

On the dynamics of phase transitions

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Abstract. The dynamics of phase transitions is described in ordinary thermodynamics i.e. the bodies are considered to be homogeneous. Stability properties of phase transitions are investigated by Lyapunov's method.

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1. Introduction

Phase transitions are interesting and important questions both in statistical physics and in thermodynamics. In this paper the thermodynamical aspects of phase transitions are examined. The dynamical description of phase transitions in the framework of continuum thermodynamics is a rapidly developing theory ([1]-[7]). That approach is based on partial differential equations. In order to get mathematically reasonable problems, in general, one is forced to assume strongly idealized conditions (one dimensional flow ([3]), isothermal phase separations ([1]) etc.). Boundary conditions are fundamental for partial differential equations; in most of the real phase transitions the volume of the material changes i.e. the limiting surfaces of materials vary with time (e.g. in the melting of ice under given ambient temperature and pressure); to avoid the rather complicated varying boundaries, one considers infinite systems ([1]) or fixed boundaries ([3],[5]).

Now we propose a description of the dynamics of phase transitions in which, instead of the spatial position of phases, we are only interested in the amount (mass) of phases as a function of time. Then we consider the materials to be homogeneous; this is a good approximation in many cases (e.g. in the usual melting of ice) and it has the advantage that we can use ordinary differential equations which are much simpler than partial differential equations. Of course, the homogeneous model is rougher than the continuum model; however, it gives results in several questions where the continuum theory seems useless because of its complexity; e.g. we can get rid of boundary conditions and we can easily treat phase transitions in

which the volume of the material changes. This approach is similar to that in the theory of chemical reactions which are mostly described by ordinary differential equations ([8]-[11]) as if the materials in chemical reactions were homogeneous though, evidently, they are far from being homogeneous. Nevertheless, a lot of basic features of chemical reactions are well reflected in such a description. Some other properties, of course, can be deduced only from a continuum theory ([12]). Then comparing the results we can see clearly where the inhomogeneity plays a fundamental role.

Different phases of a material, in general, are described by different constitutive functions ([3],[5],[7]). However, this cannot be pursued consistently ([13]), in general, because the liquid and gaseous phase intermingle over the critical point. Thus for a deep theory of phase transitions, it is indispensable to have a rigorous definition of phases and to know the exact relation of phases between which phase transitions can occur; the necessary notions and results can be found in [14].

2. Basic notions and notations

The notions and notations introduced in [14] are used in this paper. In particular, the physical dimension (unit of measurement) of quantities are written explicitly, and the derivative of thermodynamic functions is denoted by a prime. Furthermore, a *single-component substance* is a triplet (D, \mathbf{s}, R) where

- D is the *constitutive domain*, consisting of the possible values (e, v) of *specific internal energy* and *specific volume*,
- \mathbf{s} , the *specific entropy* is defined and continuously differentiable on D ,
- R , the *regular constitutive domain*, is an open subset in D , consisting of the elements (e, v) such that \mathbf{s} is twice continuously differentiable at (e, v) and $\mathbf{s}''(e, v)$ is negative definite.

The *temperature* \mathbf{T} , the *pressure* \mathbf{p} and the *chemical potential* μ , defined by the usual formulae, are continuous on D and continuously differentiable on R .

A *phase* of a substance is defined to be a maximal connected open subset of R in which $\mathbf{s}' = \left(\frac{1}{\mathbf{T}}, \frac{\mathbf{p}}{\mathbf{T}}\right)$ is injective.

Now we need the notion of a body which corresponds to a certain amount of a substance in a phase: the triplet of variables (e, v, m) describes a body where (e, v) is an element of a given phase and m is an arbitrary positive mass value. Therefore the following definition seems straightforward.

Definition 1. A *body* consisting of a single-component substance (D, \mathbf{s}, R) is $F \times (kg)^+$ where F is a phase of the substance.

It turns out that the description of processes of bodies in which mass varies will be simpler if instead of the variables e and v we use the *total internal energy* E and the *total volume* V , respectively. More precisely, we establish the smooth

bijection

$$\begin{aligned} (J/kg)^+ \times (m^3/kg)^+ \times (kg)^+ &\rightarrow (J)^+ \times (m^3)^+ \times (kg)^+, \\ (e, v, m) &\mapsto (me, mv, m) =: (E, V, m) \end{aligned}$$

whose inverse

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

is smooth as well.

In the new variables a body $F \times (kg)^+$ is represented by

$$(kg)^+ * F := \{(me, mv, m) \mid (e, v) \in F, m \in (kg)^+\}.$$

A similar notation will be applied for an arbitrary subset H of D .

Using the variables (E, V, m) , we define

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

and similar expressions for $\hat{\mathbf{p}}$ and $\hat{\mu}$ as well. For the sake of brevity and perspicuity, the usual abuse of notations will be applied further on: the simple symbol \mathbf{T} etc. will be written instead of $\hat{\mathbf{T}}$ etc. i.e. two different functions will be denoted by the same letter. Then we easily derive that

$$\frac{\partial \mathbf{T}}{\partial E} = \frac{1}{m} \frac{\partial \mathbf{T}}{\partial e}, \quad \frac{\partial \mathbf{T}}{\partial V} = \frac{1}{m} \frac{\partial \mathbf{T}}{\partial v}$$

where, according to the previously accepted abuse of notations, it is understood that the variables on the left hand side and on the right hand side are (E, V, m) and $(e, v) = (E/m, V/m)$, respectively. Moreover, we have

$$\frac{\partial \mathbf{T}}{\partial m} = -\frac{E}{m} \frac{\partial \mathbf{T}}{\partial E} - \frac{V}{m} \frac{\partial \mathbf{T}}{\partial V} \quad (*)$$

and similar formulae for \mathbf{p} and μ as well.

For the *total entropy*

$$\mathbf{S}(E, V, m) := m\mathbf{s}(E/m, V/m),$$

we get the usual equalities

$$\frac{\partial \mathbf{S}}{\partial E} = \frac{1}{\mathbf{T}}, \quad \frac{\partial \mathbf{S}}{\partial V} = \frac{\mathbf{p}}{\mathbf{T}}, \quad \frac{\partial \mathbf{S}}{\partial m} = \frac{\mu}{\mathbf{T}}.$$

Then the second derivative of the total entropy is

$$\mathbf{S}'' = -\frac{1}{\mathbf{T}^2} \begin{pmatrix} \frac{\partial \mathbf{T}}{\partial E} & \frac{\partial \mathbf{T}}{\partial V} & \frac{\partial \mathbf{T}}{\partial m} \\ \mathbf{p} \frac{\partial \mathbf{T}}{\partial E} - \mathbf{T} \frac{\partial \mathbf{p}}{\partial E} & \mathbf{p} \frac{\partial \mathbf{T}}{\partial V} - \mathbf{T} \frac{\partial \mathbf{p}}{\partial V} & \mathbf{p} \frac{\partial \mathbf{T}}{\partial m} - \mathbf{T} \frac{\partial \mathbf{p}}{\partial m} \\ -\mu \frac{\partial \mathbf{T}}{\partial E} + \mathbf{T} \frac{\partial \mu}{\partial E} & -\mu \frac{\partial \mathbf{T}}{\partial V} + \mathbf{T} \frac{\partial \mu}{\partial V} & -\mu \frac{\partial \mathbf{T}}{\partial m} + \mathbf{T} \frac{\partial \mu}{\partial m} \end{pmatrix}.$$

Since it must be symmetric, we can establish some relations among certain partial derivatives. It follows from (*) and the similar equalities for \mathbf{p} and μ that the last column of the above matrix is a linear combination of the first two ones. It is quite trivial that the inequalities expressing the negative definiteness of \mathbf{s}'' remain valid for the total quantities:

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

Then we easily derive the following result, important from the point of view of stability.

Proposition 1. $\mathbf{S}''(E, V, m)$ is negative semi-definite for all $(E, V, m) \in (kg)^+ * R$, having a one dimensional kernel spanned by (E, V, m) .

Remarks. (i) It is frequently required in the literature that the second derivative of the total entropy be negative definite (e.g. [12] page 38,[13],[14]); we see that this is not right.

(ii) The sum of two negative semi-definite forms is negative semi-definite; if the intersection of the two kernels is the zero subspace then the sum is negative definite. Thus $\mathbf{S}''(E_1, V_1, m_1) + \mathbf{S}''(E_2, V_2, m_2)$ is negative definite if and only if (E_1, V_1, m_1) and (E_2, V_2, m_2) are not parallel, or, equivalently, $(E_1/m_1, V_1/m_1) \neq (E_2/m_2, V_2/m_2)$.

3. Processes

The fundamental notion of dynamics is the *process*: the time evolution of states. As mentioned in the Introduction, we consider the materials to be homogeneous. Then a thermodynamical process of a body is a function $t \mapsto (e(t), v(t), m(t))$ or $t \mapsto (E(t), V(t), m(t))$ defined over a time interval. We assume that the processes – as in other branches of physics – are determined by differential equations ([18],[19],[20]). Such a framework of the description of processes of homogeneous bodies, called *ordinary thermodynamics*, can be outlined as follows.

The ordinary differential equations – called the dynamical law – governing the homogeneous processes can be deduced by analogy from the well working partial differential equations of continuum (irreversible) thermodynamics and have the form – in a loose notation –

$$\begin{aligned} \dot{E} &= Q - p\dot{V} + \mu\dot{m}, \\ \dot{V} &= F, \\ \dot{m} &= G \end{aligned}$$

where the heating Q , the springing F and the converting G are given by constitutive functions. As we see, the dynamical law involves the first law.

An equilibrium is a special process: a constant solution of the dynamical law. The zeroth law appears as equilibrium properties of Q , F and G : they are zero if the intensive parameters of the interacting bodies (and eventually the environment) are equal.

The second law is formulated as an analogy of the well known Clausius–Duhem inequality: it turns out to be a restriction on the constitutive functions and – roughly – is of the form

$$\dot{E} \left(\frac{1}{T} - \frac{1}{T_i} \right) + \dot{V} \left(\frac{p}{T} - \frac{p_i}{T_i} \right) + \dot{m} \left(\frac{\mu}{T} - \frac{\mu_i}{T_i} \right) \geq 0$$

where the subscript i refers to an interacting partner of the body in question; this is a well known inequality in usual equilibrium thermodynamics with dE , dV and dm (or dN where N is the particle number) instead of \dot{E} , \dot{V} and \dot{m} .

One of the major questions in ordinary thermodynamics is the description of the trend to equilibrium which is just the asymptotic stability of equilibria (see the Appendix).

We emphasize that the previous considerations form only a rough survey; the rigorous mathematical treatment will be expounded in the next sections.

First of all, note the highly important fact that the processes of a body are determined by the interactions that the body participates in; without interaction there is no non-trivial (non-constant) process. We have to distinguish between a **body** and a **system**: a system is a body or several bodies and their environment together. The processes of a body in different systems are different. It is not worth formulating the precise and rather complicated general definition of systems; we shall define several actual ones according to the following scheme: the mathematical model of a system consists of

- 1) a collection of *bodies*,
- 2) a prescription of the *environment* and/or *constraints*,
- 3) a collection of *system constitutive relations* (functions characterizing the interaction),
- 4) an actual form of the *second law* (conditions imposed on the system constitutive relations),
- 5) a *dynamical law* (differential equation governing the processes).

4. Zeroth-order (continuous) and second-order (gradual) phase transitions

In zeroth-order and second order-phase transitions ([14]) the total amount of a substance passes from one phase into another instantaneously: mass is not a dynamical variable. Therefore the treatment of such phase transitions in ordinary thermodynamics needs no new notions besides the elaborated ones ([18],[19],[20]).

To see, how to handle second-order phase transitions (zeroth-order phase transitions are trivial), let us study the simplest system: an amount of a substance having a second-order phase connection is put in an environment of constant temperature and pressure.

The following mathematical model will describe this system.

1) Two phases F_1 and F_2 of a substance (D, s, R) are considered which have a second-order phase connection C .

Put

$$U := F_1 \cup C \cup F_2, \quad \Omega := (\mathbf{T}, \mathbf{p})[U].$$

2) There is given a $(T_a, p_a) \in \Omega$ (the ambient temperature and pressure).

3) The system constitutive functions

(i) $\mathbf{q} : \Omega \rightarrow (J/kgs)$, called the *specific heating*,

(ii) $\mathbf{f} : \Omega \rightarrow (m^3/kgs)$, called the *specific springing*,

are continuously differentiable and satisfy the *equilibrium property*

$$\mathbf{q}(T_a, p_a) = 0, \quad \mathbf{f}(T_a, p_a) = 0;$$

it is worth introducing $\mathbf{w} : \Omega \rightarrow (J/kgs)$, $(T, p) \mapsto -pf(T, p)$, called the *specific working*.

4) The second law is formulated as follows:

$$-\frac{\mathbf{q}(T, p)}{T}(T - T_a) - \frac{\mathbf{w}(T, p)}{p}(p - p_a) \geq 0$$

or, equivalently,

$$(\mathbf{q}(T, p) + \mathbf{w}(T, p)) \left(\frac{1}{T} - \frac{1}{T_a} \right) + \mathbf{f}(T, p) \left(\frac{p}{T} - \frac{p_a}{T_a} \right) \geq 0$$

for all $(T, p) \in \Omega$ and equality holds if and only if $T = T_a$ and $p = p_a$,

5) A process is a continuously differentiable function $(e, v) : I \rightarrow U$ (where I is a time interval), satisfying the differential equation (dynamical law):

$$\begin{aligned} \dot{e} &= \mathbf{q}(\mathbf{T}(e, v), \mathbf{p}(e, v)) + \mathbf{w}(\mathbf{T}(e, v), \mathbf{p}(e, v)), \\ \dot{v} &= \mathbf{f}(\mathbf{T}(e, v), \mathbf{p}(e, v)). \end{aligned}$$

A second-order phase transition occurs in the process if it crosses the phase connection which is equivalent to the fact that there are $t_1, t_C, t_2 \in I$ such that $(e(t_1), v(t_1)) \in F_1$, $(e(t_C), v(t_C)) \in C$ and $(e(t_2), v(t_2)) \in F_2$.

A constant solution of the dynamical law is called an *equilibrium* of the system. $(e_o, v_o) \in U$ is an equilibrium if and only if $\mathbf{q}(\mathbf{T}(e_o, v_o), \mathbf{p}(e_o, v_o)) = 0$, $\mathbf{f}(\mathbf{T}(e_o, v_o), \mathbf{p}(e_o, v_o)) = 0$. From the equilibrium properties in 3) and from the second law 4) we deduce that (e_o, v_o) is an equilibrium if and only if

$$\mathbf{T}(e_o, v_o) = T_a, \quad \mathbf{p}(e_o, v_o) = p_a.$$

For stability investigations let us consider the function

$$\mathbf{L} : U \rightarrow (J/kgK), \quad (e, v) \mapsto \mathbf{s}(e, v) - \frac{e + p_a v}{T_a}.$$

It is quite simple that

- (i) $-\mathbf{L}$ is continuously differentiable, $\mathbf{L}' = \left(\frac{1}{\mathbf{T}} - \frac{1}{T_a}, \frac{\mathbf{p}}{\mathbf{T}} - \frac{p_a}{T_a} \right)$,
 $-\mathbf{L}'(e_o, v_o) = 0$ (the necessary condition of a local extremum of \mathbf{L} at (e_o, v_o) is satisfied),
 (ii) the derivative of \mathbf{L} along the dynamical law,

$$\dot{\mathbf{L}} := (\mathbf{q} \circ (\mathbf{T}, \mathbf{p}) + \mathbf{w} \circ (\mathbf{T}, \mathbf{p})) \left(\frac{1}{\mathbf{T}} - \frac{1}{T_a} \right) + \mathbf{f} \circ (\mathbf{T}, \mathbf{p}) \left(\frac{\mathbf{p}}{\mathbf{T}} - \frac{p_a}{T_a} \right)$$

has a minimum at the equilibrium (e_o, v_o) according to the second law; the minimum is strict if and only if the equilibrium is isolated.

Let us consider the possibilities:

1. \mathbf{L} has a strict local maximum at (e_o, v_o) ,
 2. \mathbf{L} has not a local maximum at (e_o, v_o) ,
 3. The minimum of $\dot{\mathbf{L}}$ at (e_o, v_o) is strict.
- Evidently, if 1. is satisfied then the equilibrium is isolated, so 1. implies 3.

Thus, according to Lyapunov's theory (see the Appendix),

- 1. implies asymptotic stability,
- 2. and 3. imply instability.

If the equilibrium is in one of the phases then \mathbf{s} is twice differentiable at (e_o, v_o) and $\mathbf{s}''(e_o, v_o)$ is negative definite, consequently 1. is satisfied: the equilibrium is asymptotically stable. This is an extension of the known result regarding asymptotic stability of processes without phase transitions ([18]) when the equilibrium and the initial state are in the same phase. If the equilibrium and the initial state are in different phases (but the initial state belongs to the domain of attraction of the equilibrium) then a second-order phase transition occurs in the process.

Now let us consider the case that the equilibrium is on the second-order phase connection.

Proposition 2. *If the equilibrium on the phase connection is of Tisza type ([14]) then it can be asymptotically stable, stable (without being asymptotically stable) or unstable.*

Proof. Now $\mathbf{s}''(e_o, v_o)$ is negative semidefinite. This allows the possibilities that

- a) \mathbf{L} has a strict local maximum at (e_o, v_o) ,
- b) \mathbf{L} has a local maximum at (e_o, v_o) which is not strict,
- c) \mathbf{L} has not a local maximum at (e_o, v_o) .

In the case a) the equilibrium is asymptotically stable. The case b) excludes that the equilibrium is isolated, consequently the equilibrium cannot be asymptotically stable (but it can be stable or unstable). If c) occurs and the equilibrium is isolated then the equilibrium is unstable. \square

Proposition 3. *An equilibrium in an Ehrenfest type ([14]) regular part of the second-order phase connection is asymptotically stable.*

Proof. There are continuously differentiable functions \mathbf{L}'_1 and \mathbf{L}'_2 defined on a neighbourhood N of (e_o, v_o) such that $\mathbf{L}''_1(e_o, v_o)$ and $\mathbf{L}''_2(e_o, v_o)$ are negative definite, moreover $\mathbf{L}'_1(e, v) = \mathbf{L}'(e, v)$ for $(e, v) \in N \cap F_1 \setminus \overline{F_2}$ and $\mathbf{L}'_2(e, v) = \mathbf{L}'(e, v)$ for $(e, v) \in N \cap F_2 \setminus \overline{F_1}$.

As a consequence, \mathbf{L} has a strict local minimum at (e_o, v_o) on both $F_1 \cup C$ and $F_2 \cup C$ which implies that it has a strict local minimum on $F_1 \cup C \cup F_2$. \square

5. About first-order phase transitions in general

The mass of the bodies is a dynamical variable in first-order phase transitions. We shall deal with first-order phase transitions in which only two bodies participate (e.g. ice and water or water and steam) characterized by their total internal energy, total volume and mass. Thus the two bodies together will be described by six variables: $E_1, V_1, m_1, E_2, V_2, m_2$. However, mass conservation implies $m_1 + m_2 = \text{const}$; so in fact we have at most five independent variables. Some other constraints can diminish further the number of variables; e.g. if the bodies are in a rigid box then $V_1 + V_2 = \text{const}$ and if the rigid box is heat insulated as well then, in addition, $E_1 + E_2 = \text{const}$.

There are a lot of different systems in which bodies undergo a first-order phase transition. We shall investigate two ones which correspond to realistic situations: first, the bodies are in a heat insulated rigid box; second, the bodies are in an environment of given temperature and pressure. The corresponding mathematical models will be constructed according to the scheme given in Section 3. The first item will be the same for both systems, as follows:

1) Two phases F_1 and F_2 of a substance (D, \mathbf{s}, R) are given which have a first-order phase connection (C_1, C_2) , and we consider the corresponding bodies $(kg)^+ * F_1$ and $(kg)^+ * F_2$. We disregard zeroth-order phase transitions by restricting our investigations on $H_1 := F_1 \setminus \overline{F_2}$ and $H_2 := F_2 \setminus \overline{F_1}$.

We shall use the notation

$$\vartheta_i := (\mathbf{T}, \mathbf{p})[H_i], \quad (i = 1, 2), \quad \text{and} \quad \Gamma := (\mathbf{T}, \mathbf{p})[C_1] = (\mathbf{T}, \mathbf{p})[C_2].$$

Recall that the equality $\mu_1(T, p) = \mu_2(T, p)$ holds for $(T, p) \in \vartheta_1 \cap \vartheta_2$ if and only if $(T, p) \in \Gamma$. ([14])

6. First-order phase transition in a heat insulated rigid box

The following model describes e.g. that cold water and hot steam are put together into a heat insulated rigid box: water becomes warmer, steam becomes colder, some water evaporates or some steam condenses and an equilibrium is reached.

- 1) See the previous section.
- 2) There are given

$$m_s \in (kg)^+, \quad V_s \in (m^3)^+, \quad E_s \in (J)^+,$$

and we consider the subset X of $((kg)^+ * H_1) \times ((kg)^+ * H_2)$ consisting of elements $(E_1, V_1, m_1, E_2, V_2, m_2)$ for which

$$m_1 + m_2 = m_s, \quad V_1 + V_2 = V_s, \quad E_1 + E_2 = E_s$$

hold.

- 3) The system constitutive functions, for $i = 1, 2$, defined on $\vartheta_1 \times (kg)^+ \times \vartheta_2 \times (kg)^+$,
 - (i) \mathbf{Q}_i , the *heatings*, having values in (J/s) ,
 - (ii) \mathbf{F}_i , the *springings*, having values in (m^3/s) ,
 - (iii) \mathbf{G}_i , the *convertings*, having values in (kg/s)
 are continuously differentiable, satisfy the the *constraint conditions*

$$\mathbf{G}_1 + \mathbf{G}_2 = 0, \quad \mathbf{F}_1 + \mathbf{F}_2 = 0,$$

$$(\mathbf{Q}_1 - p_1 \mathbf{F}_1 + \mu_1 \mathbf{G}_1) + (\mathbf{Q}_2 - p_2 \mathbf{F}_2 + \mu_2 \mathbf{G}_2) = 0$$

and the *equilibrium properties*

$$\mathbf{Q}_i(T_1, p_1, m_1, T_2, p_2, m_2) = 0, \quad \mathbf{F}_i(T_1, p_1, m_1, T_2, p_2, m_2) = 0,$$

$$\mathbf{G}_i(T_1, p_1, m_1, T_2, p_2, m_2) = 0$$

for arbitrary m_1, m_2 if $T_1 = T_2, p_1 = p_2, \mu_1(T_1, p_1) = \mu_2(T_2, p_2)$.

- 4) The second law, on the base of the general formula in [19], is given as follows:

$$\sum_{i=1}^2 \left((\mathbf{Q}_i - p_i \mathbf{F}_i + \mu_i \mathbf{G}_i) \left(\frac{1}{T_i} - \frac{1}{T_j} \right) + \mathbf{F}_i \left(\frac{p_i}{T_i} - \frac{p_j}{T_j} \right) + \mathbf{G}_i \left(\frac{\mu_i}{T_i} - \frac{\mu_j}{T_j} \right) \right) \geq 0$$

$(j = 1, 2)$

where

$$Q_1 := \mathbf{Q}_1(T_1, p_1, m_1, T_2, p_2, m_2), \quad \text{etc.}$$

and equality holds for arbitrary m_1, m_2 if and only if $T_1 = T_2, p_1 = p_2, \mu_1(T_1, p_1) = \mu_2(T_2, p_2)$.

5) A process is a continuously differentiable function $(E_1, V_1, m_1, E_2, V_2, m_2) : I \rightarrow X$ (where I is a time interval), governed by the dynamical law

$$\begin{aligned} \dot{E}_i &= Q_i - p_i F_i + \mu_i G_i, \\ \dot{V}_i &= F_i, \\ \dot{m}_i &= G_i \end{aligned}$$

for $i = 1, 2$ where

$$Q_i := \mathbf{Q}_i(\mathbf{T}(E_1, V_1, m_1), \mathbf{p}(E_1, V_1, m_1), m_1, \mathbf{T}(E_2, V_2, m_2), \mathbf{p}(E_2, V_2, m_2), m_2)$$

etc.

Because of the constraints given in 2), we have only three independent variables; let us choose (E_1, V_1, m_1) : from now on a process will mean a continuously differential function $(E_1, V_1, m_1) : I \rightarrow (kg)^+ * H_1$ satisfying the differential equations for $i = 1$ in 5).

According to this choice of independent variables, the second law can be reduced by the constraints to

$$(Q_1 - p_1 F_1 + \mu_1 G_1) \left(\frac{1}{T_1} - \frac{1}{T_2} \right) + F_1 \left(\frac{p_1}{T_1} - \frac{p_2}{T_2} \right) + G_1 \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) \geq 0.$$

A first-order phase transition occurs in a process (E_1, V_1, m_1) if there is a $t \in I$ such that $\dot{m}_1(t) \neq 0$.

A constant process is an equilibrium of the system.

Note that the equilibrium properties of the system constitutive relations, the second law and the remark at the end of the previous section about the equality of the chemical potentials imply that $\mathbf{Q}_i(T_1, p_1, m_1, T_2, p_2, m_2) = 0$ if and only if $(T_1, p_1) = (T_2, p_2) \in \Gamma$, and similar relations hold for \mathbf{F}_i and \mathbf{G}_i ($i = 1, 2$) as well. As a consequence, we have the following results.

Proposition 4. (E_{10}, V_{10}, m_{10}) in $(kg)^+ * H_1$ is an equilibrium if and only if $(E_{10}/m_{10}, V_{10}/m_{10})$ belongs to C_1 , or equivalently, if and only if (T_0, p_0) belongs to Γ where $T_0 := \mathbf{T}(E_{10}, V_{10}, m_{10})$, $p_0 := \mathbf{p}(E_{10}, V_{10}, m_{10})$.

Proposition 5. (E_{10}, V_{10}, m_{10}) in $(kg)^+ * H_1$ is an equilibrium if and only if

$$\begin{aligned} \mathbf{T}(E_{10}, V_{10}, m_{10}) &= \mathbf{T}(E_s - E_{10}, V_s - V_{10}, m_s - m_{10}), \\ \mathbf{p}(E_{10}, V_{10}, m_{10}) &= \mathbf{p}(E_s - E_{10}, V_s - V_{10}, m_s - m_{10}), \\ \mu(E_{10}, V_{10}, m_{10}) &= \mu(E_s - E_{10}, V_s - V_{10}, m_s - m_{10}). \end{aligned}$$

Let us introduce the function

$$\mathbf{L}(E_1, V_1, m_1) := \mathbf{S}(E_1, V_1, m_1) + \mathbf{S}(E_s - E_1, V_s - V_1, m_s - m_1)$$

defined on $(kg)^+ * H_1$. We easily find that (E_{10}, V_{10}, m_{10}) is an equilibrium if and only if $\mathbf{L}'(E_{10}, V_{10}, m_{10}) = 0$. Moreover,

$$\mathbf{L}''(E_1, V_1, m_1) = \mathbf{S}''(E_1, V_1, m_1) + \mathbf{S}''(E_s - E_1, V_s - V_1, m_s - m_1).$$

If $(E_1/m_1, V_1/m_1)$ is in H_1 then $((E_s - E_1)/(m_s - m_1), (V_s - V_1)/(m_s - m_1))$ is in H_2 which is disjoint from H_1 , consequently,

$$(E_1/m_1, V_1/m_1) \neq ((E_s - E_1)/(m_s - m_1), (V_s - V_1)/(m_s - m_1)).$$

Then it follows from the remark after Proposition 1 that $\mathbf{L}''(E_1, V_1, m_1)$ is negative definite.

Proposition 6. *Every equilibrium in $(kg)^+ * H_1$ is isolated (or locally unique, i.e. has a neighbourhood which does not contain other equilibrium).*

Proof. (E_{10}, V_{10}, m_{10}) is an equilibrium if and only if $\mathbf{L}'(E_{10}, V_{10}, m_{10}) = 0$. The derivative of \mathbf{L}' at (E_{10}, V_{10}, m_{10}) is negative definite, in particular, it is injective; then the inverse function theorem yields that \mathbf{L}' is locally injective, proving our assertion.

Proposition 7. *An equilibrium (E_{10}, V_{10}, m_{10}) in $(kg)^+ * H_1$ is asymptotically stable.*

Proof. The function \mathbf{L} defined previously is a Lyapunov function for asymptotic stability:

- it has a strict local maximum at (E_{10}, V_{10}, m_{10}) because, according to the previous proposition, its derivative at an equilibrium is zero and its second derivative is negative definite;

- its derivative along the dynamical law in 5) for $i = 1$,

$$\dot{\mathbf{L}}(E_1, V_1, m_1) =$$

$$\left(\frac{1}{\mathbf{T}(E_1, V_1, m_1)} - \frac{1}{\mathbf{T}(E_s - E_1, V_s - V_1, m_s - m_1)} \right) \times$$

$$\left(\mathbf{Q}_1((\mathbf{T}, \mathbf{p})(E_1, V_1, m_1), m_1, (\mathbf{T}, \mathbf{p})(E_s - E_1, V_s - V_1, m_s - m_1), m_s - m_1) - \text{etc.} \right)$$

+ etc.

has a strict minimum at (E_{10}, V_{10}, m_{10}) according to the second law in 4).

Remark. The existence of equilibrium of the treated system has not been stated and, really, cannot be stated: the system constitutive functions, the second law and

the dynamical law concern the physical situation when *both phases* of the material are present. Put few water and much hot steam together into a heat insulated rigid box; a process starts in which all the water evaporates: no equilibrium of that water–steam system exists. Of course, steam will be in equilibrium after the evaporation of water but this equilibrium concerns a one-body system.

The existence of equilibrium depends on the initial data.

7. First-order phase transition in a given environment

The following model describes e.g. that water and steam (or ice and water) are put together into a box surrounded by the atmosphere having constant temperature and pressure.

1) See Section 5.

2) There are given a $(T_a, p_a) \in \vartheta_1 \cap \vartheta_2$ (the ambient temperature and pressure) and an $m_s \in (kg)^+$, and we consider the subset Y of $((kg)^+ * H_1) \times ((kg)^+ * H_2)$ consisting of elements $(E_1, V_1, m_1, E_2, V_2, m_2)$ for which

$$m_1 + m_2 = m_s$$

holds.

3) The system constitutive functions, for $i = 1, 2$, defined on $\vartheta_1 \times (kg)^+ \times \vartheta_2 \times (kg)^+$,

(i) \mathbf{Q}_i , the *heatings*, having values in (J/s) ,

(ii) \mathbf{F}_i , the *springings*, having values in (m^3/s) ,

(iii) \mathbf{G}_i , the *convertings*, having values in (kg/s)

are continuously differentiable, satisfy the the *constraint condition*

$$\mathbf{G}_1 + \mathbf{G}_2 = 0$$

and the *equilibrium properties*

$$\mathbf{Q}_i(T_1, p_1, m_1, T_2, p_2, m_2) = 0, \quad \mathbf{F}_i(T_1, p_1, m_1, T_2, p_2, m_2) = 0,$$

$$\mathbf{G}_i(T_1, p_1, m_1, T_2, p_2, m_2) = 0$$

for arbitrary m_1, m_2 if $T_1 = T_2, p_1 = p_2, \mu_1(T_1, p_1) = \mu_2(T_2, p_2)$.

4) The second law, on the base of the general formula in [19] is given as follows:

$$\sum_{i=1}^2 \left((Q_i - p_i F_i + \mu_i G_i) \left(\frac{1}{T_i} - \frac{1}{T_a} \right) + F_i \left(\frac{p_i}{T_i} - \frac{p_a}{T_a} \right) + \frac{1}{2} G_i \left(\frac{\mu_i}{T_i} - \frac{\mu_j}{T_j} \right) \right) \geq 0$$

$$(j = 1, 2)$$

where Q_i etc. denote abbreviations similar to those in the previous section, and equality holds for arbitrary m_1, m_2 if and only if $T_1 = T_2 = T_a, p_1 = p_2 = p_a, \mu_1(T_1, p_1) = \mu_2(T_2, p_2)$.

5) A process is a continuously differentiable function $(E_1, V_1, m_1, E_2, V_2, m_2) : I \rightarrow Y$ (where I is a time interval), governed by the dynamical law

$$\begin{aligned} \dot{E}_i &= Q_i - p_i F_i + \mu_i G_i, \\ \dot{V}_i &= F_i, \\ \dot{m}_i &= G_i \end{aligned}$$

for $i = 1, 2$, with abbreviations similar to those in the previous section.

Because of the constraint given in 2), we have only five independent variables; let us choose $(E_1, V_1, m_1, E_2, V_2)$: from now on a process will mean a continuously differential function $(E_1, V_1, m_1, E_2, V_2)$ satisfying the differential equations

$$\begin{aligned} \dot{E}_1 &= Q_1 - p_1 F_1 + \mu_1 G_1, & \dot{E}_2 &= Q_2 - p_2 F_2 - \mu_2 G_1, \\ \dot{V}_1 &= F_1, & \dot{V}_2 &= F_2, \\ \dot{m}_1 &= G_1. \end{aligned}$$

According to this choice of independent variables, the second law can be rewritten in the form

$$\sum_{i=1}^2 \left((Q_i - p_i F_i + \mu_i G_i) \left(\frac{1}{T_i} - \frac{1}{T_a} \right) + F_i \left(\frac{p_i}{T_i} - \frac{p_a}{T_a} \right) \right) + G_1 \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) \geq 0.$$

Phase transition occurs in a process if there is a $t \in I$ such that $\dot{m}_1(t) \neq 0$.

A constant process is an equilibrium of the system.

Note that the equilibrium properties of the system constitutive relations, the second law and the remark at the end of Section 5 about the equality of the chemical potentials imply that $\mathbf{Q}_i(T_1, p_1, m_1, T_2, p_2, m_2) = 0$ if and only if $(T_1, p_1) = (T_2, p_2) = (T_a, p_a) \in \Gamma$, and similar relations hold for \mathbf{F}_i and \mathbf{G}_i ($i = 1, 2$) as well. As a consequence, we have the following result.

Proposition 8. $(E_{10}, V_{10}, m_{10}, E_{20}, V_{20})$ is an equilibrium if and only if

$$\begin{aligned} \mathbf{T}(E_{10}, V_{10}, m_{10}) &= \mathbf{T}(E_{20}, V_{20}, m_s - m_{10}) = T_a, \\ \mathbf{p}(E_{10}, V_{10}, m_{10}) &= \mathbf{p}(E_{20}, V_{20}, m_s - m_{10}) = p_a, \\ \mu(E_{10}, V_{10}, m_{10}) &= \mu(E_{20}, V_{20}, m_s - m_{10}) \end{aligned}$$

which occurs if and only if $(T_a, p_a) \in \Gamma$.

This has the following immediate consequence:

Proposition 9. If $(T_a, p_a) \in \Gamma$ then the set of equilibria is

$$\{(m_1 e_{10}, m_1 v_{10}, m_1, (m_s - m_1) e_{20}, (m_s - m_1) v_{20}) \mid 0 < m_1 < m_s\}$$

where (e_{10}, v_{10}) and (e_{20}, v_{20}) are the unique elements in C_1 and in C_2 , respectively, for which $\mathbf{T}(e_{10}, v_{10}) = \mathbf{T}(e_{20}, v_{20}) = T_a$ and $\mathbf{p}(e_{10}, v_{10}) = \mathbf{p}(e_{20}, v_{20}) = p_a$ hold.

It will be convenient to write $m_1 = \lambda m_s$ where λ is a number between 0 and 1. Then the set of equilibria can be expressed in the form

$$m_s(0, 0, 0, e_{20}, v_{20}) + \{\lambda m_s(e_{10}, v_{10}, 1, -e_{20}, -v_{20}) \mid 0 < \lambda < 1\}.$$

Contrary to the system treated in the previous section, in this case the equilibria are not isolated from each other: they form a line segment.

The physical background is clear: at a temperature of $0^\circ C$ and at an atmospheric pressure, 100g water and 100g ice as well as 150g water and 50g ice can be in equilibrium.

Since the equilibria are not isolated from each other, equilibria cannot be asymptotically stable in the usual sense. However, our everyday experience indicates that some sort of asymptotic stability (trend to equilibrium) must hold: putting together 100g of ice and 100g of water at an ambient temperature of $0^\circ C$ and atmospheric pressure, we shall have as a result some ice and water together. The amounts of resultant water and ice depend on the initial conditions and on the system; e.g. if the initial temperature of water is higher or the heat conduction between the environment and the container is slower, the resultant amount of water will be larger.

The convenient mathematical expression of such a trend to equilibrium is strict asymptotic stability of the set of equilibria (see the Appendix). Unfortunately, Lyapunov's method is not applicable at present to strict asymptotic stability; nevertheless, the function

$$\mathbf{L}(E_1, V_1, m_1, E_2, V_2) := \mathbf{S}(E_1, V_1, m_1) + \mathbf{S}(E_2, V_2, m_s - m_1) - \frac{E_1 + p_a V_1 + E_2 + p_a V_2}{T_a}$$

which is similar to the Lyapunov functions used previously, will play an important role in the following. We have that

$$\mathbf{L}'(E_1, V_1, m_1, E_2, V_2) = \left(\frac{1}{T_1} - \frac{1}{T_a}, \frac{p_1}{T_1} - \frac{p_a}{T_a}, \frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}, \frac{1}{T_2} - \frac{1}{T_a}, \frac{p_2}{T_2} - \frac{p_a}{T_a}, \right)$$

where $T_1 := \mathbf{T}(E_1, V_1, m_1)$, $T_2 := \mathbf{T}(E_2, V_2, m_s - m_1)$ etc. It is obvious that $\mathbf{L}'(E_{10}, V_{10}, m_{10}, E_{20}, V_{20}) = 0$ if and only if $(E_{10}, V_{10}, m_{10}, E_{20}, V_{20})$ is an equilibrium.

Moreover,

$$\begin{aligned}
 \mathbf{L}''(E_{10}, V_{10}, m_{10}, E_{20}, V_{20}) = & \\
 = -\frac{1}{T_a^2} & \begin{pmatrix} \frac{\partial \mathbf{T}}{\partial E} & \frac{\partial \mathbf{T}}{\partial V} & \frac{\partial \mathbf{T}}{\partial m} & 0 & 0 \\ p_a \frac{\partial \mathbf{T}}{\partial E} - T_a \frac{\partial \mathbf{P}}{\partial E} & p_a \frac{\partial \mathbf{T}}{\partial V} - T_a \frac{\partial \mathbf{P}}{\partial V} & p_a \frac{\partial \mathbf{T}}{\partial m} - T_a \frac{\partial \mathbf{P}}{\partial m} & 0 & 0 \\ -\mu_a \frac{\partial \mathbf{T}}{\partial E} + T_a \frac{\partial \mu}{\partial E} & -\mu_a \frac{\partial \mathbf{T}}{\partial V} + T_a \frac{\partial \mu}{\partial V} & -\mu_a \frac{\partial \mathbf{T}}{\partial m} + T_a \frac{\partial \mu}{\partial m} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} + \\
 -\frac{1}{T_a^2} & \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\mu_a \frac{\partial \mathbf{T}}{\partial m} + T_a \frac{\partial \mu}{\partial m} & \mu_a \frac{\partial \mathbf{T}}{\partial E} - T_a \frac{\partial \mu}{\partial E} & \mu_a \frac{\partial \mathbf{T}}{\partial V} - T_a \frac{\partial \mu}{\partial V} \\ 0 & 0 & -\frac{\partial \mathbf{T}}{\partial m} & \frac{\partial \mathbf{T}}{\partial E} & \frac{\partial \mathbf{T}}{\partial V} \\ 0 & 0 & -p_a \frac{\partial \mathbf{T}}{\partial m} + T_a \frac{\partial \mathbf{P}}{\partial m} & p_a \frac{\partial \mathbf{T}}{\partial E} - T_a \frac{\partial \mathbf{P}}{\partial E} & p_a \frac{\partial \mathbf{T}}{\partial V} - T_a \frac{\partial \mathbf{P}}{\partial V} \end{pmatrix}_2
 \end{aligned}$$

where $(\cdot)_1$ and $(\cdot)_2$ mean the value of the corresponding functions at (E_{10}, V_{10}, m_{10}) and $(E_{20}, V_{20}, m_s - m_{10})$, respectively, and $\mu_a := \mu_1(T_a, p_a) = \mu_2(T_a, p_a)$.

We get from Proposition 1 that $\mathbf{L}''(E_{10}, V_{10}, m_{10}, E_{20}, V_{20})$ is negative semidefinite and its kernel is spanned by $(E_{10}, V_{10}, m_{10}, -m_{10} \frac{E_{20}}{m_s - m_{10}}, -m_{10} \frac{V_{20}}{m_s - m_{10}})$. Since all the real multiples of m_s and m_{10} coincide, in view of Propositions 8 and 9, we can state that the kernel in question is

$$Z := \{ \lambda m_s (e_{10}, v_{10}, 1, -e_{20}, -v_{20}) \mid \lambda \in \mathbb{R} \}$$

for all equilibria. This is the one dimensional linear subspace whose translation by $m_s(0, 0, 0, e_{20}, v_{20})$ contains the set of equilibria.

The equilibrium properties and the continuous differentiability of the system constitutive relations imply that

$$\begin{aligned}
 \mathbf{Q}_i(T_1, p_1, m_1, T_2, p_2, m_2) = & \alpha_{i1}(\dots) \left(\frac{1}{T_1} - \frac{1}{T_a} \right) + \alpha_{i2}(\dots) \left(\frac{p_1}{T_1} - \frac{p_a}{T_a} \right) \\
 & + \alpha_{i3}(\dots) \left(\frac{\mu_1(T_1, p_1)}{T_1} - \frac{\mu_2(T_2, p_2)}{T_2} \right) \\
 & + \alpha_{i4}(\dots) \left(\frac{1}{T_2} - \frac{1}{T_a} \right) + \alpha_{i5}(\dots) \left(\frac{p_2}{T_2} - \frac{p_a}{T_a} \right)
 \end{aligned}$$

where $\alpha_{i1}(\dots)$ etc. denote functions of $(T_1, p_1, m_1, T_2, p_2, m_2)$; of course, similar equalities are valid for \mathbf{F}_i and \mathbf{G}_i as well with functions β_{ir} and γ_{ir} ($r=1,2,3,4,5$), respectively.

For the sake of brevity, let us now introduce $x := (E_1, V_1, m_1, E_2, V_2)$. Then we can write the dynamical law in the form

$$\dot{x} = \mathbf{C}(x)\mathbf{L}'(x)$$

where $\mathbf{C}(x)$ is a matrix whose elements are obtained from the previous α -s, β -s and γ -s in a straightforward way.

In these notations the second law has the form

$$\mathbf{L}'(x) \cdot \mathbf{C}(x)\mathbf{L}'(x) \geq 0$$

where equality holds if and only if $\mathbf{L}'(x) = 0$ (the dot denotes the usual inner product of vectors).

Let us suppose that the system constitutive relations are twice differentiable.

Then the function $x \mapsto \mathbf{C}(x)\mathbf{L}'(x)$ is differentiable and its derivative at an equilibrium $x_o := (E_{1o}, V_{1o}, m_{1o}, E_{2o}, V_{2o})$ equals $\mathbf{C}(x_o)\mathbf{L}''(x_o)$ because $\mathbf{L}'(x_o) = 0$.

Moreover,

$$\mathbf{L}'(x) \cdot \mathbf{C}(x)\mathbf{L}'(x) = (\mathbf{L}''(x_o)(x - x_o)) \cdot (\mathbf{C}(x_o)\mathbf{L}''(x_o)(x - x_o)) + O^{(3)}(x - x_o)$$

where $\lim_{x \rightarrow x_o} \frac{O^{(3)}(x - x_o)}{|x - x_o|^2} = 0$. As a consequence, we have from the second law that

$$(\mathbf{L}''(x_o)(x - x_o)) \cdot (\mathbf{C}(x_o)\mathbf{L}''(x_o)(x - x_o)) \geq 0$$

for all x in a neighbourhood of x_o which implies the inequality for all x . This means that $\mathbf{C}(x_o)$ is positive semidefinite on the range of $\mathbf{L}''(x_o)$. Since $\mathbf{L}'(x)$ is the collection of thermodynamical forces, the Onsagerian linear approximation of the dynamical law in a neighbourhood of the equilibrium is $\dot{x} = \mathbf{C}(x_o)\mathbf{L}'(x)$. Consequently, it is not hard to suppose that $\mathbf{C}(x_o)$ is symmetric.

Proposition 10. *Let $(T_a, p_a) \in \Gamma$, suppose the system constitutive functions are twice differentiable and use the previous notations. If $\mathbf{C}(x_o)$ is symmetric and positive definite for all equilibria x_o then the set of equilibria is strictly asymptotically stable.*

Proof. We apply the theorem regarding strict asymptotic stability formulated in the Appendix (for $F(x) = \mathbf{C}(x)\mathbf{L}'(x)$).

As we have seen, $F'(x_o) = \mathbf{C}(x_o)\mathbf{L}''(x_o)$ for all equilibria x_o .

Since $\mathbf{C}(x_o)$ is positive definite, we have $\text{Ker}(\mathbf{C}(x_o)\mathbf{L}''(x_o)) = \text{Ker}\mathbf{L}''(x_o)$. Moreover, $\text{Ker}\mathbf{L}''(x_o)$ is the same one dimensional linear subspace Z for all equilibria x_o .

Putting $a := m_s(0, 0, 0, e_{2o}, v_{2o})$, we know that the set of equilibria consists of the elements of $a + Z$ which are in the domain of F .

From Proposition A in the Appendix (with $C = \mathbf{C}(x_o)$, $B = \mathbf{L}''(x_o)$) we get for all equilibria x_o that the zero eigenvalue of $F'(x_o)$ has equal algebraic and geometric multiplicity and the other eigenvalues are negative.

8. Supercooling, superheating

It is fundamental in the previous treatment of first-order phase transitions that *both phases* of the material are present in the processes.

Now we wish to establish a thermodynamical model of phase appearance in a given environment by an extension of the model considered in Section 7: it will include the possibilities $m_1 = 0$ or $m_2 = 0$. Correspondingly, we shall meet $(kg)_0^+$ instead of $(kg)^+$ in the formulae. This is not a simple extension: in the problems treated earlier the domain of the differential equation was an open subset which is common in the theory of differential equations; now the domain will contain some boundary points playing an important role in superheating and supercooling.

The mathematical model is the following: take items 1)-5) from the model in Section 7, replace $(kg)^+$ with $(kg)_0^+$ everywhere, and make the following additional requirements:

1)-2) No additional requirement.

3)

$$\mathbf{Q}_1(T_1, p_1, m_1, T_2, p_2, m_2), \quad \mathbf{F}_1(T_1, p_1, m_1, T_2, p_2, m_2),$$

$$\mathbf{G}_1(T_1, p_1, m_1, T_2, p_2, m_2)$$

are independent of T_2 and p_2 if $m_2 = 0$, are zero if $m_1 = 0$, and similar relations hold for \mathbf{Q}_2 , \mathbf{F}_2 and \mathbf{G}_2 as well.

4) Equality holds

– for $m_1 m_2 \neq 0$ if and only if $T_1 = T_2 = T_a$, $p_1 = p_2 = p_a$ and $\mu_1(T_1, p_1) = \mu_2(T_2, p_2)$,

– for $m_1 m_2 = 0$ if and only if $T_1 = T_2 = T_a$ and $p_1 = p_2 = p_a$;

5) No additional requirement.

If both m_1 and m_2 take non-zero values, we get back the problem treated earlier. Evidently, we are interested in the case when one of the masses can be zero.

Let us consider the case when no material in the second phase is present i.e. $m_2 = 0$ (and consequently $E_2 = 0$, $V_2 = 0$). Then for all $(T_a, p_a) \in \vartheta_1 \cap \vartheta_2$,

$$(E_{10}, V_{10}, m_s, 0, 0, 0) \quad (*)$$

is an equilibrium if

$$\mathbf{T}(E_{10}, V_{10}, m_s) = T_a, \quad \mathbf{p}(E_{10}, V_{10}, m_s) = p_a.$$

If a process starts in such a way that only the first phase is present, i.e. the initial conditions are

$$m_2(0) = 0, \quad E_2(0) = 0, \quad V_2(0) = 0,$$

where, of course, the first one is equivalent to $m_1(0) = m_s$, then the dynamical law implies that m_2, E_2 and V_2 are zero (and $m_1 = m_s$) in all the process and the dynamical law reduces to

$$\begin{aligned} \dot{E}_1 &= Q_1 - p_1 F_1, \\ \dot{V}_1 &= F_1; \end{aligned}$$

furthermore, the second law takes the form

$$(Q_1 - p_1 F_1) \left(\frac{1}{T_1} - \frac{1}{T_a} \right) + F_1 \left(\frac{p_1}{T_1} - \frac{p_a}{T_a} \right) \geq 0$$

(with our usual abbreviation of notations) where equality holds if and only if $T_1 = T_a$ and $p_1 = p_a$.

This is the well known simple problem in ordinary thermodynamics ([18], note that $E_1 = m_1 e_1, V_1 = m_1 v_1$ and $m_1 = m_s = \text{const}$), similar to that treated in Section 4.

Thus we can state that a process with the initial conditions above tends to the equilibrium (*).

Note that this *does not mean*, in general, that the equilibrium in question is asymptotically stable. We have only that processes starting with one-phase initial values tend to one-phase equilibrium. Other processes in which the initial value of m_2 is not zero, starting even arbitrarily close to the one-phase equilibrium, may diverge from it.

The complete discussion of stability of such an equilibrium is not available yet. Recall that

$$\Gamma = \{(T, p) \in \vartheta_1 \cap \vartheta_2 \mid \mu_1(T, p) = \mu_2(T, p)\}$$

and an equilibrium in which both phases are present i.e. $m_1 m_2 \neq 0$ can exist only if $(T_a, p_a) \in \Gamma$.

Now we introduce

$$\begin{aligned} \Delta_1 &:= \{(T, p) \in \vartheta_1 \cap \vartheta_2 \mid \mu_1(T, p) < \mu_2(T, p)\}, \\ \Delta_2 &:= \{(T, p) \in \vartheta_1 \cap \vartheta_2 \mid \mu_1(T, p) > \mu_2(T, p)\} \end{aligned}$$

and we conjecture that if $(T_a, p_a) \in \Delta_1$ then the equilibrium (*) is asymptotically stable (the equilibrium is a "normal" one), if $(T_a, p_a) \in \Delta_2$ then the equilibrium (*) is unstable (the equilibrium is a superheated or supercooled one). To support this conjecture, let us study the simple particular case given by the following system constitutive functions:

$$\begin{aligned} Q_1 - p_1 F_1 + \mu_1 G_1 &= \lambda_1 m_1 \left(\frac{1}{T_1} - \frac{1}{T_a} \right) + \lambda_{12} m_1 m_2 \left(\frac{1}{T_1} - \frac{1}{T_2} \right), \\ F_1 &= \delta_1 m_1 \left(\frac{p_1}{T_1} - \frac{p_a}{T_a} \right) + \delta_{12} m_1 m_2 \left(\frac{p_1}{T_1} - \frac{p_a}{T_2} \right), \\ G_1 &= -\alpha_1 m_1 m_2 \left(\frac{\mu_1(T_1, p_1)}{T_1} - \frac{\mu_2(T_2, p_2)}{T_2} \right) \end{aligned}$$

and similar expressions for the constitutive functions with subscripts 2, where $\lambda_1, \lambda_{12}, \delta_1, \delta_{12}$ and α_1 are positive constants; the reader is asked to check that these constitutive functions satisfy all the requirements imposed in items 3)-4) if $\lambda_{12} = \lambda_{21}, \delta_{12} = \delta_{21}$ and $\alpha_1 = \alpha_2$.

Suppose $(T_a, p_a) \in \Delta_1$. If the equilibrium (*) is disturbed by a non-zero value of m_2 (by a "nucleus of the other phase") while the temperature and the pressure remain at T_a and p_a , respectively, then G_1 becomes positive, hence m_1 will increase (m_2 will decrease) and the process tends again towards an equilibrium in which $m_2 = 0$.

On the other hand, if $(T_a, p_a) \in \Delta_2$ then the perturbation by a non-zero value of m_2 yields negative value of G_1 ; consequently, m_1 will decrease (m_2 will increase): the other phase appears and begins to grow, the equilibrium is unstable.

8. Discussion

Phase transitions have been treated as processes of homogeneous bodies. The relation between phase transitions and stability has been investigated. 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" ([12] pages 136, 146).

As concerns second-order phase transitions, we see that

- there is no instability in second-order phase transitions of Ehrenfest type,
- instability may or may not occur in second-order phase transitions of Tisza type.

Moreover, it is clear even from the usual treatments 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.

Stability has the following intuitive meaning: a process is stable if a small change of the parameters - e.g. the temperature or the pressure - causes only a small change in the process. As our experience shows clearly, the everyday first-order phase transitions (freezing, melting, evaporation, condensation) are stable processes.

From a practical mathematical point of view, stability of equilibria is much simpler to study than stability of arbitrary processes. Though having dealt only with stability of equilibria, we have the convincing result that *first-order phase transitions are stable processes if both phases are present*.

The situation is quite different if only one phase of the substance is present: *the phase non-transition of a single supercooled or superheated substance is an unstable process* which is a well known phenomenon, too: a tap (a small change of the pressure) on a supercooled liquid causes a dramatic crystallization.

Our results show clearly that only the appearance of a new phase is a phenomenon related to instability and support the well known qualitative explanation of nucleation as a result of "infinitesimally small density fluctuation" ([21], [15] p.162) If only one phase is present, a new phase does not begin to grow till a nucleus (a "fluctuated portion") of that phase is not stabilized. If nucleation is hindered somehow and the process of the body crosses the curve of phase connection then an unstable equilibrium can be produced.

It is worth remarking the following. The states between the binodal line and the spinodal line – the superheated states and the supercooled ones – lie in the regular constitutive domain i.e. the conditions of intrinsic stability are satisfied; they are usually called metastable ([15],[21],[22]), and according to our results they are unstable. 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, m) : the couple (e, v) is not a state. The conditions of intrinsic stability are satisfied at all (e, v) in a phase. Considering a one-body system, we see that an equilibrium (e, v, m) is

– asymptotically stable if (e, v) is over the binodal line (which in our notations means $(\mathbf{T}(e, v), \mathbf{p}(e, v)) \in \Delta_1$),

– unstable if (e, v) is under the binodal line, i.e. (e, v) is metastable in the usual terminology (in our notations $(\mathbf{T}(e, v), \mathbf{p}(e, v)) \in \Delta_2$).

Appendix

Let n be a positive integer and suppose F is a continuously differentiable function from \mathbb{R}^n into \mathbb{R}^n and consider the differential equation

$$\dot{x} = F(x),$$

moreover suppose that x_o is in the domain of F and

$$F(x_o) = 0.$$

Then the constant function $x(t) = x_o$ ($t \in \mathbb{R}$) is a solution of the differential equation, called an equilibrium.

We say that a solution r starts from a subset H of the domain of F if $r(0)$ is in H . The solution proceeds in H if $r(t) \in H$ for all $t \geq 0$.

An equilibrium x_o is *stable* if for each neighbourhood N of x_o there is a neighbourhood U of x_o such that for every solution r starting from U proceeds in N .

An equilibrium x_o is *asymptotically stable* if it is stable and there is a neighbourhood V of x_o such that for all solutions r starting from V we have $\lim_{t \rightarrow \infty} r(t) = x_o$.

A set E of equilibria is *strictly asymptotically stable* ([24]) if

– every equilibrium in E is stable,

– every equilibrium in E has a neighbourhood V such that if r is a solution starting from V then $\lim_{t \rightarrow \infty} r(t)$ is in the closure of E .

If L is a differentiable real valued function defined in \mathbb{R}^n then its derivative (gradient) L' is a function from \mathbb{R}^n into \mathbb{R}^n . The real valued function $\dot{L}(x) := L'(x) \cdot F(x)$ defined in \mathbb{R}^n (where the dot stands for the inner product in \mathbb{R}^n) is called the *derivative of F along the differential equation*.

The following two results are well known in stability theory ([23]).

1. If x_0 is an equilibrium and there is a continuously differentiable real valued function L , defined in a neighbourhood of x_0 such that

(i) L has a strict local maximum at x_0 , i.e. $L(x) < L(x_0)$ for all x in a neighbourhood of x_0 ,

(ii) \dot{L} has a (strict) local minimum at x_0 ,
then the equilibrium x_0 is (asymptotically) stable.

2. If x_0 is an equilibrium and there is a continuously differentiable real valued function L , defined in a neighbourhood of x_0 such that

(i) L has not a local maximum at x_0 ,

(ii) \dot{L} has a strict local minimum at x_0 ,
then the equilibrium x_0 is unstable.

L is usually referred to as a Lyapunov function.

The third, less common result concerning strict asymptotic stability ([25], Section 34) reads in a convenient reformulation as follows.

3. Let H be the set of all equilibria and suppose

(i) there are a non-trivial linear subspace Z in \mathbb{R}^n , an element a of \mathbb{R}^n such that $H = (a + Z) \cap \text{Dom}F$,

(ii) for all $x_0 \in H$,
– $\text{Ker}F'(x_0) = Z$,
– the algebraic multiplicity and the geometric multiplicity of the zero eigenvalue of $F'(x_0)$ are equal,
– the real part of the non-zero eigenvalues of $F'(x_0)$ is negative.

Then H is strictly asymptotically stable.

Proposition A. *Let C and B $n \times n$ real matrices such that*

- (i) B is symmetric and negative semidefinite,
(ii) C is symmetric and positive definite.

Then

- the algebraic multiplicity and the geometric multiplicity of every eigenvalue of CB are equal,
– the non-zero eigenvalues of CB are negative.

Proof. C^{-1} is symmetric and positive definite as well. Then $\langle \xi, \eta \rangle := (C^{-1}\xi) \cdot \eta$ defines an inner product on \mathbb{R}^n . CB is symmetric and negative semidefinite with respect to this new inner product for

$$\langle \xi, CB\eta \rangle = (C^{-1}\xi) \cdot (CB\eta) = \xi \cdot B\eta = (B\xi) \cdot \eta = \langle CB\xi, \eta \rangle$$

and

$$\langle \xi, CB\xi \rangle = \xi \cdot B\xi \leq 0$$

which implies our assertion ([26], Section 78).

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