Spatial correlations in diluted gases from the viewpoint of the metric of the thermodynamic state space

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Assuming the existences of two different correlation scales in a diluted gas, the second one leads to pressure and energy corrections, which are of van der Waals type in the simplest case. The direct connection between the correlation scales and the metric of the thermodynamic state space is discussed here.

I. INTRODUCTION

Ten years ago Weinhold, in a series of papers, demonstrated that there is a Riemannian geometry behind equilibrium thermodynamics[1]; according to his own words, thermodynamics is geometry.[2] The basic idea of such a geometrization is the use of the second derivatives of the proper thermodynamic potential (i.e., for example, of energy or entropy when extensive variables are used) as a metric tensor for the thermodynamic state space; such a nondegenerate metric tensor must exist because the definiteness of the derivative matrix is just the condition for thermodynamic stability. Then the thermodynamic relations obtain simple geometric meaning.

Now, if thermodynamics is indeed a geometry, then the particularities of the equations of state must possess some geometrical meaning too. This connection can be approached in two ways. First, choosing a particular form for the thermodynamic potential one can calculate the metric tensor, and can recognize the geometric consequences of some properties of the potential. This way was chosen, e.g., by Salamon et al.[3] who have shown that (using the energy as potential) the length of a trajectory in the state space measures the change of the flow velocity of a gas when moving from one state to another. The second possibility is a somewhat inverse way, chosen by, e.g., Ruppeiner.[4] General relativity has demonstrated that in some cases the Riemannian curvature possesses genuine and direct physical meaning; Einstein's equation[5] expresses the hypothesis that some components of the curvature tensor are directly governed by matter content and interactions, and then there is a way to build up the metric from some supposed characteristics of matter. Ruppeiner started with the observation that (when using entropy as potential) the curvature vanishes for an ideal Boltzmann gas[4]; therefore the curvature must be equal to some characteristics of interparticle interactions. Hence, by assuming some version of an Einstein-type equation, one may hope to be able to construct thermodynamic potentials for different types of matter.

The problem is that neither sides of such an equation are uniquely determined beyond reasonable doubt by fundamental principles, therefore no well-founded constructive method is proposed yet. Thus here we choose a restricted goal to establish a connection between characteristic interaction ranges (or particle sizes) and the metric tensor via correlation volumes. By this way one gets some new insight into the physical meaning of the convenient and useful, but heuristic van der Waals equation of state.

In this paper we concentrate on systems near to ideal Boltzmann gases, i.e., when the entropy function has the form

$$s = s_0 n + \tfrac{3}{2} n \ln \epsilon - \tfrac{3}{2} n \ln n + \eta, \quad |\eta| \ll n, \qquad (1.1)$$

where ϵ and n are the energy and particle densities, respectively. Here s_0 is a free constant; since ideal Boltzmann gases do not obey the Third Law, its value could be fixed by a roundabout way through Fermi gases, but for our purposes s_0 is immaterial.

II. THE VAN DER WAALS EQUATION

Using the extensive densities ϵ and n as variables, the van der Waals equation of state is as follows:

$$p(\epsilon, n) = \frac{nT}{n_0 - n} - an^2, \qquad (2.1)$$

p is the pressure, T stands for the temperature, while n_0 and a are constants; they represent volume exclusion (by, e.g., hard cores of particles) and long-range interactions, respectively. The usual interpretation of the first term on the right-hand side is that there is a pressure increase due to effective decrease of the gas volume when the particles are not point like.

Equation (2.1) is a differential equation for the entropy function $s = s(\epsilon, n)$; supplemented by an energy equation as ideal as possible:

$$\epsilon = \tfrac{3}{2} nT - an^2, \qquad (2.2)$$

one obtains

$$s = s_0 n + n \ln \frac{(\epsilon + an^2)^{3/2}(n_0 - n)}{n_0 n^{5/2}}. \qquad (2.3)$$

The metric tensor defined as

$$g_{ik} = -\frac{\partial^2 s}{\partial \rho^i \partial \rho^k} \quad (\rho^1 \equiv \epsilon, \ \rho^2 \equiv n) \qquad (2.4)$$

is rather complicated, except for the special case $a = 0$, which will be henceforth discussed here; then

$$ds^2 = \frac{3}{2} n \left(\frac{1}{\epsilon} d\epsilon - \frac{1}{n} dn \right)^2 - \frac{n_0^2}{n(n_0 - n)^2} dn^2. \qquad (2.5)$$

This metric possesses a single Killing symmetry, as shown by direct calculation, representing a temperature shift (cf. the Appendix).

In the limit (1.1) one obtains

$$\eta = -\frac{n^2}{n_0} + O\left[(n/n_0)^2\right].\tag{2.6}$$

III. CORRELATION VOLUMES

It is known that the metric tensor (2.4) is intimately connected to the probability function of fluctuations[6,7]; when the fluctuating subsystem of volume $\overline{V}$ is sufficiently large, one gets

$$\langle(\rho^i - \overline{\rho}^i)(\rho^k - \overline{\rho}^k)\rangle = (1/\overline{V})g^{ik}.\tag{3.1}$$

With decreasing volume this $1/\overline{V}$ rule breaks down somewhere, thus indicating that the fluctuations of neighboring subsystems are not independent below V_c.[8] Thus V_c can be regarded as a correlation volume of the system, which must, in turn, be directly connected to the ranges of interactions establishing spatial correlations in the system. V_c is a solution of an eigenvalue equation[8]

$$(M^{ir} - V_c g^{ir})v_r = 0,\tag{3.2}$$

where, in extensive coordinates, M^{ik} is defined as

$$M^{ik} = g^{ik},_{rs}g^{rs}\tag{3.3}$$

(the comma stands for partial derivative); for general coordinates M^{ik} is rather complicated[9] and will not be used here. In the generic case there are as many different correlation volumes as the number of independent extensive densities; these volumes may represent different correlation mechanisms.

Consider a gas of one particle component with the entropy density (1.1). Then there are two correlation volumes

$$V_{c1} = \frac{4}{3}\frac{1}{n}\left[1 + O(\eta/n)\right],$$
$$V_{c2} = (x^2\varphi,_{xx} + \tfrac{2}{3}y^2\varphi,_{yy} + 2\varphi)\left[1 + O(\eta/n)\right],$$
$$\varphi = \eta,_{xx}, \quad x = n, \quad y = \epsilon/n.\tag{3.4}$$

The first correlation volume represents the indivisibility of the point particles,[8] thus only V_{c2} is connected to the interactions.

By using the first-order approximation (2.6) for the van der Waals equation of state the result is

$$V_{c2} = -\frac{4}{n_0}\left[1 + O(n/n_0)\right].\tag{3.5}$$

Since in the heuristic derivation of the van der Waals equation of state n_0 is proportional to the inverse volume of particles, one may conclude that $-V_{c2}$ is the volume excluded for other particles.

Now we take the inverse way, assuming first something for the (second) correlation volume, and then calculating the corresponding entropy function. In this paper we choose the simplest assumption

$$V_{c2} = kV_0,\tag{3.6}$$

where $k = \pm 1$, and V_0 is a constant. Observe that we are performing a first-order approximation near to ideal gases, which is physically the $n \to 0$ limit; therefore the neglection of the $x = n$ dependence in V_{c2} is not a serious oversimplification. This argument does not tell anything about the $y \sim T$ dependence; nevertheless Eq. (3.4) is of fourth order for η,

therefore one cannot hope a transparent formula for the generic case. With the assumption (3.6) the solution of Eq. (3.4) can be formally written as

$$\eta = H(x,y) + \tfrac{1}{4}kV_0x^2,\tag{3.7}$$

where $H(x,y)$ is the general solution of the homogeneous equation

$$x^2H,_{xxxx} + \tfrac{2}{3}y^2H,_{xxyy} + 2H,_{xx} = 0.\tag{3.8}$$

Now we are going to discuss the solutions.

IV. SOLUTIONS WITH TAYLOR EXPANSION

In this section we impose three restrictions on the system, neither of them seems to be too serious or aphysical. Namely (1) The deviation from the ideal gas entropy, η, possess a Taylor expansion at $x = 0$. (2) The system show an ideal gas behavior when $x \to 0$. (3) The system remain near to ideal gas state if x is moderate and $y \to \infty$ (i.e. for diluted high temperature states). From condition (1),

$$\eta = \sum_{r=0}^{\infty}\alpha_r(y)x^r.\tag{4.1}$$

According to condition (2) we require

$$\lim_{n\to 0}\frac{(s/n)}{(s/n)_{id}} = 1,$$
$$\lim_{n\to 0}\frac{(p/nT)}{(p/nT)_{id}} = 1,\tag{4.2}$$

where

$$\alpha_0 = \alpha_1 = 0.\tag{4.3}$$

Now, substituting the form (4.1) into Eqs. (3.6)–(3.8), one obtains after a lengthy but straightforward calculation:

$$\eta = x^2\left\{\frac{1}{4}kV_0 + \sum_{r=0}^{\infty}\sqrt{y}[A_r \sin(\omega_r \ln y)\right.$$
$$\left. + B_r \cos(\omega_r \ln y)]\right\}x^r,$$
$$\omega_i = \tfrac{1}{2}\sqrt{6i^2 - 6i + 11}.\tag{4.4}$$

Now, observe that this solution generally violates condition (3); in fact, with such an entropy function

$$\frac{p}{nT} = 1 - \frac{1}{4}kV_0x - x\sqrt{y}\sum_{r=0}^{\infty}(1+r)$$
$$\times [A_r \sin(\omega_r \ln y) + B_r \cos(\omega_r \ln y)]x^r\tag{4.5}$$

so at fixed small values of x there is an oscillation of growing amplitude and shrinking period with increasing temperature. Imposing then condition (3),

$$A_i = B_i = 0.\tag{4.6}$$

The remaining term in η is equivalent to the first-order approximation (2.6) of the van der Waals gas if $k = -1$.

V. INEVITABILITY OF PRESSURE CORRECTION

The previous section demonstrated that the assumption of a temperature-independent second correlation volume may be enough to result in van der Waals-type corrections in the equation of state. However, a temperature-independent coherence volume may remind us of a rigid sphere, usual in

the derivation of the van der Waals equation, and our condition (1), although mathematically decent, restricts the solutions in a physically unclear way. Now here we are going to show that the existence of a second correlation volume (of any kind of temperature dependence) inevitably leads to pressure corrections.

Assume that

$$\eta \neq 0,$$

$$p = p_{id} = nT. \tag{5.1}$$

Hence, invoking the entropy function (1.1): $\eta = x\eta_{,x}$; after integration we get

$$\eta = \omega(y)x \tag{5.2}$$

and then, via Eq. (3.4),

$$V_{c2} = 0. \tag{5.3}$$

Thus, indeed, V_{c2} is the source of the pressure correction.

VI. DIMENSIONAL CONSIDERATIONS

Here very general but only qualitative discussions are performed, based on dimensional analysis. Our starting assumptions were that the dimensionless deviation in the entropy η/n is small and that it is caused by a correlation volume. Then observe that

$$\lim_{n \to 0} V_{c2} = \infty$$

if η starts with a power lower than quadratic in n, then V_{c2} diverges in the limit $n \to 0$. Therefore we write

$$\eta(n,\epsilon) = n^2 V_0 \lambda(n,\epsilon). \tag{6.1}$$

Here λ is dimensionless, and V_0 can be chosen in such a way that λ be of order of unity (at least in the considered domain of variables). Now, a dimensionless function must depend on dimensionless arguments, i.e.,

$$\lambda = \lambda[nV_0 = x^1, \ (\epsilon/nT_0) = x^2], \tag{6.2}$$

where T_0 is a constant of energy dimension, characterizing, e.g., the energy dependence of interactions. Now, calculating the pressure and temperature from the entropy function (1.1) and (6.1), one obtains

$$\frac{P}{nT} = 1 - x^1(\lambda + x^1\lambda_{,1}). \tag{6.3}$$

At low densities and temperatures one expects that λ is either a slowly varying function (when the first term dominates in the bracket) or it is a power function (when the two terms are in the same order of magnitude). Thus, in both cases, being $\lambda \sim 1$,

$$\left(\frac{P}{nT}\right) - \left(\frac{P}{nT}\right)_{id} \sim \left(\frac{s}{n}\right) - \left(\frac{s}{n}\right)_{id} \sim nV_0. \tag{6.4}$$

For the correlation volume Eqs. (3.4) and (6.1) yield

$$\frac{V_{c2}}{V_0} = 4\lambda + 8x^1\lambda_{,1} + 14(x^1)^2\lambda_{,11} + 8(x^1)^3\lambda_{,111}$$

$$+ 2(x^1)^4\lambda_{,1111} + \tfrac{2}{3}(x^2)^2[2\lambda_{,22} + 4x^1\lambda_{,122}$$

$$+ (x^1)^2\lambda_{,1122}]. \tag{6.5}$$

Again, using the previous argumentation, $V_{c2} \sim V_0$; the factors of order of unity here and in Eq. (6.4) depend on the (here completely undefined) form of $\lambda(x^1,x^2)$.

Again an intimate connection and proportionality has been found among pressure and entropy corrections and the correlation volume. This indicates that it would be hopeful to investigate this connection on more complicated, realistic cases. The van der Waals gas is the simplest possible model system realizing this connection by $\lambda = \text{const} \sim 1$ (in first-order approximation); when nothing else is known about the interactions than the existence and order of magnitude of a second correlation volume, this model gas is the most obvious candidate according to the principle of Occam's razor.

VII. CONCLUSIONS

In this paper we have displayed some new aspects of the geometric meaning of the metric tensor of the thermodynamic state space introduced by Weinhold. We have demonstrated that the metric can, indeed, be built up from informations about the interactions in the matter. Our particular results are partly model dependent; they can be summarized as follows.

(1) In a dilute gas of almost ideal Boltzmann behavior the appearance of a correlation volume (established by interactions correlating the fluctuations in nearby space points) leads to corrections in the pressure and entropy, proportional to that correlation volume.

(2) These corrections resemble the analogous ones in van der Waals gases (when the role of the correlation volume is played by the volume occupation parameter).

While these results may be not very surprising, observe that we did not assume short-range repulsion between particles, so the pressure corrections have been produced by a more subtle mechanism.

APPENDIX: THE KILLING SYMMETRY

The Killing symmetry is a shift along a Killing vector field K^i during which the metric remains unchanged, i.e., so that

$$\mathcal{L}_K g_{ik} = 0, \tag{A1}$$

where the symbol $\mathcal{L}$ stands for the Lie derivative.[5,7] An equivalent form is

$$g_{ir}K^r_{,k} + g_{kr}K^r_{,i} + g_{ik,r}K^r = 0. \tag{A2}$$

Using the metric (2.5) one obtains the following three equations:

$$2n\epsilon K^\epsilon_{,\epsilon} - 2\epsilon^2 K^n_{,\epsilon} - \epsilon K^n - 2nK^\epsilon = 0,$$

$$nK^\epsilon_{,n} - \epsilon K^n_{,n} - \epsilon K^\epsilon_{,\epsilon}$$

$$+ \left[\frac{2}{3}\frac{n_0^2\epsilon^2}{n(n_0-n)^2} + \frac{\epsilon^2}{n}\right]K^n_{,\epsilon} + K^\epsilon = 0,$$

$$-2\frac{1}{\epsilon}K_{,n} + \left[\frac{4}{3}\frac{n_0^2}{n(n_0-n)^2} + \frac{2}{n}\right]K^n_{,n}$$

$$- \left[\frac{1}{n^2} + \frac{2}{3}\frac{n_0^2(n_0-3n)}{n^2(n_0-n)^3}\right]K^n = 0. \tag{A3}$$

One can directly see that these equations hold with

$$K^i = (A\epsilon, 0); \quad A = \text{const} \tag{A4}$$

and, integrating Eqs. (A3) step by step, the result is that the form (A4) is the general solution.

Therefore the symmetry transformation connects points in which the density is the same while the energy densities are proportional. Via Eq. (2.2) one sees that the temperatures are proportional too; note that, due to $a = 0$, now the system does not contain any phase transition which could lead to a critical temperature.

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