

New thermodynamic fluctuation theory using path integrals

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The conventional thermodynamic fluctuation theory, originated by Einstein in 1907, fails at volumes less than the correlation volume because it does not include the effects of local correlations. In this paper, a new thermodynamic fluctuation theory is developed in which an attempt is made to include local correlations by considering successive fluctuations in a sequence of systems of decreasing volume. The mathematics used is a path-integral formalism developed recently primarily for application in irreversible thermodynamics. An important result of the new theory is that it predicts the correlation length in terms of purely thermodynamic quantities, confirming a conjecture made earlier by the author on the basis of a Riemannian geometric model of thermodynamics. There is also a possibility that this new theory works at volumes less than the correlation volume and, hence, that it provides a thermodynamic theory of critical fluctuations. Unfortunately, due to mathematical difficulties, this interesting possibility is not put to a direct test in this paper.

I. INTRODUCTION

Thermodynamic fluctuation theory originated with Einstein in 1907.¹ Since then, great advances over this simple theory have been made. For the most part, however, these advances have come at the expense of adding features to the theory which lie outside the domain of thermodynamics. As an example, consider the program originated by Onsager² in 1931 of applying irreversible thermodynamics to spontaneous fluctuations; this necessitates the introduction of transport coefficients. As another example, consider renormalization-group theory in which calculations must be made by means of microscopic system models. As a working tool for dealing with fluctuations of thermodynamic quantities purely by thermodynamic methods, Einstein's theory has survived with few basic modifications.

Despite its wide range of applicability, the conventional thermodynamic fluctuation theory fails precisely where fluctuation phenomena are most important; near critical points at system dimensions of the order of the correlation length or less. It is a thesis of the present paper that this failure occurs because at small volumes the universe can no longer be separated into two homogeneous systems, one of which is the fluctuating system A_V , which I take to be an open system with fixed volume V , and the other an infinite reservoir. This separation is always made in the conventional thermodynamic fluctuation theory.³ If $V \lesssim$ (correlation volume), the thermodynamic state of A_V is strongly correlated with

that of its local surroundings. This correlation cannot be taken into account by regarding the reservoir to be homogeneous.

In this paper, I will attempt to avoid this breakdown of the conventional theory in a way using only thermodynamic information. The basic idea is to consider successive fluctuations in a sequence of systems of decreasing volume. Each system is enclosed by all the larger systems in the sequence. The smallest system is the one whose thermodynamic fluctuation probability distribution is to be determined. With this structure what is important at each volume level is not the average state of the infinite reservoir but the state of the next largest system in the hierarchy.

In order to treat this problem mathematically, I make a simple assumption about the fluctuation of successive systems which allows me to apply the recent path integral formalism developed by several authors primarily for use in irreversible thermodynamics. With this mathematics, the probability of finding a system in a certain state is the sum of the contributions of all paths leading to that state.

A major motivating factor behind the present new theory has been to develop a structure for understanding the connection between curvature and interactions in a recent Riemannian geometric model of thermodynamics.^{4,5} In this model, it appears that the curvature allows one to construct a thermodynamic function ξ_G which equals the correlation length.⁶ Previously, however, little justification was given for this construction aside from the fact that

it seems to work. In this paper, at least a start towards dealing with this problem has been made. It is demonstrated that for d -dimensional systems having volumes much greater than ξ_G^d , the path integral approach agrees with the conventional theory. At volumes of the order of ξ_G^d the conventional theory is predicted to break down and, at lesser volumes, the new theory predicts fluctuation phenomena radically different from that of the conventional theory. Such behavior is to be expected if ξ_G is indeed the correlation length.

Perhaps the most exciting aspect of this new approach is that it gives results which may be valid at volumes less than the correlation volume. If this is the case, the consequence would be a thermodynamic theory of fluctuations applicable at small volumes near critical points. Unfortunately, because of mathematical difficulties, no convincing test of this possibility is presented here.

The outline of this paper is as follows. First the conventional theory will be summarized in order to create a background for future discussion and to introduce notation. Second, the path integral approach will be developed. Finally, the new theory will be examined both by calculations in the ideal gas and the one-dimensional Ising model.

II. CONVENTIONAL THERMODYNAMIC FLUCTUATION THEORY

The basic goal of thermodynamic fluctuation theory is to determine the probability of finding a system which is somehow in contact with another system, usually an infinite reservoir, in some range of thermodynamic states. In most cases it is assumed that the state of the composite system consisting of the reservoir plus the fluctuating system is held fixed, and that fluctuations are spontaneous. Also, it is necessary to require that in a real or hypothetical experiment designed to test the theory, sufficient time is allowed between measurements for the system to have forgotten its previous state. Measurements separated by a shorter time period involve considerations of dynamics; this is beyond the scope of thermodynamics.

Consider a closed system A_{V_R} with fixed volume V_R and fixed, conserved, extensive parameters denoted by the n -tuple

$$X_R = (X_R^1, X_R^2, \dots, X_R^n).$$

The X_R^α 's are the extensive parameters in the entropy representation⁷; e.g., for fluids, to which the discussion in this section is primarily directed, X_R^1 is the total internal energy and X_R^2, \dots, X_R^n are the $n-1$ mole numbers. Throughout this paper I will use Greek indices to denote the coordinate and Arabic

indices to denote the system. Imagine now an open subsystem A_{V_0} of A_{V_R} which has a fixed volume V_0 and whose extensive parameters

$$X_0 = (X_0^1, X_0^2, \dots, X_0^n)$$

fluctuate as energy and particles flow randomly in and out. Denoted by $A_{V_0^c}$ is the system A_{V_R}/A_{V_0} . $A_{V_0^c}$, which has volume $V_0^c = (V_R - V_0)$ and extensive parameters X_0^c , acts as a reservoir for A_{V_0} .

The conventional thermodynamic fluctuation theory (cft) describes fluctuations in X_0 by means of the following three axioms:

(I). A_{V_0} and $A_{V_0^c}$ are each homogeneous systems to which the equations of state apply.

(II). The conditional probability of finding A_{V_0} in a state with extensive parameters between X_0 and $X_0 + dX_0$ provided A_{V_R} is in the state with extensive parameters X_R is given by

$$P_{\text{conv}} \left\{ \begin{matrix} X_0 \\ V_0 \end{matrix} \middle| \begin{matrix} X_R \\ V_R \end{matrix} \right\} d^n X_0 = \Omega_0 \exp[S_R(X_R, X_0)/k_B] d^n X_0, \quad (2.1)$$

where $S_R(X_R, X_0)$ is the entropy of A_{V_R} when A_{V_0} has extensive parameters X_0 , k_B is Boltzmann's constant,

$$d^n X_0 \equiv dX_0^1 dX_0^2 \cdots dX_0^n,$$

and Ω_0 is a normalization factor.

(III). Entropy is an additive function, though not a conserved one.

The axioms above are operationally equivalent to the fluctuation postulate eloquently set forth by Lewis in 1931.⁸ In the limit $V_R/V_0 \rightarrow \infty$, axioms I–III agree with Callen's⁷ postulate II'.

Some authors, including Landau and Lifshitz,⁹ are inconsistent in their statement of Eq. (2.1) by allowing the coordinate system X_0 to be arbitrary. The problem with this is seen on making a coordinate transformation from X_0 to n new coordinates Y_0 . Since the entropy is a function of state, it transforms as a scalar, but the transformation of $d^n X_0$ introduces as a multiplicative factor the Jacobian J of the coordinate transformation. Generally, J is not constant and cannot simply be absorbed in the normalization factor Ω_0 . Hence, Eq. (2.1) cannot retain the same form in all coordinate systems.

An attempt to make the form of Eq. (2.1) coordinate invariant is to approximate J by a constant. Let me explore the nature of this approximation with a simple example. Consider a system in which there is only one independent fluctuating parameter so that $X_0 = X_0^1 \equiv x$. Take the limit $V_R/V_0 \rightarrow \infty$

and let V_0 be sufficiently large that on expanding $S_R(x)$ about its maximum value at x^* in powers of $\Delta x \equiv (x - x^*)$ terms beyond the second order in Δx are negligible over the range of reasonably probable fluctuations. Making the coordinate transformation $y = y(x)$ and expanding Δx to second order in $\Delta y \equiv (y - y^*)$, where $y^* \equiv y(x^*)$, yields

$$P(\Delta y)dy = \text{const} \times x' \left[1 + \frac{x''}{x'} \Delta y \right] \times \exp \left[-\frac{1}{2} g \Delta y^2 \left[1 + \frac{x''}{x'} \Delta y \right] \right] dy, \quad (2.2)$$

where $g \equiv -(d^2 S_R / dy^2)_{y=y^*}$, and the derivatives x' and x'' of $x(y)$ are evaluated at $y = y^*$. (Here and henceforth, I express entropy in units of k_B .) It is seen that the criterion for being able to neglect the first-order term in the Jacobian is the same criterion

$$P_G \left[\begin{array}{c} \rho_0 \\ V_0 \end{array} \middle| \begin{array}{c} \rho_R \\ V_R \end{array} \right] d^n \rho_0 = \left[\frac{1}{2\pi(V_0^{-1} - V_R^{-1})} \right]^{n/2} g(\rho_R)^{1/2} \exp \left[\frac{-1}{2(V_0^{-1} - V_R^{-1})} g_{\alpha\beta}(\rho_R) \Delta \rho_0^\alpha \Delta \rho_0^\beta \right] d^n \rho_0, \quad (2.4)$$

where $\Delta \rho_0^\gamma \equiv (\rho_0^\gamma - \rho_R^\gamma)$,

$$g_{\alpha\beta}(\rho_R) \equiv \left. \frac{-\partial^2 s}{\partial \rho^\alpha \partial \rho^\beta} \right|_{\rho=\rho_R}, \quad (2.5)$$

and $g(\rho_R) \equiv \det g(\rho_R)$. Summation over repeated indices is understood throughout this paper. The matrix of response functions g is positive definite since the entropy is a maximum when $\Delta \rho_0 = 0$. Equation (2.4), which is the Gaussian approximation to the cft, will henceforth be referred to as the Gaussian fluctuation theory (Gft). In the limit $V_R/V_0 \rightarrow \infty$, Eq. (2.4) agrees with Eq. (15.50) in Callen.⁷ It should be noted that the form of (2.4) is coordinate invariant.

In practice, the Gft rather than the cft is usually used. To my knowledge, it is not clear that the cft is actually better than its Gaussian approximation. The question is whether or not the singling out of the extensive parameters X_0 as special coordinates in Eq. (2.1) is really justified. At least in the infinite reservoir limit, Callen⁷ states that the cft yields the correct third and higher moments of fluctuation, but he does not seem to give any independent criterion for deciding what is "correct." To test this issue experimentally would require a system small enough that the Gaussian term in the entropy expansion does not completely dominate the fluctuations and yet not so small as to make unreasonable the application of Axiom I. I am not aware of any such ex-

periment which has previously been carried out.

This issue will be tested in Sec. IV A by means of a numerical "experiment" on the monatomic ideal gas at small volumes. It will be seen that the cft does not yield results demonstrably superior to those of the Gft.

An interesting attempt to use higher-order terms in the entropy expansion is Smoluchowski's theory¹⁰ of critical fluctuations. This theory is, however, criticized as unsatisfactory by Klein and Tisza³ because Axiom I fails badly in the region of its application.

Let me finish this discussion of the cft with a qualitative examination of fluctuations in the interior of an infinite three-dimensional ferromagnetic Ising model (A_{V_R}).¹¹ Take the external magnetic field $h = 0$ and the temperature T greater than the critical temperature T_c so that the magnetization density of A_{V_R} is zero. If the imbedded subsystem A_{V_0} with magnetization density m_0 has volume V_0 much greater than the correlation volume ξ^3 of A_{V_R} , there is no correlation between spins on opposite sides of A_{V_0} and at any time A_{V_0} sees itself surrounded by a system with essentially the same state as that of A_{V_R} . Axiom I should be applicable in this case and the probability density $P(m_0)$ for m_0 is to a good approximation a Gaussian with a peak at $m_0 = 0$. If $V_0 \lesssim \xi^3$, however, A_{V_0} is at any time most probably

$$\rho_0 = \rho_0^c = \rho_R \equiv X_R / V_R$$

needed to enable us to neglect the third-order term in the exponential, namely, $x' \gg x'' \Delta y$ over the full range of important fluctuations.

$$\Delta \rho_0^c = -(V_0/V_0^c) \Delta \rho_0$$

and using

$$\Delta \rho_0^c = -(V_0/V_0^c) \Delta \rho_0$$

and Axiom II yields

$$\Delta \rho_0^c = -(V_0/V_0^c) \Delta \rho_0$$

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inside a cluster of spins which point predominantly either up or down. Hence, the peak at $m_0=0$ splits into two peaks which move out to $m_0=\pm 1$ as V_0 gets smaller. (Units are chosen such that the maximum value of $|m_0|$ is unity.) A qualitative sketch of $P(m_0)$ for three characteristic volumes is shown in Fig. 1.

A definitive proof that the cft cannot predict the behavior shown in Fig. 1 for small volumes is elusive. This point is probably best demonstrated with explicit model calculations. However, since the cft ignores completely local correlations by treating A_{V_0} as homogeneous, its predictions for $V_0 \lesssim \xi^3$ cannot be valid. The problem of local correlations is the one which I will attempt to overcome in this paper.

III. PATH-INTEGRAL APPROACH TO THERMODYNAMIC FLUCTUATION THEORY

A. Discussion of the Riemannian geometric model of thermodynamics

The construction of the path-integral thermodynamic fluctuation theory is motivated by a desire both to deal with local correlations and to explain the connection between curvature and interactions in the Riemannian geometric model⁴ (Rgm) of thermodynamics; as I hope to make clear, these problems are not independent. Since the Rgm plays such an important motivational role here, let me summarize it. Represent the thermodynamic states of the system A_{V_0} by points in an n -dimensional manifold or space α_{V_0} . Take V_R/V_0 to be infinite and let V_0 be large enough that the Gft is applicable. Equation (2.4) suggests that we represent fluctuations mathematically by assigning the Riemannian line element

$$(\Delta l^2)_{\text{Rgm}} \equiv V_0 g_{\alpha\beta}(\rho_R) \Delta \rho_0^\alpha \Delta \rho_0^\beta \quad (3.1)$$

to the manifold α_{V_0} at the point with coordinates $\rho_0 = \rho_R$.

The physical interpretation of this line element is evident from Eq. (2.4)—the less probable a fluctuation between states, the further apart they are. Note also that the expression for an increment of volume¹² in a Riemannian manifold with metric $V_0 g$ at the point $\rho_0 = \rho_R$,

$$[V_0^n g(\rho_R)]^{1/2} d^n \rho_0,$$

is the same "volume" which appears in (2.4).

The most interesting thing about the Riemannian manifold α_{V_0} is that for systems such as pure fluids or Ising models, where α_{V_0} is two dimension-

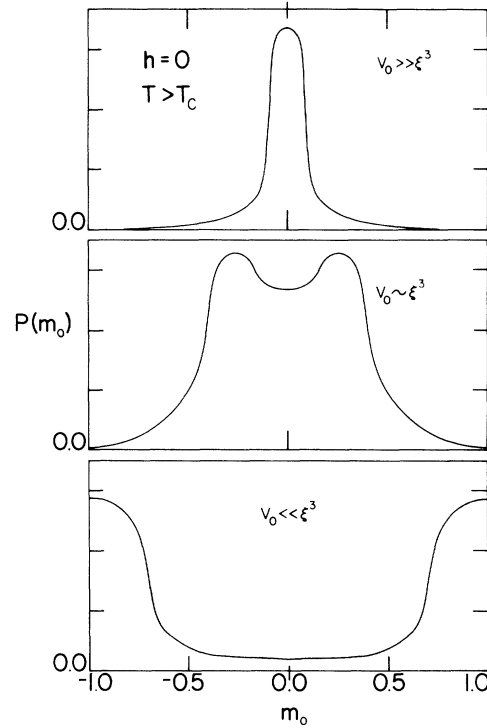


FIG. 1. Qualitative sketch of the probability amplitude $P(m_0)$ for the magnetization density m_0 of the ferromagnetic Ising system A_{V_0} for three characteristic volumes. It is seen that if $V_0 < \xi^3$, $P(m_0)$ develops two maximas which approach $m_0 = \pm 1$ as V_0 gets smaller. $P(m_0)$ is in arbitrary units and m_0 is in units such that the maximum of $|m_0|$ is unity.

al, the Gaussian curvature $[K(\rho_R)]_{\text{Rgm}}$ appears to yield the correlation length $\xi(\rho_R)$. Specifically, it appears that

$$\xi^d(\rho_R) = V_0 [K(\rho_R)]_{\text{Rgm}}, \quad (3.2)$$

where d is the spatial dimensionality of A_{V_0} . The importance of Eq. (3.2) is that it allows a calculation of the correlation length on the basis of purely thermodynamic information.

In systems tested (3.2) works to a surprising accuracy. For example, in the pure fluid along the critical isochore, both the critical exponent and the critical amplitude of the correlation length are correctly predicted.⁴ As another example, in the one-dimensional (1D) ferromagnetic Ising model the correlation length as calculated with (3.2) was never found to deviate by more than one lattice site from the statistical-mechanical correlation length which gives the range of the spin-spin correlation function.¹³

The Rgm is susceptible to criticism on two major

counts. First, Eq. (2.4), and hence the interpretation of the line element $(\Delta l^2)_{\text{Rgm}}$, has validity only if $g(\rho_0)$ is to a good approximation constant over the full range of reasonably probable fluctuations. This requires a sufficiently large volume V_0 , but it also puts a constraint on the choice of coordinate system. For any given V_0 , it is possible to find some extraordinary coordinates for α_{V_0} such that, when expressed in these coordinates, g fluctuates significantly about some point. Therefore, the physical interpretation of (3.1) is to some extent coordinate dependent and so not entirely satisfactory. Note that because of this, though the form of (2.4) is coordinate invariant its numerical predictions are not.

The second problem is the following. As I argued previously, the cft breaks down at volumes of the order of the correlation volume. How then can a mathematical model based on an approximation to this theory possibly yield the correlation length with such apparent accuracy? This contradiction of Eq. (3.2) cannot be resolved by further study of the Rgm.

My position in this paper is that the fault here lies not in the choice of line element but rather in its physical interpretation in terms of Eq. (2.4). I will construct the new theory with the line element in Eq. (3.1) only slightly modified but with a different interpretation. In this new theory, the curvature emerges naturally as the approximate volume at which the Gft fails even with the optimum choice of coordinates.

I will start the construction of the new theory with some mathematical preliminaries. First of all, since I am interested here exclusively in fluctuations in the interior of large systems where there are no extraneous constraints to impede the flow of particles and energy in any way, attention will be confined to fluctuations in the states of open systems with fixed volumes. This was also done in Sec. II. To describe the state of an open system requires two basically different types of parameters. The first is the fixed volume, which can be selected arbitrarily, and the second are fluctuating thermodynamic quantities which are characteristic of the substance in question.

It is natural to divide these different types of variables into separate, independent spaces. The first space is a parameter space which contains the volume and all scalar functions constructed solely from it. The second space is an n -dimensional Riemannian manifold α whose points represent possible values of the *intensive parameters* of any open system.

I should point out that Griffiths and Wheeler¹⁴ separate intensive parameters into two classes, "fields" and "densities," according to whether or not

they are continuous on crossing the interface between coexisting phases. Since I work here only with systems in a single phase, I will not bother to make any distinction but treat all intensive parameters on an equal footing.

Assign to α the Riemannian line element

$$dl^2 = g_{\alpha\beta}(\rho) d\rho^\alpha d\rho^\beta, \quad (3.3)$$

where

$$g_{\alpha\beta}(\rho) \equiv - \frac{\partial^2 s(\rho)}{\partial \rho^\alpha \partial \rho^\beta}, \quad (3.4)$$

and the ρ 's are the densities introduced earlier. Under a change of coordinates, $g(\rho)$ is to be transformed as a second-rank covariant tensor. With the exception of a factor of V_0 , this line element is the same as the one in Eq. (3.1) and hence the curvature of α is the same as that of α_{V_0} up to a factor of V_0^{-1} which cancels out in (3.2). The physical interpretation of dl^2 will be developed in the next few sections. Note that all thermodynamic properties of α are calculated by going to the thermodynamic limit.

B. Fluctuation within fluctuations within fluctuations ...

Let us modify Axiom I in Sec. II by including inhomogeneities in the open system A_{V_0} . Consider an open subsystem of A_{V_0} , A_{V_1} with volume $V_1 < V_0$ and densities $\rho_1 \equiv (\rho_1^1, \rho_1^2, \dots, \rho_1^n)$ not necessarily equal to the densities ρ_0 of A_{V_0} . Hence, allow for the possibility of fluctuations inside A_{V_0} .

Denote the joint conditional probability of finding the densities of A_{V_0} between ρ_0 and $\rho_0 + d\rho_0$ and of finding the densities of A_{V_1} between ρ_1 and $\rho_1 + d\rho_1$ given that the closed system A_{V_R} has densities ρ_R by

$$P \left[\begin{array}{cc|c} \rho_1 & \rho_0 & \rho_R \\ V_1 & V_0 & V_R \end{array} \right] d^n \rho_0 d^n \rho_1. \quad (3.5)$$

It is assumed that measurements of the states of A_{V_0} and A_{V_1} are made simultaneously but that successive sets of measurements are spaced at sufficiently wide intervals that the system has forgotten its previous state. The objective is to write down a thermodynamic expression for the joint conditional probability density in Eq. (3.5).

In order to make progress, it is necessary to make an important assumption about the probability density in (3.5). This assumption is that *for given values of ρ_R and ρ_0 , the probability density for ρ_1 depends only on ρ_0 and not on ρ_R ; furthermore, we can at*

least begin the task of calculating it by applying Axioms I–III as if A_{V_0} were a closed system. The first half of this statement is in probability theory called a Markov assumption.¹⁵ It allows Eq. (3.5) to be written as a product of two conditional probabilities:

$$P \left[\begin{array}{c} \rho_1 \quad \rho_0 \\ V_1 \quad V_0 \end{array} \middle| \begin{array}{c} \rho_R \\ V_R \end{array} \right] = P \left[\begin{array}{c} \rho_1 \\ V_1 \end{array} \middle| \begin{array}{c} \rho_0 \\ V_0 \end{array} \right] P \left[\begin{array}{c} \rho_0 \\ V_0 \end{array} \middle| \begin{array}{c} \rho_R \\ V_R \end{array} \right], \quad (3.6)$$

where the conditional probability for ρ_1 on the right-hand side is independent of ρ_R . The Markov assumption is here physically quite plausible since A_{V_1} samples A_{V_0} only through the intervening system A_{V_0}/A_{V_1} .

If the probability density in Eq. (3.5) is integrated over the full accessible range of ρ_0 , we must obtain

$$\begin{aligned} P_G \left[\begin{array}{c} \rho_1 \quad \rho_0 \\ V_1 \quad V_0 \end{array} \middle| \begin{array}{c} \rho_R \\ V_R \end{array} \right] &= P_G \left[\begin{array}{c} \rho_1 \\ V_1 \end{array} \middle| \begin{array}{c} \rho_0 \\ V_0 \end{array} \right] P_G \left[\begin{array}{c} \rho_0 \\ V_0 \end{array} \middle| \begin{array}{c} \rho_R \\ V_R \end{array} \right] \\ &= \left[\frac{1}{2\pi(V_0^{-1} - V_R^{-1})} \right]^{n/2} g(\rho_R)^{1/2} \left[\frac{1}{2\pi(V_1^{-1} - V_0^{-1})} \right]^{n/2} g(\rho_0)^{1/2} \\ &\quad \times \exp \left[-\frac{1}{2(V_0^{-1} - V_R^{-1})} g_{\alpha\beta}(\rho_R) \Delta\rho_0^\alpha \Delta\rho_0^\beta - \frac{1}{2(V_1^{-1} - V_0^{-1})} g_{\alpha\beta}(\rho_0) \Delta\rho_1^\alpha \Delta\rho_1^\beta \right], \quad (3.8) \end{aligned}$$

where $\Delta\rho_1^\gamma \equiv (\rho_1^\gamma - \rho_0^\gamma)$. If V_0 is sufficiently large, fluctuations in ρ_0 are small and it is possible to make the approximation $g(\rho_0) = g(\rho_R)$ for important fluctuations. With this approximation it is straightforward to show that the CK equation holds¹⁶

$$\int P_G \left[\begin{array}{c} \rho_1 \quad \rho_0 \\ V_1 \quad V_0 \end{array} \middle| \begin{array}{c} \rho_R \\ V_R \end{array} \right] d^n \rho_0 = P_G \left[\begin{array}{c} \rho_1 \\ V_1 \end{array} \middle| \begin{array}{c} \rho_R \\ V_R \end{array} \right]. \quad (3.9)$$

The program started above of considering inhomogeneities in A_{V_0} can be continued by imagining an open subsystem A_{V_2} of A_{V_1} with volume $V_2 < V_1$, an open subsystem A_{V_3} of A_{V_2} with volume $V_3 < V_2$, and so on down to the final system A_{V_m} with volume V_m . Generally, $A_{V_{i+1}}$ is an open subsystem of A_{V_i} . Figure 2 shows this structure, which is the basic idea in this paper. The ultimate goal is to write a thermodynamic expression for the fluctuation probability distribution of the final system $A_{V_f} \equiv A_{V_m}$.

Again, I make the Markov assumption that at given $\rho_R, \rho_0, \rho_1, \dots, \rho_i$ the probability distribution for

the probability density for ρ_1 alone:

$$\int P \left[\begin{array}{c} \rho_1 \quad \rho_0 \\ V_1 \quad V_0 \end{array} \middle| \begin{array}{c} \rho_R \\ V_R \end{array} \right] d^n \rho_0 = P \left[\begin{array}{c} \rho_1 \\ V_1 \end{array} \middle| \begin{array}{c} \rho_R \\ V_R \end{array} \right]. \quad (3.7)$$

In the theory of Markov processes, this is called the Chapman-Kolmogorov (CK) equation. It plays a crucial role in the development of the following theory since no distribution which violates it is viable. In Appendix A it is shown with a simple counterexample that in the absence of approximations it is not possible to satisfy the CK equation if the conditional probability densities on the rhs of (3.6) are evaluated with Axioms I–III.

In order to produce consistency with the CK equation it is necessary to go to the Gft. Using Eq. (2.4) yields

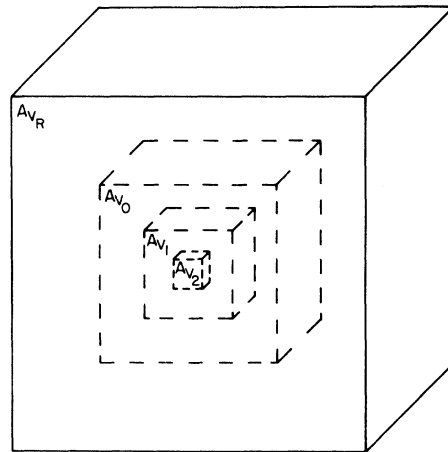


FIG. 2. Diagram of the basic structure in this paper for the case $d=3$. A large closed system A_{V_R} containing a sequence of open systems $A_{V_0}, A_{V_1}, \dots, A_{V_m}$ of decreasing size. Each system samples only the thermodynamic state of its immediate surrounding system. In this way, local correlations are taken into account. The final system A_{V_f} in the sequence is the one whose fluctuation probability distribution is to be determined.

ρ_{i+1} depends only on ρ_i and can be calculated by starting with Axioms I–III as if A_{V_i} were a closed system. This allows the conditional probability of finding A_{V_0} in a state with densities between ρ_0 and

$\rho_0 + d\rho_0$, A_{V_1} with densities between ρ_1 and $\rho_1 + d\rho_1, \dots$, and A_{V_m} with densities between ρ_m and $\rho_m + d\rho_m$, given that the densities of A_{V_R} are ρ_R , to be written as

$$P \left[\begin{array}{c|c} \rho_m & \rho_R \\ \hline V_m & V_R \end{array} \middle| \begin{array}{c|c} \rho_{m-1} & \rho_0 \\ \hline V_{m-1} & V_0 \end{array} \right] d^n \rho_0 d^n \rho_1 \cdots d^n \rho_m \\ = P \left[\begin{array}{c|c} \rho_m & \rho_{m-1} \\ \hline V_m & V_{m-1} \end{array} \right] P \left[\begin{array}{c|c} \rho_{m-1} & \rho_{m-2} \\ \hline V_{m-1} & V_{m-2} \end{array} \right] \cdots P \left[\begin{array}{c|c} \rho_0 & \rho_R \\ \hline V_0 & V_R \end{array} \right] d^n \rho_0 \cdots d^n \rho_m. \quad (3.10)$$

As previously with $m=1$, the Chapman-Kolmogorov equation can be satisfied only by first going to the Gft. Repeated applications of Eq. (2.4) on the right-hand side in (3.10) yields

$$P_G \left[\begin{array}{c|c} \rho_m & \rho_R \\ \hline V_m & V_R \end{array} \middle| \begin{array}{c|c} \rho_{m-1} & \rho_0 \\ \hline V_{m-1} & V_0 \end{array} \right] = \prod_{i=0}^{m-1} \left[\frac{1}{2\pi(V_i^{-1} - V_{i-1}^{-1})} \right]^{n/2} g(\rho_{i-1})^{1/2} \\ \times \exp \left[-\frac{1}{2} \sum_{i=0}^{m-1} \frac{1}{(V_i^{-1} - V_{i-1}^{-1})} g_{\alpha\beta}(\rho_{i-1}) \Delta\rho_i^\alpha \Delta\rho_i^\beta \right], \quad (3.11)$$

where $\Delta\rho_i^\gamma \equiv (\rho_i^\gamma - \rho_{i-1}^\gamma)$ and $A_{V_{-1}} \equiv A_{V_R}$.

If the volume V_{m-1} is sufficiently large, fluctuations in $\rho_0, \rho_1, \dots, \rho_{m-1}$ will be small and we can make the approximation $g(\rho_{m-1}) = g(\rho_{m-2}) = \cdots = g(\rho_0) = g(\rho_R)$ over the full range of reasonably probable fluctuations. With this approximation, repeated applications of the CK equation (3.9) yields the necessary relation

$$\int \int \cdots \int P_G \left[\begin{array}{c|c} \rho_m & \rho_R \\ \hline V_m & V_R \end{array} \middle| \begin{array}{c|c} \rho_0 & \rho_0 \\ \hline V_0 & V_0 \end{array} \right] d^n \rho_{m-1} \cdots d^n \rho_0 = P_G \left[\begin{array}{c|c} \rho_m & \rho_R \\ \hline V_m & V_R \end{array} \right]. \quad (3.12)$$

Take now the limit of an infinite number of systems, $m \rightarrow \infty$, in such a way that $\Delta V_i \equiv (V_i - V_{i-1}) \rightarrow 0$ for all i . Also, fix the final volume in the sequence $V_m = V_f$ and let V_0 be very large so that fluctuations in ρ_0 are negligible and $\rho_0 = \rho_R$. For simplicity, I will simply let $A_{V_0} = A_{V_R}$ which will henceforth be taken to be an infinite system. We now define the continuous parameter:

$$t \equiv V^{-1}. \quad (3.13)$$

Ultimately, the particular choice of the parameter function $t = t(V)$ makes no difference in the theory so long as it is monotonic in V . The selection made here is one of convenience; it facilitates a comparison with other path-integral theories.

Returning to Eqs. (3.11) and (3.12) and taking the limit described above we get

$$P_G \left[\begin{array}{c|c} \rho_f & \rho_R \\ \hline V_f & V_R \end{array} \right] = g^{1/2}(\rho_R) \lim_{m \rightarrow \infty} \int \int \cdots \int \frac{1}{(2\pi\tau)^{n(m+1)/2}} \prod_{i=0}^{m-1} g^{1/2}(\rho_i) d^n \rho_i \\ \times \exp \left[-\frac{1}{2} \sum_{i=0}^{m-1} \frac{1}{\tau} g_{\alpha\beta}(\rho_{i-1}) \Delta\rho_i^\alpha \Delta\rho_i^\beta \right], \quad (3.14)$$

where $\tau \equiv \Delta t_i = (V_i^{-1} - V_{i-1}^{-1})$ and $\rho_f \equiv \rho_m$. Introducing path-integral notation, we get

$$P_G \left[\begin{array}{c|c} \rho_f & \rho_R \\ \hline t_f & t_R \end{array} \right] = g^{1/2}(\rho_R) \int \int D[\rho(t)] \exp \left[-\int_0^{t_f} \mathcal{L}(\rho, \dot{\rho}) dt \right], \quad (3.15)$$

where $t_f \equiv t(V_f)$, $t_R \equiv t(V_R) = 0$ since $V_R \rightarrow \infty$,

$$D[\rho(t)] \equiv \lim_{m \rightarrow \infty} \frac{1}{(2\pi\tau)^{n(m+1)/2}} \times \prod_{i=0}^{m-1} g^{1/2}(\rho_i) d^n \rho_i, \quad (3.16)$$

and

$$\tilde{\mathcal{L}}(\rho, \dot{\rho}) \equiv \frac{1}{2} g_{\alpha\beta}(\rho) \dot{\rho}^\alpha \dot{\rho}^\beta. \quad (3.17)$$

The integration in (3.15) is the functional integration over all paths connecting the initial and final states. Equation (3.15) should be regarded purely as shorthand notation for (3.14). Note that

$$\dot{\rho} \equiv \lim_{\tau \rightarrow 0} \frac{\Delta\rho(t)}{\tau}$$

does not even exist for all paths.

Equation (3.15) manifests the beginnings of two major advantages of this approach over the conventional one. First, and most important, local correlations are taken into account since each system in the sequence samples only the state of the immediate surrounding system and not directly that of the

infinite reservoir. This gives hope of avoiding the breakdown at volumes less than the correlation volume. Second, at least a start is made towards eliminating the problem mentioned in Sec. III A of the metric \underline{g} in the Gft varying significantly over the range of fluctuations. We see from Eq. (3.11) that the size of a typical fluctuation $\Delta\rho_i^\alpha \sim O(\tau^{1/2}) \rightarrow 0$ as $\tau \rightarrow 0$. Hence, variations in \underline{g} at each step vanish in the limit regardless of the choice of coordinate systems.

If V_f is large, we can take

$$\underline{g}(\rho(t)) = \text{const} = \underline{g}(\rho_R)$$

for all paths which contribute significantly to the sum in Eq. (3.15). Finding local Cartesian coordinates x about the point ρ_R in which $\underline{g}(\rho_R)$ is the identity matrix yields

$$\tilde{\mathcal{L}} = \frac{1}{2} \sum_{\alpha=1}^n (\dot{x}^\alpha)^2. \quad (3.18)$$

Using Feynman's method¹⁷ to evaluate the functional integral in these coordinates and then transforming back to ρ coordinates yields

$$P_G \left[\begin{array}{c|c} \rho_f & \rho_R \\ t_f & 0 \end{array} \right] d^n \rho_f = (2\pi t_f)^{-n/2} g^{1/2}(\rho_R) \exp \left[-\frac{1}{2t_f} g_{\alpha\beta}(\rho_R) \Delta\rho_f^\alpha \Delta\rho_f^\beta \right] d^n \rho_f, \quad (3.19)$$

where $\Delta\rho_f^\gamma \equiv (\rho_f^\gamma - \rho_R^\gamma)$. This is in agreement with the Gft equation (2.4) as it must be since at large volumes, the Gft is correct.

For future reference, let me also point out that in the constant \underline{g} approximation, probability densities can be written in terms of the path joining the initial and final points which minimizes the "action":

$$P_G \left[\begin{array}{c|c} \rho' & \rho \\ t+\tau & t \end{array} \right] d^n \rho = \text{const} \times \exp \left[- \left[\int_t^{t+\tau} \tilde{\mathcal{L}}(\rho, \dot{\rho}) dt \right]_{\min} \right] d^n \rho. \quad (3.20)$$

This is easily verified with the coordinates x in (3.18).

Thus far, attention has been confined to volumes sufficiently large that the constant- \underline{g} approximation is satisfactory. Consider now smaller volumes. Does Eq. (3.15) still hold? Since local correlations have been included, the initial hope is that it does. In actuality, however, Eq. (3.15) is mathematically consistent only if we are in global coordinates where \underline{g} is constant. Such coordinates exist if and only if the fourth-rank Riemannian curvature tensor \underline{R} of \mathfrak{X} is zero.¹² The basic source of difficulties here is that the CK equation (3.9) fails if \underline{g} is not constant. Even in the limit $\tau \rightarrow 0$ variations in \underline{g} make a contribution. The resolution of this problem will be discussed in Sec. IV.

At this stage one may well question whether or not progress can be made by reconsidering terms higher than second order in the entropy expansions in Eq. (3.11). Earlier, such terms were dropped because of problems in satisfying the CK equation, problems which have now cropped up anyway. I believe that attempts to make progress by including higher-order terms are futile. With $\Delta\rho_i^\alpha \sim O(\tau^{1/2})$, as predicted by the Gft, it is straightforward to show that the third-order term in the i th step $\Delta^3 S_{R_i} \sim O(\tau^{-1/2})$ which diverges as $\tau \rightarrow 0$. Fourth- and higher-order terms have similar divergences.

These divergences lead to the conclusion that if higher-order terms are to be included, the Gaussian term cannot dominate in the limit $\tau \rightarrow 0$. However, it is difficult to see in this case how we could have

our resulting theory even be consistent with the Gft at large V_f . I believe that the only productive way forward is to patch up the Gaussian theory as in Sec. III C.

C. Thermodynamic fluctuation hypothesis

The resolution of the problem for $g \neq \text{const}$ is not an easy one. Fortunately, a mathematically analogous problem has been encountered and dealt with in irreversible thermodynamics. I will make use of this analogy.

The physical problem in irreversible thermodynamics is different from that in this paper since it deals with the time evolution of the thermodynamic state of a system of fixed volume. This necessitates the introduction of transport coefficients. In 1953, Onsager and Machlup¹⁸ (OM) wrote down the solution to this problem in terms of a minimum principle. The solution is represented by Eqs. (4)–(7) in their paper which for $n=1$ is formally analogous to Eq. (3.20) here if the “drift” term γ is set to zero and if we remember that here the “time” parameter t gives volume rather than real time and that their metric contains transport coefficients. The extension of the analogy for $n > 1$ is obvious.

In the Onsager-Machlup paper, constant transport coefficients and response functions are assumed; this assumption is analogous to the constant- g assumption in the previous section. Recently, several authors^{19–24} have undertaken the task of generalizing the OM formulation to regions outside this “linear” regime. I will use here the method of Grabert and Green²⁰ who start from a minimum principle rather than the Fokker-Planck equation as other authors do. The basic idea is to rewrite Eq. (3.20) in a coordinate invariant form (i.e., covariantly) in such a way that the Chapman-Kolmogorov equation is satisfied to order τ .

Define the covariant vector η with components

$$\eta_\alpha \equiv \frac{\partial \tilde{\mathcal{L}}}{\partial \dot{a}^\alpha}, \tag{3.21}$$

where the Lagrangian²⁵

$$\tilde{\mathcal{L}}(a, \dot{a}) = \frac{1}{2} g_{\alpha\beta}(a) \dot{a}^\alpha \dot{a}^\beta \tag{3.22}$$

has been written in terms of arbitrary coordinates $a = a(\rho)$. Consider now two times t and $t + \tau$, where τ is small, and two states with coordinates $a = a(t)$ and $a' = a(t + \tau)$. Joining these states there is a unique path which minimizes the action

$$\int_t^{t+\tau} \tilde{\mathcal{L}}(a, \dot{a}) dt. \tag{3.23}$$

We define the following:

$$A_\tau(a' | a) \equiv \left[\int_t^{t+\tau} \tilde{\mathcal{L}}(a, \dot{a}) dt \right]_{\min}. \tag{3.24}$$

Rather than specifying this minimum path by the endpoints a and a' , let me specify it by means of the initial state a and the initial $\eta = \eta(t)$ which gives the initial direction of the path. In this sense,

$$a' = a'(a, \eta, \tau) \tag{3.25}$$

or

$$\eta = \eta(a, a', \tau). \tag{3.26}$$

By analogy with the work of Grabert and Green, I write for small τ the *thermodynamic fluctuation hypothesis*

$$P \left[\begin{matrix} a' \\ t + \tau \end{matrix} \middle| \begin{matrix} a \\ t \end{matrix} \right] d^n a' = \frac{\exp[-A_\tau(a' | a)] d^n \eta}{\int d^n \eta \exp[-A_\tau(a' | a)]}. \tag{3.27}$$

Note that

$$d^n \eta = (\partial \eta / \partial a') d^n a',$$

where $(\partial \eta / \partial a')$ is the Jacobian of the transformation in (3.26) with a and τ held fixed.

There are three motivating features behind the fluctuation hypothesis. The first is that it reduces to (3.20) in the event that g is a constant matrix. The second is that it satisfies the Chapman-Kolmogorov equation to order τ as Grabert and Green show. The third is that it manifests covariance as can be seen by multiplying the top and bottom of the rhs by $d^n a$ and noting that $d^n a$ can be moved in or out of the integration in the denominator. The product $d^n a d^n \eta$ transforms as a scalar.²⁶

At this point, two questions occur. First, although it is certainly necessary that the numerical results of any reliable theory be independent of coordinates, is it essential that the *form* of the fluctuation hypothesis be coordinate independent? From a physical standpoint, the answer to this question does not seem clear as it is difficult to rule out special coordinates as in Eq. (2.1). The second question is whether or not (3.27) is unique given the three conditions which it satisfies. Grabert and Green give no discussion of this point.

Answers to these questions are necessary to evaluate the status of the thermodynamic fluctuation hypothesis. Is this hypothesis merely an exten-

sion of Axioms I–III dictated by necessary conditions of consistency and covariance, or is it fundamentally deeper? Further consideration of this important, and difficult, question is beyond the scope of the remainder of this paper which is devoted to an examination of the consequences of Eq. (3.27).

D. Path-integral formulation

Grabert and Green²⁰ prove that

$$P \left(\begin{matrix} a_f & a_R \\ t_f & t_R \end{matrix} \right) = \lim_{m \rightarrow \infty} \int \int \cdots \int P \left(\begin{matrix} a_f & a_{m-1} \\ t_f & t_{m-1} \end{matrix} \right) P \left(\begin{matrix} a_{m-1} & a_{m-2} \\ t_{m-1} & t_{m-2} \end{matrix} \right) \cdots P \left(\begin{matrix} a_1 & a_R \\ t_1 & t_R \end{matrix} \right) d^n a_{m-1} \cdots d^n a_1, \quad (3.29)$$

where $\tau \equiv (t_i - t_{i-1}) = t_f/m$ since $t_R = 0$. Terms of $O(\tau^{3/2})$ do not make a contribution in this limit.

A more illuminating expression is obtained on expanding the rhs of Eq. (3.27) in powers of $\Delta a^\gamma \equiv (a'^\gamma - a^\gamma)$ up to terms contributing factors of order τ . This task is straightforward but very laborious. Grabert and Green obtain

$$P \left(\begin{matrix} a_f & a_R \\ t_f & 0 \end{matrix} \right) = g^{1/2}(a_f) \int \int D[a(t)] \exp \left[- \int_0^{t_f} \mathcal{L}(a, \dot{a}) dt \right], \quad (3.30)$$

where

$$D[a(t)] \equiv \lim_{m \rightarrow \infty} \left[\frac{1}{2\pi\tau} \right]^{nm/2} \prod_{i=1}^{m-1} g^{1/2}(a_i) d^n a_i, \quad (3.31)$$

and

$$\mathcal{L}(a, \dot{a}) \equiv \frac{1}{2} g_{\alpha\beta}(a) \dot{a}^\alpha \dot{a}^\beta + \frac{1}{6} R(a); \quad (3.32)$$

here $R(a)$ is the Riemannian curvature scalar of \mathfrak{g} .²⁷

Equation (3.30) is the central result of this paper. It is designed to generalize the cft by including local correlations. So far, the application of this equation in irreversible thermodynamics does not seem to have yielded any useful new results. Here, however, Eq. (3.30) makes almost immediately a strong prediction as I will show.

Let me start by examining the case where t_f is small, and the final volume V_f large. In this event, paths which deviate appreciably from the initial point a_R contribute negligibly to the summation in Eq. (3.30) since they have large \dot{a} 's. Hence, for small t_f we can treat $R(a)$ as a constant $=R(a_R)$. With this approximation,

$$P \left(\begin{matrix} a_f & a_R \\ t_f & 0 \end{matrix} \right) = \exp \left[- \frac{R(a_R)}{6V_f} \right] \left[g^{1/2}(a_f) \int \int D[a(t)] \exp \left[- \int_0^{t_f} \frac{1}{2} g_{\alpha\beta}(a) \dot{a}^\alpha \dot{a}^\beta dt \right] \right]. \quad (3.33)$$

If $V_f \gg |R(a_R)|$, the first term on the rhs is unity. In addition, as I will demonstrate explicitly below for $n=2$, the criterion for being able to find local coordinates in which g is a constant matrix for all important paths is also $V_f \gg |R(a_R)|$. Hence, in this limit, the path-integral approach yields the Gft by the same reasoning which led to Eq. (3.19).

The Schwarz inequality²⁸ for square-integrable functions $f(t)$ and $g(t)$ is

$$\int P \left(\begin{matrix} a'' & a' \\ t+\tau & t+\tau' \end{matrix} \right) P \left(\begin{matrix} a' & a \\ t+\tau' & t \end{matrix} \right) d^n a' \\ = P \left(\begin{matrix} a'' & a \\ t+\tau & t \end{matrix} \right) [1 + O(\tau^{3/2})], \quad (3.28)$$

where $\tau > \tau'$ and the conditional probability densities are given by Eq. (3.27). Hence, repeated applications of (3.28) in the limit $\tau \rightarrow 0$ yields a result for the fluctuation probability density for noninfinitesimal time intervals which is consistent with the CK equation:

$$\left| \int_0^t f(t)g(t)dt \right|^2 \leq \int_0^t f^2(t)dt \int_0^t g^2(t)dt . \quad (3.34)$$

Letting $f(t)=(g_{\alpha\beta}\dot{\alpha}\dot{\beta})^{1/2}$ and $g(t)=1$ yields

$$\int_0^{t_f} \frac{1}{2} g_{\alpha\beta} \dot{\alpha} \dot{\beta} dt \geq \frac{r_{\max}^2}{2t_f} , \quad (3.35)$$

where the geodesic distance r_{\max} of the farthest point on the path from the starting point a_R is not greater than the total path length,

$$r_{\max} \leq \int_0^{t_f} (g_{\alpha\beta} \dot{\alpha} \dot{\beta})^{1/2} dt . \quad (3.36)$$

For a path which contributes significantly to the summation in Eq. (3.33),

$$\int_0^{t_f} \frac{1}{2} g_{\alpha\beta} \dot{\alpha} \dot{\beta} dt \lesssim 1 , \quad (3.37)$$

and hence

$$r_{\max}^2 \lesssim 2/V_f \quad (3.38)$$

for the important paths.

If a local Cartesian coordinate system in which g is constant for all important paths is to exist, the geometry must be reasonably flat over the interesting region. For the case $n=2$, it is not difficult to derive a criterion that this obtains. Imagine a circle of radius r_{\max} centered at a_R . Because α is curved, the circumference C of this circle will deviate from its Euclidean value. It can be shown²⁹ that

$$C = 2\pi r_{\max} + \frac{\pi}{6} R(a_R) r_{\max}^3 + O(r_{\max}^4) . \quad (3.39)$$

If we want the geometry to be reasonably flat, it is necessary to have the first term on the rhs of this equation dominate. This requires

$$V_f \gg |R(a_R)| , \quad (3.40)$$

which is the condition stated previously. Similar arguments can also be made in higher dimensions.³⁰

If $V_f \sim |R(a_R)|$, the Gft is predicted to fail regardless of the choice of coordinate systems. I will assume that this breakdown occurs because Axiom I in Sec. II fails rather than because not enough terms in the entropy expansion have been kept. While a general proof of this quite plausible assumption may not be possible, I show in Sec. IV A that for the monatomic ideal gas, higher-order terms in the entropy expansion make little difference even at small volumes.

Physically, Axiom I fails if V_f is of the order of the correlation volume. *The consequence of this is that $|R(a_R)|$ is predicted to be the correlation*

volume of a system in the state a_R . Since $R(a)$ is determined completely by the thermodynamics, the prediction is that the correlation length can be determined by means of thermodynamic information alone.

There is an arbitrariness involved in any definition of the correlation length; how weak must the correlation between particles or spins be before we say that they are uncorrelated? This arbitrariness shows up here as a proportionality constant between $R(a_R)$ and the volume V_f at which we decide that Eq. (3.30) no longer agrees sufficiently well with the Gft. I will select the same constant which yielded successful results in the Rgm. This gives

$$\bar{\xi}^d(a_R) = -\frac{1}{2} R(a_R) , \quad (3.41)$$

where $\bar{\xi}(a_R)$ is the thermodynamic correlation length. $\bar{\xi}$ was denoted by ξ_G in Ref. 5. Henceforth, I will use $\bar{\xi}$ since the Gaussian curvature yields ξ only if $n=2$.

Equation (3.41) is the most important consequence of the path integral theory to be presented in this paper. Note that previously this hypothesis was made and tested only for systems with $n=2$ where the scalar curvature provides complete curvature information. For $n>2$, the uniqueness arguments used in the Rgm are no longer valid. The present new theory gives the answer for all values of n . To test Eq. (3.41) in systems such as fluid mixtures, where $n>2$, would be interesting.

IV. ADDITIONAL RESULTS

A. Monatomic ideal gas

In this section I will investigate fluctuation theory at small volumes for the monatomic ideal gas. Here (Ref. 4), $R=0$ so the path-integral theory predicts that in Cartesian coordinates the Gft should work all the way down to microscopic volumes where thermodynamics ceases to have any validity. This prediction can be put to the test since exact information about fluctuations can be obtained from elementary kinetic theory. I will here also compare the cft and the Gft in a system in which such a comparison can be made exactly.

The common belief is that thermodynamic fluctuation theory is applicable only to systems containing a macroscopic number of particles. Yet, it was found in the 1D ferromagnetic Ising model⁵ that $\bar{\xi}$ and ξ agree very well with one another even if they are small; for example, if $\xi=5$ lattice sites the deviation is only about 15%. The implication is that

for weakly interacting systems, the path-integral theory works well even at microscopic volumes. This will be confirmed here for the monatomic ideal gas.

Initially, I will make the most naive choice of coordinates in the Gft and worry about the difficulties involved with a transformation to Cartesian coordinates later. Let me start by comparing the predictions of kinetic theory and the Gft for fluctuations in the particle number N of the system A_{V_f} . (For brevity, I will drop the subscript f on the parameters of A_{V_f} .) For the ideal gas it is easy to show³¹ that Eq. (2.4) yields

$$w(N)dN = (2\pi N^*)^{-1/2} \exp \left[-\frac{(N-N^*)^2}{2N^*} \right] dN \quad (4.1)$$

for the probability of finding the particle number between N and $N+dN$. Here, $N^* \equiv n_R V_f$, where n_R is the particle density of the infinite A_{V_R} . As calculated with Eq. (4.1), N^* is also the average value of N .

Kinetic theory predicts the *exact* probability of finding an integral number I of particles in A_{V_f} to be³²

$$w_I = \frac{N^{*I} e^{-N^*}}{I!} . \quad (4.2)$$

Note that (4.1) is a continuous probability density whereas the exact (4.2) is discrete.

As Landau and Lifshitz⁹ prove, the probability distributions above have the same first and second moments for all values of N^* . Hence, these moments do not provide any measure of how these distributions deviate from one another as a function of N^* . Instead, let me compare $w(N)$ and w_I by intro-

ducing the auxiliary continuous probability density

$$w'(N) \equiv \begin{cases} w_I, & I \leq N < I+1 \\ 0, & \text{if } N < 0. \end{cases} \quad (4.3)$$

The insert in Fig. 3 shows graphs of $w(N)$ and $w'(N)$ for $N^*=5$ particles. It is seen that the agreement between the two is fair even at such a small average particle number.

We define

$$\delta w \equiv \frac{1}{2} \int_{-\infty}^{\infty} |w(N) - w'(N)| dN \quad (4.4)$$

which, geometrically, is one half of the area contained under one and only one of the curves $w(N)$ and $w'(N)$. δw varies between 0 and 1; the minimum value corresponds to perfect agreement between $w(N)$ and $w'(N)$ and the maximum value to no overlap at all. δw has been calculated numerically as a function of N^* . Results are shown in Fig. 3. It is seen that δw exceeds 0.1 only if V_f is so small that $N^* < 3$. Hence, the Gft is fairly successful in predicting fluctuations in N even down to microscopic volumes.

A more complete test of the Gft is obtained if energy fluctuations are considered also. For the monatomic ideal gas the entropy per unit volume is³³

$$s(u, n) = \frac{n}{n_0} s_0 + n \ln \left[\left(\frac{u}{u_0} \right)^{3/2} \left(\frac{n_0}{n} \right)^{5/2} \right], \quad (4.5)$$

where u and n are the energy and particle densities, respectively, and $s_0 \equiv s(u_0, n_0)$ is the entropy density at some arbitrary reference state. Axioms I—III yield

$$P_{\text{conv}}(U, N) dU dN = \text{const} \times \exp \left\{ N \ln \left[\left(\frac{U}{U^*} \right)^{3/2} \left(\frac{N^*}{N} \right)^{5/2} \right] - \frac{3N^*}{2U^*} (U - U^*) + \frac{5}{2} (N - N^*) \right\} dU dN, \quad (4.6)$$

where U is the total energy in A_{V_f} and $U^* \equiv u_R V_f$. I am using an abbreviated notation for probability densities in this section. The Gaussian approximation of this is

$$P_G(U, N) dU dN$$

$$= (2\pi)^{-1} \left(\frac{3}{2} \right)^{1/2} \frac{1}{U^*} \exp \left[-\frac{5}{4N^*} (N - N^*)^2 + \frac{3}{2U^*} (U - U^*) (N - N^*) - \frac{3}{4} \frac{N^*}{(U^*)^2} (U - U^*)^2 \right] dU dN. \quad (4.7)$$

Using the Maxwell velocity distribution, we can find an exact expression for the fluctuation probability den-

sity. The details are worked out in Appendix B where it is shown that the probability of finding an integral number I of particles in A_{V_f} with total energy between U and $U + dU$ is

$$\mathcal{P}(U, I) dU = \begin{cases} \Gamma \left[\frac{3I}{2} \right]^{-1} w_I \left[\frac{3N^*}{2U^*} \right]^{3I/2} U^{(3I/2)-1} \exp \left[\frac{-3N^*}{2U^*} U \right] dU, & I \geq 1 \\ \delta(U) dU, & I = 0 \end{cases} \quad (4.8)$$

where $\delta(U)$ is the Dirac delta function of U .³⁴ In order to compare $\mathcal{P}(U, I)$ with the thermodynamic probability densities, let me again introduce an auxiliary probability density continuous in the variable N :

$$\mathcal{P}'(U, N) \equiv \begin{cases} \mathcal{P}(U, I), & I \leq N < I + 1 \\ 0, & N < 0 \text{ or } U < 0. \end{cases} \quad (4.9)$$

We define

$$\delta P_G \equiv \frac{1}{2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |P_G(U, N) - \mathcal{P}'(U, N)| dU dN. \quad (4.10)$$

Again, δP_G varies between 0 and 1 corresponding either to total agreement between $P_G(U, N)$ and $\mathcal{P}'(U, N)$ or to no overlap at all. Note, δP_G is independent of U^* since U and U^* occur always in a ratio to one another. Hence, a change of variables to U/U^* in the integration in (4.10) removes all dependence on U^* .

Figure 4 shows δP_G as a function of N^* . It is seen that for a given value of N^* , δP_G is generally larger than δw . However, it is still reasonably

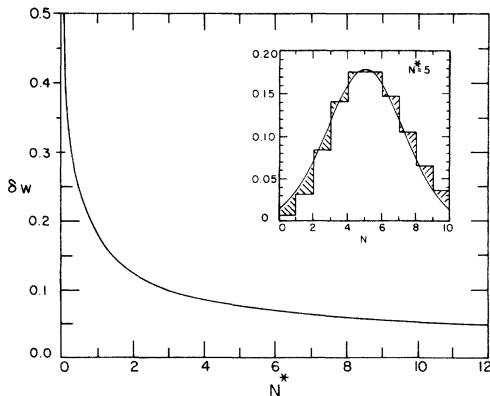


FIG. 3. A graph of δw as a function of N^* . For an average particle number $N^* > 3$, it is seen that δw drops below 0.1. Insert shows the Gaussian $w(N)$ and the step function $w'(N)$ for $N^* = 5$. Agreement between the two is seen to be fair. Area of the shaded region shown in the insert is twice δw for $N^* = 5$.

small; it drops to less than 0.15 for $N^* > 12$ particles and curves sharply upwards only for $N^* \leq 4$, where $\delta P_G \approx 0.3$. However, convergence to zero for large N^* is slow; if $N^* = 50$, $\delta P_G = 0.071$.

The conclusion here is that the Gft in (U, N) coordinates works reasonably well even down to microscopic levels. As I will show below, switching to Cartesian coordinates leads to only a slight improvement.

Also shown in Fig. 4 is a graph of

$$\delta P_{\text{conv}} \equiv \frac{1}{2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |P_{\text{conv}}(U, N) - \mathcal{P}'(U, N)| dU dN \quad (4.11)$$

as a function of N^* . (δP_{conv} is also independent of U^* .) It is seen that for $N^* > 3$, δP_{conv} is greater than δP_G indicating that, for most values of N^* , the Gft is actually better than the cft by the test used here.

The results presented here support my earlier contention that Gft fails at small volumes because of a breakdown in Axiom I rather than because of a

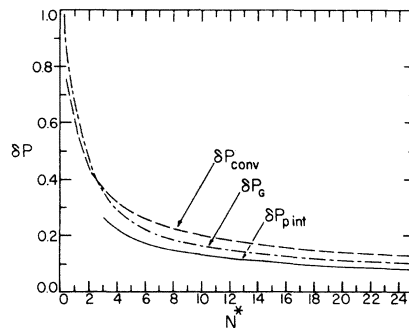


FIG. 4. A test of thermodynamic fluctuation theories as a function of N^* . Data here support the prediction that for the ideal gas the Gft should work, at least approximately, down to microscopic volumes where thermodynamics fails. Data also support the contention that third- and higher-order terms in the entropy expansion help little.

failure to take into account enough terms in the entropy expansion.

Finally, let me test the Gft by first attempting to transform into Cartesian coordinates. This will lead to an unexpected difficulty. For the monatomic ideal gas the line element of α in (T, n) coordinates is given by

$$dl^2 = \frac{3n}{2T^2} dT^2 + \frac{1}{n} dn^2, \quad (4.12)$$

where the temperature T equals $2u/3n$.

The coordinates (T, n) are convenient since there is no cross term in the line element. Making the coordinate transformation

$$\begin{aligned} x_1 &= 2\sqrt{n} \cos \ln \left[\left[\frac{T}{T_0} \right]^{\sqrt{3/8}} \right], \\ x_2 &= 2\sqrt{n} \sin \ln \left[\left[\frac{T}{T_0} \right]^{\sqrt{3/8}} \right], \end{aligned} \quad (4.13)$$

$$d = \begin{cases} 2[n_1 + n_2 - 2c(n_1 n_2)^{1/2}]^{1/2}, & \left[\frac{T_2}{T_1} \right] \leq \exp \left[\left[\frac{8}{3} \right]^{1/2} \pi \right] \\ 2(n_1)^{1/2} + 2(n_2)^{1/2}, & \left[\frac{T_2}{T_1} \right] > \exp \left[\left[\frac{8}{3} \right]^{1/2} \pi \right] \end{cases} \quad (4.16)$$

where

$$c \equiv \cos \ln \left[\left[\frac{T_2}{T_1} \right]^{\sqrt{3/8}} \right]. \quad (4.17)$$

Clearly, if $T_2/T_1 > \exp[(8/3)^{1/2}\pi]$, d depends only on differences in one coordinate, behavior not consistent with the plane. This behavior results since we can go from any point (T_1, n_1) to the line $n=0$ by moving along the geodesic segment $T=\text{const}=T_1$ which has finite length $2\sqrt{n_1}$. T can now be varied as much as desired with no cost in distance by remaining on the line $n=0$. Finally, we go out to the end point (T_2, n_2) by moving along the geodesic segment $T=\text{const}=T_2$ with length $2\sqrt{n_2}$.

To take into account these complications in the structure of α in performing the numerical evaluation of Eq. (3.30) is too difficult to attempt here. If V_f is sufficiently large it is also unnecessary since, in this case, regions far from the initial point contribute little and Eq. (4.15) works well as long as it is not applied to relatively improbable states.

Again, computations were made numerically. The distance d was evaluated with Eq. (4.16) provided T was in the range where the first part of this

where T_0 is an arbitrary constant, yields

$$dl^2 = dx_1^2 + dx_2^2, \quad (4.14)$$

the line element in Cartesian coordinates for a surface with zero curvature.

If α for the ideal gas were topologically equivalent to the two-dimensional plane, we could immediately write

$$P(x_1, x_2) dx_1 dx_2 = (2\pi t_f)^{-1} \exp \left[\frac{-d^2}{2t_f} \right] dx_1 dx_2, \quad (4.15)$$

where d is the straight line distance between the points on α corresponding to the states of A_{V_R} and A_{V_f} . However, α is more complicated. The shortest distance between points having endpoints at (T_1, n_1) and (T_2, n_2) , where $T_2 \geq T_1$ is³⁵

equation was applicable; otherwise, d was simply set to infinity. A check on the accuracy of this procedure was provided by its prediction of the normalization factor; for $N^* > 5$, it was within better than 1%. For smaller N^* the accuracy dropped off rapidly. Figure 4 shows

$$\delta P_p \text{int} \equiv \frac{1}{2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |P(U, N) - \mathcal{P}'(U, N)| dU dN, \quad (4.18)$$

which is independent of U^* , as a function of N^* . $P(U, N)$ was calculated from (4.15) by including the necessary Jacobian. As can be seen, $P(U, N)$ yields the best results.

B. 1D Ising model

Having just examined a noninteracting system, let me now consider a system in which there may be strong interactions—the 1D Ising model in zero field. A complete analysis of this problem with Eq. (3.30) is difficult and will not be attempted here. Some observations can be made, however, without a great deal of effort.

For the 1D Ising model of V_R spins, the Hamiltonian is

$$\mathcal{H} = -J \sum_{i=1}^{V_R-1} \sigma_i \sigma_{i+1} - h \sum_{i=1}^{V_R} \sigma_i, \quad (4.19)$$

where $\sigma_i = \pm 1$ is the magnetization of the i th spin, h is the external magnetic field, and J is the coupling constant between nearest-neighbor spins. In the limit of large V_R , the partition function can be shown to be³⁶

$$Z(\nu, b) = [e^\nu \cosh b + (e^{2\nu} \sinh^2 b + e^{-2\nu})^{1/2}]^{V_R}, \quad (4.20)$$

where $\nu \equiv J/T$ and $b \equiv h/T$.

For a segment of V_f spins, define the magnetization M to be the number of up spins minus the number of down spins and the magnetization density $m \equiv M/V_f$. I will regard M and m to be continuous variables. The line element for α in (T, m) coordinates is⁵

$$dl^2 = g_T dT^2 + g_m dm^2, \quad (4.21)$$

where

$$g_T = (1/T)(\partial s / \partial T)_m$$

and

$$g_m = (1/T)(\partial h / \partial m)_T.$$

All thermodynamic properties of α are calculated from the partition function in the limit $V_R \rightarrow \infty$.

For $h=0$, the correlation length can be worked out exactly³⁶:

$$\exp(-r/\xi) \equiv |\langle \sigma_i \sigma_{i+r} \rangle| = |\tanh \nu|^r. \quad (4.22)$$

As $T \rightarrow 0$, ξ diverges according to the asymptotic form $\xi \sim \frac{1}{2} \exp(2|J|/T)$.

I will first examine the case $J < 0$ and $h = 0$. For $J < 0$, ξ is less than one lattice site⁵ and hence, Eq. (3.30) predicts that the Gft should be valid down to volumes containing only a few lattice sites. However, in this example this prediction fails because fluctuations reach microscopic levels at volumes of the order of the correlation length ξ . The criterion for judging fluctuations "microscopic" is that they be of the order of the contribution of a single spin flip in which case

$$(V_f/g_m) = \langle (\Delta M)^2 \rangle \sim 1$$

and

$$(V_f/g_u) = \langle (\Delta U)^2 \rangle \sim J^2,$$

where for the second fluctuation moments I have

used the Gft prediction in (u, m) coordinates. It is straightforward to show that for $h=0$ and T small,

$$g_m = \exp(2|J|/T) = 4J^2 g_u = 2\xi. \quad (4.23)$$

Therefore, fluctuations in M and U are predicted to reach microscopic levels if $V_f \sim \xi$ and the Gft should suffer the same type of breakdown evident in Sec. IV A at small volumes.

This prediction makes good physical sense. If $V_f \sim \xi$ all the spins in the system are correlated and we can think of them as being locked into place with one another.

The above result is a most interesting one for it implies that thermodynamic information can be used to deduce the correlation length ξ also in a system where repulsive interactions dominate and $\bar{\xi} \neq \xi$. Let me point out, however, that this behavior need not necessarily obtain in higher-dimensional systems with repulsive interactions.

A comment is also in order about the provocative result⁵ $\frac{1}{2} < \bar{\xi} < 1$ for $J < 0$. This result led to the interpretation of $\bar{\xi}$ as the average length, due to interactions, of clusters of aligned spins. The picture which emerges in this paper indicates that this result is fortuitous since here Eq. (3.30) fails if $V_f \sim \xi$ and there is no basis for interpreting $\bar{\xi} \sim 1$ if $\xi \gg 1$.

The behavior exhibited at $V_f \sim \xi$ by the Ising ferromagnet ($J > 0$) differs from that of the antiferromagnet since fluctuations in M no longer merely decrease monotonically to microscopic values but rather show a crossover from the Gft to quite different behavior as shown in Fig. 1. The interesting question is whether or not Eq. (3.30) is consistent with Fig. 1. For $J > 0$, $\bar{\xi} = \xi$ to within a single lattice site so Eq. (3.30) predicts the crossover from the Gft to different behavior at $V_f \sim \xi$. A test of whether or not the crossover is to the expected probability distribution is difficult. I will present no final conclusion here, but will indicate one of the difficulties in making the calculation.

A common technique for obtaining information in path-integral theories is to examine paths of extremal action and make perturbation expansions about them. Let me show that, in at least one case, paths which extremize the action are not the most important ones, and hence, they yield little physical information. Extremal paths satisfy the Euler-Lagrange equation

$$\frac{\partial \mathcal{L}}{\partial a_i} - \frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{a}_i} = 0, \quad (4.24)$$

where $a_1 = T$ and $a_2 = m$. Since g_T , g_m , and $\bar{\xi}$ are even functions of m , the line $m=0$ satisfies the

second of Eqs. (4.24). Along this line it is easy to show that for small T , where for $J=1$, g_T has the asymptotic form

$$g_T = (4/T^4) \exp(-2/T)$$

and $\bar{\xi} = \frac{1}{2} \exp(2/T)$, the equation for T can be written

$$\frac{d^2 f}{dx^2} - \left(\frac{df}{dx} \right)^2 + \frac{2}{x} \left(\frac{df}{dx} \right) + \frac{1}{3x^4} e^{4f} = 0, \quad (4.25)$$

where $f \equiv (T^{-1} - T_R^{-1})$, $x \equiv V/\bar{\xi}(a_R)$, and $a_R = (T_R, 0)$ is the fixed state of A_{V_R} .

In Fig. 5, I show numerically generated solutions (Runge-Kutta) to Eq. (4.25). In these calculations, I selected initial values $x = 10000$ and $f = 0$ and then let x decrease. The initial value f_0 of df/dx was varied. Note that as $x \rightarrow 0$, the solution $f(x)$ becomes negative for each of the initial df/dx . This corresponds to increasing T as $x \rightarrow 0$. Physically, however, we expect the most probable state for $x \ll 1$ to have a low energy density and temperature because the spins tend to align at small volumes. Therefore, the paths which extremize the action do not provide much information about the physically important paths. Note, however, that paths with the largest actions are the ones with T small because $\bar{\xi}$ increases with decreasing T , but these paths do not satisfy the Euler-Lagrange equations. It appears that the only way to include the effects of these most important paths is to evaluate Eq. (3.30) by a direct numerical summation of paths or, more likely, by a numerical solution of the associated partial differential diffusion equation. While this task is surely difficult, it may well be tractable.

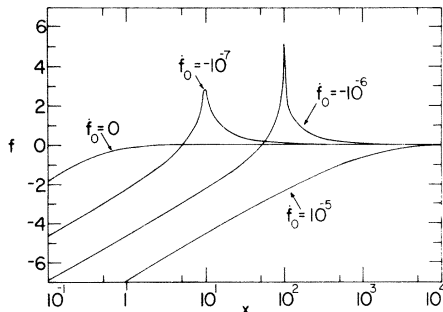


FIG. 5. Numerical solutions of the differential equation (4.25) with initial conditions $x = 10000$, $f = 0$, and four choices of f_0 . For all values of f_0 tested, f becomes negative for small x .

V. CONCLUSION

A thermodynamic fluctuation theory which includes local correlations has been developed. This theory both confirms and expands a hypothesis made earlier on the basis of a Riemannian geometric model of thermodynamics that the correlation length is a known function of the thermodynamics. In addition, since local correlations have been included, there is hope that this theory works at volumes less than the correlation volume, and hence, that it provides a thermodynamic theory of critical fluctuations.

Many problems remain. The most important one is the issue of the validity of the theory at volumes less than the correlation volume. Another important task is the calculation of the curvature scalar for systems, such as fluid mixtures, where the dimension of \mathcal{Q} is greater than two. There also remains the problem of understanding the thermodynamic fluctuation hypothesis with statistical mechanics. The attainment of this goal appears distant; my view is that a serious attack on this problem is best preceded by further tests and applications of the path-integral theory to add further confirmation that its predictions do indeed correspond to reality.

ACKNOWLEDGMENTS

The author acknowledges useful conversations with Melvin Berger, Selden Crary, Richard Ellis, and David Hoffman as well as a useful communication from Robert Osserman.

APPENDIX A: VIOLATION OF CHAPMAN-KOLMOGOROV EQUATION WITH cft

The proof will be by counterexample. Let $n = 1$ and take $s(\rho) = \ln \rho$, where $\rho > 0$. (The violation of the third law of thermodynamics is of no consequence here.) In dimensionless units, let $V_R = 4$, $V_0 = 2$, and $V_1 = 1$. It is straightforward to show that

$$P_{\text{conv}} \left(\begin{array}{c|c} \rho_1 & \rho_0 \\ \hline V_1 & V_0 \end{array} \right) = \begin{cases} \frac{3}{4} \rho_0^{-3} (2\rho_1 \rho_0 - \rho_1^2), & \\ 0 \leq \rho_1 \leq 2\rho_0, & \\ 0, & \text{otherwise} \end{cases} \quad (\text{A1})$$

and

$$P_{\text{conv}} \left[\begin{array}{c} \rho_0 \\ V_0 \end{array} \middle| \begin{array}{c} \rho_R \\ V_R \end{array} \right] = \begin{cases} \frac{15}{16} \rho_R^{-5} (2\rho_R \rho_0 - \rho_0^2)^2, \\ 0 \leq \rho_0 \leq 2\rho_R, \\ 0, \text{ otherwise.} \end{cases} \quad (\text{A2})$$

In order to derive these expressions it was necessary to use the conservation equations

$$V_1^c \rho_1^c + V_1 \rho_1 = V_0 \rho_0$$

and

$$V_0^c \rho_0^c + V_0 \rho_0 = V_R \rho_R$$

as well as the condition that all densities be positive. Note, V_1^c and ρ_1^c are the volume and density, respectively, of the system $A_{V_1^c} \equiv A_{V_0}/A_{V_1}$.

It is immediately apparent that

$$\int_{\rho_0=1/2\rho_1}^{2\rho_R} P_{\text{conv}} \left[\begin{array}{c} \rho_1 \\ V_1 \end{array} \middle| \begin{array}{c} \rho_0 \\ V_0 \end{array} \right] P_{\text{conv}} \left[\begin{array}{c} \rho_0 \\ V_0 \end{array} \middle| \begin{array}{c} \rho_R \\ V_R \end{array} \right] d\rho_0 \neq P_{\text{conv}} \left[\begin{array}{c} \rho_1 \\ V_1 \end{array} \middle| \begin{array}{c} \rho_R \\ V_R \end{array} \right] \quad (\text{A3})$$

since the left-hand side contains a term proportional to $\ln(4\rho_R/\rho_1)$ while the rhs is a polynomial in ρ_R and ρ_1 . This demonstrates the failure of the Chapman-Kolmogorov equation if probability densities are evaluated with the cft.

$$\begin{aligned} \mathcal{P}(U|I) &= \int_0^U \mathcal{P}(U-x|1) \mathcal{P}(x|I-1) dx \\ &= \left[\Gamma \left(\frac{3I}{2} \right) \right]^{-1} T_R^{-3I/2} U^{(3I/2)-1} \exp \left[-\frac{U}{T_R} \right]. \end{aligned} \quad (\text{B4})$$

Using $T_R = 2U^*/3N^*$ now yields the first part of Eq. (4.8).

Equation (B4) does not hold if $I=0$. $\mathcal{P}(U|0)=0$ if $U \neq 0$. Also, we require

$$\int_0^\infty \mathcal{P}(U|0) dU = 1. \quad (\text{B5})$$

Therefore $\mathcal{P}(U|0) = \delta(U)$.

APPENDIX B: DERIVATION OF EQ. (4.8)

From elementary probability theory

$$\mathcal{P}(U, I) dU = w_I \mathcal{P}(U|I) dU, \quad (\text{B1})$$

where $\mathcal{P}(U|I) dU$ is the conditional probability that the energy is between U and $U+dU$ given that there are I particles in A_{V_f} , and w_I is, as before, the probability that I particles are in the system. The Maxwellian velocity distribution yields⁹

$$\mathcal{P}(U|I=1) dU = \frac{2}{(\pi T_R^3)^{1/2}} \sqrt{U} \exp(-U/T_R) dU, \quad (\text{B2})$$

where T_R is the temperature of the infinite reservoir.

If there are two particles in A_{V_f} with kinetic energies e_1 and e_2 it is necessary to do a convolution integral¹⁵ to find the distribution of the random variable $U = (e_1 + e_2)$:

$$\begin{aligned} \mathcal{P}(U|2) &= \int_0^U \mathcal{P}(U-x|1) \mathcal{P}(x|1) dx \\ &= \frac{U^2}{2T_R^3} \exp(-U/T_R). \end{aligned} \quad (\text{B3})$$

Continuing to add particles yields

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¹A. Einstein, Ann. Phys. IV (Folge) **22**, 569 (1907); **33**, 1275 (1910).

²L. Onsager, Phys. Rev. **37**, 405 (1931).

³A useful try to get around this is the so-called cellular method; see, e.g., M. J. Klein and L. Tisza, Phys. Rev. **76**, 1861 (1949). However, this approach involves derivatives of the free energy with respect to variables other than its natural parameters. The values of these derivatives cannot be deduced from thermodynamic information, i.e., heat capacities, equations of state, etc.

⁴G. Ruppeiner, Phys. Rev. A **20**, 1608 (1979).

⁵G. Ruppeiner, Phys. Rev. A **24**, 488 (1981).

⁶My usage of the term "correlation length" is not entirely conventional. If attractive interactions dominate, ξ_G appears to give the range of the correlation function, and hence, is in accord with usual definitions of ξ . However, if repulsive interactions dominate, ξ_G appears to give the cluster size rather than the range of the oscillatory correlation function (see Ref. 5). This point will be discussed further in Sec. IV B.

⁷The entropy representation is discussed by H. B. Callen, *Thermodynamics* (Wiley, New York, 1960).

- ⁸G. N. Lewis, *J. Am. Chem. Soc.* **53**, 2578 (1931).
⁹L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, New York, 1977).
¹⁰M. V. Smoluchowski, *Ann. Phys. IV (Folge)* **25**, 205 (1908).
¹¹That the cft applies to magnetic systems as to fluid systems is by no means obvious because magnetic extensive quantities are not strictly conserved. This issue has been discussed in Ref. 5 where I argue that if fluctuations in a magnetic system are in some sense small, as appears to be the case for the ferromagnetic Ising model, it is possible to apply cft as if magnetic extensive quantities were conserved.
¹²I. S. Sokolnikoff, *Tensor Analysis* (Wiley, New York, 1966).
¹³See Ref. 5. I should point out again that for the 1D antiferromagnetic Ising model, the Rgm correlation length is always less than one lattice site and appears to be the average length, due to interactions, of clusters of aligned spins rather than the range of the envelope of the oscillatory correlation function.
¹⁴R. B. Griffiths and J. C. Wheeler, *Phys. Rev. A* **2**, 1047 (1970).
¹⁵See, for example, P. E. Pfeiffer, *Concepts of Probability Theory* (Dover, New York, 1978).
¹⁶This is most expeditiously proved by first diagonalizing the quadratic form in Eq. (3.8) and then using the formula

$$\int_{-\infty}^{\infty} \exp[a(x_1-x)^2 + b(x_2-x)^2] dx \\ = \left[\frac{-\pi}{(a+b)} \right]^{1/2} \exp \left[\frac{ab}{(a+b)} (x_1-x_2)^2 \right].$$

See R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965), p. 357. I should point out that $\Delta\rho_0$ is integrated between plus and minus infinity in (3.9). Since densities must be positive, however, the fixed values of ρ_1 and ρ_R set constraints on the limiting values of ρ_0 . In most cases fluctuations which send ρ_0 to one of its limiting values are so improbable that integrating $\Delta\rho_0$ between $\pm\infty$ introduces negligible inaccuracy. I will use these limits throughout this paper. A general estimate of the effect of this approximation is difficult if not impossible and will not be attempted here.

- ¹⁷In local Cartesian coordinates, Eq. (3.15) splits into n independent functional integrals of the form of Eq. (3.28) in R. P. Feynman, *Statistical Physics* (Benjamin, Reading, Massachusetts, 1976), p. 79. The same result is obtained, of course, by repeated applications of the CK equation in Eq. (3.14).
¹⁸L. Onsager and S. Machlup, *Phys. Rev.* **91**, 1505 (1953).
¹⁹R. Graham, *Z. Phys. B* **26**, 281 (1977); **26**, 397 (1977).
²⁰H. Grabert and M. S. Green, *Phys. Rev. A* **19**, 1747 (1979).
²¹H. Dekker, *Phys. Rev. A* **19**, 2102 (1979); **22**, 1315 (1980).
²²H. Dekker, *Phys. Rev. A* **24**, 3182 (1981).
²³F. Langouche, D. Roekaerts, and E. Tirapegui, *J. Phys. A* **13**, 449 (1980).
²⁴Y. Takahashi and S. Watanabe, in *Lecture Notes in Mathematics* (Springer, New York, 1981), Vol. 851, p. 433.
²⁵My notation differs from that of Grabert and Green who use the symbol O for the Lagrangian $\tilde{\mathcal{L}}$ and \underline{L} for the metric g . Also, in this paper, the drift vector $f^\alpha=0$ and the constant k of Grabert and Green is $\frac{1}{2}$.
²⁶L. D. Landau and E. M. Lifshitz, *Mechanics* (Pergamon, New York, 1976), p. 146.
²⁷Again, my notation differs slightly from that of Grabert and Green. There are several sign conventions for curvature. The fourth-rank Riemannian curvature tensor of Grabert and Green differs by a minus sign from that of Sokolnikov (Ref. 12); however, the curvature scalar $R(a)$ in these references has the same sign.
²⁸The analysis given in this paragraph is a generalization to $n > 1$ of an estimate given by Feynman (see page 77 of Ref. 17). Note that the spirit here is to embody functional integral expressions such as Eq. (3.33) with more than purely notational meanings.
²⁹D. Laugwitz, *Differential and Riemannian Geometry* (Academic, New York, 1965), p. 124. For $n=2$ the Gaussian curvature K and the Riemannian curvature scalar are related by $R = -2K$ in our sign convention.
³⁰For example, if $n=3$, surround a_R with a sphere and measure its surface area A . The relationship between R and the deviation of A from its Euclidean value is given by C. W. Misner, K. S. Thorne, and J. A. Wheeler, *Gravitation* (Freeman, San Francisco, 1973), p. 509.
³¹Reference 9, Eq. (116.1).
³²Reference 9, Eq. (116.3).
³³See Ref. 7, Eq. (D.28). Note, Callen uses N to denote mole number rather than particle number.
³⁴Let me point out that for given N^* and U^* , the exact equation (4.8) and the Gft, Eq. (4.7), have identical first and second fluctuation moments. However, the cft, Eq. (4.6), does not even predict correctly the average values of U and N .
³⁵This expression was provided to me by David Hoffman and Robert Osserman in a private communication.
³⁶See, e.g., the article by C. J. Thompson, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1972), Vol. 1, Chap. 5.