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Thermodynamic curvature of the multicomponent ideal gas

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We work out the thermodynamic curvature resulting from a Riemannian geometric approach to thermodynamics for the general multicomponent ideal gas. This Riemannian geometry is based on including fluctuation theory in thermodynamics. We find that the Riemannian curvature scalar for this system is small, on the order of the average volume per molecule, no matter how many components. This result fits in well with expectations developed earlier that the thermodynamic curvature gives a measure of the volume where classical thermodynamic fluctuation theory fails.

I. INTRODUCTION

A Riemannian geometry for thermodynamics based on thermodynamic fluctuation theory has been introduced recently and applied to a number of thermodynamic systems.[1-9] These systems were, with a few exceptions, represented by two-dimensional Riemannian geometries; for example, the single-component fluid or the Ising model. In this paper, we examine the geometry of general ideal gases consisting of more than one component. This requires a geometric representation in three or more dimensions. We are particularly interested in the Riemannian curvature scalar. Results for this geometric object are in accord with earlier expectations that the thermodynamic curvature gives the volume where classical thermodynamic fluctuation theory fails.

Thermodynamic state space was first endowed with a natural metric structure based on the laws of thermodynamics by Weinhold in 1975,[10] who introduced an inner product related to the second derivatives of the internal energy. This inner product simplified certain standard thermodynamic computations. A Riemannian metric structure representing thermodynamic fluctuation theory, and related to the second derivatives of the entropy, was introduced by Ruppeiner in 1979.[1] It offered a natural meaning for the distance between thermodynamic states and a resulting geometry with an interesting interpretation for the intrinsic curvature. It is this geometry that is the basis for this paper. Salamon *et al.*,[11] in 1980 introduced a slightly different Riemannian metric to represent thermodynamic processes in finite time.

Riemannian geometry gives rise to geometric invariants, such as the Riemannian curvature scalar, which are subject to physical interpretation. Initially, the curvature was interpreted in two-dimensional thermodynamic state spaces in terms of the correlation length.[1,2] This was followed with an interpretation in state spaces of any dimension with a covariant thermodynamic fluctuation theory developed in 1983.[3] This theory predicts that the absolute value of the curvature scalar gives the real-space volume where the classical thermodynamic fluctuation theory breaks down. In many cases, particularly near critical points, this is the correlation volume. This interpretation worked well when tried, but it was never tested beyond two dimensions in open systems.

In this paper, we calculate the thermodynamic curvature of the multicomponent ideal gas. We find full consistency with expectations.

II. GEOMETRY OF THERMODYNAMICS

In this section, we summarize the Riemannian geometry of thermodynamics, discuss its connection to the covariant thermodynamic fluctuation theory, and summarize the resulting interpretation of thermodynamic curvature.

At the outset, we must distinguish between two spaces. The first is the real physical space in which the thermodynamic system resides. The second is the thermodynamic state space, each point of which represents a thermodynamic state specified by the values of the intensive coordinates.

Consider a finite, open subsystem A' of an infinite thermodynamic fluid system A. The system A consists of n fluid components. A' has fixed volume V' and fluctuating energy and particle numbers. Denote by $\mathbf{a}=(a_0,a_1,a_2,\ldots a_n)$ the internal energy per volume of the entire system and the number of particles per volume in each of the n components of A. The n'tuple $\mathbf{a}$ constitutes the thermodynamic state of A; A' has corresponding thermodynamic state $\mathbf{a}'$. The Gaussian approximation of the classical thermodynamic fluctuation theory asserts that the probability of finding the thermodynamic state of A' between $\mathbf{a}'$ and $\mathbf{a}'+d\mathbf{a}'$ is[12]

$$W(\mathbf{a},\mathbf{a}')da_0'da_1'\cdots da_n' = \left[\frac{V'}{2\pi}\right]^{n/2}\exp\left[-\frac{V'}{2}\sum_{\mu,\nu=0}^{n} g_{\mu\nu}(\mathbf{a})\Delta a_\mu'\Delta a_\nu'\right] \times\sqrt{g(\mathbf{a})}\,da_0'da_1'\cdots da_n' \,, \tag{1}$$

where $\Delta a_\mu'=a_\mu'-a_\mu$,

$$g_{\mu\nu}(\mathbf{a})\equiv-\frac{1}{k_B}\frac{\partial^2 s(\mathbf{a})}{\partial a_\mu\partial a_\nu}\,, \tag{2}$$

$s(\mathbf{a})$ is the entropy per volume in the thermodynamic limit, k_B is Boltzmann's constant, and $g(\mathbf{a})\equiv\det[\underline{g}(\mathbf{a})]$. We use greek indices for the coordinates of the thermodynamic state space and arabic indices for the components of the fluid.

The quadratic form in Eq. (1),

$$(\Delta l)^2 = \sum_{\mu,\nu=0}^{n} g_{\mu\nu}(\mathbf{a})\Delta a'_\mu \Delta a'_\nu \ , \qquad (3)$$

constitutes a positive definite Riemannian metric on the thermodynamic state space. The positive definiteness results since the entropy is a maximum in equilibrium $\mathbf{a}'=\mathbf{a}$. Physically, the interpretation for the distance between two thermodynamic states is clear from Eq. (1): the less the probability of a fluctuation between the states, the further apart they are. Note also that the quantity in Eq. (1),

$$\sqrt{g(\mathbf{a})}da'_0 da'_1 \cdots da'_n \ , \qquad (4)$$

is the invariant Riemannian thermodynamic state space volume element.[13]

The metric defines a fourth rank Riemannian curvature tensor $\underline{R}$. For our metric the complete contraction of $\underline{R}$, the curvature scalar R, has units of real-space volume, regardless of the dimension of the state space. It is zero for the monocomponent ideal gas and diverges near the critical point of the pure interacting fluid proportional to the correlation volume.[1]

This Riemannian geometry has been grounded on a covariant thermodynamic fluctuation theory.[3,4] This theory was proposed as the correct way to extend the classical thermodynamic fluctuation theory beyond the Gaussian approximation. It also offers an interpretation for the thermodynamic curvature.[3] Janyszek and Mrugala have connected this geometry to information theory and to contact geometry.[8,14]

III. GEOMETRY OF THE MULTICOMPONENT IDEAL GAS

The Helmholtz free energy per volume of the multicomponent ideal gas is[12]

$$f(T,\rho_1,\rho_2,\ldots,\rho_n) = \sum_{i=1}^{n} \rho_i k_B T \ln(e\rho_i) + \sum_{i=1}^{n} \rho_i f_i(T) \ , \qquad (5)$$

where ρ_i equals the density a_i, and where e is the natural base of logarithms, and the $f_i(T)$'s are functions of the temperature T whose second derivatives are negative in order to assure a positive definite heat capacity.

It can be shown[12] that for any fluid system, interacting or not, the metric Eq. (3) can be written as

$$(\Delta l)^2 = \frac{1}{k_B T}\Delta T \Delta s + \frac{1}{k_B T}\sum_{i=1}^{n} \Delta\mu_i \Delta\rho_i \ , \qquad (6)$$

where the entropy per volume

$$s = -\frac{\partial f}{\partial T} \ , \qquad (7)$$

and the chemical potentials

$$\mu_i = \frac{\partial f}{\partial \rho_i} \ . \qquad (8)$$

Using Eq. (5) for the free energy and a Maxwell relation yields

$$(\Delta l)^2 = \left[\sum_{i=1}^{n} \rho_i h_i(T) \right] (\Delta T)^2 + \sum_{i=1}^{n} \frac{1}{\rho_i}(\Delta\rho_i)^2 \ , \qquad (9)$$

where

$$h_i(T) = -\frac{f_i''(T)}{k_B T} > 0 \ . \qquad (10)$$

The metric in coordinates $(T,\rho_1,\rho_2,\ldots,\rho_n)$ is therefore diagonal, with elements

$$g_{TT} = \sum_{i=1}^{n} \rho_i h_i(T) \qquad (11)$$

and

$$g_{\rho_i\rho_i} = \frac{1}{\rho_i} \ . \qquad (12)$$

The metric is diagonal necessarily only for the multicomponent ideal gas. For interacting gases, there are cross terms involving the densities $g_{ij}\Delta\rho_i\Delta\rho_j$.

The curvature tensor may be written in terms of the metric elements as

$$R^{\lambda}_{\mu\nu\kappa} = \Gamma^{\lambda}_{\mu\nu,\kappa} - \Gamma^{\lambda}_{\mu\kappa,\nu} + \sum_{\eta=0}^{n} \Gamma^{\eta}_{\mu\nu}\Gamma^{\lambda}_{\kappa\eta} - \sum_{\eta=0}^{n} \Gamma^{\eta}_{\mu\kappa}\Gamma^{\lambda}_{\nu\eta} \ , \qquad (13)$$

where the Christoffel symbols

$$\Gamma^{\lambda}_{\mu\nu} = \tfrac{1}{2}\sum_{\phi=0}^{n} g^{\lambda\phi}(g_{\phi\nu,\mu} + g_{\phi\mu,\nu} - g_{\mu\nu,\phi}) \ , \qquad (14)$$

and the comma notation $(,\mu)$ denotes the partial derivative with respect to the μth coordinate. The components of the second-rank Ricci tensor are

$$R_{\mu\nu} = \sum_{\lambda=0}^{n} R^{\lambda}_{\mu\lambda\nu} \ . \qquad (15)$$

Contracting the Ricci tensor yields the Riemannian curvature scalar

$$R = \sum_{\mu,\nu=0}^{n} g^{\mu\nu} R_{\mu\nu} \ . \qquad (16)$$

For a given metric, the sign of R may be either positive or negative depending on the sign convention used. We use the sign convention of Weinberg,[13] since this was used in Ref. 3. Though we offer no interpretation of the sign of R, it is nevertheless important to make clear what sign convention we use.

Since there is such a high degree of symmetry in the metric for the multicomponent ideal gas, many of the components in the curvature tensor are either zero or of the same functional form. Accordingly, it is not difficult to show that

$$R=\frac{\sum_{i=1}^{n} h_i(T)\sum_{j=1}^{n}\rho_j h_j(T)-\sum_{i=1}^{n}\rho_i[h_i(T)]^2}{2\left[\sum_{i=1}^{n}\rho_i h_i(T)\right]^2} . \qquad (17)$$

We emphasize that, because of the rules of Riemannian geometry, the value of R for any particular thermodynamic state is independent of the coordinate system in which it is calculated.

IV. DISCUSSION

We look first at the case where all of the $h_i(T)$'s are the same, as would be the case, for example, where all the constituents of the ideal gas are monatomic. Here, Eq. (17) reduces to

$$R=\frac{(n-1)}{2\rho} , \qquad (18)$$

where

$$\rho=\sum_{i=1}^{n}\rho_i \qquad (19)$$

is the total density. This is a surprisingly simple result, depending neither on the functional form of the $h_i(T)$'s nor on the relative densities of the component gases.

The correlation length is zero for the ideal gas and cannot be equated to the curvature, which is not zero if $n>1$. However, the interpretation of the thermodynamic curvature[3] is that its absolute value gives the real-space volume at which classical thermodynamic fluctuation theory, Eq. (1), fails. A breakdown can occur not only at length scales less that the correlation length, but if there are not enough particles for a continuous thermodynamic description. Neither of these problems can be fixed by including more terms in the series expansion of the entropy which lead to Eq. (1).[3] The curvature above is on the order of the volume where there is just a single particle present per species. At this level, classical thermodynamic fluctuation theory fails badly, as has been shown explicitly in the single-component ideal gas.[3] However, it does not require many particles in an ideal gas for classical theory to work pretty well. Hence our results for the thermodynamic curvature are consistent with expectations.

Consider now the general case. Let $h_{\max}(T)$ be the largest value of any of the functions $h_i(T)$ at temperature T and let $h_{\min}(T)$ be the smallest. It is straightforward to show that, at any temperature,

$$0\le\frac{(n-1)h_{\min}(T)}{2\rho h_{\max}(T)}\le R\le\frac{(n-1)h_{\max}(T)}{2\rho h_{\min}(T)} . \qquad (20)$$

For ideal gases, the ratio $h_{\max}/h_{\min}$ is typically between 1 and 10. Therefore a rough estimate for the general case is

$$R\approx\frac{(n-1)}{2\rho} , \qquad (21)$$

and the interpretation offered above for all equal $h_i(T)$'s remains valid.

V. CONCLUSION

We have evaluated the thermodynamic curvature for the general multicomponent ideal gas. The curvature is on the order of the volume occupied by a single particle. This result is consistent with the previously developed interpretation that the thermodynamic curvature gives a measure of the volume where classical thermodynamic fluctuation theory fails.

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