$

Note that only the nominal thermodynamical force appears explicitly on the right-hand side of the dynamical equation, i.e. the thermodynamical forces between the bodies and the environment, instead of the thermodynamical forces between the bodies themselves. Therefore, this form seems unsuitable (if the bodies are completely insulated from the environment, then $\mathbf{C}_{ia} = 0$ for all i, so neither of $\mathbf{y}_i(x_i) - \mathbf{y}_a(x_a)$ enters the dynamical equation) but later we shall see the advantage of this form.

Definition *The function* $\mathbf{B} : X_D \times \mathrm{D}_a * \mathbb{R}^+ \to \mathrm{Lin}(X^*, X)$ *given by formula* $(*)$ *is called the* **nominal conductance matrix**.

15.4.2 Remark

It is worth noting that according to mutuality

$$\begin{aligned}\mathbf{C}_{ik}(x_i,x_k)\big(\mathbf{y}_i(x_i)-\mathbf{y}_k(x_k)\big) &= -\,\mathbf{C}_{ki}(x_k,x_i)\big(\mathbf{y}_k(x_k)-\mathbf{y}_i(x_i)\big) = \\ &= \mathbf{C}_{ki}(x_k,x_i)\big(\mathbf{y}_i(x_i)-\mathbf{y}_k(x_k)\big),\end{aligned}$$

which does not imply

$$\mathbf{C}_{ik}(x_i,x_k)=\mathbf{C}_{ki}(x_k,x_i). \tag{$*$}$$

The conductance matrix, however, has a physical meaning only when multiplied by the thermodynamical force (and is not uniquely defined), therefore we do not restrict generality by assuming that $(*)$ is always satisfied.

This convention has the immediate consequence that if all the conductance matrices between the bodies have symmetric values somewhere – $\mathbf{C}_{ik}(x_i,x_k)$ is symmetric for some x_i and x_k for all i,k – then the corresponding value of the nominal conductance matrix – $\mathbf{B}(x,x_a)$ – is symmetric as well.

15.4.3 The effective conductance matrix

Let us observe two facts.

First: $\gamma(x)\mathbf{B}(x,x_a)\mathbf{F}(x,x_a)=0$ can occur if both $\gamma(x)\mathbf{B}(x,x_a)\neq 0$ and $\mathbf{F}(x,x_a)\neq 0$; in other words, $\mathrm{Ran}\mathbf{B}(x,x_a)$ is not necessarily a subset of $K(x)$.

Second: the nominal thermodynamical force cannot be replaced, in general, by the effective thermodynamical force in the representation 15.4.1 $(*)$ of $\mathbf{R}$.

Definition *The nominal conductance matrix* **fits the constraint** *if for all* $x\in X_D$, $x_a\in \mathrm{D}_a * \mathbb{R}^+$ *there is a* $\mathbf{B}_\Gamma(x,x_a)\in \mathrm{Lin}(K(x)^*,K(x))$ *such that*

$$\mathbf{B}(x,x_a)\mathbf{F}(x,x_a)=\mathbf{B}_\Gamma(x,x_a)\mathbf{F}_\Gamma(x,x_a).$$

Then the function $(x,x_a)\mapsto \mathbf{B}_\Gamma(x,x_a)$ *is called the* **effective conductance matrix** *corresponding to* Γ.

Here we have to make the same remark as in 15.3.2 about the precise definition of the effective conductance matrix.

If there is no constraint, the nominal conductance matrix and the effective one coincide.

15.4.4 Relation between the nominal conductance matrix and the effective one

We shall always suppose in the pseudolinear case that the effective conductance matrix exists (the nominal conductance matrix fits the constraint).

Using the identity embedding

$$i(x):K(x)\to X$$

(which is a linear injection) and its transpose

$$i(x)^*:X^*\to K(x)^*$$

(which is a linear surjection), we can write the relation

$$i(x)\mathbf{B}_\Gamma(x,x_a)i(x)^* = \mathbf{B}(x,x_a) \qquad (x \in X_D, x_a \in \mathrm{D}_a * \mathbb{R}^+)$$

between the two conductivity matrices.

The effective conductance matrix is the more important one from a physical point of view but the nominal conductance matrix is a simpler mathematical object, it is easier to examine its properties, which reflects the essential properties of the effective conductance matrix. Noting the evident fact that $K(x)^{\mathrm{o}}$ is the subspace spanned by $\{\gamma(x) \mid \gamma \in \Gamma\}$, we refer to App. 1 for the following results.

First of all, we know that

– the nominal conductance matrix fits the constraint if and only if $\mathrm{Ran}\mathbf{B}(x,x_a) \subset K(x)$ and $K(x)^{\mathrm{o}} \subset \mathrm{Ker}\mathbf{B}(x,x_a)$ for all x, or equivalently, $\gamma(x)\mathbf{B}(x,x_a) = 0$ and $\mathbf{B}(x,x_a)\gamma(x) = 0$ for all $\gamma \in \Gamma$ and for all x,

– if $\mathrm{Ran}\mathbf{B}(x,x_a) \subset K(x)$ and $\mathbf{B}(x,x_a)$ is symmetric for all x, then the nominal conductance matrix fits the constraint.

Moreover, we have that

– $\mathrm{Ker}\mathbf{B}_\Gamma(x,x_a) = \{0\}$ if and only if $\mathrm{Ker}\mathbf{B}(x,x_a) = K(x)^{\mathrm{o}}$.

– $\mathbf{B}_\Gamma(x,x_a)$ is symmetric if and only if $\mathbf{B}(x,x_a)$ is symmetric,

– $\mathbf{B}_\Gamma(x,x_a)$ is positive semidefinite if and only if $\mathbf{B}(x,x_a)$ is positive semidefinite.

15.5 The dissipation inequalities

From now on we suppose that workings and transferrings are ideal.

Using the notations above, we can write the dissipation inequalities (see 14.1) in the form

$$(\mathbf{y}_i(x_i) - \mathbf{y}_k(x_i))\mathbf{R}_{ik}(x_i,x_k) \geq 0 \qquad (i,k = 0,1,\ldots,n),$$

where equality holds if and only if $\mathbf{R}_{ik}(x_i,x_k) = 0$ for all i and k, from which we infer that

$$\mathbf{F}(x,x_a)\mathbf{R}(x,x_a) \geq 0 \qquad (x \in X_D,\ x_a \in \mathrm{D}_a * \mathbb{R}^+), \tag{$*$}$$

where equality holds if and only if $\mathbf{R}(x,x_a) = 0$.

$\mathbf{R}(x,x_a)$ is in $K(x)$, so the inequality above implies

$$\mathbf{F}_\Gamma(x,x_a)\mathbf{R}(x,x_a) \geq 0 \qquad (x \in X_D, x_a \in \mathrm{D}_a * \mathbb{R}^+),$$

and according to item (iii) in Definition 15.3.3, here equality holds if and only if $\mathbf{F}_\Gamma(x,x_a) = 0$.

In the pseudolinear case we have

$$\mathbf{F}(x,x_a)\mathbf{B}(x,x_a)\mathbf{F}(x,x_a) \geq 0 \qquad (x \in X_D, x_a \in \mathrm{D}_a * \mathbb{R}^+)$$

and if the nominal conductance matrix fits the constraint,

$$\mathbf{F}_\Gamma(x,x_a)\mathbf{B}_\Gamma(x,x_a)\mathbf{F}_\Gamma(x,x_a) \geq 0 \qquad (x \in X_D, x_a \in \mathrm{D}_a * \mathbb{R}^+), \tag{$**$}$$

where equality holds if and only if $\mathbf{F}_\Gamma(x,x_a) = 0$.

Note that formula $(**)$ does not imply that $\mathbf{B}_\Gamma(x,x_a)$ is positive semidefinite; this would be right only if the inequality satisfied for all elements $v(x)$ of $K(x)^*$ instead of the single $\mathbf{F}_\Gamma(x,x_a)$.

15.6 Asymptotic stability of equilibrium

Now we suppose that the environment is constant and the bodies are entropic. The function

$$\mathbf{L} : X_D \to (\mathrm{J/K}), \qquad (E_1, V_1, N_1, \ldots, E_n, V_n, N_n) \mapsto$$
$$\mapsto \sum_{i=1}^{n} \left(\mathbf{S}_i(E_i, V_i, N_i) - \frac{E_i + P_a V_i - \mu_a N_i}{T_a} \right)$$

is, up to and additive constant, the total entropy of the bodies and the environment (see 12.2.4 and 13.2.4) which, by introducing the notation

$$y_a := \mathbf{y}_a(x_a) = \left(\frac{1}{T_a}, \frac{P_a}{T_a}, -\frac{\mu_a}{T_a} \right),$$

we can write in the form

$$\mathbf{L}(x) = \sum_{i=1}^{N} \big(\mathbf{S}_i(x_i) - (y_a | x_i) \big).$$

This function is twice continuously differentiable on X_R and its derivative is the nominal thermodynamical force, i.e.

$$\mathtt{D}\mathbf{L}(x) = \mathbf{F}(x, x_a)$$

for all $x \in X_R$. Moreover, $\mathtt{D}^2\mathbf{L}(x)$ is negative semidefinite whose kernel is spanned by the vectors

$$(x_1, 0, 0, \ldots, 0), \quad (0, x_2, 0, \ldots, 0), \quad \ldots \quad (0, 0, 0, \ldots, x_n)$$

(see 8.4).

Let U be a constraint submanifold in X_R. We recall that a state x_o in U is an equilibrium if and only if $\mathbf{F}_\Gamma(x_o, x_a) = 0$, i.e. on the basis of 15.3.3 $(*)$ if and only if $\mathtt{D}\mathbf{L}(x_o)|_{T_{x_o}(U)} = 0$.

Proposition *Let us list our restrictions:*

- *there are no sources,*
- *workings and transferrings are ideal,*
- *the state of the environment is constant,*
- *the bodies are entropic,*

and let us use the previous notations. Let U be a constraint submanifold in X_R and $x_o \in U$ an equilibrium. If

(i) Ker $\big(\mathtt{D}^2\mathbf{L}(x_o)\big) \cap T_{x_o}(U) = \{0\}$,

(ii) there is a twice continuously differentiable parameterization p of U in a neighbourhood of x_o such that $\mathtt{D}\mathbf{L}(x_o)\mathtt{D}^2 p(p^{-1}(x_o))$ is negative semidefinite,

then x_o is asymptotically stable in U.

Proof The function $\Lambda := \mathbf{L} \circ p$ is twice continuously differentiable and

$$\mathtt{D}\Lambda(\xi) = \mathtt{D}\mathbf{L}(p(\xi))\mathtt{D}p(\xi), \tag{$*$}$$

$$\mathtt{D}^2\Lambda(\xi) = \mathtt{D}^2\mathbf{L}(p(\xi)) \circ \big(\mathtt{D}p(\xi) \times \mathtt{D}p(\xi)\big) + \mathtt{D}\mathbf{L}(p(\xi))\mathtt{D}^2p(\xi) \tag{$**$}$$

for all $\xi \in \mathrm{Dom}p$.

Let $\xi_o := p^{-1}(x_o)$. The range of $\mathtt{D}p(\xi_o)$ equals $T_{x_o}(U)$, so on the base of $(*)$ we have $\mathtt{D}\Lambda(p^{-1}(x_o)) = 0$.

Condition (i) implies that $\mathtt{D}^2\mathbf{L}(x_o) \circ \big(\mathtt{D}p(\xi_o) \times \mathtt{D}p(\xi_o)\big)$ is negative definite, thus $\mathtt{D}^2\Lambda(\xi_o)$ is negative definite because of $(**)$ and condition (ii).

As a consequence, Λ has a strict local maximum at ξ_o which is equivalent to that $\mathbf{L}$ has a strict local conditional maximum at x_o with respect to U.

As concerns the derivative of $\mathbf{L}$ along the dynamical equation, we have

$$\overset{\bullet}{\mathbf{L}}(x) = \mathtt{D}\mathbf{L}(x)\mathrm{R}(x, x_a) = \mathbf{F}(x, x_a)\mathrm{R}(x, x_a).$$

As a consequence of the dissipation inequalities, $\overset{\bullet}{\mathbf{L}}$ takes zero values in equilibria and negative values elsewhere; thus, it has a strict local conditional minimum in x_o with respect to U.

As a result (see Appendix 7), x_o is asymptotically stable in U.

Remarks (i) It seems at first sight that our result is not well applicable because we have no general method to assure the existence of a parameterization with the desired properties. But we know its existence in two important special cases:

– if U is a subset of an affine space, then the parameterization can be an affine function whose second derivative is zero;

– if the nominal thermodynamical force takes zero value at x_o, i.e. $\mathtt{D}\mathbf{L}(x_o) = 0$, consequently any parameterization is suitable.

(ii) Recall that the tangent space $T_{x_o}(U)$ equals the constraint subspace $K(x_o)$.

15.7 Application to special systems

Let us survey the systems treated in 12 and 13 from the point of view of this chapter.

We ask the reader to describe precisely the constraint subspaces for every system and to show that the equilibrium is characterized by the zero value of the effective thermodynamical force (the restriction of the nominal thermodynamical force onto the constraint subspace).

We can ascertain immediately that the purely extensive constraints (in which only some energy and/or volume values are fixed) and of course the empty constraint are holonomic and the constraint submanifolds are affine surfaces, thus Proposition 15.6 can be applied. Such are the systems in 12.3, 12.4, 13.3, 13.4, 13.5, 13.7 and 13.8.

The purely intensive constraints (in which only temperature or pressure is fixed) are holonomic and the nominal thermodynamical force is zero in equilibrium, thus Proposition 15.6 can be applied. Such are the systems in 12.6, 12.7, 13.11 and 13.13.

Extensive and intensive constraints are mixed in 13.12; the constraint is holonomic and a good trick allows us to apply Proposition 15.6. Namely, the pressure of the environment does not appear in the dynamical equation. The pressure of both bodies takes the same value P_o in equilibrium. Formally we can consider that the pressure of the environment is just this value, $P_a := P_o$. Then the nominal thermodynamical force is zero in equilibrium.

The constraints concerning heat insulation are mostly anholonomic. An exception is when heat insulation is accompanied by fixed volume, because in this case heat insulation is given by energy conservation, thus we get a simple extensive constraint (13.5 and 13.8). Another exception is when heat insulation is accompanied by constant pressure (13.14); the constraint is holonomic and we can apply Proposition 15.6 by a trick similar to the previous one: the temperature of the environment does not appear in the dynamical law, so we can formally consider that it equals the common equilibrium temperature of the bodies, $T_a := T_o$. Then the nominal thermodynamical force is zero in equilibrium.

The constraints concerning heat insulation in 12.5, 13.6 and 13.9 are anholonomic but there are constraint submanifolds. For the system in 12.5 we can apply Proposition 15.6 by the trick $T_a := T_o$. The working in 13.6 cannot be ideal, so that system does not satisfy the conditions of Proposition 15.6 (another method were, however, successful in proving asymptotic stability). The second derivative of the actual parameterization given in 13.9, multiplied by the nominal thermodynamical force, is negative semidefinite, thus Proposition 15.6 can be applied.

The heat insulation in 13.10 is the most awkward constraint because it is not evident what are the constraint subspaces. If we suppose that the heatings are direct, i.e. $Q_{12} = -Q_{21}$ (which does not lead to a contradiction here), then the constraint subspaces are given by $\dot{E}_1 + P_1\dot{V}_1 + \dot{E}_2 + P_2\dot{V}_2 = 0$ and it is obvious that equilibrium is determined by the zero value of the effective thermodynamical force; consequently, the constraint is well described. The constraint, however, is anholonomic, and we could not find constraint submanifolds. We could not find a convenient method to prove asymptotic stability.

15.8 Strict asymptotic stability of equilibria

Equilibria in diffusions and phase transitions, in general, are not locally unique in the constraint subspaces which is well understandable from a physical point of view. Let us take a cylinder with a movable piston in the atmosphere and suppose air can diffuse into and from the cylinder. An equilibrium can exist when the cylinder is full of air or when it is half filled, etc. Similarly, at given temperature and pressure, five grammes of water and fifteen grammes of ice, as well as ten grammess of water and ten grammes of ice can be in equilibrium. In these cases an equilibrium cannot be asymptotically stable; trend to equilibrium is then expressed by the strict asymptotic stability of the set of equilibria: if an equilibrium is disturbed, another equilibrium is realized (near to the original one).

Proposition *Let us list our restrictions:*

- *there are no sources,*
- *workings and transferrings are ideal,*
- *the state of the environment is constant,*

– *the bodies are entropic,*

and let us use the previous notations. Let U be a constraint submanifold in X_R and let Eq be the set of equilibria in U. If

(i) the dynamical quantities are pseudolinear and the nominal conductance matrix fits the constraint,

(ii) $\mathbf{B}_\Gamma(x_o, x_a)$ is symmetric and positive definite for all $x_o \in Eq$,

(iii) Eq is a submanifold,

(iv) $\mathrm{Ker}\,\big(\mathtt{D}^2\mathbf{L}(x_o)\big) \cap T_{x_o}(U) = T_{x_o}(Eq)$ for all $x_o \in Eq$,

(v) there is a twice continuously differentiable parameterization p of U in a neighbourhood of all $x_o \in Eq$ such that $\mathtt{D}\mathbf{L}(x_o)\mathtt{D}^2p(p^{-1}(x_o))$ is negative semidefinite,

then Eq is strictly asymptotically stable in U.

Proof The dynamical equation has the form

$$(x : I \to U)? \qquad \dot{x} = \mathbf{B}_\Gamma(x, x_a)(\mathtt{D}\mathbf{L})_\Gamma(x)$$

and

$$Eq = \left\{ x \in U \;\middle|\; (\mathtt{D}\mathbf{L})_\Gamma(x) = 0 \right\}.$$

Let us fix an arbitrary element x_o of Eq and let p be a twice continuously differentiable parameterization of U in a neighborhood of x_o. The function $\Lambda := \mathbf{L} \circ p$ satisfies relations $(*)$ and $(**)$ in 15.6.

The dynamical equation, reduced according to the parameterization, reads

$$\dot{\xi} = \mathtt{D}p(\xi)^{-1}\mathbf{B}_\Gamma(p(\xi), x_a)(\mathtt{D}\mathbf{L})_\Gamma(p(\xi));$$

using $\mathtt{D}p(\xi)^*\mathtt{D}\mathbf{L}(p(\xi)) = \mathtt{D}\mathbf{L}(p(\xi))\mathtt{D}p(\xi) = \mathtt{D}\Lambda(\xi)$, we can rewrite it in the form

$$\dot{\xi} = \Psi(\xi)\mathtt{D}\Lambda(\xi),$$

where

$$\Psi(\xi) := \mathtt{D}p(\xi)^{-1}\mathbf{B}_\Gamma(p(\xi), x_a)(\mathtt{D}p(\xi)^*)^{-1}.$$

The reduced dynamical equation has the set of equilibria

$$\phi := \{\xi \in \mathrm{Dom}p \mid \mathtt{D}\Lambda(\xi) = 0\}.$$

Let $\xi_o := p^{-1}(x_o)$. We show that our conditions imply

$$T_{\xi_o}(\phi) = \mathrm{Ker}\mathtt{D}^2\Lambda(\xi_o).$$

Indeed, the relation $\subset$ follows from the above form of ϕ (and the well known properties of submanifolds). The relation $\supset$ can be verified as follows: if v is in the kernel of $\mathtt{D}^2\Lambda(\xi_o)$, then condition (v) yields that v is in the kernel of both terms on the right-hand side of $(**)$, thus $\mathtt{D}p(\xi_o)v$ – an element of $T_{p(\xi_o)}(U)$ – is in the kernel of $\mathtt{D}^2\mathbf{L}(x_o)$; as a consequence of condition (iv), $\mathtt{D}p(\xi_o)v \in T_{x_o}(Eq)$ or, equivalently, $v \in T_{\xi_o}(\phi)$.

The derivative at ξ_o of the right-hand side of the reduced dynamical equation is

$$\Psi(\xi_o)\mathtt{D}^2\Lambda(\xi_o).$$

According to condition (ii), $\Psi(\xi_o)$ is symmetric and positive definite and condition (v) implies that (the symmetric) $\mathtt{D}^2\Lambda(\xi_o)$ is negative semidefinite. Consequently, (see Appendix 1)

– the kernel of $\Psi(\xi_o)\mathtt{D}^2\Lambda(\xi_o)$ equals the kernel of $\mathtt{D}^2\Lambda(\xi_o)$ which is the tangent space of ϕ at ξ_o,

– the zero eigenvalue of $\Psi(\xi_o)\mathtt{D}^2\Lambda(\xi_o)$ has the same algebraic and geometric multiplicity,

– all the other eigenvalues are negative.

Therefore, the set of equilibria of the reduced dynamical equation is strictly asymptotically stable (see Appendix 7) and so the set of equilibria in U of the dynamical equation is strictly asymptotically stable in U.

Remarks (i) We can repeat the remarks in 15.6.

(ii) It is worth noting that the tangent space $T_{x_o}(U)$ equals the constraint subspace $K(x)$. Furthermore, condition (ii) of the proposition is equivalent to

(ii)' $\mathbf{B}(x_o, x_a)$ is symmetric, positive semidefinite and $\mathrm{Ker}\mathbf{B}(x_o, x_a) = K(x_o)^o$, i.e. the kernel of $\mathbf{B}(x_o, x_a)$ is spanned by $\{\gamma(x) \mid \gamma \in \Gamma\}$.

15.9 Entropy maximum and entropy production

If the conditions of Proposition 15.6 hold, then the total entropy of the bodies and the environment has a strict local maximum in equilibrium.

If the conditions of Proposition 15.8 hold, then the total entropy of the bodies and the environment has a strict local maximum on the set of equilibria (it has the same value in every equilibrium and has a smaller value outside the equilibria).

The time rate of the total entropy in the process $t \mapsto x(t)$ is

$$(\mathbf{L}\circ x)^{\cdot} = \mathtt{D}\mathbf{L}(x)\dot{x} = \mathtt{D}\mathbf{L}(x)\mathbf{R}(x, x_a) = \overset{\bullet}{\mathbf{L}}(x);$$

that is why the function $\overset{\bullet}{\mathbf{L}}$ is called the **entropy production**.

It follows from the dissipation inequalitythat the entropy production is non-negative: the total entropy cannot decrease in any process.

The entropy maximum in equilibrium and the non-negative entropy production are independent properties which together assure trend to equilibrium. The entropy maximum is a consequence of the intrinsic stability conditions (properties of materials), the non-negative entropy production is a consequence of the dissipation inequalities of the dynamical quantitities (properties of interactions between bodies).

15.10 Exercises

1. Suppose that the constraint subspaces are the same, i.e. there is a $K \subset X$ such that $K(x) = K$ for all x. Show that the constraint submanifolds are affine subspaces over K.

2. We can modify the definition of constraint as follows: we are given a finite dimensional vector space V and a $\Phi : X_D \to \mathrm{Lin}(X, V)$ continuous map such that $\Phi(x)$ is a surjection for all x. How to define then a holonomic constraint?

Demonstrate that the conditions $\gamma(x)\mathbf{B}(x, x_a) = 0$ and $\mathbf{B}(x, x_a)\gamma(x) = 0$ $(\gamma \in \Gamma)$ in 15.4.4 are expressed by $\Phi(x)\mathbf{B}(x, x_a) = 0$ and $\mathbf{B}(x, x_a)\Phi(x)^* = 0$.

3. Explain why the effective thermodynamical force

$$\frac{1}{T} - \frac{1}{T_a} + \frac{\alpha(P_\mathrm{o} - P_a)}{T_a}$$

cannot take zero value in an isobaric process with $P_\mathrm{o} \neq P_a$. (Hint: consider the dissipation inequality).

4. Can we apply Proposition 15.6 to the systems listed in Exercise 6 of 13.17?

5. Treat the processes of two bodies with constant particle number in which (besides other constraints, such as fixed volumes) the pressure of the bodies coincide at every instant.

6. Constraints with heat insulation for more than two bodies are very difficult. Try to treat a system consisting of four bodies with constant particle number in which the bodies together are heat insulated from the environment and the first and second body together are heat insulated from the third and fourth.

7. Generalize the formulae of the present chapter for non-zero sources.

16 Remarks on some usual notions

16.1 The Onsager theory

16.1.1 The effective thermodynamical force and conductance matrix in the case of affine constraints

The domain $K(x)^*$ (and the range $K(x)$) of the effective conductance matrix $\mathbf{B}_\Gamma(x, x_a)$ (if exists, i.e. the nominal conductance matrix fits the constraint) depends on x; therefore, the effective conductance matrix cannot be independent of x except when every $K(x)$ is the same.

A constraint is called **affine** if there is a linear subspace $K \subset X$ such that $K(x) = K$ for all x. Then every constraint subspace is an affine subspace over K (in other words, a translation of K).

Thus **the effective conductance matrix can be constant only if the constraint is affine**.

The affine constraints are interesting from another point of view, too.

Let us take an affine constraint and let the process x_a of the environment be constant. If x_o is an equilibrium, then with the notations $y_a := \mathbf{y}_a(x_a)$ and $y_a^n := (y_a, \ldots, y_a)$ we have

$$0 = F_\Gamma(x_\mathrm{o}, x_a) = \big(\mathbf{y}(x_\mathrm{o}) - y_a^n\big)|_K.$$

Consequently,

$$F_\Gamma(x, x_a) = \big(\mathbf{y}(x) - \mathbf{y}(x_\mathrm{o})\big)|_K,$$

for all possible x, i.e. **if the constraint is affine, the effective thermodynamical force is represented by the difference of the intensive quantities from their equilibrium values**. This is not true for non-affine constraints, because then $\big(\mathbf{y}(x_\mathrm{o}) - y_a^n\big)|_{K(x)} \neq 0$ may be for $x \neq x_\mathrm{o}$.

Recall that the restriction of the dynamical equation onto a constraint submanifold U has the form

$$(x : I \to U)? \qquad \dot{x} = \mathbf{B}_\Gamma(x, x_a)\mathbf{F}_\Gamma(x, x_a),$$

and the dissipation inequality reads

$$\mathbf{F}_\Gamma(x, x_a)\mathbf{B}_\Gamma(x, x_a)\mathbf{F}_\Gamma(x, x_a) \geq 0 \qquad\qquad (x \in U).$$

16.1.2 Survey of the usual Onsager formalism

It was mentioned in paragraph 6 of Preface that real, time varying processes ‘near to equilibrium’ appear in classical thermodynamics, too, treated by the Onsager theory.

Onsager’s formalism is based on the relations between ‘forces and currents’. The *forces* F_k $(k = 1, \dots, n)$ driving the processes are the differences of the intensive quantities, characterizing the possible interactions, from their equilibrium values. A *current* J_k is ‘conjugated’ to each force F_k in such a way that the entropy production has the form

$$\sigma := \sum_{k=1}^{n} F_k J_k \geq 0.$$

Then a linear relation is supposed among the forces and currents: there is matrix $(B_{ik} \mid i, k = 1, \dots, n)$ such that

$$J_i = \sum_{i=1}^{n} B_{ik} F_k \qquad (i = 1, \dots, n)$$

16.1.3 Precise meaning of the Onsager formalism

The Onsager forces are “the differences of the intensive quantities, characterizing the possible interactions, from their equilibrium values". In the case of affine constraints, this is just the effective thermodynamical force. Let us consider now an affine constraint.

Let us take an affine coordinatization of a constraint submanifold U (which gives a linear coordinatization of K and K^*), let F_k and B_{ik} $(i, k = 1, \dots, n)$ denote the components of the effective thermodynamical force and the effective conductance matrix, respectively, corresponding to the coordinatization and put

$$J_i := \sum_{k=1}^{n} B_{ik} F_k \qquad (i = 1 \dots, n).$$

Then the dynamical equation becomes

$$\dot{\xi}_i = J_i(\xi) \qquad (i = 1, \dots, n)$$

and the dissipation inequality

$$\sum_{k=1}^{n} F_k(\xi) J_k(\xi) \geq 0.$$

Recall that for entropic bodies the quantity on the left-hand side above is the entropy production. We obtained the Onsager formalism in a clear setting, without the doubtful requirement 'near to equilibrium'. In the usual formalism one assumes further that the matrix B is constant (i.e. $B_{ik}(\xi)$ is the same for all ξ) and symmetric (i.e. $B_{ik} = B_{ki}$), which corresponds to a constant and symmetric $\mathbf{B}_\Gamma$.

Now we get a precise answer what and how is approximated by the Onsager theory.

Let us suppose that the constraint is affine and the effective conductance matrix exists and let us consider an equilibrium x_o. Then, for x-s in a neighborhood of x_o, the effective conductance matrix $\mathbf{B}_\Gamma(x, x_a)$ can be approximated by its equilibrium value $\mathbf{B}_\Gamma(x_\mathrm{o}, x_a)$, so

$$(x : I \to U)? \qquad \dot{x} = \mathbf{B}_\Gamma(x_\mathrm{o}, x_a)\mathbf{F}_\Gamma(x, x_a).$$

is an approximation of the dynamical equation on a constraint submanifold U whose affine coordinatization gives the usual Onsager equations.

If the constraint is not affine, however, then the effective thermodynamical force is not the difference of the intensive quantities from their equilibrium values, and $\mathbf{B}_\Gamma(x, x_a)$ cannot be replaced by $\mathbf{B}_\Gamma(x_\mathrm{o}, x_a)$ because their domains and ranges are different. In this case the usual Onsager formalism does not work. For instance, the isothermal or isobaric processes cannot be placed into the usual framework of Onsager formalism.

Therefore we can say that a generalized and clear setting of the Onsager theory is the treatise of systems for which the dynamical quantitities are pseudolinear functions of the thermodynamical forces and the effective conductance matrixexists (the nominal conductance matrix fits the constraint).

16.2 The Prigogine principle

16.2.1 Special stationary states

The following problem is of great practical importance: how to operate a heat source in a body in order to keep its temperature constant?

Let us take a body with constant volume V_o in a constant environment with temperature and pressure (T_a, P_a), and let us operate a heat source in the body, depending on the instantaneous state of the body in such a way that the temperature of the body remain constant T_o and different from T_a. Particle transport (diffusion) may occur between the body and the environment (having the same material).

Let $\mathcal{Q}$ be the heating of the body, $\mathcal{G}$ the converting, and $\mathcal{Q}_s$ the heat source (which is now a function of the state of the body). Since V_o is fixed, the temperature and the particle numberdefines the state of the body, and the dynamical equations are

$$\frac{\partial \mathcal{E}}{\partial T}\dot{T} = \mathcal{Q}_s + \mathcal{Q} + \mu\mathcal{G}$$

and

$$\dot{N} = \mathcal{G}.$$

If T_o and N_o are the temperatureand the particle number in a stationary state, then

$$\mathcal{G}(V_o,T_o,N_o)=0, \qquad \mathcal{Q}_s(V_o,T_o,N_o)+\mathcal{Q}(V_o,T_o,N_o)=0.$$

For instance, if the dynamical quantities are pseudolinear,

$$\mathcal{Q}(V,T,N)=-\lambda_Q(T-T_a)-\vartheta_Q(\mu(V,T,N)-\mu_a),$$

$$\mathcal{G}(V,T,N)=-\lambda_G(T-T_a)-\vartheta_G(\mu(V,T,N)-\mu_a)$$

where λ_Q, ϑ_Q, $\lambda_Q G$ and ϑ_G are positive constants, then for given T_o the stationary particle numberN_o is determined by

$$\mu(V_o,T_o,N_o)-\mu_a=-\frac{\lambda_G}{\vartheta_G}(T_o-T_a).$$

Since (with the usual ambiguous notation) $\mu(V,T,N)=\mu\left(\frac{V}{N},T\right)$ and so $\frac{\partial\mu}{\partial N}=-\frac{v}{N}\frac{\partial\mu}{\partial v}$, for entropic materials (see the Gibbs–Duhem relations) the chemical potential is locally strictly increasing function of the particle number. As a consequence, the stationary particle numberis locally uniquely determined.

Then the stationary heat source becomes

$$\mathcal{Q}_s(V_o,T_o,N_o)=\left(\lambda_Q-\frac{\lambda_G}{\vartheta_G}\vartheta_Q\right)(T_o-T_a)).$$

16.2.2 Minimal entropy production

As a generalization of the previous example, let us take a system with affine constraint and let the effective conductance matrix be constant. Let us suppose that the constraint subspace has the form $K=K_1\times K_2$; correspondingly, a constraint submanifold (an affine subspace) has the form $U=U_1\times U_2$. Moreover, $K^*=K_1^*\times K_2^*$, therefore, $\mathbf{F}_\Gamma=(F_1,F_2)$. Let a source $J:U\to K_1$ be given in such a way that the value of F_1 remains the same constant F_{1o}:

$$\begin{aligned}\dot{x}_1&=B_{11}F_{1o}+B_{12}F_2(x_1,x_2)+J(x_1,x_2),\\ \dot{x}_2&=B_{21}F_{1o}+B_{22}F_2(x_1,x_2).\end{aligned}$$

This is right if the linear map $\mathtt{D}_1F_1(x_1,x_2):K_1\to K_1^*$ is injective for all $(x_1,x_2)\in U$. Indeed, then the relation $\mathtt{D}_1F_1(x_1,x_2)\dot{x}_1+\mathtt{D}_2F_1(x_1,x_2)\dot{x}_2=0$ (which expresses that F_1 is constant) allows us to determine the source:

$$\begin{aligned}-J(x_1,x_2)=\Big(&B_{11}F_{1o}+B_{12}F_2(x_1,x_2)+\\ &+\mathtt{D}_1F_1(x_1,x_2)^{-1}\mathtt{D}_2F_1(x_1,x_2)\big(B_{21}F_{1o}+B_{22}F_2(x_1,x_2)\big)\Big).\end{aligned}$$

Moreover, the condition that $\mathtt{D}_1F_1(x_1,x_2)$ be injective, yields that x_1 can be given, at least locally, as a function of x_2; let ζ_1 be this function, i.e.

$F_1(\zeta_1(x_2), x_2) = F_{1\mathrm{o}}$. This reduces the dynamical equation to its second member.

If $x_{2\mathrm{o}}$ is a stationary state, then

$$\begin{aligned} &B_{21}F_{1\mathrm{o}} + B_{22}F_2(\zeta_1(x_{2\mathrm{o}}), x_{2\mathrm{o}}) =0,\\ &B_{11}F_{1\mathrm{o}} + B_{12}F_2(\zeta_1(x_{2\mathrm{o}}), x_{2\mathrm{o}}) = -\, J(\zeta_1(x_{2\mathrm{o}}), x_{2\mathrm{o}}). \end{aligned}$$

The entropy production for an entropic body is the quantity

$$\begin{aligned} x_2 \mapsto F_{1\mathrm{o}}B_{11}F_{1\mathrm{o}} + F_{1\mathrm{o}}B_{12}F_2(\zeta_1(x_2), x_2) + F_2(\zeta_1(x_2), x_2)B_{21}F_{10} + \\ + F_2(\zeta_1(x_2), x_2)B_{22}F_2(\zeta_1(x_2), x_2) =: \sigma(x_2) \end{aligned}$$

appearing in the dissipation inequality.

It is an easy task to show that if $B_{12} = B_{21}$ (the conductance matrix is symmetric), then

$$\begin{aligned} \mathtt{D}\sigma(x_2) &= 2F_2'(\zeta(x_2), x_2)\big(B_{21}F_{1\mathrm{o}} + B_{22}F_2(\zeta_1(x_2), x_2)\big),\\ \mathtt{D}^2\sigma(x_2) &= 2F_2''(\zeta(x_2), x_2)\big(B_{21}F_{1\mathrm{o}} + B_{22}F_2(\zeta_1(x_2), x_2)\big) + \\ &\quad + 2F_2'(\zeta_1(x_2), x_2)B_{22}F_2'(\zeta_1(x_2), x_2), \end{aligned}$$

where F_2' and F_2'' are first and second derivative, respectively, of the function $x_2 \mapsto F_2(\zeta_1(x_2), x_2)$.

Thus

$$\mathtt{D}\sigma(x_{2\mathrm{o}}) = 0, \qquad \mathtt{D}^2\sigma(x_{2\mathrm{o}}) = 2F_2'(\zeta_1(x_{2\mathrm{o}}), x_{2\mathrm{o}})B_{22}F_2'(\zeta_1(x_{2\mathrm{o}}), x_{2\mathrm{o}})$$

in the stationary state $x_{2\mathrm{o}}$. According to the dissipation inequality, B and so B_{22} are positive definite; consequently, if $F_2'(\zeta_1(x_{2\mathrm{o}}), x_{2\mathrm{o}}) : K_2 \to K_2^*$ is injective, then $\mathtt{D}^2\sigma(x_{2\mathrm{o}})$ is positive definite. This means that the entropy production σ has a minimum in the stationary state which is called the Prigogine principle.

We emphasize that the Prigogine principle is valid only in rather restricted circumstances: the constraint subspaces are the same (the constraint submanifolds are affine subspaces), the effective conductance matrix is constant, some conditions are imposed on certain derivatives of the thermodynamical forces.

16.3 Some thermodynamical aspects of interactions

16.3.1 The energy equation

So far we have taken into account thermal interaction, mechanical interaction (volume change) and material interaction (particle number change) but all other interactions have thermodynamical aspects: the internal energy changes in the course of any interaction (e.g. a body conducting the electric current, a body under a light beam gets warm).

The thermodynamical aspects of interactions between two bodies seem well described by the following rule:

1. Every interaction is characterized by an extensive quantity and an intensive one (e.g. the extensive quantities of electricity are the electric charge and the

dipole, and the corresponding intensive quantities are the electric potential and field, respectively), and the intensive quantities can be given as functions of the extensive ones;

2. Every interaction gives a term (a dynamical quantity) in the first law (describing the change of internal energy).

Now let us suppose that m additional interactions can occur between two bodies. Let X_i and Y_i denote formally the corresponding extensive and intensive quantities ($i = 1, \dots, m$). Then Y_i is a function of the extensive quantities, i.e.

$$Y_i = \mathcal{Y}_i(V, T, N, X_1, \dots, X_m).$$

We introduce

$$s(i) := \operatorname{sign}\left(\frac{\partial \mathcal{Y}_i}{\partial X_i}\right).$$

The dynamical quantity corresponding to the i-th interaction is called ideal if can be formally written as

$$s(i) Y_i \dot{X}_i.$$

16.3.2 Energy dissipation

A member of the thermodynamical force corresponding to an interaction is the difference of the corresponding intensive quantities of the bodies:

$$-s(i)(Y_i - (Y_*)_i,$$

where the notation introduced in Section 10.1 is used.

Every interaction gives a term in the dissipation inequality which is

$$-s(i)(Y_i - (Y_*)_i)\dot{X}_i$$

in the case of ideal interaction.

16.3.3 Interactions and entropy

The entropic property (and the first law, see 9.4) for a body is usually formulated by ‘differentials’:

$$\mathtt{d}E = T\mathtt{d}S - P\mathtt{d}V + \mu\mathtt{d}N + \sum_{i=1}^{m} s(i) Y_i \mathtt{d}X_i.$$

Expressing the real meaning of the differentials, we get the following rule for the entropic property:

$$T\frac{\partial \mathcal{S}}{\partial X_i} = \frac{\partial \mathcal{E}}{\partial X_i} - s(i)\mathcal{Y}_i \qquad (i = 1, \dots, m).$$

If $(E, V, N, X_1, \dots, X_m)$ are taken to be the independent variables, then – with obvious notations –

$$\frac{\partial \mathbf{S}}{\partial X_i} = -s(i)\frac{\mathbf{Y}_i}{\mathbf{T}}.$$

We shall see that such relations regarding entropy are doubtful in connection with electromagnetism.

16.4 Entropy and intrinsic stability

Though the entropic property is doubtful in general, it works well for composite materials; therefore, it is worth examining the second derivative of the entropy whose definiteness is strongly related to asymptotic stability. The second derivative of the total entropy as a function of the canonical variables is negative semidefinite and the second derivative of the specific entropy is negative definite. This latter one can be conceived as a multiple of the derivative of the total entropy with constant particle number.

We shall see that specific quantities cannot be defined in connection with electromagnetism. Therefore, *we examine now the total entropy with fixed particle number*. Our results remain valid for specific quantities if they exist.

Let us proceed as follows.

Let $I_0 := (\mathrm{m}^3)$, $X_0 := V$ and let I_i be a measure line whose elements are denoted by X_i $(i = 1, \dots, m)$; let us introduce $X := (X_0, \dots, X_m)$.

Let

$$(\mathrm{K})^+ \times \mathop{\mathsf{X}}_{i=0}^{m} I_i \rightarrowtail (\mathrm{J}), \quad (T, X) \mapsto \mathcal{E}(T, X),$$
$$(\mathrm{K})^+ \times \mathop{\mathsf{X}}_{i=0}^{m} I_i \rightarrowtail (\mathrm{J/K}), \quad (T, X) \mapsto \mathcal{S}(T, X)$$

be the internal energy and the entropy, respectively, as functions of temperature and the given extensive quantities (with fixed particle number).

Then the canonical variables are (E, X), $(E, X) \mapsto \mathbf{T}(E, X)$ is the temperature function and $\mathbf{S}(E, X) = \mathcal{S}(\mathbf{T}(E, X), X)$ is the entropy.

Let

$$\mathcal{K}_i : (\mathrm{K})^+ \times \mathop{\mathsf{X}}_{i=0}^{m} I_i \rightarrowtail (\mathrm{J})/I_k \quad (i = 1, \dots, m)$$

be quantities for which

$$T \frac{\partial \mathcal{S}}{\partial X_i} = \frac{\partial \mathcal{E}}{\partial X_i} - \mathcal{K}_i$$

is satisfied (this corresponds to the previous $s(i)\mathcal{Y}_i$); then in the canonical variables

$$\frac{\partial \mathbf{S}}{\partial E} = \frac{1}{\mathbf{T}}, \quad \frac{\partial \mathbf{S}}{\partial X_i} = -\frac{\mathbf{K}_i}{\mathbf{T}}, \quad (i = 0, \dots, m), \qquad (*)$$

where $\mathbf{K}_i(E, X) := \mathcal{K}_i(\mathbf{T}(E, X), X)$ and, of course, $\mathcal{K}_i(T, X) = \mathbf{K}_i(\mathcal{E}(T, X), X)$.

According to the well known formulae regarding the partial derivatives,

$$
\begin{aligned}
\frac{\partial \mathcal{K}_i}{\partial X_k}\bullet =&\frac{\partial \mathbf{K}_i}{\partial X_k} + \left(\frac{\partial \mathbf{K}_i}{\partial E}\right)\frac{\partial \mathcal{E}}{\partial X_k}\bullet \\
=&\frac{\partial \mathbf{K}_i}{\partial X_k} + \left(-\frac{\partial \mathbf{T}}{\partial E}\frac{\partial \mathbf{S}}{\partial X_i} - \mathbf{T}\frac{\partial^2 \mathbf{S}}{\partial E \partial X_i}\right)\frac{\partial \mathcal{E}}{\partial X_i}\bullet \\
=&\frac{\partial \mathbf{K}_i}{\partial X_k} + \left(\frac{\partial \mathbf{T}}{\partial E}\frac{\mathbf{K}_i}{\mathbf{T}} + \frac{1}{\mathbf{T}}\frac{\partial \mathbf{T}}{\partial X_i}\right)\frac{\partial \mathcal{E}}{\partial X_k}\bullet \\
=&\frac{\partial \mathbf{K}_i}{\partial X_k} - \frac{\mathbf{K}_k}{\mathbf{T}}\frac{\partial \mathbf{T}}{\partial X_k} - \frac{1}{\mathbf{T}\frac{\partial \mathbf{T}}{\partial E}}\frac{\partial \mathbf{T}}{\partial X_k}\frac{\partial \mathbf{T}}{\partial X_i} \\
=&-\frac{\mathbf{T}\partial^2 \mathbf{S}}{\partial X_k \partial X_i} - \frac{1}{\mathbf{T}\frac{\partial \mathbf{T}}{\partial E}}\frac{\partial \mathbf{T}}{\partial X_k}\frac{\partial \mathbf{T}}{\partial X_i}.
\end{aligned}
$$

A rearranging gives

$$
\frac{\partial^2 \mathbf{S}}{\partial X_k \partial X_i} = -\frac{1}{\mathbf{T}^2}\left(\frac{1}{\frac{\partial \mathbf{T}}{\partial E}}\frac{\partial \mathbf{T}}{\partial X_k}\frac{\partial \mathbf{T}}{\partial X_i} + \mathbf{T}\frac{\partial \mathcal{K}_i}{\partial X_k}\bullet\right),
$$

from which it follows that if

$$
\left(\frac{\partial \mathcal{K}_i}{\partial X_k} \mid i,k = 0,\dots,m\right) \tag{$**$}
$$

is positive definite, then

$$
\left(\frac{\partial^2 \mathbf{S}}{\partial X_k \partial X_i}\ \middle|\ i,k = 0,\dots,m\right)
$$

is negative definite.

Proposition *If the equalities* $(*)$ *are fulfilled for the total entropy* $\mathbf{S}$ *as a function of the canonical variables and the matrix* $(**)$ *is positive definite, then*

$$
\mathtt{D}^2\mathbf{S} = -\frac{1}{\mathbf{T}^2}\begin{pmatrix} \frac{\partial \mathbf{T}}{\partial E} & \frac{\partial \mathbf{T}}{\partial X_i} \\ \\ \frac{\partial \mathbf{T}}{\partial X_k} & \frac{1}{\frac{\partial \mathbf{T}}{\partial E}}\frac{\partial \mathbf{T}}{\partial X_k}\frac{\partial \mathbf{T}}{\partial X_i} + \mathbf{T}\frac{\partial \mathcal{K}_i}{\partial X_k}\bullet \end{pmatrix}_{i,k=0,\dots,m}
$$

is negative definite.

Proof Our condition implies that the right bottom block in the parentheses is positive definite; we have to show only that the determinant of the matrix is positive. Multiplying the first row by $\frac{1}{\frac{\partial \mathbf{T}}{\partial E}}\frac{\partial \mathbf{T}}{\partial X_k}$ and then subtracting it from the k-th row ($k = 0,\dots,m$), we get the matrix

$$
\begin{pmatrix} \frac{\partial \mathbf{T}}{\partial E} & \frac{\partial \mathbf{T}}{\partial X_i} \\ \\ 0 & \mathbf{T}\frac{\partial \mathcal{K}_i}{\partial X_k}\bullet \end{pmatrix}_{i,k=0,\dots,m}
$$

whose determinant is evidently positive. ☐

We repeat: our statement refers to the total entropy with constant particle number (the particle number is not a variable), which is reflected in the positive definiteness of the matrix $(**)$. If the particle number is considered a variable, too, then the second derivative of the total entropy is negative semidefinite.

16.5 Exercises

1. Use the notations of 16.2.1 and let N_1 be the particle number for which $\mathcal{P}(V_o/N_1, T_a) = P_a$ holds. What is the relation between N_1 and N_o?

2. Give an explicit form of $F_2'(\zeta_1(x_2), x_2)$ by the partial derivatives of F_1 and F_2 (see 16.2.2).

3. Examine in diverse simple systems: is the condition imposed on the derivative of the thermodynamical forces in the deduction of the Prigogine principle satisfied?

V SIMPLE SYSTEMS WITH PARTICLE INTERCHANGE

17 On diffusions and phase transitions

In this chapter we deal with systems in which the bodies can interchange particles; all the bodies and the environment are supposed to consist of the same material. The interchange of particle between two bodies is diffusion if the phases of the bodies coincide and is phase transition if the phases are different.

Sections 12 and 13 indicate that the more complex the system, the stronger conditions assure trend to equilibrium (asymptotic stability). Entropic property of bodies is sufficient, in general, as we have seen in Section 15.

At present we can deduce convenient results for diffusions and phase transitions only for entropic bodies and pseudolinear dynamical quantitities according to Propositions 15.6 and 15.8.

The constraint imposed on diffusions and phase transitions can be more general than the earlier ones which are of 'equality type'. Here constraints of 'inequality type' can appear in a natural way: semipermeable walls are described by non-positive or non-negative convertings. Such a problem will be treated in Section 18.7.

18 Diffusion between a body and an environment

18.1 General formulae

18.1.1 The framework of description

We examine a system consisting of a body and a given environment of the same material. The processes of the body are supposed to run in the phase coinciding with that of the environment, and diffusion can occur between the body and the environment.

Workings and transferrings are supposed to be ideal.

According to Definition 14.1, this system is described as follows.

1. There are a given body and an environment of the same material $(\mathrm{D}, \mathbf{T}, \mathbf{P}, \boldsymbol{\mu}, \mathrm{R})$.

2. There are the given heating $\mathbf{Q}$, the springing $\mathbf{F}$, the converting $\mathbf{G} \neq 0$ defined on $(\mathrm{D} * \mathbb{R}_0^+) \times (\mathrm{D} * \mathbb{R}_0^+)$; these dynamical quantitities are continuous and continuously differentiable on the interior of their domain.

The following notations will be used later on:

$$T := \mathbf{T}(E,V,N), \qquad T_a := \mathbf{T}(E_a,V_a,N_a),$$

$$P := \mathbf{P}(E,V,N), \qquad P_a := \mathbf{P}(E_a,V_a,N_a),$$

$$\mu := \boldsymbol{\mu}(E,V,N), \qquad \mu_a := \boldsymbol{\mu}(E_a,V_a,N_a),$$

and

$$Q := \mathbf{Q}(E,V,N,E_a,V_a,N_a),$$

$$F := \mathbf{F}(E,V,N,E_a,V_a,N_a),$$

$$G := \mathbf{G}(E,V,N,E_a,V_a,N_a).$$

Then the dynamical quantitities satisfy
– the equilibrium property
(I) if $N = 0$ then they have zero value,
(II) for $N \neq 0$:
if **G** can have both positive and negative values
(a) if $\mathbf{F} = 0$ and $\mathbf{Q} = 0$, then
$*$ $G = 0$ if and only if $\mu = \mu_a$,
(b) if $\mathbf{F} = 0$ and $\mathbf{Q} \neq 0$, then
$*$ $G = 0$ implies $\mu = \mu_a$,
$*$ $\mu = \mu_a$ and $Q = 0$ imply $T = T_a$,
$*\,*$ $T = T_a$ and $\mu = \mu_a$ imply $G = 0$ and $Q = 0$,
(c) if $\mathbf{F} \neq 0$ and $\mathbf{Q} = 0$, then
$*$ $G = 0$ implies $\mu = \mu_a$,
$*$ $\mu = \mu_a$ and $F = 0$ imply $P = P_a$,
$*\,*$ $P = P_a$ and $\mu = \mu_a$ imply $F = 0$ and $G = 0$,
(d) if $\mathbf{F} \neq 0$ and $\mathbf{Q} \neq 0$, then
$*$ $G = 0$ implies $\mu = \mu_a$,
$*$ $\mu = \mu_a$ and $F = 0$ imply $P = P_a$,
$*$ $\mu = \mu_a$, $P = P_a$ and $Q = 0$ imply $T = T_a$,
$*\,*\,*$ $T = T_a$, $P = P_a$ and $\mu = \mu_a$ imply $Q = 0$, $F = 0$ and $G = 0$,
– the dissipation inequality

$$-\frac{Q}{T}(T - T_a) + F(P - P_a) - G(\mu - \mu_a) \geq 0,$$

or, equivalently,

$$\big(Q - PF + \mu G)\big)\left(\frac{1}{T} - \frac{1}{T_a}\right) + F\left(\frac{P}{T} - \frac{P_a}{T_a}\right) - G\left(\frac{\mu}{T} - \frac{\mu_a}{T_a}\right) \geq 0.$$

3. There is a given phase Z of the material and a process $t \mapsto (E_a(t), V_a(t), N_a) \in \mathrm{Z} * \mathbb{R}^+$ of the environment which is a continuous function defined on a time interval.

4. There are the given heat source $t \mapsto Q_s(t)$ and the particle source $t \mapsto G_s(t)$ which are continuous functions defined on a time interval.

5. The process $t \mapsto \big(E(t), V(t), N(t)\big) \in \mathrm{Z} * \mathbb{R}_0^+$ of the body is determined by the dynamical equation

$$\begin{aligned} \dot{E} &= Q_s + \mu G_s + Q - PF + \mu G, \\ \dot{V} &= F, \\ \dot{N} &= G_s + G, \end{aligned}$$

where $Q := \mathbf{Q}(E, V, N, E_a, V_a, N_a)$, etc.

18.1.2 Other variables

(i) The formulae will often be simplified by the use of the specific quantities $e := \dfrac{E}{N}$ and $v := \dfrac{V}{N}$.

(ii) It is convenient to characterize the environment by its temperature and pressure, therefore we apply the convention in 12.2.2.

(iii) Sometimes temperature is used as a variable instead of internal energy. Then the notations $\mathcal{Q}(V, T, N, T_a, P_a)$ etc. are applied and the dynamical equation has the form

$$\begin{aligned} N\mathfrak{c}_v\dot{T} &= Q_s + \mu G_s + Q - \left(P + \frac{\partial \mathfrak{e}}{\partial v}\right) F + \mu G, \\ \dot{V} &= F, \\ \dot{N} &= G_s + G, \end{aligned}$$

where $Q := \mathcal{Q}(V, T, N, T_a, P_a)$, etc.

18.1.3 Pseudolinear dynamical quantitities

We mostly consider pseudolinear dynamical quantitities when the right hand side of the dynamical equation is written as the product of the conductance matrix and the thermodynamical force in the known form:

$$\begin{pmatrix} \lambda_A & \beta_A & \vartheta_A \\ \lambda_F & \beta_F & \vartheta_F \\ \lambda_G & \beta_G & \vartheta_G \end{pmatrix} \begin{pmatrix} \frac{1}{T} - \frac{1}{T_a} \\ \frac{P}{T} - \frac{P_a}{T_a} \\ -\frac{\mu}{T} + \frac{\mu_a}{T_a} \end{pmatrix}$$

where the matrix entries are functions of (E, V, N, T_a, P_a) and, of course, $T = \mathbf{T}(E, V, N)$ etc.

Only a single body is in the system, therefore the above quantities are the nominal conductance matrix and the nominal thermodynamical force.

18.1.4 Equilibrium

In the sequel

– the process of the environment is supposed to be constant,

$$T_a = \text{const.} \qquad P_a = \text{const.};$$

then, of course, μ_a is also constant;

– we take zero sources:

$$Q_s = 0, \qquad G_s = 0;$$

then every standstill is an equilibrium;

– we consider processes in which the particle number is not zero (the state with zero particle number is an equilibrium, because all the dynamical quantitities take zero value there).

Because the processes of the body run in the same phase in which the state of the environment is, if both the temperature and the pressure of the body and the environment coincide, their chemical potentials, too, have the same value.

The symbols e_o and v_o will denote the (uniquely determined) values of specific internal energy and specific volume, respectively, for which

$$\mathbf{T}(e_o, v_o) = T_a, \qquad \mathbf{P}(e_o, v_o) = P_a$$

hold.

18.1.5 Entropic body

The total entropy of the body and the environment equals – up to an additive constant –

$$(E, V, N) \mapsto \mathbf{L}(E, V, N) := \mathbf{S}(E, V, N) - \frac{E + P_a V - \mu_a N}{T_a}.$$

If the body is entropic, the nominal thermodynamical force is the derivative of $\mathbf{L}$:

$$\left(\frac{1}{T} - \frac{1}{T_a}, \frac{P}{T} - \frac{P_a}{T_a}, -\frac{\mu}{T} + \frac{\mu_a}{T_a}\right),$$

where $T := \mathbf{T}(E, V, N)$ etc.

Furthermore, $\mathtt{D}^2\mathbf{L}(E, V, N) = \mathtt{D}^2\mathbf{S}(E, V, N)$ is negative semidefinite, its kernel is spanned by (E, V, N).

18.2 Processes without constraint

18.2.1 The set of equilibria

Let the body and the environment be in thermal, mechanical and material interaction. Then an equilibrium is determined by the fact that the temperature and the pressure of the body equal those of the environment. There is no condition imposed on the particle number of the body, therefore with the notation of 18.1.4:

Proposition *The set of equilibria with non-zero particle number is*

$$Eq := \{N(e_o, v_o, 1) \mid N \in \mathbb{R}^+\}.$$

The equilibrium is not unique even locally; the set of equilibria is a half line: a submanifold whose tangent space at every point is spanned by $(e_o, v_o, 1)$.

18.2.2 Stability of equilibria

Proposition *If the body is entropic and the nominal conductance matrix in 18.1.3 takes symmetric and positive definite values in equilibria, then the set of equilibria is strictly asymptotically stable.*

Proof The tangent space of Eq at every point (Ne_o, Nv_o, N) equals the kernel of $\mathtt{D}^2\mathbf{L}(Ne_o, Nv_o, N)$. The constraint is void, therefore all the conditions of Proposition 15.8 are fulfilled. □

Let us imagine that the body consists of air in a completely (infinitely) deformable tyre which is in the atmosphere. Then an arbitrary amount of air inside can be in equilibrium in which the air inside has the same temperature and pressure as the atmosphere. If the air inside is hot and compressed, then molecules diffuse from the body into the atmosphere, the body cools and expands until it reaches an equilibrium. If we disturb such an equilibrium – e.g. we press the tyre a little – then a process starts and a new equilibrium is reached in which the amount of air inside will differ from the previous equilibrium amount.

18.3 Fixed volume

18.3.1 Uniqueness of equilibrium

Let us fix the volume of the body: the body and the environment are only in thermal and material interaction. Springing is zero, $\mathbf{F} = 0$; this defines a holonomic constraint:

$$\dot{V} = 0.$$

Referring to the notations of Section 15.3.3, we have now $\Gamma = \{(0,1,0)\}$. The two-dimensional constraint subspaces are spanned by the vectors $(1,0,0)$ and $(0,0,1)$ (the constraint subspace is the same at every point, the constraint is affine).

The effective thermodynamical force is

$$\left(\frac{1}{T} - \frac{1}{T_a}, -\frac{\mu}{T} + \frac{\mu_a}{T_a}\right).$$

For all $V_o \in (\mathrm{m}^3)$,

$$U(V_o) := \{(E, V_o, N) \in \mathrm{Z} \mid E \in (\mathrm{J}), N \in \mathbb{R}^+\}$$

is a constraint submanifold of the dynamical equation.

In an equilibrium, the temperature and the chemical potential of the body equal those of the environment; there is no condition imposed on the pressures. The function $\mu(T_a, \cdot)$ is locally injective by the Gibbs–Duhem relation, therefore the only equilibrium pressure in a neighbourhood of P_a is just P_a.

Proposition *If* (e_o, v_o) *is defined by 18.1.4, then with the notation*

$$N_o := \frac{V_o}{v_o}$$

the equilibrium

$$N_o(e_o, v_o, 1) \tag{$*$}$$

is locally unique in $U(V_o)$.

18.3.2 Stability of the equilibrium

Proposition *If the body is entropic, then for arbitrary* V_o *the equilibrium* $(*)$ *is asymptotically stable in* $U(V_o)$ *(even if the dynamical quantitities are not pseudolinear).*

Proof The subspace spanned by the vectors $(1,0,0)$ and $(0,0,1)$ meets the kernel of $\mathtt{D}^2\mathbf{L}(N_o(e_o,v_o,1))$ in the zero, so Proposition 15.6 can be applied.

18.4 Constant temperature

18.4.1 The constraint

Let us examine the diffusion processes in which the temperature of the body is constant, equals that of the environment. It is not obvious how to assure the constant temperature; we refer to 12.12.

The present constraint is holonomic:

$$\frac{\partial \mathbf{T}}{\partial E}\dot{E} + \frac{\partial \mathbf{T}}{\partial V}\dot{V} + \frac{\partial \mathbf{T}}{\partial N}\dot{N} = 0.$$

Using 8.3 $(*)$, we can rewrite this equality in the form

$$\frac{\partial \mathbf{T}}{\partial e}\dot{E} + \frac{\partial \mathbf{T}}{\partial v}\dot{V} - \left(e\frac{\partial \mathbf{T}}{\partial e} + v\frac{\partial \mathbf{T}}{\partial v}\right)\dot{N} = 0.$$

Referring to the notations of Section 15.3.3, we have now

$$\Gamma = \left\{\left(\frac{\partial \mathbf{T}}{\partial e}, \frac{\partial \mathbf{T}}{\partial v}, -e\frac{\partial \mathbf{T}}{\partial e} - v\frac{\partial \mathbf{T}}{\partial v}\right)\right\}.$$

The two-dimensional constraint subspaces are spanned by the vectors $\left(-\frac{\partial \mathbf{T}}{\partial v}, \frac{\partial \mathbf{T}}{\partial e}, 0\right)$ and $\left(e\frac{\partial \mathbf{T}}{\partial e} + v\frac{\partial \mathbf{T}}{\partial v}, 0, \frac{\partial \mathbf{T}}{\partial e}\right)$.

18.4.2 The effective thermodynamical force and conductance matrix

Because of $T = T_a$, we easily get that the effective thermodynamical force is

$$\frac{1}{T_a}(P - P_a, -\mu + \mu_a).$$

The nominal conductance matrix in 18.1.3 fits the constraint if and only if (see 15.4.4)

$$\begin{pmatrix} \frac{\partial \mathbf{T}}{\partial e} & \frac{\partial \mathbf{T}}{\partial v} & -e\frac{\partial \mathbf{T}}{\partial e} - v\frac{\partial \mathbf{T}}{\partial v} \end{pmatrix} \begin{pmatrix} \lambda_A & \beta_A & \vartheta_A \\ \lambda_F & \beta_F & \vartheta_F \\ \lambda_F & \beta_F & \vartheta_G \end{pmatrix} = 0,$$

$$\begin{pmatrix} \lambda_A & \beta_A & \vartheta_A \\ \lambda_F & \beta_F & \vartheta_F \\ \lambda_G & \beta_G & \vartheta_G \end{pmatrix} \begin{pmatrix} \frac{\partial \mathbf{T}}{\partial e} \\ \frac{\partial \mathbf{T}}{\partial v} \\ -e\frac{\partial \mathbf{T}}{\partial e} - v\frac{\partial \mathbf{T}}{\partial v} \end{pmatrix} = 0.$$

18.4.3 The set of equilibria

For all $T_a \in (\mathrm{K})^+$

$$U(T_a) := \{(E,V,N) \in \mathrm{Z} \mid \mathbf{T}(E,V,N) = T_a\}$$

is a constraint submanifold of the dynamical equation.

In an equilibrium, the pressure of the body and that of the environment are equal (the temperatures are equal as a matter of course) and there is no condition imposed on the particle number.

Proposition *If* (e_o, v_o) *is defined by 18.1.4 then the set of equilibria with non-zero particle number in* $U(T_a)$ *is*

$$Eq(T_a) := \{N(e_\mathrm{o}, v_\mathrm{o}, 1) \mid N \in \mathbb{R}^+\}.$$

The set of equilibria is half line: a submanifold whose tangent space at every point is spanned by $(e_\mathrm{o}, v_\mathrm{o}, 1)$.

18.4.4 Stability of equilibria

Proposition *If the body is entropic, the nominal conductance matrix in 18.1.3 fits the constraint and its value at* $(Ne_\mathrm{o}, Nv_\mathrm{o}, N)$ *is symmetric, positive semidefinite and has the kernel spanned by*

$$\left(\frac{\partial \mathbf{T}}{\partial e}, \frac{\partial \mathbf{T}}{\partial v}, -e\frac{\partial \mathbf{T}}{\partial e} - v\frac{\partial \mathbf{T}}{\partial v}\right)(Ne_o, Nv_o, N),$$

then $Eq(T_a)$ *is strictly asymptotically stable in* $U(T_a)$.

Proof Condition (ii) of Proposition 15.8 is satisfied in form (ii)' (given in the remark after the proof).

The tangent space of $Eq(T_a)$ at every point (Ne_o, Nv_o, N) equals the kernel of $\mathtt{D}^2\mathbf{L}(Ne_o, Nv_o, N)$. The nominal thermodynamical force takes zero value in equilibria. Consequently, all the conditions of Proposition 15.8 are satisfied.

18.5 Constant pressure

18.5.1 The constraint

Let us examine the diffusion processes in which the pressure of the body is constant and equals that of the environment. Again we refer to 12.12.

The present constraint is holonomic:

$$\frac{\partial \mathbf{P}}{\partial E}\dot{E} + \frac{\partial \mathbf{P}}{\partial V}\dot{V} + \frac{\partial \mathbf{P}}{\partial N}\dot{N} = 0.$$

As in the previous section, we can rewrite it in the form

$$\frac{\partial \mathbf{P}}{\partial e}\dot{E} + \frac{\partial \mathbf{P}}{\partial v}\dot{V} - \left(e\frac{\partial \mathbf{P}}{\partial e} + v\frac{\partial \mathbf{T}}{\partial v}\right)\dot{N} = 0.$$

Referring to the notations of Section 15.3.3, we have now

$$\Gamma = \left\{ \left(\frac{\partial \mathbf{P}}{\partial e}, \frac{\partial \mathbf{P}}{\partial v}, -e\frac{\partial \mathbf{P}}{\partial e} - v\frac{\partial \mathbf{P}}{\partial v} \right) \right\}.$$

The two-dimensional constraint subspaces are spanned by the vectors $\left(-\frac{\partial \mathbf{P}}{\partial v}, \frac{\partial \mathbf{P}}{\partial e}, 0\right)$ and $\left(0, e\frac{\partial \mathbf{P}}{\partial e} + v\frac{\partial \mathbf{P}}{\partial v}, \frac{\partial \mathbf{P}}{\partial v}\right)$.

18.5.2 The effective thermodynamical force and conductance matrix

Because of $P = P_a$ we easily find that

$$\left(\frac{1}{T} - \frac{1}{T_a}, -\frac{\mu}{T} + \frac{\mu_a}{T_a} \right)$$

can be considered as the effective thermodynamical force (multiples of these components appear when the nominal thermodynamical force is applied to the vectors spanning the constraint subspaces).

We can repeat what we said in the previous section about the nominal conductance matrix; the reader is asked to formulate precise necessary and sufficient conditions.

18.5.3 The set of equilibria

For all $P_a \in (\mathrm{Pa})$,

$$U(P_a) := \{(E, V, N) \in \mathrm{Z} \mid \mathbf{P}(E, V, N) = P_a\}$$

is a constraint submanifold of the dynamical equation.

In an equilibrium, the temperature of the body and that of the environment are equal (the pressures are equal as a matter of course) and there is no condition imposed on the particle number.

Proposition *If (e_o, v_o) is defined by 18.1.4, then the set of equilibria with non-zero particle number in $U(P_a)$ is*

$$Eq(P_a) := \{N(e_o, v_o, 1) \mid N \in \mathbb{R}^+\}.$$

The set of equilibria is half line: a submanifold whose tangent space at every point is spanned by $(e_o, v_o, 1)$.

18.5.4 Stability of equilibria

The following proposition can be proved as the proposition for constant temperature.

Proposition *If the body is entropic, the nominal conductance matrix in 18.1.3 fits the constraint and its value at (Ne_o, Nv_o, N) is symmetric, positive semidefinite and has the kernel spanned by*

$$\left(\frac{\partial \mathbf{P}}{\partial e}, \frac{\partial \mathbf{P}}{\partial v}, -e\frac{\partial \mathbf{P}}{\partial e} - v\frac{\partial \mathbf{P}}{\partial v} \right)(Ne_o, Nv_o, N),$$

then $Eq(P_a)$ is strictly asymptotically stable in $U(P_a)$.

18.6 Heat insulation

18.6.1 The effective thermodynamical force

Let us examine processes in which the body is heat insulated. Then the first law reads

$$\dot{E} = -P\dot{V} + \mu\dot{N}.$$

Accordingly, the constraint is given as

$$\Gamma = \{(1, P, -\mu)\}.$$

The two-dimensional constraint subspaces are spanned by $(-P, 1, 0)$ and $(\mu, 0, 1)$. The constraint is anholonomic.

The effective thermodynamical force is

$$\frac{1}{T_a}\big(P - P_a, -(\mu - \mu_a)\big).$$

18.6.2 Unsolved problem

As a consequence of the Frobenius theorem (well known in the theory of manifolds), there are no constraint submanifolds. We cannot apply Propositions 15.6 and 15.8. The problem of trend to equilibrium in the case of a heat insulated diffusing body is not yet solved.

18.7 Semipermeable wall, fixed volume

18.7.1 The set of equilibria

Let a rigid wall separate the body from the environment which lets particles only from the environment into the body; then $\mathbf{F} = 0$ and $\mathbf{G} \geq 0$. The present constraint with inequality cannot be treated in the previous framework.

Using the variables (v, T, N), we can write the dynamical equation – with ideal working and transferring – in the form

$$\mathfrak{c}\dot{T} = q - (P + \frac{\partial \mathfrak{c}}{\partial v})\dot{v},$$

$$\dot{v} = -vg, \qquad \dot{N} = Ng.$$

According to 14.1, in equilibrium the temperature of the body coincides with the temperature of the environment, and a condition on specific volume is given by

$$\boldsymbol{\mu}(v, T_a) \geq \boldsymbol{\mu}(v_a, T_a),$$

where v_a is the specific volume of the environment.

Recall that we suppose the processes running in a given phase Z. For all $V_o \in (\mathrm{m}^3)$,

$$U(V_o) := \{(v, T, N) \mid (v, T) \in Z, vN = V_o, N \in \mathbb{R}^+\}$$

is an invariant submanifold of the dynamical equation.

Only a single phase is considered, so the function $v \mapsto \boldsymbol{\mu}(v, T_a)$ is strictly monotone decreasing, thus

$$Eq(V_\mathrm{o}) := \{(v, T_a, N) \in U(V_\mathrm{o}) \mid v \leq v_a\}$$

is the set of equilibria in $U(V_\mathrm{o})$.

18.7.2 Stability of equilibria

It is reasonable to take the dynamical quantitities in the following pseudolinear form

$$\begin{aligned}
\mathfrak{q}(v, T, T_a, P_a) &= -\lambda_Q(v, T, T_a, P_a)(T - T_a) + \vartheta_Q(v, T, T_a, P_a)(\mu_a - \boldsymbol{\mu}(v, T))^+, \\
\mathfrak{g}(v, T, T_a, P_a) &= \vartheta_G(v, T, T_a, P_a)(\mu_a - \boldsymbol{\mu}(v, T))^+
\end{aligned}$$

where $(\quad)^+$ denotes the positive part of a function.

Proposition *If the dynamical quantitities have the above form, then $Eq(V_\mathrm{o})$ is strictly asymptotically stable in $U(V_\mathrm{o})$.*

Proof Let us parameterize $U(V_\mathrm{o})$ by specific volume and temperature. Then the reduced dynamical equation becomes

$$\begin{aligned}
\dot{T} &= -\alpha(v, T)(T - T_a) + \beta(v, T)(\mu_a - \boldsymbol{\mu}(v, T))^+, \\
\dot{v} &= -\gamma(v, T)(\mu_a - \boldsymbol{\mu}(v, T))^+,
\end{aligned}$$

where α, β and γ are some functions, α and β having non-negative values. The set of equilibria of the reduced equation is

$$Eq := \{(v, T_a,) \in Z \mid v \leq v_a\}.$$

The chemical potential is continuous, thus

$$A := \{(v, T) \in Z \mid \boldsymbol{\mu}(v, T) > \mu_a\}$$

is an open subset containing $Eq \setminus \{(v_a, T_a)\}$.

Let $(v_\mathrm{o}, T(0)) \in \overline{A}$, $v_\mathrm{o} < v_a$ and let $t \mapsto T(t)$ be the solution of the differential equation

$$(T - T_a)^{\boldsymbol{\cdot}} = -\alpha(v_\mathrm{o}, T)(T - T_a)$$

with initial condition $T(0)$. It is trivial that $|T - T_a|$ is monotone decreasing and $\lim\limits_{t\to\infty} T(t) = T_a$.

As a consequence, $\boldsymbol{\mu}(v_\mathrm{o}, T(t)) > \mu_a$ for all $t \geq 0$, therefore $t \mapsto (v_\mathrm{o}, T(t))$ is a solution of the reduced dynamical equation. All those imply that processes starting in A do not leave A and tend to $Eq \setminus \{(v_a, T_a)\}$, which means that the latter set is a strictly asymptotically stable set of equilibria.

Let us take now a process starting in a neighbourhood of (v_a, T_a). If the process enters $\overline{A} \setminus \{(v_a, T_a)\}$, then it proceeds as described previously. If it remains outside, then it satisfies a differential equation in which $(\boldsymbol{\mu} - \mu_a)^+ = \boldsymbol{\mu} - \mu_a$ and, according to our knowledge, (v_a, T_a) is an asymptotically stable equilibrium of such an equation.

So we can conclude that Eq, the set of equilibria of the reduced dynamical equation is strictly asymptotically stable.

18.8 Exercises

1. Treat the system without constraint in the variables (V, T, N).

2. Give the actual conditions for isothermal and isobaric processes, respectively, provided that the effective equilibrium value of the conductance matrix is symmetric and positive definite (in other words, the value of the nominal conductance matrix is symmetric and its kernel is spanned by the value of $\mathtt{D}\mathbf{T}$ and $\mathtt{D}\mathbf{P}$, respectively).

3. Suppose a non-zero material source in the body. What can be said about the stationary states? Examine the particular case of fixed volume.

4. Treat the body with semipermeable wall whose volume is not fixed.

5. Heating is determined uniquely by springing and converting for isothermal processes. Prove that in the ideal case (cf. 12.6)

$$Q = \left(P + \frac{\partial \mathfrak{e}}{\partial v}\right)F + \left(e - \mu + v\frac{\partial \mathfrak{e}}{\partial v}\right)G. \tag{$*$}$$

6. Springing is uniquely determined by heating and converting for isobaric processes. Prove that in the ideal case

$$F = \frac{1}{\mathfrak{c}_p}\left(\frac{\frac{\partial \mathcal{P}}{\partial T}}{-\frac{\partial \mathcal{P}}{\partial v}}Q + \left(\mathfrak{c}_v v + \frac{\frac{\partial \mathcal{P}}{\partial T}}{-\frac{\partial \mathcal{P}}{\partial v}}\left(\mu + v\frac{\partial e}{\partial v}\right)G\right)\right).$$

19 Diffusion between two bodies and an environment

19.1 General formulae

19.1.1 The framework of description

Considering a system consisting of two bodies of equal material and an environment characterized by its constant temperature and pressure, we shall examine processes that run in the same phases of the bodies, and both the bodies and the environment can interchange particles (diffusion can occur).

Zero sources are taken, workings and transferrings are ideal.

Constant process of the environment is supposed with temperature T_a and pressure P_a; then the chemical potential μ_a of the environment is constant, too.

This system is described according to Definition 14.1:

1. Two bodies and an environment of the same material $(\mathrm{D}, \mathbf{T}, \mathbf{P}, \boldsymbol{\mu}, \mathrm{R})$ are given.

2. There are the heatings $\mathbf{Q}_{ik}$, the springings $\mathbf{F}_{ik}$ and the convertings $\mathbf{G}_{ik}$ defined on $(\mathrm{D} * \mathbb{R}_0^+) \times (\mathrm{D} * \mathbb{R}_0^+)$ $(i = 1, 2; k = a, 1, 2)$; all the dynamical quantities are continuous and continuously differentiable on the interior of their domain and satisfy mutuality, equilibrium properties and dissipation inequalities with the notations $\mathbf{W}_{ik} := -\mathbf{P}_i\mathbf{F}_{ik}$ and $\mathbf{L}_{ik} := -\boldsymbol{\mu}_i\mathbf{G}_{ik}$.

3. There is a given phase Z of the material and the constant process $(T_a, P_a) \in (\mathbf{T}, \mathbf{P})[\mathrm{Z}]$ of the environment.

4. The sources are zero.

5. The processes, considered to run in $(\mathrm{Z}{*}\mathbb{R}^+)\times(\mathrm{Z}{*}\mathbb{R}^+)$ (zero particle numbers are excluded), are described by the dynamical equation

$$\begin{aligned}\dot{E}_1 &= Q_{1a} + Q_{12} - P_1(F_{1a} + F_{12}) + \mu_1(G_{1a} + G_{12}),\\ \dot{V}_1 &= F_{1a} + F_{12},\\ \dot{N}_1 &= G_{1a} + G_{12},\end{aligned}$$

$$\begin{aligned}\dot{E}_2 &= Q_{2a} + Q_{21} - P_2(F_{2a} + F_{21}) + \mu_2(G_{2a} + G_{21}),\\ \dot{V}_2 &= F_{2a} + F_{21},\\ \dot{N}_2 &= G_{2a} + G_{21}.\end{aligned}$$

19.1.2 The nominal conductance matrix

In the sequel we take pseudolinear dynamical quantitities. The pair conductivity matrices have the form

$$C_{ik} := \begin{pmatrix} \lambda_{ik}^A & \beta_{ik}^A & \vartheta_{ik}^A \\ \\ \lambda_{ik}^F & \beta_{ik}^F & \vartheta_{ik}^F \\ \\ \lambda_{ik}^G & \beta_{ik}^G & \vartheta_{ik}^G \end{pmatrix},$$

where $i = 1, 2$ and $k = 0, 1, 2$ and now superscripts refer to the dynamical quantitities. According to the remark in 15.4.2 we suppose that

$$\mathbf{C}_{12}(E_1, V_1, N_1, E_2, V_2, N_2) = \mathbf{C}_{21}(E_2, V_2, N_2, E_1, V_1, N_1).$$

Following 15.4.1, we introduce the conductance matrix

$$B := \begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix} := \begin{pmatrix} C_{1a} + C_{12} & -C_{12} \\ -C_{21} & C_{2a} + C_{21} \end{pmatrix}. \tag{$*$}$$

Thus, putting

$$x_1 := (E_1, V_1, N_1), \qquad x_2 := (E_2, V_2, N_2),$$

$$\mathbf{y} := \left(\frac{1}{\mathbf{T}}, \frac{\mathbf{P}}{\mathbf{T}}, -\frac{\boldsymbol{\mu}}{\mathbf{T}}\right),$$

$$y_a := \left(\frac{1}{T_a}, \frac{P_a}{T_a}, -\frac{\mu_a}{T_a}\right),$$

we obtain the dynamical equation in the form

$$\begin{pmatrix} \dot{x}_1 \\ \dot{x}_2 \end{pmatrix} = \begin{pmatrix} \mathbf{B}_{11}(x_1, x_2, y_a) & \mathbf{B}_{12}(x_1, x_2) \\ \mathbf{B}_{21}(x_1, x_2) & \mathbf{B}_{22}(x_1, x_2, y_a) \end{pmatrix} \begin{pmatrix} \mathbf{y}(x_1) - y_a \\ \mathbf{y}(x_2) - y_a \end{pmatrix}.$$

19.1.3 Entropic bodies

The total entropy of the bodies and the environment together – which plays a fundamental role in determining equilibria and their stability – equals (up to an additive constant)

$$(E_1,V_1,N_1,E_2,V_2,N_2)\mapsto \mathbf{L}(E_1,V_1,N_1,E_2,V_2,N_2):=$$
$$\mathbf{S}(E_1,V_1,N_1)+\mathbf{S}(E_2,V_2,N_2)-\frac{E_1+E_2+P_a(V_1+V_2)-\mu_a(N_1+N_2)}{T_a}.$$

The nominal thermodynamical force is the derivative of $\mathbf{L}$:

$$\left(\frac{1}{T_1}-\frac{1}{T_a},\frac{P_1}{T_1}-\frac{P_a}{T_a},-\frac{\mu_1}{T_1}+\frac{\mu_a}{T_a},\frac{1}{T_2}-\frac{1}{T_a},\frac{P_2}{T_2}-\frac{P_a}{T_a},-\frac{\mu_2}{T_2}+\frac{\mu_a}{T_a}\right),$$

where $T_1:=\mathbf{T}(E_1,V_1,N_1)$, $T_2:=\mathbf{T}(E_2,V_2,N_2)$, etc.

Furthermore, $\mathtt{D}^2\mathbf{L}(E_1,V_1,N_1,E_2,V_2,N_2)=\mathtt{D}^2\mathbf{S}(E_1,V_1,N_1)+\mathtt{D}^2\mathbf{S}(E_2,V_2,N_2)$ is negative semidefinite, having the kernel spanned by the vectors $(E_1,V_1,N_1,0,0,0)$ and $(0,0,0,E_2,V_2,N_2)$.

19.1.4 Equilibrium

Because the processes of the bodies run in the same phase in which the state of the environment is, if both the temperature and the pressure of one of the body and the environment coincide, their chemical potentials, too, have the same value; the same is true for the two bodies.

The equilibrium properties of the dynamical quantitities give mostly

$$\mathbf{T}(e_{1\mathrm{o}},v_{1\mathrm{o}})=\mathbf{T}(e_{2\mathrm{o}},v_{2\mathrm{o}}),\qquad \mathbf{P}(e_{1\mathrm{o}},v_{1\mathrm{o}})=\mathbf{P}(e_{2\mathrm{o}},v_{2\mathrm{o}})$$

for the specific quantities of the bodies. The function $(\mathbf{T},\mathbf{P})$ is injective in a phase, therefore

$$e_{1\mathrm{o}}=e_{2\mathrm{o}}=:e_\mathrm{o},\qquad v_{1\mathrm{o}}=v_{2\mathrm{o}}=:v_\mathrm{o}.$$

e_o and v_o are determined by different conditions in different systems.

19.2 System without constraint

19.2.1 The set of equilibria

Let the bodies and the environment be in thermal, mechanical and material interaction: there is no additional condition imposed on the dynamical quantities. According to 19.1.4, the equilibrium values of the specific quantities are determined uniquely by

$$\mathbf{T}(e_\mathrm{o},v_\mathrm{o})=T_a,\qquad \mathbf{P}(e_\mathrm{o},v_\mathrm{o})=P_a. \qquad (*)$$

There is no condition imposed on the particle numbers, thus we have

Proposition *The set of equilibria with non-zero particle numbers is*

$$\{(N_1e_\mathrm{o},N_1v_\mathrm{o},N_1,N_2e_\mathrm{o},N_2v_\mathrm{o},N_2)\mid N_1,N_2\in\mathbb{R}^+\}.$$

The set of equilibria is a plane quadrant: a submanifold whose tangent space at every point is spanned by the vectors $(e_\mathrm{o},v_\mathrm{o},1,0,0,0)$ and $(0,0,0,e_\mathrm{o},v_\mathrm{o},1)$.

19.2.2 Stability of equilibria

Proposition *If the bodies are entropic and the nominal conductance matrix*(∗) *in 19.1.2 takes symmetric and positive definite values in equilibria, then the set of equilibria is strictly asymptotically stable.*

Proof The set of equilibria is a submanifold, its tangent space at every point equals the kernel of the corresponding value of $\mathtt{D}^2\mathbf{L}$. The constraint is void, therefore, all the conditions of Proposition 15.8 are fulfilled.

19.3 Fixed total volume

19.3.1 The effective thermodynamical force and conductance matrix

Let the two bodies be enclosed with a heat conducting, permeable, rigid wall, i.e. the mechanical interaction between the bodies and the environment is forbidden: $\mathbf{F}_{1a} = \mathbf{F}_{2a} = 0$. Then

$$\dot{V}_1 + \dot{V}_2 = 0;$$

the constraint $\Gamma = \{(0,1,0,0,1,0)\}$ is holonomic (in fact is affine). The constraint subspaces are spanned by the vectors $(1,0,0,0,0,0)$, $(0,1,0,0,-1,0)$, $(0,0,1,0,0,0)$, $(0,0,0,1,0,0)$, $(0,0,0,0,0,1)$.

The effective thermodynamical force is

$$\left(\frac{1}{T_1} - \frac{1}{T_a}, \frac{1}{T_2} - \frac{1}{T_a}, \frac{P_1}{T_1} - \frac{P_2}{T_2}, -\frac{\mu_1}{T_1} + \frac{\mu_a}{T_a}, -\frac{\mu_2}{T_2} + \frac{\mu_a}{T_a}\right).$$

The nominal conductance matrix(∗) in 19.1.2 fits the constraint if and only if multiplied by the vector $(0,1,0,0,1,0)$ both from left and from right results in zero. In view of $C_{12} = C_{21}$, this is equivalent to that the middle row and the middle column of the matrices C_{1a} and C_{2a} are zero. This is an evident condition from a physical point of view: $\mathbf{F}_{1a} = \mathbf{F}_{2a} = 0$ imply that the middle row is zero, and the zero middle column means that the dynamical quantitities between the bodies and the environment do not depend on the pressures.

19.3.2 The set of equilibria

For all $V_\mathrm{s} \in (\mathrm{m}^3)^+$

$$U(V_\mathrm{s}) := \{(E_1, V_1, N_1, E_2, V_2, N_2) \mid V_1 + V_2 = V_\mathrm{s}\}$$

is a constraint submanifold of the dynamical equation, a part of an affine subspace.

The specific values of equilibrium quantities are determined by (∗) in 19.2.1.

Then in equilibrium we have

$$N_{1\mathrm{o}} + N_{2\mathrm{o}} = V_\mathrm{s}/v_\mathrm{o} =: N_\mathrm{o}.$$

Proposition *The set of equilibria with non-zero particle numbers in* $U(V_\mathrm{s})$ *is*

$$Eq(V_\mathrm{s}) := (N_1 e_\mathrm{o}, N_1 v_\mathrm{o}, N_1, (N_\mathrm{o} - N_1)e_\mathrm{o}, (N_\mathrm{o} - N_1)v_\mathrm{o}, N_\mathrm{o} - N_1) \mid 0 < N_1 < N_\mathrm{o}\}.$$

The set of equilibria is a straight line segment: a submanifold whose tangent space at every point is spanned by $(e_\mathrm{o}, v_\mathrm{o}, 1, -e_\mathrm{o}, -v_\mathrm{o}, -1)$.

19.3.3 Stability of equilibria

Proposition *If the bodies are entropic, the nominal conductance matrix*$(*)$ *in 19.1.2 fits the constraint and its equilibrium values are symmetric, positive semidefinite having the kernel spanned by* $(0,1,0,0,1,0)$*, then* $Eq(V_s)$ *is strictly asymptotically stable in* $U(V_s)$*.*

Proof In an arbitrary equilibrium, the kernel of $\mathtt{D}^2\mathbf{L}$ is spanned by the vectors $(e_o, v_o, 1, 0, 0, 0)$ and $(0, 0, 0, e_o, v_o, 1)$. An element which is both in this kernel and in the corresponding constraint subspace has the form $\alpha(e_o, v_o, 1, 0, 0, 0) + \beta(0, 0, 0, e_o, v_o, 1)$ in such a way that $\beta v_o = -\alpha v_o$, i.e. $\beta = -\alpha$, in other words, it is a multiple of $(e_o, v_o, 1, -e_o, -v_o, -1)$. Thus the intersection of the equilibrium kernel of $\mathtt{D}^2\mathbf{L}$ and the corresponding constraint subspace equals the corresponding tangent space of $Eq(V_s)$.

All the conditions of Proposition 15.8 are satisfied.

19.4 Fixed total particle number

19.4.1 The effective thermodynamical force and conductance matrix

Let the two bodies be enclosed with an impermeable wall, i.e. the material interaction between the bodies and the environment is forbidden: $\mathbf{G}_{1a} = \mathbf{G}_{2a} = 0$. Then

$$\dot{N}_1 + \dot{N}_2 = 0;$$

the constraint $\Gamma = \{(0,0,1,0,0,1)\}$ is holonomic (in fact is affine). The constraint subspaces are spanned by the vectors $(1,0,0,0,0,0)$, $(0,1,0,0,0,0)$, $(0,0,1,0,0,-1)$, $(0,0,0,1,0,0)$, $(0,0,0,0,1,0)$.

The effective thermodynamical force is

$$\left(\frac{1}{T_1} - \frac{1}{T_a}, \frac{1}{T_2} - \frac{1}{T_a}, \frac{P_1}{T_1} - \frac{P_a}{T_a}, \frac{P_2}{T_2} - \frac{P_a}{T_a}, -\frac{\mu_1}{T_1} + \frac{\mu_2}{T_2}\right).$$

The nominal conductance matrix $(*)$ in 19.1.2 fits the constraint if and only if multiplied by the vector $(0,0,1,0,0,1)$ both from left and from right results in zero. In view of $C_{12} = C_{21}$, this is equivalent to that the last row and the last column of the matrices C_{1a} and C_{2a} are zero. This is an evident condition from a physical point of view: $\mathbf{G}_{1a} = \mathbf{G}_{2a} = 0$ imply that the last row is zero, and the last column is zero because the dynamical quantitities between the bodies and the environment do not depend on the chemical potentials.

19.4.2 The set of equilibria

For all $N_s \in \mathbb{R}^+$

$$U(N_s) := \{(E_1, V_1, N_1, E_2, V_2, N_2) \mid N_1 + N_2 = N_s\}$$

is a constraint submanifold of the dynamical equation, a part of an affine subspace.

The specific value of the equilibrium quantities are determined by $(*)$ in 19.2.1.

Proposition *The set of equilibria with non-zero particle number in* $U(N_\mathrm{s})$ *is*

$$Eq(N_\mathrm{s}) := \{(N_1e_\mathrm{o}, N_1v_\mathrm{o}, N_1, (N_\mathrm{s}-N_1)e_\mathrm{o}, (N_\mathrm{s}-N_1)v_\mathrm{o}, N_\mathrm{s}-N_1) \mid 0 < N_1 < N_\mathrm{s}\}.$$

The set of equilibria is a straight line segment: a submanifold whose tangent space at every point is spanned by $(e_\mathrm{o}, v_\mathrm{o}, 1, -e_\mathrm{o}, -v_\mathrm{o}, -1)$.

19.4.3 Stability of equilibria

Proposition *If the bodies are entropic, the nominal conductance matrix* $(*)$ *in 19.1.2 fits the constraint and its equilibrium values are symmetric, positive semidefinite having the kernel spanned by* $(0,0,1,0,0,1)$*, then* $Eq(N_\mathrm{s})$ *is strictly asymptotically stable in* $U(N_\mathrm{s})$*.*

Proof In an arbitrary equilibrium, the kernel of $\mathtt{D}^2\mathbf{L}$ is spanned by the vectors $(e_\mathrm{o}, v_\mathrm{o}, 1, 0, 0, 0)$ and $(0,0,0,e_\mathrm{o}, v_\mathrm{o}, 1)$. An element which is both in this kernel and in the corresponding constraint subspace has the form $\alpha(e_\mathrm{o}, v_\mathrm{o}, 1, 0, 0, 0) + \beta(0,0,0,e_\mathrm{o}, v_\mathrm{o}, 1)$ in such a way that $\beta = -\alpha$, in other words, it is a multiple of $(e_\mathrm{o}, v_\mathrm{o}, 1, -e_\mathrm{o}, -v_\mathrm{o}, -1)$. Thus the intersection of the equilibrium kernel of $\mathtt{D}^2\mathbf{L}$ and the corresponding constraint subspace equals the corresponding tangent space of $Eq(N_\mathrm{s})$.

All the conditions of Proposition 15.8 are satisfied.

19.5 Fixed total volume and particle number

19.5.1 The effective thermodynamical force and conductance matrix

Let the two bodies be enclosed with a rigid and impermeable wall, i.e. both the mechanical and the material interaction are forbidden between the bodies and the environment: $\mathbf{F}_{1a} = \mathbf{F}_{2a} = 0$, $\mathbf{G}_{1a} = \mathbf{G}_{2a} = 0$. Then

$$\dot{V}_1 + \dot{V}_2 = 0, \quad \dot{N}_1 + \dot{N}_2 = 0;$$

the constraint $\Gamma = \{(0,1,0,0,1,0), (0,0,1,0,0,1)\}$ is holonomic (in fact it is affine). The constraint subspaces are spanned by the vectors $(1,0,0,0,0,0)$, $(0,1,0,0,-1,0)$, $(0,0,1,0,0,-1)$ and $(0,0,0,1,0,0)$.

The effective thermodynamical force is

$$\left(\frac{1}{T_1} - \frac{1}{T_a}, \frac{1}{T_2} - \frac{1}{T_a}, \frac{P_1}{T_1} - \frac{P_2}{T_2}, -\frac{\mu_1}{T_1} + \frac{\mu_2}{T_2}\right).$$

The nominal conductance matrix $(*)$ in 19.1.2 fits the constraint if and only if multiplied by the vectors $(0,1,0,0,1,0)$ and $(0,0,1,0,0,1)$ both from left and from right results in zero. In view of $C_{12} = C_{21}$, this is equivalent to that the only the element in the first row and first column of the matrices C_{1a} and C_{2a} is not zero.

19.5.2 The set of equilibria

For all $V_\mathrm{s} \in (\mathrm{m}^3)^+$ and $N_\mathrm{s} \in \mathbb{R}^+$

$$U(V_\mathrm{s}, N_\mathrm{s}) := \{(E_1, V_1, N_1, E_2, V_2, N_2) \mid V_1 + V_2 = V_\mathrm{s},\ N_1 + N_2 = N_\mathrm{s}\}$$

is a constraint submanifold of the dynamical equation, a part of an affine subspace.

Now we have

$$v_\mathrm{o} = \frac{V_\mathrm{s}}{N_\mathrm{s}}$$

for the equilibrium value of specific volume (see 19.1.4) which, together with

$$\mathbf{T}(e_\mathrm{o}, v_\mathrm{o}) = T_a$$

determine uniquely the equilibrium value of specific internal energy.

Proposition *The set of equilibria with non-zero particle number in* $U(V_\mathrm{s}, N_\mathrm{s})$ *is*

$$Eq(V_\mathrm{s}, N_\mathrm{s}) := \\ := \{(N_1 e_\mathrm{o}, N_1 v_\mathrm{o}, N_1, (N_\mathrm{s}-N_1)e_\mathrm{o}, (N_\mathrm{s}-N_1)v_\mathrm{o}, N_\mathrm{s}-N_1) \mid 0 < N_1 < N_\mathrm{s}\}.$$

The set of equilibria is a straight line segment: a submanifold whose tangent space at every point is spanned by $(e_\mathrm{o}, v_\mathrm{o}, 1, -e_\mathrm{o}, -v_\mathrm{o}, -1)$.

19.5.3 Stability of equilibria

The pressure of the environment does not appear in the description; we can take formally that it equals the equilibrium pressure $P_\mathrm{o} := \mathbf{P}(e_\mathrm{o}, v_\mathrm{o})$.

Furthermore, we can repeat the reasoning in the previous proofs, to arrive at the result that for entropic bodies all the conditions of 15.8 are satisfied:

Proposition *If the bodies are entropic, the nominal conductance matrix* $(*)$ *in 19.1.2 fits the constraint and its equilibrium values are symmetric, positive semidefinite having the kernel spanned by* $(0, 1, 0, 0, 1, 0)$ *and* $(0, 0, 1, 0, 0, 1)$*, then* $Eq(V_\mathrm{s}, N_\mathrm{s})$ *is strictly asymptotically stable in* $U(V_\mathrm{s}, N_\mathrm{s})$*.*

19.6 Fixed total volume, particle number and internal energy

19.6.1 The effective thermodynamical force and conductance matrix

Let the two bodies be enclosed with a wall which forbids every interaction between the bodies and the environment: $\mathbf{F}_{1a} = \mathbf{F}_{2a} = 0$, $\mathbf{G}_{1a} = \mathbf{G}_{2a} = 0$ and $\mathbf{Q}_{1a} = \mathbf{Q}_{2a} = 0$. Then

$$\dot{E}_1 + \dot{E}_2 = 0, \quad \dot{V}_1 + \dot{V}_2 = 0, \quad \dot{N}_1 + \dot{N}_2 = 0;$$

the constraint $\Gamma = \{(1, 0, 0, 1, 0, 0), (0, 1, 0, 0, 1, 0), (0, 0, 1, 0, 0, 1)\}$ is holonomic (in fact it is affine). The constraint subspaces are spanned by the vectors $(1, 0, 0, -1, 0, 0)$, $(0, 1, 0, 0, -1, 0)$, $(0, 0, 1, 0, 0, -1)$.

The effective thermodynamical force is

$$\left(\frac{1}{T_1}-\frac{1}{T_2}, \frac{P_1}{T_1}-\frac{P_2}{T_2}, -\frac{\mu_1}{T_1}+\frac{\mu_2}{T_2}\right).$$

The nominal conductance matrix $(*)$ in 19.1.2 fits the constraint if and only if multiplied by the vectors $(0,1,0,0,1,0)$ $(0,0,1,0,0,1)$ and $(1,0,0,1,0,0)$ both from left and from right results in zero. In view of $C_{12}=C_{21}$, this is equivalent to that $C_{1a}=C_{2a}=0$, which is a natural requirement.

19.6.2 The set of equilibria

For all $E_\mathrm{s} \in (\mathrm{J})^+$, $V_\mathrm{s} \in (\mathrm{m}^3)^+$ and $N_\mathrm{s} \in \mathbb{R}^+$

$$\begin{aligned} U(E_\mathrm{s}, V_\mathrm{s}, N_\mathrm{s}) := \{(E_1, V_1, N_1, E_2, V_2, N_2) \mid \\ E_1+E_2=E_\mathrm{s},\ V_1+V_2=V_\mathrm{s},\ N_1+N_2=N_\mathrm{s}\} \end{aligned}$$

is a constraint submanifold of the dynamical equation, a part of an affine subspace.

Evidently, the specific values of the equilibrium quantities (see 19.1.4) are determined by

$$e_\mathrm{o} = \frac{E_\mathrm{s}}{N_\mathrm{s}}, \qquad v_\mathrm{o} = \frac{V_\mathrm{s}}{N_\mathrm{s}}.$$

Proposition *The set of equilibria with non-zero particle number in* $U(E_\mathrm{s}, V_\mathrm{s}, N_\mathrm{s})$ *is*

$$\begin{aligned} &Eq(E_\mathrm{s}, V_\mathrm{s}, N_\mathrm{s}) := \\ &:= \{(N_1 e_\mathrm{o}, N_1 v_\mathrm{o}, N_1, (N_\mathrm{s}-N_1)e_\mathrm{o}, (N_\mathrm{s}-N_1)v_\mathrm{o}, N_\mathrm{s}-N_1) \mid 0<N_1<N_\mathrm{s}\}. \end{aligned}$$

The set of equilibria is a straight line segment: a submanifold whose tangent space at every point is spanned by $(e_\mathrm{o}, v_\mathrm{o}, 1, -e_\mathrm{o}, -v_\mathrm{o}, -1)$.

19.6.3 Stability of equilibrium

Now both the temperature and the pressure of the environment do not appear in the description; we can take formally that they equal the corresponding equilibrium values $T_\mathrm{o} := \mathbf{T}(e_\mathrm{o}, v_\mathrm{o})$ and $P_\mathrm{o} := \mathbf{P}(e_\mathrm{o}, v_\mathrm{o})$.

Furthermore, we can repeat the reasoning in the previous proofs, to arrive at the result that for entropic bodies all the conditions of 15.8 are satisfied:

Proposition *If the bodies are entropic, the nominal conductance matrix* $(*)$ *in 19.1.2 fits the constraint and its equilibrium values are symmetric, positive semidefinite having the kernel spanned by* $(0,1,0,0,1,0)$, $(0,0,1,0,0,1)$ *and* $1,0,0,1,0,0)$, *then* $Eq(E_\mathrm{s}, V_\mathrm{s}, N_\mathrm{s})$ *is strictly asymptotically stable in* $U(E_\mathrm{s}, V_\mathrm{s}, N_\mathrm{s})$.

19.7 Fixed individual volumes, total particle number and joint heat insulation

19.7.1 The effective thermodynamical force and conductance matrix

Let each body be enclosed with a rigid wall which forbids every interaction between the bodies and the environment. (Consider a container whose wall is rigid, heat insulated and impermeable, divide it in two parts by an unmovable, heat-conducting and permeable wall and fill the two parts with the same gas.) Then $\mathbf{Q}_{1a} = \mathbf{Q}_{2a} = 0$, $\mathbf{F}_{1a} = \mathbf{F}_{2a} = \mathbf{F}_{12} = 0$, $\mathbf{G}_{1a} = \mathbf{G}_{2a} = 0$, and

$$\dot{E}_1 + \dot{E}_2 = 0, \quad \dot{V}_1 = 0, \quad \dot{V}_2 = 0, \quad \dot{N}_1 + \dot{N}_2 = 0.$$

The reader is asked to describe the (affine) constraint, the constraint subspaces, the effective thermodynamical force and the conditions assuring that the nominal conductance matrix $(*)$ in 19.1.2 fits the constraint.

19.7.2 Uniqueness of equilibrium

For all $E_\mathrm{s} \in (\mathrm{J})^+$, $V_{1\mathrm{o}}, V_{2\mathrm{o}} \in (\mathrm{m}^3)^+$ and $N_\mathrm{s} \in \mathbb{R}^+$

$$U(E_\mathrm{s}, V_{1\mathrm{o}}, V_{2\mathrm{o}}, N_\mathrm{s}) := \{(E_1, V_1, N_1, E_2, V_2, N_2) \mid E_1 + E_2 = E_\mathrm{s},\ V_1 = V_{1\mathrm{o}},\ V_2 = V_{2\mathrm{o}},\ N_1 + N_2 = N_\mathrm{s}\}$$

is a constraint submanifold of the dynamical equation, a part of an affine subspace.

Then, as in the previous paragraph, the equilibrium values are determined by

$$e_\mathrm{o} = \frac{E_\mathrm{s}}{N_\mathrm{s}}, \qquad v_\mathrm{o} = \frac{V_{1\mathrm{o}} + V_{2\mathrm{o}}}{N_\mathrm{s}}$$

and, furthermore, both equilibrium particle numbers are unique:

$$N_{1\mathrm{o}} = \frac{V_{1\mathrm{o}}}{v_\mathrm{o}}, \qquad N_{2\mathrm{o}} = \frac{V_{2\mathrm{o}}}{v_\mathrm{o}}.$$

Thus

$$(N_{1\mathrm{o}}e_\mathrm{o}, N_{1\mathrm{o}}v_\mathrm{o}, N_{1\mathrm{o}}, N_{2\mathrm{o}}e_\mathrm{o}, N_{2\mathrm{o}}v_\mathrm{o}, N_{2\mathrm{o}}). \qquad (*)$$

is the only equilibrium in the above constraint submanifold.

19.7.3 Stability of the equilibrium

The reader is asked to verify that Proposition 15.6 can be applied:

Proposition *If the bodies are entropic, then the equilibrium* $(*)$ *is asymptotically stable in* $U(E_\mathrm{s}, V_{1\mathrm{o}}, V_{2\mathrm{o}}, N_\mathrm{s})$ *(even if the dynamical quantitities are not pseudolinear).*

19.7.4 Gay-Lussac's experiment

Gay-Lussac made an experiment with the system above. He took a container having rigid, heat-insulated impermeable walls, divided it in two parts by an unmovable wall with a small tap in it. Having turned the tap off, he pumped out the air of one part and then turned the tap on. The air diffused from the full part into the empty one. Gay-Lussac found that the temperature of the air before and after diffusion was the same and concluded that the internal energy of the air does not depend on volume.

We easily see his result reasoning in a reversed way: how the temperature depends on volume. Let V_1 and V_2 be the volume of the full part and the empty part, respectively. The total internal energy of the two bodies (parts) does not change during the diffusion because the two bodies are completely insulated from the environment. Consequently, $\mathbf{T}(E, V_1, N)$ and $\mathbf{T}(E, V_1 + V_2, N)$ are the temperature of the gas at the beginning and the end of the process, respectively. If these two values are equal, then temperature does not depend on volume. Nowadays it is known that Gay-Lussac's result is only a good approximation for sufficiently large specific volume, but this is true for all gases; that is why we accept that the internal energy of an ideal gas does not depend on volume.

Gay-Lussac's experiment is usually conceived as a typical process which is 'not reversible'. Namely, in the usual formalism of classical thermodynamics, the first law is written in the form

$$\mathtt{d}E = \delta Q + \delta W$$

where δQ is an 'infinitesimal heat', δW is an 'infinitesimal work'. At the same time, the entropic property implies

$$\mathtt{d}E = T\mathtt{d}S - P\mathtt{d}V \tag{$*$}$$

(tacitly assuming that the particle number is constant). A reversible process is characterized by $\delta Q = T\mathtt{d}S$ and $\delta W = -P\mathtt{d}V$.

The internal energy of the gas in Gay-Lussac's experiment is constant, the gas does not absorb heat and does not work (the two parts together are enclosed with a rigid and heat-insulated wall), thus $\delta Q = 0$ and $\delta W = 0$, implying $\mathtt{d}E = 0$, too; on the other hand, $\mathtt{d}V \neq 0$ because the gas expands, so $T\mathtt{d}S \neq 0$, too: the process is not reversible. This is an erroneous reasoning, however, because formula $(*)$ is valid only for a homogeneous body (when both temperature and pressure take the same value T and P, respectively, at every point of the body) and if the two parts are considered as a single body, then the body is not homogeneous.

Correctly, we have to consider the experiment concerning two homogeneous bodies. Then the usual relations would be valid in the form

$$\mathtt{d}E_1 = T_1\mathtt{d}S_1 - P_1\mathtt{d}V_1 + \mu_1\mathtt{d}N_1, \qquad \mathtt{d}E_2 = T_2\mathtt{d}S_2 - P_2\mathtt{d}V_2 + \mu_2\mathtt{d}N_2$$

and

$$\mathtt{d}E_1 = \delta Q_1 + \delta W_1 + \delta L_1, \qquad \mathtt{d}E_2 = \delta Q_2 + \delta W_2 + \delta L_2.$$

Moreover,

$$\mathtt{d}E_1 + \mathtt{d}E_2 = 0, \qquad \mathtt{d}V_1 = 0,\ \mathtt{d}V_2 = 0, \qquad \mathtt{d}N_1 + \mathtt{d}N_2 = 0,$$

implying $\delta W_1 = 0$, $\delta W_2 = 0$ and

$$0 = (\delta Q_1 + \delta Q_2) + (\delta L_1 + \delta L_2).$$

Since $\mu_1 \neq \mu_2$, the joint heat insulation cannot be expressed by $\delta Q_1 + \delta Q_2 = 0$ if ideal transferrings are taken.

19.8 Constant temperature, fixed total volume and particle number

19.8.1 The effective thermodynamical force and conductance matrix

Let the two bodies be enclosed with a rigid and impermeable wall which conducts heat very quickly, so that the temperature of the bodies always equals that of the environment. Then

$$\begin{aligned} &\dot V_1 + \dot V_2 = 0, \quad \dot N_1 + \dot N_2 = 0, \\ &\frac{\partial \mathbf{T}}{\partial E}\dot E_1 + \frac{\partial \mathbf{T}}{\partial V}\dot V_1 + \frac{\partial \mathbf{T}}{\partial N}\dot N_1 = 0, \\ &\frac{\partial \mathbf{T}}{\partial E}\dot E_2 + \frac{\partial \mathbf{T}}{\partial V}\dot V_2 + \frac{\partial \mathbf{T}}{\partial N}\dot N_2 = 0 \end{aligned}$$

where, of course, the partial derivatives in the upper and lower rows are to be taken at (E_1, V_1, N_1) and at (E_2, V_2, N_2), respectively.

The above equalities determine a holonomic constraint. Putting

$$\alpha_i := \frac{\partial \mathbf{T}}{\partial e}(e_i, v_i) \qquad \beta_i := \frac{\partial \mathbf{T}}{\partial e}(e_i, v_i)$$

for $i = 1, 2$ and using 8.3 $(*)$ we find that the constraint subspaces are spanned by the vectors

$$(-\beta_1\alpha_2, \alpha_1\alpha_2, 0, \alpha_1\beta_2, -\alpha_1\alpha_2, 0)$$

and

$$(\alpha_1\alpha_2 e_1 + \beta_1\alpha_2 v_1, 0, \alpha_1\alpha_2, -\alpha_1\alpha_2 e_2 - \alpha_1\beta_2 v_2, 0, -\alpha_1\alpha_2).$$

The reader is asked to find effective thermodynamical force and the conditions assuring that the nominal conductance matrix $(*)$ in 19.1.2 fits the constraint.

19.8.2 The set of equilibria

For all $V_\mathrm{s} \in (\mathrm{m}^3)^+$, $N_\mathrm{s} \in \mathbb{R}^+$ and $T_a \in (\mathrm{K})^+$

$$\begin{aligned} U(V_\mathrm{s}, N_\mathrm{s}, T_a) := \{&(E_1, V_1, N_1, E_2, V_2, N_2) \mid \\ &V_1 + V_2 = V_\mathrm{s},\ N_1 + N_2 = N_\mathrm{s},\ \mathbf{T}(E_1, V_1, N_1) = \mathbf{T}(E_2, V_2, N_2) = T_a\} \end{aligned}$$

is a constraint submanifold of the dynamical equation.

The specific value of the equilibrium quantities are determined by the equalities

$$v_\mathrm{o} = \frac{V_\mathrm{s}}{N_\mathrm{s}}, \quad \mathbf{T}(e_\mathrm{o}, v_\mathrm{o}) = T_a.$$

As in 19.5.2, we have:

Proposition *the set of equilibria with non-zero particle number in* $U(V_{\rm s}, N_{\rm s}, T_a)$ *is*

$$\begin{aligned}&Eq(V_{\rm s}, N_{\rm s}, T_a) :=\\ &\quad := \{(N_1 e_{\rm o}, N_1 v_{\rm o}, N_1, (N_{\rm s} - N_1)e_{\rm o}, (N_{\rm s} - N_1)v_{\rm o}, N_{\rm s} - N_1) \mid 0 < N_1 < N_{\rm s}\},\end{aligned}$$

The set of equilibria is a straight line segment.

19.8.3 Stability of equilibria

The constraint submanifold is not a subset of an affine subset. Because the pressure of the environment does not enter the dynamical equation, we can suppose that it equals the equilibrium pressure of the body: $P_a = \mathbf{P}(e_{\rm o}, v_{\rm o})$. Then the nominal thermodynamical force becomes zero in equilibria which admits an easy application of Proposition 15.8.

Proposition *If the bodies are entropic, the nominal conductance matrix* $(*)$ *in 19.1.2 fits the constraint, its equilibrium values are symmetric and positive semidefinite having the kernel spanned by*

$$(0, 1, 0, 0, 1, 0), \quad (0, 0, 1, 0, 0, 1),$$

$$\left(\frac{\partial \mathbf{T}}{\partial E}, \frac{\partial \mathbf{T}}{\partial V}, \frac{\partial \mathbf{T}}{\partial N}, 0, 0, 0\right) (\textit{equilibrium}),$$

$$\left(0, 0, 0\frac{\partial \mathbf{T}}{\partial E}, \frac{\partial \mathbf{T}}{\partial V}, \frac{\partial \mathbf{T}}{\partial N}\right) (\textit{equilibrium}),$$

then $Eq(V_{\rm s}, N_{\rm s}, T_a)$ *is strictly asymptotically stable in* $U(V_{\rm s}, N_{\rm s}, T_a)$.

19.9 Constant pressure, fixed total particle number

19.9.1 The effective thermodynamical force and conductance matrix

Let the two bodies be enclosed with a rigid and impermeable wall which is 'infinitely' elastic, so that the pressure of the bodies always equals that of the environment. Then

$$\dot N_1 + \dot N_2 = 0,$$

$$\frac{\partial \mathbf{P}}{\partial E}\dot E_1 + \frac{\partial \mathbf{P}}{\partial V}\dot V_1 + \frac{\partial \mathbf{P}}{\partial N}\dot N_1 = 0,$$

$$\frac{\partial \mathbf{P}}{\partial E}\dot E_2 + \frac{\partial \mathbf{P}}{\partial V}\dot V_2 + \frac{\partial \mathbf{P}}{\partial N}\dot N_2 = 0,$$

where, of course, the partial derivatives in the upper and lower rows are to be taken at (E_1, V_1, N_1) and at (E_2, V_2, N_2), respectively.

The above equalities determine a holonomic constraint. Putting

$$\alpha_i := \frac{\partial \mathbf{P}}{\partial e}(e_i, v_i) \qquad \beta_i := \frac{\partial \mathbf{P}}{\partial e}(e_i, v_i)$$

for $i = 1, 2$ and using 8.3 $(*)$ we find that the constraint subspaces are spanned by the vectors

$$(-\beta_1, \alpha_1, 0, 0, 0, 0), \qquad (0, 0, 0, -\beta_2, \alpha_2, 0)$$

and

$$(\alpha_1\alpha_2 e_1 + \beta_1\alpha_2 v_1, 0, \alpha_1\alpha_2, -\alpha_1\alpha_2 e_2 - \alpha_1\beta_2 v_2, 0, -\alpha_1\alpha_2).$$

The reader is asked to find the effective thermodynamical force and the conditions assuring that the nominal conductance matrix $(*)$ in 19.1.2 fits the constraint.

19.9.2 The set of equilibria

For all $N_\mathrm{s} \in \mathbb{R}^+$ and $P_a \in (\mathrm{Pa})$

$$U(N_\mathrm{s}, P_a) := \{(E_1, V_1, N_1, E_2, V_2, N_2) \mid \\ N_1 + N_2 = N_\mathrm{s},\ \mathbf{P}(E_1, V_1, N_1) = \mathbf{P}(E_2, V_2, N_2) = P_a\}$$

is a constraint submanifold of the dynamical equation.

The specific value of the equilibrium quantities are determined by the equalities $(*)$ in 19.2.1.

Proposition *The set of equilibria with non-zero particle number in* $U(N_\mathrm{s}, P_a)$ *is*

$$Eq(N_\mathrm{s}, P_a) := \\ := \{(N_1 e_\mathrm{o}, N_1 v_\mathrm{o}, N_1, (N_\mathrm{s} - N_1)e_\mathrm{o}, (N_\mathrm{s} - N_1)v_\mathrm{o}, N_\mathrm{s} - N_1) \mid 0 < N_1 < N_\mathrm{s}\}$$

The set of equilibria is a straight line segment.

19.9.3 Stability of equilibria

Proposition *If the bodies are entropic, the nominal conductance matrix* $(*)$ *in 19.1.2 fits the constraint, its equilibrium values are symmetric and positive semidefinite, having the kernel spanned by*

$$(0, 0, 1, 0, 0, 1),$$

$$\left(\frac{\partial \mathbf{P}}{\partial E}, \frac{\partial \mathbf{P}}{\partial V}, \frac{\partial \mathbf{P}}{\partial N}, 0, 0, 0\right) (\textit{equilibrium}),$$

$$\left(0, 0, 0\frac{\partial \mathbf{P}}{\partial E}, \frac{\partial \mathbf{P}}{\partial V}, \frac{\partial \mathbf{P}}{\partial N}\right) (\textit{equilibrium}),$$

then $Eq(N_\mathrm{s}, P_a)$ *is strictly asymptotically stable in* $U(N_\mathrm{s}, P_a)$.

19.10 Fixed total particle number and joint heat insulation

Let the bodies be enclosed with a heat-insulated and impermeable wall. Then $\mathbf{G}_{ia} = 0$, $\mathbf{Q}_{ia} = 0$ $(i = 1, 2)$. Besides

$$\dot{N}_1 + \dot{N}_2 = 0,$$

we cannot easily find other equalities describing the constraint in a convenient form. If we suppose $Q_{12} = -Q_{21}$ and ideal workings and transferring (a hard condition which now does not lead to a contradiction), then we have

$$\dot{E}_1 + P_1\dot{V}_1 - \mu_1\dot{N}_1 + \dot{E}_2 + P_2\dot{V}_2 - \mu_2\dot{N}_2 = 0.$$

The constraint is anholonomic and there are no constraint submanifolds. We cannot apply Propositions 15.6 and 15.8. The problem of trend to equilibrium in this case is not solved yet.

19.11 Fixed total particle number, joint heat insulation and mechanical separation

19.11.1 The effective thermodynamical force and conductance matrix

Let the two bodies be enclosed with a heat-insulated and impermeable wall and suppose that the bodies cannot work on each other (imagine a cylinder with two pistons which is divided in the middle by an unmovable and heat-insulated wall; the cylinder and the pistons are heat-insulated and impermeable). Then $\mathbf{G}_{ia} = 0$, $\mathbf{Q}_{ia} = 0$ and $\mathbf{F}_{ik} = 0$. Thus

$$\dot{N}_1 + \dot{N}_2 = 0,$$

and as a consequence of $(*)$ in 14.1 – because now $\dot{V}_1 = F_{1a}$ and $\dot{V}_2 = F_{2a}$ – we have

$$\dot{E}_1 + P_1\dot{V}_1 + E_2 + P_2\dot{V}_2 = 0.$$

The constraint subspaces are spanned by the vectors $(0,0,1,0,0,-1)$, $(1,0,0,-1,0,0)$, $(P_1,-1,0,0,0,0)$ and $(0,0,0,P_2,-1,0)$.

The constraint is holonomic.

The reader is asked to find the effective thermodynamical force and the conditions assuring that the nominal conductance matrix $(*)$ in 19.1.2 fits the constraint.

19.11.2 The set of equilibria

For all $N_\mathrm{s} \in \mathbb{R}^+$ and $H_\mathrm{s} \in (\mathrm{J})$

$$\begin{aligned} U(N_\mathrm{s}, H_\mathrm{s}) := \{(E_1, V_1, N_1, E_2, V_2, N_2) \mid N_1 + N_2 = N_\mathrm{s},& \\ E_1 + P_1V_1 + E_2 + P_2V_2 = H_\mathrm{s}\}& \end{aligned}$$

is a constraint submanifold of the dynamical equation.

The specific value of the equilibrium quantities are determined by $(*)$ in 19.2.1.

Proposition *The set of equilibria with non-zero particle number in* $U(N_\mathrm{s}, H_\mathrm{s})$ *is*

$$\begin{aligned} &Eq(N_\mathrm{s}, H_\mathrm{s}, P_a) := \\ &\quad := \{(N_1e_\mathrm{o}, N_1v_\mathrm{o}, N_1, (N_\mathrm{s}-N_1)e_\mathrm{o}, (N_\mathrm{s}-N_1)v_\mathrm{o}, N_\mathrm{s}-N_1) \mid 0 < N_1 < N_\mathrm{s}\}. \end{aligned}$$

The set of equilibria is straight line segment.

19.11.3 Stability of equilibria

Proposition *If the bodies are entropic, the nominal conductance matrix* $(*)$ *in 19.1.2 fits the constraint, its equilibrium values are symmetric and positive semidefinite having the kernel spanned by the vectors*

$$(0,0,1,0,0,1), \quad (1,P_1,0,1,P_2,0),$$

then $Eq(N_{\rm s},H_{\rm s})$ *is strictly asymptotically stable in* $U(N_{\rm s},H_{\rm s})$.

19.12 Cooling of gases

19.12.1 Two bodies in two environments

Let us take a cylinder with two pistons which is divided in the middle by an unmovable and heat insulated wall; the cylinder and the pistons are heat-insulated and impermeable. Let the same gas fill both parts of the cylinder and let us suppose that different constant pressures act on the pistons, and the processes are isobaric for both parts separately; that is, the pressure of the first gas is constant P_a and the pressure of the second gas is constant P_b. Let $P_a > P_b$.

Now there are two environments; this system can be treated by a slight modification of the previous scheme.

Now $\mathbf{F}_{ik} = 0$, $\mathbf{Q}_{ik} = 0$, and $\mathbf{Q}_{ia} = 0$, $\mathbf{G}_{ia} = 0$ $(i = 1,2)$, where the subscript 0 refers to any of the environments. Then we deduce, as in 19.11.1, that

$$\dot{E}_1 + P_a\dot{V}_1 + \dot{E}_2 + P_b\dot{V}_2 = 0. \qquad (*)$$

19.12.2 The direction of the diffusion

According to Proposition 14.2, if $N_1N_2 \neq 0$ and $\mathbf{P}(E_1,V_1,N_1) = P_a$, $\mathbf{P}(E_2,V_2,N_2) = P_b$, then $\mathbf{G}_{12}(E_1,V_1,N_1,E_2,V_2,N_2) < 0$ if and only if

$$\mu(T_1,P_a) - \mu(T_2,P_b) > 0. \qquad (**)$$

The function $\mu(T,\cdot)$ is locally strictly monotone increasing (Gibbs–Duhem relations), inequality $(**)$ holds if "both the pressures and the temperatures are sufficiently near to each other" because $P_a > P_b$. This means that the gas diffuses from the part with larger pressure (denoted by the subscript 1) into the part with smaller pressure (denoted by the subscript 2) (which agrees with our everyday experience).

The precise meaning of the phrase in quotation marks: if $\{(T,P) \mid P_a \geq P \geq P_b\}$ is not void and is contained in the domain of μ for some T, then T has a neighbourhood such that $(**)$ holds for all T_1 and T_2 in that neighbourhood.

There is no equilibrium with non-zero particle number.

The equilibrium in which the second body has zero particle number is instable: if the particle number in the second body is arbitrarily small, diffusion takes place increasing the particle number of the second body.

The equilibrium in which the first body has zero particle number is asymptotically stable: if the particle number in the first body is not zero then diffusion takes place decreasing the particle number number of the first body.

19.12.3 The total enthalpy is constant

Equality $(*)$ says that the sum of the enthalpies of the bodies is constant in the processes. Using temperature and pressure as variables (supposing that the processes run in a single phase), we have for the specific enthalpy $\boldsymbol{h}$ and for every instant t in the domain of the process:

$$\begin{aligned} &N_1(t)\boldsymbol{h}(T_1(t),P_a) + (N_s - N_1(t))\boldsymbol{h}(T_2(t),P_b) = \\ &\qquad\qquad = N_1(t_i)\boldsymbol{h}(T_1(t_i),P_a) + (N_s - N_1(t_i))\boldsymbol{h}(T_2(t_i),P_b), \end{aligned}$$

where t_i is the starting instant and N_s is the total particle number. The process ends (arrives at a stable equilibrium) when the particle number of the first body becomes zero: t_f is the final instant when $N_1(t_f) = 0$ (t_f can be infinity; then the further formulae are valid as limits at infinity). Then

$$N_\mathrm{s}\boldsymbol{h}(T_2(t_f),P_b) = N_1(t_i)\boldsymbol{h}(T_1(t_i),P_a) + (N_\mathrm{s} - N_1(t_i)\boldsymbol{h}(T_2(t_i),P_b).$$

If $N_1(t_i) = N_\mathrm{s}$, then

$$\boldsymbol{h}(T_2(t_f),P_b) = \boldsymbol{h}(T_1(t_i),P_a).$$

We arrived at this equality in a circuitous way; it seems, we could take $N_1(t_i) = N_s$ to have the desired result immediately. However, a process in which the particle number of the first body is N_s is an equilibrium, thus no change occurs; but this equilibrium is unstable: if the particle number of the second body is not zero – it can be arbitrarily small – then diffusion takes place. The above formulae are valid for all $N_2(t_i) = N_\mathrm{s} - N_1(t_i) > 0$ and we can consider the limit as $N_2(t_i)$ tends to zero.

19.12.4 The Joule–Thomson coefficient

Simplifying the notations, we write the previous formula in the form

$$\boldsymbol{h}(T_f,P_b) = \boldsymbol{h}(T_i,P_a).$$

This means that (T_f,P_b) and (T_i,P_a) are on an isenthalpic curve in the $T{-}P$ plane. According to Exercise 2 in 7.10 (omitting the subscript referring to the phase) we have for an entropic material

$$\frac{\partial \boldsymbol{h}}{\partial T} = \boldsymbol{c}_p(T,P), \qquad \frac{\partial \boldsymbol{h}}{\partial P} = \boldsymbol{v}(T,P) - T\frac{\partial \boldsymbol{v}(T,P)}{\partial T}.$$

Consequently, temperature can be expressed as a function of pressure (the isenthalpic curve is the graph of a function $P \mapsto \tau(P)$; the function is the solution of the differential equation

$$\frac{dT}{dP} = j(T,P)$$

with the initial condition (T_i,P_a) where

$$j(T,P) := -\frac{\frac{\partial \boldsymbol{h}(T,P)}{\partial P}}{\frac{\partial \boldsymbol{h}(T,P)}{\partial T}} = \frac{1}{\boldsymbol{c}_p(T,P)}\left(T\frac{\partial \boldsymbol{v}(T,P)}{\partial T} - \boldsymbol{v}(T,P)\right)$$

is the **Joule–Thomson coefficient** of the material.

Then we get

$$T_f = T_i + \int_{P_a}^{P_b} j(\tau(P), P)\, dP.$$

Because of $P_a > P_b$, if the Joule–Thomson coefficient on the segment of the isenthalpic curve between P_b and P_a is

- negative, then $T_f > T_i$,
- positive, then $T_f < T_i$.

The **inversion curve** of the material is the set of points in the $T-P$ plane where the Joule–Thomson coefficient is zero:

$$\{(T,P) \mid j(T,P) = 0\}.$$

19.12.5 Joule–Thomson coefficient of an ideal gas and a van der Waals material

For an ideal gas $\boldsymbol{v}(T,P) = \frac{kT}{P}$, so

$$T\frac{\partial \boldsymbol{v}}{\partial T} - \boldsymbol{v} = 0,$$

thus the Joule–Thomson coefficient of an ideal gas is zero: the temperature of an ideal gas does not change when being pressed through a porous wall.

For a van der Waals material, differentiating the equality

$$\left(P + \frac{a}{\boldsymbol{v}(T,P)^2}\right)(\boldsymbol{v}(T,P) - b) = kT \tag{$*$}$$

with respect to T, we get

$$-\frac{2a}{\boldsymbol{v}^3}\frac{\partial \boldsymbol{v}}{\partial T}(\boldsymbol{v} - b) + \left(P + \frac{a}{\boldsymbol{v}^2}\right)\frac{\partial \boldsymbol{v}}{\partial T} = k,$$

which implies

$$T\frac{\partial \boldsymbol{v}}{\partial T} - \boldsymbol{v} = \frac{kT}{P - \frac{a}{\boldsymbol{v}^2} + \frac{2ab}{\boldsymbol{v}^3}};$$

the Joule–Thomson coefficient is not identically zero.

The inversion curve of the van der Waals material can easily be found on the $v-P$ plane, i.e. the image of the inversion curve by the function $(T,P) \mapsto \big(\boldsymbol{v}(T,P), P\big)$. Replacing kT with the left-hand side of $(*)$ in the above equality, we obtain the inversion curve:

$$\left\{(v,P) \;\middle|\; P = \frac{2a}{bv} - \frac{3a}{v^2}\right\}.$$

The initial pressure P and volume v must satisfy the inequality $P < \frac{2a}{bv} - \frac{3a}{v^2}$ for cooling the gas.

It is well seen that the inversion curve lies below the isotherm corresponding to the **inversion temperature**

$$T_{inv} := \frac{2a}{bk} = \frac{27}{4}T_c$$

and goes nearer to it when v increases. Therefore an additional necessary – but not sufficient – condition is that the initial temperature of the gas be lower than the inversion temperature.

19.12.6 Remarks

(i) Instead of the integral in 19.12.4, one writes

$$\Delta T = j(T, P)\Delta P$$

in usual treatments (where $\Delta T := T_f - T_i$, $\Delta P := P_b - P_a$), which is a good approximation of the exact formula for small pressure difference.

(ii) We emphasize that two homogeneous bodies participate in the process in question and not the isenthalpic process of a single homogeneous body occurs (which is not clarified in usual treatments).

19.13 Exercises

1. Treat the following two-body systems with diffusion:
   - the temperature of the bodies is constant (isothermal processes),
   - the pressure of the bodies is constant (isobaric processes),
   - both bodies are heat insulated individually, one of the bodies has fixed volume,
   - both bodies are heat insulated individually, one of the bodies has fixed volume and diffusion does not take place between the bodies and the environment.
2. Treat diffusion systems in which – besides other constraints such as fixed total particle number, fixed total volume, etc. – the pressure of the two bodies always coincide.
3. Show that if the total particle number, the total energy and the volume of both bodies are fixed, furthermore, the bodies are heat insulated from each other, then we cannot suppose ideal transferring. What can be said about the equilibria of such a system?
4. Find the stationary states if there is a constant particle source in one of the bodies and
   - there is no constraint,
   - there is no particle interchange between the environment and the body with source,
   - there is a particle source in the other body, too, and both bodies are heat insulated individually.

(The particle source can be positive or negative.)

20 First-order phase transitions

20.1 General formulae

20.1.1 The framework of description

In first-order phase transitions the particle number is a dynamical variable which changes in time. Therefore, such processes are similar to diffusion.

Considering a system consisting of two bodies of equal material and an environment characterized by its constant temperature and pressure, we shall examine processes that run in different phases of the bodies having a first-order connection, the bodies can interchange particles (phase transition can occur) but particles cannot be interchanged between the bodies and the environment. Zero sources and ideal working, ideal transferring are taken.

The description is obtained by a little modification of that in 19.1.1:

1. There are two given bodies of the same material $(\mathrm{D}, \mathbf{T}, \mathbf{P}, \boldsymbol{\mu}, \mathrm{R})$.

2. There are the given dynamical quantitities $\mathbf{Q}_{ik}$, $\mathbf{F}_{ik}$ and $\mathbf{G}_{ik}$, $(i = 1, 2;\ k = 0, 1, 2)$, defined on $(\mathrm{D} * \mathbb{R}_0^+) \times (\mathrm{D} * \mathbb{R}_0^+)$ $(i = 1, 2; k = 0, 1, 2)$, so that

$$\mathbf{G}_{12} \neq 0, \qquad \mathbf{G}_{1a} = 0, \qquad \mathbf{G}_{2a} = 0;$$

the dynamical quantitities are continuous and continuously differentiable on the interior of their domain and satisfy mutuality, equilibrium properties and dissipation inequalities with the notations $\mathbf{W}_{ik} := -\mathbf{P}_i F_{ik}$ and $\mathbf{L}_{ik} := -\boldsymbol{\mu}_i \mathbf{G}_{ik}$.

3. There are two given phases Z_1 and Z_2 of the material and the constant process $(T_a, P_a) \in (\mathbf{T}, \mathbf{P})[\mathrm{Z}_1 \cup \mathrm{Z}_2]$ of the environment.

4. The sources are zero.

5. The processes, considered to run in $(\mathrm{Z}_1 * \mathbb{R}_0^+) \times (\mathrm{Z}_2 * \mathbb{R}_0^+)$ are described by the dynamical equation

$$\begin{aligned}
\dot{E}_1 &= Q_{1a} + Q_{12} - P_1(F_{1a} + F_{12}) + \mu_1 G_{12}, \\
\dot{V}_1 &= F_{1a} + F_{12}, \\
\dot{N}_1 &= G_{12},
\end{aligned}$$

$$\begin{aligned}
\dot{E}_2 &= Q_{2a} + Q_{21} - P_2(F_{2a} + F_{21}) + \mu_2 G_{21}, \\
\dot{V}_2 &= F_{2a} + F_{21}, \\
\dot{N}_2 &= G_{21}.
\end{aligned}$$

Because the bodies and the environment do not interchange particles, the total particle number of the bodies is constant:

$$\dot{N}_1 + \dot{N}_2 = 0. \qquad (*)$$

Phase transition occurs in a process if there is an instant t such that $\dot{N}_1(t) \neq 0$.

In the sequel

– the dynamical quantitities are supposed to be pseudolinear, so the nominal conductance matrix has the form given in 19.1.2,

– the bodies are supposed to be entropic, so 19.1.3 will be valid.

20.1.2 Equilibrium

We are interested in equilibria and their stability. Because the processes are supposed to run in given phases which are subsets of the regular domain, we can apply the results of Section 15.

In reality if phase transition occurs between two bodies, then the bodies are in direct contact, thus heat insulation between the bodies cannot be realized, moreover, the bodies change volume at each other's cost. Therefore, we do not impose additional conditions on the dynamical quantitities between the bodies (but we can do it regarding the dynamical quantitities between a body an the environment). Thus it follows from the equilibrium properties given in 14.1 that – if neither body is 'void' – $\mathbf{Q}_{12}$, $\mathbf{F}_{12}$ and $\mathbf{G}_{12}$ (and the corresponding quantities with subscripts 21) take zero value if and only if $T_1 = T_2$, $P_1 = P_2$ and $\mu_1 = \mu_2$, i.e. we have

$$\mathbf{T}(e_{1o}, v_{1o}) = \mathbf{T}(e_{2o}, v_{2o}),$$

$$\mathbf{P}(e_{1o}, v_{1o}) = \mathbf{P}(e_{2o}, v_{2o}),$$

$$\mu(e_{1o}, v_{1o}) = \mu(e_{2o}, v_{2o})$$

for the equilibrium values of the specific quantities.

In an equilibrium (outside the zeroth-order phase connection) the bodies have the same temperatureand pressure values, and the common temperature-pressure is on the phase curve Γ.

We have supposed that the two bodies are in two different phases, thus – if we consider processes avoiding the zeroth-order phase connection – (e_{1o}, v_{1o}) and (e_{2o}, v_{2o}) are in first order connection, so $(e_{1o}, v_{1o}) \neq (e_{2o}, v_{2o})$. In other words, the both the temperature and the pressure of the bodies coincide and the common temperature-pressure is on the phase curve (see 7.6).

20.2 Phase transition in a given environment

20.2.1 The effective thermodynamical force and conductance matrix

We examine a system for which no other assumption is made besides the previous ones. This corresponds to the everyday phenomenon when water freezes (ice melts) in a given atmosphere.

The constraint $\{(0,0,1,0,0,1)\}$ (resulting in $(*)$ in 20.1) is holonomic (in fact, affine). The constraint subspaces are spanned by the vectors $(1,0,0,0,0,0)$, $(0,1,0,0,0,0)$, $(0,0,1,0,0,-1)$, $(0,0,0,1,0,0)$ and $(0,0,0,0,1,0)$.

The effective thermodynamical force is

$$\left(\frac{1}{T_1} - \frac{1}{T_a}, \frac{1}{T_2} - \frac{1}{T_a}, \frac{P_1}{T_1} - \frac{P_a}{T_a}, \frac{P_2}{T_2} - \frac{P_a}{T_a}, -\frac{\mu_1}{T_1} + \frac{\mu_2}{T_2}\right)$$

and an equilibrium with non-zero particle number is characterized indeed by its zero value.

The nominal conductance matrix $(*)$ in 19.1.2 fits the constraint if and only if multiplied by $(0,0,1,0,0,1)$ both from left and from right results in zero. Because $C_{12} = C_{21}$, this is equivalent to that the last rows and last columns of the matrices C_{1a} and C_{2a} are zero, which is an evident requirement from a physical point of view.

20.2.2 The set of equilibria

For all $N_\mathrm{s} \in \mathbb{R}^+$

$$U(N_\mathrm{s}) := \{(E_1, V_1, N_1, E_2, V_2, N_2) \mid N_1 + N_2 = N_\mathrm{s}\}$$

is a constraint submanifold of the dynamical equation.

There is no restriction on the mechanical and thermal interaction between the bodies and the environment, thus besides the equalities in 20.1.2, it is necessary and sufficient for an equilibrium that the common temperature and the pressure of the bodies be equal to the temperature and pressure of the environment, respectively; this means that the temperature–pressure of the environment must be on the phase curve. Then the specific equilibrium values $(e_{1\mathrm{o}}, v_{1\mathrm{o}})$ and $(e_{2\mathrm{o}}, v_{2\mathrm{o}})$ are uniquely determined by

$$\mathbf{T}(e_{1\mathrm{o}}, v_{1\mathrm{o}}) = T_a, \qquad \mathbf{P}(e_{1\mathrm{o}}, v_{1\mathrm{o}}) = P_a,$$

$$\mathbf{T}(e_{2\mathrm{o}}, v_{2\mathrm{o}}) = T_a, \qquad \mathbf{P}(e_{2\mathrm{o}}, v_{2\mathrm{o}}) = P_a.$$

Proposition *The set of equilibria with non-zero particle number in $U(N_\mathrm{s})$ is*

$$Eq(N_\mathrm{s}) := \{(N_1 e_{1\mathrm{o}}, N_1 v_{1\mathrm{o}}, N_1, (N_\mathrm{s} - N_1)e_{2\mathrm{o}}, (N_\mathrm{s} - N_1)v_{2\mathrm{o}}, N_\mathrm{s} - N_1) \mid 0 < N_1 < N_\mathrm{s}\}.$$

The set of equilibria is a straight line segment: a submanifold whose tangent space at every point is spanned by $(e_{1\mathrm{o}}, v_{1\mathrm{o}}, 1, -e_{2\mathrm{o}}, -v_{2\mathrm{o}}, -1)$.

20.2.3 Stability of equilibria

Proposition *If the bodies are entropic, the nominal conductance matrix* $(*)$ *in 19.1.2 fits the constraint, its equilibrium value is symmetric, positive semidefinite having the kernel spanned by* $(0, 0, 1, 0, 0, 1)$*, then* $Eq(N_\mathrm{s})$ *is strictly asymptotically stable in* $U(N_\mathrm{s})$*.*

Proof In an arbitrary equilibrium, the kernel of $\mathtt{D}^2\mathbf{L}$ is spanned by the vectors $(e_{1\mathrm{o}}, v_{1\mathrm{o}}, 1, 0, 0, 0)$ and $(0, 0, 0, e_{2\mathrm{o}}, v_{2\mathrm{o}}, 1)$. An element which is both in this kernel and in the corresponding constraint subspace has the form $\alpha(e_{1\mathrm{o}}, v_{1\mathrm{o}}, 1, 0, 0, 0) + \beta(0, 0, 0, e_{2\mathrm{o}}, v_{2\mathrm{o}}, 1)$ in such a way that $\beta = -\alpha$, in other words, it is a multiple of $(e_{1\mathrm{o}}, v_{1\mathrm{o}}, 1, -e_{2\mathrm{o}}, -v_{2\mathrm{o}}, -1)$. Thus the intersection of the equilibrium kernel of $\mathtt{D}^2\mathbf{L}$ and the corresponding constraint subspace equals the corresponding tangent space of $Eq(N_\mathrm{s})$.

All the conditions of Proposition 15.8 are satisfied.

Remark The treatment of this system is similar to that of 19.4; the only difference is that here the corresponding specific quantities of the bodies do not have the same value.

20.3 Phase transition insulated from the environment

20.3.1 The effective thermodynamical force and conductance matrix

We examine a system in which the bodies are completely insulated from the environment. This corresponds to the everyday phenomenon when water boils in a closed pot.

In this case, besides the previous assumptions, we have $\mathbf{F}_{1a} = \mathbf{F}_{2a} = 0$ and $\mathbf{Q}_{1a} = \mathbf{Q}_{2a} = 0$, too, thus

$$\dot{E}_1 + \dot{E}_2 = 0, \qquad \dot{V}_1 + \dot{V}_2 = 0, \qquad \dot{N}_1 + \dot{N}_2 = 0,$$

which means a holonomic (in fact, affine) constraint. The constraint subspaces are spanned by the vectors $(1,0,0,-1,0,0)$, $(0,1,0,0,-1,0)$ and $(0,0,1,0,0,-1)$.

The effective thermodynamical force is

$$\left(\frac{1}{T_1} - \frac{1}{T_2}, \frac{P_1}{T_1} - \frac{P_2}{T_2}, -\frac{\mu_1}{T_1} + \frac{\mu_2}{T_2}\right).$$

The nominal conductance matrix $(*)$ in 19.1.2 fits the constraint if and only if multiplied by the vectors $(1,0,0,1,0,0)$, $(0,1,0,0,1,0)$ and $(0,0,1,0,0,1)$ it results in zero. Because $C_{12} = C_{21}$, this is equivalent to $C_{1a} = C_{2a} = 0$, which is a natural requirement.

20.3.2 Uniqueness of equilibrium

For all $E_\mathrm{s} \in (\mathrm{J})^+$, $V_\mathrm{s} \in (\mathrm{m}^3)^+$ and $N_\mathrm{s} \in \mathbb{R}^+$

$$U(E_\mathrm{s}, V_\mathrm{s}, N_\mathrm{s}) := \{(E_1, V_1, N_1, E_2, V_2, N_2) \mid \\ E_1 + E_2 = E_\mathrm{s},\ V_1 + V_2 = V_\mathrm{s},\ N_1 + N_2 = N_\mathrm{s}\}$$

is a constraint submanifold of the dynamical equation.

The specific equilibrium values $(e_{1\mathrm{o}}, v_{1\mathrm{o}}) \in \mathrm{C}_1$ and $(e_{2\mathrm{o}}, v_{2\mathrm{o}}) \in \mathrm{C}_2$ and the equilibrium particle numbers $N_{1\mathrm{o}}$ and $N_{2\mathrm{o}}$, besides the three equalities in 20.1.2 must satisfy the following three ones, too:

$$N_{1\mathrm{o}}e_{1\mathrm{o}} + N_{2\mathrm{o}}e_{2\mathrm{o}} = E_\mathrm{s}, \quad N_{1\mathrm{o}}v_{1\mathrm{o}} + N_{2\mathrm{o}}v_{2\mathrm{o}} = V_\mathrm{s}, \quad N_{1\mathrm{o}} + N_{2\mathrm{o}} = N_\mathrm{s}.$$

The six equilibrium quantities are not (locally) uniquely determined by the six equalities above. Nevertheless, the equilibrium is locally unique in $U(E_\mathrm{s}, V_\mathrm{s}, N_\mathrm{s})$ as it turns out from the following result on asymptotic stability.

20.3.3 Stability of equilibrium

Proposition *If the bodies are entropic, then the equilibrium*

$$(N_{1\mathrm{o}}e_{1\mathrm{o}}, N_{1\mathrm{o}}v_{1\mathrm{o}}, N_{1\mathrm{o}}, N_{2\mathrm{o}}e_{2\mathrm{o}}, N_{2\mathrm{o}}v_{2\mathrm{o}}, N_{2\mathrm{o}})$$

determined above is asymptotically stable in $U(E_\mathrm{s}, V_\mathrm{s}, N_\mathrm{s})$ *(even if the dynamical quantitities are not pseudolinear).*

Proof The equilibrium kernel of $\mathtt{D}^2\mathbf{L}$ is spanned by the vectors $(e_{1\mathrm{o}}, v_{1\mathrm{o}}, 1, 0, 0, 0)$ and $(0, 0, 0, e_{2\mathrm{o}}, v_{2\mathrm{o}}, 1)$. An element both in this kernel and in the corresponding constraint subspace has the form $\alpha(e_{1\mathrm{o}}, v_{1\mathrm{o}}, 1, 0, 0, 0) + \beta(0, 0, 0, e_{2\mathrm{o}}, v_{2\mathrm{o}}, 1)$ in such a way that $\beta e_{2\mathrm{o}} = -\alpha e_{1\mathrm{o}}$, $\beta v_{2\mathrm{o}} = -\alpha v_{1\mathrm{o}}$, $\beta = -\alpha$ which implies $\alpha = \beta = 0$ because $e_{1\mathrm{o}} \neq e_{2\mathrm{o}}$ and $v_{1\mathrm{o}} \neq v_{2\mathrm{o}}$. Thus the intersection of the equilibrium kernel of $\mathtt{D}^2\mathbf{L}$ and the corresponding constraint subspace equals zero.

All the conditions of Proposition 15.6 are satisfied.

Remark It is interesting that the treatment of this system started as that of 19.4 but ended differently: here the equilibrium in the constraint submanifold is locally unique.

20.4 Supercooling, superheating

It is well known that highly pure water can be cooled carefully below the freezing-point without being frozen or can be heated over the boiling-point without being boiled. If something disturbs the supercooled or superheated water – e.g. a lslight shock – then freezing or boiling starts ‘dramatically’.

These phenomena can be treated in our framework by taking into account equilibria with zero particle number.

20.4.1 Equilibria with zero particle number

Let us consider first-order phase transitions in a given environment described in 20.2. Then

$$(0, 0, 0, N_\mathrm{s} e_{2\mathrm{o}}, N_\mathrm{s} v_{2\mathrm{o}}, N_\mathrm{s}) \qquad (*)$$

is an equilibrium where the equilibrium specific values $e_{2\mathrm{o}}$ and $v_{2\mathrm{o}}$ are uniquely determined by

$$\mathbf{T}(e_{2\mathrm{o}}, v_{2\mathrm{o}}) = T_a, \qquad \mathbf{P}(e_{2\mathrm{o}}, v_{2\mathrm{o}}) = P_a,$$

where (T_a, P_a) can be an arbitrary element of $(\mathbf{T}, \mathbf{P})[\mathrm{Z}_2]$ (it need not be on the phase curve Γ). Of course, similar assertions are true for $(N_s e_{1\mathrm{o}}, N_\mathrm{s} v_{1\mathrm{o}}, N_\mathrm{s}, 0, 0, 0)$.

Thus if one of the bodies has zero particle number and the temperature value and the pressure value of the other body equal those of the environment, then the system is in equilibrium even if the temperature–pressure of the environment is not on the phase curve.

20.4.2 Processes with zero particle number

We can say more. Let a process start in such a way that one of the bodies has zero particle number (and then, of course, it has zero energy and zero volume). Then the process – the solution of the dynamical equation with the given initial condition – proceeds in such a way that the energy, volume and particle number always have zero value.

It seems, the problem is reduced to the one in which a body with constant particle number is in a given environment (see 12.3). We know, e.g. that in this case the equilibrium of an entropic body is asymptotically stable which implies that the process tends to the equilibrium $(*)$. This involves supercooling and superheating: a body in a given phase which is not in contact with another body in another phase can be cooled or heated arbitrarily without phase transition.

Let us see clearly what the matter is. A process starting with zero particle number of the first body, tends to the equilibrium $(*)$, and during the process the first body remains empty. This does not mean, however, that the equilibrium is asymptotically stable. Namely, it can be happen that a process starting with an 'arbitrarily small' particle number of the first body 'runs away' from the equilibrium $(*)$. And just this happens in supercooling and superheating. The mentioned disturbance – e.g. a shock – produces a 'nucleus' (a small amount of material in the other phase) which suffices to break equilibrium.

20.4.3 The question of stability

At present I cannot formulate exact statements about the stability of the equilibrium $(*)$ because this equilibrium is on the boundary of the dynamical equation and I do not know mathematical results in this respect. Nevertheless, we can make some remarks which suggest the result in accordance with our expectation.

Let $\Phi := (\mathbf{T},\mathbf{P})[\mathrm{Z}_1 \setminus \overline{\mathrm{Z}_2}] \cap (\mathbf{T},\mathbf{P})[\mathrm{Z}_2 \setminus \overline{\mathrm{Z}_1}]$ and

$$\Delta_1 := \{(T,P) \in \Phi \mid \mu_1(T,P) < \mu_2(T,P)\},$$

$$\Delta_2 := \{(T,P) \in \Phi \mid \mu_1(T,P) > \mu_2(T,P)\}.$$

According to 14.1, for $N_1N_2 \neq 0$

- if $(T,P) \in \Delta_1$, then $G_{12} > 0$,
- if $(T,P) \in \Delta_2$, then $G_{12} < 0$.

Let us suppose that $(T_a,P_a) \in \Delta_1$. If the equilibrium $(*)$ is disturbed by an 'arbitrarily small' non-zero particle number of the first body, then G_{12} becomes positive, implying that the particle number of the first body increases: the process leaves the equilibrium. This corresponds to the supercooled or superheated state.

Let us suppose that $(T_a,P_a) \in \Delta_2$. If the equilibrium $(*)$ is disturbed by a sufficiently 'small' but non-zero particle number of the first body, then G_{12} becomes negative, implying that the particle number of the first body decreases until the first body becomes empty: the process returns to the equilibrium. This corresponds to the 'normal everyday' state.

20.4.4 'Metastability'

In the literature one frequently states that phase transitions are "intimately related to the violation of stability criteria";"if the stability criteria are not satisfied, the system breaks up into two or more portions.This separation is called phase transition" [1]. It seems, this is not correct.

As concerns second-order phase transitions, we have that

- there is no instability in second-order phase transitions of the Ehrenfest type,
- instability may or may not occur in second-order phase transitions of the Tisza type.

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[1] H. B. Callen: *Thermodynamics*, John Wiley and Sons NY, 1985, pp. 136, 146

Moreover, it is clear that first-order phase transitions are not related to the violation of intrinsic stability: the curves of the first-order phase connection (‘binodal lines’) are in the regular domain of the substance.

The van der Waals materials reflect well the characteristics of the liquid phase and the gaseous phase of real materials. Let us recall Paragraph 6.3 and Figure 7.3.

The spinodal lines S_1 and S_2 delineate the boundary of the constitutive domain; the part between them does not belong to the constitutive domain. In usual treatments (where constitutive domain is not defined at all) one says that this part is the set of instable states because there the condition of intrinsic stability $\partial\mathcal{P}/\partial v < 0$ is not satisfied.

The part between the spinodal line S_1 and binodal line C_1 contains the superheated liquid states where $\mu_{\text{liquid}} > \mu_{\text{gas}}$; the part between the spinodal line S_2 and the binodal line C_2 contains the supercooled gaseous (vapour) states where $\mu_{\text{liquid}} < \mu_{\text{gas}}$.

One usually calls these states metastable (without defining the notion of metastability); this name is destined to express that these states are instable in some sense though the intrinsic stability conditions are satisfied. This confusion of ‘stable-metastable-unstable’ is based on the improper use of the notion ‘state,. Namely, the state of a body is a triplet (e, v, N): the couple (e, v) is not a state.

We emphasize that

– the conditions of intrinsic stability are satisfied at all (e, v) in a phase.

Nevertheless, an equilibrium (e, v, N) is

– asymptotically stable if (e, v) is over the binodal line (in the previous notations: $\big(\mathbf{T}(e, v), \mathbf{P}(e, v)\big) \in \Delta_1$),

– unstable if (e, v) is under the binodal line (in the previous notations: $\big(\mathbf{T}(e, v), \mathbf{P}(e, v)\big) \in \Delta_2$).

20.5 Exercise

If the entire quantities are used, then the equilibrium values (E_{1o}, V_{1o}, N_{1o}) and (E_{2o}, V_{2o}, N_{2o}) for the bodies insulated from the environment are determined by the equalities

$$\mathbf{T}(E_{1o}, V_{1o}, N_{1o}) = \mathbf{T}(E_{2o}, V_{2o}, N_{2o}),$$

$$\mathbf{P}(E_{1o}, V_{1o}, N_{1o}) = \mathbf{P}(E_{2o}, V_{2o}, N_{2o}),$$

$$\mu(E_{1o}, V_{1o}, N_{1o}) = \mu(E_{2o}, V_{2o}, N_{2o}),$$

$$E_{1o} + E_{2o} = E_s, \quad V_{1o} + V_{2o} = V_s, \quad N_{1o} + N_{2o} = N_s$$

or, equivalently,

$$\mathbf{T}(E_{1o}, V_{1o}, N_{1o}) = \mathbf{T}(E_s - E_{1o}, V_s - V_{1o}, N_s - N_{1o}),$$

$$\mathbf{P}(E_{1o}, V_{1o}, N_{1o}) = \mathbf{P}(E_s - E_{1o}, V_s - V_{1o}, N_s - N_{1o}),$$

$$\mu(E_{1o}, V_{1o}, N_{1o}) = \mu(E_s - E_{1o}, V_s - V_{1o}, N_s - N_{1o}).$$

Demonstrate (with the aid of the implicit function theorem) that the above equalities determine (E_{1o}, V_{1o}, N_{1o}) locally uniquely.

VI COMPOSITE MATERIALS (MIXTURES, SOLUTIONS)

21 Constitutive functions

21.1 Concentrations

Now we consider materials consisting of diverse neutral molecules which can be conceived as mixtures of simple materials; everyday examples are the mixtures of gases (air) and liquids (brandy), solutions, alloys, etc. Such a composite material is determined by its components. A special characteristic of a composite material is the particle proportion of the components which is expressed by the **concentrations**. If the mixture is composed of the materials denoted by $\alpha = 1, 2, ..., m$ and in a body containing N particles the particle number of the α-th component is N^α, then $c^\alpha = \frac{N^\alpha}{N}$ is the concentration of the α-th component. The concentrations are not independent: their sum equals 1 because $\sum\limits_{\alpha=1}^{m} N^\alpha = N$.

Thus, we can say that the set of possible concentrations is

$$\mathrm{C}_m := \{c = (c^1, \dots, c^m) \in \mathbb{R}^m \mid 0 < c^\alpha < 1,\ \alpha = 1, \dots, m,\ \sum_{\alpha=1}^{m} c^\alpha = 1\}.$$

In the sequel we always use the notations and relations of App. 8; moreover, if X is a set and f is a function defined in $X \times \mathrm{C}_m$, then $\frac{\partial f}{\partial c}$ denotes the partial derivative with respect to the variable in C_m (i.e. the derivative of the function $f(x, \cdot)$ with fixed x-s). It is emphasized that this partial derivative is not the collection of the partial derivatives with respect to the components of c because those make no sense.

21.2 Definition of composite materials

The fundamental thermodynamical quantities of a composite material are the specific internal energy e, the specific volume v, the temperature T, the pressure P, the concentrations $c = (c^1, \dots, c^m)$ and the chemical potentials of the components $\mu^1, \dots, \mu^m$. These quantities are related to each other characterizing the material.

Definition *Let $m \geq 2$ be a positive integer.*

A **mixture** *of the simple materials* $(D_\alpha, \mathfrak{e}_\alpha, \mathcal{P}_\alpha, \boldsymbol{\mu}_\alpha, R_\alpha)$ $(\alpha = 1,.. ..,m)$ *is* $(D, \mathfrak{e}, \mathcal{P}, \boldsymbol{\mu}^1, \dots, \boldsymbol{\mu}^m, R)$*, where* *(i)* $D \subset (\mathrm{m}^3)^+ \times (\mathrm{K})^+ \times C_m$ *is a non-void subset, the* **constitutive domain***,*

(ii) $\mathfrak{e} : D \to (\mathrm{J})^+, \qquad \mathcal{P} : D \to (\mathrm{Pa}), \qquad \mu^\alpha : D \to (\mathrm{J})\ (\alpha = 1, \dots, m),$
the **constitutive functions***, are continuous; the function* $T \mapsto \mathfrak{e}(v, T, c)$ *is strictly monotone increasing for all possible* v *and* c*, the function* $v \mapsto \mathcal{P}(v, T, c)$ *is locally strictly monotone decreasing for all possible* T *and* c*,*

(iii) R *is a non-void open dense subset of* D*, the* **regular domain***, on which the constitutive functions are continuously differentiable and satisfy the conditions of* **intrinsic stability***:*

$$\frac{\partial \mathfrak{e}}{\partial T} > 0, \qquad \frac{\partial \mathcal{P}}{\partial v} < 0,$$

$$\frac{\partial[\mu^1, \dots, \mu^m]}{\partial c} \quad \textit{is positive definite},$$

(iv) the following conditions of **purity limit** *are satisfied:*

$$\{(v, T, (1)^\alpha) \mid (v, T) \in D_\alpha\} \subset \overline{D} \qquad (\alpha = 1, \dots, m)$$

and

$$\lim_{c \to (1)^\alpha} (\mathfrak{e}, \mathcal{P}, \mu^\alpha)(v, T, c) = (\mathfrak{e}_\alpha, \mathcal{P}_\alpha, \mu_\alpha)(v, T).$$

for all α *and* $(v, T) \in D_\alpha$*.*

The third condition of intrinsic stability requires that the derivative of the function

$$[\mu^1, \dots, \mu^m](v, T, \cdot) : C_m \rightarrowtail (\mathrm{J})\mathbf{D}_m^*$$

be positive definite for all fixed v and T.

Item (*iv*) in the definition formulates the reasonable requirement that if the concentrations of all components but one tend to zero, then a pure simple material is obtained (if salt becomes less and less in a water-salt solution, then finally we get pure water).

The simple materials entering the definition of mixtures are called the **components** of the mixture.

Note: the simple materials in question are referred to by superscripts $^\alpha$ when considered as components of the mixture and by subscripts $_\alpha$ when considered as independent materials.

Sometimes we use the specific volume of the components,

$$v^\alpha = \frac{v}{c^\alpha}$$

which has the following meaning: if a body of composite material has volume V, particle number N, then $v = \frac{V}{N}$, and if N^α is the particle number of the α-th component, then $v^\alpha = \frac{V}{N^\alpha} = \frac{V}{N}\frac{N}{N^\alpha}$.

21.3 Convention about notations

Let us recall that we can easily handle the differentiation of functions of the concentrations by choosing $(m-1)$ independent concentrations – let them be the first $(m-1)$ ones – for parameterizing C_m.

For the sake of simplicity, the parameterized functions will be denoted by the same symbol as the original one; thus, according to the definition,

$$\tilde{\mathfrak{e}}(v,T,\tilde{c}) := \mathfrak{e}\left(v,T,c^1,\dots,c^{m-1},1-\sum_{\alpha=1}^{m-1}c^\alpha\right)$$

but in the sequel we write $\mathfrak{e}(v,T,c)$ instead of $\tilde{\mathfrak{e}}(v,T,\tilde{c})$ and we keep in mind that then c^m is considered as a function of $c^1,\dots,c^{m-1}$ and

$$\frac{\partial c^m}{\partial c^\beta} = -1 \qquad (\beta = 1,\dots,m-1).$$

21.4 Change coefficients

Consider processes of a mixture in which the concentrations do not change. Then the same change coefficients can be defined and treated as in Section 3 for simple materials: specific heats, compressibility factor, etc.

21.5 Canonical variables

As in the case of simple materials, temperature is a strictly monotone increasing function of specific internal energy; therefore, specific internal energy can be used instead of temperature as an independent variable. We use the customary notations:

$$\mathrm{D} := \{(\mathfrak{e}(v,T,c),c) \mid (v,T,c) \in D\}, \qquad \mathrm{R} := \{(\mathfrak{e}(v,T,c),v,c) \mid (v,T,c) \in R\},$$

furthermore, the functions $\mathbf{T}$, $\mathbf{P}$ and $\boldsymbol{\mu}^\alpha$ defined on D are the temperature, the pressure and the chemical potentials, respectively, as functions of specific internal energy, specific volume and concentrations,

$$\mathfrak{e}(v,\mathbf{T}(e,v,c),c) = e, \qquad \mathcal{P}(v,\mathbf{T}(e,v,c),c) = \mathbf{P}(e,v,c),$$
$$\mu^\alpha(v,\mathbf{T}(e,v,c),c) = \boldsymbol{\mu}^\alpha(e,v,c),$$

or

$$\mathbf{T}(\mathfrak{e}(v,T,c),v,c) = T, \qquad \mathcal{P}(v,T,c) = \mathbf{P}(\mathfrak{e}(v,T,c),v,c),$$
$$\boldsymbol{\mu}^\alpha(\mathfrak{e}(v,T,c),v,c) = \mu^\alpha(v,T,c).$$

As a consequence, a composite material will be referred to by $(\mathrm{D},\mathbf{T},\mathbf{P},\boldsymbol{\mu}^1,\dots,\boldsymbol{\mu}^m,\mathrm{R})$, too.

We have to take care only that item (*iv*) of Definition 21.2, written in a similar form for the canonical variables does not hold necessarily.

Definition *The mixture is called* **canonically good** *if*

$$\lim_{c\to(1)^\alpha} \mathbf{T}(e,v,c) = \mathbf{T}_\alpha(e,v) \qquad (*)$$

for all $(e,v) \in \mathrm{R}_\alpha$.

The mixture is canonically good, e.g. if its specific heat remains bounded when its composition tends to a pure material (see Exercise 4 in 21.8).

21.6 Entropic property

Definition *The* **specific entropy** *of the mixture in Definition 21.2 is*

$$\mathfrak{s} := \frac{\mathfrak{e} + \mathcal{P}v - \sum\limits_{\alpha=1}^{m} c^\alpha \upmu^\alpha}{T} : D \to (\mathrm{J/K})$$

The mixture is **entropic** *if*

$$T\frac{\partial \mathfrak{s}}{\partial v} = \frac{\partial \mathfrak{e}}{\partial v} + \mathcal{P}, \qquad T\frac{\partial \mathfrak{s}}{\partial T} = \frac{\partial \mathfrak{e}}{\partial T}, \qquad T\frac{\partial \mathfrak{s}}{\partial c} = \frac{\partial \mathfrak{e}}{\partial c} - [\upmu^1, \dots, \upmu^m].$$

The entropic property in the canonical variables reads as follows:

$$\frac{\partial \mathbf{s}}{\partial e} = \frac{1}{\mathbf{T}}, \qquad \frac{\partial \mathbf{s}}{\partial v} = \frac{\mathbf{P}}{\mathbf{T}}, \qquad \frac{\partial \mathbf{s}}{\partial c} = -\frac{[\boldsymbol{\mu}^1, \dots, \boldsymbol{\mu}^m]}{\mathbf{T}},$$

where, of course, $\mathbf{s}(e, v, c) := \mathfrak{s}\big(v, \mathbf{T}(e, v, c,), c\big)$.

If C_m is parameterized by the first $m-1$ components of its elements, then according to App. 8 and our convention in 21.3, the entropic property regarding concentrations becomes

$$T\frac{\partial \mathfrak{s}}{\partial c^\beta} = \frac{\partial \mathfrak{e}}{\partial c^\beta} - (\upmu^\beta - \upmu^m) \qquad (\beta = 1, \dots, m-1),$$

or

$$\frac{\partial \mathbf{s}}{\partial c^\beta} = -\frac{\boldsymbol{\mu}^\beta - \boldsymbol{\mu}^m}{\mathbf{T}} \qquad (\beta = 1, \dots, m-1).$$

The conditions of intrinsic stability and Proposition 16.4 imply the following important result:

Proposition *If the mixture is entropic, then the second derivative of the specific entropy as a function of the canonical variables is negative definite on the regular domain.*

The conditions of intrinsic stability also imply that on the regular domain – at least locally – pressure is a strictly monotone decreasing function, thus on the regular domain – at least locally – temperature, pressure and concentrations can be used as independent variables. We use symbols similar to those for simple materials: $\boldsymbol{v}$, $\boldsymbol{s}$ and μ^α denote specific volume, specific entropy and chemical potentials, respectively, as functions of temperature, pressure and concentrations on a subset corresponding to an open subset of the regular domain, e.g. $\boldsymbol{s}\big(T, \mathcal{P}(v, T, c), c\big) = \mathfrak{s}(v, T, c)$. Now temperature and pressure (and concentrations) do not characterize a whole phase (see Section 25), contrary to the case of simple materials.

These variables are the most suitable to express the **Gibbs–Duhem relations** for entropic mixtures:

$$\sum_{\alpha=1}^{m} c^\alpha \frac{\partial \mu^\alpha}{\partial T} = -\boldsymbol{s}, \qquad \sum_{\alpha=1}^{m} c^\alpha \frac{\partial \mu^\alpha}{\partial P} = \boldsymbol{v}.$$

21.7 A useful formalism

Symbolic notations similar to those in Paragraph 6.7 are useful for mixtures, too. Introducing the **Gibbs function** in the symbolic form

$$g := \sum_{\alpha=1}^{m} c^\alpha \mu^\alpha = e - Ts + Pv$$

(called sometimes specific free enthalpy) we have

$$s := \frac{e + Pv - g}{T},$$
$$f := e - Ts = g - Pv,$$
$$h := e + Pv = Ts + g$$

the specific entropy, the specific free energy and the specific enthalpy which can be actually considered as functions of (e, v, c), (v, T, c) or (T, P, c).

Then the entropic property has the symbolic form

$$T\mathtt{d}s = \mathtt{d}e + P\mathtt{d}v - \sum_{\alpha=1}^{m} \mu^\alpha \mathtt{d}c^\alpha \tag{$*$}$$

from which we easily find relations among the partial derivatives of diverse functions, as said in Paragraph 6.7. We have to be cautious only because there are no partial derivatives according to the concentrations because they are not independent which is expressed symbolically by

$$\sum_{\alpha=1}^{m} \mathtt{d}c^\alpha = 0. \tag{$**$}$$

Equalities $(*)$ and $(**)$ together give the relations among the partial derivatives with respect to concentrations chosen as independent.

The symbolic form of the Gibbs–Duhem relations – on the basis of the 'rules' $\mathtt{d}(Pv) = P\mathtt{d}v + v\mathtt{d}P$, etc. – becomes

$$\sum_{\alpha=1}^{m} c^\alpha \mathtt{d}\mu^\alpha = -s\mathtt{d}T + v\mathtt{d}P$$

or, equivalently,

$$\mathtt{d}g = v\mathtt{d}P - s\mathtt{d}T + \sum_{\alpha=1}^{m} \mu^\alpha \mathtt{d}c^\alpha.$$

21.8 Exercises

1. Let m_α be the mass of a molecule of the α-th material. Then

$$m(c) := \sum_{\alpha=1}^{m} c^\alpha m_\alpha.$$

is the ‘average mass’ of a molecule of a mixture with concentrations c.

2. In practice one often uses mass concentrations instead of particle concentrations. Using the notations of the previous exercise, prove that the mass concentration is

$$c^\alpha \frac{m_\alpha}{m(c)}.$$

3. Can the mixture of entropic materials be non-entropic? Can the mixture of non-entropic materials be entropic?

4. Let us take a mixture in canonical form. Let us suppose that for every $(e,v) \in \mathrm{R}_\alpha$, e has a neighbourhood K and $(1)^\alpha \in \overline{C}_m$ has a neighbourhood G such that

$$\sup_{e\in K, c\in G} \left| \frac{\partial \mathbf{T}}{\partial e}(e,v,c) \right| < \infty,$$

then relation $(*)$ in 21.5 is satisfied (see App. 9).

22 Ideal mixtures

22.1 Definition of an ideal mixture

Let us mix materials having the same temperature and let us suppose that the molecules of different materials do not interact. Then the internal energy of the mixture becomes the sum of the internal energies of the components; applying a symbolic notation, $Ne = N^1 e_1 + \dots + N^m e_m$, from which we get $e = c^1 e_1 + \dots + c^m e_m$. Furthermore, the pressure of the mixture will be the sum of the pressures of the components separately. As a first attempt, let us suppose that the chemical potentials of the components in the mixture do not differ significantly from the chemical potentials of the corresponding pure materials: the difference is an additive term proportional to temperature, the proportionality factor can depend on the concentrations.

We try to describe such an **ideal mixture** as follows.

Let us take the simple materials $(D_\alpha, \mathfrak{e}_a, \mathcal{P}_a, \boldsymbol{\mu}_a, R_\alpha)$ and let us recall that the specific volume of the α-th component in the mixture is $\frac{v}{c^\alpha}$.

Let us suppose that the set

$$D_0 := \left\{ (v,T,c) \in (\mathrm{m}^3) \times (\mathrm{K}) \times \mathrm{C}_m \;\middle|\; \left(\frac{v}{c^\alpha}, T\right) \in D_\alpha,\ \alpha = 1,\dots,m \right\}$$

is not void and let us define on D_0 the functions

$$\mathfrak{e}(v,T,c) := \sum_{\alpha=1}^{m} c^\alpha \mathfrak{e}_\alpha \left(\frac{v}{c^\alpha}, T\right), \tag{1}$$

$$\mathcal{P}(v,T,c) := \sum_{\alpha=1}^{m} \mathcal{P}_\alpha \left(\frac{v}{c^\alpha}, T\right), \tag{2}$$

$$\boldsymbol{\mu}^\alpha(v,T,c) := \boldsymbol{\mu}_\alpha \left(\frac{v}{c^\alpha}, T\right) + T\varphi^\alpha(c^\alpha), \tag{3}$$

where $\varphi^\alpha : [0,1] \to (\mathrm{J/K})$ is a continuously differentiable function for which $\varphi^\alpha(1) = 0$ holds ($\alpha = 1, \dots, m$).

The above functions are continuously differentiable on the set

$$R_0 := \left\{ (v, T, c) \in (\mathrm{m}^3) \times (\mathrm{K}) \times \mathrm{C}_m \;\middle|\; \left(\frac{v}{c^\alpha}, T \right) \in R_\alpha,\ \alpha = 1, \dots, m \right\}.$$

We mention that the functions

$$f_\alpha : (\mathrm{m}^3)^+ \times (\mathrm{K})^+ \times \mathrm{C}_m \to (\mathrm{m}^3)^+ \times (\mathrm{K})^+, \quad (v, T, c) \to \left(\frac{v}{c^\alpha}, T \right)$$

are infinitely differentiable and

$$D_0 = \bigcap_{\alpha=1}^{m} \overset{-1}{f_\alpha}(D_\alpha), \qquad R_0 = \bigcap_{\alpha=1}^{m} \overset{-1}{f_\alpha}(R_\alpha).$$

R_0 is open because of the continuity of f_α-s.

It is not sure that D_0 and R_0 are good for a domain and a regular domain, respectively, of a mixture because the functions (1)–(3) need not satisfy the purity limit conditions on D_0 and the stability conditions on R_0.

Definition *Let D_p be the subset of D_0 on which the functions (1)–(3) satisfy the purity limit conditions and let R_s be the subset of R_0 on which the functions (1)–(3) satisfy the intrinsic stability conditions. Supposing that the interior R of $D_p \cap R_s$ is not void, put $D := \overline{R}$. Then taking D as the constitutive domain, R as the regular domain, and the restrictions of the functions (1)–(3) onto D, we define the* **ideal mixture** *of the simple materials $(D_\alpha, \mathfrak{e}_a, \mathcal{P}_a, \boldsymbol{\mu}_a, R_\alpha)$.*

Equalities (1)–(3) give the specific entropy of the ideal mixture:

$$\mathfrak{s}(v, T, c) = \sum_{\alpha=1}^{m} c^\alpha \left(\mathfrak{s}_a \left(\frac{v}{c^\alpha}, T \right) - \varphi^\alpha(c^\alpha) \right). \tag{4}$$

In the next two paragraphs we examine what properties of the components assure that the purity limit condition and the conditions of intrinsic stability hold on (a sufficiently large subset of) D_0 and R_0, respectively.

22.2 The purity conditions

22.2.1 Mathematical formulation

First, we examine the accumulation points of D_0. Let us introduce

$$H_{T,\alpha} := \{ v \in (\mathrm{m}^3) \mid (v, T) \in D_\alpha \}$$

for all $T \in (\mathrm{K})^+$ and $\alpha = 1, \dots, m$.

Proposition 1 *Let $\alpha = 1, \dots, m$. Then $(v, T, (1)^\alpha) \in \overline{D_0}$ if and only if $(v, T) \in \overline{D_\alpha}$ and $H_{T,\beta}$ is unbounded from above for all $\beta \neq \alpha$.*

Proof Let us take $\alpha = m$. $(v, T, (1)^m) \in \overline{D_0}$ if and only if for all $\epsilon > 0$ there are positive numbers $c^1, \dots, c^{m-1} < \epsilon$ and $c_m > 1-\epsilon$ in such a way that $\left(\frac{v}{c^\alpha}, T\right) \in D_\alpha$ for all α, which is equivalent to that $(v, T) \in \overline{D_m}$ and $H_{T,\beta}$ is unbounded from above for all $\beta \neq m$.

Proposition 2 *If for all* $\alpha = 1, \dots, m$ *and* $(v, T) \in D_\alpha$ *and for all* $\beta \neq \alpha$ *we have that*

(i) $H_{T,\beta}$ *is unbounded from above,*

(ii) the function $\nu \mapsto \mathfrak{e}_\beta(\nu, T)$ *is bounded at the infinity,*

(iii) $\lim\limits_{\nu \to \infty} \mathcal{P}_\alpha(\nu, T) = 0$,

then the functions (1)–(3) satisfy the purity limit conditions on D_0.

Proof According to the previous proposition, assumption (i) implies that $(v, T, (1)^\alpha) \in \overline{D_0}$; assumptions (ii) and (iii) and $\varphi^\alpha(1) = 0$ imply that the functions (1)–(3) satisfy the limit relations in item (iv) of Definition 21.2.

22.2.2 Physical content

Let us take two liquids (say water and alcohol). At a given temperature, their specific volume can change in a relatively small (thus bounded) interval (they extend very little as pressure decreases). Therefore, their mixture cannot be ideal.

We can make this evident. Let us imagine an amount of the homogeneous mixture of the liquids in the atmosphere (at temperature T and pressure P). The pressures P_1 and P_2 of the liquids in the mixture are less than P. We can obtain the specific volumes $v^1 = v/c^1$ and $v^2 = v/c^2$ of the liquids in such a way that we consider the particles of the other liquid as missing from the recipient. So we would get pure liquids with rather large specific volume which do not exist in reality. More closely: at least one of v^1 and v^2 is greater than the specific volume of the corresponding liquid at temperature T and pressure P_1 and P_2, respectively.

22.3 The intrinsic stability conditions

Proposition *The functions (1)–(3) satisfy the conditions of intrinsic stability on the subset of* R_0 *consisting of the elements* (v, T, c) *for which*

$$-\frac{v}{(c^\alpha)^2}\frac{\partial \mu_\alpha}{\partial v}\left(\frac{v}{c^\alpha}, T\right) + T\,(\varphi^\alpha)'\,(c^\alpha) > 0$$

holds for all $\alpha = 1, \dots, m$.

Proof It is quite simple that the first and second stability conditions in Definition 21.2 are valid on R_0 because $\mathfrak{e}$ and $\mathcal{P}$ are continuously differentiable there and (with a somewhat loose notation)

$$\frac{\partial \mathfrak{e}}{\partial T} = \sum_{\alpha=1}^{m} c^\alpha \frac{\partial \mathfrak{e}_\alpha}{\partial T} > 0,$$

$$\frac{\partial \mathcal{P}}{\partial v} = \sum_{\alpha=1}^{m} \frac{1}{c^\alpha}\frac{\partial \mathcal{P}_\alpha}{\partial v} < 0.$$

To investigate the third stability condition, let us parameterize C_m by the first $m-1$ components of the elements. Then we have to show according to our convention in 21.3 and App. 8 that the matrix

$$\frac{\partial\big(\boldsymbol{\mu}^\alpha(v,T,c)-\boldsymbol{\mu}^m(v,T,c)\big)}{\partial c^\beta} \qquad (\alpha,\beta=1,\dots,m-1)$$

is positive definite. The form (3) of the chemical potentials in 22.1 gives for the above expression

$$\delta_{\alpha\beta}\left(-\frac{v}{(c^\alpha)^2}\frac{\partial\boldsymbol{\mu}_\alpha}{\partial v}(v/c^\alpha,T)+T(\varphi^\alpha)'(c^\alpha)\right)-\frac{v}{(c^m)^2}\frac{\partial\boldsymbol{\mu}_m}{\partial v}(v/c^m,T)+T(\varphi^m)'(c^m)$$

where δ is the Kronecker symbol. Introducing the notation

$$a^\alpha := -\frac{v}{(c^\alpha)^2}\frac{\partial\boldsymbol{\mu}_\alpha}{\partial v}(v/c^\alpha,T)+T(\varphi^\alpha)'(c^\alpha) \qquad (\alpha=1,\dots,m),$$

we get that the matrix

$$\begin{pmatrix} a^1+a^m & a^m & \dots & a^m \\ a^m & a^2+a^m & \dots & a^m \\ \vdots & \vdots & \ddots & \vdots \\ a^m & a^m & \dots & a^{m-1}+a^m \end{pmatrix}$$

must be positive definite which is satisfied if $a^\alpha > 0$ for all $\alpha = 1,\dots,m$.

22.4 Ideal mixture of entropic materials

Proposition *Let the materials in Paragraph 22.1 be entropic. Their ideal mixture is entropic if and only if there is an* $\eta \in (\mathrm{J/K})$ *such that*

$$\varphi^\alpha = -\eta\log \qquad (\alpha=1,\dots,m). \tag{$*$}$$

Proof The specific entropy (4) in 22.1 satisfies the relations

$$\begin{aligned} T\frac{\partial\mathfrak{s}}{\partial v} &= T\sum_{\alpha=1}^m \frac{\partial\mathfrak{s}_\alpha}{\partial v} = \sum_{\alpha=1}^m\left(\frac{\partial\mathfrak{e}_\alpha}{\partial v}+\mathcal{P}_\alpha\right) = \frac{\partial\mathfrak{e}}{\partial v}+\mathcal{P}, \\ T\frac{\partial\mathfrak{s}}{\partial T} &= T\sum_{\alpha=1}^m c^\alpha\frac{\partial\mathfrak{s}_\alpha}{\partial T} = \sum_{\alpha=1}^m c^\alpha\frac{\partial\mathfrak{e}_\alpha}{\partial T} = \frac{\partial\mathfrak{e}}{\partial T}; \end{aligned}$$

furthermore, according to Paragraph 21.3,

$$\frac{\partial\mathfrak{s}}{\partial c^\beta} = \mathfrak{s}_\beta - \frac{v}{c^\beta}\frac{\partial\mathfrak{s}_\beta}{\partial v_\beta} - \varphi_\beta - c^\beta(\varphi_\beta)' - \mathfrak{s}_m + \frac{v}{c^m}\frac{\partial\mathfrak{s}_m}{\partial v_m} + \varphi_m + c^m(\varphi_m)',$$

and

$$\frac{\partial\mathfrak{e}}{\partial c^\beta} = \mathfrak{e}_\beta - \frac{v}{c^\beta}\frac{\partial\mathfrak{e}_\beta}{\partial v_\beta} - \mathfrak{e}_m + \frac{v}{c^m}\frac{\partial\mathfrak{e}_m}{\partial v_m}.$$

Then we infer from the entropic property of the components that

$$T\frac{\partial \mathfrak{s}}{\partial c^\beta}=\frac{\partial \mathfrak{e}}{\partial c^\beta}-(\mu_\beta-\mu_m)-c^\beta(\varphi^\beta)'+c^m(\varphi_m)'.$$

We see that the mixture is entropic if and only if $c^\beta(\varphi^\beta)'(c^\beta)=c^m(\varphi^m)'(c^m)$ for all $\beta=1,\dots,m-1$, which implies the existence of a constant η such that $c^\alpha(\varphi^\alpha)'(c^\alpha)=-\eta$ (the negative sign is chosen for later convenience) for all $\alpha=1,\dots,m$ which is equivalent to equality $(*)$.

Warning η is not an overall constant, it can depend on the materials composing the mixture.

22.5 Ideal mixture of ideal gases

Let us take m ideal gases with constant specific heats $\lambda_1 k,\dots,\lambda_m k$. Then conditions of Proposition 2 in 22.2 are satisfied on $D:=(\mathrm{m}^3)^+\times(\mathrm{K})^+\times\mathrm{C}_m$. Then the formulae of 2.1 yield that if $(\varphi^\alpha)'(c^\alpha)\geq-\frac{k}{c^\alpha}$ then the stability conditions hold on $R:=D$. Then

$$\mathcal{P}(v,T,c)=\sum_{\alpha=1}^m\frac{c^\alpha kT}{v}=\frac{kT}{v},$$

$$\mathfrak{e}(v,T,c)=\sum_{\alpha=1}^m c^\alpha\lambda_\alpha kT=\lambda(c)kT,$$

where

$$\lambda(c):=\sum_{\alpha=1}^m c^\alpha\lambda_\alpha,$$

If, moreover, the mixture is entropic, then

$$\begin{aligned}\mu^\alpha(v,T,c)=&kT\left(\lambda_\alpha+1-\log\left(\left(\frac{T}{T_0}\right)^{\lambda_\alpha}\frac{v}{c^\alpha v_0}\right)\right)-\eta T\log c^\alpha=\\ =&kT\left(\lambda_\alpha+1-\log\left(\left(\frac{T}{T_0}\right)^{\lambda_\alpha}\frac{v}{v_0}\right)\right)+(k-\eta)T\log c^\alpha=\\ =&\mu_\alpha(v,T)+(k-\eta)T\log c^\alpha,\end{aligned}$$

and

$$\begin{aligned}\mathfrak{s}(v,T,c)=&\sum_{\alpha=1}^m c^\alpha\left(k\log\left(\left(\frac{T}{T_0}\right)^{\lambda_\alpha}\frac{v}{c^\alpha v_0}\right)+\eta\log c^\alpha\right)=\\ =&\sum_{\alpha=1}^m c^\alpha\left(\mathfrak{s}_\alpha(v,T)-(k-\eta)\log c^\alpha\right).\end{aligned}$$

In processes in which the concentrations c are constant (e.g. no diffusion occurs) such an ideal gas mixture behaves as a simple ideal gas with specific heat $\lambda(c)k$.

We have
$$\mathcal{P}_\alpha\left(\frac{v}{c^\alpha}, T\right) = c^\alpha \mathcal{P}(v, T)$$
for the partial pressure of the components in the mixture: the partial pressures are proportional to concentrations and the pressure, which is called **Dalton's law**.

22.6 Ideal mixture of identical materials

22.6.1 Relations for the constitutive functions

Let us consider an ideal mixture of identical materials (oxygen is mixed with oxygen, water is mixed with water, etc.). It is natural to expect that the mixture be equal to the original material: the constitutive functions must be independent of the concentrations and must equal the original constitutive functions. Thus, if $(D, \mathfrak{e}, \mathcal{P}, \mathfrak{u}, R)$ is the original material, then for all $(v, T) \in D$ and $c \in \mathrm{C}_m$ we must have $\left(\frac{v}{c^\alpha}, T\right) \in D \quad (\alpha = 1, \ldots, m)$ and

$$\mathfrak{e}(v, T) = \sum_{\alpha=1}^{m} c^\alpha \mathfrak{e}\left(\frac{v}{c^\alpha}, T\right), \tag{1}$$

$$\mathcal{P}(v, T) = \sum_{\alpha=1}^{m} \mathcal{P}\left(\frac{v}{c^\alpha}, T\right), \tag{2}$$

$$\mathfrak{u}(v, T) = \sum_{\alpha=1}^{m} c^\alpha \left(\mathfrak{u}\left(\frac{v}{c^\alpha}, T\right) + T\varphi^\alpha(c^\alpha)\right), \tag{3}$$

which imply

$$\mathfrak{s}(v, T) = \sum_{\alpha=1}^{m} c^\alpha \left(\mathfrak{s}\left(\frac{v}{c^\alpha}, T\right) - \varphi^\alpha(c^\alpha)\right). \tag{4}$$

These relations impose very strong conditions on the constitutive domain and functions. For instance,
$$\{v \in (\mathrm{m}^3) \mid (v, T) \in D\}$$
is either void or an interval unbounded from above because if it contains v, then it also contains $\frac{v}{\gamma}$ for all $\gamma \in]0, 1[$.

Proposition *The ideal mixture of identical materials can exist only if the specific internal energy of the simple material in question does not depend on specific volume.*

Proof For the sake of brevity, fixing an arbitrary T, let us introduce the notation

$$f : \{v \in (\mathrm{m}^3) \mid (v, T) \in R\} \to (\mathrm{J})^+, \quad v \mapsto \mathfrak{e}(v, T).$$

Equality (1) gives for $n = 2$

$$f(v) = cf\left(\frac{v}{c}\right) + (1 - c)f\left(\frac{v}{1 - c}\right), \tag{5}$$

or

$$f(v) - f\left(\frac{v}{1-c}\right) = cf\left(\frac{v}{c}\right) - cf\left(\frac{v}{1-c}\right). \tag{6}$$

for all $v \in \mathrm{Dom} f$ and $c \in]0,1[$.

f is continuously differentiable; differentiating equality (5) with respect to v and c, we get

$$f'(v) = f'\left(\frac{v}{c}\right) + f'\left(\frac{v}{1-c}\right), \tag{7}$$

and

$$0 = f\left(\frac{v}{c}\right) - \frac{v}{c}f'\left(\frac{v}{c}\right) - f\left(\frac{v}{1-c}\right) + \frac{v}{1-c}f'\left(\frac{v}{1-c}\right), \tag{8}$$

respectively. Combining equalities (6), (7) and (8), we conclude that

$$f(v) - vf'(v) = f\left(\frac{v}{1-c}\right) - \frac{v}{1-c}f'\left(\frac{v}{1-c}\right).$$

As a consequence, the function $v \mapsto f(v) - vf'(v)$ is constant, which implies that there are constants a and b such that $f(v) = av + b$. But equality (5) can hold only if $a = 0$.

Thus we have: for all T the function $v \mapsto \mathfrak{e}(v,T)$ is constant on the set for which $(v,T) \in R$. Then this is true for $(v,T) \in D$ because $\mathfrak{e}$ is continuous and R is dense in D.

22.6.2 Explanation

We have got that if the internal energy depends on volume then the material cannot be the ideal mixture of itself; e.g. the van der Waals material.

This fact is clear. In an ideal mixture the molecules of the different components do not interact. In a ‘self-mixture’ a part of molecules must be considered ‘alien’ to the others; but this is impossible if the molecules do interact which is reflected in the fact that internal energy depends on volume.

In order to avoid misunderstanding, we emphasize that two different van der Waals materials can be mixed ideally.

22.7 The Gibbs paradox

Equalities (1) and (2) in paragraph 22.6.1 are satisfied for an ideal gas; equalities (3) and (4) are valid only if

$$\eta = k.$$

In usual treatments of thermodynamics one takes it for granted that the chemical potential in the ideal mixture of the components equals the chemical potential of the corresponding pure materials, i.e. $\varphi^\alpha = 0$ for all α in Definition 22.5 which is equivalent to $\eta = 0$ if the mixture is entropic. More precisely, one always considers entropy, and takes it for granted that the entropy of an ideal mixture is the sum of the individual entropies:

$$\mathfrak{s}(v,T,c) = \sum_{\alpha=1}^{m} c^\alpha \mathfrak{s}_\alpha\left(\frac{v}{c^\alpha}, T\right). \tag{$*$}$$

Then for an ideal gas as a self-mixture one gets

$$\mathfrak{s}(v,T) \neq \sum_{\alpha=1}^{m} c^\alpha \mathfrak{s}\left(\frac{v}{c^\alpha}, T\right) = \mathfrak{s}(v,T) - k \sum_{\alpha=1}^{m} c^\alpha \log c^\alpha.$$

This is the Gibbs paradox that can be formulated as follows: if identical ideal gases are mixed in identical states, then nothing happens, the state of the 'mixture' (which is not a mixture in reality) will be the original state of the components, thus entropy cannot change in mixing; nevertheless, the entropy of the mixture – on the basis of the 'evidently valid' equality $(*)$, i.e. $\eta = 0$ – will be larger because $-k \sum\limits_{\alpha=1}^{m} c^\alpha \log c^\alpha > 0$.

Like all paradoxes, this one, too, is based on a false 'evidence'; the paradox points out that the 'evidence' is not true.

The Gibbs paradox is solved if we take $\eta = k$ in an ideal self-mixture of an ideal gas. This need not hold, however, in every ideal mixture.

The theory, besides the case of the ideal self-mixture of an ideal gas, does not specify η (in general φ^α). Only experience may answer the question which η gives a good description of the mixture.

According to experience, $\eta = 0$ (in general $\varphi^\alpha = 0,\ \alpha = 1, \dots, m$) is the good choice for ideal mixtures of different materials.

We can say that η corresponding to ideal mixtures of ideal gases does not depend continuously on the mixed gases (see Exercise 3).

22.8 Exercises

1. Examine the conditions of Propositions 1 and 2 in 22.2 for (different) van der Waals materials.

2. Give the ideal mixture of van der Waals materials with constant specific heats $\lambda_1, \dots, \lambda_m$.

3. Does a van der Waals material satisfy equality (2) in 22.6.1?

4. What conditions are imposed on the pressure constitutive function if a material can be considered as a self-mixture?

5. Two ideal gases are different if and only if they have different specific heats. Let us take two ideal gases with constant specific heats $\lambda_1 k$ and $\lambda_2 k$ and let $\eta(\lambda_1, \lambda_2)$ be the constant corresponding to their mixture according to Proposition 22.4. Then experience indicates that $\eta(\lambda_1, \lambda_2) = 0$ if $\lambda_1 \neq \lambda_2$ and $\eta(\lambda_1, \lambda_2) = k$ if $\lambda_1 = \lambda_2$. As a consequence, the function $(\lambda_1, \lambda_2) \mapsto \eta(\lambda_1, \lambda_2)$ is not continuous.

6. Give the specific heat at constant volume and the isothermal compressibility factor of an ideal mixture.

7. Is the ideal mixture of

– two different ideal gases,

– two different van der Waals materials,

– an ideal gas and a van der Waals material?

canonically good (see 21.5)?

23 Non-ideal mixtures

23.1 Partial pressures, Henry law

The theory of non-ideal mixtures (solutions, alloys), very important from a practical point of view, has a vast literature; now we shall deal with some basic relations, considering mixtures of different materials.

The most important characteristics of mixtures are the chemical potentials of the components that are usually given as functions of (T, P, c) which is always possible locally in the regular domain: if $(T, P, c) \mapsto \boldsymbol{v}(T, P, c)$ is the specific volume as function of temperature, pressure and concentrations, then

$$\mu^\alpha(T, P, c) := \boldsymbol{\mu}^\alpha(v(T, P, c), T, c).$$

Sometimes $(T, P^1, \dots, P^m)$ are used as independent variables where P^α is the partial pressure of the α-th material in the mixture, which makes sense in the following way: we know the partial pressures as functions $(v, T, c) \mapsto (\mathcal{P}^\alpha(v, T, c) \mid \alpha = 1, \dots, m)$ or $(T, P, c) \mapsto \big(\boldsymbol{P}^\alpha(T, P, c) \mid \alpha = 1, \dots, \big)$, supposed locally injective for every given T, thus we can use their inverses. The function $(T, P^1, \dots, P^m) \mapsto \mu^\alpha(T, P^1, \dots, P^m)$ is defined by

$$\mu^\alpha\big(T, \mathcal{P}^1(v, T, c), \dots, \mathcal{P}^m(v, T, c)\big) = \boldsymbol{\mu}^\alpha(v, T, c).$$

A possible expression for partial pressures is

$$\mathcal{P}^\alpha(v, T, c) = \mathcal{P}_\alpha\left(\frac{v}{c^\alpha}, T\right) \qquad (\alpha = 1, \dots, m),$$

known for ideal mixtures.

In general, the *Henry law* is accepted: for every α there is a function K^α such that

$$\lim_{c \to (1)^\alpha} K^\alpha(T, P, c) = P$$

and

$$\boldsymbol{P}^\alpha(T, P, c) = c^\alpha K^\alpha(T, P, c).$$

In the ideal mixture of ideal gases $K^\alpha(T, P, c) = P$.

23.2 Fugacities, Lewis–Randall rule

In an ideal mixture of ideal gases

$$\boldsymbol{v}(T, P, c) = \frac{kT}{P},$$

and

$$\boldsymbol{P}^\alpha(T, P, c) = c^\alpha P,$$

thus

$$\frac{\boldsymbol{v}(T, P, c)}{c^\alpha} = \frac{kT}{c^\alpha P} = \frac{kT}{P^\alpha}.$$

Therefore, Paragraph 22.5 yields (with $\eta = 0$) for the chemical potential of the α-th component

$$\mu^\alpha(T,P,c) = \boldsymbol{\mu}^\alpha(v(T,P,c),T,c) = \mu_\alpha(T,P) + kT\log c^\alpha,$$

where μ_α is the chemical potential of the α-th pure gas as a function of temperature and pressure. Using the partial pressures, we have

$$\mu^\alpha(T,P^1,\dots,P^m) = \nu^\alpha(T) + kT\log\frac{P^\alpha}{P_0},$$

where ν^α is a well-determined simple function and P_0 is a fixed pressure value.

In analogy, a mixture is usually called ideal if the chemical potentials have the form

$$\mu^\alpha(T,P,c) = \mu_\alpha(T,P) + kT\log c^\alpha \tag{1}$$

or

$$\mu^\alpha(T,P^1,\dots,P^m) = \nu^\alpha(T) + kT\log\frac{P^\alpha}{P_0}. \tag{2}$$

This terminology differs from ours and is ambiguous because the above two relations are not equivalent. That is why we shall apply the names **semi-ideal** of type (1) and (2).

In general it is supposed that the chemical potentials of the components have the form

$$\mu^\alpha(T,P,c) = \mu_\alpha(T,P) + kT\log c^\alpha J^\alpha(T,P,c), \tag{$*$}$$

where J^α is a continuously differentiable function for which

$$\lim_{c\to(1)^\alpha} J^\alpha(T,P,c) = 1,$$

$$\lim_{c\to(1)^\alpha} \frac{\partial J^\alpha(T,P,c)}{\partial c} = 0.$$

According to another usual assumption,

$$\mu^\alpha(T,P^1,\dots,P^m) = \nu^\alpha(T) + kT\log\frac{P^\alpha L^\alpha(T,P^1,\dots,P^m)}{P_0}, \tag{$**$}$$

where ν^α is a given function and L^α is a continuously differentiable function for which

$$\lim_{P\to 0} L^\alpha(T,P^1,\dots,P^m) = 1,$$

$$\lim_{P\to 0} \frac{\partial L^\alpha(T,P^1,\dots,P^m)}{\partial P_\alpha} = 0,$$

where $P\to 0$ means that all P^α tend to zero.

The function

$$(T,P^1\dots,P^m) \mapsto P^\alpha L^\alpha(T,P^1,\dots,P^m) =: f^\alpha(T,P^1,\dots,P^m)$$

is called the **fugacity** of the α-th component.

If we express fugacities as functions of (T,P,c), then the Henry law yields – with evident notations – the **Lewis–Randall rule**:

$$f^\alpha(T,P,c) = c^\alpha K^\alpha(T,P,c)L^\alpha(T,P,c).$$

24 Some phenomena connected with mixing

24.1 Experimental facts

It is well known that the mixture of certain materials – e.g. water and alcohol – has smaller volume (at a given temperature and pressure) than the sum of the volumes of the mixed materials. It is also well known that mixing of certain materials – e.g. water and sulphuric acid – raises the temperaturesignificantly; in other words, if we want to assure constant temperature, then we have to 'extract heat'. Another everyday fact is that the freezing point of some solutions – e.g. salt in water – becomes lower than that of the corresponding pure liquid. Osmosis, the basic fact in the life of plants, is connected with mixtures, too.

24.2 Change of quantities in mixing

We examine how the internal energy, the volume, etc. change when a mixture is produced from m materials with concentrations $c^1, \dots, c^m$ at given temperature T and pressure P. In practice we take given amounts, according to the concentrations, of the materials and mix them. If N^α particles are taken from the α-th material and v_α is the corresponding specific volume, then $\sum\limits_{\alpha=1}^{m} N^\alpha v_\alpha$ is the entire volume of the materials to be mixed, which is compared with the entire volume V after mixing. Dividing these quantities by the entire number of particles, we get that $\sum\limits_{\alpha=1}^{m} c^\alpha v_\alpha$ (the average specific volume before mixing) is to be compared with the specific volume v after mixing.

Thus the change of volume, internal energy and entropy is measured by

$$\boldsymbol{v}(T, P, c) - \sum_{n=1}^{m} c^\alpha \boldsymbol{v}_\alpha(T, P),$$

$$\boldsymbol{e}(T, P, c) - \sum_{n=1}^{m} c^\alpha \boldsymbol{e}_\alpha(T, P),$$

$$\boldsymbol{s}(T, P, c) - \sum_{n=1}^{m} c^\alpha \boldsymbol{s}_\alpha(T, P),$$

respectively. We point out that $\boldsymbol{v}_\alpha(T, P)$ is not equal to $\frac{\boldsymbol{v}(T,P,c)}{c^\alpha}$, often met previously. $\boldsymbol{v}_\alpha(T, P)$ is the specific volume of the α-th pure material (before mixing) and $\frac{\boldsymbol{v}(T,P,c)}{c^\alpha}$ is the specific volume of that material in the mixture (after mixing).

24.3 Mixing heat

As usual, corresponding to 3.12), the **mixing heat** is defined to be

$$T\left(\boldsymbol{s}(T,P,c)-\sum_{n=1}^{m}c^{\alpha}\boldsymbol{s}_{\alpha}(T,P)\right)=\boldsymbol{e}(T,P,c)-\sum_{n=1}^{m}c^{\alpha}\boldsymbol{e}_{\alpha}(T,P)+$$
$$+P\left(\boldsymbol{v}(T,P,c)-\sum_{n=1}^{m}c^{\alpha}\boldsymbol{v}_{\alpha}(T,P)\right)-\sum_{n_1}mc^{\alpha}(\mu^{\alpha}(T,P,c)-\mu_{\alpha}(T,P).$$

Note that here the mixing heat refers to a particle; in practice the mixing heat refers to a unit mass, which equals this mixing heat divided by $m(c)$.

24.4 Freezing-point decrease

Now we indicate in advance that a first-order phase connection is determined by the equal values of temperature, pressure and the chemical potentials of the components in the two phases (see 25.2).

Let us consider a two-component liquid mixture and let us suppose that during freezing only one of the components enters the solid phase (a pure material arises); for the sake of clarity and brief formulation, let us speak about freezing of water-salt solution, where the solid phase is pure ice. Accordingly, the solid phase and the corresponding liquid phase are denoted by the subscript i and w, respectively. If the concentration of the water in the solution is $c\in]0,1[$, relation $(*)$ in 23.2 gives that the first-order phase connection of the ice and the solution is characterized by

$$\mu_i(T,P)=\mu^w(T,P,c)=\mu_w(T,P)+kT\log cJ(T,P,c).$$

This allows us to express temperature as a function of pressure and concentration; let $\boldsymbol{T}$ be this function. On the basis of the implicit function theorem,

$$\frac{\partial\boldsymbol{T}}{\partial c}=-\frac{\frac{kT}{cJ}\left(J+c\frac{\partial J}{\partial c}\right)}{\frac{\partial\mu_w}{\partial T}-\frac{\partial\mu_i}{\partial T}+k\log cJ+\frac{kT}{J}\frac{\partial J}{\partial T}}\bullet\,. \tag{$*$}$$

We deduce from the Gibbs–Duhem relation

$$\frac{\partial\mu_w}{\partial T}-\frac{\partial\mu_i}{\partial T}=-\boldsymbol{s}_w(T,P)+\boldsymbol{s}_i(T,P)=\frac{q_{iw}(T,P)}{T},$$

where $q_{iw}(T,P)$ is the freezing heat of water (see 3.12).

If the solution is sufficiently diluted, i.e. c is near to 1, then the expression $(*)$ can be approximated by its limit as $c\to 1$ which equals

$$-\frac{k\boldsymbol{T}(P,1)^2}{q_{iw}\,\boldsymbol{T}(P,1),P)}<0,$$

according to 23.2.

This shows that freezing point – at a given pressure – decreases as concentration increases.

24.5 Osmosis

Now we inidicate in advance that two mixtures with equal temperature values are in equilibrium if the chemical potentials of the interchangeable components take equal values (see 29.1).

Let us suppose that a two-component solution is enclosed with a wall permeable only for one of the components and that the material is on the other side of the wall. For the sake of clarity and brief formulation, let us speak about water–salt solution where only water can pass through the wall. Let both bodies have the same temperature T. Following our previous notations, if $c \in]0,1[$ is the concentration of water in the solution, we have in equilibrium

$$\mu_w(T, P_w) = \mu^w(T, P_s, c),$$

where P_w is the pressure of pure water and P_s is the pressure of the solution. Using relation $(*)$ in 23.2, we infer

$$\mu_w(T, P_w) = \mu_w(T, P_s) + kT \log cJ(T, P_s, c).$$

According to the Gibbs–Duhem relation, the partial derivative of chemical potential with respect to pressure – at a given temperature – is specific volume, therefore,

$$\mu_w(T, P_s) = \mu_w(T, P_w) + \int_{P_w}^{P_s} \boldsymbol{v}(T, P)\, dP.$$

As a consequence,

$$\int_{P_w}^{P_s} \boldsymbol{v}(T, P)\, dP = -kT \log cJ(T, P_s, c).$$

If the integrand is approximated by a middle value v_m, the integral becomes $v_m(P_s - P_w)$. If the solution is sufficiently diluted, i.e. c is near to 1, then $J(T, P_s, c)$ is near to 1, too; in this way we obtain **van t'Hoff's formula** for the pressure difference:

$$P_s - P_w \approx -\frac{kT \log c}{v_m} \approx \frac{kT(1-c)}{v_m}.$$

24.6 Saturation

A piece of salt in water dissolves till the water–salt solution reaches saturation. In saturation the pure salt and the water–salt solution are in equilibrium. Thus, if c denotes the concentration of salt in the solution, the saturation concentration c_s at given temperature T and pressure P is determined by

$$\mu^{\mathrm{t}}(T, P, c_s, 1 - c_s) = \mu_{\mathrm{t}}(T, P),$$

where the indices t refer to salt.

If the mixture is semi-ideal of type (1), then

$$\mu_{\mathrm{t}}(T,P) + kT\log c_s = \mu_{\mathrm{t}}(T,P)$$

yields $c_s = 1$ which is impossible: no saturation occurs for semi-ideal mixtures of type (1). Thus the experimental fact of saturation shows that the mixtures are not semi-ideal. In fact, semi-ideal mixtures are good approximations only for concentrations near to 0 or 1, according to the sense.

Saturation can exist if the mixture is not semi-ideal. Then, according to Paragraph 23.2,

$$c_s J^{\mathrm{t}}(T,P,c_s) = 1$$

determines the saturation concentration. The conditions imposed on J^{t} imply that if c is large enough, then

$$J^{\mathrm{t}}(T,P,c) + c\frac{\partial J^{\mathrm{t}}(T,P,c)}{\partial c} > 0,$$

thus, the implicit function theorem allows us to give the saturation concentration as a function $\boldsymbol{c}_s$ of temperature and pressure. Moreover,

$$\frac{\partial \boldsymbol{c}_s}{\partial T} = -\frac{c\frac{\partial J^{\mathrm{t}}}{\partial T}}{J^{\mathrm{t}} + c\frac{\partial J^{\mathrm{t}}}{\partial c}} \bullet .$$

The denominator is positive; then the experimental fact that the saturation concentration increases as temperature increases (at a given pressure) points out that $\frac{\partial J^{\mathrm{t}}}{\partial T} < 0$.

24.7 Exercises

1. Demonstrate that internal energy and volume do not change in preparing ideal mixture of ideal gases; the mixing heat is zero.
2. Verify that the entropy increases in preparing ideal mixture of different ideal gases and the entropy does not change if the mixed gases are identical (of course, $\eta = 0$ in the first case and $\eta = k$ in the second case).
3. Give an estimation for the difference of the freezing points of the water-salt solution and the pure water, i.e. for $\boldsymbol{T}(P,c) - \boldsymbol{T}(P,1)$ when c is near to 1 (in other words, $1-c$ is near to 0).
4. Deduce a formula for the boiling point increase on the analogy of Paragraph 24.4: boiling a water–salt solution, only water enters the vapour.

25 Phases, phase connections

25.1 Phases

Phases and phase connections of composite materials are defined formally in the same manner as those of simple materials. Now $\mathcal{T}$ denotes the function $D \to (\mathrm{K})$, $(v,T,c) \mapsto T$.

Definition *A* **phase** *of the composite material* $(D, \mathfrak{e}, \mathcal{P}, \mu^1, \dots, \mu^m, R)$ *is a connected open subset* Z *of* R *on which* $(\mathcal{T}, \mathcal{P}, [\mu^1, \dots, \mu^m])$ *is injective, and* Z *is maximal with this properties, i.e. if* N *is a connected open subset of* R *on which* $(\mathcal{T}, \mathcal{P}, [\mu^1, \dots, \mu^m])$ *is injective and* $Z \subset N$*, then* $Z = N$.

Proposition *Every element of* R *is contained in a phase.*

Thus temperature, pressure and a convenient equivalence class of chemical potentials can be taken as independent variables in a phase. The latter is a rather involved and hardly manageable quantity, so these independent variables – contrary to the case of simple materials where only temperature and pressure appear – are useless in practice.

25.2 Phase connections

The zeroth-order and second-order phase connections of two phases Z and Z' of a composite material are defined in the same way as those of a simple material (see Definitions 7.2 and 7.3) and the same can be said about them, therefore, we do not go into details.

Definition 1 *Let* Z *and* Z' *be two phases of a composite material. We say that* $(v, T, c) \in Z \setminus \overline{Z'}$ *and* $(v', T, c') \in Z' \setminus \overline{Z}$ *are in a* **first-order connection with each other** *if* $\mathcal{P}(v, T, c) = \mathcal{P}(v', T, c')$ *and* $\mu^\alpha(v, T, c) = \mu^\alpha(v', T, c')$ *for all* $\alpha = 1, \dots, m$.

Definition 2 *Let* C *be the subset of states in* $Z \setminus \overline{Z'}$ *which are in first-order connection with some states in* $Z' \setminus \overline{Z}$ *and let* C' *be the similar set in* $Z' \setminus \overline{Z}$*. The* **first-order connection** *of the phases* Z *and* Z' *is the pair* (C, C')*. The phases are in first-order connection if the sets* C *and* C' *are not void.*

Recall that $[\mu^1, \dots, \mu^m]$ is the composition of a surjection and $(\mu^1, \dots, \mu^m)$. As a consequence – because $(\mathcal{T}, \mathcal{P}, [\mu^1, \dots, \mu^m])$ is injective on Z – every state in C is in first-order phase connection with exactly one state in C' and vice versa. In other words, 'being in first-order connection' is a bijection between C and C'.

Proposition *Let* (C, C') *be the first-order phase connection of* Z *and* Z'*. Then* C *and* C' *are* m*-dimensional submanifolds in* Z *and in* Z'*, respectively.*

Proof Let f and f' denote the restriction of the functions $(\mathcal{T}, \mathcal{P}, [\mu^1, \dots, \mu^m])$ onto $Z \setminus \overline{Z'}$ and $Z' \setminus \overline{Z}$, respectively. Applying the implicit function theorem for the function $(v, T, c, v', T', c') \mapsto f(v, T, c) - f'(v', T', c')$, we get by the intrinsic stability conditions that there is a continuously differentiable function $\vartheta : Z \rightarrowtail Z'$ in a neighbourhood of every point of C in such a way that $f(v, T, c) - f'(\vartheta(v, T, c)) = 0$. It is evident that the restriction of ϑ onto C is just the previously mentioned bijection $C \to C'$ in the neighbourhood in question. It is clear from the definition of $[\mu^1, \dots, \mu^m]$ that $C = \{(v, T, c) \in Z \mid \mu^\alpha(v, T, c) - \mu^\alpha(\vartheta(v, T, c)) = 0\}$ for an arbitrarily chosen $\alpha = 1, \dots, m$. Again the conditions of intrinsic stability imply that for all (v, T, c) there is an α such that the derivative of μ^α at (v, T, c) is not zero.

All those imply that C is an m-dimensional submanifold, and the same is true for C'.

25.3 Phase surfaces

25.3.1 The notion of phase surface

It follows then that $(\mathcal{T},\mathcal{P},[\mu^1,\ldots,\mu^m])[C] = (\mathcal{T},\mathcal{P},[\mu^1,\ldots,\mu^m])[C']$ is an m-dimensional submanifold in $(\mathrm{K})\times(\mathrm{Pa})\times(\mathrm{J})D_m^*$; this corresponds to the phase line of a simple material in $(\mathrm{K})\times(\mathrm{Pa})$ that are described by the Clausius–Clapeyron equation. This submanifold is of little importance because $[\mu^1,\ldots,\mu^m]$ is a rather involved and hardly manageable quantity. On the contrary, the **phase surfaces**

$$\Gamma := (\mathcal{T},\mathcal{P},\mathfrak{c})[C] \subset (\mathrm{K})\times(\mathrm{Pa})\times C_m,$$
$$\Gamma' := (\mathcal{T},\mathcal{P},\mathfrak{c})[C'] \subset (\mathrm{K})\times(\mathrm{Pa})\times C_m,$$

which are m-dimensional submanifolds, too, have a clear meaning and great practical importance; here and in the sequel

$$\mathfrak{c} : D \to C_m, \qquad (v,T,c)\mapsto c. \tag{$*$}$$

The bijection between C and C' establishes a bijection $\Gamma\to\Gamma'$ whose restriction to $\Gamma\cap\Gamma'$ is the identity. Thus if $\big(T,P,c(1)\big),\big(T,P,c(2)\big)\in\Gamma$ and $(T,P,c'(1))$, $(T,P,c'(2))$ are the corresponding points in Γ', then $c(1)\neq c(2)$ implies $c'(1)\neq c'(2)$. Therefore, at a given temperature and pressure the concentrations belonging to states in a first-order phase connection are uniquely determined. We shall see that the first-order phase connections express the equilibrium of bodies in different phases. Thus, we can say that at given temperature and pressure the concentrations of bodies in equilibrium in different phases are uniquely determined.

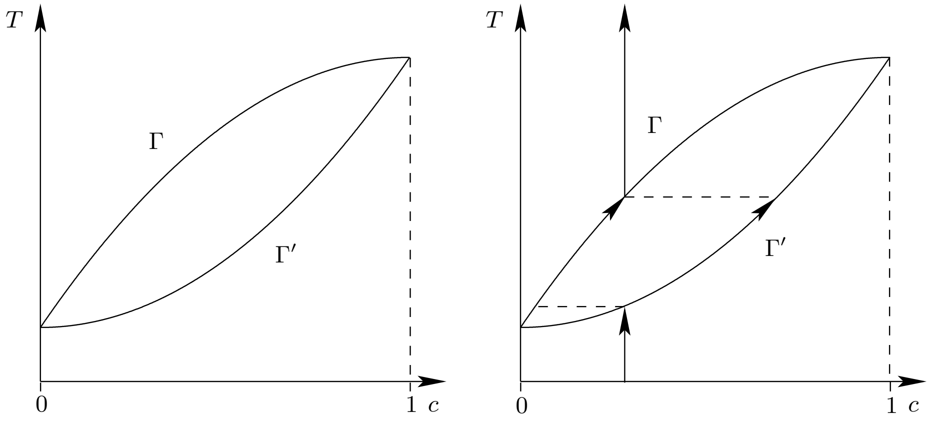

Figure 25.1

25.3.2 Illustration of phase surfaces

Figure 25.1 illustrates phase surfaces (Γ and Γ') of a two-component material. The horizontal axis shows the concentration c of one of the components (the concentration of the other component is $1-c$), the vertical axis shows temperature. The lines on the figure represent intersections of the phase surface and the planes with constant pressure. The two figures correspond to two different pressures.

For the sake of easier formulation, let Z and Z' be the liquid phase and the gaseous phase and let the two components be alcohol and water. Let us draw a vertical line at a given concentration c and let us proceed on the line upwards from the bottom; this corresponds to the process that the alcohol-water solution in which water has concentration c is heated at constant pressure. When the vertical line reaches the surface Γ, then boiling starts, the gaseous phase appears whose temperature equals the temperature of the liquid but has a different (smaller) concentration of water. As temperature is raised, the boiling continues, the water concentration in the vapour is always less than in the liquid (always less water enters the vapour than alcohol), consequently, the water concentration in the liquid becomes higher. If the process is slow enough, then liquid and vapor are nearly in equilibrium. The process 'splits' in two branches, proceeds on the surfaces Γ and Γ' 'upwards' ('to the right') in such a way that the points corresponding to each other are on a horizontal line (have the same temperature). When boiling is finished (the liquid phase disappears), the two branches of the process unite into a vertical line in the gaseous phase.

25.4 Phase connections of different mixtures

Up to now the first-order phase connections of different phases of the same mixture have been considered. It is an everyday experience that phase transition occurs between different mixtures; e.g. freezing-point decrease is connected with such a phenomenon. To treat phase connections between phases of different mixtures, we need the notion of mixture families that will be given in the next section whose notations and results are applied here.

Let us take the mixture family $\big(D, \mathfrak{e}, \mathcal{P}, (\mu^\alpha \mid \alpha = 1, \dots, m), R\big)$ of the simple materials $(D_\alpha, \mathfrak{e}_\alpha, \mathcal{P}_\alpha, \mu_\alpha, R_\alpha)$ $(m = 1, \dots, m)$. The notions and results of the previous paragraph concern phases and phase connections of a composition $\mathcal{F}$ of the mixture family. The zeroth-order and second-order connections of the phases Z and Z' of the compositions $\mathcal{F}$ and $\mathcal{F}'$, respectively, are defined formally in the known way when the compositions coincide. The first-order phase connections, too, are defined similarly:

Definition 1 *Let Z and Z' be phases of the composition $\mathcal{F}$ and $\mathcal{F}'$, respectively. We say that $(v, T, c) \in Z \setminus \overline{Z'}$ and $(v', T, c') \in Z' \setminus \overline{Z}$ are in a* **first-order connection with each other** *if $\mathcal{P}(v, T, c) = \mathcal{P}(v', T, c')$ and $\mu^\alpha(v, T, c) = \mu^\alpha(v', T, c')$ for all $\alpha \in \mathcal{F} \cap \mathcal{F}'$.*

Definition 2 *Let C be the subset of states in $Z \setminus \overline{Z'}$ which are in first-order connection with some states in $Z' \setminus \overline{Z}$ and let C' be the similar set in $Z' \setminus \overline{Z}$. The* **first-order connection** *of the phases Z and Z' is the pair (C, C'). The phases are in first-order connection if the sets C and C' are not void.*

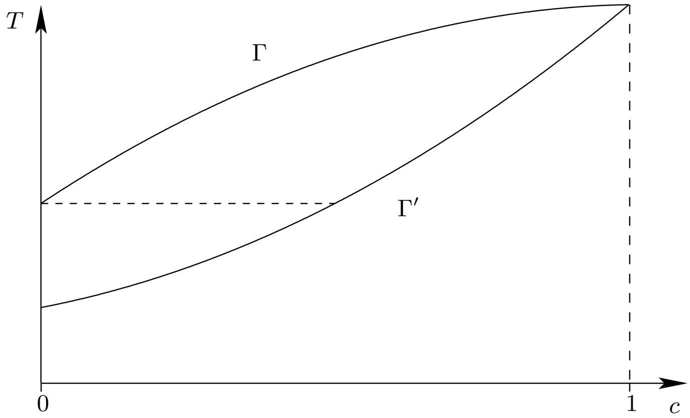

Figure 25.2

Now a state in C can be in a first-order connection with more states in C' and vice versa.

We introduce the sets

$$\Gamma := (\mathcal{T}, \mathcal{P}, \mathfrak{c})[C] \subset (\mathrm{K})^{+} \times (\mathrm{Pa}) \times C_{\mathcal{F}},$$

$$\Gamma' := (\mathcal{T}, \mathcal{P}, \mathfrak{c})[C'] \subset (\mathrm{K})^{+} \times (\mathrm{Pa}) \times C_{\mathcal{F}'}.$$

Let us investigate the case $\mathcal{F} \subset \mathcal{F}'$ in more detail. Then $\mathcal{F} \cap \mathcal{F}' = \mathcal{F}$; because $\big(\mathcal{T}, \mathcal{P}, (\mu^{\alpha} \mid \alpha \in \mathcal{F})\big)$ is injective on Z, every state in C' is in first-order connection with exactly one state in C; this is not true, however, interchanging the role of C and C'. In other words, now ‘being in first-order connection’ is a surjection from C' onto C which establishes a surjection $\Gamma' \to \Gamma$, too. This means that in a phase equilibrium at given temperature and pressure the concentrations of the mixture having less components is uniquely determined while the concentrations of the mixture having more components are not unique, in general.

Figure 25.2 shows the boiling of a liquid mixture when only the material ‘2’ enters the gaseous phase until the concentration of the material ‘1’ in the liquid is less than 1/2.

25.5 Exercises

1. Define the critical points of a composite material according to Definition 7.8 and show that a critical point is in the second-order phase connection.

2. Discuss the phase surfaces in Figure 25.3.

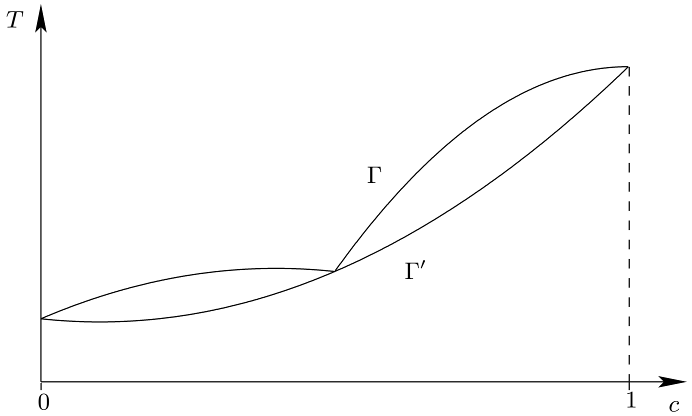

Figure 25.3

26 Mixture families

26.1 Definition of a mixture family

For the sake of simpler formulation, we introduce the notation $\mathcal{A} := \{1, \dots, m\}$ for the time being, where $m \geq 2$ is a given positive integer.

Note that it is mathematical convenience only that components in Definition 21.2 are labelled by numbers from 1 to m; we could give them arbitrary names (as in the case of actual mixtures, e.g. the mixture of salt and water), i.e. we could take an arbitrary finite set instead of $\mathcal{A}$.

We have to renounce this convenience if we wish to describe that some components of a mixture disappear completely during a process and a mixture of less components remains, because the components of the remaining mixture cannot be labelled consistently from 1 to .... If, for instance, the first and the m-th component disappear, then the remaining mixture has $m-2$ components which are not labelled by numbers from 1 to $m-2$ but by numbers from 2 to $m-1$. It is suitable to consider this mixture having concentrations of the form $(0, c^2, \dots, c^{m-1}, 0)$ where $0 < c^\alpha < 1$ for $\alpha = 2, \dots, m-1$ and $\sum\limits_{\alpha=2}^{m-1} c^\alpha = 1$.

In general, if $\mathcal{F}$ is a subset of $\mathcal{A}$ that contains at least two elements, we introduce the notation

$$\mathrm{C}_{\mathcal{F}} := \{c \in \overline{\mathrm{C}}_m \mid 0 < c^\alpha < 1 \text{ if } \alpha \in \mathcal{F}, \ \sum_{\alpha \in \mathcal{F}} c^\alpha = 1\};$$

if $\mathcal{F}$ has only one element, let $C_{\mathcal{F}} := \{1\}$.

Note that if $\mathcal{F}$ and $\mathcal{F}'$ are different non-void subsets of $\mathcal{A}$, then $\mathrm{C}_{\mathcal{F}} \cap \mathrm{C}_{\mathcal{F}'} = \emptyset$. Furthermore, it is trivial that $\overline{\mathrm{C}}_m = \bigcup\limits_{\emptyset \neq \mathcal{F} \subset \mathcal{A}} \mathrm{C}_{\mathcal{F}}$.

If we wish to consider mixtures of m simple materials in which some of the materials are not present, then we have to take a whole family of mixtures: we have to give the mixture of the materials corresponding to every non-void subset $\mathcal{F}$ of $\mathcal{A}$ (the mixture corresponding to a singleton is really a pure material). The constitutive domain of the mixture corresponding to $\mathcal{F}$ is a subset of $(\mathrm{m}^3)^+ \times (\mathrm{K})^+ \times \mathrm{C}_{\mathcal{F}}$. The above remarks indicate us that the constitutive domains of the mixtures of different composition are disjoint and their union is a subset of $(\mathrm{m}^3)^+ \times (\mathrm{K})^+ \times \overline{\mathrm{C}}_m$.

'Putting together' the constitutive domains and constitutive functions of the mixtures of different compositions, we arrive at the following definition.

Definition *Let $m \geq 2$ be a positive integer, $\mathcal{A} := \{1, \dots, m\}$.*

A **mixture family** *of the simple materials $(D_\alpha, \mathfrak{e}_\alpha, \mathcal{P}_\alpha, \boldsymbol{\mu}_\alpha, R_\alpha)$ $(\alpha \in \mathcal{A})$ is an object*

$$(D, \mathfrak{e}, \mathcal{P}, (\boldsymbol{\mu}^\alpha \mid \alpha \in \mathcal{A}), R)$$

where

- *both D and R are non-void subsets of $(\mathrm{m}^3)^+ \times (\mathrm{K})^+ \times \overline{\mathrm{C}}_m$,*
- *$\mathfrak{e} : D \to (\mathrm{J})^+$, $\mathcal{P} : D \to (\mathrm{Pa})$,*
- *$\boldsymbol{\mu}^\alpha : D \rightarrowtail (\mathrm{J})$ having the domain $\{(v, T, c) \in D \mid c^\alpha \neq 0\}$,*

are continuous functions and if $\emptyset \neq \mathcal{F} \subset \mathcal{A}$, then $(D_{\mathcal{F}}, \mathfrak{e}_{\mathcal{F}}, \mathcal{P}_{\mathcal{F}}, (\boldsymbol{\mu}^\alpha_{\mathcal{F}} \mid \alpha \in \mathcal{F}), R_{\mathcal{F}})$ is a mixture according to Definition 21.2, called the **mixture of composition** *$\mathcal{F}$, where*

$$D_{\mathcal{F}} := D \cap \big((\mathrm{m}^3)^+ \times (\mathrm{K})^+ \times \mathrm{C}_{\mathcal{F}}\big), \quad R_{\mathcal{F}} := R \cap \big((\mathrm{m}^3)^+ \times (\mathrm{K})^+ \times \mathrm{C}_{\mathcal{F}}\big),$$

$$\mathfrak{e}_{\mathcal{F}} := \mathfrak{e}|_{D_{\mathcal{F}}} \qquad \mathcal{P}_{\mathcal{F}} := \mathcal{P}|_{D_{\mathcal{F}}} \qquad \boldsymbol{\mu}^\alpha_{\mathcal{F}} := \boldsymbol{\mu}^\alpha|_{D_{\mathcal{F}}}.$$

Remarks (i) We point out that the same symbol denotes the mixture family here and a single mixture in Definition 21.2; the single mixture there is the 'largest' member of the present family. Hopefully, this ambiguity does not lead to confusion.

(ii) Note that the chemical potential of the α-th material is not defined everywhere in D, in other words, not for all members of the family; it is defined only for the compositions that contains the α-th material as a component.

(iii) The continuity of the constitutive functions imply that a larger composition is reduced in limit to a smaller one; more closely, if $\emptyset \neq \mathcal{H} \subset \mathcal{F}$ and the components corresponding $\mathcal{F} \setminus \mathcal{H}$ disappear from the mixture of composition $\mathcal{F}$, then we get the mixture with composition $\mathcal{H}$: for all $\alpha \in \mathcal{H}$ and $c_{\mathcal{H}} \in \mathrm{C}_{\mathcal{H}}$ (see Appendix 8):

$$\lim_{c_{\mathcal{F}} \to c_{\mathcal{H}}} (\mathfrak{e}_{\mathcal{F}}, \mathcal{P}_{\mathcal{F}}, (\boldsymbol{\mu}^\alpha_{\mathcal{F}} \mid \alpha \in \mathcal{H}))(v, T, c_{\mathcal{F}}) = (\mathfrak{e}_{\mathcal{H}}, \mathcal{P}_{\mathcal{H}}, (\boldsymbol{\mu}^\alpha_{\mathcal{H}} \mid \alpha \in \mathcal{H}))(v, T, c_{\mathcal{H}}).$$

This is a generalization of item *(iv)* in Definition 21.2.

26.2 Canonical variables

Of course, a mixture family, too, can be defined in canonical variables as an object $(\mathrm{D}, \mathbf{T}, \mathbf{P}, (\boldsymbol{\mu}^\alpha \mid \alpha \in \mathcal{A}), \mathrm{R})$, where

- both D and R are non-void subsets of $(\mathrm{J})^+ \times (\mathrm{m}^3)^+ \times \overline{\mathrm{C}}_m$,

- $\mathbf{T} : \mathrm{D} \to (\mathrm{K})^+$, $\mathbf{P} : \mathrm{D} \to (\mathrm{Pa})$,
- $\boldsymbol{\mu}^\alpha : \mathrm{D} \rightarrowtail (\mathrm{J})$ having the domain $\{(e, v, c) \in \mathrm{D} \mid c^\alpha \neq 0\}$

and if $\emptyset \neq \mathcal{F} \subset \mathcal{A}$, then $(\mathrm{D}_\mathcal{F}, \mathbf{T}_\mathcal{F}, \mathbf{P}_\mathcal{F}, (\boldsymbol{\mu}^\alpha_\mathcal{F} \mid \alpha \in \mathcal{F}), \mathrm{R}_\mathcal{F})$ is a mixture similar to Paragraph 21.5, where

$$\mathrm{D}_\mathcal{F} := \mathrm{D} \cap \big((\mathrm{J})^+ \times (\mathrm{m}^3)^+ \times \mathrm{C}_\mathcal{F}\big), \quad \mathrm{R}_\mathcal{F} := \mathrm{R} \cap \big((\mathrm{J})^+ \times (\mathrm{m}^3)^+ \times \mathrm{C}_\mathcal{F}\big),$$

$$\mathbf{T}_\mathcal{F} := \mathbf{T}|_{\mathrm{D}_\mathcal{F}} \qquad \mathbf{P}_\mathcal{F} := \mathbf{P}|_{D_\mathcal{F}} \qquad \boldsymbol{\mu}^\alpha_\mathcal{F} := \boldsymbol{\mu}^\alpha|_{D_\mathcal{F}}.$$

The temperature in canonical variables corresponding to different compositions need not have a limit relation similar to that described in item (*iii*) of the previous remark (see 21.5); if

$$\lim_{c_\mathcal{F} \to c_\mathcal{H}} \mathbf{T}_\mathcal{F}(e, v, c_\mathcal{F}) = \mathbf{T}_\mathcal{H}(e, v, c_\mathcal{H}),$$

for all $\mathcal{F}$ and $\mathcal{H}$, $\mathcal{H} \subset \mathcal{F}$, then the mixture family is called **canonically good**.

26.3 Entropic mixture families

The mixture family treated previously is called **entropic**, if every composition in the family is entropic.

The chemical potential μ^α is defined only for the concentrations that the α-th component is present in, i.e. $c^\alpha \neq 0$. Let us put $c^\alpha \mu^\alpha := 0$ if $c^\alpha = 0$; then the Gibbs function

$$g := \sum_{\alpha=1}^{m} c^\alpha \mu^\alpha$$

and consequently, the specific entropy

$$\mathfrak{s} := \frac{\mathfrak{e} + \mathcal{P}v - g}{T}$$

is defined on the whole D. If the mixture family is entropic, then the partial derivative of specific entropy satisfies the formal relations given in Paragraph 21.6.

26.4 Exercises

1. Give the ideal mixture family of three different ideal gases.
2. Is the mixture family of the previous exercise canonically good?

27 Bodies

27.1 Definition of a body

The bodies of composite materials are more complicated than those of simple materials. Namely, only one extreme possibility exists there: the body becomes empty, i.e. its particle number reduces to zero. Now we have to take into account the cases when some of the components of a body disappear; thus the notion of a body requires a mixture family as given in Paragraph 26.1.

A mixture body, besides its material, is characterized by its particle number. Therefore, the following definition is straightforward.

Definition *A* **body** *composed of the simple materials* $(D_\alpha, \mathfrak{e}_\alpha, \mathcal{P}_\alpha, \boldsymbol{\mu}_\alpha, R_\alpha)$ $(\alpha \in \mathcal{A})$ *is*

$$\big(D \times \mathbb{R}_0^+, \mathfrak{e}, \mathcal{P}, (\boldsymbol{\mu}^\alpha \mid \alpha \in \mathcal{A}), R\big),$$

where $\big(D, \mathfrak{e}, \mathcal{P}, (\boldsymbol{\mu}^\alpha \mid \alpha \in \mathcal{A}), R\big)$ *is a mixture family of the materials in question.*

The elements of $D \times \mathbb{R}^+$ and the set $D \times \{0\}$ are called the states of the body.

The body is **entropic** if the corresponding mixture family is entropic.

27.2 The entire quantities

A state of a composite body is $(v, T, c, N) \in (\mathrm{J})^+ \times (\mathrm{m}^3)^+ \times \overline{\mathrm{C}}_m \times \mathbb{R}_0^+$: specific volume, temperature, concentrations and particle number(denoted by N). As in the case of simple bodies, it is convenient to introduce the entire quantities:

$N^\alpha := Nc^\alpha$, the particle number of the α-th component (the α-th **partial particle number**),

$V := Nv$, the entire volume of the body,

and to use them for describing states. The relation between the specific quantities and the entire ones is realized by the infinitely differentiable mapping

$$\begin{aligned}&(\mathrm{m}^3)^+ \times (\mathrm{K})^+ \times \overline{\mathrm{C}}_m \times \mathbb{R}_0^+ \to (\mathrm{J})^+ \times (\mathrm{m}^3)_0^+ \times (\mathbb{R}_0^+)^m,\\ &\qquad\qquad (v, T, c, N) \mapsto (Nv, T, Nc^1, \dots, Nc^m) =: (V, T, N^1, \dots, N^m).\end{aligned}$$

This functions maps the set $D \times \{0\}$ (the state with zero particle number) into a subset of $\{0\} \times (\mathrm{K})^+ \times \{(0, 0 \dots, 0)\}$ and establishes a bijection between $(\mathrm{m}^3)^+ \times (\mathrm{K})^+ \times \overline{\mathrm{C}}_m \times \mathbb{R}^+$ and $(\mathrm{m}^3)^+ \times (\mathrm{K})^+ \times (\mathbb{R}^+)^m$; its inverse is infinitely differentiable, too:

$$(V, T, N^1, \dots, N^m) \mapsto (V/N, T, N^1/N \dots, N^m/N, N),$$

where, of course, $N = \sum_{\alpha=1}^{m} N^\alpha$ is the entire particle number.

We stress that the **partial particle numbers** N^α $(\alpha = 1, \dots, m)$ are independent variables, contrary to the concentrations.

Using the entire variables – supposing that $N \neq 0$ – we apply the ambiguous notation similar to that for simple materials:

$$\mathcal{P}(V, T, N^1, \dots, N^m) = \mathcal{P}(V/N, T, N^1/N, \dots, N^m/N)$$

and a similar one for $\boldsymbol{\mu}^\alpha$, too. Furthermore,

$\mathcal{E}(V, T, N^1, \dots, N^m) := N\mathfrak{e}(V/N, T, N^1/N, \dots, N^m/N)$ is the entire energy,

$\mathcal{S}(V, T, N^1, \dots, N^m) := N\mathfrak{s}(V/N, T, N^1/N, \dots, N^m/N)$ is the entire entropy,

and the entire enthalpy $\mathcal{H}$, the entire free energy $\mathcal{F}$ and the entire Gibbs function $\mathcal{G}$ are defined similarly (we apologize: the symbols $\mathcal{F}$ and $\mathcal{H}$ appeared in connection with mixture families, too, with a different meaning).

Then – taking the first $(m-1)$ concentrations as independent –

$$\frac{\partial \mathcal{P}}{\partial V} = \frac{1}{N}\frac{\partial \mathcal{P}}{\partial v},$$

$$\frac{\partial \mathcal{P}}{\partial N^\beta} = \frac{1}{N}\left(-v\frac{\partial \mathcal{P}}{\partial v} + \frac{\partial \mathcal{P}}{\partial c^\beta} - \sum_{\gamma=1}^{m-1} c^\gamma \frac{\partial \mathcal{P}}{\partial c^\gamma}\right) \qquad (\beta = 1, \dots, m-1),$$

$$\frac{\partial \mathcal{P}}{\partial N^m} = \frac{1}{N}\left(-v\frac{\partial \mathcal{P}}{\partial v} - \sum_{\gamma=1}^{m-1} c^\gamma \frac{\partial \mathcal{P}}{\partial c^\gamma}\right).$$

Moreover,

$$\frac{\partial \mathcal{E}}{\partial V} = \frac{\partial \mathfrak{e}}{\partial v}, \qquad \frac{\partial \mathcal{E}}{\partial T} = N\frac{\partial \mathfrak{e}}{\partial T},$$

$$\frac{\partial \mathcal{E}}{\partial N^\beta} = \mathfrak{e} - v\frac{\partial \mathfrak{e}}{\partial v} + \frac{\partial \mathfrak{e}}{\partial c^\beta} - \sum_{\gamma=1}^{m-1} c^\gamma \frac{\partial \mathfrak{e}}{\partial c^\gamma} \qquad (\beta = 1, \dots, m-1),$$

$$\frac{\partial \mathcal{E}}{\partial N^m} = \mathfrak{e} - v\frac{\partial \mathfrak{e}}{\partial v} - \sum_{\gamma=1}^{m-1} c^\gamma \frac{\partial \mathfrak{e}}{\partial c^\gamma},$$

and similar relations hold also for $\mathcal{S}$, $\mathcal{F}$, $\mathcal{H}$ and $\mathcal{G}$.

As a consequence, the partial derivatives of the entire quantities with respect to volume and temperature satisfy the same relations as those of the specific quantities, i.e. for entropic bodies

$$T\frac{\partial \mathcal{S}}{\partial V} = \frac{\partial \mathcal{E}}{\partial V} + \mathcal{P}, \qquad T\frac{\partial \mathcal{S}}{\partial T} = \frac{\partial \mathcal{E}}{\partial T},$$

$$\frac{\partial \mathcal{F}}{\partial V} = -\mathcal{P}, \qquad \frac{\partial \mathcal{F}}{\partial T} = -\mathcal{S},$$

furthermore, for all $\alpha = 1, \dots, m$

$$T\frac{\partial \mathcal{S}}{\partial N^\alpha} = \frac{\partial \mathcal{E}}{\partial N^\alpha} - \boldsymbol{\mu}^\alpha, \qquad \frac{\partial \mathcal{F}}{\partial N^\alpha} = \boldsymbol{\mu}^\alpha.$$

27.3 The entire canonical variables

Of course, a body can be given in canonical variables, too, as $\big(\mathrm{D} \times \mathrm{R}_0^+, \mathbf{T}, \mathbf{P}, (\boldsymbol{\mu}^\alpha \mid \alpha \in \mathcal{A}), \mathrm{R}\big)$.

The relation between the specific quantities and the entire ones is realized by the infinitely differentiable mapping

$$(\mathrm{J})^+ \times (\mathrm{m}^3)^+ \times \overline{\mathrm{C}}_m \times \mathbb{R}_0^+ \to (\mathrm{J})^+ \times (\mathrm{m}^3)_0^+ \times (\mathbb{R}_0^+)^m,$$
$$(e, v, c, N) \mapsto (Ne, Nv, Nc^1, \dots, Nc^m) =: (E, V, N^1, \dots, N^m).$$

This function maps the set $\mathrm{D} \times \{0\}$ (the state with zero particle number) into the single element $(0,0,0\dots,0)$ and establishes a bijection between $(\mathrm{J})^+ \times (\mathrm{m}^3)^+ \times \overline{\mathrm{C}}_m \times \mathbb{R}^+$ and $(\mathrm{J})^+ \times (\mathrm{m}^3)^+ \times (\mathbb{R}^+)^m$ having the infinitely differentiable inverse

$$(E, V, N^1, \dots, N^m) \mapsto (E/V, V/N, N^1/N \dots, N^m/N, N).$$

Using the entire canonical variables – supposing that $N \neq 0$ – we apply the ambiguous notation similar to that for simple materials:

$$\mathbf{T}(E, V, N^1, \dots, N^m) = \mathbf{T}(E/N, V/N, N^1/N, \dots, N^m/N)$$

and similar ones for $\mathbf{P}$ and $\boldsymbol{\mu}^\alpha$, too. These functions are defined on

$$\mathbb{R}^+\mathrm{D} := \{(Ne, Nv, Nc) \mid (e, v, c) \in \mathrm{D}, N \in \mathbb{R}^+\}$$

and are continuously differentiable on

$$\mathbb{R}^+\mathrm{R} := \{(Ne, Nv, Nc) \mid (e, v, c) \in \mathrm{R}, N \in \mathbb{R}^+\}.$$

Then – taking the first $(m-1)$ concentrations as independent –

$$\frac{\partial \mathbf{T}}{\partial E} = \frac{1}{N}\frac{\partial \mathbf{T}}{\partial e}, \qquad \frac{\partial \mathbf{T}}{\partial V} = \frac{1}{N}\frac{\partial \mathbf{T}}{\partial v},$$

$$\frac{\partial \mathbf{T}}{\partial N^\beta} = \frac{1}{N}\left(-e\frac{\partial \mathbf{T}}{\partial e} - v\frac{\partial \mathbf{T}}{\partial v} + \frac{\partial \mathbf{T}}{\partial c^\beta} - \sum_{\gamma=1}^{m-1} c^\gamma \frac{\partial \mathbf{T}}{\partial c^\gamma}\right) \qquad (\beta = 1, \dots, m-1), \qquad (*)$$

$$\frac{\partial \mathbf{T}}{\partial N^m} = \frac{1}{N}\left(-e\frac{\partial \mathbf{T}}{\partial e} - v\frac{\partial \mathbf{T}}{\partial v} - \sum_{\gamma=1}^{m-1} c^\gamma \frac{\partial \mathbf{T}}{\partial c^\gamma}\right)$$

and similar formulae hold for $\mathbf{P}$ and $\boldsymbol{\mu}^\alpha$, too.

Let us observe that

$$\sum_{\beta=1}^{m} c^\beta \frac{\partial \mathbf{T}}{\partial N^\beta} = \frac{1}{N}\left(-e\frac{\partial \mathbf{T}}{\partial e} - v\frac{\partial \mathbf{T}}{\partial v}\right).$$

Furthermore, we easily deduce for the entire entropy

$$\mathbf{S}(E, V, N^1, \dots, N^m) := N\mathbf{s}(E/N, V/N, N^1/N, \dots, N^m/N)$$

that

$$\frac{\partial \mathbf{S}}{\partial E} = \frac{\partial \mathbf{s}}{\partial e}, \qquad \frac{\partial \mathbf{S}}{\partial V} = \frac{\partial \mathbf{s}}{\partial v}$$

and

$$\frac{\partial \mathbf{S}}{\partial N^\beta} = \mathbf{s} - e\frac{\partial \mathbf{s}}{\partial e} - v\frac{\partial \mathbf{s}}{\partial v} + \frac{\partial \mathbf{s}}{\partial c^\beta} - \sum_{\gamma=1}^{m-1} c^\gamma \frac{\partial \mathbf{s}}{\partial c^\gamma} \qquad (\beta = 1, \dots, m-1), \qquad (*)$$

$$\frac{\partial \mathbf{S}}{\partial N^m} = \mathbf{s} - e\frac{\partial \mathbf{s}}{\partial e} - v\frac{\partial \mathbf{s}}{\partial v} - \sum_{\gamma=1}^{m-1} c^\gamma \frac{\partial \mathbf{s}}{\partial c^\gamma}$$

and similar equalities for the entire free energy $\mathbf{F}(E, V, N^1, \dots, N^m) := N\mathbf{f}(E/N, V/N, N^1/N, \dots, N^m/N)$, the entire enthalpy $\mathbf{H}$ and the entire Gibbs function $\mathbf{G}$.

27.4 Entropic property in the entire canonical variables

Formulae in Paragraphs 21.6 and 27.3 give for entropic bodies

$$\frac{\partial \mathbf{S}}{\partial E} = \frac{1}{\mathbf{T}}, \quad \frac{\partial \mathbf{S}}{\partial V} = \frac{\mathbf{P}}{\mathbf{T}}, \quad \frac{\partial \mathbf{S}}{\partial N^\alpha} = -\frac{\boldsymbol{\mu}^\alpha}{\mathbf{T}} \qquad (\alpha = 1, \dots, m),$$

in other words,

$$\mathtt{D}\mathbf{S} = \left(\frac{1}{\mathbf{T}}, \frac{\mathbf{P}}{\mathbf{T}}, -\frac{\boldsymbol{\mu}^1}{\mathbf{T}}, \dots, -\frac{\boldsymbol{\mu}^m}{\mathbf{T}} \right).$$

The second derivative of the entire entropy is similar to that in Paragraph 8.4: the last column (and last row) is to be replaced with m similar columns (and rows): instead of $\boldsymbol{\mu}$ and $\frac{\partial}{\partial N}$ we have to write $\boldsymbol{\mu}^\alpha$ and $\frac{\partial}{\partial N^\beta}$ for $\alpha, \beta = 1, \dots, m$.

Then Proposition 21.6 implies the following important result:

Proposition *For all* $(E, V, N^1, \dots, N^m)$ *in* $\mathbb{R}^+\mathrm{R}$, $\mathtt{D}^2\mathbf{S}(E, V, N^1 \dots, N^m)$ *is negative semidefinite having the kernel spanned by* $(E, V, N^1 \dots, N^m)$.

27.5 A useful formalism

Using the familiar symbolic notations, we can write the entropic property in the form

$$T\mathtt{d}S = \mathtt{d}E + P\mathtt{d}V - \sum_{\alpha=1}^{m} \mu^\alpha \mathtt{d}N^\alpha$$

which allows us to easily deduce the relations among partial derivatives in different variables.

The symbolic form of the Gibbs–Duhem relations – based on the 'rules' $\mathtt{d}(PV) = P\mathtt{d}V + V\mathtt{d}P$ etc. – becomes

$$\sum_{\alpha=1}^{m} N^\alpha \mathtt{d}\mu^\alpha = -S\mathtt{d}T + V\mathtt{d}P,$$

or, with the entire Gibbs function

$$G := \sum_{\alpha=1}^{m} N^\alpha \mu^\alpha = E - TS + PV$$

(called sometimes free enthalpy, too)

$$\mathtt{d}G = V\mathtt{d}P - S\mathtt{d}T + \sum_{\alpha=1}^{m} \mu^\alpha \mathtt{d}N^\alpha.$$

27.6 Exercises

1. Deduce relations for the partial derivatives of the entire free energy of an entropic composite body in the canonical variables.

2. Take a body mixed ideally of two different ideal gases. Give its pressure, entire internal energy and entire entropy as a function of (V, T, N^1, N^2); give its pressure, temperature and entire entropy as a function of (E, V, N^1, N^2).

28 Thermodynamical forces

28.1 Problems of definition

Let us take two bodies composed of the same materials in the form of Definition 27.1. We would think that the thermodynamical force between them consists of the temperature difference, the pressure difference and the chemical potential difference of the components. The temperature difference is a trivially defined quantity. The pressure difference is all right as a function defined on $D \times D$; if the states of a body are denoted by the usual letters and the states of the other body are denoted by a subscript $*$ to the letters, then $\mathcal{P}(v, T, c) - \mathcal{P}(v_*, T_*, c_*)$ is the pressure component of the thermodynamical force.

The chemical potentials, however, are not defined on the whole D; in the case of different compositions of the bodies, the difference of the chemical potentials of the components that are not common is not defined. This would roughly mean that only the common components could pass from one body to the other though it is an everyday phenomenon that salt diffuses from a water–salt solution into pure water.

Let us see the problem more closely. The domain of the difference of the α-th chemical potentials is not the whole $D \times D$: $\boldsymbol{\mu}^\alpha(v, T, c) - \boldsymbol{\mu}^\alpha(v_*, T_*, c_*)$ is defined only if $c^\alpha \neq 0$ and $c_*^\alpha \neq 0$. Moreover, according to the usual assumptions treated in Paragraph 23.2, the limit of that expression is $-\infty$ as $c^\alpha \to 0$ which makes doubtful the definition of the thermodynamical force.

28.2 Solution of the problems

Let us recall Paragraph 11: we see that the thermodynamical force never appears alone, it is always multiplied by the conductance matrix. Therefore, we can hope that the product of the coefficient functions and the difference of chemical potentials possesses a convenient limit as a concentration tends to zero. More closely, if the member

$$-\vartheta_\alpha(v, T, c, N, v_*, T_*, c_*, N_*)\big(\boldsymbol{\mu}^\alpha(v, T, c) - \boldsymbol{\mu}^\alpha(v_*, T_*, c_*)\big)$$

appears in the converting of the α-th component where, of course, $c^\alpha \neq 0$ and $c_*^\alpha \neq 0$, then there exist

$$\lim_{c^\alpha \to 0} \vartheta_\alpha(v, T, c, N, v_*, T_*, c_*, N_*)\big(\boldsymbol{\mu}^\alpha(v, T, c) - \boldsymbol{\mu}^\alpha(v_*, T_*, c_*)\big),$$

$$\lim_{c_*^\alpha \to 0} \vartheta_\alpha(v, T, c, N, v_*, T_*, c_*, N_*)\big(\boldsymbol{\mu}^\alpha(v, T, c) - \boldsymbol{\mu}^\alpha(v_*, T_*, c_*)\big).$$

For the sake of simplicity, in the sequel we write

$$\big(-(T - T_*), P - P_*, -(\mu^\alpha - \mu_*^\alpha \mid \alpha = 1, \dots, m)\big),$$

for the thermodynamical force which multiplied by the matrix

$$\begin{pmatrix} \lambda_Q & \beta_Q & (\vartheta_Q^\alpha \mid \alpha = 1, \dots, m) \\ \lambda_F & \beta_F & (\vartheta_F^\alpha \mid \alpha = 1 \dots, m) \\ \lambda_G & \beta_G & (\vartheta_G^\alpha \mid \alpha = 1, \dots, m) \end{pmatrix}$$

gives the heating Q, the springing F and the convertings G^α $(\alpha = 1, \dots, m)$ of the components between the bodies, and we keep in mind that neither the thermodynamical force (the difference of certain chemical potentials) nor the conductance matrix (its certain entries) are meaningful for different compositions of the bodies, only their product has a meaning.

The same is true for the canonical thermodynamical force

$$\left(\frac{1}{T} - \frac{1}{T_*}, \frac{P}{T} - \frac{P_*}{T_*}, -\left(\frac{\mu^\alpha}{T} - \frac{\mu_*^\alpha}{T_*} \,\middle|\, \alpha = 1, \dots, m\right)\right)$$

which is more often used.

29 System of bodies

29.1 Definition of a system

Now we are in a position to formulate the mathematical model of interacting systems of composite bodies. If the particle transport is forbidden between the bodies, then we have a system treated in Chapter III. If the bodies can interchange particles, we can consider that each body is the mixture of the same materials (at most the actual composition of the bodies differ).

We simplify the formulation by taking only ideal workings and ideal transferrings; someone familiar with the description of such systems, can easily give the generalization for non-ideal cases.

Definition *A system of bodies composed of given materials with given sources under the action of a given environment consists of the following*

0. *A positive integer* $m \geq 2$ *and simple materials* $(\mathrm{D}_\alpha, \mathbf{T}_\alpha, \mathbf{P}_\alpha, \boldsymbol{\mu}_\alpha, \mathrm{R}_\alpha)$ $\quad(\alpha = 1 \dots, m)$.

1. *A positive integer* n *and a collection of bodies marked by the symbols* $\{a, 1, \dots, n\}$*; the a-th body is called the* **environment**.

Each body is represented in the form

$$\big(\mathrm{D} \times \mathbb{R}_0^+, \mathbf{T}, \mathbf{P}, (\boldsymbol{\mu}^\alpha \mid \alpha = 1, \dots, m), \mathrm{R}\big)$$

according to Definition 27.1 and the notation $\mathbf{c} : \mathrm{D} \to \overline{\mathrm{C}}_m, \quad (e, v, c) \mapsto c$ *will be used.*

2. *For all* $i, k = a, 1, \dots, n$ *the* **dynamical quantitities**

$$\mathbf{Q}_{ik} : (\mathbb{R}_0^+\mathrm{D}) \times (\mathbb{R}_0^+\mathrm{D}) \to (\mathrm{J/s}),$$

$$\mathbf{F}_{ik} : (\mathbb{R}_0^+\mathrm{D}) \times (\mathbb{R}_0^+\mathrm{D}) \to (\mathrm{m}^3/\mathrm{s}),$$

$$\mathbf{G}_{ik}^\alpha : (\mathbb{R}_0^+\mathrm{D}) \times (\mathbb{R}_0^+\mathrm{D}) \to (1/\mathrm{s}), \quad (\alpha = 1, \dots, m),$$

which are continuous, moreover continuously differentiable on the interior of their domain.

With the notation

$$Q_{ik} := \mathbf{Q}_{ik}(E_i, V_i, N_i^1, \dots, N_i^m, E_k, V_k, N_k^1, \dots, N_k^m), \qquad \textit{etc.},$$

$$A_{ik} := Q_{ik} - P_i F_{ik} + \sum_{\alpha=1}^{m} \mu_i^\alpha G_{ik}$$

and other similar simplified notations, the dynamical quantitities satisfy

– **mutuality***:*

$$A_{ik} = -A_{ki}, \quad F_{ik} = -F_{ki}, \quad G_{ik}^\alpha = -G_{ki}^\alpha \quad (\alpha = 1, \dots, m),$$

– *the* **equilibrium property** $\left(N_i := \sum\limits_{\alpha=1}^{m} N_i^\alpha\right)$

(I) if $N_i N_k = 0$ *then* $Q_{ik} = 0$, $F_{ik} = 0$, $G_{ik}^\alpha = 0$ $(\alpha = 1, \dots, m)$,

(II) for $N_i N_k \neq 0$

1) if $\mathbf{G}_{ik}^\alpha = 0$ *for all* $\alpha = 1, \dots, m$

(a) and $\mathbf{F}_{ik} = 0$, $\mathbf{Q}_{ik} \neq 0$, *then*

$*$ $Q_{ik} = 0 \iff T_i = T_k$,

(b) and $\mathbf{Q}_{ik} = 0$, $\mathbf{F}_{ik} \neq 0$, *then*

$*$ $F_{ik} = 0 \iff P_i = P_k$,

(c) if $\mathbf{F}_{ik} \neq 0$, $\mathbf{Q}_{ik} \neq 0$, *then*

$*$ $F_{ik} = 0 \implies P_i = P_k$,

$*$ $Q_{ik} = 0$ *and* $P_i = P_k \implies T_i = T_k$,

$**$ $T_i = T_k$ *and* $P_i = P_k \implies Q_{ik} = 0$ *and* $F_{ik} = 0$;

2) if there is an α *such that* $\mathbf{G}_{ik}^\alpha \neq 0$ *and can have both positive and negative values*

(a) and $\mathbf{F}_{ik} = 0$, $\mathbf{Q}_{ik} = 0$, *then*

$*$ $G_{ik}^\alpha = 0 \iff \mu_i^\alpha = \mu_k^\alpha$;

(b) and $\mathbf{F}_{ik} = 0$, $\mathbf{Q}_{ik} \neq 0$, *then*

$*$ $G_{ik}^\alpha = 0 \implies \mu_i^\alpha = \mu_k^\alpha$;

$*$ $\mu_i^\alpha = \mu_k^\alpha$ *and* $Q_{ik} = 0 \implies T_i = T_k$

(which imply that if $G_{ik}^\alpha = 0$ *and* $Q_{ik} = 0$, *then* $\mu_i^\alpha = \mu_k^\alpha$ *and* $T_i = T_k$*),*

$**$ $\mu_i^\alpha = \mu_k^\alpha$ *and* $T_i = T_k \implies G_{ik}^\alpha = 0$ *and* $Q_{ik} = 0$;

(c) and $\mathbf{F}_{ik} \neq 0$, $\mathbf{Q}_{ik} = 0$, *then*

$*$ $G_{ik}^\alpha = 0 \implies \mu_i^\alpha = \mu_k^\alpha$;

$*$ $\mu_i^\alpha = \mu_k^\alpha$ *and* $F_{ik} = 0 \implies P_i = P_k$

(which imply that if $G_{ik}^\alpha = 0$ *and* $F_{ik} = 0$, *then* $\mu_i^\alpha = mu_k^\alpha$;

$*$ $\mu_i^\alpha = \mu_k^\alpha$ *and* $P_i = P_k \implies G_{ik}^\alpha = 0$ *and* $F_{ik} = 0$;

(d) and $\mathbf{F}_{ik} \neq 0$, $\mathbf{Q}_{ik} \neq 0$, *then*

$*$ $G_{ik}^\alpha = 0 \implies \mu_i^\alpha = \mu_k^\alpha$;

$*$ $\mu_i^\alpha = \mu_k^\alpha$ *and* $F_{ik} = 0 \implies P_i = P_k$,

$*$ $\mu_i^\alpha = mu_k^\alpha$, $P_i = P_k$, *and* $Q_{ik} = 0 \implies T_i = T_k$

(which imply that if $G^\alpha_{ik} = 0$, $F_{ik} = 0$ *and* $Q_{ik} = 0$, *then* $\mu^\alpha_i = \mu^\alpha_k$, $P_i = P_k$ *and* $T_i = T_k$*),*

$* * *\ \mu^\alpha_i = \mu^\alpha_k$, $P_i = P_k$ *and* $T_i = T_k \implies G^\alpha_{ik} = 0$, $F_{ik} = 0$ *and* $Q_{ik} = 0$*;*

3) if there is an α *such that* $\mathbf{G}^\alpha_{ik} \geq 0$ *(or* $\mathbf{G}^a_{ik} \leq 0$*), then the previous relations (a) to (d) are satisfied in such a way that* $\mu^\alpha_i \geq \mu^\alpha_k$ *(or* $\mu^\alpha_i \geq \mu^\alpha_k$*) appears everywhere instead of* $\mu^\alpha_i = \mu^\alpha_k$*.*

– *the* **dissipation inequalities***:*

$$-\frac{Q_{ik}}{T_i}(T_i - T_k) + F_{ik}(P_i - P_k) - \sum_{\alpha=1}^{m} G^\alpha_{ik}(\mu^\alpha_i - \mu^\alpha_k) \geq 0,$$

where equality holds if and only if $Q_{ik} = 0$, $F_{ik} = 0$ *and* $G^\alpha_{ik} = 0 \quad (\alpha = 1, \dots, m)$ *or, equivalently,*

$$A_{ik}\left(\frac{1}{T_i} - \frac{1}{T_k}\right) + F_{ik}\left(\frac{P_i}{T_i} - \frac{P_k}{T_k}\right) - \sum_{\alpha=1}^{m} G^\alpha_{ik}\left(\frac{\mu^\alpha_i}{T_i} - \frac{\mu^\alpha_k}{T_k}\right) \geq 0.$$

3. *A* **process of the environment***, a continuous function* $t \mapsto (E_a(t), V_a(t), N^1_a(t), \dots, N^m_a(t)) \in \mathbb{R}^+\mathrm{D}_a$ *defined on a time interval.*

4. *For all* $i = 1, \dots, n$ *and* $\alpha = 1, \dots, m$ *the* **sources***, continuous functions* $t \mapsto Q_{i,s}(t) \in (\mathrm{J/s})$ *and* $t \mapsto G^\alpha_{i,s}(t) \in (1/\mathrm{s})$ *defined on a time interval.*

5. *The* **dynamical equation** *for* $(i = 1, \dots, n)$*:*

$$\dot{E}_i = Q_i - P_i F_i + \sum_{\alpha=1}^{m} \mu^\alpha_i G^\alpha_i \qquad \dot{V}_i = F_i, \qquad \dot{N}^\alpha_i = G^\alpha_i \quad (\alpha = 1, \dots, m),$$

where

$$Q_i = Q_{i,s} + \sum_{k=a,1}^{n} Q_{ik}, \quad F_i = \sum_{k=a,1}^{n} F_{ik}, \quad G^\alpha_i = G^\alpha_{i,s} + \sum_{k=a,1}^{n} G^\alpha_{ik}.$$

Systems of composite bodies are described formally in the same way as systems of simple bodies; the only difference is that now convertings of each component is to be taken into account. Remarks in 14.1 remain valid.

29.2 Summarizing formulae

The description of systems can be put in an abstract framework similar to that treated in Section 15.

For the sake of simplicity, we suppose that the sources are zero; besides the results concerning the equilibria, everything can be repeated for non-zero sources, too.

According to paragraph 27.2, the states of the bodies are elements of the subset

$$\mathop{\times}_{i=1}^{n} (\mathbb{R}^+_0 \mathrm{D}_i)$$

of the vector space

$$X := \Big((\mathrm{J}) \times (\mathrm{m}^3) \times \mathbb{R}^m\Big)^n;$$

a state will be denoted by

$$x := \Big(x_i := (E_i, V_i, N_i^1, \dots, N_i^m) \;\Big|\; i = 1, \dots, n\Big).$$

Again kT is taken instead of T; then the Cartesian product of the intensive quantities of the bodies is the function

$$\mathbf{y} := \mathop{\times}_{i=1}^{n} \mathbf{y}_i := \mathop{\times}_{i=1}^{n} \left(\frac{1}{k\mathbf{T}}, \frac{\mathbf{P}}{k\mathbf{T}}, -\frac{\boldsymbol{\mu}^1}{k\mathbf{T}}, \dots, -\frac{\boldsymbol{\mu}^m}{k\mathbf{T}}\right) : X \rightarrowtail X^*.$$

As in Section 15, the dynamical equation can be written in the form

$$(x : I \to X_{R_S})? \qquad \dot{x} = \mathbf{R}(x, x_a).$$

We can define the nominal thermodynamical force $\mathbf{F}$ and the nominal conductance matrix $\mathbf{B}$ as in Section 15 (with a little care because of Paragraph 28.1) and then

$$\mathbf{R}(x, x_a) = \mathbf{B}(x, x_a)\mathbf{F}(x, x_a).$$

Constraints, holonomic and anholonomic ones, the effective thermodynamical force and conductance matrix are defined as in Section 15, and we can repeat what we know about the relation between the nominal conductance matrix and the effective one.

The entropy of the environment – in usual loose notations – is

$$S_a = \frac{E_a + P_a V_a - \sum\limits_{\alpha=1}^{m} \mu_a^a N_a^\alpha}{T_a}.$$

The bodies and the environment together form a ‘closed system’, i.e. their total energy, total volume and total particle numbers are constant,

$$\sum_{k=a,1}^{n} E_k = \text{const}, \qquad \sum_{k=a,1}^{n} V_k = \text{const}, \qquad \sum_{k=a,1}^{n} N_k^\alpha = \text{const} \quad (\alpha = 1, \dots, m).$$

Thus, if the process of the environment is constant, the total entropy of the bodies and the environment equals, up to an additive constant,

$$\mathbf{L}(E_1, V_1, N_1^1 \dots, N_1^m, \dots, \dots, E_n, V_n, N_n^1, \dots, N_n^m) :=$$
$$\sum_{i=1}^{n} \left(\mathbf{S}_i(E_i, V_i, N_i^1, \dots, N_i^m) - \frac{E_i + P_a V_i - \sum\limits_{\alpha=1}^{m} \mu_a^\alpha N_i^\alpha}{T_a}\right).$$

This function is twice differentiable on $\times_{i=1}^{n}(\mathbb{R}_0^+\mathrm{R}_i)$, $\mathtt{D}\mathbf{L}$ is the nominal force for entropic bodies, moreover, $\mathtt{D}^2\mathbf{L}(x)$ is negative semidefinite for all x having the kernel spanned by the vectors

$$(x_1, 0, 0, \dots, 0), \quad (0, x_2, 0, \dots, 0), \quad \dots \quad (0, 0, 0, \dots, x_N)$$

(cf. 15.6).

Therefore, Propositions 15.6 and 15.8 and remarks to them remain valid. Finally, we can repeat Paragraph 15.9 about extremum properties.

30 A body in a given environment

30.1 The framework of description

The processes of a body composed of the materials $(\mathrm{D}_\alpha, \mathbf{T}_\alpha, \mathbf{P}_\alpha, \boldsymbol{\mu}_\alpha, \mathrm{R}_\alpha)$ $(\alpha = 1, \dots, m)$ will be examined in an environment composed of the same materials. The given constant process of the environment will be characterized by the temperature T_a, the pressure P_a and the concentrations $c_a \in \overline{\mathrm{C}}_m$. We shall use the notations introduced earlier, and μ^α will be the chemical potential of the α-th component as a function of temperature, pressure and concentrations in a neighbourhood of (T_a, P_a, c_a) and

$$\mu_a^\alpha := \mu^\alpha(T_a, P_a, c_a) \qquad (\alpha = 1, \dots, m).$$

The processes of the body are supposed to run in the phase that the environment is in. If there is no restriction on the convertings, such a system is treated as the ones in Section 18; as a sample, we present the constraint-free system. We faced a new problem, however, if the converting of some components is forbidden. This will be illustrated by two examples.

30.2 System without constraint

Let us exclude states in which some particle numbers are zero and let us suppose that the composition of the body and the environment coincide. We can suppose that all components are present in the processes, i.e. $c_a \in C_m$.

The dynamical equation has the form

$$\dot{E} = Q - PF + \sum_{\alpha=1}^{m} \mu^\alpha G^\alpha, \quad \dot{V} = F,$$

$$\dot{N}^\alpha = G^\alpha \qquad (\alpha = 1, \dots, m).$$

The equilibrium values of the specific quantities and the concentration are uniquely determined by

$$\mathbf{T}(e_o, v_o, c_o) = T_a, \quad \mathbf{P}(e_o, v_o, c_o) = P_a,$$

$$\boldsymbol{\mu}^\alpha(e_o, v_o, c_o) = \mu_a^\alpha \qquad (\alpha = 1, \dots, m).$$

Because the phase of the body coincedes with that of the environment, we have $c_o = c_a$.

There is no condition on the particle number of the body.

Proposition 1 *The set of equilibria with non-zero particle number is*

$$\{N(e_\mathrm{o}, v_\mathrm{o}, c_a) \mid N \in \mathbb{R}^+\}.$$

We can prove as Proposition 18.2.2:

Proposition 2 *If the body is entropic and the equilibrium values of the (nominal) conductance matrix are symmetric and positive definite, then the set of equilibrium is strictly asymptotically stable.*

30.3 Selective converting, fixed volume

We consider a two-component body in a one-component environment; the body is enclosed with a rigid wall which passes through only the component corresponding to the environment. Let the set of components be $\mathcal{A} = \{\mathrm{w}, \mathrm{t}\}$ ('(w)ater' and 'sal(t)') and let the environment be pure water (salt cannot permeate the wall), i.e. $\mathcal{F} = \{\mathrm{w}, \mathrm{t}\}$, $\mathcal{F}_a = \{\mathrm{w}\}$; the latter means that $c_a = (1, 0)$.

The dynamical equation has the form

$$\dot{E} = Q + \mu^\mathrm{w} G^\mathrm{w}, \quad \dot{V} = 0, \quad \dot{N}^\mathrm{w} = G^\mathrm{w}, \quad \dot{N}^\mathrm{t} = 0.$$

Let V_o and N_o^t denote the constant volume and salt particle number of the body, respectively. Then

$$U(V_\mathrm{o}, N_\mathrm{o}^\mathrm{t}) := \{(E, V_\mathrm{o}, N^\mathrm{w}, N_\mathrm{o}^\mathrm{t}) \mid E \in (\mathrm{J})^+, N^\mathrm{w} \in \mathbb{R}^+\}$$

is an invariant submanifold of the dynamical equation.

If there is an equilibrium with non-zero water particle number, then the equilibrium values E_o and N_o^w of internal energy and water particle number, respectively, of the body are determined by

$$\mathbf{T}(E_\mathrm{o}, V_\mathrm{o}, N_\mathrm{o}^\mathrm{w}, N_\mathrm{o}^\mathrm{t}) = T_a, \qquad \boldsymbol{\mu}^\mathrm{w}(E_\mathrm{o}, V_\mathrm{o}, N_\mathrm{o}^\mathrm{w}, N_\mathrm{o}^\mathrm{t}) = \mu_\mathrm{w}(T_a, P_a).$$

Proposition *If the body is entropic, then the equilibrium $(E_\mathrm{o}, V_\mathrm{o}, N_\mathrm{o}^\mathrm{w}, N_\mathrm{o}^\mathrm{t})$ (if exists) is asymptotically stable in $U(V_\mathrm{o}, N_\mathrm{o}^\mathrm{t})$.*

Proof The conditions of Proposition 15.6 are satisfied, but we can prove directly that

$$(E, N^\mathrm{w}) \mapsto \mathbf{S}(E, V_\mathrm{o}, N^\mathrm{w}, N_\mathrm{o}^\mathrm{t}) - \frac{E - \mu_a^\mathrm{w} N^\mathrm{w}}{T_a}$$

is a Liapunov function for the asymptotic stability of the equilibrium $(E_\mathrm{o}, N_\mathrm{o}^\mathrm{w})$ of the reduced dynamical equation

$$\dot{E} = Q + \mu^\mathrm{w} G^\mathrm{w}, \quad \dot{N}^\mathrm{w} = G^\mathrm{w}.$$

Remark Returning to the specific quantities, we find that in equilibrium

$$\mu^\mathrm{w}(T_a, P_a, c^\mathrm{w}, 1 - c^\mathrm{w}) = \mu_\mathrm{w}(T_a, P_a),$$

thus the water reaches the saturation concentration in the body (cf. 24.6). Thus equilibrium can exist only if the solution is not semi-ideal. The same is true for the system in the next paragraph.

30.4 Selective converting

We consider a system similar to the previous one but the wall is not rigid.

The dynamical equation has the form

$$\dot{E} = Q - PF + \mu^{\mathrm{w}} G^{\mathrm{w}}, \quad \dot{V} = F, \quad \dot{N}^{\mathrm{w}} = G^{\mathrm{w}} \quad \dot{N}^{\mathrm{t}} = 0.$$

Let $N_{\mathrm{o}}^{\mathrm{t}}$ denote the constant salt particle number in the body. Then

$$U(N_{\mathrm{o}}^{\mathrm{t}}) := \{(E, V, N^{\mathrm{w}}, N_{\mathrm{o}}^{\mathrm{t}}) \mid E \in (\mathrm{J})^+, V \in (\mathrm{m}^3)^+, N^{\mathrm{w}} \in \mathbb{R}^+\}$$

is an invariant submanifold of the dynamical equation.

If there is an equilibrium with non-zero value of water particle number, then the equilibrium values E_{o}, V_{o} and $N_{\mathrm{o}}^{\mathrm{w}}$ of internal energy, volume and water particle number, respectively, of the body are determined by

$$\mathbf{T}(E_{\mathrm{o}}, V_{\mathrm{o}}, N_{\mathrm{o}}^{\mathrm{w}}, N_{\mathrm{o}}^{\mathrm{t}}) = T_a, \qquad \mathbf{P}(E_{\mathrm{o}}, V_{\mathrm{o}}, N_{\mathrm{o}}^{\mathrm{w}}, N_{\mathrm{o}}^{\mathrm{t}}) = P_a,$$

$$\boldsymbol{\mu}^{\mathrm{w}}(E_{\mathrm{o}}, V_{\mathrm{o}}, N_{\mathrm{o}}^{\mathrm{w}}, N_{\mathrm{o}}^{\mathrm{t}}) = \mu_{\mathrm{w}}(T_a, P_a).$$

As in the previous paragraph, we can prove that if the body is entropic, then the equilibrium (if exists) is asymptotically stable.

30.5 Exercises

1. Treat the isothermal and the isobaric processes of a body in an environment if there is no constraint, and the body and the environment have the same composition (follow the line of Paragraphs 18.4 and 18.5).
2. How does the treatment of the isothermal and the isobaric processes change if the body is pure 'water' and the environment is 'water-salt' solution (i.e. the salt particles cannot enter into the body).
3. Compare the result in Paragraph 30.3 with Paragraph 24.5 about osmosis.

31 Two bodies in a given environment

31.1 The framework of description

Te processes of two bodies composed of the materials $(\mathrm{D}_\alpha, \mathbf{T}_\alpha, \mathbf{P}_\alpha, \boldsymbol{\mu}_\alpha, \mathrm{R}_\alpha)$ $(\alpha = 1, \dots, m)$ will be examined in an environment; the bodies and the environment cannot interchange particles (the bodies together are enclosed with an impermeable wall). We shall use the previous notations.

If there is no restriction on the convertings, such systems are treated as the ones in Section 18; as a sample, we present the system in which the bodies can interact freely (without constraint) but they are completely isolated from the environment. As in the previous section, we face a new problem, however, if the converting of some components is forbidden, which is illustrated by two examples.

31.2 Fixed total energy and total volume

31.2.1 The dynamical equation

The bodies are completely isolated from the environment.

The dynamical equation has the form

$$\dot{E}_1 = Q_1 - P_1F_1 + \sum_{\alpha=1}^{m} \mu^\alpha G_1^\alpha, \qquad \dot{V}_1 = F_1,$$

$$\dot{N}_1^\alpha = G_1^\alpha \qquad (\alpha = 1, \dots, m),$$

$$\dot{E}_2 = Q_2 - P_2F_2 + \sum_{\alpha=1}^{m} \mu^\alpha G_2^\alpha, \qquad \dot{V}_2 = F_2,$$

$$\dot{N}_2^\alpha = G_2^\alpha \qquad (\alpha = 1, \dots, m).$$

The constraint (isolation from the environment) is described by

$$\dot{E}_1 + \dot{E}_2 = 0, \qquad \dot{V}_1 + \dot{V}_2 = 0, \qquad \dot{N}_1^\alpha + \dot{N}_2^\alpha = 0 \quad (\alpha = 1, \dots, m).$$

Consequently, for all $E_\mathrm{s} \in (\mathrm{J})^+$, $V_\mathrm{s} \in (\mathrm{m}^3)^+$ and $N_\mathrm{s}^\alpha \in \mathbb{R}^+ \quad (\alpha = 1, \dots, m)$,

$$\begin{aligned} U(E_\mathrm{s}, V_\mathrm{s}, N_\mathrm{s}^1, \dots, N_\mathrm{s}^m) := \{ &(E_1, V_1, N_1^1, \dots, N_1^m), (E_2, V_2, N_2^1, \dots, N_2^m) \mid \\ &E_1 + E_2 = E_\mathrm{s},\ V_1 + V_2 = V_\mathrm{s},\ N_1^\alpha + N_2^\alpha = N_\mathrm{s}^\alpha\ (\alpha = 1, \dots, m) \} \end{aligned}$$

is an invariant submanifold of the dynamical equation.

The equilibrium values of specific quantities and concentrations satisfy

$$\mathbf{T}(e_{1\mathrm{o}}, v_{1\mathrm{o}}, c_{1\mathrm{o}}) = \mathbf{T}(e_{2\mathrm{o}}, v_{2\mathrm{o}}, c_{2\mathrm{o}}), \qquad \mathbf{P}(e_{1\mathrm{o}}, v_{1\mathrm{o}}, c_{1\mathrm{o}}) = \mathbf{P}(e_{2\mathrm{o}}, v_{2\mathrm{o}}, c_{2\mathrm{o}}),$$

$$\boldsymbol{\mu}^\alpha(e_{1\mathrm{o}}, v_{1\mathrm{o}}, c_{1\mathrm{o}}) = \boldsymbol{\mu}^\alpha(e_{2\mathrm{o}}, v_{2\mathrm{o}}, c_{2\mathrm{o}}) \quad (\alpha = 1, \dots, m).$$

31.2.2 Identical phases

If the equilibrium states of the bodies are in the same phase, then – because the joint of the functions in the previous equalities is injective –

$$e_{1\mathrm{o}} = e_{2\mathrm{o}} =: e_\mathrm{o} = \frac{E_\mathrm{s}}{N_\mathrm{s}}, \quad v_{1\mathrm{o}} = v_{2\mathrm{o}} =: v_\mathrm{o} = \frac{V_\mathrm{s}}{N_\mathrm{s}},$$

$$c_{1\mathrm{o}} = c_{2\mathrm{o}} =: c_\mathrm{o} = \frac{(N_\mathrm{s}^1, \dots, N_\mathrm{s}^m)}{N_\mathrm{s}}$$

where

$$N_\mathrm{s} := \sum_{\alpha=1}^{m} N_\mathrm{s}^\alpha.$$

There is no restriction on the entire particle numbers of the bodies, i.e. on $N_1 := \sum_{\alpha=1}^{m} N_1^\alpha$ and $N_2 := \sum_{\alpha=1}^{m} N_2^\alpha$, thus the set of equilibria with non-zero particle number in $U(E_\mathrm{s}, V_\mathrm{s}, N_\mathrm{s}^1, \dots, N_\mathrm{s}^m)$ is

$$\{(N_1 e_\mathrm{o}, N_1 v_\mathrm{o}, N_1 c_\mathrm{o}, (N_\mathrm{s} - N_1)e_\mathrm{o}, (N_\mathrm{s} - N_1)v_\mathrm{o}, (N_\mathrm{s} - N_1)c_\mathrm{o}) \mid 0 < N_1 < N_\mathrm{s}\}.$$

A proposition similar to that in 19.6 can be proved for the strict asymptotic stability of the set of equilibria.

31.2.3 Different phases

If the equilibrium states of the two bodies are in different phases, then the equalities at the end of 31.2.1 are supplemented by

$$N_{1\mathrm{o}} e_{1\mathrm{o}} + N_{2\mathrm{o}} e_{2\mathrm{o}} = E_\mathrm{s}, \quad N_{1\mathrm{o}} v_{1\mathrm{o}} + N_{2\mathrm{o}} v_{2\mathrm{o}} = V_\mathrm{s},$$
$$N_{1\mathrm{o}}^\alpha + N_{2\mathrm{o}}^\alpha = N_\mathrm{s}^\alpha \quad (\alpha = 1, \dots, m),$$

where

$$N_{1\mathrm{o}} := \sum_{\alpha=1}^{m} N_{1\mathrm{o}}^\alpha, \qquad N_{2\mathrm{o}} := \sum_{\alpha=1}^{m} N_{2\mathrm{o}}^\alpha.$$

As in Paragraph 20.2, we can prove that if the bodies are entropic, then the equilibrium is asymptotically stable (so locally unique) in $U(E_\mathrm{s}, V_\mathrm{s}, N_\mathrm{s}^1, \dots, N_\mathrm{s}^m)$.

31.3 Selective converting, fixed total energy and fixed individual volumes

The two bodies are completely isolated from the environment and there is a rigid wall between the bodies which does not allow certain components to pass through. Let us suppose that one of the bodies has two components and the other body has a pure material: $\mathcal{F}_1 = \{\mathrm{w}, \mathrm{t}\}$, $\mathcal{F}_2 = \{\mathrm{w}\}$ (the first body is a 'water–salt' solution, the second body is pure 'water', salt particles cannot get into the second body).

The dynamical equation has the form

$$\dot{E}_1 = Q_1 + \mu_1^\mathrm{w} G_1^\mathrm{w}, \quad \dot{V}_1 = 0, \quad \dot{N}_1^\mathrm{w} = G_1^\mathrm{w}, \quad \dot{N}_1^\mathrm{t} = 0,$$
$$\dot{E}_2 = Q_2 + \mu_2^\mathrm{w} G_2^\mathrm{w}, \quad \dot{V}_2 = 0, \quad \dot{N}_2^\mathrm{w} = G_2^\mathrm{w}, \quad \dot{N}_2^\mathrm{t} = 0.$$

The chemical potential of water in the second body equals that of the pure material: $\mu_2^\mathrm{w} = \mu_\mathrm{w}$. The given volumes $V_{1\mathrm{o}}$ and $V_{2\mathrm{o}}$ of the bodies, the salt particle numbers $N_{1\mathrm{o}}^\mathrm{t}$ and 0 in the bodies, the total energy E_s of the bodies and the total particle number of water N_s^w in the bodies define an invariant submanifold $U(V_{1\mathrm{o}}, V_{2\mathrm{o}}, N_{1\mathrm{o}}^\mathrm{t}, 0, E_\mathrm{s}, N_\mathrm{s}^\mathrm{w})$ of the dynamical equation which can be parameterized by the variables E_1 and N_1^w. Then the reduced dynamical equation becomes

$$\dot{E}_1 = Q_1 + \mu_1^\mathrm{w} G_1^\mathrm{w}, \quad \dot{N}_1^\mathrm{w} = G_1^\mathrm{w}.$$

The equilibrium value $E_{1\mathrm{o}}$ and $N_{1\mathrm{o}}^\mathrm{w}$ of internal energy and water particle number, respectively, are determined by

$$\mathbf{T}_1(E_{1\mathrm{o}}, V_{1\mathrm{o}}, N_{1\mathrm{o}}^\mathrm{w}, N_{1\mathrm{o}}^\mathrm{t}) = \mathbf{T}_2(E_\mathrm{s} - E_{1\mathrm{o}}, V_{2\mathrm{o}}, N_\mathrm{s}^\mathrm{w} - N_{1\mathrm{o}}^\mathrm{w}, 0),$$
$$\boldsymbol{\mu}_1^\mathrm{w}(E_{1\mathrm{o}}, V_{1\mathrm{o}}, N_{1\mathrm{o}}^\mathrm{w}, N_{1\mathrm{o}}^\mathrm{t}) = \boldsymbol{\mu}_\mathrm{w}(E_\mathrm{s} - E_{1\mathrm{o}}, V_{2\mathrm{o}}, N_\mathrm{s}^\mathrm{w} - N_{1\mathrm{o}}^\mathrm{w}, 0).$$

Proposition *The equilibrium (if exists)* $(E_{1o}, V_{1o}, N^{w}_{1o}, N^{t}_{1o}, E_s - E_{1o}, V_{2o}, N^{w}_{s} - N^{w}_{1o}, 0)$ *is asymptotically stable in* $U(V_{1o}, V_{2o}, N^{t}_{1o}, 0, E_s, N^{w}_{s})$*.*

Proof The conditions of Proposition 15.8 are satisfied, but we can prove directly that

$$(E_1, N^{w}_{1}) \mapsto \mathbf{S}_1(E_1, V_{1o}, N^{w}_{1}, N^{t}_{1o}) + \mathbf{S}_2(E_s - E_1, V_{2o}, N^{w}_{s} - N^{w}_{1}, 0)$$

is a Liapunov function for asymptotic stability.

31.4 Selective converting

The two bodies are separated by a wall which does not allow certain components to pass through (and there is no particle interchange between the bodies and the environment).

The 'wall' can be imaginary: previously we considered water–salt solution and pure water. In the case of water–salt solution and pure salt (a piece of salt dissolves in water) the selective converting is realized without a wall: salt enters the solution but water does not enter the piece of salt. Now we shall treat such processes; the first body is the pure salt and the second body is the water–salt solution.

The dynamical equation has the form

$$\dot{E}_1 = Q_1 - P_1 F_1 + \mu^{t}_{1} G^{t}_{1}, \quad \dot{V}_1 = F_1, \quad \dot{N}^{t}_{1} = G^{t}_{1}, \quad \dot{N}^{w}_{1} = 0,$$

$$\dot{E}_2 = Q_2 - P_2 F_2 + \mu^{t}_{2} G^{t}_{2}, \quad \dot{V}_2 = F_2, \quad \dot{N}^{t}_{2} = G^{t}_{2}, \quad \dot{N}^{w}_{2} = 0.$$

The chemical potential of salt in the first body equals the chemical potential of the pure material: $\mu^{t}_{1} = \mu_z$. The water particle numbers 0 and N^{w}_{2o} in the bodies, the total particle number of salt N^{t}_{s} in the bodies define an invariant submanifold $U(0, N^{w}_{2o}, N^{t}_{s})$ of the dynamical equation which can be parameterized by the variables $(E_1, V_1, N^{t}_{1}, E_2, V_2)$. The the reduced dynamical equation becomes

$$\begin{aligned} \dot{E}_1 &= Q_1 - P_1 F_1 + \mu_t G^{t}_{1}, \quad \dot{V}_1 = F_1, \quad \dot{N}^{t}_{1} = G^{t}_{1}, \\ \dot{E}_2 &= Q_2 - P_2 F_2 - \mu^{t}_{2} G^{t}_{1}, \quad \dot{V}_2 = F_2. \end{aligned}$$

The equilibrium values are determined by

$$\mathbf{T}_1(E_{1o}, V_{1o}, N^{t}_{1o}, 0) = T_a, \quad \mathbf{P}_1(E_{1o}, V_{1o}, N^{t}_{1o}, 0) = P_a,$$

$$\mathbf{T}_2(E_{2o}, V_{2o}, N^{t}_{s} - N^{t}_{1o}, N^{w}_{2o}) = T_a, \quad \mathbf{P}_2(E_{2o}, V_{2o}, N^{t}_{s} - N^{t}_{1o}, N^{w}_{2o}) = P_a,$$

$$\boldsymbol{\mu}_t(E_{1o}, V_{1o}, N^{t}_{1o}, 0) = \boldsymbol{\mu}^{t}_{2}(E_{2o}, V_{2o}, N^{t}_{s} - N^{t}_{1o}, N^{w}_{2o}).$$

Asymptotic stability can be assured as in the previous paragraph; the reader is asked to prove a corresponding proposition.

Remark As in Paragraph 30.3, we find that in equilibrium salt reaches the saturation concentration in the solution (second body).

31.5 Supersaturated solutions

Let us consider the previous system: salt dissolves in water at given temperature T and pressure P. Let us chose the salt concentration in the solution as independent variable, denoting it simply by c, and let c_s be the saturation concentration.

If $c < c_t$, then salt dissolves from the piece; if $c > c_t$ then salt precipitates from the solution. It is known that at given pressure the saturation concentration is a strictly monotone increasing function of temperature. Let us take a saturated equilibrium between a piece of salt and a water–salt solution; if temperature increases (at constant pressure), then salt particles leave the piece and enter the solution; if temperature decreases, then salt particles leave the solution and enter the piece.

This is true, evidently, if there is a piece of salt in contact with the solution, i.e. if the body of pure material has non-zero particle number. It is known that a water–salt solution which is not in contact with a piece of salt (the body of pure material has zero particle number) can be cooled carefully below the saturation temperature whitout precipitation. If something disturbs such a supersaturated solution – e.g a slight shock – then precipitation starts 'dramatically'.

These phenomena can be treated in our framework by taking into account equilibria with zero particle number. As to the instability of supersaturated solutions, we can repeat what we said in Paragraph 20.4 about superheating and supercooling.

31.6 Exercises

1. Treat the processes of two bodies in a given environment corresponding to the constraint in Section 18, supposing that the compositions of the bodies and the environment are equal (no constraint is imposed on convertings).
2. Treat the selective converting between two bodies completely isolated from the environment if the volumes of the bodies are not fixed.
3. Suppose that 'water' in Paragraph 31.3 is an ideal gas with constant specific heat λk, the 'water–salt' solution is an ideal mixture, and give explicitly the equilibrium.
4. Compare the result in Paragraph 31.3 with Paragraph 24.5 about osmosis.
5. What can be said about saturation in the system treated in Paragraph 31.3?

VII CHEMICAL REACTIONS

32 Characteristics of chemical reactions

32.1 Introductory remarks

So far we tacitly excluded chemical reactions from the processes of composite materials by considering the partial particle numbers as independent. The particle number of bodies changes in diffusion and in phase transition in such a way that particles flow from a body to another because of interaction between the bodies. In chemical reactions (if diffusion and phase transition do not take place) the partial particle numbers of a body change because of interactions inside the body.

Therefore, examining chemical reactions, we consider a single body as defined in 27.1 which can be coupled with the environment only mechanically and thermally (interchange of particles is forbidden). The environment is characterized by its temperature and pressure. Moreover, for the time beeing, we suppose that only one chemical reaction can occur and all the materials take place in that reaction.

32.2 Stoichiometric coefficients

The chemical reactions have the well-known properties that determined proportions of materials participating in them. For instance, two molecules of hydrogen, one molecule of oxygen and two molecules of water participate in a reaction:

$$2\mathrm{H}_2 + \mathrm{O}_2 \rightleftharpoons 2\mathrm{H}_2\mathrm{O}.$$

The minimal particle numbers necessary for a reaction are called **stoichiometric coefficents** of the reaction. These corresponding to input and output materials are negative and positive, respectively. In the previous example, the stoichiometric coefficents of hydrogen, oxygen and water are -2, -1 and 2. Of course, it is our choice, which side is chosen as input and output, respectively (the symbol $\rightleftharpoons$ shows that the reaction can proceed in both directions depending on the circumstances).

Therefore, if the materials $1, \dots, m$ participate in a reaction, then we can assign the stoichiometric coefficents $\nu^1, \dots, \nu^m$ to the materials in such a way that the change of particle numbers $N^1 \dots, N^m$ is always a multiple of $\nu^1, \dots, \nu^m$. Thus, the particle numbers of the materials in the body (if particles do not enter and leave the body) are of the form

$$(N(0)^1 + J\nu^1, \dots, N(0)^m + J\nu^m)$$

where J is a non-negative integer and $N(0)^1$, etc. are the initial particle numbers.

32.3 Chemical affinity

If the body and the environment do not interchange particles, the particle change in the chemical reaction is described by the equation

$$\dot{N}^\alpha = \dot{J}\nu^\alpha \qquad (\alpha = 1, \dots, m). \tag{$*$}$$

The change of internal energy due to the change of particle numbers is

$$\sum_{\alpha=1}^{m} \mu^\alpha \dot{N}^\alpha = \left(\sum_{\alpha=1}^{m} \nu^\alpha \mu^\alpha \right) \dot{J}.$$

The quantity in parentheses on the right-hand side plays a fundamental role in the description of chemical reactions. Its negative is the chemical affinity, defined precisely as follows.

Definition *The* **chemical affinity** *of the composite material* $\big(D, \mathfrak{e}, \mathcal{P}, \boldsymbol{\mu}^1 \dots, \boldsymbol{\mu}^m, R\big)$ *corresponding to the stoichiometric coefficents* $(\nu^1, \dots, \nu^m) \in \mathbb{Z}^m$ *is*

$$\mathcal{A} := -\sum_{\alpha=1}^{m} \nu^\alpha \boldsymbol{\mu}^\alpha.$$

Of course, chemical affinity can be given in canonical variables, too, or locally as a function of temperature, pressure and concentrations.

32.4 The degree of reaction

If the body and the environment do not interchange particles, we have, instead of the particle numbers $(N^1, \dots, N^m)$, the single independent variable J called the **degree of reaction**. Accordingly, the states of the body are characterized by (V, T, J) or (E, V, J) or, in a phase, by (T, P, J).

The constitutive functions, as functions of the above variables, will be denoted by the customary letters; hopefully, this ambiguity does not cause confusion. Thus, e.g.

$$\begin{aligned}
\mathbf{S}(E, V, J) &:= \mathbf{S}(E, V, N(0)^1 + J\nu^1, \dots, N(0)^m + J\nu^m), \\
\mathcal{S}(V, T, J) &:= \mathcal{S}(V, T, N(0)^1 + J\nu^1, \dots, N(0)^m + J\nu^m), \\
\boldsymbol{S}(T, P, J) &:= \boldsymbol{S}(T, P, N(0)^1 + J\nu^1, \dots, N(0)^m + J\nu^m).
\end{aligned}$$

Then the partial derivatives with respect to V, E, T and P retain their original relations, and the partial derivative with respect to J obeys the following symbolic equality:

$$\frac{\partial}{\partial J} = \sum_{\alpha=1}^{m} \nu^\alpha \frac{\partial}{\partial N^\alpha}.$$

We note that everything depends on the initial particle numbers $N(0)^1, N(0)^2$ etc., too, but we omit this from the notations.

We say that (V, T, J) is in the regular domain if $(V/N, T, N(0)^1 + J\nu^1, \dots, N(0)^m + J\nu^m)$ is in it, where

$$N := \sum_{\alpha=1}^{m} (N(0)^\alpha + J\nu^\alpha).$$

It has a similar meaning that (E, V, J) is in the canonical regular domain.

32.5 Entropic body

Our formulae imply for entropic bodies

$$\frac{\partial \mathbf{S}}{\partial E} = \frac{1}{\mathbf{T}}, \qquad \frac{\partial \mathbf{S}}{\partial V} = \frac{\mathbf{P}}{\mathbf{T}}, \qquad \frac{\partial \mathbf{S}}{\partial J} = \frac{\mathbf{A}}{\mathbf{T}},$$

and

$$\frac{\partial \mathcal{F}}{\partial J} = -\mathcal{A}, \qquad \frac{\partial \boldsymbol{G}}{\partial J} = -\boldsymbol{A}.$$

Furthermore,

$$\mathtt{D}^2\mathbf{S} = -\frac{1}{\mathbf{T}^2} \begin{pmatrix} \frac{\partial \mathbf{T}}{\partial E} & \frac{\partial \mathbf{T}}{\partial V} & \frac{\partial \mathbf{T}}{\partial J} \\ \mathbf{P}\frac{\partial \mathbf{T}}{\partial E} - \mathbf{T}\frac{\partial \mathbf{P}}{\partial E} & \mathbf{P}\frac{\partial \mathbf{T}}{\partial V} - \mathbf{T}\frac{\partial \mathbf{P}}{\partial V} & \mathbf{P}\frac{\partial \mathbf{T}}{\partial J} - \mathbf{T}\frac{\partial \mathbf{P}}{\partial J} \\ \mathbf{A}\frac{\partial \mathbf{T}}{\partial E} - \mathbf{T}\frac{\partial \mathbf{A}}{\partial E} & \mathbf{A}\frac{\partial \mathbf{T}}{\partial V} - \mathbf{T}\frac{\partial \mathbf{A}}{\partial V} & \mathbf{A}\frac{\partial \mathbf{T}}{\partial J} - \mathbf{T}\frac{\partial \mathbf{A}}{\partial J} \end{pmatrix}.$$

This result can be obtained in another way, too: the second derivative described in Paragraph 27.4 (where entropy is considered as a function of the partial particle numbers) is to be multiplied from the right by the matrix

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \nu^1 \\ \vdots & \vdots & \vdots \\ 0 & 0 & \nu^m \end{pmatrix}$$

and from the left by the transpose of this matrix.

Thus (a, b, c) is in the kernel of $\mathtt{D}^2\mathbf{S}(E, V, J)$ if and only if $(a, b, \nu^1 c, \dots, \nu^m c)$ is parallel to $(E, V, N(0)^1 + J\nu^1, N(0)^m + J\nu^m)$. This would imply that $N(0)^\alpha/\nu^\alpha$ is the same number for all α which is impossible because the particle numbers are non-negative and some of the stoichiometric coefficents are positive, some of them are negative. As a consequence, we have:

Proposition *If the body is entropic, then* $\mathtt{D}^2\mathbf{S}(E, V, J)$ *is negative definite for* (E, V, J) *in the regular domain.*

32.6 Exercises

1. Give relations for the partial derivatives of $(V, T, J) \mapsto \mathcal{S}(V, T, J)$ in the case of an entropic body.

2. Give the constitutive functions in the variables (V, T, J) for a body of ideal mixture.

33 Dynamics of chemical reactions

33.1 The dynamical equation

Equality $(*)$ in 32.3 means that the converting G^α is proportional to ν^α and the proportionality coefficient is the same for all α, in other words, there is a quantity K called the **reaction rate** in such a way that $G^\alpha = K\nu^a \quad (\alpha = 1, \dots, m)$. Thus $\sum\limits_{\alpha=1}^{m} \mu^\alpha G^\alpha = -AK$, and the dynamical equation becomes

$$\dot{E} = Q - PF - AK, \qquad \dot{V} = F, \qquad \dot{J} = K,$$

where, of course, the dynamical quantitities must be given as functions of (E, V, J) and the state (T_a, P_a) of the environment. We have considered only ideal working which does not lead to contradiction even if the body is heat insulated. The generalization to non-ideal working is straightforward.

33.2 Thermodynamical forces

We accept that the 'driving force' of chemical reaction is the chemical affinity. Thus the thermodynamical force acting on the body is

$$(-(T - T_a), P - P_a, A)$$

and the canonical thermodynamical force is

$$\left(\frac{1}{T} - \frac{1}{T_a}, \frac{P}{T} - \frac{P_a}{T_a}, \frac{A}{T}\right).$$

We define pseudolinear dynamical quantitities as earlier:

$$\begin{pmatrix} Q \\ F \\ K \end{pmatrix} = \begin{pmatrix} \lambda_Q & \beta_Q & \vartheta_Q \\ \lambda_F & \beta_F & \vartheta_F \\ \lambda_K & \beta_K & \vartheta_K \end{pmatrix} \begin{pmatrix} -(T - T_a) \\ P - P_a \\ A \end{pmatrix} = \begin{pmatrix} \lambda_Q^c & \beta_Q^c & \vartheta_Q^c \\ \lambda_F^c & \beta_F^c & \vartheta_F^c \\ \lambda_K^c & \beta_K^c & \vartheta_K^c \end{pmatrix} \begin{pmatrix} \frac{1}{T} - \frac{1}{T_a} \\ \frac{P}{T} - \frac{P_a}{T_a} \\ \frac{A}{T} \end{pmatrix}.$$

33.3 The role of affinity

We accepted that affinity is the driving force of the chemical reactions; this means that the sign of reaction rate equals 'essentially' the sign of affinity. In the pseudolinear case this is reflected in $\vartheta_K \geq 0$. Later we make this more precise (see 35.2).

Let us see more closely the relation between affinity and the direction of the reaction. For the sake of brevity, we consider only three materials. Roughly, the sign of the affinity

$$|\nu^1|\mu^1 + |\nu^2|\mu^2 - |\nu^3|\mu^3$$

determines the direction of the reaction, and its zero value characterizes equilibrium. In practice, however, most equilibria regarding chemical reactions is not realized by a peaceful coexistence of the three materials but in such a way that one or two materials become exhausted. This corresponds to a boundary point of the domain of the dynamical equation: one or more particle numbers are zero. The affinity is not defined for such states; the problem is similar to that in Paragraph 28.1. Fortunately, now the situation is more favourable. For instance, let the concentration of the first material tend to zero; then μ^1 tends to $-\infty$ and the other two chemical potential remain finite. Consequently, affinity takes zero value at a sufficiently small concentrationof the first material. Thus equilibrium is always realized (at least in the mathematical model) by sufficiently small non-zero particle numbers, we never need to take into account states with zero particle number.

Note that the thermodynamical force contains

– in diffusion: the difference of chemical potentials corresponding to states in the *same* phase of the *same* material,

– in phase transition: the difference of chemical potentials corresponding to states in *different* phases of the *same* material,

– in chemical reaction: the linear combination of chemical potentials corresponding to states of *different* materials.

Recall that specific internal energy and chemical potential as functions of (v, T) are determined only up to an additive constant (see 1.1 and 2.1). This additive constant is just the energy of chemical bond of a molecule. Let us say now that the chemical potential consists of a diffusion part and a bond part. The bond part drops out in the difference of values of the same chemical potential (diffusion and phase transition) but plays a fundamental role in the linear combination of different chemical potentials.

Let e_1, e_2 and e_3 denote the energy of chemical bonds of molecules of the materials. If

$$|\nu^1|e_1 + |\nu^2|e_2 - |\nu^3|e_3 > 0,$$

then in the reaction 1+2 → 3 (e.g. hydrogen + oxygen → water) a part of chemical energy is released (is transformed into another form of energy). In order to realize the chemical reaction, the molecules must be pulled out from their medium which requires energy (as in diffusion); this energy is given by the diffusion parts of the chemical potentials. Then it is quite obvious that affinity is just the specific energy that is released in the reaction.

The above inequality regarding the chemical bonds does not imply that affinity, too, is greater than zero. A good example: at sufficiently low temperature and pressure hydrogen and oxygen exist together without reacting; increasing the temperature, however, affinity becomes positive, the reaction starts and we know how much energy is released.

The reactions in which chemical energy gets free are called **exothermic**; burning is a typical exothermic reaction.

On the other hand, it may happen that

$$|\nu^1|e_1 + |\nu^2|e_2 - |\nu^3 e_3| < 0$$

but the affinity is positive; then the reaction starts but during the reaction other forms of energy are transformed into the energy of chemical bonds. Such reactions are called **endothermic**. Baking is a typical endothermic reaction.

33.4 Catalysators

There are materials whose reaction starts only at high temperature and pressure. Then a **catalysator** can help to realize the chemical reaction: this is a material which influences the reaction without participating in it. We can see how this works as follows. Let us take the mixture of the three materials considered previously and a mixture which contains the three materials and another one, the catalysator. In this mixture the stoichiometric coefficient of the catalysator is zero but the presence of the catalysator influences significantly the chemical potentials of the original materials in the mixture. Thus,

$$|\nu^1|\mu^1 + |\nu^2|\mu^2 - |\nu^3|\mu^3,$$

is the affinity without catalysator and

$$|\nu^1|\mu^1_{kat} + |\nu^2|\mu^2_{kat} - |\nu^3|\mu^3_{kat}$$

is the affinity with catalysator. It may be that at given temperature, pressure and concentrations the first affinity is zero (the reaction does not take place) but the second affinity is positive (the reaction is produced).

33.5 The law of mass action

According to Paragraph 23.2, the chemical affinity in a semi-ideal mixture of type (1) has the form

$$\begin{aligned}\boldsymbol{A}(T,P,c) &= -\sum_{\alpha=1}^{m} \nu^\alpha \left(\mu_\alpha(T,P) + kT\log c^\alpha\right) = \\ &= -\sum_{\alpha=1}^{m} \nu^\alpha \mu_\alpha(T,P) - kT\log\prod_{\alpha=1}^{m} \left(c^\alpha\right)^{\nu^\alpha}.\end{aligned}$$

In a chemical equilibrium the affinity takes zero value (see 35.2), thus in equilibrium we have

$$\prod_{\alpha=1}^{m} \left(c^\alpha\right)^{\nu^\alpha} = \exp\left(-\frac{\sum\limits_{\alpha=1}^{m} \nu^\alpha \mu_\alpha(T,P)}{kT}\right) =: \kappa(T,P).$$

This relation is called the **law of mass action**: the product of the stoichiometric power of the equilibrium concentrations depends only on temperature and pressure. $\kappa(T,P)$ is usually called the equilibrium constant (a 'constant' which depends on temperature and pressure).

On the basis of Exercise 4 in 7.10, we have

$$\mu_\alpha(T,P) = kT\left((\lambda_\alpha+1) - \log\left(\left(\frac{T}{T_0}\right)^{\lambda_\alpha+1}\frac{P_0}{P}\right)\right) + e_\alpha$$

for ideal gases with constant specific heats, thus for their semi-ideal mixture we obtain

$$\kappa(T,P) = \exp\left(-\sum_{\alpha=1}^{m}\left(\nu^\alpha(\lambda_\alpha+1)+\frac{e_\alpha}{kT}\right)\right)\prod_{\alpha=1}^{m}\left(\left(\frac{T}{T_0}\right)^{\lambda+1}\frac{P_0}{P}\right)^{\nu^\alpha}.$$

33.6 Exercises

1. Take a semi-ideal mixture of three materials with stoichiometric coefficents $\nu^1 < 0$, $\nu^2 < 0$ and $\nu^3 > 0$. Then

$$\mu^\alpha(T,P,N^1,N^2,N^3) = \mu_\alpha(T,P) + kT\log\frac{N^\alpha}{N^1+N^2+N^3} \qquad (\alpha = 1,2,3),$$

thus

$$\boldsymbol{A}(T,P,N^1,N^2,N^3) = -\sum_{\alpha=1}^{3}\nu^\alpha\mu_\alpha(T,P) - kT\sum_{\alpha=1}^{3}\nu^\alpha\log\frac{N^\alpha}{N^1+N^2+N^3}.$$

Let a ‘zeroth’ material (catalysator) be mixed, too, with particle number N^0 and stoichiometric coefficient 0. Compare the new affinity with the one above.

2. Give $\kappa(T,P)$ for semi-ideal mixture of ideal gases whose specific heat is not constant (cf. 2.1).

3. Deduce the law of mass action for mixtures which are not semi-ideal.

34 Reaction heats

34.1 Energy change of an isolated body

If a body is completely isolated from the environment, then $\dot{E} = -AK$: the time rate of internal energy change is proportional to the reaction rate (the particle change per unit time) and affinity is the proportionality coefficient. This corresponds to what has been said in Paragraph 33.3.

34.2 Energy change of a body at constant volume and temperature

If the volume is fixed, then

$$\dot{E} = Q - AK. \tag{$*$}$$

Let V_o be the constant volume. Let us suppose that the reaction takes place at the constant temperature T_a of the environment. Then the variables (V,T,J) are suitable:

$$\dot{E} = \frac{\partial\mathcal{E}(V_o,T_a,J)}{\partial J}\dot{J}.$$

If the body is entropic, then using the relations

$$\mathcal{E} = \mathcal{F} - T\frac{\partial\mathcal{F}}{\partial T} \quad\text{and}\quad \frac{\partial\mathcal{F}}{\partial J} = -\mathcal{A}$$

for the free energy $\mathcal{F}$, we get

$$\dot{E} = -AK + \left(T_a \frac{\partial \mathcal{A}}{\partial T}\right) K,$$

where, of course, all the quantities are to be taken at (V_{o}, T_a, J). Comparing this equality with $(*)$, we see that heating is proportional to the reaction rate; the proportionality coefficient is

$$T_a \frac{\partial \mathcal{A}}{\partial T}(V_{\mathrm{o}}, T_a, J)$$

called the **reaction heat at constant volume and constant temperature**.

34.3 Energy change of a body at constant temperature and pressure

If the reaction takes place at the constant pressure P_a of the environment and the working is ideal, then $\dot{E} + P_a\dot{V} = \dot{H}$, where H stands for the enthalpy of the body, thus

$$\dot{H} = Q - AK. \tag{$*$}$$

Let us suppose that the reaction takes place at the constant temperature T_a of the environment. Then the variables (T, P, J) are suitable:

$$\dot{H} = \frac{\partial \boldsymbol{H}(T_a, P_a, J)}{\partial J}\dot{J}.$$

If the body is entropic, then using the relations

$$\boldsymbol{H} = \boldsymbol{G} - T\frac{\partial \boldsymbol{G}}{\partial T} \quad \text{és} \quad \frac{\partial \boldsymbol{G}}{\partial J} = -\boldsymbol{A}$$

for the Gibbs functions $\boldsymbol{G}$, we get

$$\dot{H} = -AK + \left(T_a \frac{\partial \boldsymbol{A}}{\partial T}\right) K,$$

where, of course, every quantity is to be taken at (T_a, P_a, J). Comparing this equality with $(*)$, we see that heating is proportional to the reaction rate; the proportionality coefficient is

$$T_a \frac{\partial \mathcal{A}}{\partial T}(T_a, P_a, J)$$

called the **reaction heat at constant temperature and constant pressure**.

35 Description of chemical reactions

35.1 Introductory remarks

Up to now we have spoken loosely about chemical reactions in a body. That heuristics supports the exact definition to be done in this section.

We emphasize that if particles enter or leave the body, then we have to take the particle numbers as variables. The degree of reaction as a single variable is justified only if there is no particle interchange between the body and the environment. But even in this case every quantity depends on the initial particle numbers in the body and different reactions are realized with different initial particle numbers: e.g. the reaction hydrogen + oxygen → water starting with one litre of hydrogen and one litre of oxigen proceeds differently than starting with one litre of hydrogen and hundred litre of oxygen.

Avoiding a too clumsy formulation, we remain in the framework when the body and the environment do not interchange particles and we do not denote the dependence on the initial particle numbers.

35.2 Definition of a chemical reaction

Definition *A chemical system consisting of*

- *a body mixed of given materials,*
- *a given environment,*
- *a given heat source*

is the following:

1. *The body with composite material* $\left(\mathrm{D}\times\mathbb{R}_0^+, \mathbf{T}, \mathbf{P}, \boldsymbol{\mu}^1, \dots, \boldsymbol{\mu}^m, \mathrm{R}\right)$ *and the stoichiometric coefficents* $(\nu^1, \dots, \nu^m) \in \mathbb{Z}^m$*, where* $m \geq 3$ *is a positive integer,*

2. *The* **dynamical quantitities**

$$(\mathbf{Q}, \mathbf{F}, \mathbf{K}) : (\mathrm{D} * \mathbb{R}_0^+) \times (\mathrm{K})^+ \times (\mathrm{Pa}) \to (\mathrm{J/s}) \times (\mathrm{m}^3/\mathrm{s}) \times (1/\mathrm{s}),$$

the **heating***, the* **springing** *and the* **reaction rate***, which are continuous and continuously differentiable on the interior of their domain,*

$$\mathbf{K} \neq 0,$$

furthermore, with the customary simplified notations

$$Q := \mathbf{Q}(E, V, J, T_a, P_a), \quad \textit{etc.},$$

$$A := \mathbf{A}(E, V, J), \quad \textit{etc.}$$

the dynamical quantitities satisfy

- *the* **equilibrium property** *for*

(a) if $\mathbf{F} = 0$, $\mathbf{Q} = 0$*, then*

$*$ $K = 0 \iff A = 0$*;*

(b) if $\mathbf{F} = 0$, $\mathbf{Q} \neq 0$*, then*

$*$ $K = 0 \implies A = 0$,

$*$ $A = 0$ *and* $Q = 0 \implies T = T_a$,

(which imply that if $K = 0$ *and* $Q = 0$*, then* $A = 0$ *and* $T = T_a$*),*

$**$ $A = 0$ *and* $T = T_a \implies K = 0$ *and* $Q = 0$*;*

(c) if $\mathbf{F} \neq 0$, $\mathbf{Q} = 0$*, then*

$*$ $K = 0 \implies A = 0$*;*

$*$ $A = 0$ *and* $F = 0 \implies P = P_a$

(which imply that if $K = 0$ *and* $F = 0$*, then* $A = 0$*);*

$* *$ *$A = 0$ and $P = P_a \implies K = 0$ and $F = 0$;*

(d) if $\mathbf{F} \neq 0$, $\mathbf{Q} \neq 0$, then

$*$ *$K = 0 \implies A = 0$;*

$*$ *$A = 0$ and $F = 0 \implies P = P_a$,*

$*$ *$A = 0$, $P = P_a$, and $Q = 0 \implies T = T_a$*

(which imply that if $K = 0$, $F = 0$ and $Q = 0$, then $A = 0$, $P = P_a$ and $T = T_a$),

$* * *$ *$A = 0$, $P = P_a$ and $T = T_a \implies K = 0$, $F = 0$ and $Q = 0$;*

– *the* **dissipation inequality***:*

$$-\frac{Q}{T}(T - T_a) + F(P - P_a) + AK \geq 0,$$

where equality holds if and only if $Q = 0$, $F = 0$ and $K = 0$ or, equivalently,

$$(Q - PF - AK)\left(\frac{1}{T} - \frac{1}{T_a}\right) + F\left(\frac{P}{T} - \frac{P_a}{T_a}\right) + K\frac{A}{T} \geq 0.$$

3. *The* **process of the environment***, a continuous function $t \mapsto \big(T_a(t), P_a(t)\big)$ defined on a time interval.*

4. *The* **heat source***, a continuous function $t \mapsto Q_s(t)$ defined on a time interval.*

5. *The* **dynamical equation**

$$\begin{aligned}\dot{E} &= Q_s + Q - PF - AK\\ \dot{V} &= F,\\ \dot{J} &= K,\end{aligned}$$

where

$$Q := \mathbf{Q}(E, V, J, T_a, P_a), \quad \textit{etc.}$$

It is a simple fact that if the heat source is zero, then every standstill is an equilibrium.

35.3 Consequences of the equilibrium property and the dissipation inequality

We deduce as in Paragraph 14.2:

Proposition *(a) if $\mathbf{F} = 0$ and $\mathbf{Q} = 0$, then $K > 0$ if and only if $A > 0$,*

(b) if $\mathbf{F} = 0$ and $\mathbf{Q} \neq 0$, then if $A > 0$ and $T = T_a$, then (E, V, J) has a neighbourhood in which for all (E', V', J') the strict inequality $\mathbf{K}(E', V', J', T_a, P_a) > 0$ holds,

(c) if $\mathbf{F} \neq 0$ and $\mathbf{Q} = 0$, then if $A > 0$ and $P = P_a$, then (E, V, J) has a neighbourhood in which for all (E', V', J') the strict inequality $\mathbf{K}(E', V', J', T_a, P_a) > 0$ holds,

(d) if $\mathbf{F} \neq 0$ and $\mathbf{Q} \neq 0$, then if $A > 0$ and $T = T_a$, $P = P_a$, then (E, V, J) has a neighbourhood in which for all (E', V', J') the strict inequality $\mathbf{K}(E', V', J', T_a, P_a) > 0$ holds,

and the same assertions are true with reversed inequalities.

35.4 Summarizing formulae

35.4.1 The framework of description

The description of chemical reactions can be put in an abstract framework similar to that in Section 15.

For the sake of simplicity, we suppose that the heat source is zero; besides the results concerning the equilibria, everything can be repeated for non-zero heat source, too. Moreover, the temperature T_a and the pressure P_a of the environment are taken to be constant.

The states of the body are in the vector space

$$X := (\mathrm{J}) \times (\mathrm{m}^3) \times \mathbb{R};$$

a state will be denoted by

$$x := (E, V, J)$$

(do not confuse the symbol J = *Joule* in the definition of X with the above J).

Again kT is taken instead of T; then the collection of the intensive quantities is the function

$$\mathbf{y} := \left(\frac{1}{k\mathbf{T}}, \frac{\mathbf{P}}{k\mathbf{T}}, \frac{\mathbf{A}}{k\mathbf{T}}\right) : X \rightarrowtail X^*,$$

whose domain is denoted by X_D.

The intensive quantities of the environment are denoted by

$$y_a := \left(\frac{1}{kT_a}, \frac{P_a}{kT_a}, 0\right) \in X^*.$$

Then referring to the process of the environment by the intensive quantities, we can write the dynamical equation in the form

$$(x : I \to X_D)? \qquad \dot{x} = \mathbf{R}(x, y_a).$$

In the pseudolinear case, the nominal thermodynamical force

$$\mathbf{F}(x, y_a) := \mathbf{y}(x) - y_a$$

and the nominal conductance matrix matrix $\mathbf{B}(x, y_a) \in \mathrm{Lin}(X^*, X/\mathrm{s})$ give

$$\mathbf{R}(x, y_a) = \mathbf{B}(x, y_a)\mathbf{F}(x, y_a).$$

35.4.2 Constraints

Constraints, holonomic and anholonomic ones, the effective thermodynamical force and conductance matrix are defined as in Section 15, and we can repeat what we know about the relation between the nominal conductance matrix and the effective one.

Thus if the nominal conductance matrix fits the constraint, then – using the notations of Paragraphs 15.3 and 15.4.3 – we get the dynamical equation in the form

$$(x : I \to X_D)? \qquad \dot{x} = \mathbf{B}_\Gamma(x, y_a)\mathbf{F}_\Gamma(x, y_a).$$

We infer from the dissipation inequality that

$$\mathbf{F}(x, y_a)\mathbf{B}(x, y_a)\mathbf{F}(x, y_a) \geq 0 \qquad (x \in X_D, y_a \in X^*),$$

or

$$\mathbf{F}_\Gamma(x, y_a)\mathbf{B}_\Gamma(x, y_a)\mathbf{F}_\Gamma(x, y_a) \geq 0 \qquad (x \in X_D, y_a \in X^*),$$

where equality holds if and only if $\mathbf{F}_\Gamma(x, y_a) = 0$.

35.4.3 Stability of equilibria

The total entropy of the body and environment equals, up to an additive constant, the function

$$\mathbf{L} : X_D \to (J/K), \qquad (E, V, J) \mapsto \mathbf{S}(E, V, J) - \frac{E + P_a V}{T_a}$$

which is twice differentiable on the regular domain and $\mathbf{F}(x, y_a) = \mathtt{D}\mathbf{L}(x)$ if the body is entropic; furthermore, $\mathtt{D}^2 L = \mathtt{D}^2\mathbf{S}$ is negative definite on the regular domain.

A simple reformulation of Proposition 15.6 yields:

Proposition *Let U be a constraint submanifold in the regular domain, x_o is an equilibrium in U. Let the body be entropic. If U has a parameterization p around x_o for which $\mathtt{D}\mathbf{L}(x_\mathrm{o})\mathtt{D}^2 p(p^{-1}(x_\mathrm{o}))$ is negative semidefinite, then x_o is asymptotically stable in U.*

36 Special chemical reactions

36.1 Reactions without constraint

The body is coupled with the environment both mechanically and thermally, the environment temperature T_a and pressure P_a being constant. As a consequence of the equilibrium properties of the dynamical quantitities, $(E_\mathrm{o}, V_\mathrm{o}, J_\mathrm{o})$ in the regular domain is an equilibrium of an entropic body if and only if $\mathtt{D}\mathbf{L}(E_\mathrm{o}, V_\mathrm{o}, J_\mathrm{o}) = 0$. As a consequence, we can apply Proposition 35.4.3.

36.2 Fixed volume

The volume of the body does not change, $\mathbf{F} = 0$. The constraint is affine, the constraint subspaces are spanned by the vectors $(1, 0, 0)$ and $(0, 0, 1)$. Thus the effective thermodynamical force is

$$\left(\frac{1}{T} - \frac{1}{T_a}, \frac{A}{T}\right).$$

If V_o is the fixed volume of the body, then as a consequence of the equilibrium properties of the dynamical quantitities, $(E_\mathrm{o}, V_\mathrm{o}, J_\mathrm{o})$ is an equilibrium if and only if the corresponding value of the effective thermodynamical force is zero:

$$\mathbf{T}(E_\mathrm{o}, V_\mathrm{o}, J_\mathrm{o}) = T_a, \qquad \mathbf{A}(E_\mathrm{o}, V_\mathrm{o}, J_\mathrm{o}) = 0.$$

For all $V_o \in (\mathrm{m}^3)^+$

$$U(V_o) := \{(E, V_o, J) \mid E \in (\mathrm{J})^+, J \in \mathbb{R}^+\}$$

is a constraint submanifold, a subset of an affine subspace, thus Proposition 35.4.3 can be applied for the equilibrium in $U(V_o)$.

36.3 Constant temperature

The temperature of the body is kept constant (equal to the temperature T_a of the environment). The constraint subspace corresponding to (E, V, J) is spanned by the vectors

$$\left(-\frac{\partial \mathbf{T}}{\partial V}, \frac{\partial \mathbf{T}}{\partial E}, 0\right), \qquad \left(-\frac{\partial \mathbf{T}}{\partial J}, 0, \frac{\partial \mathbf{T}}{\partial E}\right).$$

Thus the effective thermodynamical force is

$$\left(\frac{P}{T_a} - \frac{P_a}{T_a}, \frac{A}{T_a}\right).$$

As a consequence of the equilibrium properties of the dynamical quantitities, (E_o, V_o, J_o) is really an equilibrium if and only if the corresponding value of the effective thermodynamical force is zero:

$$\mathbf{P}(E_o, V_o, J_o) = P_a, \qquad \mathbf{A}(E_o, V_o, J_o) = 0$$

and, of course,

$$\mathbf{T}(E_o, V_o, J_o) = T_a.$$

For all $T_a \in (\mathrm{K})^+$

$$U(T_a) := \{(E, V, J) \mid \mathbf{T}(E, V, J) = T_a\}$$

is a constraint submanifold. The nominal thermodynamical force, too, is zero in equilibrium, thus Proposition 35.4.3 can be applied for the equilibrium in $U(T_a)$.

36.4 Constant pressure

The pressure of the body is kept constant (equal to the pressure of the environment). The constraint subspace corresponding to (E, V, J) is spanned by the vectors

$$\left(-\frac{\partial \mathbf{P}}{\partial V}, \frac{\partial \mathbf{P}}{\partial E}, 0\right), \qquad \left(-\frac{\partial \mathbf{P}}{\partial J}, 0, \frac{\partial \mathbf{P}}{\partial E}\right).$$

Thus the effective thermodynamical force is

$$\left(\frac{1}{T} - \frac{1}{T_a}, \frac{A}{T}\right).$$

As a consequence of the equilibrium properties of the dynamical quantitities, (E_o, V_o, J_o) is really an equilibrium if and only if the corresponding value of the effective thermodynamical force is zero:

$$\mathbf{T}(E_o, V_o, J_o) = T_a, \qquad \mathbf{A}(E_o, V_o, J_o) = 0$$

and, of course,

$$\mathbf{P}(E_o, V_o, J_o) = P_a.$$

For all $P_a \in (\mathrm{Pa})$

$$U(P_a) := \{(E, V, J) \mid \mathbf{P}(E, V, J) = P_a\}$$

is a constraint submanifold. The nominal thermodynamical force, too, is zero in equilibrium, thus Proposition 35.4.3 can be applied for the equilibrium in $U(P_a)$.

36.5 Heat insulation

The body is heat insulated from the environment. The constraint subspace corresponding to (E, V, J) is spanned by the vectors $(-\mathbf{P}(E, V, J), 1, 0)$ and $(-\mathbf{A}(E, V, J), 0, 1)$. Thus, the effective thermodynamical force is given by

$$\left(-\frac{P}{T} + \frac{P}{T_a}\right) + \left(\frac{P}{T} - \frac{P_a}{T_a}\right) = \frac{P}{T_a} - \frac{P_a}{T_a},$$

$$\left(-\frac{A}{T} + \frac{A}{T_a}\right) + \frac{A}{T} = \frac{A}{T_a}.$$

As a consequence of the equilibrium properties of the dynamical quantitities, (E_o, V_o, J_o) is really an equilibrium if and only if the corresponding value of the effective thermodynamical force is zero:

$$\mathbf{P}(E_o, V_o, J_o) = P_a, \qquad \mathbf{A}(E_o, V_o, J_o) = 0.$$

The temperature of the environment does not play any role, thus we can take formally $T_a := \mathbf{T}(E_o, V_o, J_o)$. Then the nominal thermodynamical force, too, is zero in equilibrium. Then we can apply Proposition 35.4.3: if the body is entropic, then for all constraint submanifold U in the regular domain, every equilibrium in U is asymptotically stable in U.

The question, however, remains open: how to give a constraint submanifold (can it be given at all)?

36.6 Exercises

1. Treat chemical reactions when
- the volume and the temperature are constant,
- the temperature and the pressure are constant,
- the pressure is constant and the body is heat insulated.

2. Suppose that a particle source is in the body (e.g. the reaction is combustion, the fuel and oxygen flow in and the combustion product flows out continuously). If the source provides the materials proportionally to the stoichiometric coefficents, i.e. $K_s \nu^\alpha$ is the particle number of the α-th material put in the body in unit time where K_s is a given function of time, then we can continue to use the variable J.

Let the reaction take place at constant temperature T_a and constant pressure P_a. Give the heat extracted from the body in unit time in a stationary state.

VIII EXTENDED ORDINARY THERMODYNAMICS

37 Thermo-mechanical interaction

37.1 Problems of the description

Let us take a cylinder with a piston containing a gas. It is a trivial experimental fact that the piston will oscillate after a push. Let us try to describe such an oscillation.

Let N be the particle number of the gas, m the mass of the piston, A the area of the piston. Let the exterior temperature T_a and pressure P_a be constant. If P is the pressure of the gas, then $A(P - P_a)$ is the force acting on the piston. Let x denote the distance of the piston from the bottom of the cylinder. Then we have the Newtonian equation $m\ddot{x} = A(P - P_a)$. The gas has volume $V = Ax$, specific volume $v = V/N$, thus the equation

$$\ddot{v} = \frac{A^2}{Nm}(\mathbf{P}(e, v) - P_a) \qquad (*)$$

supplements the equations

$$\dot{e} = \mathbf{q}(e, v, T_a, P_a) + \mathbf{w}(e, v, T_a, P_a), \qquad \dot{v} = \mathbf{f}(e, v, T_a, P_a)$$

describing the process of the gas.

Unfortunately, the mechanical equation of the piston and the thermodynamical equations of the gas are not compatible. This is evident in the simple case when $\mathbf{f}(e, v, T_a, P_a) = \beta(\mathbf{P}(e, v) - P_a)$ where $\beta > 0$ is constant, so besides the equation $(*)$, we would have

$$\dot{v} = \beta(\mathbf{P}(e, v) - P_a),$$

consequently,

$$\ddot{v} = \frac{A^2}{Nm\beta}\dot{v},$$

and so the volume of the body grows exponentially in time.

This nonsense comes from the fact that the internal motion of the bodies is neglected in ordinary thermodynamics. Let us recall the Introduction: we built up ordinary thermodynamics from the continuum theory by considering the quantities homogeneous in space and by taking the velocity field constant; because of the latter assumption, the equations of ordinary thermodynamics exclude momentum transfer.

37.2 A new dynamical equation

There are phenomena in which the thermodynamical body can be considered homogeneous but the momentum transfer is not negligible. To describe them, we must approach the problem in a new way [1]. Let us recall the balance equations of continuum physics:

$$\begin{aligned}\mathtt{D}_{\boldsymbol{u}}e &= -\,v(\nabla\cdot\boldsymbol{k}+\boldsymbol{P}:\nabla\boldsymbol{u}),\\ \mathtt{D}_{\boldsymbol{u}}\boldsymbol{u} &= -\,v\nabla\cdot\boldsymbol{P},\\ \mathtt{D}_{\boldsymbol{u}}v &= v\nabla\cdot\boldsymbol{u}.\end{aligned}$$

If we consider the quantities homogeneous,

$$\dot e = q + w$$

undoubtedly corresponds to the first equation. Now, contrary to Paragraph 6 of Introduction, let us argue as follows. The third equation concerns the time derivative of specific volume: an expression containing the velocity field stands on the right-hand side, and the time derivative of the velocity field enters the second equation. Combining these two equations audaciously for the homogenous case, we get an equation of form

$$\ddot v = f, \tag{$*$}$$

where f is a given function.

These equations and the Newtonian equation of the piston are compatible if $f = \frac{A^2}{Nm}(P - P_a)$.

This f, however, is not good because it is not meaningful in the limiting case when the piston has zero mass, i.e. when the thermodynamical body is not coupled with a mechanical body, though we should like to have well-working equations in this case, too.

The essence of equation $(*)$ is that we wish to take into account the internal momentum of the thermodynamical body but this is left out from the arguments in 37.1 Let us try to express somehow that the pressure difference moves the particles of the gas, too, not only the piston.

Let F_a, F_d denote the forces acting on the piston due to the environment and the gas, respectively and let F_g be the force acting on the gas due to the bottom of the cylinder. If the pressure were homogeneous, then F_d and F_g would be equal. We know that pressure is not homogeneous in reality.

Let us imagine the gas condensed in its mass centre denoted by x_g; let m_g be the entire mass of the gas. Then we can set up purely mechanical equations:

$$m\ddot x = F_d - F_a, \qquad m_g\ddot x_g = F_g - F_d.$$

Supposing the gas to be homogeneous, we have $x_g = \frac{x}{2}$. Thus summing the two equations, we obtain

$$\left(m + \frac{m_g}{2}\right)\ddot x = F_g - F_a.$$

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[1] This chapter is based on the paper P. Ván: Other Dynamic Laws in Thermodynamics, *Physics Essays*, 8(1995)457-4675

Now we can consider the pressure homogeneous; then $F_d = F_g = AP$, $F_a = AP_a$, so

$$\ddot{v} = \frac{A^2}{N(m + m_g/2)}\big(\mathbf{P}(e, v) - P_a\big) \tag{**}$$

which is appropriate: if the mass of the gas is small relative to the mass of the piston (the mass of the gas tends to zero), we regain the equation in 37.1 and we get a meaningful equation in the limit, too, when the mass of the piston tends to zero.

37.3 Exercises

1. If the cylinder is heat insulated, then the process of the gas is adiabatic, thus the temperature of the gas can be given by a function $v \mapsto \mathcal{T}(v)$ which satisfies the differential equation (see 4.2)

$$\frac{dT}{dv} = -\frac{\mathfrak{l}_v(v, T)}{\mathfrak{c}_v(v, T)},$$

thus,

$$\ddot{v} = \frac{A^2}{N(m + m_g/2)}\left(\mathcal{P}(v, \mathcal{T}(v)) - P_a\right).$$

If the gas is of normal dilation (see 3.9), then the derivative of the right-hand side satisfies

$$-b(v) := \left(\frac{\partial \mathcal{P}}{\partial v} - \frac{\partial \mathcal{P}}{\partial T}\frac{\mathfrak{l}_v}{\mathfrak{c}_v}\right)(v, \mathcal{T}(v)) < 0.$$

It is well known from stability theory that the equilibrium v_o that $\mathcal{P}(v_\mathrm{o}, \mathcal{T}(v_\mathrm{o})) = P_a$ holds for is stable and the processes near to it are periodic. For the quantity $z := v - v_\mathrm{o}$ we have the approximate equation

$$\ddot{z} = -\frac{A^2}{m + m_g/2}b(v_\mathrm{o})z,$$

whose solutions are harmonic oscillations.

2. If the gas in the cylinder is ideal with specific heat λk, then $\mathcal{T}(v) = a/v^\lambda$ where $a > 0$ is constant and

$$b(v) = \frac{ka(\lambda + 1)}{v_\mathrm{o}^{\lambda+2}\lambda}.$$

Using this relation, estimate the specific heat on the base of the frequency of the oscillation.

3. Let the wall of the cylinder conduct heat very fast, i.e. consider the process of the gas isothermal. Describe the oscillation of the piston and estimate the specific heat on the basis of the frequency.

4. Put the gas in a ball whose wall can extend and contract freely. Describe the equation of motion for the volume change. Hint: let m be the mass of the wall and let m_g and N be the mass and particle number of the gas. If r is the radius of the ball and A is a small surface area, then $Am_g/4r^2\pi$ is the mass of gas portion

in the corresponding spherical cone, having the mass centre at distance $r/3$ from the centre of the ball. The mass of the wall in the surface area is $Am/4r^2\pi$. We derive

$$\frac{m + \frac{2m}{3}}{4r^2\pi}\ddot{r} = P - P_a$$

from the Newton equations as in 37.2. Express r by v and substitute $\mathcal{P}(v, T)$ for P.

38 Extended thermodynamical processes

38.1 Introductory remarks

Equation $(*)$ in 37.2 can be written in a first-order form:

$$\dot{v} = u, \qquad \dot{u} = f.$$

The **volume rate** u is of great importance beyond the formal transcription of the second-order equation: it will be a new independent variable in **extended ordinary thermodynamics** where a process is (v, T, u) or (e, v, u) as a function of time and the dynamical quantitities, the heating q, the working w and the **forcing** f are to be given as functions of (v, T, u) or (e, v, u).

In other words, a state of a material in extended ordinary thermodynamics is (v, T, u) or (e, v, u). This implies that the volume rate u appears as a variable in the constitutive functions, too.

It is a question, however, whether we can choose either (v, T, u) or (e, v, u) for independent variable. Now we suppose that internal energy is not influenced by the volume rate which allows us a simpler (but sufficiently general) treatment. We emphasize that doing so we do not exclude that the energy of the material is influenced by the volume rate; indeed, now we can define kinetic energy due to the volume rate, so the energy becomes the sum of internal energy and kinetic energy (see Exercise 2 in 38.4).

The stress tensor in continuum theory is the sum of an elastic part and a viscous part. The elastic part corresponds to the customary pressure in thermodynamics and the viscous part is expressed by the gradient of the velocity field. The divergence of the velocity field (the trace of the gradient) is related to the time derivative of the specific volume. Therefore, we accept in extended ordinary thermodynamics that the pressure has the form

$$\mathcal{P}(v, T, u) = \mathcal{P}_r(v, T) + \mathcal{P}_s(v, T, u),$$

where $\mathcal{P}_r$ is the known customary pressure, the elastic part and $\mathcal{P}_s$ is the viscous part that satisfies $\mathcal{P}_s(v, T, 0) = 0$.

We shall see that the extended thermodynamical description works well only for bodies with constant particle number, thus it will be unimportant whether chemical potential is influenced by volume rate or not.

38.2 The extended thermodynamical material

Definition $(D, \mathfrak{e}, \mathcal{P}_r, \boldsymbol{\mu}, R, \mathcal{P}_s)$ *is an* **extended** *simple material if* $(D, \mathfrak{e}, \mathcal{P}_r, \boldsymbol{\mu}, R)$ *is a simple material and*

$$\mathcal{P}_s : D \times (\mathrm{m}^3/\mathrm{s}) \to (\mathrm{Pa})$$

is a continuous function, continuously differentiable on $R \times (\mathrm{m}^3/\mathrm{s})$ *and* $\mathcal{P}_s(v, T, 0) = 0$ *is satisfied for all* $(v, T) \in D$. $\mathcal{P} := \mathcal{P}_r + \mathcal{P}_s$ *is the pressure of the extended material.*

The extended thermodynamical material is

- **entropic** *if the corresponding simple material is entropic,*
- **viscous** *if* $\mathcal{P}_s(v, T, u) = 0$ *if and only if* $u = 0$.

The conditions imply the existence of a continuous function $\eta : R \times (\mathrm{m}^3/\mathrm{s}) \to (\mathrm{Pa\ s/m}^3)$ such that

$$\mathcal{P}_s(v, T, u) = -\eta(v, T, u)u \qquad \big((v, T, u) \in R \times (\mathrm{m}^3/\mathrm{s})\big). \tag{$*$}$$

The extended material is viscous if and only if $u \neq 0$ imply $\eta(v, T, u) \neq 0$.

Of course, the extended material can be given in canonical form, because temperature can be expressed as a function of specific internal energy and specific volume in the known way: $\mathbf{T}(\mathfrak{e}(v, T), v) = T$. Then we apply the symbols $\mathbf{P}_r$, $\mathbf{P}_s$, $\mathbf{P} = \mathbf{P}_r + \mathbf{P}_s$ for the functions in the variables (e, v, u):

$$\mathbf{P}_r(e, v) = \mathcal{P}_r(v, \mathbf{T}(e, v)), \qquad \mathbf{P}_s(e, v, u) = \mathcal{P}_s(v, \mathbf{T}(e, v), u).$$

The extended thermodynamical body is defined formally in the known way: $(D \times \mathbb{R}_0^+, \mathfrak{e}, \mathcal{P}_r, \boldsymbol{\mu}, R, \mathcal{P}_s)$ or $(\mathrm{D} \times \mathbb{R}_0^+, \mathbf{T}, \mathbf{P}_r, \boldsymbol{\mu}, \mathrm{R}, \mathbf{P}_s)$.

38.3 Description of processes

We consider bodies whose particle number is constant. Then a process of a body is a function $t \mapsto \big(e(t), v(t), u(t)\big)$ defined on a time interval and obeying the dynamical equation

$$\dot{e} = q + w, \qquad \dot{v} = u, \qquad \dot{u} = f.$$

The quantities on the right-hand side are

- the **specific heating** q, **the specific working** w,
- the **specific forcing** f,

which depend on (e, v, u) and the quantities of the environment.

Now we use the specific quantities (contrary to the previous sections) for having a clear parallelism with Paragraph 37.1; moreover, we shall see that phenomena whose description would require the entire quantities cannot be treated in extended ordinary thermodynamics (see 40).

Working is ideal if

$$w = -P\dot{v} = -(P_r + P_s)u.$$

Replacing P_s with π, we get a form similar to the non-ideal working (cf. Paragraph 9.3) but the difference is essential: there, π is a dynamical quantity characterizing interaction and so depending on both the state of the body and the state of another body (or environment) and it takes zero value at equal values of the pressures; here, P_s is a constitutive function characterizing the body and so depending only on the (extended) state of the body and it takes zero value at the zero value of the volume rate.

38.4 Exercises

1. Show that the same problem arises as in Paragraph 10.4 even in the presence of the viscous pressure.

2. Generalize the notion of extended simple material by giving a 'kinetic energy' $\mathfrak{e}_k : (\mathrm{m}^3/\mathrm{s}) \to (\mathrm{J})_0^+$ in such a way that the extended internal energy equals $\hat{\mathfrak{e}}(v,T,u) := \mathfrak{e}(v,T) + \mathfrak{e}_k(u)$. What are the natural conditions to be imposed on $\mathfrak{e}_k$? How the function $(\hat{e}, v, u) \to \mathbf{T}(\hat{e}, v, u)$ can be given?

39 A body in a given environment

39.1 The dynamical quantitities

Let us consider the processes of an extended thermodynamical body in which

- the particle number of the body is constant,
- the body is coupled with an environment both mechanically and thermally,
- the working is ideal.

Characterizing the environment by its temperature and pressure, we give the dynamical quantitities as continuous functions

$$(v,T,u,T_a,P_a) \mapsto \mathfrak{q}(v,T,u,T_a,P_a), \qquad (v,T,u,T_a,P_a) \mapsto \mathfrak{f}(e,v,u,T_a,P_a)$$

or

$$(e,v,u,T_a,P_a) \mapsto \mathbf{q}(e,v,u,T_a,P_a), \qquad (e,v,u,T_a,P_a) \mapsto \mathbf{f}(e,v,u,T_a,P_a),$$

which are continuously differentiable in the interior of their domain.

39.2 The equilibrium properties

The equilibrium properties of the dynamical quantitities are formulated according to the following ideas: 1) momentum transfer is determined by pressure difference, 2) we can consider direct heating. Thus we accept that

$*$ if $\mathfrak{f} \neq 0$, then $\mathfrak{f}(v,T,0,T_a,P_a) = 0$ if and only if $\mathcal{P}(v,T,0) = P_a$ or, equivalently, $\mathcal{P}_r(v,T) = P_a$,

$*$ if $\mathfrak{q} \neq 0$, then $\mathfrak{q}(v,T,0,T_a,P_a) = 0$ if and only if $T = T_a$.

39.3 The dissipation inequalities

The dissipation inequalities for the dynamical quantitities are formulated on the basis of the Clausius–Duhem inequality (see Paragraph 7 of the Introduction). Now we find convenient to require separate inequalities.

The inequality concerning heating will be the same as previously:

$$-\mathfrak{q}(v,T,u,T_a,P_a)(T-T_a)\geq 0 \qquad \text{or} \qquad \mathbf{q}(e,v,u,T_a,P_a)\left(\frac{1}{\mathbf{T}(e,v)}-\frac{1}{T_a}\right)\geq 0,$$

where equality holds if and only if $\mathfrak{q}(v,T,u,T_a,P_a)=0$ or $\mathbf{q}(e,v,u,T_a,P_a)=0$.

The part concerning working in the Clausius–Duhem inequality contains the viscous pressure, thus its counterpart in the present case will be more straightforward as previously:

$$-\mathcal{P}_s(v,T,u)u\geq 0,$$

where equality holds if and only if $\mathcal{P}_s(v,T,u)=0$.

Furthermore, we accept an inequality expressing a strong relation between forcing and pressure difference:

$$\mathfrak{f}(v,T,u,T_a,P_a)(\mathcal{P}(v,T,u)-P_a)\geq 0$$

where equality holds if and only if $\mathfrak{f}(v,T,u,T_a,P_a)=0$.

The equilibrium properties and the conditions of equalities in the dissipation inequalities are not independent and do not contradict each other.

The second inequality implies that $\eta\geq 0$ in the form $(*)$ of Paragraph 38.2.

39.4 The dynamical equation

The system in Section 37 can be well treated in the framework of extended ordinary thermodynamics, even we can generalize it by writing the extended pressure in the equation $(**)$ of Paragraph 37.2.

In the sequel we suppose that, besides the conditions imposed earlier,

- the temperature T_a and pressure P_a of the environment is constant,
- the forcing has the form

$$\mathfrak{f}(v,T,u,T_a,P_a)=\delta(\mathcal{P}(v,T,u)-P_a), \tag{$*$}$$

where δ is constant, greater than zero because of the dissipation inequality,

- processes run in the regular domain of the body.

Then the dynamical equation reads:

$$\begin{aligned}\dot e&=\mathbf{q}(e,v,u,T_a,P_a)-\mathbf{P}(e,v,u)u,\\ \dot v&=u,\\ \dot u&=\delta(\mathbf{P}(e,v,u)-P_a)\end{aligned}$$

or

$$\begin{aligned}\dot v&=u,\\ \dot T&=\frac{1}{\mathfrak{c}_s(v,T)}\left(\mathfrak{q}(v,T,u,T_a,P_a)-\left(\frac{\partial\mathfrak{e}(v,T)}{\partial v}+\mathcal{P}(v,T,u)\right)u\right),\\ \dot u&=\delta(\mathcal{P}(v,T,u)-P_a).\end{aligned}$$

39.5 Processes without constraint

39.5.1 Uniqueness of equilibrium

$(e_\mathrm{o}, v_\mathrm{o}, 0)$ is an equilibrium if and only if

$$\mathbf{T}(e_\mathrm{o}, v_\mathrm{o}) = T_a, \qquad \mathbf{P}_r(e_\mathrm{o}, v_\mathrm{o}) = P_a$$

or $(v_\mathrm{o}, T_\mathrm{o}, 0)$ is an equilibrium if and only if

$$T_\mathrm{o} = T_a, \qquad \mathcal{P}_r(v_\mathrm{o}, T_\mathrm{o}) = P_a.$$

These equalities determine equilibrium in a phase uniquely.

39.5.2 Stability of equilibrium

Proposition *Let*

$$\mathfrak{q}(v, T, u, T_a, P_a) = -\lambda(T - T_a)$$

where $\lambda > 0$ *is constant. If the body is of normal dilation, then the equilibrium is asymptotically stable.*

Proof The derivative of the right-hand side of the dynamical equation at $(v_\mathrm{o}, T_\mathrm{o}, 0)$ equals

$$\begin{pmatrix} 0 & 0 & 1 \\ 0 & -\frac{\lambda}{c_\mathrm{o}} & -\frac{n_\mathrm{o}}{c_\mathrm{o}} \\ -\delta b_\mathrm{o} & \delta a_\mathrm{o} & -\delta\eta_\mathrm{o} \end{pmatrix},$$

where $c_\mathrm{o} := \mathfrak{c}_v(v_\mathrm{o}, T_\mathrm{o})$ (the equilibrium value of the specific heat), $\eta_\mathrm{o} := \eta(v_\mathrm{o}, T_\mathrm{o}, 0)$,

$$n := \frac{\partial \mathfrak{e}}{\partial v} + \mathcal{P}_r, \qquad a := \frac{\partial \mathcal{P}}{\partial T}, \qquad b := -\frac{\partial \mathcal{P}}{\partial v},$$

and the subscript o denotes their equilibrium values. Note that here $\mathcal{P}_r$ appears instead of $\mathcal{P}$ because $u = 0$ in equilibrium. This matrix has the characteristic polinomial

$$x \mapsto x^3 + \left(\frac{\lambda}{c_\mathrm{o}} + \delta\eta_\mathrm{o}\right) x^2 + \delta\left(a_\mathrm{o}\frac{n_\mathrm{o}}{c_\mathrm{o}} + \eta_\mathrm{o}\frac{\lambda}{c_\mathrm{o}} + b_\mathrm{o}\right) x + \delta b_\mathrm{o}\frac{\lambda}{c_\mathrm{o}}.$$

The conditions of intrinsic stability imply $c_\mathrm{o} > 0$ and $b_\mathrm{o} > 0$, the normal dilation implies $a_\mathrm{o} n_\mathrm{o} \geq 0$ and $\eta_\mathrm{o} \geq 0$ because of the dissipation inequality; thus we infer from the Ruth–Hurwitz criterion that the eigenvalues of the matrix have negative real part, consequently, the equilibrium is asymptotically stable.

39.5.3 Stability of equilibrium of an entropic body

Proposition *If the body is entropic, then the equilibrium is stable and if, moreover, the body is viscous, then the equilibrium is asymptotically stable.*

Proof Let us use now the specific internal energy as a variable. Let $\mathbf{s}$ be the specific entropy of the simple material in question. The derivative of the function

$$(e,v,u)\mapsto \mathbf{L}(e,v,u):=\mathbf{s}(e,v)-\frac{e+P_av}{T_a}-\frac{u^2}{2\delta T_a},$$

that is

$$\frac{\partial \mathbf{L}}{\partial e}=\frac{1}{\mathbf{T}}-\frac{1}{T_a},\qquad \frac{\partial \mathbf{L}}{\partial v}=\frac{\mathbf{P}_r}{\mathbf{T}}-\frac{P_a}{T_a},\qquad \frac{\partial \mathbf{L}}{\partial u}=-\frac{u}{\delta T_a},$$

is zero in equilibrium and

$$\mathtt{D}^2\mathbf{L}=\begin{pmatrix}\mathtt{D}^2\mathbf{s} & \mathbf{0}\\ \mathbf{0} & -\frac{1}{\delta T_a}\end{pmatrix}$$

is negative definite (where, of course, $\mathtt{D}^2\mathbf{s}$ is a 2×2 matrix). Therefore, $\mathbf{L}$ has a strict maximum in equilibrium.

The derivative of $\mathbf{L}$ along the dynamical equation, the function – with a loose notation –

$$\overset{\bullet}{\mathbf{L}}=\left(\frac{1}{T}-\frac{1}{T_a}\right)(q-Pu)+\left(\frac{P_r}{T}-\frac{P_a}{T_a}\right)u-\frac{P-P_a}{T_a}u=q\left(\frac{1}{T}-\frac{1}{T_a}\right)-\frac{P_su}{T},$$

has a minimum in equilibrium which is strict if the body is viscous.

39.6 Isothermal processes

39.6.1 Uniqueness of equilibrium

For isothermal processes – the temperature of the body is the constant T_a – the first law serves to determine the heating:

$$\mathfrak{q}(v,T_a,u,T_a,P_a)=\left(\frac{\partial\mathfrak{e}(v,T_a)}{\partial v}+\mathcal{P}(v,T_a,u)\right)u.$$

Then

$$U(T_a):=\{(v,T_a,u)\mid v\in(\mathrm{m}^3)^+,u\in(\mathrm{m}^3/\mathrm{s})\}$$

is an invariant submanifold of the dynamical equation that can be parameterized by (v,u) in a natural way. Then we get the reduced dynamical equation

$$\dot v=u,\qquad \dot u=\delta(\mathcal{P}(v,T_a,u)-P_a).$$

$(v_\mathrm{o},0)$ is an equilibrium of this equation if and only if $\mathcal{P}_r(v_\mathrm{o},T_a)=P_a$ which determines v_o uniquely in a phase.

39.6.2 Stability of equilibrium

Proposition *If $\eta_\mathrm{o}:=\eta(v_\mathrm{o},T_a,0)>0$, then every equilibrium in $U(T_a)$ is asymptotically stable in $U(T_a)$.*

Proof The derivative of the reduced dynamical equation in equilibrium is

$$\begin{pmatrix}0 & 1\\ -\delta b_\mathrm{o} & -\delta\eta_\mathrm{o}\end{pmatrix},$$

whose eigenvalues have negative real part (b_o is given in Proposition 39.5.2).

39.6.3 Stability of equilibrium of an entropic body

Proposition *If the body is entropic, then an equilibrium in* $U(T_a)$ *is stable in* $U(T_a)$ *and if, moreover, the body is viscous, then the equilibrium is asymptotically stable.*

Proof Taking the function introduced in the previous paragraph and putting

$$(v, u) \mapsto \Lambda(v, u) := T_a \mathbf{L}(\mathfrak{e}(v, T_a), v, u),$$

we get a Liapunov function for the equilibrium of the reduced dynamical equation. Its first derivative

$$\Big(\mathcal{P}_r(v, T_a) - P_a, -\frac{u}{\delta}\Big)$$

is zero in equilibrium, its second derivative

$$\begin{pmatrix} \frac{\partial \mathcal{P}_r}{\partial v} & 0 \\ 0 & -\frac{1}{\delta} \end{pmatrix}$$

is evidently negative definite, thus Λ has a strict maximum in equilibrium.

The derivative of Λ along the reduced dynamical equation, the function $(v, u) \mapsto -\mathcal{P}_s(v, T_a, u)u$ has a minimum in equilibrium because of the dissipation inequality and the minimum is strict if the body is viscous.

39.6.4 Remark

If $\mathcal{P}_s = 0$ (the body is highly non viscous), then the reduced dynamical equation is

$$\dot{v} = u, \qquad \dot{u} = \delta(\mathcal{P}_r(v, T_a) - P_a).$$

The right-hand side of the second equation is negative; it is well known in stability theory that the equilibrium is stable and processes near equilibrium are periodic.

Such an equation enters Exercise 3 of 37.3 (where, of course, $\mathcal{P}$ denoted the elastic pressure).

39.7 Adiabatic processes

39.7.1 Equilibrium of a body without viscous pressure

Now $\mathcal{P}_s = 0$. Then the first law – with $\mathbf{q} = 0$ – gives the usual differential equation for the adiabats, i.e. processes run on the usual adiabats. An adiabat C is obtained as the graph of a solution $v \mapsto \mathcal{T}(v)$ of the differential equation in Paragraph 4.2. The set $C \times (\mathrm{m}^3/\mathrm{s})$ is an invariant submanifold of the dynamical equation which can be parameterized by the function $(v, u) \mapsto (v, \mathcal{T}(v), u)$. The the reduced dynamical equation becomes

$$\dot{v} = u, \qquad \dot{u} = \delta\big(\mathcal{P}_r(v, \mathcal{T}(v)) - P_a\big).$$

$(v_\mathrm{o}, 0)$ is an equilibrium of the reduced dynamical equation if and only if $\mathcal{P}_r(v_\mathrm{o}, \mathcal{T}(v_\mathrm{o})) = P_a$; the equilibrium in an adiabat and in a phase is unique.

Essentially this equation was examined in Exercise 1 of 37.3 (where, of course, $\mathcal{P}$ denoted the elastic pressure). We can then state:

Proposition *If the viscous pressure of the body is zero and the body has the normal dilation property and C is an adiabat of the body, then every equilibrium in $C \times (\mathrm{m}^3/\mathrm{s})$ is stable in $C \times (\mathrm{m}^3/\mathrm{s})$.*

39.7.2 Equilibrium of a viscous body

If $\mathcal{P}_s \neq 0$, then the first law is not linear in $u = \dot{v}$, and we cannot give invariant submanifolds, so we cannot reduce the dynamical equation. The equilibria of the original dynamical equation constitute the set

$$Eq := \{(v_{\mathrm{o}}, T_{\mathrm{o}}, 0) \mid \mathcal{P}_r(v_{\mathrm{o}}, T_{\mathrm{o}}) = P_a\}$$

which is a one-dimensional submanifold. The tangent space of Eq at $(v_{\mathrm{o}}, T_{\mathrm{o}}, 0)$ is spanned by the vector $(a_{\mathrm{o}}, b_{\mathrm{o}}, 0)$, where the notations of Proposition 39.5.2 are used.

Proposition *Let us suppose that $\eta_{\mathrm{o}} := \eta(v_{\mathrm{o}}, T_{\mathrm{o}}, 0) > 0$ for all $(v_{\mathrm{o}}, T_{\mathrm{o}}, 0) \in Eq$. Then Eq is strictly asymptotically stable.*

Proof We get the derivative of the right-hand side of the dynamical equation in an equilibrium $(v_{\mathrm{o}}, T_{\mathrm{o}}, 0)$ by substituting 0 for λ in the matrix in 39.5.2. The eigenvector of the zero eigenvalue of this matrix is $(a_{\mathrm{o}}, b_{\mathrm{o}}, 0)$ – a tangent vector of Eq at the given point – and the non-zero eigenvalues are negative. Thus we have got the desired result by App. 7.

39.8 Isobaric processes

39.8.1 Uniqueness of equilibrium

Now

$$U(P_a) := \{(e, v, u) \mid \mathbf{P}(e, v, u) = P_a\}$$

is an invariant set of the dynamical equation.

Let us take the simple case when η does not depend on the volume rate and $\eta > 0$. Then in $U(P_a)$

$$u = \frac{\mathbf{P}_r(e, v) - P_a}{\eta(e, v)}$$

thus, $U(P_a)$ can be parameterized by (e, v) and the reduced dynamical equation becomes

$$\begin{aligned} \dot{e} &= \mathbf{q}\left(e, v, \frac{\mathbf{P}_r(e, v) - P_a}{\eta(e, v)}, T_a, P_a\right) - P_a \frac{\mathbf{P}_r(e, v) - P_a}{\eta(e, v)}, \\ \dot{v} &= \frac{\mathbf{P}_r(e, v) - P_a}{\eta(e, v)}. \end{aligned}$$

$(e_{\mathrm{o}}, v_{\mathrm{o}})$ is an equilibrium of the reduced dynamical equation if and only if

$$\mathbf{T}(e_{\mathrm{o}}, v_{\mathrm{o}}) = T_a, \qquad \mathbf{P}_r(e_{\mathrm{o}}, v_{\mathrm{o}}) = P_a;$$

the equilibrium is uniquely determined in a phase.

Proposition *If* η *does not depend on the volume rate,* $\eta > 0$ *and the body is entropic, then every equilibrium in* $U(P_a)$ *is asymptotically stable in* $U(P_a)$*.*

Proof It is a routine to check that the function

$$(e, v) \mapsto \mathbf{L}(e, v) := \mathbf{s}(e, v) - \frac{e + P_a v}{T_a}$$

has a strict maximum in equilibrium.

The derivative of $\mathbf{L}$ along the reduced dynamical equation – with the customary loose notations – is

$$\overset{\bullet}{\mathbf{L}} = \left(\frac{1}{T} - \frac{1}{T_a}\right)\left(q - P_a\frac{P_r - P_a}{\eta}\right) + \left(\frac{P}{T} - \frac{P_a}{T_a}\right)\left(\frac{P_r - P_a}{\eta}\right) =$$
$$= \left(\frac{1}{T} - \frac{1}{T_a}\right)q + \frac{(P_r - P_a)^2}{T\eta}.$$

The first term is the expression in the first dissipation inequality, consequently, $\overset{\bullet}{\mathbf{L}}$ has a strict minimum in equilibrium.

39.9 Limiting case of the extended dynamical equation

The question arises, how we can formulate a relation – if it exists – between extended ordinary thermodynamics and ordinary thermodynamics.

Let us consider the simple case when $\eta > 0$ is constant. Then the dynamical equation (in a loose notation) is

$$\dot{e} = q - (P_r - \eta u)u, \quad \dot{v} = u, \quad \dot{u} = \delta(P_r - \eta u - P_a). \tag{$*$}$$

In the special case of Paragraph 37.2 we have

$$\delta = \frac{A^2}{N(m + m_g/2)}.$$

Momentum transfer in ordinary thermodynamics is neglected which corresponds to zero masses. This is expressed in the general case by δ tending to infinity, or in a more suitable form, by letting $1/\delta$ tend to zero in the equation

$$\frac{1}{\delta}\dot{u} = P_r - \eta u - P_a.$$

Then we get formally that $u = \frac{P_r - P_a}{\eta}$ yielding

$$\dot{e} = q - P_a f, \qquad \dot{v} = f := \frac{P_r - P_a}{\eta}. \tag{$**$}$$

The partial derivative with respect to u of the right-hand side of the third equation in ($*$) is negative, therefore, equation ($**$) is a good approximation of ($*$) for small $\frac{1}{\delta}$ (see App. 6).

Because equation ($**$) is an approximation of the dynamical equation in ordinary thermodynamics if P_r nearly equals P_a (because now P_a stands in the first law instead of P), we can say that – at least in the present special case – the extended description of a body in a given environment is approximated by the non-extended description if the masses tend to zero and the pressure of the body is near to that of the environment.

39.10 Exercises

1. Show that for isochoric processes (volume is constant) the extended description gives back the non-extended description.

2. Verify that Proposition 39.5.2 remains valid if λ and δ are not constant but take positive value in equilibrium.

Furthermore, the proposition remains valid if forcing has the form $\delta(P-P_a)+\phi(u)$, where ϕ is differentiable and $\phi(0)=0$, $\phi'(0)=0$.

3. Treat Exercise 4 in 37.3 in extended ordinary thermodynamics. What can be said about the stability of equilibrium?

4. Describe the isobaric processes in the variables (v,T,u) and prove a stability statement by the linearization method.

5. Treat all the systems in Section 39 accepting a generalized definition of extended material according to Exercise 2 in 38.4.

40 Bounds of extended thermodynamics

Extended ordinary thermodynamics provides good results for a body with constant particle number in a given environment (though forcing has a rather special form). Unfortunately, it does not work well for the description of interaction of more bodies because the volume rate is an independent variable assigned to the body, thus it cannot be split into the sum of quantities assigned to interacting pairs. For a system consisting of bodies with constant particle number, ordinary thermodynamics writes

$$\dot{V}_i = F_i = \sum_{k=1}^{m} F_{ik},$$

and extended ordinary thermodynamics would write

$$\dot{V}_i = \dot{N}_i v_i + N_i u_i =: U_i,$$

and u_i is a constitutive variable of the i-th body. Consequently, the dissipation inequality – which involves the volume rate – cannot be formulated for interacting pairs. We could try to formulate the dissipation inequality for each body (in the non-extended theory this means that the inequalities concerning a body are summed up). Then Paragraph 39.3 suggests requiring for three bodies

$$-\frac{Q_{12}}{T_2}(T_1-T_2)-\frac{Q_{13}}{T_3}(T_1-T_3)\geq 0$$

or

$$Q_{12}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)+Q_{13}\left(\frac{1}{T_1}-\frac{1}{T_3}\right)\geq 0.$$

The two inequalities are not equivalent; we have to decide which of them should be accepted.

We have to select, of course, the one assuring stability at least in simple cases. In the simplest case, however, when two entropic bodies interact completely isolated from the environment and the two inequalities are indeed equivalent, we cannot find a modification of the entropy (similar to that in Paragraph 39.5.2) that would be a Liapunov function for stability (it was the temperature of the environment that appeared in the modifying term).

Moreover, at present, we have no convenient dissipation inequality for varying particle number, thus diffusions and phase transitions cannot be treated in extended ordinary thermodynamics.

IX ELECTROMAGNETIC PHENOMENA IN THERMODYNAMICS

41 Introductory remarks

It is an everyday phenomenon that a body conducting electric current becomes warmer. Another well-known phenomenon that metals becomes warmer when being magnetized. The resistance of bodies, an important quantity in electric circuits, depends on temperature. The magnetic permeability, too, depends on temperature.

In this chapter we examine how the thermodynamic states of bodies are influenced by electromagnetism and how electromagnetic phenomena depend on the thermodynamic state of bodies.

We emphasize that here we only have a restricted possibility: we deal with homogeneous bodies, thus the electromagnetic quantities, too must be considered homogeneous, which is rarely a good approximation, e.g. the electric field even in equilibrium is hardly ever homogeneous. Nevertheless, the homogeneous model gives good qualitative results in a surprisingly great number of cases.

We point out that electric field, magnetic field, electric dipole, magnetic momentum, etc. are relative notions i.e. depend on observers. The absolute quantities are the electromagnetic field, the electromagnetic momentum, etc. Electric charge, too, is absolute. Because a thermodynamical body presupposes an observer in which it rests, we shall speak about electric field etc. which will mean the electric field, etc. with respect to the body.

Finally, we have to mention the electromagnetic units. Up to now we have used the SI units and we do not want to deviate from them too much but the electromagnetic formulae are somewhat clumsy because of the everywhere present vacuum permittivity ϵ_0 and vacuum permeability μ_0. That is why we use, instead of some electric quantities, their multiple by $\sqrt{\epsilon_0}$ or $1/\sqrt{\epsilon_0}$ and instead of some magnetic quantities their multiple by $\sqrt{\mu_0}$ or $1/\sqrt{\mu_0}$. Of course, a precise mathematical meaning can be assigned to $\sqrt{\epsilon_0}$ and $\sqrt{\mu_0}$ which we do not detail here. The magnetic units in SI are mistaken because formerly one confused the physical role of the magnetic quantities $\mathbb{H}$ and $\mathbb{B}$. On the basis of electric analogy, one took $\mathbb{H}$ for the magnetic field in such a way that $\mathbf{m} \times \mathbb{H}$ is the torque acting on a magnetic momentum $\mathbf{m}$. This error survives in SI though both theory and practice have proved that $\mathbb{B}$ is the magnetic field. The units in SI are chosen in such a way that the unit of magnetic momentum $\mathbf{m}$ multiplied by the unit of $\mathbb{H}$ be J (*joule*). Now we modify here the SI in such a way that the product of the units of $\mathbf{m}$ and $\mathbb{B}$ be *joule*. Moreover, we achieve that ϵ_0 and μ_0 be missing from all formulae.

The symbols we use for electromagnetic quantities and their SI units are the following:

C electric charge:	As,
U electric potential:	V,
$\mathbb{E}$ electric field:	V/m,
$\mathbb{D}$ electric frame:	$\mathrm{As/m^2}$,
$\mathbf{p}$ electric dipole:	As m,
$\mathbb{P}$ electric polarization:	$\mathrm{As/m^2}$,
ϵ_0 vacuum permittivity:	As/Vm,
$\mathbb{B}$ magnetic field:	$\mathrm{Vs/m^2}$,
$\mathbb{H}$ magnetic frame:	A/m,
$\mathbf{m}$ magnetic momentum:	$\mathrm{A\,m^2}$,
$\mathbb{M}$ magnetization:	A/m,
μ_0 vacuum permeability:	Vs/Am.

Using the notations $\hat{\mathrm{A}} := \mathrm{A}/\sqrt{\epsilon_0}$, $\hat{\mathrm{V}} := \sqrt{\epsilon_0}\mathrm{V}$, $\breve{\mathrm{A}} := \sqrt{\mu_0}\mathrm{A}$, $\breve{\mathrm{V}} := \mathrm{V}/\sqrt{\mu_0}$, the units we use are the following:

C electric charge:	$\hat{\mathrm{A}}\mathrm{s} := \mathrm{As}/\sqrt{\epsilon_0}$,
U electric potential:	$\hat{\mathrm{V}} := \sqrt{\epsilon_0}\mathrm{V}$,
$\mathbb{E}$ electric field:	$\hat{\mathrm{V}}/\mathrm{m} := \sqrt{\epsilon_0}\mathrm{V/m}$,
$\mathbb{D}$ electric frame:	$\hat{\mathrm{A}}\mathrm{s/m^2} := \mathrm{As}/(\mathrm{m^2}\sqrt{\epsilon_0})$,
$\mathbf{p}$ electric dipole:	$\hat{\mathrm{A}}\mathrm{sm} := \mathrm{Asm}/\sqrt{\epsilon_0}$,
$\mathbb{P}$ electric polarization:	$\hat{\mathrm{A}}\mathrm{s/m^2} := \mathrm{As}/(\mathrm{m^2}\sqrt{\epsilon_0})$,
$\mathbb{B}$ magnetic field:	$\breve{\mathrm{V}}\mathrm{s/m^2} := \mathrm{Vs}/(\mathrm{m^2}\sqrt{\mu_0})$,
$\mathbb{H}$ magnetic frame:	$\breve{\mathrm{A}}/\mathrm{m} := \sqrt{\mu_0}\mathrm{A/m}$,
$\mathbf{m}$ magnetic momentum:	$\breve{\mathrm{A}}\mathrm{m^2} := \sqrt{\mu_0}\mathrm{Am^2}$,
$\mathbb{M}$ magnetization:	$\breve{\mathrm{A}}/\mathrm{m} := \sqrt{\mu_0}\mathrm{A/m}$.

Thus, if in our formulae the symbols in the left column below are replaced with the symbols in the right column, then we obtain the corresponding formulae in SI:

C	$C/\sqrt{\epsilon_0}$,
U	$\sqrt{\epsilon_0}U$,
$\mathbb{E}$	$\sqrt{\epsilon_0}\mathbb{E}$,
$\mathbb{D}$	$\mathbb{D}/\sqrt{\epsilon_0}$,
$\mathbf{p}$	$\mathbf{p}/\sqrt{\epsilon_0}$,
$\mathbb{P}$	$\mathbb{P}/\sqrt{\epsilon_0}$,
$\mathbb{B}$	$\mathbb{B}/\sqrt{\mu_0}$,
$\mathbb{H}$	$\sqrt{\mu_0}\mathbb{H}$,
$\mathbf{m}$	$\sqrt{\mu_0}\mathbf{m}$,
$\mathbb{M}$	$\sqrt{\mu_0}\mathbb{M}$.

Because

$$(\epsilon_0) = \left(\frac{\text{As}}{\text{Vm}}\right), \qquad (\mu_0) = \left(\frac{\text{Vs}}{\text{Am}}\right),$$

it is easy to see that

$$(\text{As}/\sqrt{\epsilon_0}) = (\sqrt{\text{Jm}}), \qquad (\sqrt{\epsilon_0}\text{V}) = (\sqrt{\text{J/m}}),$$

$$(\sqrt{\epsilon_0}\text{V/m}) = (\text{As/m}^2\sqrt{\epsilon_0}) = (\text{Vs/m}^2\sqrt{\mu_0}) = (\sqrt{\mu_0}\text{A/m}) = (\sqrt{\text{J/m}^3}),$$

thus, $\mathbb{E}$, $\mathbb{D}$, $\mathbb{P}$, $\mathbb{B}$, $\mathbb{H}$ and $\mathbb{M}$ have the same unit.

42 Electrically chargeable bodies

42.1 The potential of a charged body

Charges produce electric field. If we deal with phenomena in which the macroscopic flow of charges in the body is not too fast, then the magnetic field can be neglected and the electric field can be considered static, thus having a potential. Charge is the extensive quantity characterizing electricity and potential is the corresponding intensive quantity.

A body can be charged in two different microscopic ways:

1) charges are bound to molecules (insulators),

2) charges move freely among the molecules (conductors).

Let us recall some elementary facts of electrostatics.

Let us put a charge C on a ball with radius R. If the ball is a conductor, then in equilibrium the charge is distributed on the surface of the ball and the potential in the ball is constant having the value

$$U = \frac{1}{4\pi}\frac{C}{R}$$

or

$$U = \gamma_c C, \qquad \gamma_c := \frac{1}{\sqrt[3]{3(4\pi)^2 V}},$$

where V is the volume of the body. The potential depends on the charge and the volume. Now the potential is homogeneous in the body, the charge is not. Nevertheless, let us consider as if it were homogeneous. If N is the particle number of the ball, then C/N is the specific charge, V/N is the specific volume. We see that the potential cannot be expressed as a function of the specific quantities only.

If the ball is an insulator, then we can realize a homogeneous charge distribution on it. Then the potential is not constant in the ball; it is spherically symmetric, its value at a distance r from the centre is

$$U(r) = \frac{1}{4\pi\epsilon}\frac{Cr^2}{R^3},$$

where ϵ is the (relative) permittivity of the material. Now the charge distribution is homogeneous and the potential is not. Nevertheless, let us consider as if it were homogeneous and let us replace it with its average value

$$\frac{1}{4\pi\epsilon}\frac{C}{3R},$$

which is obtained by integrating from 0 to R and then dividing it by R. Then we have

$$U = \gamma_i C, \qquad \gamma_i := \frac{1}{3\epsilon\sqrt[3]{3(4\pi)^2 V}} = \frac{\gamma_c}{3\epsilon}.$$

We can see, as previously, that the potential depends on charge and volume but cannot be expressed as a function of the specific quantities only.

These simple examples show that the assumption of homogeneity is rather rough. Note also that our results apply for a ball; other forms yield other formulae: the potential depends not only on the volume of the body but also on its form.

Moreover, besides the volume, the potential depends on other thermodynamical quantities of the body, too. The formula for the insulator contains the permittivity which depends on the phase of the body and in a given phase it depends on temperature and pressure.

Based on straightforward assumptions on the molecular structure of materials, we can deduce the Clausius–Mosotti formula (see 48.4):

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{\alpha}{3v},$$

where α is a constant and v is specific volume. Rearranging we get

$$\epsilon(v, T) = 1 + \frac{3\alpha}{3v - \alpha},$$

i.e. the permittivity depends only on specific volume and not on temperature. This seems strange because it is well know that permittivity depends on temperature. Of course, it will depend on temperature if – corresponding to practice – we take a given phase and the variables temperature and pressure in the phase. The the specific volume will be a function of temperature and pressure, and in our customary notations

$$\epsilon(T, P) = 1 + \frac{3\alpha}{3\boldsymbol{v}(T, P) - \alpha}.$$

The Clausius–Mosotti formula, of course being only a good approximation in many cases, has no overall validity. There are materials whose permittivity cannot be defined at all but it is true generally that the potential produced by charges on a body depends on its thermodynamical state.

42.2 The pressure of a charged body

The identical microcharges on a body repulse each other, which makes the body extend, or a greater pressure is necessary to keep the volume constant. Thus pressure depends on the charge of the body which will be illustrated as follows.

Let us distribute homogeneously a charge C in a ball of volume V. The potential U and the electric field $\mathbb{E}$ are spherically symmetric and the pressure P_c due to the charge can be taken spherically symmetric, too. The charge density is C/V, so the electric force acting on a small piece between the radii r and $r + \Delta r$ with surface area A is approximately

$$A\Delta r \frac{C}{V}|\mathbb{E}(r)|.$$

In equilibrium this equals the force deriving from the pressure:

$$-P_c(r+\Delta r)A + P_c(r)A.$$

The equality of these expressions gives in the limit $\Delta r \to 0$ that

$$P_c'(r) = -\frac{C}{V}|\mathbb{E}(r)| = \frac{C}{V}U'(r),$$

from which we find that

$$P_c(r) = \frac{CU(r)}{V}$$

(the constant of integration is zero because of spherical symmetry).

Neither the potential nor the pressure due to the charge is homogeneous. Nevertheless, let us consider them to be homogeneous. Then the additional pressure becomes

$$P_c = \frac{CU}{V} = \frac{\gamma_i C^2}{V}$$

or a suitable multiple of it (see 42.9).

42.3 The internal energy of a charged body

The electric interaction of microcharges results in electric energy which is a part of the internal energy of the body; thus the internal energy, too, depends on the charge of the body. It is an elementary fact that the electric energy of the charge distribution ρ is

$$\frac{1}{2}\int U(x)d\rho(x),$$

where U is the potential produced by the charge distribution. Thus, the charged conductor ball and insulator ball have electric energy

$$E_c := \frac{C^2}{8\pi R} = \frac{\gamma_c C^2}{2} \qquad \text{and} \qquad E_c := \frac{C^2}{24\pi\epsilon R} = \frac{\gamma_i C^2}{2},$$

respectively.

42.4 Extensive and intensive quantities

The previous heuristic considerations disclose that neither the potential nor the pressure can be given as a function of specific volume and specific charge only. Consequently, the potential and the pressure, though being intensive quantities, do not have the usual property: if a homogeneous body is split into two parts and the two parts are removed, then the potential and the pressure in the two halves are not equal to the original ones.

Neither is internal energy a usual extensive quantity, specific internal energy cannot be defined: if a homogeneous body is split into two parts and the two parts are removed, then the internal energy of each half is not the half of the original internal energy.

Charge, however, is a usual extensive quantity: half of the original charge will be in each half part.

42.5 Definition of a chargeable body

As mentioned, we can define only an electrically chargeable body, not material. Moreover, the electrically charged homogeneous body is a strong idealization. Besides its known thermodynamical quantities, it is characterized by its charge and electric potential. If its charge is zero, then the body possesses the known thermodynamical properties.

Definition $(D \times \mathbb{R}^+ \times (\hat{\mathrm{A}}\mathrm{s}), \mathfrak{e}_b, \mathcal{P}_b, \mu_b, R, \mathcal{E}_c, \mathcal{P}_c, \mu_c, \mathcal{U})$ *is called an* **electrically chargeable body** *if* $(D, \mathfrak{e}_b, \mathcal{P}_b, \mu_b, R)$ *is a simple material,*

$$\mathcal{E}_c : D \times \mathbb{R}^+ \times (\hat{\mathrm{A}}\mathrm{s}) \to (\mathrm{J})^+, \qquad \mathcal{P}_c : D \times \mathbb{R}^+ \times (\hat{\mathrm{A}}\mathrm{s}) \to (\mathrm{Pa}),$$

$$\mu_c : D \times \mathbb{R}^+ \times (\hat{\mathrm{A}}\mathrm{s}) \to (\mathrm{J}), \qquad \mathcal{U} : D \times \mathbb{R}^+ \times (\hat{\mathrm{A}}\mathrm{s}) \to (\hat{\mathrm{V}}),$$

are continuous functions, continuously differentiable on $R \times \mathbb{R}^+ \times (\hat{\mathrm{A}}\mathrm{s})$*,*

– $T \mapsto \mathcal{E}_c(v, T, N, C)$ *is monotone increasing for all* v*,* N *and* C*,*

– $v \mapsto \mathcal{P}_c(v, T, N, C)$ *is locally monotone decreasing for all* T*,* N *and* C*,*

– $C\mathcal{U}(v, T, N, C) > 0$ *if* $C \neq 0$ *and* $C \mapsto \mathcal{U}(v, T, N, C)$ *is strictly monotone increasing for all* v*,* T *and* N*, its derivative is everywhere positive,*
moreover $\mathcal{E}_c(v, T, N, 0) = 0$*,* $\mathcal{P}_c(v, T, N, 0) = 0$*,* $\mu_c(v, T, N, 0) = 0$*,* $\mathcal{U}(v, T, N, 0) = 0$ *for all* (v, T, N) *in* $D \times \mathbb{R}^+$ *.*

The function $\mathcal{U}$ *is the* **potential** *of the body, and the functions*

$$\mathcal{E}(v, T, N, C) := N\mathfrak{e}_b(v, T) + \mathcal{E}_c(v, T, N, C),$$

$$\mathcal{P}(v, T, N, C) := \mathcal{P}_b(v, T) + \mathcal{P}_c(v, T, N, C),$$

$$\mu(v, T, N, C) := \mu_b(v, T) + \mu_c(v, T, N, C)$$

are the **internal energy***, the* **pressure** *and the* **chemical potential** *of the body.*

The subscript b refers to the basic quantities related to the material of the body.

It follows from the definition that the inequalities

$$\frac{\partial \mathcal{E}}{\partial T} > 0, \qquad \frac{\partial \mathcal{P}}{\partial v} < 0, \qquad \frac{\partial \mathcal{U}}{\partial C} > 0 \tag{$*$}$$

hold on the regular domain, more precisely on $R \times \mathbb{R}^+ \times (\hat{\mathrm{A}}\mathrm{s})$.

We emphasized before the definition that we can define only an electrically chargeable body, not a material because the quantities connected to electricity cannot be described by specific data. The definition involves the material of the body which is related to the thermodynamical quantities only. There can be quantities related to electricity which depend only on v and T; they are considered to characterize the material. Such a quantity is the permittivity of the material. The formula in Paragraph 42.1 in the present notation reads

$$\mathcal{U}(v, T, N, C) = \frac{C}{3\epsilon(v, T)\sqrt[3]{3(4\pi)^2 N v}}.$$

In the definition and in quantities related to the material, the specific volume is the convenient variable. In formulae concerning the body – as in the case of a neutral body – the entire volume is more suitable.

Applying the customary ambiguous notation, we shall write either v *or* V *as a variable in a function.*

42.6 Canonical variables

The conditions imposed on the constitutive functions allow us to give temperature as a function of internal energy, volume, particle number and charge, i.e. internal energy can be used as an independent variable instead of temperature. Thus, we have, as earlier

$$\mathbf{T}(\mathcal{E}(V,T,N,C),V,N,C) = T, \qquad \mathcal{E}(V,\mathbf{T}(E,V,N,C),N,C) = E,$$

$$\begin{aligned} \mathbf{P}(E,V,N,C) &= \mathcal{P}(V,\mathbf{T}(E,V,N,C),N,C), \\ \boldsymbol{\mu}(E,V,N,C) &= \mu(V,\mathbf{T}(E,V,N,C),N,C), \\ \mathbf{U}(E,V,N,C) &= \mathcal{U}(V,\mathbf{T}(E,V,N,C),N,C). \end{aligned}$$

42.7 Entropic property

According to the usual ‘rule’ (see Paragraph 16.3), the entropy $(V,T,N,C) \mapsto \mathcal{S}(V,T,N,C)$ of a chargeable body should obey the relations

$$T\frac{\partial \mathcal{S}}{\partial T} = \frac{\partial \mathcal{E}}{\partial T}, \qquad T\frac{\partial \mathcal{S}}{\partial V} = \frac{\partial \mathcal{E}}{\partial V} + \mathcal{P}, \qquad T\frac{\partial \mathcal{S}}{\partial N} = \frac{\partial \mathcal{E}}{\partial N} - \mu, \tag{1}$$

$$T\frac{\partial \mathcal{S}}{\partial C} = \frac{\partial \mathcal{E}}{\partial C} - \mathcal{U}. \tag{2}$$

If internal energy is used as a variable (in other words, canonical variables are applied), then the function $\mathbf{S}(E,V,N,C) := \mathcal{S}(V,\mathbf{T}(E,V,N,C),N,C)$ satisfies

$$\frac{\partial \mathbf{S}}{\partial E} = \frac{1}{\mathbf{T}}, \qquad \frac{\partial \mathbf{S}}{\partial V} = \frac{\mathbf{P}}{\mathbf{T}}, \qquad \frac{\partial \mathbf{S}}{\partial N} = -\frac{\boldsymbol{\mu}}{\mathbf{T}},$$

$$\frac{\partial \mathbf{S}}{\partial C} = -\frac{\mathbf{U}}{\mathbf{T}}.$$

Definition *An electrically chargeable body in Definition 42.5 is* **entropic** *if there is a function* $\mathcal{S}$, *the* **entropy** *of the body, satisfying equalities* (1) *and* (2) *on* $R \times \mathbb{R}^+ \times$ (Âs).

If the entropy is twice differentiable, then Young’s theorem yields the known equality

$$T\frac{\partial \mathcal{P}}{\partial T} = \frac{\partial \mathcal{E}}{\partial V} + \mathcal{P} \tag{3}$$

and the additional equalities

$$\frac{\partial \mathcal{E}}{\partial C} = -T\frac{\partial \mathcal{U}}{\partial T} + \mathcal{U}, \qquad \frac{\partial \mathcal{P}}{\partial C} = -\frac{\partial \mathcal{U}}{\partial V}, \qquad \frac{\partial \mu}{\partial C} = \frac{\partial \mathcal{U}}{\partial N}. \tag{4}$$

Applying Proposition 16.4, we can state that the second derivative of entropy as a function of the canonical variables, if particle number is fixed,

$$-\frac{1}{\mathbf{T}^2}\begin{pmatrix} \frac{\partial \mathbf{T}}{\partial E} & \frac{\partial \mathbf{T}}{\partial V} & \frac{\partial \mathbf{T}}{\partial C} \\ \mathbf{P}\frac{\partial \mathbf{T}}{\partial E}-\mathbf{T}\frac{\partial \mathbf{P}}{\partial E} & \mathbf{P}\frac{\partial \mathbf{T}}{\partial V}-\mathbf{T}\frac{\partial \mathbf{P}}{\partial V} & \mathbf{P}\frac{\partial \mathbf{T}}{\partial C}-\mathbf{T}\frac{\partial \mathbf{P}}{\partial C} \\ -\mathbf{U}\frac{\partial \mathbf{T}}{\partial E}+\mathbf{T}\frac{\partial \mathbf{U}}{\partial E} & -\mathbf{U}\frac{\partial \mathbf{T}}{\partial V}+\mathbf{T}\frac{\partial \mathbf{U}}{\partial V} & -\mathbf{U}\frac{\partial \mathbf{T}}{\partial C}+\mathbf{T}\frac{\partial \mathbf{U}}{\partial C} \end{pmatrix}$$

is negative definite and if particle number is allowed to vary, too, then the second derivative is negative semidefinite.

42.8 Conventional chargeable body

According to our knowledge in electrostatics (see 42.1), potential can be taken proportional to charge, the proportionality coefficient can depend on the thermodynamical state of the body. Then (see 42.2) the additional pressure due to the charge and the electric energy are proportional to the square of the charge. These suggest the following definition.

Definition *The chargeable body* $(D\times\mathbb{R}^+\times(\hat{\mathrm{A}}\mathrm{s}), \mathfrak{e}_b, \mathcal{P}_b, \boldsymbol{\mu}_b, R, \mathcal{E}_c, \mathcal{P}_c, \boldsymbol{\mu}_c, \mathcal{U})$ *is called* **conventional** *if there are continuous functions* η, π, ξ *and* γ *defined on* $D\times\mathbb{R}^+$ *(mapping into convenient measure lines), continuously differentiable on* $R\times\mathbb{R}^+$ *so that*

$$\mathcal{E}_c(V,T,N,C) := \frac{\eta(V,T,N)C^2}{2}, \qquad \mathcal{P}_c(V,T,N,C) := \frac{\pi(V,T,N)C^2}{2},$$

$$\boldsymbol{\mu}_c(V,T,N,C) := \frac{\xi(V,T,N)C^2}{2}, \qquad \mathcal{U}(V,T,N,C) := \gamma(V,T,N)C.$$

γ has positive values because potential is a strictly monotone increasing function of charge. $\frac{1}{\gamma}$ is called the **capacity** of the body.

42.9 Remarks on the entropic property

42.9.1 Doubts

Equalities (3) and (4) in Paragraph 42.7 give the necessary conditions

$$\eta = -T\frac{\partial\gamma}{\partial T}+\gamma, \qquad \pi = -\frac{\partial\gamma}{\partial V}, \qquad \xi = \frac{\partial\gamma}{\partial N} \tag{$*$}$$

for a conventional body to be entropic.

Let

$$\gamma(V,T,N) := \frac{a}{\epsilon(V,T,N)\sqrt[3]{V}},$$

as in 42.1 where $a > 0$ is a constant, and of course, according to our customary notation, $\epsilon(V,T,N) := \epsilon(V/N,T)$, furthermore,

$$\pi(V,T,N) := b\frac{\gamma(V,T,N)}{V},$$

as in 42.2 where b is a constant. If the body is entropic, then the middle equality in $(*)$ yields

$$\frac{ba}{\epsilon\sqrt[3]{V^4}} = \frac{a\frac{\partial\epsilon}{\partial V}}{\epsilon^2\sqrt[3]{V}} + \frac{a}{3\epsilon\sqrt[3]{V^4}}$$

implying

$$V\frac{\partial\epsilon}{\partial V} = (b - 1/3)\epsilon; \qquad (**)$$

as a consequence, there is a $c(T,N)$ such that

$$\epsilon(V,T,N) = c(T,N)V^{b-1/3}.$$

Then we can state that the following four conditions cannot simultaneously hold:

1. the body is entropic,
2. the formula $\mathcal{U}(V,T,N,C) = \frac{aC}{\epsilon(V,T,N)\sqrt[3]{V}}$ well-known from electrostatics is valid (where a is a positive constant),
3. the formula $b\frac{CU}{V}$ deduced in 42.2 for the additional pressure due to the charge is valid (where b is a constant),
4. the Clausius–Mosotti formula is valid for the permittivity.

Conditions 2 and 3 are consequences of fundamental relations in electricity and mechanics. Condition 4 is based on fundamental relations in electricity and ‘natural assumptions’ on the molecular structure of bodies and it turns out to be a good approximation of reality; the Clausius–Mosotti formula, however, differs significantly from (is not a good approximation of) $(**)$. Thus if the common conditions 2–4 are valid, then the body is not entropic. Conversely, if the body is entropic, one of the three common conditions 2–4 is not valid.

This makes it doubtful whether it is reasonable to require that a chargeable body be entropic. Of course, we cannot exclude that entropic property is a really good one but then we have to revise our knowledge on electrostatics.

42.9.2 On the form of entropy

Note that we have not defined the actual form of entropy of a chargeable body: only some properties of entropy are settled.

Let us suppose in analogy of our earlier formulae that

$$\mathcal{S} := \frac{\mathcal{E} + \mathcal{P}V - \mu N - \mathcal{U}C}{T}.$$

We infer from (2) in 42.7 that if the body is entropic, then

$$\frac{\partial\mathcal{P}_c}{\partial C}V - \frac{\partial\mu_c}{\partial C}N - \frac{\partial\mathcal{U}}{\partial C}C = 0$$

which gives

$$\pi V - \xi N = \gamma \qquad (**)$$

for a conventional body, so

$$\mathcal{S} = \mathcal{S}_b + \frac{(\eta - \gamma)C^2}{2T},$$

where $\mathcal{S}_b$ is the entropy of the body without charge.

Combining formula $(*)$ in the previous paragraph and $(**)$, we get

$$-V\frac{\partial\gamma}{\partial V} - N\frac{\partial\gamma}{\partial N} = \gamma.$$

It is known from the theory of first-order quasi-linear partial differential equations that γ satisfies the above equality if and only if there are functions α and β of temperature such that

$$\gamma(V, T, N) = \frac{\alpha(T)}{V} + \frac{\beta(T)}{N}.$$

This contradicts the forms of γ in 42.1.

42.10 Two customary conditions

In practice (electrotechnics) one always takes $U = \gamma C$ and $E_c = \frac{CU}{2} = \frac{\gamma C^2}{2}$. Moreover, γ is considered to be independent of temperature (which seems a good approximation in a large interval). For a conventional body, these assumptions give

$$\eta = \gamma, \qquad \frac{\partial\gamma}{\partial T} = 0.$$

As a generalization, we suppose in the sequel that

$$\frac{\partial\mathcal{E}}{\partial C} = \mathcal{U}, \qquad \frac{\partial\mathcal{U}}{\partial T} = 0. \tag{$*$}$$

42.11 Exercises

1. Take the balls treated in Paragraph 42.1. Cut them in two equal parts and make from both parts a new ball. Show that the potential of a new ball differs from the original potential (potential and pressure have not the usual properties of an intensive quantity) and the electrostatic energy of a new ball is not the half of the original electrostatic energy (internal energy is not a usual extensive quantity, specific internal energy makes no sense).

2. Using the exact value of the potential (instead of the average one), show that the electrostatic energy of a homogeneously charged ball is

$$E_c = \frac{3C^2}{40\pi\epsilon R}.$$

3. Demonstrate that the assumptions $U = \gamma C$ and $E_c = \frac{CU}{2}$ of electrostatics imply that γ (so the capacity) does not depend on temperature if the body is entropic.

4. Give the function $\mathbf{T}$ (temperature as a function of internal energy, volume, particle number and charge) for a conventional body if γ does not depend on temperature.

5. In practice the properties of bodies are examined in a given phase at given temperature and pressure (in the atmosphere). Let $\boldsymbol{V}$ denote the volume of the

body in a phase as a function of (T, P, N, C). "We expect" that for given T, P and N if the charge is increased, then the body extends. Formulate such an assertion and show how it is related to the fact that for given V, T and N more charge results in larger pressure.

6. Define the electrically chargeable composite body.

43 Processes of electrically chargeable bodies

Now we outline the description of a thermodynamical system of chargeable bodies; on this basis an exact formulation can be given as in Paragraph 14.1.

43.1 Dynamical equation, dynamical quantitities

A process of a chargeable body is a function $t \mapsto \big(V(t), T(t), N(t), C(t)\big)$ or $t \mapsto \big(E(t), V(t), N(t), C(t)\big)$ defined on a time interval and obeying the dynamical equation

$$\dot{E} = Q + W + L + D, \qquad \dot{V} = F, \qquad \dot{N} = G, \qquad \dot{C} = J,$$

where, besides the known quantities, J is the **electric current** and D the **electric energy transport**.

The electric energy transport is ideal (see 16.3) if $D = UJ$.

If $n \geq 2$ bodies interact in a given environment, then the process of the system is the joint of the processes of the bodies: $\big((E_i, V_i, N_i) \mid i = 1, \dots, n\big)$ obeys the dynamical equation

$$\dot{E}_i = Q_i + W_i + L_i + D_i, \qquad \dot{V}_i = F_i \qquad \dot{N}_i = G_i, \qquad \dot{C}_i = J_i$$

$$(i = 1, \dots, n).$$

As all the other dynamical quantitities, the electric current J_i in the i-th body consists of the currents coming from (or going to) the other bodies and of the current due to a **charge source**:

$$J_i = J_{i,s} + \sum_{k=a,1}^{n} J_{ik},$$

and similarly,

$$D_i = \sum_{k=a,1}^{n} D_{ik}.$$

As earlier, we accept that the dynamical quantitities between the i-th and the k-th body – so J_{ik}, too – depend only on the states of the corresponding bodies.

Furthermore, we accept the mutuality property for F_{ik}, G_{ik}, J_{ik} and

$$A_{ik} := Q_{ik} + W_{ik} + L_{ik} + D_{ik},$$

e.g. in a symbolic form $J_{ik} = -J_{ki}$.

43.2 Equilibrium properties, thermodynamical force

The equilibrium properties of the dynamical quantitities specify the connection among the zero value of the dynamical quantitities and that of the thermodynamical forcewhich is formulated intiuitively as follows:

The zero value of the dynamical quantitities describing the admitted interactions (which characterize equilibrium) imply the zero value of the corresponding thermodynamical force (the effective thermodynamical force), and the zero value of the thermodynamical force belonging to the admitted interactions imply the zero value of the corresponding dynamical quantitities.

A precise formulation is rather complicated even for neutral bodies and is more complicated for chargeable bodies. Therefore, we do not give it in details; by the way, it is not worth doing so because homogeneity is a too strong assumption for electromagnetic phenomena. We shall formulate the equilibrium properties in each special case treated in the sequel.

Now we describe only the thermodynamical force in more detail.

Following the method outlined in Paragraph 10.1, we choose two bodies, the quantities of one of them are denoted by the usual symbols and those of the other are distinguished by a subscript $*$. Thus heating, etc. is the function

$$(E,V,N,C,E_*,V_*,N_*,C_*)\mapsto \mathbf{Q}(E,V,N,C,E_*,V_*,N_*,C_*),$$

etc.

Recall that the potential is the intensive quantity corresponding to electricity; the difference of the intensive quantities of the bodies, more closely,

$$\big(-(T-T_*),P-P_*,-(\mu-\mu_*),-(U-U_*)\big)$$

is the **thermodynamical force** acting on the body due to the other body and

$$\left(\frac{1}{T}-\frac{1}{T_*},\frac{P}{T}-\frac{P_*}{T_*},-\left(\frac{\mu}{T}-\frac{\mu_*}{T_*}\right),-\left(\frac{U}{T}-\frac{U_*}{T_*}\right)\right)$$

is the **canonical thermodynamical force**.

The dynamical quantitities are pseudolinear if

$$\begin{pmatrix}Q\\F\\G\\J\end{pmatrix}=\begin{pmatrix}\lambda_Q&\beta_Q&\vartheta_Q&\sigma_Q\\\lambda_F&\beta_F&\vartheta_F&\sigma_F\\\lambda_G&\beta_G&\vartheta_G&\sigma_G\\\lambda_J&\beta_J&\vartheta_J&\sigma_J\end{pmatrix}\begin{pmatrix}-(T-T_*)\\P-P_*\\-(\mu-\mu_*)\\-(U-U_*)\end{pmatrix}=$$

$$=\begin{pmatrix}\lambda^c_Q&\beta^c_Q&\vartheta^c_Q&\sigma^c_Q\\\lambda^c_F&\beta^c_F&\vartheta^c_F&\sigma^c_F\\\lambda^c_G&\beta^c_G&\vartheta^c_G&\sigma^c_G\\\lambda^c_J&\beta^c_J&\vartheta^c_J&\sigma^c_J\end{pmatrix}\begin{pmatrix}\frac{1}{T}-\frac{1}{T_*}\\\frac{P}{T}-\frac{P_*}{T_*}\\-\left(\frac{\mu}{T}-\frac{\mu_*}{T_*}\right)\\-\left(\frac{U}{T}-\frac{U_*}{T_*}\right)\end{pmatrix},$$

where the entries in the matrix, too, are functions of $(E,V,N,C,E_*,V_*,N_*,C_*)$.

If $\lambda_J=0$, $\beta_J=0$, $\vartheta_J=0$, then $J=\sigma_J(U_*-U)$, which is exactly Ohm's law: σ_J is the electric conductance, $\frac{1}{\sigma_J}$ is the resistance between the bodies.

We mention that according to our usual knowledge, resistance is a property of a body but here resistance characterizes the interaction of two bodies. This follows from the fact that the quantities are considered homogeneous: the value of the potential is constant on a body. In continuum physics we can take into account that the potential has different values in different points of the body, thus the resistance can be assigned to a single body.

43.3 Dissipation inequality

The dissipation inequality in the ideal cases is required in the form

$$-\frac{Q}{T}(T-T_*)+F(P-P_*)-G(\mu-\mu_*)-J(U-U_*)\geq 0,$$

or, equivalently,

$$(Q-Pf+\mu L+UJ)\left(\frac{1}{T}-\frac{1}{T_*}\right)+ \\ +F\left(\frac{P}{T}-\frac{P_*}{T_*}\right)-G\left(\frac{\mu}{T}-\frac{\mu_*}{T_*}\right)-J\left(\frac{U}{T}-\frac{U_*}{T_*}\right)\geq 0,$$

where equality holds if and only if every dynamical quantity takes zero values.

Now we find a new member in the dissipation inequality, the power of the electric current: $-J(U-U_*)$.

43.4 Concluding remarks

Standstills, equilibria and stationary states of a system consisting of n chargeable bodies are defined as in Paragraph 14.3.

Introducing

$$X:=\Big((\mathrm{J})\times(\mathrm{m}^3)\times\mathbb{R}\times(\hat{\mathrm{A}}\mathrm{s})\Big)^n,$$

we can apply the formalism of Paragraph 15; the results, however, are applicable only for entropic bodies. The entropic property is a doubtful assumption for chargeable bodies, therefore we shall not require it in the sequel.

We shall treat only some special systems consisting of a body in a given environment. We shall impose diverse constraints; without constraints we should get hardly tractable formulae and the same is true for two-body systems even for reasonable constraints.

44 Some special systems

44.1 General formulae

We treat the processes of a body with constant particle number N_{o} in a given environment. The environment is supposed to have constant temperature T_a, pressure P_a and potential U_a. Ideal working and electric energy transport are taken; thus the dynamical equation becomes

$$\dot{E} = Q - PF + UJ, \qquad \dot{V} = F, \qquad \dot{C} = J.$$

Moreover, we accept the conditions $(*)$ in Paragraph 42.10 from which

$$\frac{\partial \mathcal{E}}{\partial C} = \mathcal{U} \tag{$*$}$$

plays a fundamental role. In particular, if temperature is used instead of internal energy as a variable, the first law will have the form

$$\frac{\partial \mathcal{E}}{\partial T}\dot{T} = Q - \left(P + \frac{\partial \mathcal{E}}{\partial V}\right)\dot{V}.$$

44.2 Fixed volume

The volume has the fixed value V_o, and the dynamical equation, reduced to the variables T and C is very simple:

$$\frac{\partial \mathcal{E}}{\partial T}\dot{T} = Q, \qquad \dot{C} = J. \tag{1}$$

Let us suppose that

$$Q = -\lambda_Q(T - T_a) - \sigma_Q(U - U_a), \qquad J = -\lambda_J(T - T_a) - \sigma_J(U - U_a), \tag{2}$$

where λ_Q, σ_Q etc. are constant. The dissipation inequality gives

$$\lambda_Q > 0, \qquad \sigma_J > 0, \qquad \lambda_Q\sigma_J - \sigma_Q\lambda_J > \frac{(\sigma_Q + T\lambda_J)^2}{4t}.$$

The last inequality implies $\lambda_Q\sigma_J > \sigma_Q\lambda_J$: σ_Q and λ_J are not too large which has the physical meaning that the cross effects – the heating due to the potential difference and the electric current induced by the temperature difference – are smaller than the direct effects.

The above form of the dynamical quantitities implies that (T_o, C_o) is an equilibrium of the reduced dynamical equation if and only if

$$T_o = T_a, \qquad \mathcal{U}(V_o, T_a, N_o, C_o) = U_a.$$

Potential is a strictly monotone increasing function of charge, thus the equilibrium is unique.

If $(V_o/N_o, T_a)$ is in the regular domain, then the right hand side of the reduced dynamical equation is differentiable, its derivative in the equilibrium is

$$\begin{pmatrix} -\frac{\lambda_Q}{c} & -\frac{\sigma_Q b}{c} \\ -\lambda_J & -\sigma_J b \end{pmatrix}$$

where

$$b := \frac{\partial \mathcal{U}}{\partial C}(V_o, T_a, N_o, C_o), \qquad c := \frac{\partial \mathcal{E}}{\partial T}(V_o, T_a, N_o, C_o).$$

This matrix has the characteristic polynomial

$$x \mapsto cx^2 + (\lambda_Q + \sigma_J bc)x + (\lambda_Q \sigma_J - \sigma_Q \lambda_J)b.$$

All the coefficients are positive: $c > 0$ and $b > 0$ by the fundamental properties of the body, $\lambda_Q > 0$, $\sigma_J > 0$ and $\lambda_Q \sigma_J - \sigma_Q \lambda_J > 0$ by the dissipation inequality, thus the eigenvalues of the matrix have negative real part:

Proposition *If condition* $(*)$ *in Paragraph 44.1 holds and the dynamical quantitities have the form (2), then the equilibrium* (T_a, C_{o}) *of the reduced dynamical equation (1) is asymptotically stable.*

44.3 Constant pressure

The chargeable body has constant pressure P_a.

Using

$$\frac{\partial \mathcal{P}}{\partial V}\dot{V} + \frac{\partial \mathcal{P}}{\partial T}\dot{T} + \frac{\partial \mathcal{P}}{\partial C}\dot{C} = 0$$

to eliminate $\dot{V}$, we can reduce the dynamical equation to the variables T and C:

$$\left(\frac{\partial \mathcal{E}}{\partial T} + \left(P_a + \frac{\partial \mathcal{E}}{\partial V}\right)\frac{\frac{\partial \mathcal{P}}{\partial T}}{-\frac{\partial \mathcal{P}}{\partial V}}\right)\dot{T} = Q - \left(\left(P_a + \frac{\partial \mathcal{E}}{\partial T}\right)\frac{\frac{\partial \mathcal{P}}{\partial C}}{-\frac{\partial \mathcal{P}}{\partial V}}\right)J, \qquad \dot{C} = J. \tag{1}$$

We take again the dynamical quantitities

$$Q = -\lambda_Q(T - T_a) - \sigma_Q(U - U_a), \qquad J = -\lambda_J(T - T_a) - \sigma_J(U - U_a), \tag{2}$$

where λ_Q, σ_Q, etc. are constant for which the dissipation inequality gives the same relations as in the previous paragraph.

The above form of the dynamical quantitities imply that $(T_{\mathrm{o}}, C_{\mathrm{o}})$ is an equilibrium of the reduced dynamical equation if and only if

$$T_{\mathrm{o}} = T_a, \qquad \mathcal{U}(V_{\mathrm{o}}, T_a, N_{\mathrm{o}}, C_{\mathrm{o}}) = U_a,$$

where V_{o} is determined by $\mathcal{P}(V_{\mathrm{o}}, T_a, N_{\mathrm{o}}, C_{\mathrm{o}}) = P_a$. The equilibrium is locally unique.

Now we get asymptotic stability, as previously, if the polynomial

$$x \mapsto cx^2 + (\lambda_Q + \sigma_J bc + \lambda_J h) + (\lambda_Q \sigma_J - \sigma_Q \lambda_J)b$$

has negative roots, where

$$b := \frac{\partial \mathcal{U}}{\partial C}(V_{\mathrm{o}}, T_{\mathrm{o}}, N, C_{\mathrm{o}}), \qquad c := \left(\frac{\partial \mathcal{E}}{\partial T} + \left(P_a + \frac{\partial \mathcal{E}}{\partial V}\right)\frac{\frac{\partial \mathcal{P}}{\partial T}}{-\frac{\partial \mathcal{P}}{\partial V}}\right)(V_{\mathrm{o}} T_a, N, C_{\mathrm{o}}),$$

$$h := -\left(\left(P_a + \frac{\partial \mathcal{E}}{\partial T}\right)\frac{\frac{\partial \mathcal{P}}{\partial C}}{-\frac{\partial \mathcal{P}}{\partial V}}\right)(V_{\mathrm{o}}, T_a, N, C_{\mathrm{o}}).$$

In the previous paragraph c is the specific heat at constant volume which is necessarily positive; now c is the specific heat at constant pressure which is positive, e.g. if the body is of normal dilation.

Proposition *If condition* $(*)$ *in Paragraph 44.1 holds, the body is of normal dilation and the dynamical quantitities have the form (2), then the equilibrium* (T_a, C_o) *of the reduced dynamical equation (1) is asymptotically stable if*

$$-\lambda_J h < \lambda_Q + \sigma_J bc.$$

The inequality above imposes a condition on λ_J – on a cross effect – to be sufficiently small.

44.4 Constant temperature

The chargeable body has constant temperature T_a and the dynamical equation reduced to the variables V and C is very simple:

$$\dot{V} = F, \qquad \dot{C} = J. \tag{1}$$

Let us suppose that

$$F = \beta_F(P - P_a), \qquad J = \beta_J(P - P_a) - \sigma_J(U - U_a), \tag{2}$$

where β_F, etc. are constant. Then the dissipation inequality gives

$$\beta_F > 0, \qquad \sigma_J > 0, \qquad \beta_F\sigma_J - \frac{\beta_J^2}{4} > 0.$$

The above form of the dynamical quantitities imply that (V_o, C_o) is an equilibrium of the reduced dynamical equation if and only if

$$\mathcal{P}(V_o, T_a, N_o, C_o) = P_a, \qquad \mathcal{U}(V_o, T_a, N_o, C_o) = U_a.$$

The equilibrium is locally unique.

If $(V_o/N, T_a)$ is in the regular domain, then the right-hand side of the reduced dynamical equation is differentiable, its derivative in the equilibrium is

$$\begin{pmatrix} -\beta_F k & \beta_F z \\ -\beta_J k - \sigma_J u & \beta_J z - \sigma_J b \end{pmatrix},$$

where

$$k := -\frac{\partial\mathcal{P}}{\partial V}(V_o, T_a, N_o, C_o), \qquad z := \frac{\partial\mathcal{P}}{\partial C}(V_o, T_a, N_o, C_o),$$

$$u := \frac{\partial\mathcal{U}}{\partial V}(V_o, T_a, N_o, C_o), \qquad b := \frac{\partial\mathcal{U}}{\partial C}(V_o, T_a, N_o, C_o).$$

This matrix has the characteristic polynomial

$$x \mapsto x^2 + (\beta_F k + \sigma_J b - \beta_J z)x + \beta_F\sigma_J(kb - zu).$$

Because $k > 0$ and $b > 0$ by the fundamental properties of the body and $\beta_F > 0$ and $\sigma_J > 0$ by the dissipation inequality, we have the following:

Proposition *If the dynamical quantitities have the form (2), then the equilibrium* (V_o, C_o) *of the reduced dynamical equation (1) is asymptotically stable if*

$$\beta_J z < \beta_F k + \sigma_J b, \qquad zu < kb.$$

Thus, asymptotic stability is assured if β_J, z and u are 'sufficiently small': the electric current induced by the pressure difference is not too large, the pressure of the body and the potential do not change too heavily by the change of charge and volume, respectively.

44.5 Direct currents

If a constant charge source J_s is in the body, then the dynamical equation has the form

$$\dot{E} = Q - PF + U(J_s + J), \qquad \dot{V} = F, \qquad \dot{C} = J_s + J.$$

Then a stationary state can exist if $J = -J_s$: a constant current (direct current) flows from the body into the environment.

Let us take the simplest case when the temperature of the body is constant and let Q, F and J as in the previous paragraphs. Then the stationary state is determined by

$$\mathcal{P}(V_o, T_a, N_o, C_o) = P_a \qquad \sigma_J\big(\mathcal{U}(V_o, T_a, N_o, C_o) - U_a\big) = J_s$$

Replacing U_a with $U_a + J_s/\sigma_J$, we get formally the previous problem; thus the corresponding conditions imply that the stationary state is asymptotically stable.

44.6 Exercises

1. If the temperature of the body is constant, then heating is determined by springing and current.
2. What relations λ_Q, σ_Q, λ_J and σ_J have if the conductance matrix defined according to Paragraph 11.4 is symmetric?
3. What can be said about asymptotic stability if λ_Q, etc. are not constant? (Hint: the dissipation inequality does not imply the strict positivity relations).
4. What restrictions give the treated conditions of asymptotic stability for the quantities γ, etc. of a conventional body?
5. Treat the isothermal–isobaric processes of a chargeable body.
6. Treat the adiabatic processes of a chargeable body.

45 Some important thermoelectric effects

45.1 Basic assumptions

Let us take two bodies interacting only thermally and electrically (the particle number and the volume of the bodies are constant). Let us suppose that the dynamical quantitities are pseudolinear:

$$Q = -\lambda_Q(T - T_*) - \sigma_Q(U - U_*),$$
$$J = -\lambda_J(T - T_*) - \sigma_J(U - U_*),$$

where λ_Q, etc. are continuous functions of temperature and charge.

If σ_J is nowhere zero, then

$$U - U_* = -\frac{1}{\sigma_J}\big(J + \lambda_J(T - T_*)\big), \tag{$*$}$$

thus,

$$Q = -\frac{\Delta}{\sigma_J}(T - T_*) + \frac{\sigma_Q}{\sigma_J}J, \tag{$**$}$$

where $\Delta := \lambda_Q\sigma_J - \lambda_J\sigma_Q$ (the determinant of the coefficient matrix).

The thermoelectric effects are based on the fact that $\sigma_Q \neq 0$ and $\lambda_J \neq 0$, i.e. heating is influenced by potential difference and electric current is influenced by temperature difference.

45.2 The Seebeck effect

The Seebeck effect is that temperature difference can induce electric current: $\lambda_J \neq 0$.

If no current flows, then the potential difference between contacting bodies, given by $(*)$ of the previous paragraph, is

$$U - U_* = -\frac{\lambda_J}{\sigma_J}(T - T_*).$$

45.3 The Peltier effect

The Peltier effect is that electric current results in heating between bodies having the same temperature; we get from $(**)$ of Paragraph 45.1

$$Q = \frac{\sigma_Q}{\sigma_J}J.$$

45.4 The Thomson effect

Equality $(*)$ of Paragraph 45.1 gives

$$J(U_* - U) = \frac{1}{\sigma_J}J^2 + \frac{\lambda_J}{\sigma_J}(T - T_*)J$$

for the power of the electric current. The first term on the right-hand side is the well-known Joule effect, the second term is the Thomson effect. In special circumstances, they result in the Joule heat and the Thomson heat, respectively.

If the two bodies are completely insulated from the environment, then

$$\dot{E} = Q + UJ, \qquad \dot{E}_* = Q_* - U_*J$$

and $\dot{E} + \dot{E}_* = 0$, thus,

$$Q + Q_* = J(U_* - U), \tag{$*$}$$

i.e. the power of the current results in heating.

Let the constant charge source J_s be in one of the bodies and $-J_s$ in the other and let the bodies be in thermal contact with the environment:

$$\dot{E} = Q_a + Q + U(J_s + J), \qquad \dot{E}_* = Q_{*a} + Q_* - U_*(J_s + J).$$

In a stationary state $J = -J_s$, $\dot{E} = \dot{E}_* = 0$, thus

$$Q_a = -Q, \qquad Q_{*a} = -Q_*.$$

Supposing $(*)$, we deduce

$$-(Q_a + Q_{*a}) = J(U_* - U),$$

i.e. the heat emitted in unit time by the bodies together to the environment equals the power of the current.

45.5 Concluding remarks

We emphasize again that homogeneity is a rather rough approximation for electric phenomena. Processes of chargeable bodies and thermoelectric effects are really well described only if inhomogeneity is taken into account.

It is the most conspicuous that here the resistance is a mutual property of two bodies while the potentials on the bodies have constant value. It is an elementary fact, however, that the resistance is a property of a body and the potential of a body is not constant (e.g. it changes linearly along the path of a direct current).

45.6 Exercise

Using the canonical thermodynamical force, we have

$$\begin{pmatrix} Q + UJ \\ J \end{pmatrix} = \begin{pmatrix} \lambda_Q^c + U\lambda_J^c & \sigma_Q^c + U\sigma_J^c \\ \lambda_J^c & \sigma_J^c \end{pmatrix} \begin{pmatrix} \frac{1}{T} - \frac{1}{T_*} \\ -\left(\frac{U}{T} - \frac{U_*}{T_*}\right) \end{pmatrix}.$$

The matrix on the right-hand side – if the volume and the particle number of the body are constant – is the canonical conductance matrix between the bodies. Show that

$$\begin{pmatrix} Q \\ J \end{pmatrix} = \begin{pmatrix} \alpha_Q^c & \sigma_Q^c \\ \alpha_J^c & \sigma_J^c \end{pmatrix} \begin{pmatrix} \frac{1}{T} - \frac{1}{T_*} \\ -\frac{U-U_*}{T_*} \end{pmatrix},$$

where $\alpha_Q^c := \lambda_Q^c - U\sigma_Q^c$, $\alpha_J^c := \lambda_J^c - U\sigma_J^c$.

The conductance matrix is of the Onsager type if $\sigma_Q^c + U\sigma_J^c = \lambda_J^c$, or equivalently, $\sigma_Q^c = \alpha_J^c$.

Give the treated thermoelectric effects with the aid of these coefficients and consider the special case of the Onsager type conductance matrix.

46 Extended chargeable bodies

46.1 Definition of an extended chargeable body

So far we have examined phenomena in which the change of electric field is slow enough and the electric field can be considered static, i.e. having a potential.

If the change is faster but ‘not too fast’, we can describe the electric field by a potential but we have to take into account the time rate of the current, too.

This is formulated in electromagnetism as follows: varying charge (current) induces an electromagnetic field which reacts on the current. If the charge does not vary too fast – the current is **quasi-stationary** – then the reaction of the induced electromagnetic field can be described by the time derivative of the current (the second time derivative of charge) while the electric field has a potential.

This is on analogy to the faster volume change discussed in Section 38: the dynamical equation refers to the second derivative of the volume, consequently, the volume rate must be included into the collection of state variables. If the charge varies in a quasi-stationary way, then current must be considered an independent variable, i.e. the state of the body will be (V, T, N, C, J). We shall take the simplest case when all the constitutive quantities but the potential do not depend on the current.

Definition $(D \times \mathbb{R}^+ \times (\hat{\mathrm{A}}\mathrm{s}) \times (\hat{\mathrm{A}}), \mathfrak{e}_b, \mathcal{P}_b, \mu_b, R, \mathcal{E}_c, \mathcal{P}_c, \mu_c, \mathcal{U}_c, \mathcal{U}_x)$ *is an* **extended electrically chargeable simple body** *if*

– $(D \times \mathbb{R}^+ \times (\hat{\mathrm{A}}\mathrm{s}), \mathfrak{e}_b, \mathcal{P}_b, \mu_b, R, \mathcal{E}_c, \mathcal{P}_c, \mu_c, \mathcal{U}_c)$ *is an electrically chargeable simple body,*

– $\mathcal{U}_x : D \times \mathbb{R}^+ \times (\hat{\mathrm{A}}\mathrm{s}) \times (\hat{\mathrm{A}}) \to (\hat{\mathrm{V}})$ *is a continuous function, continuously differentiable on* $R \times \mathbb{R}^+ \times (\hat{\mathrm{A}}\mathrm{s}) \times (\hat{\mathrm{A}})$ *and* $\mathcal{U}_x(v, T, N, C, 0) = 0$ *for all* v, T, N *and* C.

The function $\mathcal{U} := \mathcal{U}_c + \mathcal{U}_x$ *is the* **potential** *of the extended body.*

46.2 Dynamical equation, dissipation inequalities

A process of an extended chargeable body is $t \mapsto \big(E(t), V(t), N(t), C(t), J(t)\big)$ obeying the dynamical equation (in the ideal case)

$$\dot{E} = Q - PF + \mu G + UJ, \quad \dot{V} = F, \quad \dot{N} = G,$$

$$\dot{C} = J, \qquad \dot{J} = K,$$

where (without sources) Q, F, G and K are functions of (E, V, N, C, J).

For more bodies, of course, a process is the joint of the processes. The mutuality of the dynamical quantitities is formulated as previously. The dissipation inequalities – on the analogy of those in Paragraph 39.3 – are obtained in such a way that the terms containing J are omitted from the inequality in Paragraph 43.3 and two other inequalities are required:

$$-\frac{Q}{T}(T - T_*) + F(P - P_*) - G(\mu - \mu_*) \geq 0,$$

$$JU_x \geq 0, \qquad -K(U - U_*) \geq 0,$$

where equality holds if and only if Q, F, G, U_x and K take zero value.

The first inequality can be written in the other usual form

$$(Q - PF + \mu G)\left(\frac{1}{T} - \frac{1}{T_*}\right) + F\left(\frac{P}{T} - \frac{P_*}{T_*}\right) - G\left(\frac{\mu}{T} - \frac{\mu_*}{T_*}\right) \geq 0.$$

46.3 Quasi-stationary currents

We treat the processes of a body with constant volume V_o and particle number N_o in a given environment which is supposed to have constant temperature T_a, pressure P_a and potential U_a.

Accepting the relations $(*)$ in 42.10, we get the first law in the form

$$\frac{\partial \mathcal{E}}{\partial T}\dot{T} = Q + U_x J.$$

We take

$$\mathcal{U}_c(V, T, N, C) = \gamma C, \tag{1}$$

where $\gamma > 0$ is a constant and

$$\mathcal{U}_x(V, T, N, C, J) := RJ, \tag{2}$$

where R is a constant (the ohmic resistance of the body), positive because of the second dissipation inequality. Then

$$U = \gamma C + RJ.$$

The dynamical quantitities are taken in the form

$$Q = -\lambda(T - T_a), \qquad K = -\frac{1}{L}(U - U_a), \tag{3}$$

where λ and L (the coefficient of self-induction) are constant, positive because of the first and third dissipation inequalities.

The the dynamical equation reduced to the variables (T, C, J) reads

$$\frac{\partial \mathcal{E}(V_o, T, N_o, C)}{\partial T}\dot{T} = -\lambda(T - T_a) + RJ^2, \tag{4}$$

$$\dot{C} = J, \qquad L\dot{J} = -\gamma C - RJ + U_a. \tag{5}$$

The two members of equation (5) can be united into

$$L\ddot{C} + R\dot{C} + \gamma C = U_a. \tag{6}$$

46.4 Constant exterior potential

46.4.1 The equilibrium

If U_a is constant, then (T_o, C_o, J_o) is an equilibrium if and only if

$$T_o = T_a, \qquad C_o = \frac{U_a}{\gamma}, \qquad J_o = 0.$$

46.4.2 Stability of equilibrium: linearization

The derivative of the right-hand side of the dynamical equation (4)–(5) in equilibrium is

$$\begin{pmatrix} -\frac{\lambda}{c} & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -\frac{\gamma}{L} & -\frac{R}{L} \end{pmatrix}$$

where

$$c := \frac{\partial \mathcal{E}}{\partial T}(V_o, T_a, N_o, C_o).$$

The matrix has the characteristic polynomial

$$x \mapsto x^3 + \left(\frac{\lambda}{c} + \frac{R}{L}\right)x^2 + \frac{\lambda R}{cL}x + \frac{\gamma\lambda}{cL}.$$

All the coefficients are positive, therefore the eigenvalues of the matrix have negative real part if

$$\frac{\lambda}{c} \geq \frac{\gamma L - R^2}{LR}. \tag{3}$$

Proposition *If U_a is constant in the reduced dynamical equation (4)–(5), then the equilibrium $(T_o, C_o, 0)$ is asymptotically stable if inequality $(*)$ holds.*

Thus asymptotic stability holds if the ohmic resistance R is sufficiently large.

46.4.3 Stability of equilibrium: a special method

Equation (6) is a second-order inhomogeneous linear differential equation with constant coefficients. It is well known that its every solution has the form

$$C(t) = \frac{U_a}{\gamma} + a_1 e^{-\alpha_1 t} + a_2 e^{-\alpha_2 t},$$

where

$$\alpha_1 := \frac{R + \sqrt{R^2 - 4L\gamma}}{2L} > 0, \qquad \alpha_2 := \frac{R - \sqrt{R^2 - 4L\gamma}}{2L} > 0$$

and a_1, a_2 are constants. Then

$$J(t) = -\alpha_1 a_1 e^{-\alpha_1 t} - \alpha_2 a_2 e^{-\alpha_2 t}.$$

The charge exponentially tends to its equilibrium value U_a/γ and the current exponentially tends to zero.

Putting the above functions into the equation (4) of the previous paragraph, we get an equation for T. If we suppose that the specific heat is constant,

$$c := \frac{\partial \mathcal{E}}{\partial T} = \text{const}.$$

then we get the inhomogeneous first-order linear differential equation with constant coefficients

$$c(T - T_a)^{\cdot} + \lambda(T - T_a) = \vartheta,$$

where ϑ is a linear combination of exponentially damping functions. It is well known that its every solution has the form

$$T(t) - T_a = \alpha e^{-\lambda t/c} + \theta(t),$$

where α is a constant and θ is a linear combination of functions that are products of exponentially damping functions and polynomials, thus θ, too, is a damping function. As a consequence, the temperature tends to its equilibrium value T_a.

Moreover, because of the properties of polynomials and exponential functions, processes that “start sufficiently near to equilibrium, remain near to it", thus the equilibrium is asymptotically stable.

It is worth comparing the present result with that in the previous paragraph. Here we imposed a condition only on the specific heat, no restriction is necessary to γ, λ, L and R (besides their being positive). The previous result cannot be improved by assuming constant specific heat. This shows that the linearization method is rather rough in some cases.

46.5 Periodic exterior potential

46.5.1 Solution of the dynamical equation

Let us suppose now that

$$U_a(t) = U_m \cos \omega t,$$

where $\omega \in (1/\mathrm{s})^+$ and U_m (the maximal value of the voltage) are constants. Then equation (6) becomes an inhomogeneous second-order linear differential equation in which the inhomogeneity is a trigonometric function. Instead of it, we consider the equation of same type for the current:

$$L\ddot{J} + R\dot{J} + \gamma J = \dot{U}_a.$$

It is well known that its every solution has the form

$$J(t) = J_m \cos(\omega t + \phi) + \vartheta(t),$$

where

$$\mathrm{tg}\phi = \frac{X}{R}, \qquad J_m = \frac{U_m}{\sqrt{R^2 + X^2}}$$

with

$$X := \omega L - \frac{\gamma}{\omega} \tag{$*$}$$

and ϑ is a linear combination of products of exponentially damping functions and trigonometric functions.

Then charge, too, is a similar function: the sum of a function and a damping function. We should like to have a similar result for temperature, too. This is obtained easily if the specific heat of the body is constant; let it be c. Then we have the differential equation for the temperature:

$$c\dot{T} = -\lambda(T - T_a) + RJ_m^2 \cos^2(\omega t + \phi) + \theta(t),$$

where θ is a linear combination of products of exponentially damping functions and trigonometric functions. Using well-known trigonometric relations, we can rewrite the equation in the form

$$c\left(T - T_a - \frac{RJ_m^2}{2\lambda}\right)^{\boldsymbol{\cdot}} = -\lambda\left(T - T_a - \frac{RJ_m^2}{2\lambda}\right) + \frac{1}{2}RJ_m^2 \cos 2(\omega t + \phi) + \theta(t).$$

Finally, we get

$$T(t) = T_a + \frac{RJ_m^2}{2\lambda} + \frac{RJ_m^2}{2\omega} \sin 2(\omega t + \phi) + \Theta(t),$$

where Θ is a linear combination of products of exponentially damping and trigonometric functions.

Thus we have shown that if specific heat of the body is constant, then the temperature of the body, too, becomes periodic as time passes.

46.5.2 Heating effect of alternating current

Let us consider the periodic state

$$T(t) = T_a + \frac{RJ_m^2}{2\lambda} + \frac{RJ_m^2}{2\omega} \sin 2(\omega t + \phi);$$

the temperature of the body oscillates around a temperature larger than the temperature of the environment. Then the heating has values

$$Q(t) = -\lambda(T(t) - T_a) = -\frac{RJ_m^2}{2} - \frac{\lambda RJ_m^2}{2\omega}\sin 2(\omega t + \phi).$$

If $\overline{Q}$ denotes the average heating (heating integrated on the time period π/ω and then divided by it), then

$$-\overline{Q} = \frac{RJ_m^2}{2}.$$

Introducing the effective voltage and current

$$U_e := \frac{U_m}{\sqrt{2}}, \qquad J_e := \frac{J_m}{\sqrt{2}},$$

we get

$$-\overline{Q} = U_e J_e \cos\phi = \frac{U_e^2 R}{R^2 + X^2},$$

the formula well known in electrotechnics.

Remark Note that in the case of an alternating current it is enough to consider a single body in an environment for obtaining the known formula of Joule heat whereas in the case of a direct current two bodies and an environment are necessary. This is so, as mentioned earlier, because homogeneity is a rough approximation but ‘extended homogeneity’ is a better one.

46.5.3 Complex resistance

The formulae regarding alternating currents can be simplified by using complex quantities whose real part corresponds to physical quantities. Now we refer to the complex quantities by a tilde.

Then

$$\tilde{U}_a(t) = U_m e^{i\omega t},$$

and differentiating

$$L\dot{\tilde{J}} + R\tilde{J} + \gamma\tilde{C} = U_m e^{i\omega t}$$

we get the equation

$$L\ddot{\tilde{J}} + R\dot{\tilde{J}} + \gamma\tilde{J} = i\omega U_m e^{i\omega t}$$

whose periodic solution has the form $\tilde{J}_m e^{i\omega t}$, where

$$\tilde{J}_m = \frac{U_m}{Z}$$

and (with the notation $(*)$ of Paragraph 46.5)

$$Z := R + iX$$

is the complex resistance (or impedance).

Then $\cos\phi = \frac{R}{|Z|}$ and

$$Z = |Z|e^{i\phi}, \qquad \mathrm{Re}J(t) = |\tilde{J}_m|\cos(\omega t + \phi) = \frac{U_m \cos\phi}{R}\cos(\omega t + \phi),$$

thus $|\tilde{J}_m| = J_m$.

Lastly, the energy dissipation (average heating) can be written in the form

$$-U_e^2 \frac{R}{R^2 + X^2}.$$

We see that it is determined essentially by the real part of the complex resistance (the ohmic resistance): the less the real part compared with the imaginary part, the less the energy dissipation.

46.6 Exercises

1. Is it true that periodic exterior potential implies that the temperature of the body becomes periodic as time passes if the pressure of the body is constant? Is the constant pressure of the body (see 12.12) physically realizable?

2. Show directly that the average of $t \mapsto RJ(t)^2$ equals the average heating of the body.

3. Take the differential equation

$$L\ddot{\tilde{C}} + R\dot{\tilde{C}} + \gamma\tilde{C} = U_m e^{i\omega t}$$

for the charge and solve it by the method of Paragraph 46.5.3.

Of course, knowing the current, we obtain the charge by integration. For the periodic solution we have

$$\tilde{C}(t) = \tilde{C}_m e^{i\omega t}$$

where

$$\tilde{C}_m = \frac{\tilde{J}_m}{i\omega} = \frac{U_m}{i\omega Z}.$$

Then we can say that

$$i\omega Z = \gamma - \omega^2 L + i\omega R$$

is the reciprocal of the 'complex capacity'. Give the real part and the imaginary part of the complex capacity.

47 Bodies consisting of ions

Up to now we have treated bodies that can be charged – in principle – arbitrarily. There are bodies consisting of charged particles, ions. For such a body the particle number and the charge are not independent: charge is proportional to particle number, $C = \alpha N$. Correspondingly, $J = \alpha G$ (which is Faraday's law: converting is proportional to the current), thus the dynamical equation becomes

$$\dot{E} = Q - PF + (\mu + \alpha U)G, \qquad \dot{V} = F, \qquad \dot{N} = G.$$

For such a body the chemical potential μ never appears in itself, it has no physical meaning, it is replaced with the **electrochemical potential** $\mu + \alpha U$. Then the difference of electrochemical potentials constitutes a part of the thermodynamical force, too, and equilibrium is determined by the equality of electrochemical potentials. Thus in such an equilibrium a potential difference can exist between the bodies (this is the base of the galvanic batteries).

So far we have considered chargeable bodies of simple material but the most interesting bodies consist of more ions (and neutral molecules). A lot of solutions are ion mixtures; their chemical properties are strongly related to electricity, chemical reactions are influenced by electric phenomena and vice versa. Well-known examples are the galvanic batteries (electric current produced by chemical reaction) and electrolysis (chemical reaction due to electric current).

The detailed treatment of ionic bodies and their processes are beyond the scope of this book.

48 Electrically polarizable bodies

48.1 Electric field of a polarized body

Besides charges, also electric dipoles induce electric field. An insulator in an electric field is polarized and, as a consequence, the electric field is modified, so the electric energy, the dynamics of precesses etc. are modified, too. Some of these modifications can be taken into account by permittivity and others can be neglected (in the presence of charges). In this section we examine just the thermodynamical aspects of polarization when charge is zero.

Electric dipole as a self-consistent quantity makes sense only when the dipole is at rest with respect to the body in question. Resting dipoles produce pure electric field; varying dipoles produce magnetic field, too. If the change of dipoles is not too fast, we can neglect the magnetic effects. Then electric dipole is the extensive quantity, electric field is the corresponding intensive quantity.

Dipoles are space vectors having unit $\hat{\mathrm{A}}$sm. Electric field is a space vector, too, having unit $\hat{\mathrm{V}}$/m. Polarization, the density of dipoles, is a space vector having unit $\hat{\mathrm{A}}\mathrm{s}/\mathrm{m}^2$.

Let us recall the following elementary knowledge of electrostatics.

Let us take a ball with homogeneous polarization $\mathbb{P}$. The electric field produced by this polarization will be homogeneous inside the ball having value $-\mathbb{P}/3$; in particular, the polarization and the produced electric field have opposite directions (outside the body the electric field is not homogeneous).

More generally, if an ellipsoid is endowed with a homogeneous polarization parallel to an axis of the ellipsoid, then the produced electric field in the body is proportional to the polarization (so is homogeneous). The electric field produced by homogeneous polarization in bodies of other form is not homogeneous.

We shall consider in the sequel (except Paragraph 50.3) as if a homogeneous polarization in a body produced a homogeneous electric field in the body (similarly, as we considered previously as if a homogeneous charge distribution produced a homogeneous potential).

48.2 Polarization in an exterior field

The polarization of a body is determined by the dipoles of the molecules which depends strongly on the electric field acting on the body.

Bodies can be polarized in two ways:

1) The molecules have no intrinsic dipole but an exterior electric field deforms the molecules inducing dipoles on them that are more or less parallel to the exterior field; these microscopic dipoles result in a macroscopic polarization.

2) The molecules have an intrinsic dipole whose macroscopic effect – the polarization of the body – depends on the average direction of the dipoles; if the dipoles are totally disordered (the average direction is zero), then no macroscopic polarization is observed. Exterior electric field orders the dipoles, so it induces a polarization. Polarization – ordered dipoles – can exist even without an exterior field (ferroelectric and ferrielectric materials).

An electric field moves a positive charge in the direction of the field and moves a negative charge oppositely. Thus in both cases 1) and 2) the direction of the polarization induced by an exterior field equals the direction of the field, and the electric field inside the body becomes smaller than the exterior field.

48.3 Fundamental assumptions

Let us consider a system of polarized bodies. The electric field produced by a body penetrates into the other bodies, thus the bodies modify their polarization mutually: interaction at a distance plays a fundamental role in processes. This differs significantly from the previous cases where only contact interaction appeared (of course, it is true that the charge of a body interacts at a distance with the charge of another body but this interaction does not change the amount of charges but only their distribution which is not relevant because it is always considered homogeneous, therefore, we could leave out of consideration interaction at a distance). Now interaction at a distance is an essential feature of phenomena: polarization changes as a consequence of interaction at a distance and not as a consequence of dipole transport between the bodies.

The polarization of a body produces electric field in and outside the body, which modifies the polarization of other bodies, the electric field produced by the other bodies modifies the polarization of the body in question, therefore, its electric field is modified as well, thus the polarization of the other bodies will be modified again ... and so on. The description of a system of polarized bodies seems to be too complicated.

According to the previous and the present paragraphs,

– **we shall examine only a single body in a homogeneous exterior field (which can depend on time)**.

– **the electric field in the body produced by a homogeneous polarization is taken to be parallel and opposite to the polarization**,

– **the polarization induced in the body by an exterior field is considered to be parallel to the field and to have the same direction**.

Consequently, the electric fields, the polarization and dipoles can be treated as scalars (except Paragraph 50.3), so the symbols of these quantities represent values with respect to a given direction (the value can be either positive or negative).

48.4 The Clausius–Mosotti formula

Let us take a body whose molecules do not have intrinsic dipole and let us put it in a constant exterior electric field $\mathbb{E}_a$; the molecules are deformed and become dipoles. Let $\mathbb{P}$ be the polarization of the body in equilibrium (when no change occurs). It seems a good assumption that the dipole $\mathbf{p}_m$ of a molecule in equilibrium is proportional to the electric field acting on the molecule (this is not necessarily true outside equilibrium: if the electric field changes, then the dipole changes, too, but its change does not follow immediately that of the electric field because of inertia); let $\alpha > 0$ be the proportionality coefficient. Let $\mathbb{E}$ be the electric field in the body. The electric field acting on a molecule is not $\mathbb{E}$ because this field contains the field produced by the molecule, too. We obtain the field acting on the molecule by 'removing' the molecule and calculating the field produced without the molecule. This can be done as follows. Let us remove a small piece of the body around the molecule, i.e. let us imagine that a small cavity exists in the body. The electric field produced by the small piece is supposed to be $-\delta_c\mathbb{P}$ (which is true if the piece is an ellipsoid), where δ_c can depend on the thermodynamical state of the body. Then the electric field in the cavity is

$$\mathbb{E} + \delta_c\mathbb{P}.$$

Contracting the cavity to the point of the molecule in such a way that δ_c is constant (this is the case if all cavities are balls), we get the electric field acting on the molecule. Thus the dipole of a molecule is

$$\mathbf{p}_m = \alpha(\mathbb{E} + \delta_c\mathbb{P}).$$

If there are N molecules in the volume V, then $\mathbb{P} = \frac{N\mathbf{p}_m}{V} = \mathbf{p}_m v$, therefore,

$$\mathbb{P} = \frac{\alpha}{v}(\mathbb{E} + \delta_c\mathbb{P})$$

which yields

$$\mathbb{P} = \chi\mathbb{E},$$

where

$$\chi := \frac{\alpha}{v - \alpha\delta_c}$$

is the **electric susceptibility**.

If the electric field produced by the body equals $-\delta\mathbb{P}$ (which is true if the body is an ellipsoid), then

$$\mathbb{E} = \mathbb{E}_a - \delta\mathbb{P},$$

thus,

$$\mathbb{P} = \kappa\mathbb{E}_a,$$

where

$$\kappa := \frac{\chi}{1 + \delta\chi} = \frac{\alpha}{v + \alpha(\delta - \delta_c)}$$

is the **electric susceptance**.

We see that χ and κ depend on the form of the cavity. If the cavity is a ball, then $\delta_c = 1/3$ and

$$\chi = \frac{3\alpha}{3v - \alpha}$$

or

$$\frac{3\chi}{3+\chi} = \frac{\alpha}{v}.$$

Introducing the **electric permittivity** $\epsilon := 1 + \chi$, we get the **Clausius–Mosotti formula**:

$$\frac{\epsilon - 1}{\epsilon + 1} = \frac{\alpha}{3v}.$$

It seems, the ball form cavity can be motivated by homogeneity; the action on a molecule, however, does not have a spherical symmetry, thus the more general formula – δ_c instead of $1/3$ – is not superfluous.

Of course, the Clausius–Mosotti formula does not have an overall validity: it gives a qualitatively good approximation for certain materials in certain thermodynamical states.

48.5 The notion of induced polarization

The previous considerations concern equilibrium (for the time being, let equilibrium be an intuitive notion). Let us imagine that the body is in equilibrium in an exterior field. The field deformed the molecules (or ordered the dipoles), a polarization is established by the exterior field. Let the exterior field change abruptly; then the deformation of the molecules (or the ordering of the dipoles) changes, too, but this change is behind the change of the exterior field: outside equilibrium the actual polarization differs from the equilibrium polarization corresponding to the actual exterior field. If a new constant exterior field is established, then a new equilibrium polarization will come into being which can depend on the former equilibrium polarization.

Let us introduce the notion of induced polarization: this is **the equilibrium polarization realized by a constant exterior field from an initial polarization**.

48.6 Definition of a polarizable body

Polarization is the dipole density. Thus if polarization $\mathbb{P}$ is on the body of volume V, then the body has the dipole

$$\mathbf{p} := \mathbb{P}V \in (\hat{\mathrm{A}}\mathrm{sm}).$$

It is convenient to use this quantity as a variable of the polarizable body.

Definition *$\left(D \times \mathbb{R}^+ \times (\hat{\mathrm{A}}\mathrm{sm}), \mathfrak{e}_b, \mathcal{P}_b, \mu_b, R, \mathcal{E}_p, \mathcal{P}_p, \mu_p, \mathbb{E}_g, \mathbb{P}_{in}\right)$ is called a* **simple polarizable body** *if $(D, \mathfrak{e}_b, \mathcal{P}_b, \mu_b, R)$ is a simple material,*

$$\mathcal{E}_p : D \times \mathbb{R}^+ \times (\hat{\mathrm{A}}\mathrm{sm}) \to (\mathrm{J})^+, \qquad \mathcal{P}_p : D \times \mathbb{R}^+ \times (\hat{\mathrm{A}}\mathrm{sm}) \to (\mathrm{Pa}),$$

$$\mu_p : D \times \mathbb{R}^+ \times (\hat{\mathrm{A}}\mathrm{sm}) \to (\mathrm{J}), \qquad \mathbb{E}_g : D \times \mathbb{R}^+ \times (\hat{\mathrm{A}}\mathrm{sm}) \to (\hat{\mathrm{V}}/\mathrm{m}),$$

are continuous functions, continuously differentiable on $R \times \mathbb{R}^+ \times (\hat{\mathrm{A}}\mathrm{sm})$*,*

– $T \mapsto \mathcal{E}_p(v, T, N, \mathbf{p})$ *is monotone increasing for all possible* v*,* N *and* $\mathbf{p}$*,*

– $v \mapsto \mathcal{P}_p(v, T, N, \mathbf{p})$ *is locally monotone decreasing for all possible* T*,* N *and* $\mathbf{p}$*,*

– $\mathbf{p}\mathbb{E}_g(v, T, N, \mathbf{p}) < 0$ *if* $\mathbf{p} \neq 0$ *and* $\mathbf{p} \mapsto \mathbb{E}_g(v, T, N, \mathbf{p})$ *is strictly monotone decreasing for all possible* v*,* T *and* N*, having everywhere negative derivative,*

furthermore,

$$\mathcal{E}_p(v, T, N, 0) = 0, \quad \mathcal{P}_p(v, T, N, 0) = 0, \quad \mu_p(v, T, N, 0) = 0, \quad \mathbb{E}_g(v, T, N, 0) = 0$$

for all elements (v, T, N) *of* $D \times \mathbb{R}^+$*,*

lastly,

$$\mathbb{P}_{in} : D \times \mathbb{R}^+ \times (\hat{\mathrm{A}}\mathrm{sm}) \times (\hat{\mathrm{V}}/\mathrm{m}) \to (\hat{\mathrm{A}}\mathrm{s}/\mathrm{m}^2)$$

is a continuous function, continuously differentiable on $R \times \mathbb{R}^+ \times (\hat{\mathrm{A}}\mathrm{sm}) \times (\hat{\mathrm{V}}/\mathrm{m})$*,*

– $\mathbb{E}_a\mathbb{P}_{in}(v, T, N, \mathbf{p}, \mathbb{E}_a) > 0$ *if* $\mathbb{E}_a \neq 0$ *and* $\mathbb{E}_a \mapsto \mathbb{P}_{in}(v, T, N, \mathbf{p}, \mathbb{E}_a)$ *is strictly monotone increasing for all possible* v*,* T*,* N *and* $\mathbf{p}$*, having everywhere negative derivative.*

$\mathbb{E}_g$ *is the* **electric field produced by the body***,*

$$\mathcal{E}(v, T, N, \mathbf{p}) := N\mathfrak{e}_b(v, T) + \mathcal{E}_p(v, T, N, \mathbf{p}),$$

$$\mathcal{P}(v, T, N, \mathbf{p}) := \mathcal{P}_b(v, T) + \mathcal{P}_p(v, T, N, \mathbf{p}),$$

$$\mu(v, T, N, \mathbf{p}) := \mu_b(v, T) + \mu_p(v, T, N, \mathbf{p})$$

are the **internal energy***, the* **pressure** *and the* **chemical potential***, respectively, of the body.*

$\mathbb{P}_{in}$ *is the* **polarization induced by the exterior field***.*

As a consequence of the definition, the inequalities

$$\frac{\partial \mathcal{E}}{\partial T} > 0, \qquad \frac{\partial \mathcal{P}}{\partial v} < 0, \qquad \frac{\partial \mathbb{E}_g}{\partial \mathbf{p}} < 0$$

hold on the regular domain $R \times \mathbb{R}^+ \times (\hat{\mathrm{A}}\mathrm{sm})$.

The **electric susceptance** of the body

$$\kappa(v, T, N, \mathbf{p}, \mathbb{E}_a) := \frac{\partial \mathbb{P}_{in}(v, T, N, \mathbf{p}, \mathbb{E}_a)}{\partial \mathbb{E}_a}$$

is positive (and is defined if $(v, T) \in R$).

Let us compare the present definition with the definition of chargeable bodies. $\mathbf{p} \in (\hat{\mathrm{A}}\mathrm{sm})$ here corresponds to $C \in (\hat{\mathrm{A}}\mathrm{s})$ there; $\mathbb{E}_g$ corresponds to $\mathcal{U}$ there; conditions imposed on the corresponding quantities are similar. There is an important difference, however: the induced polarization $\mathbb{P}_{in}$ has no counterpart in a chargeable body. The treatment of processes will reveal its importance: **if the exterior field is constant, then the equilibrium polarization of the body equals the induced polarization**:

$$\frac{\mathbf{p}}{V} = \mathbb{P}_{in}(V, T, N, \mathbf{p}, \mathbb{E}_a).$$

It is worth emphasizing that we can define only a polarizable body, not a material because the quantities connected to electricity cannot be described by specific data. The definition involves the material of the body which is related to the thermodynamical quantities only.

In the definition and in quantities related to the material, the specific volume is the convenient variable. In formulae concerning the body – as in the case of a chargeable body – the entire volume is more suitable.

Applying the customary ambiguous notation, we shall write either v or V as a variable in a function.

48.7 Canonical variables

The conditions imposed on the constitutive functions allow us to give temperature as a function of internal energy, volume, particle number and charge, i.e. internal energy can be used as an independent variable instead of temperature. Thus, we have, as earlier

$$\mathbf{T}(\mathcal{E}(V,T,N,\mathbf{p}),V,N,\mathbf{p}) = T, \qquad \mathcal{E}(V,\mathbf{T}(E,V,N,\mathbf{p}),N,\mathbf{p}) = E,$$

$$\mathbf{P}(E,V,N,\mathbf{p}) = \mathcal{P}(V,\mathbf{T}(E,V,N,\mathbf{p}),N,\mathbf{p}),$$

$$\boldsymbol{\mu}(E,V,N,\mathbf{p}) = \mu(V,\mathbf{T}(E,V,N,\mathbf{p}),N,\mathbf{p}),$$

$$\mathbb{E}_g(E,V,N,\mathbf{p}) = \mathbb{E}_g(V,\mathbf{T}(E,V,N,\mathbf{p}),N,\mathbf{p})$$

(the same symbol $\mathbb{E}_g$ appeared on both sides of the last equality for different functions because of scarcity of letters).

48.8 Entropic property

According to the usual ‘rule’ (see Paragraph 16.3) the entropy $(V,T,N,\mathbf{p}) \mapsto \mathcal{S}(V,T,N,\mathbf{p})$ of a polarizable body should obey the relations

$$T\frac{\partial\mathcal{S}}{\partial T} = \frac{\partial\mathcal{E}}{\partial T}, \qquad T\frac{\partial\mathcal{S}}{\partial V} = \frac{\partial\mathcal{E}}{\partial V} + \mathcal{P}, \qquad T\frac{\partial\mathcal{S}}{\partial N} = \frac{\partial\mathcal{E}}{\partial N} - \mu, \tag{1}$$

$$T\frac{\partial\mathcal{S}}{\partial\mathbf{p}} = \frac{\partial\mathcal{E}}{\partial\mathbf{p}} + \mathbb{E}_g. \tag{2}$$

If internal energy is employed as a variable (in other words, canonical variables are used), then the function $\mathbf{S}(E,V,N,\mathbf{p}) := \mathcal{S}(V,\mathbf{T}(E,V,N,\mathbf{p}),N,\mathbf{p})$ satisfies

$$\frac{\partial\mathbf{S}}{\partial E} = \frac{1}{\mathbf{T}}, \qquad \frac{\partial\mathbf{S}}{\partial V} = \frac{\mathbf{P}}{\mathbf{T}}, \qquad \frac{\partial\mathbf{S}}{\partial N} = -\frac{\boldsymbol{\mu}}{\mathbf{T}},$$

$$\frac{\partial\mathbf{S}}{\partial\mathbf{p}} = \frac{\mathbb{E}_g}{\mathbf{T}}.$$

Definition *The polarizable body in Definition 48.6 is* **entropic** *if there is a function $\mathcal{S}$, the* **entropy** *of the body, satisfying equalities* (1) *and* (2) *on* $R \times \mathbb{R}^+ \times (\hat{\mathrm{A}}\mathrm{sm})$.

If the entropy is twice differentiable, then Young's theorem yields the known equality

$$T\frac{\partial \mathcal{P}}{\partial T} = \frac{\partial \mathcal{E}}{\partial V} + \mathcal{P} \tag{3}$$

and the additional equalities

$$\frac{\partial \mathcal{E}}{\partial \mathbf{p}} = T\frac{\partial \mathbb{E}_g}{\partial T} - \mathbb{E}_g, \qquad \frac{\partial \mathcal{P}}{\partial \mathbf{p}} = \frac{\partial \mathbb{E}_g}{\partial V}, \qquad \frac{\partial \mu}{\partial \mathbf{p}} = -\frac{\partial \mathbb{E}_g}{\partial N}. \tag{4}$$

We shall see in Paragraph 51.4 that it is doubtful whether it is reasonable to require that a polarizable body be entropic.

48.9 Conventional polarizable body

According to our knowledge in electrostatics (see 48.1), the electric field $\mathbb{E}_g$ produced by a polarization $\mathbb{P}$ can be taken to be proportional to the polarization, the constant of proportionality can depend on the thermodynamical state of the body. Then electrostatics says that the electric energy density equals $-\frac{1}{2}\mathbb{E}_g \cdot \mathbb{P}$, thus the energy density is proportional to the square of polarization. Then an analogy with chargeable bodies suggests the following definition.

Definition *The polarizable body defined in 48.6 is called* **conventional** *if there are continuous functions η, π, ξ and γ defined on $D\times\mathbb{R}^+$ (mapping into convenient measure lines), continuously differentiable on $R \times \mathbb{R}^+$ so that*

$$\mathcal{E}_p(V,T,N,\mathbf{p}) := \frac{\eta(V,T,N)\mathbf{p}^2}{2}, \qquad \mathcal{P}_p(V,T,N,\mathbf{p}) := \frac{\pi(V,T,N)\mathbf{p}^2}{2},$$

$$\mu_p(V,T,N,\mathbf{p}) := \frac{\xi(V,T,N)\mathbf{p}^2}{2}, \qquad \mathbb{E}_g(V,T,N,\mathbf{p}) := -\gamma(V,T,N)\mathbf{p}.$$

γ is positive because the produced electric field is a strictly monotone decreasing function of polarization. $\delta := \gamma V$ is the **depolarization factor** of the body.

This corresponds formally to a conventional chargeable body: C and $\mathcal{U}$ are to be replaced with $\mathbf{p}$ and $-\mathbb{E}_g$, respectively.

48.10 Two customary conditions

In practice (electrotechnics) one always takes $\mathbb{E}_g = -\gamma\mathbf{p} = -\delta\mathbb{P}$ and $\mathcal{E}_p = -\frac{1}{2}\mathbb{E}_g\mathbf{p} = -\frac{\gamma\mathbf{p}^2}{2}$. Moreover, γ is considered to be independent of temperature. For a conventional body these assumptions give

$$\eta = \gamma, \qquad \frac{\partial \gamma}{\partial T} = 0.$$

As a generalization, we suppose in the sequel that

$$\frac{\partial \mathcal{E}}{\partial \mathbf{p}} = -\mathbb{E}_g, \qquad \frac{\partial \mathbb{E}_g}{\partial T} = 0. \tag{$*$}$$

48.11 Exercises

1. Cut a conventional body in two equal parts and form both parts to a body having the same depolarization coefficient as has the original body. Show that the electric field in the new bodies coincide with the original one (electric field has the usual property of an intensive quantity); on the contrary, the electrostatic energy of one of the halves is not the half of the original electrostatic energy (internal energy is not a usual extensive quantity, specific internal energy makes no sense).

2. Verify that

$$\eta = -T\frac{\partial\gamma}{\partial T} + \gamma, \qquad \pi = -\frac{\partial\gamma}{\partial V}, \qquad \xi = -\frac{\partial\gamma}{\partial N}$$

for an entropic polarizable body.

If the depolarization factor $\delta = \gamma V$ does not depend on the thermodynamical state of the body, then

$$\pi = -\frac{\delta}{V^2}.$$

3. Give the function $\mathbf{T}$ (temperature as a function of internal energy, volume, particle number and dipole) for a conventional body if γ does not depend on temperature.

49 Induced polarization

49.1 Dielectric bodies

The Clausius–Mosotti formula shows that for certain bodies (whose molecules do not have intrinsic dipole) the induced polarization in equilibrium is proportional to the exterior field; the following is obtained by supposing this is true outside equilibrium, too.

Definition *A simple polarizable body is called* **dielectric** *if there is a continuous function* $\kappa : D \times \mathbb{R}^+ \to \mathbb{R}^+$, *continuously differentiable on* $R \times \mathbb{R}^+$ *such that*

$$\mathbb{P}_{in}(v, T, N, \mathbf{p}, \mathbb{E}_a) = \kappa(v, T, N)\mathbb{E}_a.$$

In other words, a polarizable body is dielectric if its susceptance (see 48.6) does not depend on the exterior field and the dipole (or polarization) of the body.

The equilibrium polarization $\mathbb{P}$ of a dielectric body is

$$\mathbb{P} = \kappa\mathbb{E}_a. \tag{$*$}$$

If the body is conventional, then

$$\mathbb{E} = \mathbb{E}_a - \delta\mathbb{P}$$

is the electric field in the body, thus we get

$$\mathbb{P} = \chi\mathbb{E}, \tag{$**$}$$

for the **equilibrium polarization**, where

$$\chi := \frac{\kappa}{1-\delta\kappa}$$

is the **electric susceptibility**. It is worth noting the inverse relation, too:

$$\kappa = \frac{\chi}{1+\delta\chi}.$$

We have to bear in mind that κ, δ and χ are functions of (v, T, N).

Warning (i) The actual polarization (outside equilibrium) of a body can differ from the induced one and it need not be proportional to the actual electric field in the body, as explained below. Let the body be in equilibrium in an exterior field $\mathbb{E}_{a1}$. Let the exterior field change abruptly to $\mathbb{E}_{a2}$ at the instant t_1. Then the polarization $\mathbb{P}$ of the body will vary in time in such a way that $\mathbb{P}(t_1) = \kappa\mathbb{E}_{a1}$ and $\mathbb{P}(t_2) = \kappa\mathbb{E}_{a2}$ for some instant t_2 (which can be infinity; see later in Section 51). Then the instantaneous electric field at the instant t between t_1 and t_2 is $\mathbb{E}(t) = \mathbb{E}_{a2} - \delta\mathbb{P}(t)$ but $\mathbb{P}(t) \neq \kappa\mathbb{E}_{a2}$, so $\mathbb{P}(t) \neq \chi\mathbb{E}(t)$.

Thus relations $(*)$ and $(**)$ are valid only in equilibrium.

(ii) In the usual literature some notions are confused. In general, susceptance is not defined at all, susceptibility is defined by $\mathbb{P} = \chi\mathbb{E}$ (and considered true even outside equilibrium) and then one often takes as if $\mathbb{P} = \chi\mathbb{E}_a$ held.

49.2 Langevin–Weiss induced polarization

In the previous paragraph we considered bodies whose molecules do not have an intrinsic dipole. If the molecules have an intrinsic dipole π, then some heuristics (not detailed here) results in the **Langevin–Weiss formula**

$$\mathbb{P}_{in}(v, T, N, \mathbf{p}, \mathbb{E}_a) = \frac{1}{v}\left(\alpha(\mathbb{E}_a - \lambda(v,T,N)\mathbb{P}) + \pi L\left(\frac{\pi(\mathbb{E}_a - \lambda(v,T,N)\mathbb{P})}{kT}\right)\right),$$

where $\lambda := \delta - \delta_c$ (δ and δ_c are the depolarization factors used in 48.4), α is the Clausius–Mosotti constant, $\mathbb{P} := \frac{\mathbf{P}}{V}$ and

$$L : \mathbb{R} \to \mathbb{R}, \quad x \mapsto \begin{cases} \mathrm{cth} x - \frac{1}{x} & \text{if} \quad x \neq 0, \\ 0 & \text{if} \quad x = 0 \end{cases}$$

is the Langevin function.

A body whose induced polarization is given by the above formula, is called a **Langevin–Weiss body**.

Thus the equilibrium polarization $\mathbb{P}$ of a Langevin–Weiss body is determined by the Langevin–Weiss equation

$$\mathbb{P} = \frac{1}{v}\left(\alpha(\mathbb{E}_a - \lambda(v,T,N))\mathbb{P} + \pi L\left(\frac{\pi(\mathbb{E}_a - \lambda(v,T,N)\mathbb{P})}{kT}\right)\right)$$

The solution of this equation is, in general, not unique which will be shown in detail in the theory of magnetization because Langevin–Weiss magnetization corresponds to an everyday phenomenon but Langevin–Weiss polarization is not frequent: there are few materials whose molecules have a significant intrinsic dipole but there are a lot of them whose molecules have a significant intrinsic magnetic momentum.

49.3 Properties of the Langevin function

It is a simple fact that L is odd, i.e. $L(-x) = -L(x)$, moreover L is analytic,

$$L(x) = \frac{x}{3} - \frac{x^3}{45} + \dots,$$

$$L'(x) = \begin{cases} -\frac{1}{\mathrm{sh}^2 x} + \frac{1}{x^2} > 0 & \text{if} \quad x \neq 0, \\ \frac{1}{3} & \text{if} \quad x = 0, \end{cases}$$

$$L''(x) = \begin{cases} 2\left(\frac{\mathrm{ch} x}{\mathrm{sh}^3 x} - \frac{1}{x^3}\right) & \text{if} \quad x \neq 0, \\ 0 & \text{if} \quad x = 0. \end{cases}$$

It is quite evident that $L' > 0$ and $L''(x) < 0$ if $x > 0$, $L''(x) > 0$ if $x < 0$, thus L is strictly monotone increasing and is concave on the positive half line (convex on the negative half line), consequently,

$$L(x) < \frac{x}{3} \qquad (x > 0).$$

Lastly, we have

$$\lim_{x\to\infty} L(x) = 1.$$

49.4 Exercises

1. Use the properties of the Langevin function to verify that if $\lambda = 0$ and the exterior field is not too strong – precisely: if $\pi\mathbb{E}_a \ll kT$ – then the induced polarization is approximately proportional to the exterior field, the susceptance is

$$\kappa \approx \frac{1}{v}\left(\alpha + \frac{\pi^2}{3kT}\right).$$

2. Give the susceptibility in the previous case.

3. Demonstrate that the Langevin–Weiss induced polarization satisfies the requirement of Definition 48.6: the derivative of $\mathbb{P}_{in}$ with respect to $\mathbb{E}_a$ (the susceptance) is positive.

50 Further observations

50.1 Equilibrium relations

In equilibrium the polarization of the body equals the induced polarization:

$$\frac{\mathbf{p}}{V} = \mathbb{P}_{in}(V, T, N, \mathbf{p}, \mathbb{E}_a).$$

Let us suppose that this allows us to express the equilibrium dipole $\mathbf{p}_{eq}$ – at least locally – as a function of the thermodynamical state of the body and the exterior field:

$$(V, T, N, \mathbb{E}_a) \mapsto \mathbf{p}_{eq}(V, T, N, \mathbb{E}_a). \qquad (*)$$

The electric field in the body in equilibrium is

$$\mathbb{E}_{eq}(V, T, N, \mathbb{E}_a) = \mathbb{E}_a + \mathbb{E}_g(V, T, N, \mathbf{p}_{eq}(V, T, N, \mathbb{E}_a))$$

If this allows us to express the exterior field as a function of the field in the body, i.e. to give a function $(V, T, N, \mathbb{E}_{eq}) \mapsto \mathbb{E}_a(V, T, N, \mathbb{E}_{eq})$, then we arrive at the equilibrium dipole function

$$(V, T, N, \mathbb{E}_{eq}) \mapsto \mathbf{p}_{eq}(V, T, N, \mathbb{E}_{eq}). \qquad (**)$$

Then the equilibrium susceptibility is defined to be

$$\chi(V, T, N, \mathbb{E}_{eq}) := \frac{\partial(V\mathbf{p}_{eq}(V, T, N, \mathbb{E}_{eq}))}{\partial\mathbb{E}_{eq}}.$$

We stress that susceptance is defined generally (see 48.6) whereas susceptibility is meaningful only in equilibrium (which was mentioned in Paragraph 49.1 for dielectric bodies).

Putting the expression $(*)$ for the equilibrium dipole $\mathbf{p}_{eq}$ in the constitutive functions of the body, we get the equilibrium quantities corresponding to a given exterior field; e.g.

$$(V, T, N, \mathbb{E}_a) \mapsto \mathcal{P}(V, T, N, \mathbf{p}_{eq}(V, T, N, \mathbb{E}_a))$$

is the equilibrium pressure as a function of the thermodynamical state of the body and the exterior field.

50.2 Remarks on usual treatments

The notion of induced polarization and that of the electric field produced by the polarization do not appear in usual treatments of thermodynamics. Electric field there means either the exterior field $\mathbb{E}_a$ or the field $\mathbb{E}$ in the body, and they are often confused. Polarization always means its equilibrium value, i.e. one of the functions $(*)$ or $(**)$ of the previous paragraph.

Furthermore, it is required (the bodies are supposed to be entropic) that $-\mathbb{E}_a$ or $-\mathbb{E}$ stand instead of the formulae of Paragraph 48.8.

If $-\mathbb{E}_a$ is taken, then

$$T\frac{\partial\mathcal{S}}{\partial\mathbf{p}} - \frac{\partial\mathcal{E}}{\partial\mathbf{p}} = -\mathbb{E}_a. \qquad (*)$$

This is impossible because the left-hand side is independent of the exterior field (it depends only on the thermodynamical state and polarization of the body). The same is true if $-\mathbb{E} = -\mathbb{E}_a - \mathbb{E}_g$ is taken.

Because usually one always considers only equilibrium, we can make the relations in question meaningful if the exterior field is considered as a function of the quantities of the body in the following way: we give the exterior field inducing the equilibrium dipole $\mathbf{p}$ in the thermodynamical state (V, T, N) of the body; in other words, the function

$$(V, T, V, \mathbf{p}) \mapsto \mathbb{E}_{a,eq}(V, T, N, \mathbf{p})$$

defined implicitly by $\mathbf{p}/V = \mathbb{P}_{in}(V, T, N, \mathbf{p}, \mathbb{E}_a)$.

This seems rather artificial; nevertheless, it would be acceptable if entropy were suitable for a Liapunov function assuring asymptotic stability. We shall see that this is not satisfied.

50.3 Vectorial quantities

We can modify the notion of a polarized body in such a way that the dipole $\mathbf{p}$, the electric fields $\mathbb{E}_a$ and $\mathbb{E}_g$ and the induced polarization $\mathbb{P}_{in}$ are considered as vectors. Then $(\hat{\mathrm{A}}\mathrm{sm})$ and $(\hat{\mathrm{V}}/\mathrm{m})$ in Definition 48.6 is replaced with $\mathbf{N}(\hat{\mathrm{A}}\mathrm{sm})$ and $\mathbf{N}(\hat{\mathrm{V}}/\mathrm{m})$, respectively, where $\mathbf{N}$ is the Euclidean space of spacelike vectors without physical dimension: e.g. $\mathbf{p} \in \mathbf{N}(\hat{\mathrm{A}}\mathrm{sm})$.

Besides the above formal changes, we have to make the following alteration:

– if $\mathbf{p} \neq 0$, then $\mathbf{p} \cdot \mathbb{E}_g(v, T, N, \mathbf{p}) < 0$ (the dot denotes scalar product), moreover, the function $\alpha \mapsto -|\mathbb{E}_g(v, T, N, \alpha\mathbf{p})|$ defined for real α-s is strictly monotone decreasing for all possible v, T and N, having negative derivative.

The entropic property, the conventional body, the dielectric body are defined formally as earlier but the Langevin–Weiss body cannot be defined.

50.4 Exercises

1. Give a relation between the susceptance defined in 48.6 and the susceptibility defined in 50.1. Apply the result for a Langevin–Weiss body.

2. In practice the equilibrium quantities (in a phase) are usually given as functions of temperature, pressure, particle number and electric field (exterior or in the body) without referring to polarization. The volume – at least locally – can be given as a function $(T, P, N, \mathbf{p}) \mapsto \boldsymbol{V}(T, P, N, \mathbf{p})$. Replacing here $\mathbf{p}$ with the equilibrium function $\mathbf{p}_{eq}$ obtained in 50.1, we get the desired function for volume:

$$V_{eq}(T, P, N, \mathbb{E}_a) := \boldsymbol{V}\big(T, P, N, \mathbf{p}_{eq}(V, T, N, \mathbb{E}_a)\big)$$

or

$$V_{eq}(T, P, N, \mathbb{E}_{eq}) := \boldsymbol{V}\big(T, P, N, \mathbf{p}_{eq}(V, T, N, \mathbb{E}_{eq})\big).$$

Define the equilibrium susceptance and the equilibrium susceptibility as a function of temperature, pressure, particle number and electric field.

51 Processes of a polarizable body

51.1 Dynamical equation, dynamical quantitities

A process of a polarizable body in a given environment is a function $t \mapsto \big(E(t), V(t), N(t), \mathbf{p}(t)\big)$ defined on a time interval obeying the dynamical equation

$$\dot{E} = Q - PF + \mu G - \mathbb{E}_g \mathbf{r},$$

$$\dot{V} = F, \qquad \dot{N} = G, \qquad \dot{\mathbf{p}} = \mathbf{r}$$

(in the ideal case, see Paragraph 16.3), where Q, F, G and $\mathbf{r}$ are given as functions of the state of the body and the state of the environment. For instance, if the environment is characterized by its temperature T_a, pressure P_a (which determine the chemical potential μ_a) and by the exterior field $\mathbb{E}_a$, then the heating is a function

$$(E, V, N, \mathbf{p}, T_a, P_a, \mathbb{E}_a) \mapsto \mathbf{Q}(E, V, N, \mathbf{p}, T_a, P_a, \mathbb{E}_a)$$

or

$$(V, T, N, \mathbf{p}, T_a, P_a, \mathbb{E}_a) \mapsto \mathcal{Q}(V, T, N, \mathbf{p}, T_a, P_a, \mathbb{E}_a).$$

51.2 Equilibrium properties, thermodynamical force

If the environment is constant, then an equilibrium of the body is a constant process in which every dynamical quantity takes zero value.

As said, electric field is the intensive quantity corresponding to polarization. Polarization phenomena have the particular feature – as a consequence of the action at a distance – that **equilibrium is not characterized by the equality of the intensive quantities**: neither the electric field $\mathbb{E}_g$ produced by the body polarization nor the electric field $\mathbb{E} = \mathbb{E}_a + \mathbb{E}_g$ in the body is equal to the exterior field $\mathbb{E}_a$ in equilibrium.

Equilibrium is characterized by the fact that the actual polarization of the body equals the induced polarization. Thus we accept that if no constraint is imposed on the precesses, then $(V_\mathrm{o}, T_\mathrm{o}, N_\mathrm{o}, \mathbf{p}_\mathrm{o})$ is an equilibrium if and only if

$$T_\mathrm{o} = T_a, \qquad \mathcal{P}(V_\mathrm{o}, T_\mathrm{o}, N_\mathrm{o}, \mathbf{p}_\mathrm{o}) = P_a, \qquad \boldsymbol{\mu}(V_\mathrm{o}, T_\mathrm{o}, N_\mathrm{o}, \mathbf{p}_\mathrm{o}) = \mu_a,$$

$$\frac{\mathbf{p}_\mathrm{o}}{V_\mathrm{o}} = \mathbb{P}_{in}(V_\mathrm{o}, T_\mathrm{o}, N_\mathrm{o}, \mathbf{p}_\mathrm{o}, \mathbb{E}_a).$$

As a consequence, the difference $\mathbf{p}/V - \mathbb{P}_{in}$ offers itself for the component of the thermodynamical force corresponding to electricity. This is, however, not an intensive quantity. We look for convenient intensive quantities. The fundamental properties of the body imply that the polarization and the electric field produced by it determine each other uniquely; therefore, we accept the difference of the electric fields produced by $\mathbf{p}/V$ and $\mathbb{P}_{in}$ as a convenient member of the thermodynamical force, as follows.

If $\mathbb{E}_h$ denotes the (fictitious) electric field produced by the induced polarization, i.e.

$$\mathbb{E}_h(V, T, N, \mathbf{p}, \mathbb{E}_a) := \mathbb{E}_g(V, T, N, V\mathbb{P}_{in}(V, T, N, \mathbf{p}, \mathbb{E}_a)),$$

then (with the customary symbolic notations)

$$\big(-(T - T_a), P - P_a, -(\mu - \mu_a), \mathbb{E}_g - \mathbb{E}_h\big)$$

is the **thermodynamical force** acting on the body and

$$\left(\frac{1}{T} - \frac{1}{T_a}, \frac{P}{T} - \frac{P_a}{T_a}, -\left(\frac{\mu}{T} - \frac{\mu_a}{T_a}\right), \frac{\mathbb{E}_g}{T} - \frac{\mathbb{E}_h}{T_a}\right)$$

is the **canonical thermodynamical force**.

We note that the last member of the thermodynamical force is not the difference of a quantity concerning the body only and a quantity concerning the environment only: $\mathbb{E}_h$ depends on the body state, too.

The dynamical quantitities are pseudolinear if

$$\begin{pmatrix} Q \\ F \\ G \\ \mathbf{r} \end{pmatrix} = \begin{pmatrix} \lambda_Q & \beta_Q & \vartheta_Q & \rho_Q \\ \lambda_F & \beta_F & \vartheta_F & \rho_F \\ \lambda_G & \beta_G & \vartheta_G & \rho_G \\ \lambda_r & \beta_r & \vartheta_r & \rho_r \end{pmatrix} \begin{pmatrix} -(T-T_a) \\ P-P_a \\ -(\mu-\mu_a) \\ \mathbb{E}_g - \mathbb{E}_h) \end{pmatrix} =$$

$$= \begin{pmatrix} \lambda^c_Q & \beta^c_Q & \vartheta^c_Q & \rho^c_Q \\ \lambda^c_F & \beta^c_F & \vartheta^c_F & \rho^c_F \\ \lambda^c_G & \beta^c_G & \vartheta^c_G & \rho^c_G \\ \lambda^c_r & \beta^c_r & \vartheta^c_r & \rho^c_r \end{pmatrix} \begin{pmatrix} \frac{1}{T} - \frac{1}{T_a} \\ \frac{P}{T} - \frac{P_a}{T_a} \\ -\left(\frac{\mu}{T} - \frac{\mu_a}{T_a}\right) \\ \frac{\mathbb{E}_g}{T} - \frac{\mathbb{E}_h}{T_a} \end{pmatrix},$$

where the matrix entries are functions of $(E, V, N, \mathbf{p}, T_a, P_a, \mathbb{E}_a)$ (or $(V, T, N, \mathbf{p}, T_a, P_a, \mathbb{E}_a)$).

The equilibrium properties of the dynamical quantitities specify the connection among the zero value of the dynamical quantitities and that of the thermodynamical forcewhich is formlated intuitively as followls:

The zero value of the dynamical quantitities describing the admitted interactions (which characterizes equilibrium) imply the zero value of the corresponding thermodynamical force (the effective thermodynamical force), and the zero value of the thermodynamical force belonging to the admitted interactions implies the zero value of the corresponding dynamical quantitities.

A precise formulation is rather complicated even for neutral bodies and is more complicated for polarizable bodies. Therefore, we do not give it in detail; by the way, it is not worth doing so because homogeneity is a too strong assumption for electromagnetic phenomena. We shall formulate the equilibrium properties in each special case treated in the sequel.

51.3 Dissipation inequality

The dissipation inequality – on the analogy of earlier inequalities – is required in the form

$$-\frac{Q}{T}(T - T_a) + F(P - P_a) - G(\mu - \mu_a) + \mathbf{r}(\mathbb{E}_g - \mathbb{E}_h) \geq 0,$$

where equality holds if and only if all the dynamical quantitities take zero value. Equivalently,

$$(Q - PF + \mu G - \mathbb{E}_g\mathbf{r})\left(\frac{1}{T} - \frac{1}{T_a}\right) + \\ + F\left(\frac{P}{T} - \frac{P_a}{T_a}\right) - G\left(\frac{\mu}{T} - \frac{\mu_a}{T_a}\right) + \mathbf{r}\left(\frac{\mathbb{E}_g}{T} - \frac{\mathbb{E}_h}{T_a}\right) \geq 0.$$

51.4 Electrostriction

If the processes are slow enough, we can consider that they are isothermal–isobaric: the body temperature and pressure are constant T_a and P_a, respectively. If, moreover, the particle number is constant, too, then the change of polarization determines that of volume by the relation

$$\frac{\partial \mathcal{P}}{\partial V}\dot{V} + \frac{\partial \mathcal{P}}{\partial \mathbf{p}}\dot{\mathbf{p}} = 0, \tag{$*$}$$

thus

$$\dot{V} = \frac{\frac{\partial \mathcal{P}}{\partial \mathbf{p}}}{-\frac{\partial \mathcal{P}}{\partial V}}\dot{\mathbf{p}}.$$

Experience shows that the body contracts as its polarization grows which is called **electrostriction**. The denominator in the right-hand side above is positive, electrostriction implies that the numerator is negative (for positive $\mathbf{p}$).

If the body is entropic, then $\frac{\partial \mathcal{P}}{\partial \mathbf{p}} = \frac{\partial \mathbb{E}_g}{\partial V}$. Experience indicates that the right-hand side here is positive; e.g. if the body is conventional and the depolarization factor δ is independent of the state of the body, then $\frac{\partial \mathbb{E}_g}{\partial V} = \frac{\delta}{V^2}\mathbf{p}$.

Thus the phenomenon of electrostriction and the fact that the electric field produced by a given dipole decreases as the volume of the dipole increases are not compatible with the entropic property.

52 Some special systems

52.1 General formulae

We treat the processes of a body with constant particle number N_o in a given environment. The environment is supposed to have constant temperature T_a, pressure P_a and exterior field $\mathbb{E}_a$. Thus, the dynamical equation becomes

$$\dot{E} = Q - PF - \mathbb{E}_g\mathbf{r}, \qquad \dot{V} = F, \qquad \dot{\mathbf{p}} = \mathbf{r}.$$

Moreover, we accept the conditions $(*)$ in Paragraph 48.10 from which

$$\frac{\partial \mathcal{E}}{\partial \mathbf{p}} = -\mathbb{E}_g \tag{$*$}$$

plays a fundamental role. In particular, if temperature is used instead of internal energy as a variable, the first law will have the form

$$\frac{\partial \mathcal{E}}{\partial T}\dot{T} = Q - \left(P + \frac{\partial \mathcal{E}}{\partial V}\right)\dot{V}.$$

The entropic property is a doubtful assumption for polarizable bodies, moreover, the canonical thermodynamical force is not obtained as the derivative of the total entropy of the body and the environment, therefore, we cannot apply the results of Paragraph 15; some special systems will be treated without entropy.

52.2 Fixed volume

The volume has the fixed value V_o, and the dynamical equation, reduced to the variables T and $\mathbf{p}$ is very simple:

$$\frac{\partial \mathcal{E}}{\partial T}\dot{T} = Q, \qquad \dot{\mathbf{p}} = \mathbf{r}. \tag{1}$$

Let us suppose that

$$Q = -\lambda_Q(T - T_a) - \rho_Q(\mathbb{E}_h - \mathbb{E}_g), \qquad \mathbf{r} = -\lambda_r(T - T_a) - \rho_r(\mathbb{E}_h - \mathbb{E}_g) \tag{2}$$

where λ_Q, ρ_Q etc. are constant. The dissipation inequality gives

$$\lambda_Q > 0, \qquad \rho_r > 0, \qquad \lambda_Q\rho_r - \rho_Q\lambda_r > \frac{(\rho_Q - T\lambda_r)^2}{4T}.$$

The above form of the dynamical quantitities implies that $(T_o, \mathbf{p}_o)$ is an equilibrium of the reduced dynamical equation if and only if

$$T_o = T_a, \qquad \mathbf{p}_o = V_o\mathbb{P}_{in}(V_o, T_a, N_o, \mathbf{p}_o, \mathbb{E}_a).$$

If $(V_o/N_o, T_a)$ is in the regular domain, then the right-hand side of the reduced dynamical equation is differentiable, its derivative in the equilibrium is

$$\begin{pmatrix} -\frac{\lambda_Q+\rho_Q ba}{c} & -\frac{\rho_Q b(1-d)}{c} \\ -\lambda_r - \rho_r ba & -\rho_r b(1-d) \end{pmatrix},$$

where

$$c := \frac{\partial \mathcal{E}}{\partial T}(V_o, T_a, N_o, \mathbf{p}_o), \qquad b := -\frac{\partial \mathbb{E}_g}{\partial \mathbf{p}}(V_o, T_a, N_o, \mathbf{p}_o),$$

$$a := \frac{\partial \mathbb{P}_{in}}{\partial T}(V_o, T_a, N_o, \mathbf{p}_o, \mathbb{E}_a), \qquad d := V_o\frac{\partial \mathbb{P}_{in}}{\partial \mathbf{p}}(V_o, T_a, N_o, \mathbf{p}_o, \mathbb{E}_a).$$

If the eigenvalues of this matrix, i.e. the roots of the characteristic polynomial

$$x \mapsto cx^2 + (\lambda_Q + \rho_Q ba + \rho_r bc(1-d))x + (\lambda_Q\rho_r - \lambda_r\sigma_Q)b(1-d)$$

have negative real parts, then the equilibrium is asymptotically stable; if there is an eigenvalue having positive real value, then the equilibrium is unstable. Because the basic properties of the body imply that $c > 0$ and $b > 0$, and the dissipation inequality implies that $\lambda_Q > 0$, $\rho_r > 0$ and $\lambda_Q\rho_r - \rho_Q\lambda_r > 0$, we have the following result.

Proposition *If condition* $(*)$ *in Paragraph 52.1 holds and the dynamical quantitities have the form (2), then the equilibrium* $(T_a, \mathbf{p}_o)$ *of the reduced dynamical equation (1) is*

– asymptotically stable if

$$1 - d > 0, \qquad -\rho_Q ba < \lambda_Q + \rho_r bc(1-d),$$

– instable if

$$1 - d < 0.$$

Thus, the question of stability–instability is decided essentially by the sign of $1-d$. For a dielectric body $d=0$, thus the condition of stability is satisfied. For a Langevin–Weiss body the physical meaning of the sign of $1-d$ will be clarified later in connection with magnetic processes.

52.3 Constant pressure

Similarly to Paragraph 44.3, the dynamical equation reduced to the variables T and $\mathbf{p}$ is

$$\left(\frac{\partial\mathcal{E}}{\partial T} + \left(P_a + \frac{\partial\mathcal{E}}{\partial V}\right)\frac{\frac{\partial\mathcal{P}}{\partial T}}{-\frac{\partial\mathcal{P}}{\partial V}}\right)\dot{T} = Q - \left(\left(P_a + \frac{\partial\mathcal{E}}{\partial T}\right)\frac{\frac{\partial\mathcal{P}}{\partial\mathbf{p}}}{-\frac{\partial\mathcal{P}}{\partial V}}\right)\mathbf{r}, \qquad \dot{\mathbf{p}} = \mathbf{r}.$$

Let the dynamical quantitities be as in the previous paragraph. Then $(T_\mathrm{o}, \mathbf{p}_\mathrm{o})$ is an equilibrium if and only if

$$T_\mathrm{o} = T_a, \qquad \mathbf{p}_\mathrm{o} = V_\mathrm{o}\mathbb{P}_{in}(V_\mathrm{o}, T_a, N_\mathrm{o}, \mathbf{p}_\mathrm{o}, \mathbb{E}_a)$$

where V_o is determined by $\mathcal{P}(V_\mathrm{o}, T_a, N_\mathrm{o}, \mathbf{p}_\mathrm{o}) = P_a$. The equilibrium is locally unique.

If the equilibrium is in the regular domain, then the right-hand side of the reduced dynamical equation is differentiable and its derivative in equilibrium has the characteristic polynomial

$$x \mapsto cx^2 + \big(\lambda_Q + h\lambda_r + (\rho_Q + h\rho_r)ba + \rho_r(1-d)bc\big)x + (\lambda_Q\rho_r - \lambda_r\rho_Q)(1-d)b,$$

where a, b and d are the quantities introduced in the previous paragraph and

$$c := \left(\frac{\partial\mathcal{E}}{\partial T} + \left(P_a + \frac{\partial\mathcal{E}}{\partial V}\right)\frac{\frac{\partial\mathcal{P}}{\partial T}}{-\frac{\partial\mathcal{P}}{\partial V}}\right)(V_\mathrm{o}, T_a, N_\mathrm{o}, \mathbf{p}_\mathrm{o}),$$

$$h := -\left(\left(P_a + \frac{\partial\mathcal{E}}{\partial T}\right)\frac{\frac{\partial\mathcal{P}}{\partial\mathbf{p}}}{-\frac{\partial\mathcal{P}}{\partial V}}\right)(V_\mathrm{o}, T_a, N_\mathrm{o}, \mathbf{p}_\mathrm{o}).$$

If the roots of the characteristic polynomial have negative real parts, then the equilibrium is asymptotically stable; if a root has positive real part, then the equilibrium is unstable. The reader is asked to discuss the possibilities.

52.4 Constant temperature

The dynamical equation reduced to the variables V and $\mathbf{p}$ is

$$\dot{V} = F, \qquad \dot{\mathbf{p}} = \mathbf{r}.$$

Let us suppose that

$$F = \beta_F(P - P_a), \qquad \mathbf{r} = \beta_r(P - P_a) - \rho_r(\mathbb{E}_g - \mathbb{E}_h),$$

where β_F, β_r and ρ_r are constant. The dissipation inequality implies

$$\beta_F > 0, \qquad \rho_r > 0, \qquad \beta_F\rho_r - \frac{\beta_r^2}{4} > 0.$$

The above form of the dynamical quantitities implies that $(V_o, \mathbf{p}_o)$ is an equilibrium of the reduced dynamical equation if and only if

$$\mathcal{P}(V_o, T_a, N_o, \mathbf{p}_o) = P_a, \qquad \mathbf{p}_o = V_o\mathbb{P}_{in}(V_o, T_a, N_o, \mathbf{p}_o, \mathbb{E}_a).$$

If $(V_o/N, T_a)$ is in the regular domain, then the right-hand side of the reduced dynamical equation is differentiable, its derivative in the equilibrium is

$$\begin{pmatrix} -\beta_F k & \beta_F z \\ -\beta_r k - \rho_r bw & \beta_r z - \rho_r(1-d)b \end{pmatrix},$$

where

$$k := -\frac{\partial\mathcal{P}}{\partial V}(V_o, T_a, N_o, \mathbf{p}_o), \qquad z := \frac{\partial\mathcal{P}}{\partial\mathbf{p}}(V_o, T_a, N_o, \mathbf{p}_o),$$

$$w := \frac{\partial\mathbb{P}_{in}}{\partial V}(V_o, T_a, N_o, \mathbf{p}_o, \mathbb{E}_a), \qquad b := -V\frac{\partial\mathbb{E}_g}{\partial\mathbf{p}}(V_o, T_a, N_o, \mathbf{p}_o).$$

This matrix has the characteristic polynomial

$$x \mapsto x^2 + (\beta_F k + \rho_r(1-d)b - \beta_r z)x + \beta_F\rho_r b\big((1-d)k - wz\big).$$

The reader is asked to discuss stability–instability of equilibrium.

52.5 Exercises

1. If both temperature and pressure are constant (and the particle number is fixed), then we have a relation between polarization change and the dipole change (see Paragraph 51.4), thus the dynamical equation can be reduced to $\mathbf{p}$. Suppose that

$$\mathbb{E}_g = -\frac{\delta}{V}\mathbf{p}, \qquad \mathbb{P}_{in} = \frac{\alpha}{v}\mathbb{E}_a, \qquad \mathbf{r} = \eta V(\mathbb{E}_g - \mathbb{E}_h)$$

where δ, α and η are positive constants. Solve the reduced dynamical equation.

2. Treat the adiabatic processes of a polarizable body.

53 Extended polarizable bodies

53.1 Definition of an extended polarizable body

Up to now we have investigated phenomena in which the polarization and the electric field can be considered as static because they change slowly enough. If the change is faster, then we have to take into account that the polarization produces a magnetic field too, which in turn induces an electric field. If the change is not too fast, then magnetic effects can be left out by taking an electric field consisting of two parts, one is due to the polarization, the other is due to the time rate of the polarization.

This is done on a clear analogy to Paragraph 46.1: the time rate of the dipole is to be an independent variable, i.e. the state of a body – the variables of the constitutive functions – will be $(V, T, N, \mathbf{p}, \mathbf{r})$. Now we shall consider the simple case when only the electric field depends explicitly on the time rate of the dipole.

Definition $(D \times \mathbb{R}^+ \times (\hat{\mathrm{A}}\mathrm{sm}) \times (\hat{\mathrm{A}}\mathrm{m}), \mathfrak{e}_b, \mathcal{P}_b, \boldsymbol{\mu}_b, R, \mathcal{E}_p, \mathcal{P}_p, \boldsymbol{\mu}_p, \mathbb{E}_g, \mathbb{P}_{in}, \mathbb{E}_{gx})$ *is an* **extended simple polarizable body** *if*

– $(D \times \mathbb{R}^+ \times (\hat{\mathrm{A}}\mathrm{sm}), \mathfrak{e}_b, \mathcal{P}_b, \boldsymbol{\mu}_b, R, \mathcal{E}_p, \mathcal{P}_p, \boldsymbol{\mu}_p, \mathbb{E}_{gp}, \mathbb{P}_{in})$ *is a simple polarizable body,*

– $\mathbb{E}_{gx} : D \times \mathbb{R}^+ \times (\hat{\mathrm{A}}\mathrm{sm}) \times (\hat{\mathrm{A}}\mathrm{m}) \to (\hat{\mathrm{V}}/\mathrm{m})$ *is a continuous function, continuously differentiable on* $R \times \mathbb{R}^+ \times \hat{\mathrm{A}}\mathrm{sm}) \times (\hat{\mathrm{A}}\mathrm{m})$ *and* $\mathbb{E}_{gx}(v, T, N, \mathbf{p}, 0) = 0$ *for all possible* v*,* T*,* N *and* $\mathbf{p}$.

The function $\mathbb{E}_g := \mathbb{E}_{gp} + \mathbb{E}_{gx}$ *is the* **electric field produced by the polarization**.

53.2 Dynamical equation, dissipation inequalities

A process of an extended polarizable body in a given environment is a function $t \mapsto \big(E(t), V(t), N(t), \mathbf{p}(t), \mathbf{r}(t)\big)$ obeying the dynamical equation

$$\dot{E} = Q - PF + \mu G - \mathbb{E}_g \mathbf{r}, \quad \dot{V} = F, \quad \dot{N} = G,$$

$$\dot{\mathbf{p}} = \mathbf{r}, \qquad \dot{\mathbf{r}} = \mathbf{z}$$

where (without sources) Q, F, G and $\mathbf{z}$ are functions of $(E, V, N, \mathbf{p}, \mathbf{r})$.

The dissipation inequalities are required on the analogy to those in Paragraph 46.2:

$$-\frac{Q}{T}(T - T_a) + F(P - P_a) - G(\mu - \mu_a) \geq 0,$$

$$-\mathbf{r}\mathbb{E}_{gx} \geq 0, \qquad \mathbf{z}(\mathbb{E}_g - \mathbb{E}_h) \geq 0$$

where equality holds if and only if Q, F, G, $\mathbb{E}_{gx}$ and $\mathbf{z}$ take zero value.

53.3 Processes of special systems

As in the case of quasi-stationary currents, instead of giving the complicated general treatment, we illustrate the processes of extended polarizable bodies by the following special example: the volume V_o and particle number N_o and the body are fixed, the environment is supposed to have constant temperature T_a, pressure P_a and electric field $\mathbb{E}_a$.

Furthermore, we assume that

$$\mathbb{P}_{in}(V, T, N, \mathbf{p}, \mathbb{E}_a) = \kappa \mathbb{E}_a, \tag{1}$$

where $\kappa > 0$ is constant,

$$\mathbb{E}_{gp}(V, T, N, \mathbf{p}) = -\frac{\delta \mathbf{p}}{V}, \tag{2}$$

where $\delta > 0$ is constant and

$$\mathbb{E}_{gx}(V, T, N, \mathbf{p}, \mathbf{r}) := -\frac{\alpha \mathbf{r}}{V}, \tag{3}$$

where $\alpha > 0$ is constant. Then

$$\mathbb{E}_g = -\frac{\delta\mathbf{p}}{V} - \frac{\alpha\mathbf{r}}{V}.$$

The dynamical quantititities are

$$Q = -\lambda(T - T_a), \qquad \mathbf{z} = -\frac{V}{\rho}(\hat{\mathbb{E}}_g - \mathbb{E}_h), \tag{4}$$

where $\lambda > 0$ and $\rho > 0$ are constant.

Let us recall that

$$\mathbb{E}_h = -\delta\kappa\mathbb{E}_a.$$

Then the dynamical equation reduced to the variables $(T, \mathbf{p}, \mathbf{r})$ is

$$\frac{\partial\mathcal{E}(V_\mathrm{o}, T, N_\mathrm{o}, \mathbf{p})}{\partial T}\dot{T} = -\lambda(T - T_a) + \frac{\alpha\mathbf{r}^2}{V_\mathrm{o}},$$

$$\dot{\mathbf{p}} = \mathbf{r}, \qquad \rho\dot{\mathbf{r}} = -\delta\mathbf{p} - \alpha\mathbf{r} + \delta\kappa V_\mathrm{o}\mathbb{E}_a. \tag{5}$$

The last two equations can be united in

$$\rho\ddot{\mathbf{p}} + \alpha\dot{\mathbf{p}} + \delta\mathbf{p} = \delta\kappa V_\mathrm{o}\mathbb{E}_a. \tag{6}$$

53.4 Constant or periodic exterior field

We have the same formal relations and equations as in Paragraph 46.3: L, R, γ and U_a are replaced with ρ, α, δ and $\delta\kappa V_\mathrm{o}\mathbb{E}_a$, respectively. Therefore, the results of Paragraphs 46.4 and 46.5 remain valid for constant and periodic exterior fields.

If the field is periodic, then both the dipole $\mathbf{p}$ of the body and the time rate $\mathbf{r}$ of the dipole are sums of a periodic function and an exponentially damping function and this is true for the temperature, too, if specific heat is constant.

If $\mathbb{E}_a(t) = E_m \cos\omega t$ or with the use of complex quantities, $\tilde{\mathbb{E}_a}(t) = E_m e^{i\omega t}$, then the periodic solution has the form

$$\tilde{\mathbf{p}}(t) = \tilde{p}_m e^{i\omega t}$$

where

$$\frac{\tilde{p}_m}{V_\mathrm{o}} = \frac{\delta\kappa}{\omega\left(i\alpha - \left(\rho\omega - \frac{\delta}{\omega}\right)\right)} E_m. \tag{$*$}$$

Thus the real solution is

$$\mathbf{p}(t) = |\tilde{p}_m| \sin(\omega t + \phi),$$

where

$$\mathrm{tg}\phi := \frac{\alpha}{\rho\omega - \frac{\delta}{\omega}}.$$

53.5 Complex susceptance

The coefficient of E_m in $(*)$ of the previous paragraph can be considered as a complex susceptance; this is real if and only if $\alpha = 0$.

Similarly to 46.5.2, we get for the average heating

$$-\overline{Q} = \frac{\delta^2\kappa^2 V_\text{o}^2 E_m^2 \alpha}{2\omega^2\left(\alpha^2 + \left(\omega\rho - \frac{\delta}{\omega}\right)^2\right)}.$$

Energy dissipation (the average heating) depends essentially on the imaginary part of the complex susceptance: the less the imaginary part compared to the real part, the less the heating.

It might be strange that here the imaginary part plays a similar role to the real part of complex resistance for alternating currents. The complex susceptance, however, is analogous to the complex capacity (see Exercise 3 of 46.6) and not to the complex resistance, and the imaginary part of the complex capacity is proportional to the ohmic resistance.

53.6 Exercises

1. Define complex susceptibility, describe its actual form and give a relation between complex susceptance and complex susceptibility.

2. Admit arbitrary induced polarization instead of (3) in 53.3 and prove that in the case of a constant electric field the equilibrium is asymptotically stable if $1 - d > 0$ and is instable if $1 - d < 0$, where d is the quantity introduced in 52.2.

54 Magnetizable bodies

54.1 Magnetic field of a magnetized body

Electromagnetic field is produced by electric charges and electromagnetic dipoles. An electromagnetic dipole appears to an observer (a body) as an electric dipole and a magnetic dipole. Previously, we have treated electric dipoles, now we come to magnetic dipoles, called generally magnetic momentums. We can repeat what we said in Paragraph 48.1: magnetic momentums resting with respect to the body produce only magnetic fields. Magnetic momentum is the extensive quantity, magnetic field is the intensive quantity characterizing magnetism from a thermodynamical point of view though the latter does not have all the usual properties of an intensive quantity.

Magnetic momentums and magnetic fields are usually considered to be space vectors though they are in fact antisymmetric tensors; their units are Ăm^2 abd V̆s/m^2, respectively. Magnetization, the density of magnetic momentums has the unit Ă/m.

Let us recall the following elementary knowledge of magnetostatics.

Let us take a ball with homogeneous magnetization $\mathbb{M}$. The magnetic field produced by this magnetization will be homogeneous inside the ball having value

$2\mathbb{M}/3$; in particular, the magnetization and the produced magnetic field have equal directions (outside the body the magnetic field is not homogeneous).

More generally, if an ellipsoid is endowed with a homogeneous magnetization parallel to an axis of the ellipsoid, then the produced magnetic field in the body is proportional to the magnetization (so is homogeneous). The magnetic field produced by homogeneous magnetization in bodies of other form is not homogeneous. We shall consider in the sequel as if a homogeneous magnetization in a body produced a homogeneous magnetic field in the body.

54.2 Magnetization in an exterior field

A body can be magnetized (similarly to polarization) in two ways:

1) The molecules have no intrinsic magnetic momentum but an exterior magnetic field, modifying the currents inside the molecules, induces magnetic momentums that are more or less parallel to the exterior field; these microscopic magnetic momentums result in a macroscopic magnetization.

2) The molecules have an intrinsic magnetic momentum whose macroscopic effect – the magnetization of the body – depends on the average direction of the magnetic momentums; if the magnetic moments are totally disordered (the average direction is zero), then no macroscopic magnetization is observed. Exterior magnetic field orders the magnetic moments, so it induces a magnetization. Magnetization – ordered magnetic moments – can exist even without an exterior field (ferromagnetic and ferrimagnetic materials).

We have essentially repeated what we said for polarization but there is a significant difference in item 1).

An electric field moves a positive charge in the direction of the field and moves a negative charge oppositely. Thus **the direction of the dipole of a molecule induced by an exterior field equals the direction of the field**.

We know that a current i running around a surface area F has a magnetic momentum iF whose direction is such that vectors of the current, the radius and the magnetic momentum are right handed. If such a circle-current is put into a magnetic field having the same direction as the magnetic moment, then the Lorentz force displaces the current towards the centre, the encircled area becomes smaller, so the magnetic momentum decreases.

The electron movements in the molecules can be roughgly considered as circle-currents. If the magnetic momentums of such circle-currents (and the spins of the electrons) give zero resultant magnetic momentum, then the molecules do not have intrinsic magnetic momentum. An exterior magnetic field decreases the magnetic momentum of circle-currents having the same direction as the field has and increases the magnetic momentum of circle-currents having opposite direction. Thus (if spin plays a negligible role) **the direction of the magnetic moment of a molecule induced by an exterior field is opposite to the direction of the field**.

The magnetic moment due to the spin of electrons can modify the situation, so it may happen that the induced magnetic moment and the exterior field have the same direction.

Thus the magnetic moment induced by a magnetic field can either have opposite or equal direction to the direction of the field. If the directions are opposite, the magnetic field in the body becomes smaller than the exterior field; if the directions coincide, then the magnetic field in the body becomes larger than the exterior field.

54.3 Fundamental assumptions

We can repeat what we said in Paragraph 48.2: magnetization strongly depends on exterior effects, changes due to action at a distance. Therefore, we do not deal with systems consisting of more bodies. As in the electric case,

– **we shall examine only a single body in a homogeneous exterior magnetic field (which can depend on time)**,

– **the magnetic field in the body produced by a homogeneous magnetization is taken to be parallel to the magnetization and to have the same direction**,

– **the magnetization induced in the body by an exterior field is considered to be parallel to the field**.

Consequently, the magnetic fields, the magnetization and magnetic momentum can be considered as scalar quantities, so their symbols will represent values with respect to a given direction (the value can either be positive or negative).

54.4 The Clausius–Mosotti formula

The Clausius–Mosotti formula for materials whose molecules do not have intrinsic magnetic moment can be derived on the analogy to the electric case. Let $\mathbb{M}$ be the equilibrium magnetization of the body in a homogeneous exterior field $\mathbb{B}_a$. Let us suppose that the magnetic moment $\mathbf{m}_m$ of a molecule is proportional to the magnetic field $\mathbb{B}_m$ acting on the molecule; let $-\alpha < 0$ be the proportionality coefficient. If $\mathbb{B}$ is the magnetic field in the body, then the 'cavity method' applied in Paragraph 48.4 – if the piece corresponding to the cavity produces magnetic field $\delta_c\mathbb{M}$ – results in that the field acting on a molecule becomes

$$\mathbb{B} - \delta_c\mathbb{M}.$$

The proportionality

$$\mathbf{m}_m = -\alpha(\mathbb{B} - \delta_c\mathbb{M})$$

gives for the magnetization $\mathbb{M} = \mathbf{m}_m v$

$$\mathbb{M} = \chi\mathbb{B},$$

where

$$\chi := -\frac{\alpha}{v - \alpha\delta_c}$$

is the **magnetic susceptibility**.

If the magnetic field produced by the body equals $\delta\mathbb{M}$ (which is true if the body is an ellipsoid), then

$$\mathbb{B} = \mathbb{B}_a + \delta\mathbb{M},$$

thus

$$\mathbb{M} = \kappa \mathbb{B}_a,$$

where

$$\kappa := \frac{\chi}{1-\delta\chi} = \frac{-\alpha}{v + \alpha(\delta - \delta_c)}$$

is the **magnetic susceptance**.

The classical formula is obtained for ball cavities when $\delta_c = 2/3$,thus

$$\chi = -\frac{3\alpha}{3v - 2\alpha},$$

or

$$\frac{3\chi}{3-2\chi} = -\frac{\alpha}{v}.$$

Introducing the **magnetic permeability** $\mu := \frac{1}{1-\chi}$, we get the **Clausius–Mosotti formula**:

$$\frac{\mu - 1}{\mu + 1} = \frac{\alpha}{3v}.$$

54.5 Definition of a magnetizable body

Magnetization is the magnetic moment density. Thus if magnetization $\mathbb{M}$ is on the body of volume V, then the body has the magnetic moment

$$\mathbf{m} := \mathbb{M}V \in (\breve{\mathrm{A}}\mathrm{m}^2).$$

Definition $(D \times \mathbb{R}^+ \times (\breve{\mathrm{A}}\mathrm{m}^2), \mathfrak{e}_b, \mathcal{P}_b, \boldsymbol{\mu}_b, R, \mathcal{E}_m, \mathcal{P}_m, \boldsymbol{\mu}_m, \mathbb{B}_g, \mathbb{M}_{in})$ *is called a* **simple magnetizable body** *if* $(D, \mathfrak{e}_b, \mathcal{P}_b, \boldsymbol{\mu}_b, R)$ *is a simple material,*

$$\mathcal{E}_m : D \times \mathbb{R}^+ \times (\breve{\mathrm{A}}\mathrm{m}^2) \to (\mathrm{J})^+, \qquad \mathcal{P}_m : D \times \mathbb{R}^+ \times (\breve{\mathrm{A}}\mathrm{m}^2) \to (\mathrm{Pa}),$$

$$\boldsymbol{\mu}_m : D \times \mathbb{R}^+ \times (\breve{\mathrm{A}}\mathrm{m}^2) \to (\mathrm{J}), \qquad \mathbb{B}_g : D \times \mathbb{R}^+ \times (\breve{\mathrm{A}}\mathrm{m}^2) \to (\breve{\mathrm{V}}\mathrm{s}/\mathrm{m}^2)$$

are continuous functions, continuously differentiable on $R \times \mathbb{R}^+ \times (\breve{\mathrm{A}}\mathrm{m}^2)$,

– $T \mapsto \mathcal{E}_m(v, T, N, \mathbf{m})$ *is monotone increasing for all possible* v, N *and* $\mathbf{m}$,

– $v \mapsto \mathcal{P}_m(v, T, N, \mathbf{m})$ *is locally monotone decreasing for all possible* T, N *and* $\mathbf{m}$,

– $\mathbf{m}\mathbb{B}_g(v, T, N, \mathbf{m}) > 0$ *if* $\mathbf{m} \neq 0$ *and* $\mathbf{m} \mapsto \mathbb{B}_g(v, T, N, \mathbf{m})$ *is strictly monotone increasing for all possible* v, T *and* N, *having everywhere positive derivative, furthermore,*

$$\mathcal{E}_m(v,T,N,0){=}0, \quad \mathcal{P}_m(v,T,N,0){=}0, \quad \boldsymbol{\mu}_m(v,T,N,0){=}0, \quad \mathbb{B}_g(v,T,N,0){=}0$$

for all elements (v, T, N) *of* $D \times \mathbb{R}^+$,
lastly,

$$\mathbb{M}_{in} : D \times \mathbb{R}^+ \times (\breve{\mathrm{A}}\mathrm{m}^2) \times (\breve{\mathrm{V}}\mathrm{s}/\mathrm{m}^2) \to (\breve{\mathrm{A}}/\mathrm{m}),$$

is a continuous function, continuously differentiable on $R \times \mathbb{R}^+ \times (\breve{\mathrm{A}}\mathrm{m}^2) \times (\breve{\mathrm{V}}\mathrm{s}/\mathrm{m}^2)$ *such that* $\mathbb{B}_a \mapsto \mathbb{M}_{in}(v, T, N, \mathbf{m}, \mathbb{B}_a)$ *is strictly monotonic (increasing or decreasing) for all possible* v, T, N *and* $\mathbf{m}$, *having everywhere non-zero derivative.*

$\mathbb{B}_g$ *is the* **magnetic field produced by the body**

$$\mathcal{E}(v,T,N,\mathbf{m}) := N\mathfrak{e}_b(v,T) + \mathcal{E}_m(v,T,N,\mathbf{m}),$$
$$\mathcal{P}(v,T,N,\mathbf{m}) := \mathcal{P}_b(v,T) + \mathcal{P}_m(v,T,N,\mathbf{m}),$$
$$\mu(v,T,N,\mathbf{m}) := \mu_b(v,T) + \mu_m(v,T,N,\mathbf{m})$$

are the **internal energy***, the* **pressure** *and the* **chemical potential***, respectively, of the body.*

$\mathbb{M}_{in}$ *is the* **magnetization induced by the exterior field**.

As a consequence of the definition, the inequalities

$$\frac{\partial\mathcal{E}}{\partial T} > 0, \qquad \frac{\partial\mathcal{P}}{\partial v} < 0, \qquad \frac{\partial\mathbb{B}_g}{\partial\mathbf{m}} > 0$$

hold on the regular domain $R \times \mathbb{R}^+ \times (\breve{\mathrm{A}}\mathrm{m}^2)$.

The **magnetic susceptance** of the body

$$\kappa(v,T,N,\mathbf{m},\mathbb{B}_a) := \frac{\partial\mathbb{M}_{in}(v,T,N,\mathbf{m},\mathbb{B}_a)}{\partial\mathbb{B}_a}$$

is defined if $(v,T) \in R$.

The present definition is nearly an exact copy of the definition of a polarizable body. There are two differences: 1. The produced electric field is a decreasing function of polarization whereas the produced magnetic field is an increasing function of magnetization. 2. The induced polarization is an increasing function of the exterior field whereas the induced magnetization can either be an increasing or a decreasing function of the exterior field.

The induced magnetization has the same physical meaning as induced polarization: **the equilibrium magnetization realized by a constant exterior field from an initial magnetization**; thus

$$\frac{\mathbf{m}}{V} = \mathbb{M}_{in}(V,T,N,\mathbf{m},\mathbb{B}_a)$$

holds for the equilibrium magnetic moment. Here and often in the sequel, as in the electric case, we find it convenient to use the entire volume instead of the specific volume and *applying the customary ambiguous notation, we shall write either v or V as a variable in a function.*

We emphasize again that we can define only a magnetizable body, not a material because the quantities connected to magnetism cannot be described by specific data. The definition involves the material of the body which is related to the thermodynamical quantities only.

54.6 Canonical variables, entropic property

We can repeat what we said about polarizable bodies: temperature can be expressed as a function of internal energy, volume, particle number and magnetic moment, in other words, we can use the canonical variables $(E,V,N,\mathbf{m})$.

Entropic property is defined similarly by replacing $\mathbf{p}$ with $\mathbf{m}$ and $-\mathbb{E}_g$ with $\mathbb{B}_g$; the different signs correspond to the rule in Paragraph 16.3.

It is doubtful, here again, whether entropic property is a really good requirement, because of arguments similar to those in Paragraph 50.2.

54.7 Conventional magnetizable body

Based on the known results of magnetostatics, the magnetic field $\mathbb{B}_g$ produced by a magnetization $\mathbb{M}$ can be taken proportional to the magnetization (cf. 54.1), the proportionality coefficient can depend on the thermodynamical state of the body. Moreover, the magnetostatical energy density is $\frac{1}{2}\mathbb{B}_g \cdot \mathbb{M}$, thus the energy density is proportional to the square of the magnetic moment. These suggest the following definition.

Definition *The magnetizable body defined in 54.5 is called* **conventional** *if there are continuous functions η, π, ξ and γ defined on $D \times \mathbb{R}^+$ (mapping into convenient measure lines), continuously differentiable on $R \times \mathbb{R}^+$ so that*

$$\mathcal{E}_m(V,T,N,\mathbf{m}) := \frac{\eta(V,T,N)\mathbf{m}^2}{2}, \qquad \mathcal{P}_m(V,T,N,\mathbf{m}) := \frac{\pi(V,T,N)\mathbf{m}^2}{2},$$

$$\mu_m(V,T,N,\mathbf{m}) := \frac{\xi(V,T,N)\mathbf{m}^2}{2}, \qquad \mathbb{B}_g(V,T,N,\mathbf{m}) := \gamma(V,T,N)\mathbf{m}.$$

γ is positive because the produced magnetic field is a strictly monotone increasing function of magnetization. $\delta := \gamma V$ is the **demagnetization factor** of the body.

This corresponds exactly to a conventional polarizable body: $\mathbf{p}$ and $-\mathbb{E}_g$ are replaced with $\mathbf{m}$ and $\mathbb{B}_g$, respectively.

54.8 Two customary conditions

In practice one always takes $\mathbb{B}_g = \gamma\mathbf{m} = \delta\mathbb{M}$ and $\mathcal{E}_m = \frac{1}{2}\mathbb{B}_g\mathbf{m} = \frac{\gamma\mathbf{m}^2}{2}$. Moreover, γ is considered to be independent of temperature. For a conventional body these assumptions give

$$\eta = \gamma, \qquad \frac{\partial\gamma}{\partial T} = 0.$$

As a generalization, we suppose in the sequel that

$$\frac{\partial\mathcal{E}}{\partial\mathbf{m}} = \mathbb{B}_g, \qquad \frac{\partial\mathbb{B}_g}{\partial T} = 0. \tag{$*$}$$

54.9 Exercises

Formulate the counterpart of the exercises in 48.11.

55 Induced magnetization

55.1 Diamagnetic and paramagnetic bodies

The Clausius–Mosotti formula shows that for certain bodies (whose molecules do not have intrinsic magnetic moment) the induced magnetization in equilibrium is proportional to the exterior field.

Definition *A simple magnetizable body is called* **diamagnetic** *or* **paramagnetic** *if there is a continuous function* $\kappa : D \times \mathbb{R}^+ \to \mathbb{R}^-$ *or* $\mathbb{R}^+$*, respectively, continuously differentiable on* $R \times \mathbb{R}^+$ *and*

$$\mathbb{M}_{in}(v, T, N, \mathbf{m}, \mathbb{B}_a) = \kappa(v, T, N)\mathbb{B}_a.$$

In other words, a magnetizable body is diamagnetic or paramagnetic if its susceptance (see 54.5) does not depend on the exterior field and the magnetic moment (or magnetization) of the body.

The names may seem curious because in electricity the positive susceptance (the only possibility) is di(a)electric whereas in magnetism the negative susceptance is diamagnetic. The dielectric and diamagnetic bodies have in common the property that **the produced field is opposite to the exterior field**, in other words, the field in the body becomes smaller than the exterior field.

The equilibrium magnetization $\mathbb{M}$ of a diamagnetic or paramagnetic body is

$$\mathbb{M} = \kappa \mathbb{B}_a. \tag{$*$}$$

If the body is conventional, then

$$\mathbb{B} = \mathbb{B}_a + \delta \mathbb{M},$$

is the magnetic field in the body, thus we get

$$\mathbb{M} = \chi \mathbb{B}, \tag{$**$}$$

for the **equilibrium magnetization** where

$$\chi := \frac{\kappa}{1 + \delta\kappa}$$

is the **magnetic susceptibility**. It is worth noting the inverse relation, too:

$$\kappa = \frac{\chi}{1 - \delta\chi}.$$

We have to bear in mind that κ, δ and χ are functions of (v, T, N).

We emphasize that equalities $(*)$ and $(**)$ are valid only in equilibrium, and we can repeat the warning in Paragraph 49.1.

In the usual literature some notions and formulae regarding susceptibility are confused as in the case of electricity. Moreover, earlier (and sometimes even nowadays) one takes erroneously $\mathbb{H}$ instead of $\mathbb{B}$, i.e. one writes $\mathbb{M} = \chi \mathbb{H}$ though arguments based on the molecular structure of materials clearly show that magnetization is proportional to $\mathbb{B}$.

55.2 Langevin–Weiss induced magnetization

For bodies whose molecules have an intrinsic magnetic moment, a formula similar to that in Paragraph 49.2 can be deduced; if the intrinsic magnetic moment of a molecule is π, then with the notations $\lambda := \delta - \delta_c$ and $\mathbb{M} := \mathbf{m}/V$ we get the **Langevin–Weiss formula**:

$$\mathbb{M}_{in}(v,T,N,\mathbf{m},\mathbb{B}_a) = \frac{1}{v}\left(-\alpha(\mathbb{B}_a+\lambda(v,T,N)\mathbb{M})+\pi L\left(\frac{\pi(\mathbb{B}_a+\lambda(v,T,N)\mathbb{M})}{kT}\right)\right).$$

A body whose induced magnetization is given by the above formula, is called a **Langevin–Weiss body**.

55.3 Approximate solution of the Langevin–Weiss equation

The actual magnetization of the body and the induced magnetization are equal in equilibrium, thus the equilibrium magnetization of a Langevin–Weiss body is determined by the Langevin–Weiss equation

$$\mathbb{M} = \frac{1}{v}\left(-\alpha(\mathbb{B}_a + \lambda\mathbb{M}) + \pi L\left(\frac{\pi(\mathbb{B}_a + \lambda\mathbb{M})}{kT}\right)\right).$$

Using the properties of the Langevin function (see 49.3), we get for $\pi(\mathbb{B}_a + \lambda\mathbb{M}) \ll kT$ that

$$\mathbb{M} \approx \frac{1}{v}\left(-\alpha(\mathbb{B}_a + \lambda\mathbb{M}) + \frac{\pi^2}{3kT}(\mathbb{B}_a + \lambda\mathbb{M})\right).$$

Thus, if

$$\lambda\left(-\alpha + \frac{\pi^2}{3kT}\right) \neq v,$$

we can define the equilibrium susceptance:

$$\kappa(v,T,N) \approx \frac{-\alpha + \frac{\pi^2}{3kT}}{v - \lambda(v,T,N)\left(-\alpha + \frac{\pi^2}{3kT}\right)}.$$

Taking $\lambda = 0$, we obtain the formula

$$\kappa \approx \frac{1}{v}\left(-\alpha + \frac{\pi^2}{3kT}\right)$$

known in the literature.

On the other hand, taking $\alpha = 0$, $\lambda \neq 0$ and putting

$$C := \frac{\pi^2}{3k}, \qquad \Theta(v,T,N) := \frac{C\lambda(v,T,N)}{v},$$

we arrive at the **Curie–Weiss formula**

$$\kappa(v,T,N) \approx \frac{1}{v}\frac{C}{T - \Theta(v,T,N)}.$$

The susceptibility has a similar form; with the notation

$$\hat{\Theta} := \Theta + \frac{\delta C}{v} = \frac{C(\lambda + \delta)}{v}$$

we have

$$\chi(v,T,N) \approx \frac{1}{v}\frac{C}{T-\hat{\Theta}(v,T,N)}.$$

Note that both Θ and $\hat{\Theta}$ can depend on the thermodynamical state of the body which is seldom mentioned in the usual literature.

55.4 Examination of the Langevin–Weiss equation

Let us study the solutions of the Langevin–Weiss equation for a given (v,T,N), excluding the trivial case $\lambda(v,T,N)=0$ and let $\alpha=0$ for the sake of simplicity (the case $\alpha\neq 0$ can be treated in the same way, only the combination of constants will be more complicated). Using the notation Θ introduced in the previous paragraph and

$$r := \frac{\mathbb{B}_a}{\pi\lambda}, \qquad x := \frac{\pi(\mathbb{B}_a+\lambda\mathbb{M})}{kT},$$

we can rewrite the equation in the form

$$\frac{T}{3\Theta}x - r = L(x).$$

The solutions are given by the points that the straight line determined by the left-hand side and the graph of the Langevin function have in common. We know (see Paragraph 49.3) that $L'(x) < L'(0) = 1/3$ if $x \neq 0$; as a consequence, if $T \geq \Theta$, then the straight line meets the graph of L in a single point: there is a unique solution. If $T < \Theta$, then there are two or three solutions. Two solutions exist if the straight line touches and then cuts the curve; three solutions exist if the straight line cuts the curve in three points (Figure 55.1).

If there are three solutions, x_-, x_m and x_+ so that $x_- < x_m < x_+$, then the slope of the curve in the middle solution is larger than the slope of the straight line and the slopes in the other two solutions are less, i.e.

$$L'(x_m) > \frac{T}{3\Theta}, \qquad L'(x_\pm) < \frac{T}{3\Theta}.$$

If there are two solutions, x_t and x_c where x_t corresponds to the touching point, then

$$L'(x_t) = \frac{T}{3\Theta}, \qquad L'(x_c) < \frac{T}{3\Theta}.$$

If there is only one solution x_c, then

$$L'(x_c) < \frac{T}{3\Theta}.$$

In particular, there are three solutions if $T < \Theta$ and $r = 0$: $x_- = -x_+$ and $x_m = 0$. $r = 0$ means that the exterior magnetic field is zero. The magnetization corresponding to the non-zero solutions is called spontaneous magnetization. Thus, the Langevin–Weiss equation gives account of the well-known experimental fact that bodies of certain materials (e.g. iron) can have equilibrium magnetization even if the exterior field is zero.

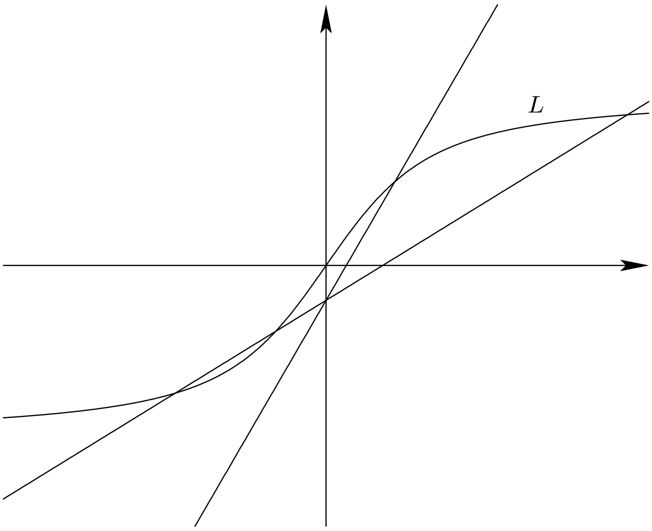

Figure 55.1

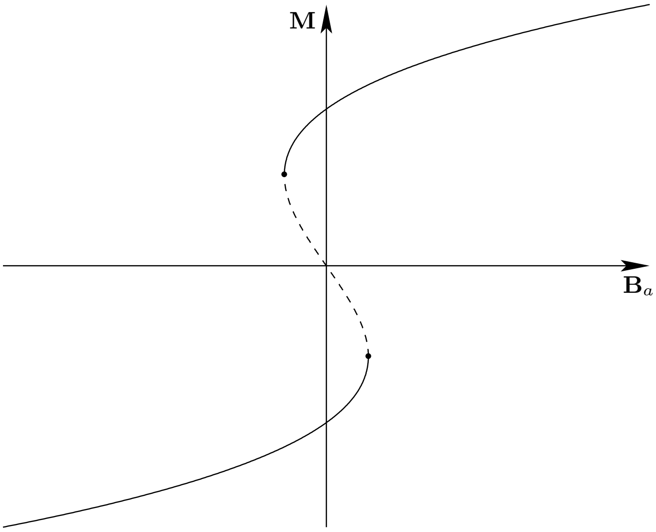

Figure 55.2

Figure 55.2 illustrates the possible equilibrium magnetizations in the presence of a given exterior field. The continuous lines contains the pairs $(\mathbb{B}_a, \mathbb{M})$ for which

$$L'\left(\frac{\pi(\mathbb{B}_a + \lambda\mathbb{M})}{kT}\right) < \frac{T}{3\Theta},$$

the dashed line contains the pairs for which

$$L'\left(\frac{\pi(\mathbb{B}_a + \lambda\mathbb{M})}{kT}\right) > \frac{T}{3\Theta}$$

and the circles show the points for which

$$L'\left(\frac{\pi(\mathbb{B}_a + \lambda\mathbb{M})}{kT}\right) = \frac{T}{3\Theta}.$$

55.5 Exercises

1. Corresponding to Paragraph 50.1, define the equilibrium constitutive functions for the variables $(v, T, N, \mathbb{B}_a)$ with the aid of the equilibrium magnetic moment$(v, T, N, \mathbb{B}_a) \mapsto \mathbf{m}_{eq}(v, T, N, \mathbb{B}_a)$. Define the equilibrium susceptibility in general.

2. Formulate and solve the exercise corresponding to Exercise 2 in 50.4.

3. If specific volume in the previous exercise depends negligibly on the magnetic field, then the specific volume $\boldsymbol{v}$ of the material of the body can be used as a function of temperature and pressure.

Take the ‘reference values’ T_0 and P_0 (say the temperature and the pressure of the atmosphere) and put $v_0 := \boldsymbol{v}(T_0, P_0)$,

$$\alpha_0 := -\frac{1}{v_0}\frac{\frac{\partial \mathcal{P}_b}{\partial T}}{\frac{\partial \mathcal{P}_b}{\partial v}}(v_0, T_0), \qquad \kappa_0 := -\frac{1}{v_0}\frac{1}{\frac{\partial \mathcal{P}_b}{\partial v}}(v_0, T_0)$$

(α_0 is the isothermal expansion coefficient and κ_0 is the isothermal compressibility factor, and, of course, they have nothing to do with the proportionality coefficient for molecular magnetic moments and susceptance denoted by the same letters). Then

$$\boldsymbol{v}(T, P) = v_0\big(1 + \alpha_0(T - T_0) - \kappa_0(P - P_0)\big) + \mathrm{ordo}(T - T_0, P - P_0).$$

Give an explicit formula how susceptibility and susceptance depend on temperature and pressure near to the reference values.

4. Define magnetizable bodies considering the magnetic quantities as vectors (antisymmetric tensors) (cf. 50.3).

56 Processes of a magnetizable body

56.1 Dynamical equation, dynamical quantitities

A process of a magnetizable body in a given environment is a function $t \mapsto \big(E(t), V(t), N(t), \mathbf{m}(t)\big)$ defined on a time interval obeying the dynamical equation

$$\dot{E} = Q - PF + \mu G + \mathbb{B}_g\mathbf{r},$$

$$\dot{V} = F, \qquad \dot{N} = G, \qquad \dot{\mathbf{m}} = \mathbf{r}$$

(in the ideal case, see Paragraph 16.3) where the dynamical quantitities Q, F, G and $\mathbf{r}$ are given as functions of the state of the body and the state of the environment. For instance, if the environment is characterized by its temperature T_a, pressure P_a (which determine the chemical potential μ_a) and by the exterior field $\mathbb{B}_a$, then the heating is a function

$$(E, V, N, \mathbf{m}, T_a, P_a, \mathbb{B}_a) \mapsto \mathbf{Q}(E, V, N, \mathbf{m}, T_a, P_a, \mathbb{B}_a)$$

or

$$(V, T, N, \mathbf{m}, T_a, P_a, \mathbb{B}_a) \mapsto \mathcal{Q}(V, T, N, \mathbf{m}, T_a, P_a, \mathbb{B}_a).$$

56.2 Equilibrium properties, thermodynamical force

If the environment is constant, then an equilibrium of the body is a constant process in which every dynamical quantity takes zero value.

Equilibrium is characterized – from a magnetic point of view – by the fact that the actual magnetization of the body equals the induced magnetization. Thus we accept that if no constraint is imposed on the processes, then $(V_o, T_o, N_o, \mathbf{m}_o)$ is an equilibrium if and only if

$$T_o = T_a, \qquad \mathcal{P}(V_o, T_o, N_o, \mathbf{m}_o) = P_a, \qquad \boldsymbol{\mu}(V_o, T_o, N_o, \mathbf{m}_o) = \mu_a,$$

$$\frac{\mathbf{m}_o}{V_o} = \mathbb{M}_{in}(V_o, T_o, N_o, \mathbf{m}_o, \mathbb{B}_a).$$

Let us introduce, similarly to the electric case, the (fictitious) magnetic field $\mathbb{B}_h$ produced by the induced magnetization, i.e.

$$\mathbb{B}_h(V, T, N, \mathbf{m}, \mathbb{B}_a) := \mathbb{B}_g(V, T, N, V\mathbb{M}_{in}(V, T, N, \mathbf{m}, \mathbb{B}_a)).$$

Then (with the customary symbolic notations)

$$\big(-(T - T_a), P - P_a, -(\mu - \mu_a), -(\mathbb{B}_g - \mathbb{B}_h)\big)$$

is the **thermodynamical force** acting on the body and

$$\left(\frac{1}{T} - \frac{1}{T_a}, \frac{P}{T} - \frac{P_a}{T_a}, -\left(\frac{\mu}{T} - \frac{\mu_a}{T_a}\right), -\left(\frac{\mathbb{B}_g}{T} - \frac{\mathbb{B}_h}{T_a}\right)\right)$$

is the **canonical thermodynamical force**.

We should point out as in the electric case, that here the last member of the thermodynamical force is not the difference of a quantity concerning the body only and a quantity concerning the environment only: $\mathbb{B}_h$ depends on the body state, too. Moreover, the sign of the last member of the thermodynamical force is opposite to that of the corresponding member in Paragraph 51.2 because the polarization and the produced electric field have opposite directions whereas the magnetization and the produced magnetic field have equal directions.

Pseudolinear dynamical quantitities are defined as in 51.2, $\mathbb{E}_g - \mathbb{E}_h$ replaced with $-(\mathbb{B}_g - \mathbb{B}_h)$.

The equilibrium properties of the dynamical quantitities specify the connection among the zero value of the dynamical quantitities and that of the thermodynamical force which is formulated intuitively as follows:

The zero value of the dynamical quantitities describing the admitted interactions (which characterizes equilibrium) imply the zero value of the corresponding thermodynamical force (the effective thermodynamical force), and the zero value of the thermodynamical force belonging to the admitted interactions implies the zero value of the corresponding dynamical quantitities.

A precise formulation is rather complicated even for neutral bodies and is more complicated for magnetizable bodies. Therefore, we do not give it in details; by the way, it is not worth doing so because homogeneity is a too strong assumption for electromagnetic phenomena. We shall formulate the equilibrium properties in each special case treated in the sequel.

56.3 Dissipation inequality

The dissipation inequality – on the analogy of earlier inequalities – is required in the form

$$-\frac{Q}{T}(T-T_a)+F(P-P_a)-G(\mu-\mu_a)-\mathbf{r}(\mathbb{B}_g-\mathbb{B}_h)\geq 0,$$

where equality holds if and only if all the dynamical quantitities take zero value. Equivalently,

$$(Q-PF+\mu G-\mathbb{E}_g\mathbf{r})\left(\frac{1}{T}-\frac{1}{T_a}\right)+ \\ +F\left(\frac{P}{T}-\frac{P_a}{T_a}\right)-G\left(\frac{\mu}{T}-\frac{\mu_a}{T_a}\right)+\mathbf{r}\left(\frac{\mathbb{B}_g}{T}-\frac{\mathbb{B}_h}{T_a}\right)\geq 0.$$

56.4 Magnetic cooling

Magnetostriction, a well-known experimental fact, can be treated as electrostriction (see 51.4); as a consequence, we get that $\partial\mathcal{P}/\partial\mathbf{m}<0$.

Another interesting phenomenon is that the adiabatic decreasing of magnetization results in a temperature decrease which gives an efficient method for cooling near absolute zero temperature: a large magnetization is induced in the body by a strong magnetic field at constant temperature; then the body gets heat insulated, the exterior field is switched off and the body pressure is kept constant. The magnetization collapses and the body cools.

This is described as follows.

The body has fixed particle number, constant pressure P_a and is heat insulated. Thus the relation

$$\frac{\partial\mathcal{P}}{\partial V}\dot{V}+\frac{\partial\mathcal{P}}{\partial T}\dot{T}+\frac{\partial\mathcal{P}}{\partial\mathbf{m}}\dot{\mathbf{m}}=0,$$

the first law

$$\dot{E}=-P_a\dot{V}+\mathbb{B}_g\dot{\mathbf{m}}$$

and the customary condition

$$\frac{\partial \mathcal{E}}{\partial \mathbf{m}} = \mathbb{B}_g$$

yield that

$$\left(\frac{\partial \mathcal{E}}{\partial T} + \left(P_a + \frac{\partial \mathcal{E}}{\partial V}\right)\frac{\frac{\partial \mathcal{P}}{\partial T}}{-\frac{\partial \mathcal{P}}{\partial V}}\right)\dot{T} = \left(P_a + \frac{\partial \mathcal{E}}{\partial V}\right)\frac{-\frac{\partial \mathcal{P}}{\partial \mathbf{m}}}{-\frac{\partial \mathcal{P}}{\partial V}}\dot{\mathbf{m}}.$$

The coefficient of $\dot{T}$ is the specific heat at constant pressure which can be supposed positive. If the expansion heat is positive, then the coefficient of $\dot{\mathbf{m}}$ is positive as well. Thus $\dot{T}$ and $\dot{\mathbf{m}}$ have the same sign. Decreasing magnetization causes decreasing temperature.

56.5 On the negative temperature

Absolute temperature is defined in such a way that zero is the smallest temperature value. Sometimes, however, one asserts that negative temperature can be achieved in special circumstances by increasing temperature beyond plus infinity.

The argument is the following. Take a body whose molecules have an intrinsic magnetic moment and put it in an exterior field. The field induces magnetization on the body by ordering the molecular dipoles in the direction of the field. Temperature influences the ordering; if the temperature increases, then the ordering decreases, at ‘infinite’ temperature the disorder is complete, magnetization disappears (this is reflected in the Curie–Weiss law, too).

Now let us consider the situation from the point of view of energy. The magnetic moment $\mathbf{m}$ in the magnetic field $\mathbb{B}_a$ has energy $-\mathbb{B}_a\mathbf{m}$: this increases as $\mathbf{m}$ decreases. Let $\mathbb{B}_a > 0$. If $\mathbf{m} > 0$ (magnetization and the exterior field have the same direction), then the decrease of $\mathbf{m}$ – the increase of energy – means the increase of disorder. On the contrary, if $\mathbf{m} < 0$ (magnetization and the exterior field have opposite directions), then the increase of $\mathbf{m}$ – the decrease of energy – means the increase of disorder. According to statistical physics, entropy is a measure of disorder. Thus if the magnetization and the exterior field have the same direction, then the increase of energy implies the increase of entropy. On the contrary, if the magnetization and the exterior field have opposite directions, then the decrease of energy implies the increase of entropy. As a consequence, in the latter case the partial derivative of entropy (at constant volume) with respect to energy is negative, so because of

$$\frac{\partial \mathbf{S}}{\partial E} = \frac{1}{\mathbf{T}}, \tag{$*$}$$

the temperature, too, is negative. Thus negative temperature is achieved in a simple way: put a magnetizable body in an exterior field, wait until it is magnetized and then reverse the direction of the field abruptly.

One usually says that a state with negative temperature is unstable, a process starts in which the body passes into a state with positive temperature but not through the zero temperature but the infinite temperature; the states with negative temperature are ‘beyond’ plus infinity.

Such an argument for the negative temperature is mistaken for more reasons.

First: The relation between entropy and disorder appears intuitively without exact formulae. Perhaps this flaw could be eliminated.

Second: The temperature of a body is the property of the body alone (at least up to now) but now it would be a common property of the body and the exterior field because it depends on the mutual direction of the magnetization and the field. Nothing changes in the body, only the direction of the exterior field is reversed, and does the temperature become negative? If it does, the temperature depends on the exterior field; then the entropy, too, must depend on the exterior field because of the equality $(*)$. But there is no hint in the argument that entropy, the measure of disorder, depends on the exterior field.

Third: The energy and the internal energy are confused. The internal energy, the entropy and the temperature of the body have the known relation $(*)$ (if the body is entropic) and the internal energy cannot be replaced with another energy. The magnetic part of internal energy comes from the magnetic interaction of the molecules. Besides this internal energy the body can have a magnetic potential energy because of an exterior field; this energy, however, is not a part of internal energy. An analogy: the energy of molecules deriving from their gravitation interaction is a part of internal energy but their potential energy due to the gravitation of the earth is not a part of internal energy. The quantity $-\mathbb{B}_a\mathbf{m}$ in the argument is the magnetic potential energy which is not a part of internal energy; the magnetic internal energy $\frac{1}{2}\mathbb{B}_g\mathbf{m}$ is independent of the exterior field.

Fourth: The argument is based on usual treatments in which every formula refers to equilibrium when the magnetization of the body and the exterior field are related, $\mathbb{M} = \kappa\mathbb{B}_a$ (the body is paramagnetic). In the argument, however, the magnetization and the exterior field are independent.

Fifth: Formulae valid exclusively in equilibrium are applied for non-equilibrium. Let us see it more closely, it is very instructive.

Saying that the exterior field orders the magnetic moments and so induces a magnetization, and saying that smaller magnetization corresponds to higher temperature, one has in mind equilibrium. As in Paragraph 50.2, we can give an equilibrium relation

$$(V, T, N, \mathbb{B}_a) \mapsto \mathbb{M}_{eq}(V, T, N, \mathbb{B}_a),$$

which for non-zero $\mathbb{B}_a$ is a strictly monotonically decreasing function of T and tends to zero az T tends to infinity (see Paragraph 55.3). This is all right but is not true outside equilibrium.

The internal energy, the entropy (if exists!) and the temperature of the body having magnetic moment $\mathbf{m}$ are well-defined quantities regardless the exterior field, they are the same in every exterior field. The negative temperature, on the cited arguments, is a false notion.

If a magnetizable body is in equilibrium in an exterior field and the field is reversed abruptly, then the quantities of the body (temperature, internal energy, etc.) remain unchanged but a non-equilibrium or possibly an unstable equilibrium is established, thus a process starts tending to an asymptotic stable equilibrium (where the magnetization and the exterior field have the same direction) as we shall see in the next paragraph.

57 Some special systems

57.1 General formulae

As said, it is not reasonable to suppose that a magnetizable body is entropic. On the analogy of Paragraph 52.1, we can treat several systems consisting of a body with constant particle number N_o in a given environment having constant temperature T_a, pressure P_a and homogeneous magnetic field $\mathbb{B}_a$.

We accept the relations in 54.8 implying that if temperature is used as a variable, then the first law will have the form

$$\frac{\partial \mathcal{E}}{\partial T}\dot{T} = Q - \left(P + \frac{\partial \mathcal{E}}{\partial V}\right)\dot{V}.$$

57.2 Fixed volume

The volume has the fixed value V_o and the dynamical equation reduced to the variables T and $\mathbf{m}$ is very simple:

$$\frac{\partial \mathcal{E}}{\partial T}\dot{T} = Q \qquad \dot{\mathbf{m}} = \mathbf{r}.$$

Let us suppose that

$$Q = -\lambda_Q(T - T_a) + \rho_Q(\mathbb{B}_g - \mathbb{B}_h), \qquad \mathbf{r} = -\lambda_{\mathbf{R}}(T - T_a) + \rho_r(\mathbb{B}_g - \mathbb{B}_h), \qquad (*)$$

where λ_Q, ρ_Q, etc. are constant. The dissipation inequality gives

$$\lambda_Q > 0, \qquad \rho_r > 0, \qquad \lambda_Q\rho_r - \rho_Q\lambda_r > \frac{(\rho_Q - T\lambda_r)^2}{4T}.$$

The above form of the dynamical quantitities implies that $(T_o, \mathbf{m}_o)$ is an equilibrium of the reduced dynamical equation if and only if

$$T_o = T_a, \qquad \mathbf{m}_o = V_o\mathbb{M}_{in}(V_o, T_o, N_o, \mathbf{m}_o, \mathbb{B}_a).$$

If $(V_o/N_o, T_a)$ is in the regular domain, then the right-hand side of the reduced dynamical equation is differentiable, its derivative in the equilibrium is

$$\begin{pmatrix} -\frac{\lambda_Q - \rho_Q ba}{c} & -\frac{\rho_Q b(1-d)}{c} \\ -\lambda_r - \rho_r ba & -\rho_r b(1-d) \end{pmatrix},$$

where

$$c := \frac{\partial \mathcal{E}}{\partial T}(V_o, T_a, N_o, \mathbf{m}_o), \qquad b := \frac{\partial \mathbb{B}_g}{\partial \mathbf{m}}(V_o, T_a, N_o, \mathbf{m}_o),$$

$$a := \frac{\partial \mathbb{M}_{in}}{\partial T}(V_o, T_a, N_o, \mathbf{m}_o, \mathbb{B}_a), \qquad d := V\frac{\partial \mathbb{M}_{in}}{\partial \mathbf{m}}(V_o, T_a, N_o, \mathbf{m}_o, \mathbb{B}_a).$$

This matrix is formally the same as the one in 52.2, therefore, the conditions for asymptotic stability and instability are the same as well.

The question of stability–instability is decided essentially by the sign of $1 - d$. For a diamagnetic or paramagnetic body $d = 0$, thus the condition of stability is satisfied.

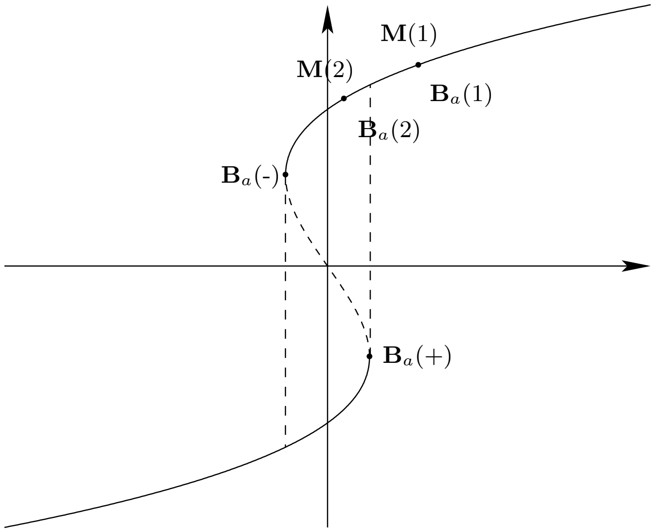

Figure 57.1

57.3 Hysteresis

Let us examine the stability conditions of the previous paragraph for a Langevin–Weiss body. Let us introduce the notation $\Theta_o := \Theta(V_o, T_a, N_o)$ and let us recall that if $T_a \geq \Theta_o$, then there is only one equilibrium magnetization; if $T_a < \Theta_o$, then there are two or three.

A simple calculation yields that

$$d = L'\left(\frac{\pi(\mathbb{B}_a + \lambda\mathbf{m}_o/V_o}{kT_a}\right)\frac{3\Theta_o}{T_a},$$

therefore, the sign of $1 - d$ equals the sign of

$$\frac{T_a}{3\Theta_o} - L'\left(\frac{\pi(\mathbb{B}_a + \lambda\mathbf{m}_o/V_o}{kT_a}\right).$$

Figure 55.2 shows the possible equilibrium magnetizations for given $\mathbb{B}_a$. According to Paragraph 55.4 we see that the equilibria on the continuous line are asymptotically stable, the equilibria on the dashed line are instable, and the linearization method does not give information about the stability–instability of the two equilibria corresponding to the circles.

Our result reflects the well-known phenomenon of hysteresis for $T_a < \Theta_o$. Let us consider a given $\mathbb{B}_a(1)$ to which the equilibrium magnetization $\mathbb{M}(1)$ corresponds on the upper continuous line in Figure 57.1. Let the exterior field decrease to $\mathbb{B}_a(2)$; then $\mathbb{M}(1)$ is not an equilibrium magnetization, so a process starts. Three equilibrium magnetizations correspond to $\mathbb{B}_a(2)$, the middle one is instable. The attraction domain of $\mathbb{M}(2)$ is above the dashed line. Thus, the process starting from $\mathbb{M}(1)$ tends to $\mathbb{M}(2)$. The same happens if the exterior field decreases until $\mathbb{B}_a(-)$. If the exterior field becomes less than this value, then the equilibrium magnetization 'jumps down' to the lower line, i.e. the process starting from a magnetization on the upper continuous line tends to an equilibrium on the lower continuous line. Similar statements are valid if we increase the exterior field corresponding to equilibria on the lower continuous line. The new equilibrium magnetization remain on the lower continuous line until the exterior remains less than $\mathbb{B}_a(+)$; if the exterior field becomes larger than this value, then the equilibrium magnetization 'jumps up' to the upper continuous line.

57.4 Theory and experience

The properties of a Langevin–Weiss body reflect well the experimental fact: bodies of certain materials (e.g. iron) can have magnetization without exterior field (spontaneous magnetization) and exhibit a hysteresis under a determined temperature (for higher temperaturethe hysteresis disappears). Materials not showing hysteresis are characterized by $\Theta < 0$.

The temperature Θ in which the spontaneous magnetization disappears is called the Curie temperature.

The bodies above the Curie temperature are paramagnetic as it is well seen by the formulae of 55.4. Of course, the Langevin–Weiss body draws only a qualitatively good picture of reality. The hysteresis curves in reality do not run vertically up and down; moreover, the zero spontaneous magnetization is unstable here which does not fit experience.

Three different behaviours can be distinguished below the Curie temperature: **ferromagnetic**, **ferrimagnetic** and **antiferromagnetic**. The Langevin–Weiss magnetization cannot give account of these behaviours.

57.5 Exercises

1. Treat the isobaric and isothermal processes of a magnetizable body with fixed particle number in a given environment.
2. Formulate Exercise 1 in 52.5 for a magnetizable body and solve it.
3. Define the extended magnetizable body, give the dynamical equation, the dissipation inequality for such a body in a given environment, and treat the processes in a periodic exterior field.

Tables of the most important relations

58 Simple materials

1. Formal symbols

e specific internal energy,
v specific volume,
T temperature,
P pressure,
μ chemical potential,
$s := \dfrac{e + Pv - \mu}{T}$ specific entropy,
$h := e + Pv = \mu + Ts$ specific enthalphy,
$f := e - Ts = \mu - Pv$ specific free energy.

Entropic property:

$$T\mathtt{d}s = \mathtt{d}e + P\mathtt{d}v.$$

Gibbs–Duhem relation (equivalent to the entropic property):

$$\mathtt{d}\mu = v\mathtt{d}P - s\mathtt{d}T.$$

2. Notations of functions

	variables (v, T)	variables (e, v)	variables (T, P)
specific internal energy	$\mathfrak{e}$	e	$\boldsymbol{e}$
specific volume	v	v	$\boldsymbol{v}$
temperature	T	$\mathbf{T}$	T
pressure	$\mathcal{P}$	$\mathbf{P}$	P
chemical potential	$\mathfrak{\mu}$	$\boldsymbol{\mu}$	μ
specific entropy	$\mathfrak{s}$	$\mathbf{s}$	$\boldsymbol{s}$
specific enthalpy	$\mathfrak{h}$	$\mathbf{h}$	$\boldsymbol{h}$
specific free energy	$\mathfrak{f}$	$\mathbf{f}$	$\boldsymbol{f}$

3. Relations among partial derivatives with respect to the variables (v, T) and the variables (e, v):

$$\frac{\partial \mathbf{T}}{\partial e} = \frac{1}{\frac{\partial \mathfrak{e}}{\partial T}}\bullet, \qquad \frac{\partial \mathbf{T}}{\partial v} = -\frac{\frac{\partial \mathfrak{e}}{\partial v}}{\frac{\partial \mathfrak{e}}{\partial T}}\bullet,$$

$$\frac{\partial \mathbf{P}}{\partial e} = \frac{\frac{\partial \mathcal{P}}{\partial T}}{\frac{\partial \mathfrak{e}}{\partial T}}\bullet, \qquad \frac{\partial \mathbf{P}}{\partial v} = \left(\frac{\partial \mathcal{P}}{\partial v} - \frac{\partial \mathcal{P}}{\partial T}\frac{\frac{\partial \mathfrak{e}}{\partial v}}{\frac{\partial \mathfrak{e}}{\partial T}}\right)\bullet,$$

$$\frac{\partial \mathfrak{e}}{\partial T} = \frac{1}{\frac{\partial \mathbf{T}}{\partial e}}\bullet, \qquad \frac{\partial \mathfrak{e}}{\partial v} = -\frac{\frac{\partial \mathbf{T}}{\partial v}}{\frac{\partial \mathbf{T}}{\partial e}}\bullet,$$

$$\frac{\partial \mathcal{P}}{\partial T} = \frac{\frac{\partial \mathbf{P}}{\partial e}}{\frac{\partial \mathbf{T}}{\partial e}}\bullet, \qquad \frac{\partial \mathcal{P}}{\partial v} = \left(\frac{\partial \mathbf{P}}{\partial v} - \frac{\partial \mathbf{P}}{\partial e}\frac{\frac{\partial \mathbf{T}}{\partial v}}{\frac{\partial \mathbf{T}}{\partial e}}\right)\bullet$$

4. Relations among partial derivatives with respect to the variables (v, T) and the variables (T, P) (in a phase):

$$\frac{\partial \boldsymbol{v}}{\partial P} = \frac{1}{\frac{\partial \mathcal{P}}{\partial v}}\bullet, \qquad \frac{\partial \boldsymbol{v}}{\partial T} = -\frac{\frac{\partial \mathcal{P}}{\partial T}}{\frac{\partial \mathcal{P}}{\partial v}}\bullet,$$

$$\frac{\partial \boldsymbol{e}}{\partial P} = \frac{\frac{\partial \mathfrak{e}}{\partial v}}{\frac{\partial \mathcal{P}}{\partial v}}\bullet, \qquad \frac{\partial \boldsymbol{e}}{\partial T} = \left(\frac{\partial \mathfrak{e}}{\partial T} - \frac{\partial \mathfrak{e}}{\partial v}\frac{\frac{\partial \mathcal{P}}{\partial T}}{\frac{\partial \mathcal{P}}{\partial v}}\right)\bullet,$$

$$\frac{\partial \mathcal{P}}{\partial v} = \frac{1}{\frac{\partial \boldsymbol{v}}{\partial P}}\bullet, \qquad \frac{\partial \mathcal{P}}{\partial T} = -\frac{\frac{\partial \boldsymbol{v}}{\partial T}}{\frac{\partial \boldsymbol{v}}{\partial P}}\bullet,$$

$$\frac{\partial \mathfrak{e}}{\partial v} = \frac{\frac{\partial \boldsymbol{e}}{\partial P}}{\frac{\partial \boldsymbol{v}}{\partial P}}\bullet, \qquad \frac{\partial \mathfrak{e}}{\partial T} = \left(\frac{\partial \boldsymbol{e}}{\partial T} - \frac{\partial \boldsymbol{e}}{\partial P}\frac{\frac{\partial \boldsymbol{v}}{\partial T}}{\frac{\partial \boldsymbol{v}}{\partial P}}\right)\bullet .$$

5. Conditions of intrinsic stability:
- in the variables (v, T):

$$\frac{\partial \mathfrak{e}}{\partial T} > 0, \qquad \frac{\partial \mathcal{P}}{\partial v} < 0;$$

- in the variables (e, v):

$$\frac{\partial \mathbf{T}}{\partial e} > 0, \qquad \frac{\partial \mathbf{P}}{\partial v}\frac{\partial \mathbf{T}}{\partial e} - \frac{\partial \mathbf{P}}{\partial e}\frac{\partial \mathbf{T}}{\partial v} = \det\mathtt{D}(\mathbf{T}, \mathbf{P}) < 0.$$

6. Entropic property
- in the variables (v, T):

$$T\frac{\partial \mathfrak{s}}{\partial T} = \frac{\partial \mathfrak{e}}{\partial T}, \qquad T\frac{\partial \mathfrak{s}}{\partial v} = \frac{\partial \mathfrak{e}}{\partial v} + \mathcal{P};$$

- in the variables (e, v):

$$\frac{\partial \mathbf{s}}{\partial e} = \frac{1}{\mathbf{T}}, \qquad \frac{\partial \mathbf{s}}{\partial v} = \frac{\mathbf{P}}{\mathbf{T}}.$$

The Gibbs–Duhem relation (equivalent to the entropic property):
– in the variables (v, T):

$$\frac{\partial \boldsymbol{\mu}}{\partial v} = v\frac{\partial \mathcal{P}}{\partial v}, \qquad \frac{\partial \boldsymbol{\mu}}{\partial T} = -\mathfrak{s} + v\frac{\partial \mathcal{P}}{\partial T};$$

– in the variables (T, P) (in a phase):

$$\frac{\partial \mu}{\partial T} = -\boldsymbol{s}, \qquad \frac{\partial \mu}{\partial P} = \boldsymbol{v}.$$

7. Necessary condition for entropic property if entropy is twice differentiable:
– in the variables (v, T):

$$T\frac{\partial \mathcal{P}}{\partial T} = \frac{\partial \mathfrak{e}}{\partial v} + \mathcal{P};$$

– in the variables (e, v):

$$\frac{\partial \mathbf{T}}{\partial v} = \mathbf{P}\frac{\partial \mathbf{T}}{\partial e} - \mathbf{T}\frac{\partial \mathbf{P}}{\partial e}.$$

8. The second derivative of specific entropy in the variables (e, v) for an entropic material:

$$\mathtt{D}^2\mathbf{s} = -\frac{1}{\mathbf{T}^2}\begin{pmatrix} \frac{\partial \mathbf{T}}{\partial e} & \frac{\partial \mathbf{T}}{\partial v} \\ \mathbf{P}\frac{\partial \mathbf{T}}{\partial e} - \mathbf{T}\frac{\partial \mathbf{P}}{\partial e} & \mathbf{P}\frac{\partial \mathbf{T}}{\partial v} - \mathbf{T}\frac{\partial \mathbf{P}}{\partial v} \end{pmatrix}.$$

This implies that

$$\det \mathtt{D}^2\mathbf{s} = -\frac{1}{\mathbf{T}^3}\det \mathtt{D}(\mathbf{T}, \mathbf{P}) > 0.$$

9. Thermal expansion property:

$$\left(\frac{\partial \mathfrak{e}}{\partial v} + \mathcal{P}\right)\frac{\partial \mathcal{P}}{\partial T} \geq 0.$$

10. Specific heats:

$$\mathfrak{c}_v = \frac{\partial \mathfrak{e}}{\partial T}, \qquad \mathfrak{c}_p = \mathfrak{c}_v + \left(\frac{\partial \mathfrak{e}}{\partial v} + \mathcal{P}\right)\frac{\frac{\partial \mathcal{P}}{\partial T}}{-\frac{\partial \mathcal{P}}{\partial v}} = \mathfrak{c}_v + T\frac{\left(\frac{\partial \mathcal{P}}{\partial T}\right)^2}{-\frac{\partial \mathcal{P}}{\partial v}};$$

the third equality holds for entropic material.

11. Noteworthy relations among certain partial derivatives if the material is entropic:
– in the variables (v, T):

$$\frac{\partial \mathfrak{f}}{\partial v} = -\mathcal{P}, \qquad \frac{\partial \mathfrak{f}}{\partial T} = -\mathfrak{s},$$

$$\mathfrak{e} = \mathfrak{f} - T\frac{\partial \mathfrak{f}}{\partial T};$$

– in the variables (T, P) (in a phase):

$$\frac{\partial \boldsymbol{h}(T, P)}{\partial T} = \boldsymbol{c}_p(T, P),$$

$$\boldsymbol{h} = \mu - \frac{\partial \mu}{\partial T}.$$

59 Simple bodies

1. Formal symbols:

N particle number,
$E = Ne$ (entire) internal energy,
$V = Nv$ (entire) volume,
$S := N\mathbf{s} = \frac{E+PV-\mu N}{T}$ (entire) entropy,
$H := Nh = E + PV = \mu N + TS$ (entire) enthalpy,
$F := Nf = E - TS = \mu N - PV$ (entire) free energy.

Entropic property:

$$T\mathtt{d}S = \mathtt{d}E + P\mathtt{d}V - \mu\mathtt{d}N.$$

Gibbs–Duhem relation (equivalent to the entropic property):

$$N\mathtt{d}\mu = V\mathtt{d}P - S\mathtt{d}T.$$

2. Notations of functions (the exclamation mark calls attention that the same letter denotes two different – but strongly related – functions):

– in the variables (V, T, N):

$\mathcal{E}$ internal energy	$\mathcal{E}(V,T,N) = N\mathfrak{e}(V/N,T)$
$\mathcal{P}$ pressure	$\mathcal{P}(V,T,N) = \mathcal{P}(V/N,T)$ (!)
$\upmu$ chemical potential	$\upmu(V,T,N) = \upmu(V/N,T)$ (!)
$\mathcal{S}$ entropy	$\mathcal{S}(V,T,N) = N\mathfrak{s}(V/N,T)$
$\mathcal{H}$ enthalpy	$\mathcal{H}(V,T,N) = N\mathfrak{h}(V/N,T)$
$\mathcal{F}$ free energy	$\mathcal{F}(V,T,N) = N\mathfrak{f}(V/N,T)$

– in the variables (E, V, N):

$\mathbf{T}$ temperature	$\mathbf{T}(E,V,N) = \mathbf{T}(E/N,V/N)$ (!)
$\mathbf{P}$ pressure	$\mathbf{P}(E,V,N) = \mathbf{P}(E/N,V/N)$ (!)
$\boldsymbol{\mu}$ chemical potential	$\boldsymbol{\mu}(E,V,N) = \boldsymbol{\mu}(E/N,V/N)$ (!)
$\mathbf{S}$ entropy	$\mathbf{S}(E,V,N) = N\mathbf{s}(E/N,V/N)$
$\mathbf{H}$ enthalpy	$\mathbf{H}(E,V,N) = N\mathbf{h}(E/N,V/N)$
$\mathbf{F}$ free energy	$\mathbf{F}(E,V,N) = N\mathbf{f}(E/N,V/N)$

3. Partial derivatives in the variables (V, T, N) (ambiguous notation: the variables (V, T, N) on the left-hand side and the variables (v, T) and N on the right-hand side):

$$\frac{\partial\mathcal{P}}{\partial V} = \frac{1}{N}\frac{\partial\mathcal{P}}{\partial v}, \qquad \frac{\partial\mathcal{P}}{\partial N} = \frac{1}{N}\left(-v\frac{\partial\mathcal{P}}{\partial v}\right),$$

and similar equalities for $\upmu$, too;

$$\frac{\partial\mathcal{E}}{\partial V} = \frac{\partial\mathfrak{e}}{\partial v}, \qquad \frac{\partial\mathcal{E}}{\partial T} = N\frac{\partial\mathfrak{e}}{\partial T}, \qquad \frac{\partial\mathcal{E}}{\partial N} = e - v\frac{\partial\mathfrak{e}}{\partial v},$$

and similar equalities for $\mathcal{S}$, $\mathcal{F}$ and $\mathcal{H}$.

If the body is entropic:

$$T\frac{\partial\mathcal{S}}{\partial V}=\frac{\partial\mathcal{E}}{\partial V}+\mathcal{P},\qquad T\frac{\partial\mathcal{S}}{\partial T}=\frac{\partial\mathcal{E}}{\partial T},\qquad T\frac{\partial\mathcal{S}}{\partial N}=\frac{\partial\mathcal{E}}{\partial N}-\mu,$$

$$\frac{\partial\mathcal{F}}{\partial V}=-\mathcal{P},\qquad \frac{\partial\mathcal{F}}{\partial T}=-\mathcal{S},\qquad \frac{\partial\mathcal{F}}{\partial N}=\mu,$$

$$\mathcal{E}=\mathcal{F}-T\frac{\partial\mathcal{F}}{\partial T}.$$

4. Partial derivatives in the variables (E,V,N) (ambiguous notation: the variables (E,V,N) on the left-hand side and the variables (e,v) and N on the right-hand side):

$$\frac{\partial\mathbf{T}}{\partial E}=\frac{1}{N}\frac{\partial\mathbf{T}}{\partial e},\qquad \frac{\partial\mathbf{T}}{\partial V}=\frac{1}{N}\frac{\partial\mathbf{T}}{\partial v},\qquad \frac{\partial\mathbf{T}}{\partial N}=\frac{1}{N}\left(-e\frac{\partial\mathbf{T}}{\partial e}-v\frac{\partial\mathbf{T}}{\partial v}\right),$$

and similar equalities for $\mathbf{P}$ and $\boldsymbol{\mu}$, too;

$$\frac{\partial\mathbf{S}}{\partial E}=\frac{\partial\mathbf{s}}{\partial e},\qquad \frac{\partial\mathbf{S}}{\partial V}=\frac{\partial\mathbf{s}}{\partial v},\qquad \frac{\partial\mathbf{S}}{\partial N}=\mathbf{s}-e\frac{\partial\mathbf{s}}{\partial e}-v\frac{\partial\mathbf{s}}{\partial v},$$

and similar equalities for $\mathbf{H}$ and $\mathbf{F}$, too.

If the body is entropic:

$$\frac{\partial\mathbf{S}}{\partial E}=\frac{1}{\mathbf{T}},\qquad \frac{\partial\mathbf{S}}{\partial V}=\frac{\mathbf{P}}{\mathbf{T}},\qquad \frac{\partial\mathbf{S}}{\partial N}=-\frac{\boldsymbol{\mu}}{\mathbf{T}}.$$

5. The second derivative of the entropy in the variables (E,V,N) for an entropic body:

$$\mathtt{D}^2\mathbf{S}=-\frac{1}{\mathbf{T}^2}\begin{pmatrix}\frac{\partial\mathbf{T}}{\partial E} & \frac{\partial\mathbf{T}}{\partial V} & \frac{\partial\mathbf{T}}{\partial N}\\ \mathbf{P}\frac{\partial\mathbf{T}}{\partial E}-\mathbf{T}\frac{\partial\mathbf{P}}{\partial E} & \mathbf{P}\frac{\partial\mathbf{T}}{\partial V}-\mathbf{T}\frac{\partial\mathbf{P}}{\partial V} & \mathbf{P}\frac{\partial\mathbf{T}}{\partial N}-\mathbf{T}\frac{\partial\mathbf{P}}{\partial N}\\ -\boldsymbol{\mu}\frac{\partial\mathbf{T}}{\partial E}+\mathbf{T}\frac{\partial\boldsymbol{\mu}}{\partial E} & -\boldsymbol{\mu}\frac{\partial\mathbf{T}}{\partial V}+\mathbf{T}\frac{\partial\boldsymbol{\mu}}{\partial V} & -\boldsymbol{\mu}\frac{\partial\mathbf{T}}{\partial N}+\mathbf{T}\frac{\partial\boldsymbol{\mu}}{\partial N}\end{pmatrix}.$$

60 Composite materials (mixtures, solutions)

1. Formal symbols:

e specific internal energy,
v specific volume,
$c=(c^1,\dots,c^n)$ concentrations,
T temperature,
P pressure,
μ^α chemical potential of the α-th component in the mixture,

$g := \sum_{\alpha=1}^{m} \mu^\alpha c^\alpha$ specific Gibbs function,
$s := \dfrac{e + Pv - g}{T}$ specific entropy,
$h := e + Pv = g + Ts$ specific enthalpy,
$f := e - Ts = g - Pv$ specific free energy.

Entropic property:

$$T\mathtt{d}s = \mathtt{d}e + P\mathtt{d}v - \sum_{\alpha=1}^{m} \mu^a \mathtt{d}c^\alpha.$$

The Gibbs–Duhem relation (equivalent to the entropic property):

$$\sum_{\alpha=1}^{m} c^\alpha \mathtt{d}\mu^\alpha = -s\mathtt{d}T + v\mathtt{d}P,$$

or

$$\mathtt{d}g = -s\mathtt{d}T + v\mathtt{d}P + \sum_{\alpha=1}^{m} \mu^\alpha \mathtt{d}c^\alpha.$$

2. Notation of functions in the variabales (v, T, c), in the variables (e, v, c) and in the variabales (T, P, c) is the same as for simple materials, i.e. $\mathfrak{e}$, $\mathbf{T}$, $\boldsymbol{v}_Z$ etc.; furthermore, the notation of the Gibbs function (in the given order of the variables):

$$\mathfrak{g}, \qquad \mathbf{g}, \qquad \boldsymbol{g}.$$

3. Entropic property
– in the variables (v, T, c):

$$T\frac{\partial \mathfrak{s}}{\partial T} = \frac{\partial \mathfrak{e}}{\partial T}, \qquad T\frac{\partial \mathfrak{s}}{\partial v} = \frac{\partial \mathfrak{e}}{\partial v} + \mathcal{P}, \qquad T\frac{\partial \mathfrak{s}}{\partial c} = \frac{\partial \mathfrak{e}}{\partial c} - [\mathfrak{\mu}^1, \dots, \mathfrak{\mu}^m];$$

– in the variables (e, v, c):

$$\frac{\partial \mathbf{s}}{\partial e} = \frac{1}{\mathbf{T}}, \qquad \frac{\partial \mathbf{s}}{\partial v} = \frac{\mathbf{P}}{\mathbf{T}}, \qquad \frac{\partial \mathbf{s}}{\partial c} = -\frac{[\boldsymbol{\mu}^1, \dots, \boldsymbol{\mu}^m]}{\mathbf{T}}.$$

The Gibbs–Duhem relation (equivalent to the entropic property):
– in the variables (v, T, c):

$$\sum_{\alpha=1}^{m} c^\alpha \frac{\partial \mathfrak{\mu}^\alpha}{\partial v} = v\frac{\partial \mathcal{P}}{\partial v}, \qquad \sum_{\alpha=1}^{m} c^\alpha \frac{\partial \mathfrak{\mu}^\alpha}{\partial T} = -\mathfrak{s} + v\frac{\partial \mathcal{P}}{\partial T},$$

or

$$\frac{\partial \mathfrak{g}}{\partial v} = v\frac{\partial \mathcal{P}}{\partial v}, \qquad \frac{\partial \mathfrak{g}}{\partial T} = -\mathfrak{s} + v\frac{\partial \mathcal{P}}{\partial T}, \qquad \frac{\partial \mathfrak{g}}{\partial c} = v\frac{\partial \mathcal{P}}{\partial c} + [\mathfrak{\mu}^1, \dots, \mathfrak{\mu}^m];$$

– in the variables (T, P, c) (locally in a phase):

$$\sum_{\alpha=1}^{m} c^\alpha \frac{\partial \mu^\alpha}{\partial T} = -\boldsymbol{s}, \qquad \sum_{\alpha=1}^{m} c^\alpha \frac{\partial \mu^\alpha}{\partial P} = \boldsymbol{v},$$

or

$$\frac{\partial \boldsymbol{g}}{\partial T} = -\boldsymbol{s}, \quad \frac{\partial \boldsymbol{g}}{\partial P} = \boldsymbol{v}, \qquad \frac{\partial \boldsymbol{g}}{\partial c} = [\mu^1, \dots, \mu^n].$$

4. Noteworthy relations among certain partial derivatives if the mixture is entropic:

– in the variables (v, T, c):

$$\frac{\partial \mathfrak{f}}{\partial v} = -\mathcal{P}, \qquad \frac{\partial \mathfrak{f}}{\partial T} = -\mathfrak{s}, \qquad \frac{\partial \mathfrak{f}}{\partial c} = [\boldsymbol{\mu}^1, \dots, \boldsymbol{\mu}^n],$$

$$\mathfrak{e} = \mathfrak{f} - T\frac{\partial \mathfrak{f}}{\partial T};$$

– in the variables (T, P, c) (locally in a phase):

$$\frac{\partial \boldsymbol{h}(T, P, c)}{\partial T} = \boldsymbol{c}_p(T, P, c),$$

$$\boldsymbol{h} = \boldsymbol{g} - \frac{\partial \boldsymbol{g}}{\partial T}.$$

61 Composite bodies

1. Formal symbols:

N^α particle numberof the α-th component,
$N := \sum_{\alpha=1}^{n} N^\alpha$ entire particle number, $N^\alpha = Nc^\alpha$,
$E = Ne$ (entire) internal energy,
$V = Nv$ (entire) volume,
$G := Ng = \sum_{\alpha=1}^{m} \mu^\alpha N^\alpha$ (entire) Gibbs function,
$S := Ns = \dfrac{E + PV - G}{T}$ (entire) entropy,
$H := Nh = E + PV = G + TS$ (entire) enthalpy,
$F := Nf = E - TS = G - PV$ (entire) free energy.

Entropic property:

$$T\mathtt{d}S = \mathtt{d}E + P\mathtt{d}V - \sum_{\alpha=1}^{m} \mu^\alpha \mathtt{d}N^\alpha.$$

The Gibbs–Duhem relation (equivalent to the entropic property):

$$\sum_{\alpha=1}^{m} N^\alpha \mathtt{d}\mu^\alpha = -S\mathtt{d}T + V\mathtt{d}P,$$

or

$$\mathtt{d}G = -S\mathtt{d}T + V\mathtt{d}P + \sum_{\alpha=1}^{m} \mu^\alpha \mathtt{d}N^\alpha.$$

2. Notation of functions, $\overline{N} := (N^1, \dots, N^m)$ (the exclamation mark calls attention that the same letter denotes two different – but strongly related – functions):

– in the variables $(V, T, \overline{N})$:

$\mathcal{E}$ internal energy	$\mathcal{E}(V,T,\overline{N}) = N\mathfrak{e}(V/N, T, N^1/N, \dots, N^m/N)$
$\mathcal{P}$ pressure	$\mathcal{P}(V,T,\overline{N}) = \mathcal{P}(V/N, T, N^1/N, \dots, N^m/N)$ (!)
$\upmu^\alpha$ chemical potential of the α-th component	$\upmu^\alpha(V,T,\overline{N}) = \upmu^\alpha(V/N, T, N^1/N, \dots, N^m/N)$ (!)
$\mathcal{G}$ Gibbs function	$\mathcal{G}(V,T,\overline{N}) = N\mathfrak{g}(V/N, T, N^1/N, \dots, N^m/N)$
$\mathcal{S}$ entropy	$\mathcal{S}(V,T,\overline{N}) = N\mathfrak{s}(V/N, T, N^1/N, \dots, N^m/N)$
$\mathcal{H}$ enthalpy	$\mathcal{H}(V,T,\overline{N}) = N\mathfrak{h}(V/N, T, N^1/N, \dots, N^m/N)$
$\mathcal{F}$ free energy	$\mathcal{F}(V,T,\overline{N}) = N\mathfrak{f}(V/N, T, N^1/N, \dots, N^m/N)$

– in the variables $(E, V, \overline{N})$:

$\mathbf{T}$ temperature	$\mathbf{T}(E,V,\overline{N}) = \mathbf{T}(E/N, V/N, N^1/N, \dots, N^m/N)$ (!)
$\mathbf{P}$ pressure	$\mathbf{P}(E,V,\overline{N}) = \mathbf{P}(E/N, V/N, N^1/N, \dots, N^m/N)$ (!)
$\boldsymbol{\mu}^\alpha$ chemical potential of the α-th component	$\boldsymbol{\mu}^\alpha(E,V,\overline{N}) = \boldsymbol{\mu}^\alpha(E/N, V/N, N^1/N, \dots, N^m/N)$ (!)
$\mathbf{G}$ Gibbs function	$\mathbf{G}(E,V,\overline{N}) = N\mathbf{g}(E/N, V/N, N^1/N, \dots, N^m/N)$
$\mathbf{S}$ entropy	$\mathbf{S}(E,V,\overline{N}) = N\mathbf{s}(E/N, V/N, N^1/N, \dots, N^m/N)$
$\mathbf{H}$ enthalpy	$\mathbf{H}(E,V,\overline{N}) = N\mathbf{h}(E/N, V/N, N^1/N, \dots, N^m/N)$
$\mathbf{F}$ free energy	$\mathbf{F}(E,V,\overline{N}) = N\mathbf{f}(E/N, V/N, N^1/N, \dots, N^m/N)$

– in the variables $(T, P, V, \overline{N})$ (locally in a phase):

μ^α chemical potential of the α-th component	$\mu^\alpha(T,P,\overline{N}) = \mu^\alpha(T, P, N^1/N, \dots, N^m/N)$ (!)
$\boldsymbol{G}$ Gibbs function	$\boldsymbol{G}(T,P,\overline{N}) = N\boldsymbol{g}(T, P, N^1/N, \dots, N^m/N)$
$\boldsymbol{H}$ enthalpy	$\boldsymbol{H}(T,P,\overline{N}) = N\boldsymbol{h}(T, P, N^1/N, \dots, N^m/N)$

3. Partial derivatives in the variables $(V, T, \overline{N})$ with resepcet to V and T are the same as for simple bodies, furthermore, if the first $m-1$ concentrations are taken to be independent,

$$\frac{\partial \mathcal{P}}{\partial N^\beta} = \frac{1}{N}\left(-v\frac{\partial \mathcal{P}}{\partial v} + \frac{\partial \mathcal{P}}{\partial c^\beta} - \sum_{\gamma=1}^{m-1} c^\gamma \frac{\partial \mathcal{P}}{\partial c^\gamma}\right) \qquad (\beta = 1, \dots, m-1),$$

$$\frac{\partial \mathcal{P}}{\partial N^m} = \frac{1}{N}\left(-v\frac{\partial \mathcal{P}}{\partial v} - \sum_{\gamma=1}^{m-1} c^\gamma \frac{\partial \mathcal{P}}{\partial c^\gamma}\right),$$

and similar equalities for μ^α, too;

$$\frac{\partial \mathcal{E}}{\partial N^\beta} = \mathfrak{e} - v\frac{\partial \mathfrak{e}}{\partial v} + \frac{\partial \mathfrak{e}}{\partial c^\beta} - \sum_{\gamma=1}^{m-1} c^\gamma \frac{\partial \mathfrak{e}}{\partial c^\gamma} \qquad (\beta = 1, \dots, m-1),$$

$$\frac{\partial \mathcal{E}}{\partial N^m} = \mathfrak{e} - v\frac{\partial \mathfrak{e}}{\partial v} - \sum_{\gamma=1}^{m-1} c^\gamma \frac{\partial \mathfrak{e}}{\partial c^\gamma},$$

and similar euqalities for $\mathcal{S}$, $\mathcal{F}$ and $\mathcal{H}$, too.

If the body is entropic:

$$T\frac{\partial \mathcal{S}}{\partial V} = \frac{\partial \mathcal{E}}{\partial V} + \mathcal{P}, \qquad T\frac{\partial \mathcal{S}}{\partial T} = \frac{\partial \mathcal{E}}{\partial T}, \qquad T\frac{\partial \mathcal{S}}{\partial N^\alpha} = \frac{\partial \mathcal{E}}{\partial N^\alpha} - \mu^\alpha \quad (\alpha = 1, \dots, m),$$

$$\frac{\partial \mathcal{F}}{\partial V} = -\mathcal{P}, \qquad \frac{\partial \mathcal{F}}{\partial T} = -\mathcal{S}, \qquad \frac{\partial \mathcal{F}}{\partial N^\alpha} = \mu^\alpha \quad (\alpha = 1, \dots, m),$$

$$\mathcal{E} = \mathcal{F} - T\frac{\partial \mathcal{F}}{\partial T}.$$

4. Partial derivatives in the variables $(E, V, \overline{N})$ with respect to E and V are the same as for simple materials, furthermore, if the first $m-1$ concentrations are taken to be independent,

$$\frac{\partial \mathbf{T}}{\partial N^\beta} = \frac{1}{N}\left(-e\frac{\partial \mathbf{T}}{\partial e} - v\frac{\partial \mathbf{T}}{\partial v} + \frac{\partial \mathbf{T}}{\partial c^\beta} - \sum_{\gamma=1}^{m-1} c^\gamma \frac{\partial \mathbf{T}}{\partial c^\gamma}\right) \qquad (\beta = 1, \dots, m-1),$$

$$\frac{\partial \mathbf{T}}{\partial N^m} = \frac{1}{N}\left(-e\frac{\partial \mathbf{T}}{\partial e} - v\frac{\partial \mathbf{T}}{\partial v} - \sum_{\gamma=1}^{m-1} c^\gamma \frac{\partial \mathbf{T}}{\partial c^\gamma}\right),$$

and similar equalitries for $\mathbf{P}$ and $\boldsymbol{\mu}^\alpha$, too,

$$\frac{\partial \mathbf{S}}{\partial N^\beta} = \mathbf{s} - e\frac{\partial \mathbf{s}}{\partial e} - v\frac{\partial \mathbf{s}}{\partial v} + \frac{\partial \mathbf{s}}{\partial c^\beta} - \sum_{\gamma=1}^{m-1} c^\gamma \frac{\partial \mathbf{s}}{\partial c^\gamma} \qquad (\beta = 1, \dots, m-1),$$

$$\frac{\partial \mathbf{S}}{\partial N^m} = \mathbf{s} - v\frac{\partial \mathbf{s}}{\partial e} - v\frac{\partial \mathbf{s}}{\partial v} - \sum_{\gamma=1}^{m-1} c^\gamma \frac{\partial \mathbf{s}}{\partial c^\gamma},$$

and similar equalities for $\mathbf{H}$ and $\mathbf{F}$.

If the body is entropic:

$$\frac{\partial \mathbf{S}}{\partial E} = \frac{1}{\mathbf{T}}, \qquad \frac{\partial \mathbf{S}}{\partial V} = \frac{\mathbf{P}}{\mathbf{T}}, \qquad \frac{\partial \mathbf{S}}{\partial N^\alpha} = -\frac{\boldsymbol{\mu}^\alpha}{\mathbf{T}} \quad (\alpha = 1, \ldots, m).$$

5. Some important relations in the variables $(T, P, \overline{N})$:

$$\frac{\partial \boldsymbol{G}}{\partial T} = -\boldsymbol{S}, \qquad \frac{\partial \boldsymbol{G}}{\partial P} = \boldsymbol{V}, \qquad \frac{\partial \boldsymbol{G}}{\partial N^\alpha} = \mu^\alpha \quad (\alpha = 1, \ldots, m),$$

$$\boldsymbol{H} = \boldsymbol{G} - T\frac{\partial \boldsymbol{G}}{\partial T},$$

$$\frac{\partial \boldsymbol{H}(T, P, N^1 \ldots, N^m)}{\partial T} = N\boldsymbol{c}_p(T, P, \overline{N}).$$

Appendix

0 Equalities and equations

Serious misunderstandings can arise from the fact that equalities and equations, two different objects, denoted by similar symbols, are frequently confused.

First olf all, let us fix some elementary notations. Let A and B two sets; then $f : A \rightarrowtail B$ denotes a function whose domain, $\mathrm{Dom} f$ is a subset of A and its range, $\mathrm{Ran} f$ is a subset of B; if the domain of f equals A, we write $f : A \to B$.

0.1 Let us consider two functions, $f : A \rightarrowtail B$ and $g : A \rightarrowtail B$. The **equality**

$$g = f$$

means that we **assert** that the two functions are equal, i.e. $\mathrm{Dom} g = \mathrm{Dom} f$ and $g(x) = f(x)$ for all x in the common domain. One frequently writes

$$g(x) = f(x)$$

for expressing this equality.

For example,

$$\sin 2x = 2 \sin x \cos x$$

and

$$(x-2)(x-3) = x^2 - 5x + 6$$

are such equalities.

0.2 Let us consider two functions, $f : A \rightarrowtail B$ and $g : A \rightarrowtail B$. The **equation**

$$(x \in A)? \qquad g(x) = f(x) \tag{$*$}$$

means that we **define** the subset of A consisting of the elements, belonging to both $\mathrm{Dom} f$ and $\mathrm{Dom} g$, at which the two (different) functions g and f take the same values. In other words, the above equation means the set

$$\{x \in A \mid g(x) = f(x)\}.$$

One frequently writes simply

$$g(x) = f(x)$$

for expressing this equation, so eqality and equation appear in the same form.

A **solution** of the above equation is just an element of the set in question. There is no solution if the set is void and the solution is unique if the set is a singleton.

For example,

$$(x \in \mathbb{R})? \qquad \sin 2x = \sin x + \cos x$$

and

$$(x \in \mathbb{R})? \qquad (x-2)(x-3) = 2x^2 + 3$$

are such equations.

It may happen that the sets A and B consist of functions, thus f and g are functions of functions. For instance, let both A and B be the set of continuously differentiable functions defined on some interval of the real line and having values in a finite dimensional vector space X; so, if $x \in A$, then it is a function $x : \mathbb{R} \rightarrowtail X$ whose domain is an interval. Let $R : X \rightarrowtail X$ be a continuously differentiable function. Denoting the differentiation by a dot and putting $g(x) := \dot{x}$, $f(x) := R \circ x$, the equation $(*)$ gives a usual ordinary differential equation, for which we will use the notation

$$(x : \mathbb{R} \rightarrowtail X)? \qquad \dot{x} = R(x).$$

0.3 In the same sense, we must distinguish between **inequalities** and **inequations** for functions having real values.

The inequality

$$g < f$$

meanS that the two functions have the same domain, $\mathrm{Dom} g = \mathrm{Dom} f$, and $g(x) < f(x)$ for all x in the common domain.

The inequation

$$(x \in A)? \qquad g(x) < f(x)$$

means that we define the subset of A consisting of the elements, belonging to both $\mathrm{Dom} f$ and $\mathrm{Dom} g$, at which the the values of g are less than the values of f.

0.4. Lastly, we mention the defining equality $:=$ which means that an object – a set, a function etc. – arising in the text in a complicated or compound form and put on the side of $=$ will be denoted in the sequel by the simpler symbol appearing on the side of :. For example,

$$s(x) := \frac{\sin x + x^2}{x^2 + 3}.$$

1 Vector spaces and linear maps

1.1 The notions and elementary results regarding vector spaces and linear maps are supposed to be known. All the vector spaces in the following will be real and finite dimensional. The set of linear maps $X \to Y$ is denoted by $\mathrm{Lin}(X, Y)$.

If K is a linear subspace of the vector space X, then its translations, the sets of the form $x + K = \{x + m \mid m \in K\}$ $(x \in X)$ are called **affine subspaces** of X over K.

1.2 The **dual** of the vector space X is

$$X^* := \mathrm{Lin}(X, \mathbb{R}).$$

If $p \in X^*$ and $x \in X$, now we write $px = xp$ for the value of p at x.

A linear map $A : X \to X^*$ is **symmetric**, if $yAx = xAy$ for all $x, y \in X$; it is
– positive (negative) definite if $xAx > 0$ (< 0) for all $0 \neq x \in X$,
– positive (negative) semidefinite if $xAx \geq 0$ (≤ 0) for all $x \in X$.

We can define similarly that a linear map $X^* \to X$ is symmetric, positive definite, etc.

On the contrary, the notion of symmetricity, positive definiteness etc. are not meaningful for a linear map $X \to X$ or $X^* \to X^*$ unless an inner product is given on X.

If an inner product $<,>$ is given on X, then a linear map $L : X \to X$ is symmetric with respect to the inner product if $< y, Lx >=< Ly, x >=< x, Ly >$ for all $x, y \in X$, and it is positive definite with respect to the inner product if $< x, Lx > > 0$ for all $0 \neq x \in X$.

1.3 The real number λ is the **eigenvalue** of the linear map $L : X \to X$ if there is a non-zero vector $x \in X$ such that $Lx = \lambda x$.

The linear subspace $\{x \in X \mid Lx = \lambda x\}$ is called the **eigenspace** of L corresponding to λ.

The **geometric multiplicity** of an eigenvalue is the dimension of the corresponding eigenspace.

λ is an eigenvalue of L if and only if $\det(L - \lambda I) = 0$ where I is the identity map. The **algebraic multiplicity** of λ is the multiplicity of the root λ of the polynomial $\xi \mapsto \det(L - \xi I)$.

The geometric multiplicity is less or equal to the algebraic multiplicity.

We can define similary the eigenvalues, etc. of a linear map $X^* \to X^*$.

On the contrary, the notion of eigenvalue is not meaningful for a linear map $X \to X^*$ or $X^* \to X$.

1.4

Proposition *Let*
(i) $B \in \mathrm{Lin}(X^*, X)$ be symmetric and positive definite,
(ii) $F \in \mathrm{Lin}(X, X^*)$ be symmetric and negative semidefinite.
Then $BF \in \mathrm{Lin}(X, X)$ has the following properties:
– the algebraic and geometric multiplicities of all eigenvalues are equal,
– the non-zero eigenvalues are negative.

Proof Now $B^{-1} \in \mathrm{Lin}(X, X^*)$ is symmetric and positive definite, too. As a consequence,

$$(x, y) \mapsto < x, y > := (B^{-1}x)y$$

is an inner product on X. BF is symmetric and negative semidefinite with respect to this inner product because

$$< x, BFy >= (B^{-1}x)(BFy) = xFy = (Fx)y =< BFx, y >;$$

and

$$< x, BFx >= xFx \leq 0.$$

Then well-known results regarding linear operators in Euclidean spaces (vector spaces with inner product) imply our assertions.

1.5 Let K be a linear subspace of X and let $i : K \to X$ be the canonical (identity) embedding. Then $i^* : X^* \to K^*$ is the linear surjection defined by $i^*p = pi := p \circ i = p|_K$.

The **annullator** of K,

$$K^{\mathrm{o}} := \{p \in X^* \mid i^*p = 0\}$$

is a linear subspace in X^* and $\mathrm{dim}K^{\mathrm{o}} = \mathrm{dim}X - \mathrm{dim}K$.

In the following three propositions $B_K : K^* \to K$ is a given linear map and $B := iB_Ki^* : X^* \to X$.

Proposition 1 $\mathrm{Ker}B_K = \{0\}$ *if and only if* $\mathrm{Ker}B = K^{\mathrm{o}}$.

Proof $\mathrm{Ker}B_K = \{0\}$ is equivalent to $B_Ki^*p = 0$ if and only if $i^*p = 0$, i.e. $p \in K^{\mathrm{o}}$. Because i is injective the kernel of B_Ki^* equals the kernel of B.

Proposition 2 *B_K is symmetric if and only if if B is symmetric.*

Proof If B_K is symmetric, then

$$qBp = qiB_Ki^*p = (i^*q)B_K(i^*p) = (i^*p)B_K(i^*q) = pBq$$

for all $p, q \in X^*$. If B is symmetric, then – beacuse for all $h, k \in K^*$ there are $p, q \in X^*$ so that $h = i^*p$, $k = i^*q$ –,

$$kB_Kh = i^*qB_Ki^*p = qBp = pBq = hB_Kk.$$

Proposition 3 *B_K is positive semidefinite if and only if B is positive semidefinite.*

Proof If B is positive semidefinite, then – because for all $h \in K^*$ there is a $p \in X^*$ such that $h = i^*p$ –, $hB_Kh = i^*pB_Ki^*p = pBp \geq 0$. If B_K is positive semidefinite, then $pBp = piB_Ki^*p = (i^*p)B_K(i^*p) \geq 0$ for all $p \in X^*$.

In the following two propositons $B : X^* \to X$ is a given linear map.

Proposition 4 *If* $\mathrm{Ran}B \subset K$ *and B is symmetric, then there is a linear map $B_K : K^* \to K$ such that $iB_Ki^* = B$.*

Proof The linear map B_K is well defined by $B_Ki^*p := Bp$ $(p \in K)$ because if $i^*p_1 = i^*p_2$, then $(p_1 - p_2)B = 0$ and the the symmetricity of B implies $B(p_1 - p_2) = 0$ i.e. $B_Ki^*p_1 = B_Ki^*p_2$.

Proposition 5 *There is a linear map $B_K : K^* \to K$ such that $iB_Ki^* = B$ if and only if* $\mathrm{Ran}B \subset K$ *and* $K^{\mathrm{o}} \subset \mathrm{Ker}B$.

Proof The conditions are evidently necessary. If the conditons are satisfied, then $B_K i^* p := Bp$ $(p \in K^*)$ is a good definition because $i^* p = 0$ implies $Bp = 0$.

1.6 Let $m, n \in \mathbb{N}$ and $I_1, \dots, I_m$, $J_1, \dots, J_n$ one-dimensional real vector spaces. Then a linear map $L : \mathop{\times}\limits_{i=1}^{m} I_i \to \mathop{\times}\limits_{k=1}^{n} J_k$ can be represented by a matrix

$$\{L_{ki} \in J_k \otimes I_i^* \mid k = 1, \dots n,\ i = 1, \dots, m)$$

according to the usual rules of matrix multiplication.

In particular, if $m = n$, then L is square matrix. Its symmetricity makes sense only if $J_k = I_k^*$ for all $k = 1, \dots, n$ (or, equivalently, $I_i = J_i^*$ for all $i = 1, \dots, n$). Then the definiteness of such a matrix is determined by the sign of its minors in the known way.

2 Measure lines

The values of a physical quantity constitute a **measure line**, an oriented one-dimensional real vector space, i.e. every value is a unique multiple of an arbitrarily chosen non-zero element and the positive values are distinguished. For instance, the the measure line of distances is the multiple of 'meter' and the positive multiples have a physical meaning.

Thus if D is a measure line, then for all $0 < \mathrm{m} \in D$ we have $D = \{\alpha\mathrm{m} \mid \alpha \in \mathbb{R}\}$. The element m represents the unit of measurement. We find suitable to refer to a measure line by the corresponding unit, i.e. we shall write (m) instead of D; the positive and non-negative values will be denoted by $(\mathrm{m})^+$ and $(\mathrm{m})_0^+$, respectively; thus, $(\mathrm{m})^+ := \{\alpha\mathrm{m} \mid \alpha > 0\}$.

A precise meaning can be given for the product of measure lines, denoted by $\otimes$, which obeys the usual rules; e.g. $(m) \otimes (\mathrm{kg}) = (\mathrm{m\,kg})$.

The dual of a measure line is its "reciprocal"; e.g. $(\mathrm{m})^* = \left(\frac{1}{\mathrm{m}}\right)$. An element of a measure line, multiplied by an element of the dual, results in a real number. The division by a measure line is defined by the multiplication by the dual, e.g.

$$\frac{(\mathrm{m})}{(\mathrm{s})} := (\mathrm{m}) \otimes (1/\mathrm{s}) = \left(\frac{\mathrm{m}}{\mathrm{s}}\right).$$

3 Inverse function theorem and implicit function theorem

3.1 Let X and Y be finite dimensional vector spaces. The function $f : X \rightarrowtail Y$ is differentiable at the interior point a of its domain if there is a linear map $\mathtt{D}f(a) : X \to Y$ (the derivative of f at a) such that

$$\lim_{x \to a} \frac{f(x) - f(a) - \mathtt{D}f(a)(x - a)}{|x - a|} = 0,$$

where $|\ |$ is an arbitrary norm on X.

The derivative of f is the function $X \rightarrowtail \mathrm{Lin}(X, Y)$, $a \mapsto \mathtt{D}f(a)$. If this function is continuous, f is called continuously differentiable. If $\mathtt{D}f$ is differentiable, f

is called twice differentiable. The second derivative of f at a is a linear map $\mathtt{D}^2f(a) : X \to \mathrm{Lin}(X, Y)$ which is considered in the ususal way as a bilinear map $X \times X \to Y$.

Let X_1, X_2 and Y be finite dimensional vector spaces. The function $f : X_1 \times X_2 \rightarrowtail Y$ is partially differentiable with respect to the first variable at the interior point of its domain (a_1, a_2) if the function $X_1 \rightarrowtail Y$, $x_1 \mapsto f(x_1, a_2)$ is differentiable at a_1; this partial derivative is denoted by $\mathtt{D}_1 f(a_1, a_2)$ or $\partial_1 f(a_1, a_2)$. The partial derivative with respect to the second (third, fourth, etc. if there are more variables) variable is defined similarly.

3.2

Proposition (Inverse function theorem) *Let X and Y be vector spaces having equal finite dimension and $f : V \rightarrowtail U$ a continuously differentiable function. If $a \in \mathrm{Dom}f$ and $\mathtt{D}f(a)$ is injective, then a has a neighbourhood G such that $f|_G$ is injective, $f[G]$ is open and $(f|_G)^{-1}$ is continuously differentiable.*

Note that $\mathtt{D}f(a)$ is bijective because the vector spaces have equal dimension.

Proposition (Implicit function theorem) *Let X_1, X_2 and Y be finite dimensional vector spaces,* $\mathrm{dim}X_1 = \mathrm{dim}Y$ *and $f : X_1 \times X_2 \rightarrowtail Y$ a continuously differentiable function. If $(a_1, a_2) \in$* Dom$f$ *and $\mathtt{D}_1 f(a_1, a_2)$ is injective, then a_2 has a neighbourhood $G \subset X_2$ and there is a uniquely determined continuously differentiable function $\varphi : G \to X_1$ such that* Graph$\varphi \subset$ Dom$f$, *$\varphi(a_2) = a_1$ and*

$$f(\varphi(x_2), x_2) = f(a_1, a_2) \qquad (x_2 \in G);$$

furthermore,

$$\mathtt{D}\varphi(x_2) = -\left(\mathtt{D}_1 f(\varphi(x_2), x_2)\right)^{-1} \mathtt{D}_2 f(\varphi(x_2), x_2).$$

The implicit function theorem says that the given conditions allow us to express x_1 as function of x_2 (locally, in a neighbourhood of (a_1, a_2)) from the equation $f(x_1, x_2) = f(a_1, a_2)$.

3.3 For the sake of thermodyanamical applications, we formulate a special form of the above theorems.

Let $m, n \in \mathbb{N}$ and let $I_1, \dots, I_m$ and $J_1, \dots, J_n$ be one dimensional vector spaces.

If $f = (f_1, \dots, f_n) : \mathop{\mathsf{X}}_{i=1}^{m} I_i \rightarrowtail \mathop{\mathsf{X}}_{k=1}^{n} J_k$ is differentiable at $a = (a_1, \dots, a_m)$, then the matrix of the linear map $\mathtt{D}f(a) : \mathop{\mathsf{X}}_{i=1}^{m} I_i \to \mathop{\mathsf{X}}_{k=1}^{n} J_k$ is

$$\{\partial_i f_k(a_1, \dots, a_m) \mid k = 1, \dots n,\ i = 1, \dots, m\}.$$

In applications of the inverse function theorem $m = n$ and the injectivity of $\mathtt{D}f(a)$ is equalent to the fact that the determinant of the matrix

$$\{\partial_i f_k(a_1, \dots, a_n) \mid k, i = 1, \dots, n\}$$

is not zero.

In applications of the implicit function theorem $m > n$ and in view of the identification

$$\mathop{\times}_{i=1}^{m} I_k \equiv \left(\mathop{\times}_{i=1}^{n} I_k\right) \times \left(\mathop{\times}_{i=n+1}^{m} I_i\right),$$

the partial derivative of f with respect to the first n variables at $(a_1, \dots, a_m)$ is the linear map $\mathop{\times}_{i=1}^{n} I_i \to \mathop{\times}_{k=1}^{n} J_k$, whose matrix is

$$\{\partial_i f_k(a_1, \dots, a_m) \mid k = 1, \dots, n,\, i = 1, \dots, n\}. \tag{$*$}$$

Similarly, the partial derivative of f with respect to the last $m - n$ variables at the given point is the linear map $\mathop{\times}_{i=n+1}^{m} I_i \to \mathop{\times}_{k=1}^{n} J_k$ whose matrix is

$$\{\partial_i f_k(x_1, x_2) \mid k = 1, \dots, n,\, i = n+1, \dots, m\}.$$

The first n variables can be expessed as a function of the last $m - n$ variables if the determinant of the matrix $(*)$ is not zero.

Of course – by rearranging the variables – we can formulate a similar assertion for arbitrary n variables.

3.4 Now we consider a special form of the implicit function theorem in order to introduce a convention about notations. For the sake of simplicity, we take real functions. Let $\mathbb{R}^3 \rightarrowtail \mathbb{R}$, $\quad (x, y, z) \mapsto f(x, y, z)$ be a continuously differentiable function and let us suppose that $\partial_3 f(x_0, y_0, z_0) \neq 0$. Then there is a uniquely determined continuously differentiable function $\mathrm{z} : \mathbb{R}^2 \rightarrowtail \mathbb{R}$ defined in a neighbourhood of (x_0, y_0) such that $\mathrm{z}(x_0, y_0) = z_0$ and $f(x, y, \mathrm{z}(x, y)) = f(x_0, y_0, z_0)$ for all (x, y) in the domain of z.

The partial derivatives of z satisfy

$$\partial_i \mathrm{z}(x, y) = -\frac{\partial_i f(x, y, \mathrm{z}(x, y))}{\partial_3 f(x, y, \mathrm{z}(x, y))} \qquad (i = 1, 2)$$

As usual, these relations are written in the form

$$\frac{\partial \mathrm{z}}{\partial x} = -\frac{\frac{\partial f}{\partial x}}{\frac{\partial f}{\partial z}}, \qquad \frac{\partial \mathrm{z}}{\partial y} = -\frac{\frac{\partial f}{\partial y}}{\frac{\partial f}{\partial z}}.$$

This is, however, rather misleading becasue the function on the right-hand side is defined in $\mathbb{R}^3$ whereas the function on the left-hand side is defined in $\mathbb{R}^2$. Correctly the third variable on the right-hand side should be replaced with the implicit function z.

We shall use a similar notation, supplemented by the symbol $\bullet$ which reminds us of the fact that the right-hand side must be composed by the graph function $(x, y) \mapsto (x, y, \mathrm{z}(x, y))$:

$$\frac{\partial \mathrm{z}}{\partial x} = -\frac{\frac{\partial f}{\partial x}}{\frac{\partial f}{\partial z}} \bullet \qquad \frac{\partial \mathrm{z}}{\partial y} = -\frac{\frac{\partial f}{\partial y}}{\frac{\partial f}{\partial z}} \bullet .$$

4 Legendre transformation

Let X be a finite dimensional real vector space and $\Phi : X \rightarrowtail \mathbb{R}$ a twice continuously differentiable function. Then $\mathtt{D}\Phi : X \rightarrowtail X^*$ is continuously differentiable. Let us suppose that the linear map $\mathtt{D}^2\Phi(x) : X \to X^*$ is injective (consequently bijective) for all $x \in \mathrm{Dom} f$. Then the function

$$X \times X^* \rightarrowtail X^*, \qquad (x, p) \mapsto \mathtt{D}\Phi(x) - p$$

is continuously differentiable, its partial derivative with respect to the first variable, $D^2\Phi$ is everywhere injective, thus the implicit relation

$$\mathtt{D}\Phi(x) = p$$

allows us to express x locally as a function of p; such a function $\hat{x} : X^* \rightarrowtail X$ is continuously differentiable and

$$\mathtt{D}\hat{x}(p) = \big(\mathtt{D}\Phi(\hat{x}(p))\big)^{-1}. \tag{$*$}$$

Definition *The* **Legendre transform** *of* Φ *is*

$$\Psi : X^* \rightarrowtail \mathbb{R}, \qquad p \mapsto \Phi(\hat{x}(p)) - p\hat{x}(p).$$

Using well-known simple results of the differential calculus, we can easily prove:

Proposition Ψ *is twice continuously differentiable and*

$$\mathtt{D}\Psi = -\hat{x} \tag{$**$}$$

It is worth noting that equalities $(*)$ and $(**)$ imply: if $\mathtt{D}^2\Phi(\hat{x}(p))$ is negative definite, then $\mathtt{D}^2\Psi(p)$ is positive definite.

Let us repeat the above formulae in the usual loose way: we leave the variable x for its ‘conjugate’ variable

$$p = \frac{\partial \Phi}{\partial x}$$

meanwhile the function Φ is replaced with the function $\Psi = \Phi - px$ for which

$$-x = \frac{\partial \Psi}{\partial p}$$

holds.

5 Submanifolds

Let $n, m, k \in \mathbb{N}$, $m \leq n$. A subset U of the n dimensional vector space X is called an m**-dimensional** C^k**-submanifold** if for every point x of U there is a (local) **parameterization** $p : \mathbb{R}^m \rightarrowtail X$ such that

- p is injective and p^{-1} is continuous,
- p is k times continuously differentiable (thus also p is continuous),
- $\mathtt{D}p(\xi)$ is injective for all $\xi \in \mathrm{Dom}p$,

– $x \in \mathrm{Ran}p$.

A submanifold will mean a C^1-submanifold.

The m-dimensional linear subspace

$$T_x(U) := \mathrm{Ran}\mathtt{D}p(p^{-1}(x))$$

is called the **tangent space** of U at x. It can be shown that the tangent space is independent of the parameterization.

If $F : X \rightarrowtail \mathbb{R}^{n-m}$ is k times continuously differentiable, then for all $a \in \mathrm{Ran}F$

$$U_a := \{x \in \mathrm{Dom}F \mid F(x) = a,\ \mathtt{D}F(x) \text{ is surjective}\}$$

is a C_k-submanifold and

$$T_x(U_a) = \mathrm{Ker}\mathtt{D}F(x).$$

6 Differential equations

6.1 Let X be a finite dimensional vector space, $R : X \to X$ a continuously differentiable function.

The notions and elementary results regarding the differential equation

$$(x : \mathbb{R} \rightarrowtail X)? \qquad \dot{x} = R(x)$$

are supposed to be known.

6.2 Let $F : X \times \mathbb{R} \rightarrowtail X$ and $\phi, \psi : X \times \mathbb{R} \rightarrowtail \mathbb{R}$ be continuously differentiable functions such that

$$\frac{\partial \phi(x,\xi)}{\partial \xi} < 0.$$

If (a, α) is in the domain of the above functions and $\phi(a, \alpha) = 0$, then the implicit function theorem assures the existence of a continuously differentiable function $\hat{\xi} : X \rightarrowtail \mathbb{R}$ such that $\phi(x, \hat{\xi}(x)) = 0$.

Let us consider the differential equations

$$\big((x,\xi) : \mathbb{R} \rightarrowtail X \times \mathbb{R}\big)? \qquad \begin{aligned} \dot{x} &= F(x,\xi), \\ \sigma\dot{\xi} &= \phi(x,\xi) + \sigma\psi(x,\xi) \end{aligned} \tag{1}$$

for $\sigma > 0$ and

$$(x : \mathbb{R} \rightarrowtail X)? \qquad \dot{x} = F(x, \hat{\xi}(x)). \tag{2}$$

Let us suppose that there are positive numbers σ_0 and T so that for all $0 < \sigma < \sigma_0$ there are solutions

– $(r_\sigma, \rho_\sigma) : [0, T] \to X \times \mathbb{R}$ of the differential equation (1) with the initial condition $r_\sigma(0) = a$, $\rho_\sigma(0) = \alpha$,

– $r : [0, T] \to X$ of the differential equation (2) with the initial condition $r(0) = a$.

Then

$$\lim_{\sigma \to 0} r_\sigma(t) = r(t), \qquad \lim_{\sigma \to 0} \rho_\sigma(t) = \hat{\xi}(r(t))$$

for all $t \in [0, T]$.

7 Stability theory

7.1 Let us consider the differential equation

$$(x:\mathbb{R} \rightarrowtail X)? \qquad \dot{x} = R(x) \tag{$*$}$$

where $R : X \rightarrowtail X$ is a continuously differentiable function.

$x_{\mathrm{o}} \in \mathrm{Dom}R$ is called an *equilibrium* if $R(x_{\mathrm{o}}) = 0$. (In thermodynamics such an element is called a standstill, equilibrium is a special type of standstill.)

A subset U of $\mathrm{Dom}R$ is an *invariant set* of the differential equation if for all solutions r $\mathrm{Ran}r \cap U \neq \emptyset$ implies $\mathrm{Ran}r \subset U$.

Let U be an invariant set and $x_{\mathrm{o}} \in U$ an equilibrium.

The equilibrium x_{o} is **stable** in U if for all neighbourhood G of x_{o} there is another neighbourhood D such that every solution starting from $D \cap U$ runs in G (in fact in $G \cap U$ because of the invariance of U), i.e. if $r(t_0) \in D \cap U$, then $r(t) \in G \cap U$ for all $t > t_0$.

The equilibrium x_{o} is **asymptotically stable** in U if it is stable in U and x_{o} has a neighbourhood Δ such that $\lim\limits_{t\to\infty} r(t) = x_{\mathrm{o}}$ for all solutions r starting from $\Delta \cap U$.

A set E of equilibria in U is **strictly asymptotically stable** in U if all $x_{\mathrm{o}} \in E$

– is stable in U,

– has a neighbourhood Δ such that $\lim\limits_{t\to\infty} r(t) \in \overline{E}$ for all solutions R starting from $\Delta \cap U$.

Of course, $U = \mathrm{Dom}R$ is possible; then we do not say 'in U'.

7.2 The fundamental theorems of stability theory are the following.

Let $L : X \rightarrowtail \mathbb{R}$ be a continuously differentiable function and let us introduce the function

$$\overset{\bullet}{L} := \mathtt{D}L \cdot R : X \rightarrowtail \mathbb{R},$$

called the **derivative of L along the differential equation**.

If r is a solution of the differential equation, then

$$(L \circ r)^{\cdot} = \overset{\bullet}{L} \circ r.$$

If x_{o} is an equilibrium, then $\overset{\bullet}{L}(x_{\mathrm{o}}) = 0$.

Proposition 1 *Let x_{o} be an equilibrium of the differential equation $(*)$ in 7.1. If there is a continuously differentiable real function L defined in a neighbourhood of x_{o} such that*

– L has a strict local maximum at x_{o},

– $\overset{\bullet}{L}$ has a (strict) local minimum at x_{o},

then x_{o} is (asymptotically) stable.

If

– L has not a local maximum at x_{o},

– $\overset{\bullet}{L}$ has a strict local minimum at x_{o},

then x_{o} is instable.

Such an L is called a *Liapunov function* for the (asymptotic) stability or instability of the equilibrium.

Proposition 2 *Let $R(x) = Ax$ where $A : X \to X$ is a linear map and $Ax_o = 0$.*

(i) If the real part of every eigenvalue of A is negative, then x_o is an asymptotically stable equilibrium.

(ii) If A has an eigenvalue with positive real part, then x_o is an instable equilibrium.

(iii) If the real part of every eigenvalue of A is non-positive, furthermore,

– the eigenvalues with zero real part have equal algebraic and geometric multiplicity, then x_o is a stable equilibrium,

– there is an eigenvalue with zero real part whose algebraic multiplicity is not equal to the geometric multiplicity, then x_o is an instable equilibrium.

(iv) Ker$A$ *is strictly asymptotically stable if and only if the zero eigenvalue of A has equal algebraic and geometric multiplicity, all the other eigenvalues have negative real part.*

Proposition 3 *Let x_o be an equilibrium of the differential equation $(*)$ in 7.1. If*

(i) all the eigenvalues of the linear map $\mathtt{D}R(x_o)$ have negative real part, then x_o is asymptotically stable,

(ii) an eigenvalue of the linear map $\mathtt{D}R(x_o)$ has positive real part, then x_o is instable.

Proposition 4 *Let $H := \{x_o \in \mathrm{Dom}R \mid R(x_o) = 0\}$ and let us suppose that*

(i) there is a non-zero linear subspace V in X such that $H = V \cap \mathrm{Dom}R$,

(ii) for all $x_o \in H$

– $\mathrm{Ker}\mathtt{D}R(x_o) = V$,

– *the zero eigenvalue of $\mathtt{D}R(x_o)$ has equal algebraic and geometric multiplicity,*

– *all the non-zero eigenvalues of $\mathtt{D}R(x_o)$ have negative real part.*

Then H is strictly asymptotically stable.

7.3 Let an u-dimensional submanifold U be an invariant set of the differential equation $(*)$ in 7.1. If $p : \mathbb{R}^u \rightarrowtail X$ is a (local) parameterization of U, then the restriction of the differential equation onto U (onto Ran$p$) is **reduced** to the differential equation

$$(\xi : \mathbb{R} \rightarrowtail \mathbb{R}^u)? \qquad \dot{\xi} = \mathtt{D}p(\xi)^{-1} R(p(\xi)) \tag{$*$}$$

which means that ξ satisfies the above equation if and only if $x = p \circ \xi$ satisfies the original equation.

Proposition 1 *If U is an invariant submanifold of the differential equation and there is a continuously differentiable function $L : X \rightarrowtail \mathbb{R}$ defined in a neighbourhood of the equilibrium $x_o \in U$ and*

(i) L has a strict local conditional maximum at x_o with respect to U,

(ii) $\overset{\bullet}{L}$ has a (strict) local conditional minimum at x_o with respect to U,

then x_o is (asymptotically) stable in U.

Proof Recall that conditional extremum with respect to U means that the restriction of the functions onto U has an extremum.

Let p be a parameterization of U in a neighbourhood of x_o. It is evident that $\xi_\mathrm{o} := p^{-1}(x_\mathrm{o})$ is an equilibrium of the reduced equation. Furthermore, $\Lambda := L \circ p$ has a strict maximum at ξ_o.

Because $\mathtt{D}\Lambda = (\mathtt{D}L \circ p)\mathtt{D}p$, the derivative of Λ along the reduced equation,

$$\overset{\bullet}{\Lambda} = (\mathtt{D}L \circ p)(f \circ p) = \overset{\bullet}{L} \circ p$$

has a (strict) minimum at ξ_o.

Consequently, ξ_o is an (asymptotically) stable equilibrium of the reduced differential equation which implies immediately that x_o is (asymptotically) stable in U.

Proposition 2 *Let U be an invariant submanifold of the differential equation and let E be the set of equilibria in U. Let us suppose that*

(1) E is a submanifold,

(2) for all $x \in E$,

(i) the kernel of the linear map $\mathtt{D}R(x)|_{T_x(U)} : T_x(U) \to T_x(U)$ equals $T_x(E)$,

(ii) the zero eigenvalue of $\mathtt{D}R(x)|_{T_x(U)}$ has equal algebraic and geometric multiplicity,

(iii) all the non-zero eigenvalues have negative real part.

Then E is strictly asymptotically stable in U.

Proof Let e and u be the dimension of E and U, respectively. There is a (local) parameterization $p : \mathbb{R}^e \times \mathbb{R}^{u-e} \rightarrowtail X$ of U such that $p(\cdot, 0) : \mathbb{R}^e \rightarrowtail X$ is a (local) parameterization of E. Then

$$\mathrm{Ran}\left(\mathtt{D}p(\eta, 0)|_{\mathbb{R}^e \times \{0\}}\right) = T_{p(\eta,0)}(E).$$

The set of equilibria of the reduced equation $(*)$ is

$$p^{-1}(E) = (\mathbb{R}^e \times \{0\}) \cap \mathrm{Dom}p,$$

whose tangent space at $(\eta, 0)$ equals

$$\mathbb{R}^e \times \{0\} = \mathtt{D}p(\eta, 0)^{-1}[T_{p(\eta,0)}(E)].$$

The derivative of the right-hand side of the reduced equation at an equilibrium $(\eta, 0)$ is

$$D(\eta, 0) := \mathtt{D}p(\eta, 0)^{-1}\mathtt{D}R(p(\eta, 0))\mathtt{D}p(\eta, 0).$$

Thus the spectral properties of $D(\eta, 0)$ coincide with the spectral properties of $\mathtt{D}R(p(\eta, 0))$ (they have the same eigenvalues and corresponding multiplicities) and

$$\mathrm{Ker}D(\eta, 0) = \left(\mathtt{D}p(\eta, 0)\right)^{-1}[\mathrm{Ker}\mathtt{D}R(p(\eta, 0))] = \mathbb{R}^e \times \{0\};$$

consequently, the set of equilibria of the reduced differential equation is strictly asymptotically stable according to Propoposition 4 in 7.2.

8 Concentrations

8.1 Let $m \in \mathbb{N}$. Then

$$\mathbf{D}_m := \left\{ (x^1, \dots, x^m) \in \mathbb{R}^m \;\middle|\; \sum_{\alpha=1}^{n} x^\alpha = 0 \right\}$$

is an $m-1$ dimensional linear subspace. It is evident, that for arbitrary $\alpha = 1, \dots, m$, omitting the α-th component, we establish a linear bijection between $\mathbf{D}_m$ and $\mathbb{R}^{m-1}$ i.e. we give a coordinatization of $\mathbf{D}_m$. For instance,

$$\boldsymbol{K}_m : \mathbf{D}_m \to \mathbb{R}^{m-1}, \quad (x^1, \dots, x^m) \mapsto (x^1, \dots, x^{m-1})$$

is such a coordinatization, whose inverse

$$\boldsymbol{P}_m : \mathbb{R}^{m-1} \to \mathbf{D}_m, \quad (x^1, \dots, x^{m-1}) \mapsto (x^1, \dots, x^{m-1}, -\sum_{\alpha=1}^{m-1} x^\alpha)$$

is the corresponding parameterization.

Let $i : \mathbf{D}_m \to \mathbb{R}^m$ denote the canonical (identity) embedding; its transpose $i^* : (\mathbb{R}^m)^* \to \mathbf{D}_m^*$ is a linear surjection. As usual, the dual of $\mathbb{R}^m$ is identified with $\mathbb{R}^m$. Let us introduce the notation

$$[p] := [p^1, \dots, p^m] := i^*(p^1, \dots, p^m) \qquad (p \in \mathbb{R}^m).$$

Thus if $p \in \mathbb{R}^m$ and $x \in \mathbf{D}_m$, then

$$[p]x = \sum_{\alpha=1}^{n} p^\alpha x^\alpha.$$

It is a simple fact that $[p] = [q]$ if and only if there is an $a \in \mathbb{R}$ such that $p^\alpha - q^\alpha = a$ for all $\alpha = 1, \dots, m$.

The coordinatization $\boldsymbol{K}_m$ determines a coordinatization of $\mathbf{D}_m^*$, too:

$$(\boldsymbol{K}_m^{-1})^* : \mathbf{D}_m^* \to \mathbb{R}^{m-1}, \quad [p] \mapsto (p^1 - p^m, \dots, p^{m-1} - p^m).$$

8.2

$$\mathrm{B}_m := \left\{ (c^1, \dots, c^m) \in \mathbb{R}^m \;\middle|\; \sum_{\alpha=1}^{n} c^\alpha = 1 \right\}$$

is an $m-1$ dimensional affine subspace over $\mathbf{D}_m$. This affine subspace, too, can be coordinatized by omitting an arbitrary component; for instance,

$$K_m : \mathrm{B}_m \to \mathbb{R}^{m-1}, \quad (c^1, \dots, c^m) \mapsto (c^1, \dots, c^{m-1}),$$

whose inverse

$$P_m : \mathbb{R}^{m-1} \to \mathrm{B}_m, \quad (c^1, \dots, c^{m-1}) \mapsto (c^1, \dots, c^{m-1}, 1 - \sum_{\alpha=1}^{m-1} c^\alpha)$$

is the corresponding parameterization.

If $f : \mathrm{B}_m \rightarrowtail \mathbb{R}$ is a differentiable function, then $\mathtt{D}f(c) \in \mathbf{D}^*_m$. It is important: *the partial derivatives of f make no sense* because $c^1, \dots, c^m$ do not vary independently in B_m. Thus $\mathtt{D}f$ cannot be obtained as the joint of its partial derivatives. If B_m is coordinatized, then $\mathtt{D}f$ can be represented by partial derivatives but these partial derivatives depend on the coordinatization. More closely, if $\mathtt{D}f(c) = [p]$, then

$$\frac{\partial f(P_m(c^1, \dots, c^{m-1}))}{\partial c^\alpha} = p^\alpha - p^m \qquad (\alpha = 1, \dots, m-1).$$

If $\phi : \mathrm{B}_m \rightarrowtail \mathbf{D}^*_m$ is a differentiable function, then $\mathtt{D}\phi(c) \in \mathrm{Lin}(\mathbf{D}_m, \mathbf{D}^*_m)$, thus its positive (negative) definiteness is a meaningful notion. If $\phi = [\phi^1, \dots, \phi^m]$ and B_m is coordinatized by the first $m-1$ components, then $\mathtt{D}\phi$ positive definite if and only if the matrix

$$\left\{ \frac{\partial\big((\phi^\beta - \phi^m) \circ P_m\big)}{\partial c^\alpha} \;\middle|\; \alpha, \beta = 1, \dots, m-1 \right\}$$

is positive definite.

8.3 Let us consider

$$\mathrm{C}_m := \{c \in \mathrm{B}_m \mid c^\alpha > 0,\ \alpha = 1, \dots, m\}.$$

C_m is an open subset in B_m whose closure is

$$\overline{\mathrm{C}_m} = \{c \in \mathrm{B}_m \mid c^\alpha \geq 0,\ \alpha = 1, \dots, n\}.$$

It is evident that if c is in C_m or $\overline{\mathrm{C}_m}$, then $0 < c^\alpha < 1$ and $0 \leq c^\alpha \leq 1$ $(\alpha = 1, \dots, m)$, respectively.

Note that if $c \in \overline{\mathrm{C}_m}$ and there is an α such that $c^\alpha = 1$, then the other components of c are zero. We introduce the notation

$$(1)^\alpha := \{\text{the } \alpha\text{-th component is 1, the other are 0}\}.$$

Let $n < m$. If $c \in \mathrm{C}_n$, then $(c^1, \dots, c^n, 0, \dots, 0) \in \overline{\mathrm{C}_m}$, where, of course, $(m-n)$ zeros are between the parantheses. In this way we consider C_n as a subset of $\overline{\mathrm{C}_m}$; consequently, the elements of C_n are accumulation points of C_m.

9 Something else

Proposition *Let I be an open interval and $f_n : I \to \mathbb{R}$ $(n \in \mathbb{N})$ injective continuous functions so that $f := \lim_n f_n$ exists and is an injective continuous function. If f_n^{-1} is differentiable for all n and $y \in \mathrm{Ran} f$ has a neighbourhood K such that*

$$L := \sup \left\{ \left| \left(f_n^{-1}\right)'(z) \right| \mid z \in K,\ n \in \mathbb{N} \right\} < \infty,$$

then $\lim_n f_n^{-1}(y) = f^{-1}(y)$.

Proof The injective continuous functions on an interval are strictly monotone; let us suppose that the functions in question are strictly monotone increasing.

Let $y \in \operatorname{Ran} f$, i.e. $y = f(x)$ for some $x \in I$. If $x_1, x_2 \in I$ and $x_1 < x < x_2$, then $\lim\limits_n f_n(x_1) = f(x_1) < y < \lim\limits_n f_n(x_2) = f(x_2)$. Thus, there are an $\eta > 0$ and an $n_\mathrm{o} \in \mathbb{N}$ such that $f_n(x_1) < y - \eta,\ \ y + \eta < f_n(x_2)$ for all $n > n_\mathrm{o}$.

The continuous image of an interval is an interval, therefore the previous inequalities tell us that y (even a neighbourhood of y) is in the range of f_n if $n > n_\mathrm{o}$.

Furthermore, $f = \lim\limits_n f_n$ implies that for every neighbourhood U of y there is an $n_U \in \mathbb{N}$ such that $f_n(f^{-1}(y)) \in U$ for all $n > n_U$.

Then if $n > \max\{n_\mathrm{o}, n_K\}$, it follows from the mean value theorem that

$$\left|f_n^{-1}(y) - f^{-1}(y)\right| = \left|f_n^{-1}(y) - f_n^{-1}(f_n(f^{-1}(y)))\right| \le L|y - f_n(f^{-1}(y))|$$

and the right-hand side tends to zero az n tends to infinity.

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