Riemannian geometry in thermodynamic fluctuation theory

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Although thermodynamic fluctuation theory originated from statistical mechanics, it may be put on a completely thermodynamic basis, in no essential need of any microscopic foundation. This review views the theory from the macroscopic perspective, emphasizing, in particular, notions of covariance and consistency, expressed naturally using the language of Riemannian geometry. Coupled with these concepts is an extension of the basic structure of thermodynamic fluctuation theory beyond the classical one of a subsystem in contact with an infinite uniform reservoir. Used here is a hierarchy of concentric subsystems, each of which samples only the thermodynamic state of the subsystem immediately larger than it. The result is a covariant thermodynamic fluctuation theory which is plausible beyond the standard second-order entropy expansion. It includes the conservation laws and is mathematically consistent when applied to fluctuations inside subsystems. Tests on known models show improvements. Perhaps most significantly, the covariant theory offers a qualitatively new tool for the study of fluctuation phenomena: the Riemannian thermodynamic curvature. The thermodynamic curvature gives, for any given thermodynamic state, a lower bound for the length scale where the classical thermodynamic fluctuation theory based on a uniform environment could conceivably hold. Straightforward computation near the critical point reveals that the curvature equals the correlation volume, a physically appealing finding. The combination of the interpretation of curvature with a well-known proportionality between the free energy and the inverse of the correlation volume yields a purely thermodynamic theory of the critical point. The scaled equation of state follows from the values of the critical exponents. The thermodynamic Riemannian metric may be put into the broader context of information theory.

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I. OVERVIEW

The formula for entropy

$$S=k_B \ln \Omega \tag{1.1}$$

inscribed on Boltzmann's gravestone[1] is one of the mainstays of statistical mechanics. The inversion of this formula by Einstein,

$$\Omega=\exp\left[\frac{S}{k_B}\right], \tag{1.2}$$

is the starting point for thermodynamic fluctuation theory, now found in almost every textbook on statistical mechanics. What could possibly be new about this topic?

This question is addressed here in a review of a number of ideas which have followed the founding of the classical thermodynamic fluctuation theory. This review is organized as follows: first, a relatively simple and comprehensive introduction that provides a nontechnical discussion of the basic physical ideas; second, a summary of the classical thermodynamic fluctuation theory, including a discussion of its limitations; third, a review of work adding covariance, consistency, and the Riemannian geometry to the theory; fourth, simple examples computing fluctuations for models where methods from statistical mechanics offer an exact comparison; finally, a discussion of the Riemannian thermodynamic curvature and the curvature theory of the critical point. Since many of the ideas of Riemannian geometry are not familiar in the thermodynamic context, some care will be taken in developing them.

In this era when computers are increasingly being used to perform symbolic mathematics, a note is in order about their role in this review. Though many of the results have been checked with such programs, all the non-numerical calculations were performed by hand, with the exception of those in Sec. VI.C.

Table I gives the general notation in this review.

II. INTRODUCTION

A. Fluctuations with one variable

Consider a very large closed thermodynamic system A_{V_0} in thermodynamic equilibrium. It has fixed volume V_0 and fixed energy per volume u_0. Let A_V, with fixed volume V, be some subsystem of A_{V_0} (see Fig. 1). The energy per volume of A_V is u, which is not fixed by any explicit constraint[2]; all the other independent thermodynamic parameters of A_V are held fixed. An example of such a case is a pure fluid subsystem of A_{V_0} with closed boundaries, in which only the exchange of heat is allowed with the environment. Another example in which a single fluctuating variable suffices is a paramagnetic spin system.

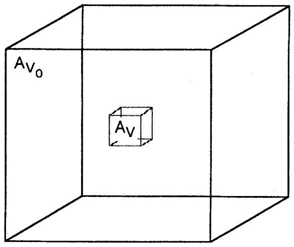

FIG. 1. Usual setup in the classical thermodynamic fluctuation theory. A single subsystem A_V, with volume V, of a much larger closed environment A_{V_0}. Both A_V and its reservoir A_{V_0}/A_V are regarded as uniform systems. This structure is also used in canonical ensembles in statistical mechanics.

The usual statement of the second law of thermodynamics says that u takes on that value which maximizes the entropy $S_0(u,u_0)$ of A_{V_0} (Callen, 1985). However, statistical mechanics says more; it describes fluctuations around this state of maximum entropy (Landau and Lifshitz, 1977). Let us argue from the microcanonical ensemble. Here the basic postulate is that all accessible microstates[3] of A_{V_0} occur with equal probability. Therefore the probability of finding the internal energy of A_V between u and $u+du$ is proportional to the number of microstates of A_{V_0} corresponding to this range:

$$P_V(u\,|\,u_0)du=C\Omega_V(u,u_0)du\ , \tag{2.1}$$

where $\Omega_V(u,u_0)$ is the density of states, and C is a normalization constant.[4]

Now, by Eq. (1.1), Boltzmann's constant k_B times the natural logarithm of $\Omega_V(u,u_0)$ is the entropy of A_{V_0}, so

$$P_V(u\,|\,u_0)du=C\exp\left[\frac{S_0(u,u_0)}{k_B}\right]du\ . \tag{2.2}$$

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[1] This is the modern notation; actually appearing is $S=k\log W$ (Broda, 1983).

[2] Some texts leave the fluctuating function unspecified (e.g., Landau and Lifshitz, 1977). However, it is difficult to envision a single thermodynamic quantity fluctuating at fixed energy; so there seems to be no essential loss in generality in taking it to be the energy density, or some function of the energy density.

[3] A microstate is the specification of the quantum numbers of all the atomic constituents of the subsystem. A macrostate consists just of the specification of the independent macroscopic parameters, such as energy or particle density. Generally, a microstate determines uniquely a macrostate, but not vice versa.

[4] This probability is for finding a state in a small range at *some specific instant in time,* with no knowledge about the history of the subsystem. Information about history improves the chances of guessing the state, since states are correlated over time. But time correlations belong to the domain of dynamic phenomena and are beyond the scope of either equilibrium statistical mechanics or thermodynamic fluctuation theory.

TABLE I. Notation for symbols appearing in more than one place in this review. Because of the large number of symbols in thermodynamics, we occasionally use the same symbol for different quantities. The usage should be clear from the context.

Notation	Meaning
A_V	open subsystem of A_{V_0} with volume V
A_{V_0}	large closed thermodynamic system with volume V_0
A_{V_c}	environment $A_{V_0}\setminus A_V$, with volume $V_c=V_0-V$, of A_V in A_{V_0}
$F=(1/T,-\mu^1/T,-\mu^2/T,\ldots,\mu^r/T)$	intensive parameters in the entropy representation
$F_e=(1/T,-\mu^1/T,\ldots,-p/T,\ldots,\mu^r/T)$	extended list of intensive parameters
K^α	drift vector
M	magnetization
N	number of atoms in a single-component system
N^i	number of molecules of the ith species
$P=(T,\mu^1,\mu^2,\ldots,\mu^r)$	intensive parameters in the energy representation
$P=P_V(x\vert x_0)=P_t(x\vert x_0)$	probability density with $V_0\rightarrow\infty$
$P=P\left[\begin{matrix} x & \vert & x_0 \\ t & \vert & t_0 \end{matrix}\right]$	probability density with nonzero t_0
$P_e=(T,\mu^1,\ldots,-p,\ldots,\mu^r)$	extended list of intensive parameters
$S_0=S_0(x,x_0)$	entropy of A_{V_0} when A_V is in the state x
T	temperature of A_V
T_c	critical temperature
U	internal energy of A_V
V,V_c,V_0	volumes of A_V, A_{V_c}, and A_{V_0}, respectively
$X=(U,N^1,N^2,\ldots,N^r)$	extensive parameters in the entropy representation
$X_e=(U,N^1,\ldots,V,\ldots,N^r)$	extended list of extensive parameters
$Y_e=(S,N^1,\ldots,V,\ldots,N^r)$	extended list of extensive parameters
$a=X/V=(u,\rho^1,\rho^2,\ldots,\rho^r)$	standard densities of A_V in the entropy representation
a_0,a_c	standard densities of A_{V_0} and A_{V_c}, respectively
$a_e=(U/X_e^n,N^1/X_e^n,\ldots,1)$	extended list of densities
d	spatial dimension
$f=u-Ts$	Helmholtz free energy
g	determinant of $g_{\alpha\beta}$
$g_{\alpha\beta}$	metric elements
$g^{\alpha\beta}$	inverse of the metric elements
h	magnetic field
k_B	Boltzmann's constant
$m=M/N$	magnetization per spin
$n=r+1$	dimension of the thermodynamic state space
p	pressure
r	number of fluid components
$s=s(a)$	entropy per volume
$t=1/V$	"time" parameter
$t=(T-T_c)/T_c$	reduced temperature
$u=U/V$	internal energy per volume of A_V
u_0	internal energy per volume of A_{V_0}
$x=(x^1,x^2,\ldots,x^n)$	general coordinates
$x'=(x'^1,x'^2,\ldots,x'^n)$	general coordinates
$\Delta x^\alpha=x^\alpha-x_0^\alpha$	coordinate differential
$\Omega_V(a,a_0)$	density of states
$\kappa=\kappa_1\kappa_2$	constant of proportionality between R and ϕ^{-1}
κ_1	constant of proportionality between ϕ and ξ^{-d}
κ_2	constant of proportionality between R and ξ^d
μ	chemical potential of a single fluid component
μ^i	chemical potential of ith fluid component
ξ^d	correlation volume
$\xi_G^d=-R/2$	Gaussian curvature
ρ	single-component fluid density
ρ^i	density of the ith fluid component
$\phi=s-u/T+\mu\rho/T$	thermodynamic potential, or free energy, per volume
$\omega=u-Ts-\mu\rho$	thermodynamic potential, or free energy, per volume

If we regard entropy as a thermodynamic quantity equal to the sum of the entropies of A_V and its environment $A_{V_0} \setminus A_V$, then we have arrived at the classical theory of thermodynamic fluctuations (Einstein, 1907, 1910). The next step is usually to take $V_0 \rightarrow \infty$ and to approximate the probability density $P_V(u|u_0)$ by expanding the entropy to second order about its maximum at $u=u_0$. A standard exercise (Landau and Lifshitz, 1977; see also Sec. III.B of this review) reveals

$$P_V(u|u_0)du$$
$$=\sqrt{Vg(u_0)/(2\pi)}\exp\left[-\frac{V}{2}g(u_0)(u-u_0)^2\right]du , \tag{2.3}$$

where

$$g(u_0) \equiv -\frac{1}{k_B}\frac{d^2s}{du^2}\bigg|_{u=u_0} , \tag{2.4}$$

and $s=s(u)$ is the entropy per volume in the thermodynamic limit. This Gaussian approximation is adequate for small deviations of u from u_0.

B. Some technical problems

Despite its effectiveness, this line of thought leads to difficulties when pursued beyond the Gaussian approximation. First, instead of characterizing the thermodynamic state of A_V with the energy density u, suppose we choose some other thermodynamic parameter $x=x(u)$? The counting of the microstates which led to Eq. (2.1) can be done equally well with x. If we simply take the entropy again to be proportional to the logarithm of the density of states, the result should be the same expression as Eq. (2.2) with x's in place of u's. Indeed, Landau and Lifshitz (1977) presented this equation with a general coordinate x, since, as they put it, "the discussion made no use of any specific property of the energy."

But we obtain a different expression if instead we start with Eq. (2.2) and make a straightforward coordinate transformation $u \rightarrow x(u)$. The left-hand side goes to

$$P_V(u|u_0)du=\left[P_V(u|u_0)\left[\frac{du}{dx}\right]\right]dx \equiv P_V(x|x_0)dx , \tag{2.5}$$

which gives the probability of finding the new parameter in the range from x to $x+dx$. On the right-hand side of Eq. (2.2) the thermodynamic entropy is a function of state, invariant with respect to a coordinate transformation. Therefore

$$P_V(x|x_0)dx=C\left[\frac{du}{dx}\right]\exp\left[\frac{S_0(x,x_0)}{k_B}\right]dx , \tag{2.6}$$

which does not have the form of Eq. (2.2), since the derivative of u on the right-hand side is not generally a constant and may not simply be absorbed in the normalization factor C.

Consequently, if we argue using statistical mechanics, we get one expression, but if we argue using mathematics in the purely thermodynamic regime, we get another. Indeed, the latter argument reveals clearly that the *form* of the thermodynamic fluctuation formula (2.2) depends on the coordinates; we say that the equation fails to be covariant. This suggests possible problems not only with Eq. (2.2), but with the statistical mechanical argument that produced it.

At first, this may appear to be a minor issue, open to several possible solutions. Perhaps the somewhat offhand presentation given here of the statistical mechanical derivation of the theory has overlooked some special feature of the energy density, which sets it apart from other variables.[5] Hence the prefactor of the exponential term in Eq. (2.6) might simply always happen to be a constant in energy coordinates. But it is not easy to frame an argument as to why this should be so. Indeed, the proposition that theory equation (2.2) is correctly stated in terms of the energy density is easy to test with simple examples. As will be seen in Sec. V, results do not offer much support for such a point of view.

A second try is simply to back out of this issue by saying that, at large enough volumes, fluctuations in the intensive parameters[6] become very small, and the Gaussian approximation, free of this difficulty, as we show below, is adequate. Furthermore, we cannot expect more from thermodynamics. We hope to convince the reader, however, that this viewpoint is unnecessarily limiting.

Let us look at another class of problems with Eq. (2.2), which we refer to as a lack of consistency. First, we define the average value of a thermodynamic function as

$$\langle f \rangle = \int f(x)P_V(x|x_0)dx . \tag{2.7}$$

There is nothing in the entropy function to ensure that

$$\langle u \rangle = u_0 \tag{2.8}$$

if $V_0 \rightarrow \infty$. Physically, Eq. (2.8) must hold for *all V*, as will be shown in Sec. III.C, but it clearly will not hold with Eq. (2.2) unless $S_0(u,u_0)$ is an even function of $u-u_0$. There is nothing in the laws of thermodynamics which demands that the entropy be such, beyond the Gaussian approximation.

In Sec. II.D we shall see yet another problem in the category of consistency: the Chapman-Kolmogorov equation is not satisfied by Eq. (2.2). This equation emerges when we go to the next level and consider fluc-

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[5] Indeed, the discussion of the microcanonical ensemble is frequently given in the context of Liouville's theorem of classical mechanics, where the energy does have a special role.

[6] An *intensive* parameter is one that does not scale up with the system size, for example, density, temperature, or pressure. An *extensive* parameter scales up in proportion to the system size, for example, internal energy, mole numbers, or entropy.

tuations inside the subsystem A_V.

It must be emphasized that these issues are not confined merely to very small subsystems. Fluctuations near the critical point become very large, and the Gaussian approximation to the classical thermodynamic fluctuation theory becomes inadequate, for subsystems of *macroscopic* size.

Before proceeding, let us show that the Gaussian approximation (2.3) has a number of very positive features that allow it to serve as an essential building block for a correct theory. First, it becomes exact as the subsystem volume V becomes very large, since in this limit fluctuations of the intensive quantities become very small. Second, the Gaussian approximation is covariant in form. A straightforward coordinate transformation $u \rightarrow x(u)$ in Eq. (2.3) establishes that, to second order in the displacement from $x_0[=x(u_0)]$,

$$P_V(x|x_0)dx = \sqrt{Vg(x_0)/(2\pi)} \times \exp\left[-\frac{V}{2}g(x_0)(x-x_0)^2\right]dx\ , \tag{2.9}$$

where[7]

$$g(x_0) = \left[\frac{du}{dx}\right]^2 g(u_0)\ . \tag{2.10}$$

Fluctuations are small in the regime of validity of the Gaussian approximation; so the derivative of u with respect to x is constant over the range of reasonably probable states. Therefore Eq. (2.9) is of precisely the same form as Eq. (2.3) in energy coordinates. Third, from the symmetry of the Gaussian distribution, the average value of x is x_0, for any choice of coordinate, including the energy density.

C. A physical difficulty

Let us depart for now from these somewhat formal mathematical technicalities and turn to a problem at the heart of the physics. For specificity, let A_{V_0} be a very large closed pure-fluid system with known, and fixed, thermodynamic state. Open the boundary of the enclosed subsystem A_V to the exchange of particles, as well as energy, with its environment $A_{V_0} \setminus A_V$.

A standard assumption in classical thermodynamic fluctuation theory is that the environment $A_{V_0} \setminus A_V$ of A_V is uniform. However, there are certainly departures from homogeneity. Especially significant are those of the local surroundings of A_V, which tend to fluctuate along with A_V. These fluctuations raise questions about the assumption of a uniform environment.

For simplicity, pitch the discussion entirely in terms of density fluctuations, even though doing so is not really correct, since the energy fluctuates independently of density. But this assumption does serve as an educational device and is not completely removed from realistic cases, since, near the critical point, density fluctuations are much larger than energy fluctuations. The full formalism is discussed in Sec. IV.

Consider first a fairly large volume V. Sample the detailed microscopic state of A_{V_0} at some given instant in time. At this instant, we might find A_V locally surrounded by a region of density higher all around than average, or lower all around than average. But, as is not uncommon in statistics, there are more ways to get "mixed" situations than situations in which things go all one way (see Fig. 2). Such mixed situations have densities whose averages all around at some instant in time tend to be close to that of the whole environment. If mixed situations are dominant, then the assumption that the environment is uniform has some plausibility.

But let V get smaller and such logic runs afoul of the spatial correlations in the positions of the molecules, particularly those contributed by the attractive parts of the intermolecular forces. According to the canonical distribution in statistical mechanics, the probabilistic weight of a microstate in some region of A_{V_0} is increased if the energy is lowered. Unless the molecules are packed very closely, bringing a pair of molecules closer together lowers the energy. The attractive intermolecular interactions thus tend to cause molecules to cluster together loosely, with local density higher than average (see Fig. 3). Of course, over a long period of time, the average density at any point in A_{V_0} must be ρ_0; so clustering must come at the expense of regions with correspondingly lowered densities.

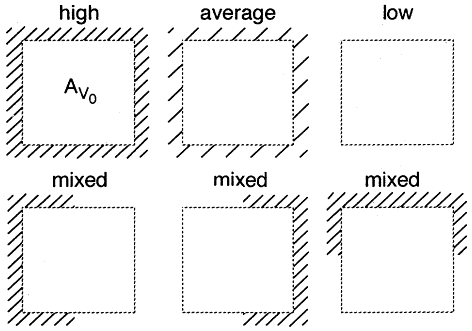

FIG. 2. Possible densities surrounding A_V at a given instant in time. If V is very large, then there will be more mixed-type situations, with regions of both high and low densities, than those with the density all around less or greater than average. Mixed situations tend to have average densities close to ρ_0. For smaller volumes, however, the high- and the low-density configurations are favored because of molecular spatial correlations, and the subsystem A_V rarely sees itself surrounded by an environment represented by the overall state of the system A_{V_0}.

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[7] Equation (2.10) is the transformation rule for a second-rank tensor. This transformation rule appears in standard treatments of the Gaussian approximation (Landau and Lifshitz, 1977) and is in no sense new to thermodynamics.

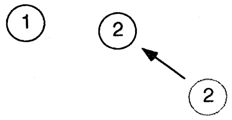

FIG. 3. Two nearby molecules in the fluid. In comparison with the ideal gas, attractive intermolecular interactions tend to increase their probability of being found close to each other at any instant in time.

The average size of these clusters of raised and lowered density is called the correlation length ξ. It may be considerably greater than the range of the intermolecular interaction, even approaching infinity at the critical point. In statistical mechanics, ξ is usually defined as the range of the exponentially decaying envelope of the correlation function (Landau and Lifshitz, 1977; Fisher, 1983). In some parts of this review, such a strict interpretation is what is intended; but in most places the meaning is a bit looser. Rice and Chang (1974) roughly defined the correlation length as the average distance between a region of density fluctuation in one direction and a region of fluctuation in the other. Widom (1974) has given a similar definition. The quantity ξ^d, where d is the spatial dimensionality, is called the correlation volume.

If $V<\xi^d$, A_V tends to find itself, at any instant in time, with increased probability inside either a cluster of increased density or a relatively depleted region. This has the effect of enhancing the probability of the "high" and the "low" density boundary configurations in Fig. 2, at the expense of the "mixed" configurations. The local surroundings of A_V, at any instant of time, then usually deviate widely from the overall state of the infinite environment.

One might argue that these details of the local environment of A_V will somehow all average out over time, and that the assumption of a uniform environment remains sound even in these volume regimes. But this seems too much to hope for since, in the typical case, the interaction of the subsystem A_V with the infinite medium is entirely through the local surroundings. Such profound fluctuations likely make a difference.

In the canonical ensemble of rigorous statistical mechanics (Ruelle, 1969; Griffiths, 1972), this issue is evaded by taking the thermodynamic limit $V\to\infty$. However, this limit defines away the problem of thermodynamic fluctuations. The canonical ensemble, with finite volume V, may be used to calculate fluctuation moments (Reif, 1965). But without the thermodynamic limit, the canonical ensemble is vulnerable to the same difficulties as those mentioned above. Indeed, Greene and Callen (1951) proved that the fluctuation moments computed with the statistical mechanical ensembles (with finite V) are the same as those computed with the classical thermodynamic fluctuation theory. Statistical mechanics does deal rigorously with fluctuations through correlation functions, but these do not provide the same information as thermodynamic fluctuation theory.

At this point, we add that the problem of physical concern here must be distinguished from the thermodynamics of finite-sized systems (Hill, 1963, 1964) and from the finite-scaling theory of critical phenomena (Barber, 1983). In both these theories, the basic structure is a uniform environment surrounding some finite subsystem. This is physically justified in the problems they deal with, such as small liquid droplets surrounded by air, or a fluid enclosed in a copper sample cell.

D. Towards a solution

Let us now work towards a common solution to the problems that have been raised. The first step is to introduce another open subsystem A_{V_1} of A_{V_0}. It, in turn, contains A_V (see Fig. 4). For pedagogical reasons, we again oversimplify and concentrate just on density fluctuations. We regard the fixed thermodynamic state of A_{V_0} as known.

Imagine sampling the thermodynamic state of A_{V_1} at some instant in time, and let us say that its density is ρ_1. Given this information, what is the probability that A_V will have a density between ρ and $\rho+d\rho$ at this instant in time? Clearly, knowing the density ρ_1 should narrow the possibilities over just knowing ρ_0. To find out how, start with a basic assumption about fluctuations: at some instant in time, the probability of finding the density of A_V between ρ and $\rho+d\rho$, given the density of A_{V_1}, depends only on ρ_1, and not on ρ_0.

This assumption is called Markovicity. Basically, it states that, at some instant in time, the situation inside a subsystem is determined solely by the thermodynamic state of that subsystem at that instant in time. Markovicity allows us to invoke the mathematics of Markov processes, which offers at least a good start for the theory. Though one would not expect Markovicity to hold exactly, there is some direct evidence for its validity (see Sec. IV.A.2).

We shall denote the conditional probability density for finding the density of A_V between ρ and $\rho+d\rho$ at some instant of time, given the density ρ_1 of A_{V_1} at that instant of time, as

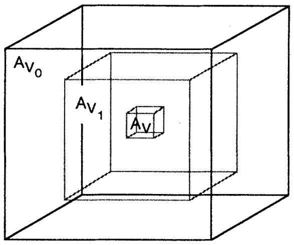

FIG. 4. Introduction of an intermediate open subsystem A_{V_1}. It is contained by A_{V_0} and in turn contains A_V.

$$P\left[\begin{matrix}\rho\\ t\end{matrix}\,\middle|\,\begin{matrix}\rho_1\\ t_1\end{matrix}\right]d\rho\,, \tag{2.11}$$

where

$$t=\frac{1}{V} \tag{2.12}$$

is the inverse of the volume (and in no sense a measure of real time). Subscripts on t refer to the corresponding subscripts on V. Using the inverse of the volume rather than the volume as the size parameter makes the connection to a diffusion-type equation (below) very natural. We shall use the notation of Eq. (2.11) for the probability density when t_1 is not necessarily zero, with the notation of Eq. (2.1) reserved for cases when it is.

A necessary self-consistency principle is the Chapman-Kolmogorov equation:

$$P\left[\begin{matrix}\rho\\ t\end{matrix}\,\middle|\,\begin{matrix}\rho_0\\ t_0\end{matrix}\right]=\int P\left[\begin{matrix}\rho\\ t\end{matrix}\,\middle|\,\begin{matrix}\rho_1\\ t_1\end{matrix}\right]P\left[\begin{matrix}\rho_1\\ t_1\end{matrix}\,\middle|\,\begin{matrix}\rho_0\\ t_0\end{matrix}\right]d\rho_1\,. \tag{2.13}$$

In words, if we integrate out the intermediate density ρ_1, we are left with the conditional probability density for ρ, given ρ_0. This principle may be invoked not just when the largest of the three systems is the infinite closed A_{V_0}, with fixed thermodynamic state, but when it is yet another finite open subsystem whose state is sampled at some instant in time. Ruppeiner (1983b) showed with a simple example that the Chapman-Kolmogorov equation does not hold in the classical thermodynamic fluctuation theory beyond the Gaussian approximation.

To determine the conditional probability densities requires a resolution to the problems discussed in the previous section. Fortunately, as a foundation for a correct theory, a relatively simple situation presents itself. This has t_1 nearly t. Nearly equal volumes allow for very little uncertainty in the value for ρ, for given value of ρ_1, and we expect that a simple Gaussian probability density would be adequate. Define

$$\Delta t=t-t_1 \tag{2.14}$$

and

$$\Delta\rho=\rho-\rho_1\,. \tag{2.15}$$

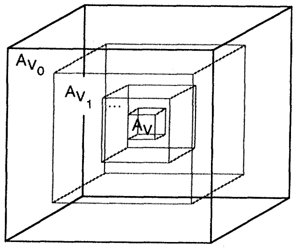

FIG. 5. Hierarchy of open concentric subsystems $A_{V_1}\supset A_{V_2}\supset\cdots\supset A_{V_M}\supset A_V$ of decreasing size. Each subsystem samples only the thermodynamic state of its immediate surrounding neighbor.

If $t_1=0$ (an infinite system), we can immediately write, by analogy with Eq. (2.3),

$$P\left[\begin{matrix}\rho\\ t\end{matrix}\,\middle|\,\begin{matrix}\rho_1\\ t_1\end{matrix}\right]=\left[\frac{g(\rho_1)}{2\pi\Delta t}\right]^{1/2}\exp\left[-\frac{1}{2\Delta t}g(\rho_1)(\Delta\rho)^2\right], \tag{2.16}$$

where

$$g(\rho_1)\equiv-\frac{1}{k_B}\frac{d^2s}{d\rho^2}\bigg|_{\rho=\rho_1}\,. \tag{2.17}$$

This becomes exact for small Δt. Equation (2.16) is predicted by statistical mechanics as well, and holds even if we drop the assumption that the energy is fixed.

If $t_1>0$, the situation is less clear, and to make headway we assume that Eq. (2.16) holds as well, with Δt given by Eq. (2.14). Implicit in this is that $g(\rho)$ has no explicit volume dependence. These assumptions are called translational invariance, and the reader may verify, with a logical application of the rules of the classical thermodynamic fluctuation theory presented in Sec. III.B, that it is actually predicted in the Gaussian approximation of this theory. However, this assumption is too simple to hold at volumes less than the order of the correlation volume, as we shall see in Sec. IV.D. But, since we have nothing better, we use this for now. The probability distribution in the limit $\Delta t\to 0$ is called the short-time propagator.

The two probability densities in the integrand of Eq. (2.13) are not short-time propagators. There are two ways to bring these in. The first is to introduce more subsystems in the hierarchy of systems: $A_{V_0}\supset A_{V_1}\supset A_{V_2}\supset\cdots\supset A_{V_M}\supset A_V$ (see Fig. 5). Take the limit as $M\to\infty$ and let all the adjacent subsystem volumes approach one another. Assuming Markovicity at every level, and repeatedly applying Eq. (2.13), leads to

$$P\left[\begin{matrix}\rho\\ t\end{matrix}\,\middle|\,\begin{matrix}\rho_0\\ t_0\end{matrix}\right]=\int P\left[\begin{matrix}\rho\\ t\end{matrix}\,\middle|\,\begin{matrix}\rho_M\\ t_M\end{matrix}\right]P\left[\begin{matrix}\rho_M\\ t_M\end{matrix}\,\middle|\,\begin{matrix}\rho_{M-1}\\ t_{M-1}\end{matrix}\right]\cdots P\left[\begin{matrix}\rho_1\\ t_1\end{matrix}\,\middle|\,\begin{matrix}\rho_0\\ t_0\end{matrix}\right]d\rho_M\cdots d\rho_1\,, \tag{2.18}$$

where the integration is over the M intermediate variables $\rho_1, \rho_2, \ldots, \rho_M$. In the limit considered, all the quantities in the integrand are short-time propagators. Physically, the picture is fluctuations inside fluctuations inside fluctuations..., as each subsystem in the hierarchy samples only the thermodynamic state of the subsystem immediately larger than it.[8] Mathematically, such an approach can be expressed in terms of the path-integral formalism (Schulman, 1981), where one thinks of the probability of finding a density ρ in a large environment with density ρ_0 as a sum over all parametrized paths $\rho(t)$ in density space leading from ρ_0 to ρ.

The second way to bring in the short-time propagator appears technically easier. Again, we start with Eq. (2.13) and let t_1 be very close to t. We may write

$$P\left[\begin{matrix}\rho\\ t\end{matrix}\,\middle|\,\begin{matrix}\rho_0\\ t_0\end{matrix}\right]=\int P\left[\begin{matrix}\rho\\ t\end{matrix}\,\middle|\,\begin{matrix}\rho-\Delta\rho\\ t-\Delta t\end{matrix}\right]P\left[\begin{matrix}\rho-\Delta\rho\\ t-\Delta t\end{matrix}\,\middle|\,\begin{matrix}\rho_0\\ t_0\end{matrix}\right]d(\Delta\rho)\;. \tag{2.19}$$

Using now the short-time propagator equation (2.16), expanding the second quantity in the integrand of Eq. (2.19) to first order in Δt and to second order in $\Delta\rho$, and doing the Gaussian integrals leads to

$$\frac{\partial P}{\partial t}=\frac{1}{2}g^{-1}(\rho)\frac{\partial^2 P}{\partial\rho^2}\;. \tag{2.20}$$

This is a diffusion-type equation, with the inverse of the volume playing the role of the time.[9,10]

We shall not press this somewhat loose derivation further. Again, it is not really correct, since it ignores energy fluctuations as well as a number of subtleties regarding path integrals, whose resolution requires Riemannian geometry. But this argument does serve to advance a diffusion-type equation in connection with thermodynamic fluctuations.

E. Covariant and consistent theory with one variable

Guided by the above discussion, we shall postulate a partial differential equation that contains a set of desired principles. We shall return to the general variable x and let the initial condition be $t=0$, corresponding to the infinite system A_{V_0}.

First, note that a diffusion-type equation, Eq. (2.20), with delta-function "initial condition,"

$$P_{t=0}(x\,|\,x_0)=\delta(x-x_0)\;, \tag{2.21}$$

is mathematically analogous to that governing the diffusion of a small drop of ink in a capillary filled with water (Arfken, 1970). The one-dimensional space of all thermodynamic states parametrized by x corresponds to the water, and the concentration of ink to the probability distribution of thermodynamic states. As the volume decreases, the thermodynamic probability distribution broadens just as the ink spreads with increasing real time.

As the basis for a physical principle, Eq. (2.20) has a serious shortcoming. It does not preserve the normalization of the probability, unless $g(\rho)$ is a constant function, as the argument below shows. However, this is easily resolved by writing the equation in the more general form

$$\frac{\partial P}{\partial t}=-\frac{\partial}{\partial x}[K(x)P]+\frac{1}{2}\frac{\partial^2}{\partial x^2}[g^{-1}(x)P]\;, \tag{2.22}$$

where $K(x)$ is a function of x to be determined, and $g(x)$ turns out to be the coefficient in the Gaussian distribution equation (2.9).[11] For small Δt, this has a Gaussian solution precisely of the form of Eq. (2.16).

Let us examine some general consequences of this equation. We denote by x_a and x_b the limits of the thermodynamic phase space, the smallest and the largest values of x, respectively. By successive multiplications by x, and integration by parts,

$$\frac{d}{dt}\int_{x_a}^{x_b}P\,dx=-(KP)\Big|_{x_a}^{x_b}+\tfrac{1}{2}\frac{\partial}{\partial x}(g^{-1}P)\Big|_{x_a}^{x_b}\;, \tag{2.23}$$

$$\frac{d}{dt}\langle x\rangle=\langle K\rangle-(xKP)\big|_{x_a}^{x_b}+\tfrac{1}{2}x\frac{\partial}{\partial x}(g^{-1}P)\Big|_{x_a}^{x_b}-\frac{1}{2}(g^{-1}P)\Big|_{x_a}^{x_b}\;, \tag{2.24}$$

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[8] Kadanoff (1976) gave a qualitative discussion along these lines, though it was limited to volumes less than the correlation volume and with no assumption of Markovicity.

[9] The spirit of this derivation, which reduces a problem to a small "time" step and ends up with a diffusion equation, dates back at least to Einstein's work on Brownian movement (Einstein, 1905b). Of course, the physical problem there was quite different from that here.

[10] One might think that the use of the inverse volume in the role of a "time" in a diffusion-type equation is somewhat far-fetched. But unusual variables in this role occur also in the Schrödinger equation of quantum mechanics, where one uses the square root of -1 times the real time, and in the density-matrix formulation of statistical mechanics (Feynman, 1972), where one uses the inverse of the temperature.

[11] We could write the equation as well in the form

$$\frac{\partial P}{\partial t}=c_0(x)P+c_1(x)\frac{\partial P}{\partial x}+\frac{1}{2}c_2(x)\frac{\partial^2 P}{\partial x^2}\;,$$

with the functions $c_0(x)$, $c_1(x)$, and $c_2(x)$ simply related to $K(x)$ and $g(x)$. However, as we shall see, the form of the equation in (2.22) has several advantages, including automatic inclusion of normalization for arbitrary functions $K(x)$ and $g(x)$.

and

$$\frac{d}{dt}\langle x^2\rangle = \langle g^{-1}\rangle + 2\langle xK\rangle + \text{boundary terms} . \tag{2.25}$$

Returning momentarily to u coordinates, we evaluate $K(u)$. By Eq. (2.8),

$$\frac{d}{dt}\langle u\rangle = 0 , \tag{2.26}$$

and Eq. (2.24) in u coordinates certainly indicates that we must set

$$K(u)=0 \tag{2.27}$$

for all u, since for small t the boundary terms are negligible, and the average of $K(u)$ is just $K(u_0)$.

Before turning to the state space boundary terms in Eq. (2.24), it helps to consider first the requirement of normalization of the probability density at all volumes. We need

$$\frac{d}{dt}\int_{x_a}^{x_b} P dx = 0 , \tag{2.28}$$

which, with $K(u)=0$ and Eq. (2.23), requires us to set

$$\frac{\partial}{\partial u}(g^{-1}P) \tag{2.29}$$

to zero at the boundary.

Consider now the effect of the boundaries on $\langle u\rangle$. We cannot explicitly demand that the function $g^{-1}P$ and its first derivative *both* be zero at the boundaries, since that would overdetermine the boundary conditions. If, however, g^{-1} happens to vanish at the edges, then all the boundary terms in Eq. (2.24) will vanish, and $\langle u\rangle$ will remain fixed even if fluctuations are large enough to reach the state space boundaries. A zero g^{-1} corresponds to vanishing second fluctuation moments, not unusual at the boundaries; see, for example, Sec. V.A.

We return now to the discussion in general coordinates. If the distribution is tightly concentrated about some point, then Eqs. (2.24) and (2.25) lead to

$$\langle (x-x_0)^2\rangle = \frac{1}{V} g^{-1}(x_0) . \tag{2.30}$$

This is exactly the same as that of the Gaussian fluctuation theory, as the reader may readily verify, establishing the identity of $g(x)$ with the coefficient in the Gaussian approximation.

All that remains is to determine how $K(x)$ and $g(x)$ transform under a change of variables $x \to x'(x)$. Covariance demands that the form of the equation be the same in any coordinate system; so we expect

$$\frac{\partial P'}{\partial t} = -\frac{\partial}{\partial x'}[K'(x')P'] + \frac{1}{2}\frac{\partial^2}{\partial x'^2}[g'^{-1}(x')P'] . \tag{2.31}$$

From Eq. (2.5),

$$P' = \frac{dx}{dx'} P . \tag{2.32}$$

On substituting Eq. (2.32) into Eq. (2.31), writing the partial derivative with respect to x' in terms of x, dividing by dx/dx', and equating coefficients of the derivatives of P with those in Eq. (2.22), we can show that g and K must transform as

$$g' = \left[\frac{dx}{dx'}\right]^2 g \tag{2.33}$$

and

$$K' = K\frac{dx'}{dx} + \frac{1}{2} g^{-1}\frac{d^2x'}{dx^2} . \tag{2.34}$$

The former expression matches Eq. (2.10) As we shall see, this is the metric transformation rule in Riemannian geometry. Hence this geometry emerges naturally from the requirement of covariance of the fluctuation equation.

We have assumed that neither $K(x)$ nor $g(x)$ depends on volume, an element of the hypothesis of translational invariance.

The modified thermodynamic fluctuation theory yields better probability distributions than the classical one in a number of simple cases which may be worked out exactly; the reader may turn immediately to the example in Sec. V.A for a simple case involving one parameter. If this were all there were to it, however, the results would amount to merely a quantitative improvement over the classical theory. But the Riemannian thermodynamic curvature offers more: a new tool for looking at the subject of fluctuations. The addition of another independent fluctuating thermodynamic parameter brings this out.

F. Riemannian geometry and fluctuations with two independent variables

Here we discuss fluctuations with two independent variables. This situation occurs, for example, if the pure-fluid subsystem and its environment exchange particles as well as energy. Two independent fluctuating variables allow a Riemannian geometry with nonzero thermodynamic curvature.

As an introduction, we present some of the essential ingredients of Riemannian geometry in two dimensions, since it is not conventionally encountered in thermodynamics.[12] Riemannian geometry has a reputation for being somewhat difficult. Contributing to this perception is its use in general relativity, where four-dimensional

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[12] A semipopular account of Riemannian geometry is given by Le Corbeiller (1954).

"spacetimes" with non-positive-definite metrics occur.[13] But the situation in thermodynamics is considerably easier. There are simple examples with two-dimensional geometries and positive-definite metrics.

The first element of a two-dimensional Riemannian geometry is a two-dimensional surface or manifold, which is, roughly speaking, a set of points parametrized smoothly by two coordinates $x=(x^0,x^1)$. We refer the interested reader to a text on Riemannian geometry for a rigorous definition, including precise statements of smoothness and regularity (Laugwitz, 1965). In physics, points on a manifold represent physical quantities (here thermodynamic states) with a meaning beyond those of the coordinates.

The second element of a Riemannian geometry is a rule for distance, or line element, Δl between each pair of neighboring points with coordinate differences Δx^α. The line element is expressed as a quadratic form:

$$(\Delta l)^2=\sum_{\mu,\nu=0}^{1} g_{\mu\nu}(x)\Delta x^\mu \Delta x^\nu , \tag{2.35}$$

where the matrix of coefficients $g_{\alpha\beta}(x)$ is called the metric tensor. A manifold with a rule for distance in the form of Eq. (2.35) is called a Riemannian manifold. A key requirement is that for a given pair of points Δl must be independent of the coordinate system used to specify the points. Distance must also be a concept that transcends the coordinate system!

It is important to emphasize that there is absolutely no requirement that these two-dimensional Riemannian manifolds be surfaces that can be embedded in flat three-dimensional spaces, although the latter are certainly examples of Riemannian manifolds. All that is essential are points and distances on the manifold itself.

A familiar example of a Riemannian manifold is the Euclidean plane, which in Cartesian coordinates has line element

$$(\Delta l)^2=(\Delta x^0)^2+(\Delta x^1)^2 . \tag{2.36}$$

Points in the plane may also be represented by polar coordinates, with line element

$$(\Delta l)^2=(\Delta r)^2+r^2(\Delta\theta)^2 , \tag{2.37}$$

where r denotes the distance from the origin, and θ the angle with respect to the abscissa.

An example involving an entirely different Riemannian manifold is the two-dimensional sphere of radius a, which in spherical coordinates has line element

$$(\Delta l)^2=a^2(\Delta\theta)^2+a^2\sin^2\theta(\Delta\phi)^2 , \tag{2.38}$$

where θ is the angle with respect to the z axis and ϕ is the azimuthal angle.

With these examples, we raise a question of central concern in Riemannian geometry: how can we tell from the metric elements whether or not two given metrics correspond to the same manifold? As we shall see in Sec. IV.C.2, this question leads to the Riemannian curvature, the third essential element of a Riemannian geometry. Two coordinate systems describe the same manifold if their curvatures at corresponding points are the same.

Curvature is induced when the definition for distance is applied, and measures at any point on the manifold the local deviation from flat Euclidean geometry. Consider the simple example of a small circle of radius r drawn on the surface of the two-dimensional sphere (see Fig. 6). The radius r is measured along great circles, since sections of great circles correspond to paths of minimum distance on the sphere. In Riemannian geometry, distance is generally measured only within the manifold! Because the sphere is intrinsically curved, the circumference of the circle differs from that of a circle of the same radius on the flat plane. Indeed, it is a fairly elementary exercise for us to use the sphere to show that

$$C=2\pi r+\frac{\pi}{6}Rr^3+O(r^4) , \tag{2.39}$$

where $R=-2/a^2$ is called the Riemannian curvature scalar of the sphere.

A sphere has the property that the curvature on its surface is the same at all points, a property which certainly does not hold in general—witness, for example, the surface of an egg. But with the appropriate local value of R, Eq. (2.39) actually holds in the neighborhood of any point on a two-dimensional Riemannian manifold.

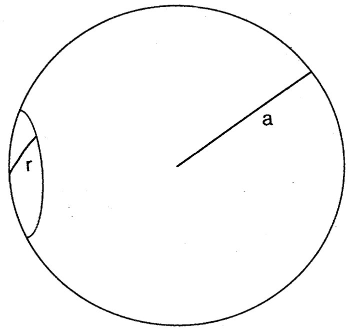

FIG. 6. Sphere with radius a on which is drawn a small circle with radius r. The circle's radius is measured along great circles of the sphere, and its circumference is less than that of a circle of the same radius on the plane, reflecting the intrinsic curvature of the sphere.

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[13] Here is a reminiscence of E. G. Strauss passed on to A. Pais (1982, p. 213): "Einstein told Grossmann that he needed a geometry which allowed for the most general transformations that leave [the line element] invariant. Grossman replied that Einstein was looking for Riemannian geometry. But, Grossmann added, that it is a terrible mess which physicists should not be involved with. Einstein then asked if there were any other geometries he could use. Grossmann said no, and pointed out to Einstein that the differential equations of Riemannian geometry are nonlinear, which he considered a bad feature. Einstein replied to this last remark that he thought, on the contrary, that this was a great advantage."

Going further, the Riemannian curvature provides the answer to all questions about the intrinsic deviation from Euclidean geometry. As another example, of both practical and theoretical interest to Gauss (1827), consider a triangle composed of three geodesic (curves of minimum length) segments. By how much does the sum of the interior angles deviate from π? The curvature gives the answer.

We shall take these issues up further in Sec. IV.C. Let us add that because the scalar curvature contains all information in two dimensions, any theory based on curvature must be based on R. But in higher dimensions, the situation is more complicated, and we might conceivably need several components of the fourth-rank Riemann tensor.

To represent a physical problem with a Riemannian manifold, it is necessary to have a set of physical objects that corresponds to the set of points of the manifold, and a rule for distance in the form of a scalar quadratic form. Distance should be physically motivated and to some degree unique. If this obtains, there is, in addition to other possible insights, the possibility that the induced intrinsic curvature might offer a new tool for the formulation of physical principles. That is certainly the case in general relativity, and the extent to which this is effective in thermodynamics is part of the discussion in this review.

Return now to thermodynamic fluctuation theory. Generalize the discussion by considering again an *open* pure-fluid subsystem A_V of the infinite closed system A_{V_0}. An exchange of particles is now allowed, and both the energy per volume a^0 and the number of particles per volume a^1 fluctuate. Again, issues of covariance and consistency exist, and ways of dealing with them are identical in style to those for one variable; details are deferred to Sec. IV.A. We concentrate here on the thermodynamic Riemannian curvature scalar.

Expanding the total entropy to second order about its maximum yields

$$P_V(a|a_0)da^0da^1=\left[\frac{V}{2\pi}\right]\exp\left[-\frac{V}{2}\sum_{\mu,\nu=0}^{1} g_{\mu\nu}(a_0)\Delta a^\mu \Delta a^\nu\right]\sqrt{g(a_0)}\,da^0da^1 \ , \tag{2.40}$$

where $\Delta a^\alpha = a^\alpha - a_0^\alpha$,

$$g_{\alpha\beta}(a_0) = -\frac{1}{k_B}\frac{\partial^2 s}{\partial a^\alpha \partial a^\beta} \ , \tag{2.41}$$

and

$$g(a_0)=\det[g_{\alpha\beta}(a_0)] \ . \tag{2.42}$$

This result follows from a standard calculation (Landau and Lifshitz, 1977), which is presented in detail in Sec. III.B.

For two given neighboring states, the value of the positive-definite quadratic form,

$$(\Delta l)^2 = \sum_{\mu,\nu=0}^{1} g_{\mu\nu}(a_0)\Delta a^\mu \Delta a^\nu \ , \tag{2.43}$$

is independent of the choice of coordinate system, since the entropy difference between two states is independent of the coordinate system used to represent those states. This is, of course, necessary, since the probability of a fluctuation depends only on the thermodynamic states. Equation (2.43) has the properties of a Riemannian metric between thermodynamic states, including, as we shall see, the transformation property. In the next section we discuss the physical significance of the induced thermodynamic curvature.

Let us add that the units of the square of the thermodynamic length are those of inverse volume. This differs from Riemann geometry in, say, general relativity, where the units are meters squared.

G. Thermodynamic Riemannian curvature

The thermodynamic Riemannian curvature was first evaluated for several cases by Ruppeiner (1979, 1981). It has units of volume. It is zero for the monoatomic ideal gas, where there are no interparticle interactions.[14] The curvature goes to infinity at the critical point in the same way as the correlation volume ξ^d. These properties suggest that it is a measure of effective interactions. The situation is shown schematically in Fig. 7.

The theory presented in Sec. IV indicates that curvature is a measure of the smallest volume where classical thermodynamic fluctuation theory based on the assumption of a uniform environment could conceivably work. Near the critical point, we expect this volume to be ξ^d, so we expect a proportionality between the curvature and the correlation volume:

$$R=\kappa_2\xi^d \ , \tag{2.44}$$

where κ_2 is a dimensionless constant of order unity.

The thermodynamic curvature connects with another aspect of thermodynamic fluctuation theory, one which is not usually stressed in the standard treatments. First, we

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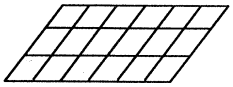
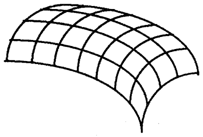
[14] Ingarden *et al.* (1979) independently found zero curvature for a similar ideal-gas metric, in the context of information theory. They did not, however, connect this result to any general statement of the relation between curvature and interactions.



(a) no interactions



(b) interactions

FIG. 7. The physical meaning of Riemannian thermodynamic curvature. If interactions between molecules are absent, as in the ideal gas, the space of thermodynamic states is flat, or nearly so. If interactions are present, the space curves in proportion. The curvature goes to infinity near the critical point and has units of volume. It appears to be related to the statistical mechanical correlation length.

introduce the thermodynamic potential or free energy per volume:

$$\phi = s - \left[\frac{1}{T}\right] u + \left[\frac{\mu}{T}\right] \rho \ , \tag{2.45}$$

where T is the temperature and μ is the chemical potential. It is a straightforward exercise, using the conservation of the energy and of the number of particles, to prove that the deviation of the entropy from its maximum value is

$$\Delta S_0 = V\left[\Delta s - \left[\frac{1}{T_0}\right]\Delta u + \left[\frac{\mu_0}{T_0}\right]\Delta\rho\right] \ , \tag{2.46}$$

where the 0 subscript refers to the parameters of the very large A_{V_0}.

Near the critical point, usual treatments (Landau and Lifshitz, 1977) show that fluctuations in the temperature and the chemical potential go to zero, while those of the entropy and the standard extensive quantities become very large. Hence the quantity in brackets in Eq. (2.46) is very nearly the differential of $\Delta\phi$ and

$$\Delta S_0 \approx V\Delta\phi \ . \tag{2.47}$$

But for typical fluctuations,

$$|\Delta S_0| \approx k_B \ , \tag{2.48}$$

and so

$$|\Delta\phi| \approx \frac{k_B}{V} \ . \tag{2.49}$$

Assume now that at the correlation volume ξ^d fluctuations in the thermodynamic potential per volume ϕ become of the same order as the quantity itself:

$$\Delta\phi \approx \phi \ . \tag{2.50}$$

Combining with Eq. (2.49) yields

$$\phi = -\frac{\kappa_1 k_B}{\xi^d} \ , \tag{2.51}$$

where κ_1 is a dimensionless constant with absolute value of order unity.

In the modern theory of critical phenomena, this is usually referred to as the "hyperscaling" assumption (Kadanoff, 1966; Widom, 1974). Here, ϕ denotes just the "singular part" of the free energy, that associated with the long-ranged correlations between parts of the system. This must go to zero at the critical point, since ξ diverges. Hence ϕ may be determined, at least to leading order, by subtracting from the free energy its value at the critical point.[15] We add that Einstein (1904) used, in his treatment of the Planck radiation law, an argument such as that which leads to Eq. (2.50).

When Eq. (2.44) is used to eliminate the correlation volume with Eq. (2.51), we obtain

$$R = -\kappa\frac{k_B}{\phi} \ , \tag{2.52}$$

where

$$\kappa = \kappa_1\kappa_2 \ . \tag{2.53}$$

In words, this geometric equation states that *the thermodynamic curvature is proportional to the inverse of the free energy.* This principle may be expressed as a partial differential equation for the free energy, the solution of which is discussed in Sec. VI.C. It leads to a form of the free energy near the critical point which has several features expected from the modern theory of critical phenomena.

There exists a rough analogy between the geometric equation and the field equations in general relativity. In the latter case, the simplest law connecting mass-energy to curvature is chosen. Here, it is interactions which produce the curvature, and Eq. (2.52) appears to be the simplest relation connecting them. It seems, at least, a good start.

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[15] This relation has a somewhat unsettled status in the modern theory of critical phenomena. Fisher (1983) gave a somewhat different argument to arrive at Eq. (2.51): "The argument we use may, perhaps, be regarded as not very plausible, but it does lead to the desired result, and other arguments are not much more convincing!" This statement would appear to apply equally well to the derivation presented here.

An interesting approach is by Goodstein (1975), who proposed a simple postulate for critical-point phenomena: "Nothing matters except ξ." This, together with dimensional analysis, led him to Eq. (2.51). All the relationships between the critical indices were shown to follow from this postulate. It is unclear, however, if Goodstein's postulate can be used to derive the scaled form of the free energy.

III. CLASSICAL THERMODYNAMIC FLUCTUATION THEORY

In this section we summarize the basics of the classical thermodynamic fluctuation theory, with particular emphasis on its Gaussian approximation. Since the covariant thermodynamic fluctuation theory must be equivalent to the classical theory for very large subsystem sizes, the classical theory naturally forms an essential part of the discussion. Also included is a brief discussion of the origin of the subject, and other related recent literature.

A. Origin

The origin of thermodynamic fluctuation theory is closely connected with that of statistical mechanics. It is usually attributed to Einstein, who used it as early as 1904 to assist in understanding blackbody radiation. With what is now called the canonical partition function, he calculated the second moment of the energy fluctuation $\langle (\Delta U)^2 \rangle$ with the Planck blackbody law and related it to the heat capacity. He derived the volume at which the energy fluctuations reach the same magnitude as the energy, and reasoned that it must correspond to a physically significant length scale. Einstein found this length scale to be of the same order as the wavelength λ_m at the peak of the blackbody curve. The calculation used the value of Boltzmann's constant from the kinetic theory of gases, and the success of the connection between what were thought to be waves on the one hand and particles on the other, prior to the general notion of wave-particle duality, appeared to have had considerable impact on Einstein's thinking. Einstein (1904) concluded his paper: "One can see that both the kind of dependence on the temperature and the order of magnitude of $[\lambda_m]$ can be correctly determined from the general molecular theory of heat, and considering the broad generality of our assumptions, we believe that this agreement must not be ascribed to chance."[16]

Einstein first expressed probabilities in the form of the exponential of the entropy equation (1.2) in 1907 in connection with a proposed experiment to determine Boltzmann's constant by measuring voltage fluctuations across a shorted capacitor. Einstein's thoughts on thermodynamic fluctuation theory reached fruition in 1910 with his analysis of light scattering near the critical point; and the theory developed here in Sec. III.B differs little from Einstein's in its essential points.[17] Thermodynamic fluctuations formed a part of Einstein's larger program of exploring atomic properties, and in this connection his work (Einstein, 1956) on Brownian motion must be mentioned.[18]

Smoluchowski (1908) applied thermodynamic fluctuation theory to fluids, including an analysis of the near critical point. This paper led Einstein (1910) to his more detailed work.

Gibbs (1902) actually wrote down the thermodynamic formula for the second moments of the energy fluctuations before Einstein, who was not aware of Gibbs's work when he published his early papers on statistical mechanics. Einstein (1911) said later that had he known of it, he would not have published his own work on statistical mechanics. With regard to thermodynamic fluctuation theory, however, the motivation of these two individuals was quite different, and giving Einstein credit for its founding, as most texts do, seems not unfair. Gibbs was interested primarily in establishing that fluctuations vanish in the thermodynamic limit. This, while anticipating the concerns of modern statistical mechanics, did little to advance the thermodynamic fluctuation theory in its own right. Klein (1967) and Pais (1982) have discussed these historical issues. Gearhart (1990) has also written a recent history of Einstein's early work on statistical mechanics. In addition, the ongoing publication of the Einstein papers (1987, 1989, 1993) is a valuable resource.

It was subsequently argued by Szilard (1925), Lewis (1931), Callen (1960), Tisza and Quay (1963), and Mandelbrot (1964) that thermodynamic fluctuation theory can stand alone and is in no essential need of statistical mechanics for its foundation. This is certainly the philosophy in this review. The place of thermodynamic fluctuation theory in the totality of physics has been discussed by Tisza (1963). In addition, Tisza (1966) has published a collection of his papers on thermodynamics, including fluctuation theory.

B. The Gaussian approximation to the classical thermodynamic fluctuation theory

This section is intended primarily to set the context and notation in this review. It is in no way intended to

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[16] Though this result may have been a guiding factor in Einstein's (1905a) Nobel Prize–winning work on the photoelectric effect, it was not essential to its development. The key in that paper was the analogy between the expressions for the entropy resulting from the Planck blackbody law and that of the ideal gas.

[17] The classical theory has been slow to change, as pointed out by Callen (1965): "When I was asked by Professor Prigogine to review and comment on my work on the theory of fluctuations I was flattered, for my first thought was that this is truly a field for gentlemen. Few fields have been so leisurely in their pace, so untouched by the frantic rush of publication, or so graced by the illustriousness of their founders. Almost all we know today was foreshadowed in the work of Einstein half a century ago."

[18] A semipopular account of both Brownian motion and thermodynamic fluctuations has been given by Lavenda (1985).

be as complete and logically rigorous in establishing the foundations of the classical thermodynamic fluctuation theory as, for example, Tisza and Quay (1963). It is also specific to systems with the volume as the fixed scale and with all other variables fluctuating. For a compact exposition of the general formalism, see Greene and Callen (1951), whose derivation is summarized in Sec. III.C.

At the outset, we distinguish between two spaces. The first is the real physical space, with dimension d. The second is the thermodynamic state space, with dimension n, each point of which represents a thermodynamic state.

The thermodynamics in this section is done on open fluid subsystems, with fluctuating energy and particle numbers. Open subsystems seem essential in this approach, since, in probing the intrinsic properties of fluids, artificial internal boundaries, occurring, for example, if the mole numbers are held fixed, should be avoided. The extensive volume V is held separate as a nonfluctuating parameter. This formalism is easily adapted to magnetic systems (see Sec. III.G).

We distinguish between two types of parameters for specifying the thermodynamic state of a subsystem. The first type consists of *mechanical parameters,* such as the energy, particle number, or magnetization, which at any instant of time can be computed directly by elementary sums over microscopic quantities. The second are purely *thermodynamic parameters,* such as the temperature, chemical potential, and entropy. These are related to distributions over microscopic quantities and, in contrast to the mechanical parameters, are not directly related to microscopic quantities. The former are the most convenient for specifying the thermodynamic state of subsystems.

We turn now to fluctuations and consider an open subsystem A_V, with fixed volume V, of a thermodynamic fluid system A_{V_0} with a very large (approaching infinity) volume V_0, as in Fig. 1. The system A_{V_0} consists of r fluid components (assumed to be chemically noninteracting) and is in equilibrium. Denote by the n-tuple $a_0=(a_0^0, a_0^1, a_0^2, \ldots, a_0^r)$ the internal energy per volume and the number of particles per volume of the r components of A_{V_0}. These mechanical parameters are the *standard densities* in the entropy representation (Callen, 1985); they constitute the thermodynamic state of A_{V_0}. The subsystem A_V has the corresponding thermodynamic state a.

The classical thermodynamic fluctuation theory (Landau and Lifshitz, 1977) can be stated in the form of three basic axioms.

Axiom 1. A_V and its reservoir $A_{V_c}=A_{V_0}\setminus A_V$, with volume $V_c=V_0-V$, are each homogeneous systems described by the thermodynamics in the thermodynamic limit.

Axiom 2. The conditional probability of finding A_V in a state with parameters between a and $a+da$, provided A_{V_0} is in the state a_0, is

$$P_V(a|a_0)da^0da^1\cdots da^r = C\exp\left[\frac{S_0(a,a_0)}{k_B}\right]da^0da^1\cdots da^r\,, \quad (3.1)$$

where $S_0(a,a_0)$ is the entropy of the system A_{V_0} when its subsystem A_V is in the state a, and C is a normalization factor.[19]

Axiom 3. Entropy is additive, but not conserved. The standard extensive parameters (internal energy and particle numbers) are both additive and conserved.

The next step is generally to expand the entropy to second order about the homogeneous state, where $a=a_0$. By Axioms 1 and 3,

$$S_0(a,a_0)=Vs(a)+V_cs(a_c)\,, \quad (3.2)$$

where $s(a)$ is the entropy per volume and a_c denotes the standard densities of A_{V_c}. By Axiom 3,

$$a_c^\alpha=\frac{(V_0a_0^\alpha-Va^\alpha)}{V_c}\,. \quad (3.3)$$

Expanding the entropy densities in Eq. (3.2) about $a_c^\alpha=a_0^\alpha=a^\alpha$ yields

$$\begin{aligned}S_0(a,a_0)=&\,Vs(a_0)+V_cs(a_0)+V\frac{\partial s}{\partial a^\mu}(a^\mu-a_0^\mu)\\&+V_c\frac{\partial s}{\partial a^\mu}(a_c^\mu-a_0^\mu)\\&+\frac{1}{2}V\frac{\partial^2 s}{\partial a^\mu\partial a^\nu}(a^\mu-a_0^\mu)(a^\nu-a_0^\nu)\\&+\frac{1}{2}V_c\frac{\partial^2 s}{\partial a^\mu\partial a^\nu}(a_c^\mu-a_0^\mu)(a_c^\nu-a_0^\nu)+\cdots\,,\end{aligned} \quad (3.4)$$

where the derivatives are all evaluated at a_0. Here and henceforth, we use the Einstein summation convention, which asserts that repeated indices in products are assumed to be summed over their full range $(0,\ldots,r)$. We use as well the convention that the list of unsummed indices in any expression starts with α, and summed, or dummy, indices start with μ.

Substituting Eq. (3.3) into Eq. (3.4) and letting $V_c\to\infty$ yields

$$S_0(a,a_0)=V_0s(a_0)+\frac{1}{2}V\frac{\partial^2 s}{\partial a^\mu\partial a^\nu}\Delta a^\mu\Delta a^\nu+\cdots\,, \quad (3.5)$$

where

$$\Delta a^\alpha\equiv a^\alpha-a_0^\alpha\,. \quad (3.6)$$

The cancellation of the first-order terms reveals that the

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[19] $S_0(a,a_0)$ also depends on the two volumes, but this is not explicitly denoted with the notation.

state $a = a_0$ corresponds to an extremum of the total entropy. The usual thermodynamic stability relations (Landau and Lifshitz, 1977) establish that it corresponds to a maximum of the entropy. Alternately, the stability relations may be forced by demanding that the entropy be a maximum if $a = a_0$.

The form of Eq. (3.5) holds only in the standard densities (or linear transformations of these densities), because additivity is specific to these coordinates. To express S_0 in a general set of thermodynamic coordinates $x = x(a)$ requires special care.[20] Expanding the entropy to second order about the maximum at $x = x_0 \equiv x(a_0)$ yields[21]

$$S_0(x,x_0) = S_0(x_0,x_0) + \frac{1}{2}\frac{\partial^2 S_0}{\partial x^\mu \partial x^\nu}\Delta x^\mu \Delta x^\nu , \tag{3.7}$$

where $\Delta x^\alpha = x^\alpha - x_0^\alpha$.

The second derivatives here are not typical thermodynamic derivatives, in contrast to those in Eq. (3.5), since $S_0(x,x_0)$ depends on two distinct thermodynamic systems with different states. As a first step in expressing these derivatives in terms of thermodynamic quantities, we transform them to some other coordinate system $x' = x'(x)$. Through the chain rule

$$\frac{\partial}{\partial x^\alpha} = \frac{\partial x'^\mu}{\partial x^\alpha}\frac{\partial}{\partial x'^\mu} , \tag{3.8}$$

it is easy to show that

$$\frac{\partial^2 S_0}{\partial x^\alpha \partial x^\beta} = \frac{\partial^2 x'^\mu}{\partial x^\alpha \partial x^\beta}\frac{\partial S_0}{\partial x'^\mu} + \frac{\partial x'^\mu}{\partial x^\alpha}\frac{\partial x'^\nu}{\partial x^\beta}\frac{\partial^2 S_0}{\partial x'^\mu \partial x'^\nu} . \tag{3.9}$$

At the maximum of S_0, this becomes

$$\frac{\partial^2 S_0}{\partial x^\alpha \partial x^\beta} = \frac{\partial x'^\mu}{\partial x^\alpha}\frac{\partial x'^\nu}{\partial x^\beta}\frac{\partial^2 S_0}{\partial x'^\mu \partial x'^\nu} , \tag{3.10}$$

the transformation rule for the components of a second-rank tensor.[22]

It is now possible to express the general second derivatives in terms of purely thermodynamic functions. Comparing Eqs. (3.5) and (3.10) yields

$$\frac{\partial^2 S_0}{\partial x^\alpha \partial x^\beta} = V\frac{\partial a^\mu}{\partial x^\alpha}\frac{\partial a^\nu}{\partial x^\beta}\frac{\partial^2 s}{\partial a^\mu \partial a^\nu} . \tag{3.11}$$

Although in actual calculations this expression does not see much use, it does establish that the second derivatives of S_0 may be expressed in terms of familiar thermodynamic variables no matter what the coordinates. It also shows that these derivatives vary linearly with the volume.

Using the quadratic expansion, we may write the Gaussian approximation to the thermodynamic fluctuation theory:

$$\begin{aligned} P_V(x|x_0)dx^0 dx^1 \cdots dx^r &= \left[\frac{V}{2\pi}\right]^{n/2} \exp\left[-\frac{V}{2} g_{\mu\nu}(x_0)\Delta x^\mu \Delta x^\nu\right] \\ &\quad \times \sqrt{g(x_0)}dx^0 dx^1 \cdots dx^r , \end{aligned} \tag{3.12}$$

where

$$g_{\alpha\beta}(x_0) \equiv -\frac{1}{Vk_B}\frac{\partial^2 S_0}{\partial x^\alpha \partial x^\beta}\bigg|_{x=x_0} \tag{3.13}$$

and

$$g(x_0) \equiv \det[g_{\alpha\beta}(x_0)] . \tag{3.14}$$

The normalization factor was worked out with a straightforward evaluation of Gaussian integrals (Landau and Lifshitz, 1977).[23]

We may readily compute the average values

$$\langle \Delta x^\alpha \rangle = 0 \tag{3.15}$$

and

$$\langle \Delta x^\alpha \Delta x^\beta \rangle = \frac{g^{\alpha\beta}(x_0)}{V} , \tag{3.16}$$

where $g^{\alpha\beta}$ denotes the elements of the inverse of the matrix $g_{\alpha\beta}$.

It is easy to verify that the quadratic form in the argument of the exponential in Eq. (3.12) transforms as a scalar under a coordinate transformation. To first order,

$$\Delta x^\alpha = \frac{\partial x^\alpha}{\partial x'^\mu}\Delta x'^\mu , \tag{3.17}$$

which is the transformation rule for a first-rank contravariant tensor. Substituting into the quadratic form and using transformation rule (3.10), with primes and unprimes switched, reveals the invariance. This is necessary, since neither the probability of a fluctuation be-

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[20] We shall assume, without explicitly saying so on each occasion, that coordinate transformations are continuous and differentiable and have nonzero Jacobians, except possibly at special points, such as critical points.

[21] Alternately, we could use Eq. (3.2), which holds as well with $a \rightarrow x$, to expand the entropy densities of A_V and its environment separately; however, this requires the expansion of $(x_c^\mu - x_0^\mu)$ in powers of $(x^\mu - x_0^\mu)$, which is difficult to interpret, since additivity equation (3.3) does not hold in general coordinates.

[22] A tensor is any indexed quantity that transforms as

$$W^{ij\cdots}_{\alpha\beta\cdots} = \frac{\partial x'^\mu}{\partial x^\alpha}\frac{\partial x'^\nu}{\partial x^\beta}\cdots\frac{\partial x^i}{\partial x'^m}\frac{\partial x^j}{\partial x'^n}\cdots W'^{mn\cdots}_{\mu\nu\cdots}$$

under a coordinate transformation $x' \rightarrow x(x')$ (Weinberg, 1972). Upper indices are called contravariant indices, and lower ones are called covariant indices. The rank of a tensor is the total number of its indices. Since both x and x' denote sets of arbitrary coordinates, one may exchange primes with unprimes and still have a valid expression.

[23] The method requires the diagonalization of $g_{\alpha\beta}(x_0)$ to bring the quadratic form to a sum of uncoupled quadratic terms, and then the evaluation of simple Gaussian integrals.

tween two states nor the entropy difference should depend on the system of coordinates used to represent those states.

The quadratic form

$$(\Delta l)^2 \equiv g_{\mu\nu}(x_0)\Delta x^\mu \Delta x^\nu \tag{3.18}$$

constitutes a positive-definite Riemannian metric on thermodynamic state space (Ingarden *et al.*, 1979; Ruppeiner, 1979, 1981). It is independent of V by Eqs. (3.11) and (3.13). Physically, the interpretation for distance between two thermodynamic states is clear: *the less the probability of a fluctuation between two states, the further apart they are.* Note as well that

$$\sqrt{g(x_0)}dx^0 dx^1 \cdots dx^r \tag{3.19}$$

is the invariant volume element on a Riemannian manifold (Weinberg, 1972, p. 99).

The requirement that the line element be positive for any set of values of the coordinate differentials, except where they are all zero, sets conditions on the metric elements $g_{\alpha\beta}$. First, clearly all of the diagonal metric elements must be positive. These elements are, for example, heat capacities or compressibilities. The requirement that they be positive is a manifestation of thermodynamic stability, or Le Chatelier's principle.

Positive diagonal metric elements are not enough to ensure a positive-definite line element, however. A necessary and sufficient condition (Eves, 1966) is that the leading principle minors of the metric elements, defined by

$$p_0 \equiv 1 , \tag{3.20}$$

$$p_1 \equiv g_{00} , \tag{3.21}$$

$$p_2 \equiv \begin{vmatrix} g_{00} & g_{01} \\ g_{10} & g_{11} \end{vmatrix} , \tag{3.22}$$

$$p_3 \equiv \begin{vmatrix} g_{00} & g_{01} & g_{02} \\ g_{10} & g_{11} & g_{12} \\ g_{20} & g_{21} & g_{22} \end{vmatrix} , \tag{3.23}$$

and so on, and finally

$$p_n \equiv |g| , \tag{3.24}$$

all be positive.

Tisza (1951, 1961, 1966) has discussed at length the implications of the positivity of forms constructed from second derivatives of thermodynamic potentials, with particular attention focused on what happens in the neighborhood of phase transitions.

Before returning to the physics, let us explore the form of the thermodynamic metric in several coordinate systems. For assistance, we derive two helpful intermediate relations. First, we denote by $F=(1/T, -\mu^1/T, -\mu^2/T, \ldots, -\mu^r/T)$ the standard intensive quantities in the entropy representation (Callen, 1985)[24]:

$$F^\alpha = \frac{\partial s(a)}{\partial a^\alpha} . \tag{3.25}$$

Here, T is the temperature and μ^i the chemical potential of the ith fluid component. The F^α's are a complete set of n coordinates on the thermodynamic phase space. The pressure p, conjugate to the fixed volume V and expressible in terms of the other coordinates, is not included.[25]

With the aid of Eq. (3.5), we have

$$(\Delta l)^2 = -\frac{1}{k_B}\Delta F^\mu \Delta a^\mu , \tag{3.26}$$

which is a convenient starting point for expressing the metric in several coordinate systems.[26] Another convenient intermediate expression results from the variables of the energy representation, where s replaces u as the zeroth coordinate and the conjugate intensive variables are $P=(T,\mu^1,\mu^2,\ldots,\mu^r)$. Substituting

$$\Delta a^0 = \Delta u = T\Delta s + \sum_{i=1}^{r} \mu^i \Delta a^i , \tag{3.27}$$

$$\Delta F^0 = -\frac{1}{T^2}\Delta T , \tag{3.28}$$

and

$$\Delta F^i = \frac{\mu^i}{T^2}\Delta T - \frac{1}{T}\Delta \mu^i , \tag{3.29}$$

with $1 \le i \le r$, into Eq. (3.26) leads to

$$(\Delta l)^2 = \frac{1}{k_B T}\Delta T \Delta s + \frac{1}{k_B T}\sum_{i=1}^{r} \Delta\mu^i \Delta a^i . \tag{3.30}$$

To express the metric in F coordinates, we write

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[24] The coordinates F^α look like the components of the gradient of the entropy, geometric objects that have covariant (lower) indices. This is deceiving, however. Definition (3.25) has no implication for the transformation properties. The differentials dF^α transform as contravariant vectors, with upper indices, like the differentials of all coordinates. In symplectic-type thermodynamic geometries, where one desires to preserve conjugate relations between "extensive" and "intensive" variables, one would use quite a different transformation rule.

[25] This certainly does not mean that p is fixed, however. Its fluctuations are related to those of the other thermodynamic parameters through equations of state.

[26] The sum over the two contravariant indices looks awkward. Indeed, this is not a natural metric expression on the n-dimensional thermodynamic state space, since twice as many coordinate differentials appear as there are independent coordinates. This expression is used here only as a computational aid. Mrugała *et al.* (1990) have used such expressions as metrics in $2n$-dimensional contact spaces. Such geometries can be used to embed the Riemannian geometries of thermodynamics in higher-dimensional flat spaces.

$$\Delta a^{\alpha}=\frac{\partial a^{\alpha}}{\partial F^{\mu}}\Delta F^{\mu} \tag{3.31}$$

and substitute into Eq. (3.26). This yields

$$(\Delta l)^2=\frac{1}{k_B}\frac{\partial^2\phi}{\partial F^{\mu}\partial F^{\nu}}\Delta F^{\mu}\Delta F^{\nu}\ , \tag{3.32}$$

where

$$\phi(F^0,F^1,\ldots,F^r)=s-F^{\mu}a^{\mu}\ . \tag{3.33}$$

It is a relatively simple exercise to show that

$$\phi=p/T\ . \tag{3.34}$$

This thermodynamic potential is k_B/V times the logarithm of the grand canonical partition function. Diósi *et al.* (1984) and Janyszek and Mrugała (1989b) used F^{μ} as their coordinate system.

To express the metric in $(T,a^1,a^2,\ldots,a^r)$ coordinates, we write

$$\Delta s=\left(\frac{\partial s}{\partial T}\right)\Delta T+\sum_{i=1}^{r}\left(\frac{\partial s}{\partial a^i}\right)\Delta a^i\ , \tag{3.35}$$

and

$$\Delta\mu^i=\left(\frac{\partial\mu^i}{\partial T}\right)\Delta T+\sum_{j=1}^{r}\left(\frac{\partial\mu^i}{\partial a^j}\right)\Delta a^j\ . \tag{3.36}$$

Using the Maxwell relation

$$\left(\frac{\partial s}{\partial\rho^i}\right)=-\left(\frac{\partial\mu^i}{\partial T}\right) \tag{3.37}$$

and substituting into Eq. (3.30), we obtain

$$(\Delta l)^2=\frac{1}{k_BT}\left(\frac{\partial s}{\partial T}\right)(\Delta T)^2+\frac{1}{k_BT}\sum_{i,j=1}^{r}\left(\frac{\partial\mu^i}{\partial a^j}\right)\Delta a^i\Delta a^j\ . \tag{3.38}$$

This line element is diagonal for the pure fluid $r=1$, as well as for the multicomponent ideal gas. Ruppeiner and Davis (1990) used these coordinates.

To express the metric in P coordinates, we write

$$\Delta s=\left(\frac{\partial s}{\partial T}\right)\Delta T+\sum_{i=1}^{r}\left(\frac{\partial s}{\partial\mu^i}\right)\Delta\mu^i \tag{3.39}$$

and

$$\Delta a^i=\left(\frac{\partial a^i}{\partial T}\right)\Delta T+\sum_{j=1}^{r}\left(\frac{\partial a^i}{\partial\mu^j}\right)\Delta\mu^j\ . \tag{3.40}$$

Substituting into Eq. (3.30) yields

$$(\Delta l)^2=-\frac{1}{k_BT}\frac{\partial^2\omega}{\partial P^{\mu}\partial P^{\nu}}\Delta P^{\mu}\Delta P^{\nu}\ , \tag{3.41}$$

where

$$\omega(T,\mu^1,\mu^2,\ldots,\mu^r)=u-Ts-\sum_{i=1}^{r}\mu^i\rho^i\ . \tag{3.42}$$

It is easy to show that

$$\omega=-p=-\phi T\ . \tag{3.43}$$

A more difficult case, not considered in detail here, was encountered in the Takahashi gas (Ruppeiner and Chance, 1990). This system has $r=1$ and allows for the explicit evaluation of the Gibbs free energy $\Phi=\Phi(T,p,N)$, but not for the other potentials in terms of their natural parameters. The problem with the Gibbs free energy in this application is that the fluctuating particle number N, rather than the fixed volume V, is one of the natural parameters. The condition of fixed V leads to an implicit relation between T, p, and N, which must be taken into account.

See Table II for a summary of the metrics in various coordinate systems.

C. The general classical thermodynamic fluctuation theory

The full formalism for classical thermodynamic fluctuation theory was worked out by Greene and Callen (1951) and elaborated upon by Callen (1965). They worked out the case where the fixed subsystem scale is not necessarily the volume, and where independent variables in addition to the subsystem scale might be fixed, for example, by a semipermeable partition. In addition, they established that (1) fluctuation moments to all orders computed with the full classical thermodynamic fluctuation theory are the same as those computed with the appropriate statistical mechanical ensemble; and that

TABLE II. Thermodynamic potentials, or free energies, and the Riemannian line elements in four coordinate systems.

Coordinates	Potential	Line element $(\Delta l)^2$
$a=(u,\rho^1,\rho^2,\ldots,\rho^r)$	s	$-\frac{1}{k_B}\frac{\partial^2 s}{\partial a^{\mu}\partial a^{\nu}}\Delta a^{\mu}\Delta a^{\nu}$
$F=(1/T,-\mu^1/T,\ldots-\mu^r/T)$	$\phi(F)=s-F^{\mu}a^{\mu}$	$\frac{1}{k_B}\frac{\partial^2\phi}{\partial F^{\mu}\partial F^{\nu}}\Delta F^{\mu}\Delta F^{\nu}$
$P=(T,\mu^1,\mu^2,\mu^r)$	$\omega(P)=u-Ts-\sum_{i=1}^{r}\mu^i a^i$	$-\frac{1}{k_BT}\frac{\partial^2\omega}{\partial P^{\mu}\partial P^{\nu}}\Delta P^{\mu}\Delta P^{\nu}$
$(T,\rho^1,\rho^2,\ldots\rho^r)$	$f=u-Ts$	$\frac{1}{k_BT}\left(\frac{\partial s}{\partial T}\right)(\Delta T)^2+\frac{1}{k_BT}\sum_{i,j=1}^{r}\frac{\partial\mu^i}{\partial a^j}\Delta a^i\Delta a^j$

(2) second fluctuation moments computed with the Gaussian fluctuation approximation to thermodynamic fluctuation theory agree with those above, but higher-order moments do not.

Since Greene and Callen (1951) allowed for the possibility of volume fluctuations, let us add V to the list of standard extensive parameters X, defined in Table I.[27] This addition results in an *extended* list of variables, denoted by $X_e=(U,N^1,\ldots,V,\ldots,N^r)$. The internal energy U of the subsystem is first on the list, but the remaining parameters occur in no particular order, except that the variables that are fixed are placed at the end of the list. In thermodynamics one extensive variable must always be fixed as the subsystem scale (Callen, 1985), so there will be at most $n=r+1$ independent variables.

Dividing X_e by the fixed subsystem scale X_e^n results in an extended list of n densities $a_e=(U/X_e^n, N^1/X_e^n,\ldots,V/X_e^n,\ldots,1)$. Define as well the corresponding extended list of conjugate intensive quantities:

$$F_e^\alpha=\frac{\partial S}{\partial X_e^\alpha}\ , \tag{3.44}$$

which results in $F_e=(1/T,\ -\mu^1/T,\ldots,p/T,\ldots,-\mu^r/T)$. The Gibbs-Duhem relation (Callen, 1985) allows us to express any one of these variables in terms of the others. The dependent variable, or, indeed, any other intensive thermodynamic function, may also be expressed in terms of the n densities a_e, or some mixture of n variables selected from the sets F_e and a_e. In keeping with the general philosophy of thermodynamics, Greene and Callen (1951) implicitly assumed that relations among intensive variables are worked out in the thermodynamic limit and do not depend on the volume. Tisza and Quay (1963) criticized such an assumption.

Before presenting the details of the generalized classical thermodynamic fluctuation theory, let us prove an important theorem. Consider momentarily, again, a completely open subsystem A_V, where the volume V is the fixed scale, and where all of the other independent variables are allowed to fluctuate. We show that the average standard densities must equal the environment densities at all volumes V.

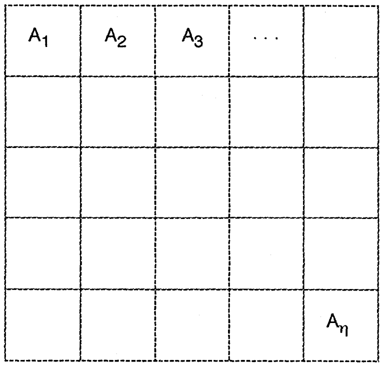

FIG. 8. System A_{V_0} broken into η identical subsystems. The boundary conditions for A_{V_0} are periodic, so each subsystem has the same average properties.

For the argument, let the very large A_{V_0} have periodic boundary conditions; the nature of the boundary conditions should be irrelevant in the limit as $V_0\rightarrow\infty$, so long as the system A_{V_0} is in a single phase not at the critical point. Imagine A_{V_0} to be composed of a set of η identical open systems $A_1,A_2,\ldots,A_\eta$, each with volume V_0/η (see Fig. 8). Let X_0 denote some extensive parameter of A_{V_0} and let X_i be the corresponding extensive parameter of A_i at some time. Define $a_0=X_0/V_0$ and $a_i=\eta X_i/V_0$. It follows from additivity that, at any time,

$$a_0=\frac{1}{\eta}\sum_{i=1}^{\eta}a_i\ . \tag{3.45}$$

But, because the boundary of A_{V_0} is periodic, $\langle a_i\rangle$ is independent of i. When the ensemble average in Eq. (3.45) is taken, it follows that

$$\langle a_i\rangle=\langle a\rangle=a_0\ , \tag{3.46}$$

proving the theorem.

It is essential in such an argument that A_{V_0} be an infinite system, to which periodic boundary conditions can be applied without affecting the subsystems; but the subsystems may be of any size. This argument is restricted, however, to standard densities. For thermodynamic variables such as the temperature, which are not additive, it does not work and the result does not hold beyond the Gaussian approximation.

When the subsystem is not open but has a boundary barring passage of some of the chemical species, this argument will also be inadequate. In this case the environment is generally not equivalent to one evenly partitioned into subsystems with boundaries. However, Greene and Callen (1951) implicitly assumed the result anyway:

$$\langle a_e^\alpha\rangle=\frac{\langle X_e^\alpha\rangle}{X_e^n}=a_{e0}^\alpha\ , \tag{3.47}$$

and we shall proceed under this assumption.

Consider the situation in which the variables $X_e^0, X_e^1,\ldots,X_e^j$ $(1\leq j<n)$ all fluctuate, but the variables $X_e^{j+1},\ldots,X_e^n$ are fixed. The grand canonical probability of finding the subsystem in its ith discrete microstate is[28]

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[27] The notation here differs from that of Greene and Callen (1951). They used lower-case x's for the instantaneous values of the standard extensive quantities, which are denoted by capital X's here. Green and Callen reserved capital letters for average values, denoted simply by $\langle X\rangle$ in this review.

[28] See Landau and Lifshitz (1977), p. 102, Eq. (35.2) for the case with $r=1$; the extension to more thermodynamic variables is immediate.

$$w_i = \exp\left[-\frac{1}{k_B}\left[S[F^0_{e0},\ldots,F^j_{e0}] + \sum_{\mu=0}^{j} F^\mu_{e0} X^\mu_e \right]\right] , \tag{3.48}$$

where

$$S[F^0_{e0},\ldots,F^j_{e0}] \equiv S - \sum_{\mu=0}^{j} F^\mu_{e0} \langle X^\mu_e \rangle . \tag{3.49}$$

The thermodynamic parameters F^α_{e0} are characteristic of the infinite reservoir, and the parameters X^α_e are characteristic of the subsystem in its ith microstate. The average of a general function over the microstates f_i is defined by

$$\langle f \rangle = \sum_i f_i w_i , \tag{3.50}$$

where the sum is over all of the microstates. The entropy S is the entropy of the subsystem in the state corresponding to that of the intensive variables of the environment:

$$S = X^n_e s(a^0_{e0}, a^1_{e0}, \ldots, a^{n-1}_{e0}) . \tag{3.51}$$

Using Eqs. (3.44), (3.47), and (3.51), we may verify that

$$\frac{\partial}{\partial F^\alpha_{e0}} S[F^0_{e0},\ldots,F^j_{e0}] = -\langle X^\alpha_e \rangle \tag{3.52}$$

for $k=0, 1, \ldots, j$. The theorem

$$\frac{\partial w_i}{\partial F^\alpha_{e0}} = -\frac{1}{k_B}(X^\alpha_e - \langle X^\alpha_e \rangle) w_i \tag{3.53}$$

follows easily. We then take the second derivatives of $\sum_i w_i$ and set the result to zero, since the probability is normalized. This yields

$$\langle \Delta X^\alpha_e \Delta X^\beta_e \rangle = k_B \frac{\partial^2}{\partial F^\alpha_{e0} \partial F^\beta_{e0}} S[F^0_{e0},\ldots,F^j_{e0}] , \tag{3.54}$$

where

$$\Delta X^\alpha_e = X^\alpha_e - \langle X^\alpha_e \rangle . \tag{3.55}$$

Green and Callen (1951) showed that this result for the second fluctuation moments is the same as that calculated with the Gaussian approximation to the thermodynamic fluctuation theory.

Differentiating $\sum_i w_i$ again yields the third fluctuation moments

$$\langle \Delta X^\alpha_e \Delta X^\beta_e \Delta X^\gamma_e \rangle = -k_B^2 \frac{\partial^3}{\partial F^\alpha_{e0} \partial F^\beta_{e0} \partial F^\gamma_{e0}} S[F^0_{e0},\ldots,F^j_{e0}] . \tag{3.56}$$

The expressions for the higher-order fluctuation moments are more complicated, but there is a hierarchy of equations which yields them all in terms of thermodynamic quantities.

In addition, Greene and Callen (1951) went to the continuum approximation and worked out the fluctuation moments to all orders using the full classical fluctuation theory equation (3.1) in standard density coordinates. They demonstrated that these moments are exactly the same as those calculated with the grand canonical distribution, but differ beyond the second order from those calculated with the Gaussian approximation.

D. Higher-order entropy expansions

A natural try at improving the Gaussian approximation to the classical thermodynamic fluctuation theory is to include more terms in the expansion of the entropy. The literature does not pay much attention to this, but there is certainly a body of opinion that more terms help.

Smoluchowski (1908) expanded the entropy about the critical point in powers of the density only. He noted that in the van der Waals model, both the first and second derivatives of the pressure with respect to the density vanish at the critical point. Therefore the fourth-order density term in the entropy expansion is needed to keep the second moments of the density fluctuations finite. However, in addition to the difficulties with entropy expansions beyond the second order raised in this review (Secs. II.B and II.C), such an expansion must be questioned in light of present-day thinking that the thermodynamic functions at the critical point are nonanalytic.[29]

A survey of textbooks on statistical mechanics and statistical thermodynamics finds that most contain some treatment of thermodynamic fluctuation theory. The standard discussion begins with an expression of the second fluctuation moments of the energy density $\langle (\Delta u)^2 \rangle$ of systems closed to density fluctuations in terms of the heat capacity, using the canonical ensemble. It is usually noted that these fluctuations go to zero in the thermodynamic limit, as required. Many texts also evaluate the second moment of the density fluctuations $\langle (\Delta \rho)^2 \rangle$ for open systems with the grand canonical ensemble. They usually point out that, because of the diverging isothermal compressibility, density fluctuations at all length scales become very large near the critical point, resulting in, for example, critical opalescence. Many texts give the Einstein fluctuation formula (3.1) and show that in the thermodynamic limit the second fluctuation moments are the same as those calculated with the statistical mechanical ensembles.

Most textbooks do not deal with the expansion of the entropy beyond second order, and none we have read attempt to relate results of such expansions to quantitative experimental measurements. Tolman (1938) emphasizes

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[29] Nonanalyticity of the thermodynamic functions at the critical point is now well accepted (Fisher, 1983). Onsager (1944) was the first to find rigorous proof of nonanalyticity at the critical point in a statistical mechanical model, the two-dimensional Ising model. Tisza (1951) gave an early thermodynamic argument for nonanalyticity in ferroelectrics.

that the Einstein thermodynamic fluctuation theory is only an approximation, giving valid results for the second moments, but not beyond that. Fowler (1955) discusses thermodynamic fluctuation theory extensively, including a critical examination of the Boltzmann formula relating entropy and probability. Rice (1967) works out the third-order term in the entropy expansion for density fluctuations and gives some estimates of when it might become important, particularly near the critical point. Fowler (1955), King (1962), ter Haar (1966), and Lee, Sears, and Turcotte (1973) present Smoluchowski's (1908) expansion about the critical point.

We might attempt to argue that the results of Green and Callen (1951) establishing the equivalence between the fluctuation moments computed with the canonical ensemble and the full classical thermodynamic fluctuation theory equation (3.1) prove that classical thermodynamic fluctuation theory is exact at all volumes in standard density coordinates. But this equivalence is deceptive because the thermodynamic limit must be invoked in all calculations with statistical mechanical ensembles; specifically, the subsystem must become infinite in size. Only here is statistical mechanics consistent in that different ensembles give the same results (Ruelle, 1969; Griffiths, 1972). But, in this limit, the Gaussian theory also becomes exact, and the deviation Greene and Callen (1951) found between the full thermodynamic fluctuation theory and its Gaussian approximation must become impossible to detect.

Another attempt at expanding the entropy is to recognize that the thermodynamic functions are smoothly varying and to include gradients of the density in the expansion. This line of thought leads to the Ornstein-Zernike theory of critical fluctuations (Landau and Lifshitz, 1977).

E. Shortcomings of the classical thermodynamic fluctuation theory

The classical thermodynamic fluctuation theory suffers from several problems at volumes not large enough for its Gaussian approximation to be valid. These were discussed in Sec. II, and we elaborate here.

The first problem with the classical thermodynamic fluctuation theory concerns Axiom 1, which contains the assertion that the environment of subsystem A_V may be characterized only by its intensive parameters. As was discussed in Sec. II.C, this assumption is reasonable provided that there is negligible spatial correlation between molecules on opposite sides of A_V, which will be the case if $V \gg \xi^d$. Here A_V will at any time see itself surrounded by an environment that at any instant in time looks similar to A_{V_0}. But this is not so at smaller volumes, and Axiom 1 ceases to be plausible.

The second, more formal problem with classical thermodynamic fluctuation theory is that it fails to be covariant, since a coordinate transformation $x \rightarrow x'(x)$ introduces the Jacobian of the transformation in the thermodynamic state space volume element $dx^0 dx^1 \cdots dx^r$ in Eq. (3.1), as was argued in Sec. II.B. The Jacobian is generally not constant[30] and cannot simply be absorbed in the normalization constant C. Neither can it be absorbed in the entropy $S_0(a,a_0)$, which transforms as a scalar. Therefore we must assert that there is some special coordinate system in which Eq. (3.1) works. However, neither the classical thermodynamic fluctuation theory nor statistical mechanics offers any guidance as to what such a special coordinate system might be.

The third problem with the classical thermodynamic fluctuation theory is that it yields incorrect average values for the standard densities beyond second order in the entropy expansion. As was shown in Eq. (3.46), we expect

$$\langle a^\alpha \rangle = a_0^\alpha \ , \tag{3.57}$$

if V_0 is infinite, by the conservation of the standard extensive parameters. However, this is not what Eq. (3.1) predicts, unless $S_0(a,a_0)$ is an even function of $a^\alpha - a_0^\alpha$. But, there is nothing in the laws of thermodynamics that demands that this be so. This problem is classified under a lack of consistency. The importance of conservation laws in the context of thermodynamic fluctuation theory was emphasized by Diósi and Lukács (1985a).

The fourth problem with classical thermodynamic fluctuation theory is that it does not satisfy the Chapman-Kolmogorov consistency relation (2.13). This condition arose when we extended the thermodynamic fluctuation theory to include fluctuations inside the subsystem.

F. Physical meaning of fluctuating thermodynamic parameters

A natural question is the physical meaning of thermodynamic parameters for subsystems. Other than in the thermodynamic limit, statistical mechanics offers no unique definition for these quantities, and their physical meaning has been disputed. The operational viewpoint in this review is that of Landau and Lifshitz (1977), in which equations of state (from the thermodynamic limit) are used to assign values of thermodynamic parameters to subsystems from the known values of the mechanical parameters. This operating method comes from the hypothesis of "translational invariance" and is discussed in Sec. II.D. It is at least implicit in most textbook discussions of thermodynamic fluctuations. Other viewpoints are discussed briefly in this section.

The meaning of temperature for fluctuating subsystems has recently been debated from several points of view (Feshbach, 1987; Kittel, 1988; Mandelbrot, 1989). Feshbach (1987) discussed the use of temperature to analyze

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[30] Ruppeiner (1983b) argued that treating the Jacobian as a constant is consistent with stopping the entropy expansion at second order.

heavy nuclei collision data.[31] The basic picture is that of an excited nucleus ("subsystem") in an environment consisting of other excited nuclei ("heat reservoir"). Feshbach cautions that the use of temperature in the analysis of collision products requires that the temperature fluctuations of any given nucleus be small, so that the decay products of each nucleus will be characteristic of those of the whole ensemble. Temperature fluctuations were estimated with what Feshbach presents as a "thermodynamic uncertainty relation"

$$\Delta U \Delta \left[\frac{1}{T}\right] = k_B \ . \qquad (3.58)$$

The energy may be expressed in terms of the temperature using the Fermi-gas model, and Feshbach finds that in typical cases of interest temperature fluctuations are only about an order of magnitude less than the temperature, large enough to raise questions about quantitative thermodynamic results from nuclear collisions.

Kittel (1988), writing in apparent response to Feshbach, argued that the phrase "temperature fluctuation" is an "oxymoron" because temperature is defined only in the thermodynamic limit, where it does not fluctuate. He stated that the temperature of a subsystem must be that of the infinite surrounding heat reservoir.

Mandelbrot (1989), however, argued that the temperature of fluctuating subsystems is a very well-defined concept if one is willing to go a step beyond elementary probability theory and use the theory of estimators of statistical parameters (Mandelbrot, 1962, 1964). The basic idea is that the temperature of a subsystem can be determined by examining its energies at various times and making the best guess at the temperature of the reservoir with which it might have been in contact. The uncertainty in the answer is taken as ΔT. These arguments are basically connected with the theory of thermometry. Lavenda (1991) has given an extensive discussion of this idea, including its history.

Lindhardt (1986), referring to a lecture by Bohr (1932, p. 401),[32] argued that Eq. (3.58) may be regarded as a "thermodynamic uncertainty principle" for energy and temperature, but only in the sense discussed by Mandelbrot (1989), and not in the sense of Landau and Lifshitz (1977), where the energy and the temperature are related by an equation of state. A proper uncertainty relation requires independent variables.

It is tempting to seek a conflict between these two points of view and to argue that the validity of the one negates the other. But there does not seem to be any incompatibility, since in one case the temperature being interpreted is that of the reservoir, and in the other it is that of the subsystem.

Chui *et al.* (1992) found direct experimental evidence for the validity of the Landau and Lifshitz (1977) equation-of-state interpretation. They measured temperature fluctuations in a paramagnetic crystal at low temperatures with high-resolution thermometers. The temperature measurement was made directly of the subsystem, and the energy was deduced from the magnetization.

Klein (1960) examined pressure fluctuations from several points of view, both statistical and thermodynamic, and concluded that the thermodynamic approach (Landau and Lifshitz, 1977) is basically correct.

Kratky (1985) reviewed fluctuations of thermodynamic parameters, with particular emphasis on pressure fluctuations. He concluded that in the microcanonical ensemble, all mechanical and thermodynamic parameters are fixed; but in other ensembles, the thermodynamic parameters fluctuate according to the fluctuations of the mechanical parameters, in a way consistent with Landau and Lifshitz (1977).

Schlögl (1988) discussed the thermodynamic uncertainty relations for the case of more than one pair of fluctuating variables.

G. Magnetic-fluid analogy

A class of physical systems parallel to fluid systems are magnetic systems. Thermodynamically, there is a simple analogy between these classes of systems, which we now examine for the case $n=2$. Consider a magnetic system of N spins in a magnetic field h. Let M be the magnetization, which is the sum of the magnetic moments of all the spins in the system. We may show (Kittel, 1958) that the differential of the internal energy is

$$dU = T\,dS + h\,dM \ . \qquad (3.59)$$

Here, the field h, but not the magnet that produces it, is taken to be a part of the system. For the pure fluid with the volume V fixed,

$$dU = TdS + \mu\,dN \ . \qquad (3.60)$$

Hence the formal analogy

$$N \leftrightarrow V, \quad M \leftrightarrow N, \quad h \leftrightarrow \mu, \quad m \leftrightarrow \rho \ , \qquad (3.61)$$

where $m = M/N$ is the magnetization per spin.

A problem with this analogy may appear at first to be the difficulty of fixing the energy and magnetization of the large system A_{V_0}, because it is not isolated from the magnet, which is *not* part of the system. By contrast, for fluids we may at least conceptually fix both the energy and the particle number simply by physically closing the

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[31] A semipopular account of this subject, with particular emphasis on nuclear phases and phase transitions, is given by Greiner and Stöcker (1985).

[32] Heisenberg (1971, p. 103) presents conversations with Bohr on complementarity principles and how the relation between equilibrium thermodynamics and statistical mechanics is connected to the relation between classical mechanics and quantum mechanics.

boundary around the system. This raises the question of the validity of Axiom 3 in Sec. III.B for magnetic systems, since that axiom, used in Eq. (3.3), asserts the conservation laws for energy and particle numbers.

The resolution of this difficulty may be found in the equivalence of the canonical and the microcanonical ensembles in the thermodynamic limit (Ruelle, 1969; Griffiths, 1972). In the former, we fix the thermodynamic parameters of the environment, and in the latter, we fix the standard densities of the subsystem. The resulting thermodynamic properties are the same. Magnetic systems are most naturally described with the canonical ensemble. The equivalence to the microcanonical ensemble assures us that there will be no error in proceeding as if the standard extensive quantities for very large magnetic systems are strictly conserved.

H. Other results concerning classical fluctuation theory

Klein and Tisza (1949) pointed out the inadequacy of Axiom 1 of the classical theory near the critical point and addressed it with a thermodynamic theory based on a subdivision of the system A_{V_0} into equal-sized cells arranged on a regular spatial array, as in Fig. 8. In this construction, the subsystem A_V is one of the cells, and it samples the universe only through the thermodynamic states of its immediate neighbors. This formalism yields information about the pair-correlation function, including, with suitable approximations, the Ornstein-Zernike theory. Klein and Tisza (1949) argued that their theory also produces finite density fluctuations near the critical point, in contrast to the unphysical infinite density fluctuations produced by the diverging isothermal compressibility in the Gaussian approximation.[33] The symmetry properties also may be used to make deductions, particularly about λ points in solids. The authors criticized the approach of Smoluchowski (1908) in expanding the entropy beyond second order in the density, because (in the language of this review) of the breakdown in Axiom 1 of Sec. III.B.

Bonner (1956) discussed the application of thermodynamic fluctuation theory to self-gravitating spherical masses of gas. The onset of instability resulting in collapse was predicted. Some discussion was given of the role of fluctuations in the formation of the nebula early in the universe.

Glansdorff and Prigogine (1971) discussed thermodynamic fluctuation theory in systems far from equilibrium.

Jou and Careta (1982) applied thermodynamic fluctuation theory to extended irreversible thermodynamics. The entire subject of extended irreversible thermodynamics, including fluctuation theory, was recently reviewed by Jou, Casas-Vazquez, and Lebon (1988).

Pavón and Rubí (1983, 1985) applied thermodynamic fluctuation theory to the thermodynamics of black holes.

Schlögl (1985) related the thermodynamic metric to the scheme of bit-number cumulants of probability distributions.

Levine (1986) described a formalism for generalizing thermodynamic Riemannian geometry. Use was made of a Euclidean geometry for classical thermodynamics.

Debenedetti (1986a, 1986b) has worked out an explicit formalism of thermodynamic fluctuations as far as the Gaussian terms in multicomponent fluid mixtures. This includes a geometric representation, though not of the type in this review (Debenedetti, 1986b). This work was extended by Panagiotopoulos and Reid (1986) and by Yan and Chen (1992).

Compagner (1989) compared the thermodynamic limit obtained by approaching infinite volume with that obtained by the continuum limit $k_B \to 0$, where fluctuations disappear. Particular attention was given to capillary phenomena, but there was little discussion of phase transitions and the critical point.

IV. COVARIANT AND CONSISTENT THERMODYNAMIC FLUCTUATION THEORY

In this section, the covariant and consistent thermodynamic fluctuation theory is presented. Motivated by the discussion in Sec. II.E, we postulate that the probability density for thermodynamic fluctuations is the solution to a second-order linear parabolic partial differential equation, whose coefficients are determined by the requirement that the solution match the classical theory in the thermodynamic limit. A lower bound on the volume where this theory could agree with the classical theory based on a uniform environment is given by the Riemannian thermodynamic curvature. Routine calculations of the curvature, from known thermodynamics, reveal that in several cases the curvature is proportional to the correlation volume, a physically appealing finding.

The basic philosophy in the theory is similar in style to that in theories of quantum mechanics, where the usual starting points are postulated partial differential equations which fit a set of desired general principles.

A. Thermodynamic fluctuation partial differential equation

We begin with the assumption that the fluctuation probability density satisfies a generalized diffusion-type partial differential equation,[34]

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[33] Of course, keeping higher-order terms in the entropy expansion also holds the density fluctuations finite.

[34] One may present a derivation for this equation similar in spirit to that presented in Sec. II.D. A useful addition to this argument is a logical application of Axioms 1–3 of the classical thermodynamic fluctuation theory (Ruppeiner, 1983a, 1983b; Diósi and Lukács, 1985a). Diósi and Lukács are especially clear in their derivation of a Fokker-Planck-type equation emphasizing the conservation laws.

$$\frac{\partial P}{\partial t}=c_0(x)P+c_1^{\mu}(x)\frac{\partial P}{\partial x^{\mu}}+\frac{1}{2}c_2^{\mu\nu}(x)\frac{\partial^2 P}{\partial x^{\mu}\partial x^{\nu}} \, . \tag{4.1}$$

The "time" t is in no sense a measure of the real time, but of the volume:

$$t=1/V \, . \tag{4.2}$$

The equation should be linear in P, to accommodate a normalization constant (Wehner and Wolfer, 1987). The form of Eq. (4.1) does not explicitly preserve normalization, however. It appears as an implicit relation among the coefficients. A form that preserves normalization is

$$\frac{\partial P}{\partial t}=-\frac{\partial}{\partial x^{\mu}}[K^{\mu}(x)P]+\frac{1}{2}\frac{\partial^2}{\partial x^{\mu}\partial x^{\nu}}[g^{\mu\nu}(x)P] \, , \tag{4.3}$$

which is the thermodynamic fluctuation equation that will be used henceforth. This partial differential equation is formally identical to the Fokker-Planck equation in irreversible thermodynamics (Graham, 1977a). It seems to be the simplest general type of mathematical structure that accommodates thermodynamic fluctuation theory. The first application of a partial differential equation for thermodynamic fluctuation theory appears to have been by Ruppeiner (1983a, 1983b). Diósi and Lukács (1985a) were the first to emphasize the role of conservation laws in determining the coefficients $K^{\alpha}(x)$.

K^{α} is called the drift vector and $g^{\alpha\beta}$ is the inverse of the metric tensor, which is assumed to be symmetric under an exchange of indices. The standard terminology and notation are somewhat misleading here, since the quantity K^{α} does not, in fact, transform as a first-rank contravariant tensor, as we shall see. For a form of the equation in which everything transforms as a tensor, see Graham (1977b) and Diósi and Lukács (1985a).[35] Mathematically, these coefficients could be allowed to depend on t as well as on x. The absence of time dependence is the hypothesis of "translational invariance."

1. Average values

Let us now use Eq. (4.3) to work out average values, which are generally defined by

$$\langle f\rangle \equiv \int fP dx \, , \tag{4.4}$$

where

$$dx \equiv dx^0 dx^1 \cdots dx^r \, . \tag{4.5}$$

It is straightforward to show (Graham, 1977b) by multiplication of Eq. (4.3) by the coordinates, and integration by parts that

$$\frac{d}{dt}\int P\, dx=0 \, , \tag{4.6}$$

$$\frac{d}{dt}\langle x^{\alpha}\rangle=\langle K^{\alpha}\rangle \, , \tag{4.7}$$

and

$$\frac{d}{dt}\langle x^{\alpha}x^{\beta}\rangle=\langle x^{\alpha}K^{\beta}\rangle+\langle x^{\beta}K^{\alpha}\rangle+\langle g^{\alpha\beta}\rangle \, . \tag{4.8}$$

Boundary terms have been omitted for brevity; see Wehner and Wolfer (1983b) for their inclusion. For probability distributions tightly clustered near some point, they are irrelevant. For large fluctuations, boundary conditions are chosen to conserve the normalization, as in Sec. II.

Consider next the classical theory in the thermodynamic limit $t\to 0$. The initial condition is a Dirac delta function:

$$P_{t\to 0}(x|x_0)=\delta(x-x_0) \, , \tag{4.9}$$

where x_0 is the state of the infinite environment. From Eqs. (4.7) and (4.8),

$$\lim_{t\to 0}\frac{d}{dt}\langle (x^{\alpha}-x_0^{\alpha})(x^{\beta}-x_0^{\beta})\rangle=g^{\alpha\beta}(x_0) \, ; \tag{4.10}$$

so, to leading order in t,

$$\langle \Delta x^{\alpha}\Delta x^{\beta}\rangle=g^{\alpha\beta}(x_0)t \, , \tag{4.11}$$

which is identical to Eq. (3.16). Here, $\Delta x^{\alpha}=x^{\alpha}-x_0^{\alpha}$. Equation (4.11) shows that $g^{\alpha\beta}$ in this section must be the same as the thermodynamic metric of Sec. III.

The average values of the *standard density coordinates* do not depend on t, by Eq. (3.46). For small t the average value for $K^{\alpha}(x)$ is very nearly its value evaluated at x_0; and Eq. (4.7) leads us to conclude that

$$K^{\alpha}(a)=0 \, . \tag{4.12}$$

This, together with the transformation rules for $K^{\alpha}(x)$ and $g^{\alpha\beta}(x)$, presented below, determines the equation coefficients uniquely in any coordinate system.

2. Thermodynamic Markovicity

Let us explore some basic principles that follow from Eq. (4.3). First, note that, in a parabolic partial differential equation, a unique solution exists in some domain, given an initial condition for P at some time t_0 (not necessarily zero) and a boundary condition (Morse and Feshbach, 1953). The boundary condition may consist either of the specification of the probability density on the boundary of the domain, or of the normal derivative of the probability density, or be some linear combination of the two.

Mathematically, the history that has led to a given initial condition at $t=t_0$ is irrelevant. In the theory of random processes, such a statement is called a Markov rule (Reif, 1965), and it motivates using the following notation for the probability density:

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[35] There is a small error in Eq. (3.10) of the latter paper.

$$P\left[\begin{array}{c|c} x & x_0 \\ t & t_0 \end{array}\right], \tag{4.13}$$

as in Sec. II.D. We always assume a Dirac delta function initial condition if $t \rightarrow t_0$, since in this limit the system A_V is the same as A_{V_0}. Markovicity has an immediate strong physical implication: given a subsystem at some instant in time in some thermodynamic state, the probability of a fluctuation inside that subsystem at that instant in time depends only on the subsystem's thermodynamic state and not on that of the exterior environment. Computer experiments on the two-dimensional Ising model support Markovicity at all length scales (Ruppeiner, 1985a, 1986).

As was discussed in Sec. II.D, thermodynamic Markovicity, along with a short-time propagator, offers an alternative foundation for the theory, in terms of the path-integral formalism of Ruppeiner (1983b). The detailed mathematics behind this was worked out by Grabert and Green (1979), though in a different physical context.

Markovicity can only be an approximation, likely to be most effective in cases with short-ranged intermolecular potentials and for subsystems not too small. The hope is that the validity of Markovicity will not be diminished by the diverging range ξ of the pair-correlation function of A_{V_0} near the critical point. One might argue that this cannot be so, because if the correlation length of A_{V_0} is very large, then the effect of any one spin will be felt over long distances, and certainly a spin inside A_V could sample spins well outside A_V. Such an attempt at refutation fails, however, because the pair-correlation function is formed by computing long-time averages over *all* of the microstates of the *infinite system* A_{V_0}. On the other hand, Markovicity addresses the ensemble of microstates of just the *subsystem* A_V with macroscopic variables restricted to some small range.

Markovicity is implicit in the canonical ensemble in statistical mechanics which assigns equal probabilities for all microstates with given macroscopic parameters. But the canonical ensemble is valid only in the thermodynamic limit. The hope is that the weaker statement of Markovicity will remain valid to a good approximation even down to very small volumes.

3. Chapman-Kolmogorov equation

Another condition satisfied by solutions to Eq. (4.3) is the Chapman-Kolmogorov equation

$$P\left[\begin{array}{c|c} x & x_0 \\ t & t_0 \end{array}\right] = \int P\left[\begin{array}{c|c} x & x_1 \\ t & t_1 \end{array}\right] P\left[\begin{array}{c|c} x_1 & x_0 \\ t_1 & t_0 \end{array}\right] dx_1 , \tag{4.14}$$

with $t > t_1 > t_0$. Its proof consists of two steps. First, it is easily verified that the right-hand side of Eq. (4.14) is a solution to Eq. (4.3) if

$$P\left[\begin{array}{c|c} x & x_1 \\ t & t_1 \end{array}\right] \tag{4.15}$$

is a solution. Second, the Dirac delta-function initial condition implies

$$\lim_{t\rightarrow t_1, x=x_1} \int P\left[\begin{array}{c|c} x & x_1 \\ t & t_1 \end{array}\right] P\left[\begin{array}{c|c} x_1 & x_0 \\ t_1 & t_0 \end{array}\right] dx_1 = P\left[\begin{array}{c|c} x_1 & x_0 \\ t_1 & t_0 \end{array}\right], \tag{4.16}$$

the necessary initial condition. The uniqueness theorem for solutions of Eq. (4.3) (Morse and Feshbach, 1953) then completes the proof.

The classical thermodynamic fluctuation theory does not satisfy the Chapman-Kolmogorov equation, as was explicitly demonstrated with a simple example (Ruppeiner, 1983b). The Gaussian approximation to the theory does satisfy it, so long as we do not allow variation of the metric elements with the thermodynamic state.

4. Covariance

Consider now the covariance of the thermodynamic fluctuation partial differential equation.[36,37] What is meant by covariance under a coordinate transformation from one set of thermodynamic variables x to another set $x'(x)$? First of all, if we, working with the new coordinates, were to formulate a theory of our own, our equation would look formally like Eq. (4.3). Second, there exists an explicit prior prescription that relates the probability density in the new coordinates to those in the old coordinates:

$$P dx = P' dx' . \tag{4.17}$$

This equation follows from the requirement that the probability of finding the thermodynamic state in some range of states be independent of the particular coordinates used to specify that range of states. Third, using the foregoing prescription, we must be able to show that the thermodynamic fluctuation equation in the new coordinates not only looks like the fluctuation equation in the old coordinates, but is equivalent to it. That the form of Eq. (4.3) satisfies all these conditions is, *a priori*, not clear, but it does, as the following demonstrates.

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[36] This discussion on covariance paraphrases that of Sakurai (1980) in connection with the derivation of the transformation properties of the Dirac equation. I consider only coordinate transformations independent of t.

[37] Many of the tensor calculations in Sec. IV were checked with the computer program MathTensor (Parker and Christensen, 1991).

In x' coordinates,

$$\frac{\partial P'}{\partial t}=-\frac{\partial}{\partial x'^{\mu}}(K'^{\mu}P')+\frac{1}{2}\frac{\partial^2}{\partial x'^{\mu}\partial x'^{\nu}}(g'^{\mu\nu}P') \ . \tag{4.18}$$

To resolve the issue of how K'^{α} and $g'^{\alpha\beta}$ are related to K^{α} and $g^{\alpha\beta}$, we systematically compare Eqs. (4.3) and (4.18). First, a standard theorem in advanced calculus lets us rewrite Eq. (4.17) as

$$P'=\left|\frac{\partial x}{\partial x'}\right|P \ , \tag{4.19}$$

where the coefficient of P on the right-hand side is the Jacobian. We then substitute this into Eq. (4.18) and express derivatives with respect to x' with

$$\frac{\partial}{\partial x'^{\alpha}}=\frac{\partial x^{\mu}}{\partial x'^{\alpha}}\frac{\partial}{\partial x^{\mu}} \ . \tag{4.20}$$

We compare with Eq. (4.3) by differentiating, dividing by the Jacobian, and equating corresponding coefficients of the derivatives of P. The calculation is aided by the identities (Sokolnikoff, 1964)

$$\frac{\partial}{\partial x^{\alpha}}\left|\frac{\partial x}{\partial x'}\right|=-\left|\frac{\partial x}{\partial x'}\right|\frac{\partial x^{\nu}}{\partial x'^{\mu}}\frac{\partial^2 x'^{\mu}}{\partial x^{\alpha}\partial x^{\nu}} \ , \tag{4.21}$$

$$\frac{\partial}{\partial x^{\alpha}}\left[\frac{\partial x^{\beta}}{\partial x'^{\gamma}}\right]=-\frac{\partial x^{\mu}}{\partial x'^{\gamma}}\frac{\partial x^{\beta}}{\partial x'^{\nu}}\frac{\partial^2 x'^{\nu}}{\partial x^{\alpha}\partial x^{\mu}} \ , \tag{4.22}$$

and

$$\frac{\partial x^{\alpha}}{\partial x'^{\mu}}\frac{\partial x'^{\mu}}{\partial x^{\beta}}=\frac{\partial x'^{\alpha}}{\partial x^{\mu}}\frac{\partial x^{\mu}}{\partial x'^{\beta}}=\delta^{\alpha}_{\beta} \ , \tag{4.23}$$

where the Kronecker delta function

$$\delta^{\alpha}_{\beta}=\begin{cases}0 & \text{if } \alpha\neq\beta,\\ 1 & \text{if } \alpha=\beta \ .\end{cases} \tag{4.24}$$

All derivatives with respect to x'^{α} may be placed into either the Jacobian or factors of

$$\frac{\partial x^{\alpha}}{\partial x'^{\beta}} \ . \tag{4.25}$$

Equating the n^2 second derivatives of P yields

$$g'^{\alpha\beta}=\frac{\partial x'^{\alpha}}{\partial x^{\mu}}\frac{\partial x'^{\beta}}{\partial x^{\nu}}g^{\mu\nu} \ . \tag{4.26}$$

Equating the n first derivatives of P yields

$$K'^{\alpha}=\frac{\partial x'^{\alpha}}{\partial x^{\mu}}K^{\mu}+\frac{1}{2}g^{\mu\nu}\frac{\partial^2 x'^{\alpha}}{\partial x^{\mu}\partial x^{\nu}} \ . \tag{4.27}$$

At this point all of the equation coefficients have been determined. Factors with just P now equate as well, indicating consistency and completing the calculation.[38]

The covariance of the equation was clearly discussed by Graham (1977b), who derived both it and transformation rules (4.26) and (4.27) from the microscopic Langevin equation to deal with the problem of irreversible thermodynamics. In this review, of course, not only is the context quite different, but the starting point is macroscopic. Essentially, requirements of covariance, consistency, and the thermodynamic limit take the place of microscopic equations!

5. Translational invariance

There is yet another feature in the theory: neither K^{α} nor $g^{\alpha\beta}$ depends explicitly on t. This assumption of "translational invariance," implicit in the notation, is not demanded by the mathematics. It is just the simplest assumption that may be made about the volume dependence. In the classical theory, translational invariance is contained in Axiom 1 in Sec. III.B. The thermodynamics in the thermodynamic limit offers little guidance as to possible alternatives. As is discussed in Sec. IV.D, this assumption is reasonable at volumes above the correlation volume, but not at lesser volumes.

6. Summary of rules of the covariant and consistent thermodynamic fluctuation theory

To conclude this section, here is a review of the theory. The discussion began with the choice of a particular partial differential equation, one motivated by the considerations in Sec. II. While deducing properties from this equation is instructive, this presentation nevertheless leaves a sense that the choice of the original equation was somewhat arbitrary. Therefore let us go the other way and begin with the desired principles of the theory:

(1) volume independence of the average standard densities;

(2) Chapman-Kolmogorov consistency equation;

(3) covariance; and

(4) consistency with the classical thermodynamic fluctuation theory in the limit of very large volumes.

In addition, a fifth assumption was added for the purposes of simplicity:

(5) translational invariance.

This fifth assumption has a lesser status than the first four and, in fact, fails at small volumes.

As we have argued, Eq. (4.3) satisfies all these princi-

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[38] Not just any equation will satisfy requirements of covariance; it is possible that no transformation rule for $g^{\alpha\beta}$ and K^{α} would have worked. "When we know the transformation properties of a certain quantity [in our case P in Eq. (4.17)], we can often guess the laws which govern its behavior merely from the requirement that physical laws must be covariant under transformation from one coordinate system to another; at least, the number of possible such laws is greatly reduced" Joseph (1965).

ples. Note as well that the equation was taken to be linear to accommodate an arbitrary normalization constant. The question of uniqueness remains and is not explored in generality here. Nevertheless, the choice of equations is severely limited by principles 1–5. Of course, alternate theories may be constructed by modifying these basic assumptions, but our hope is that they, and Eq. (4.3), form at least a good start.

To conclude this section, note that the Gaussian approximation to the classical thermodynamic fluctuation theory satisfies principles 1–5. However, this approximation is limited to very large volumes. Beyond the Gaussian approximation, the full classical thermodynamic fluctuation theory equation (3.1) fails to satisfy the first three principles.

B. Fluctuations at large volumes

The solution to the thermodynamic fluctuation equation separates naturally into different volume regimes: large, intermediate, and small. Start with large volumes, where t is small. In this case, the probability distribution is strongly centered near the initial point x_0, and the drift K^α and the metric elements $g^{\alpha\beta}$ will not vary much over the region of significance. As a first try, simply evaluate the equation coefficients at x_0 and write

$$\frac{\partial P}{\partial t} = -K^\mu \frac{\partial P}{\partial x^\mu} + \frac{1}{2} g^{\mu\nu} \frac{\partial^2 P}{\partial x^\mu \partial x^\nu} \, . \tag{4.28}$$

It is straightforward to verify that a normalized solution with Dirac delta-function initial condition is

$$P\left[\begin{array}{c|c} x & x_0 \\ t & 0 \end{array}\right] = \left[\frac{1}{2\pi t}\right]^{n/2} \sqrt{g} \exp\left[-\frac{1}{2t} g_{\mu\nu}(\Delta x^\mu - K^\mu t)(\Delta x^\nu - K^\nu t)\right] . \tag{4.29}$$

Such an approximate solution has been used (in a different context), for example, by Dekker (1976) and by Wehner and Wolfer (1985).

For any given Δx^α, with t becoming small, this equation becomes equivalent to the Gaussian approximation to the classical theory equation (3.12):

$$P\left[\begin{array}{c|c} x & x_0 \\ t & 0 \end{array}\right] = \left[\frac{1}{2\pi t}\right]^{n/2} \sqrt{g} \times \exp\left[-\frac{1}{2t} g_{\mu\nu} \Delta x^\mu \Delta x^\nu\right] . \tag{4.30}$$

This confirms that in the thermodynamic limit, the covariant thermodynamic fluctuation theory approaches the classical theory. Any deviation of the covariant thermodynamic fluctuation theory from the Gaussian approximate expression signals a disagreement with the classical thermodynamic fluctuation theory, which is not covariant beyond second order in the entropy expansion.

A somewhat awkward problem with the approximation equation (4.28) is that it neglects the fact that the first derivatives of $g^{\alpha\beta}$ are formally as important as the drift K^α. To see this, perform the derivatives out explicitly in Eq. (4.3) before setting the coefficients to constants:

$$\frac{\partial P}{\partial t} = \left[\frac{1}{2} g^{\mu\nu}{}_{,\mu\nu} - K^\mu_{,\mu}\right] P + (g^{\mu\nu}{}_{,\nu} - K^\mu) \frac{\partial P}{\partial x^\mu} + \frac{1}{2} g^{\mu\nu} \frac{\partial^2 P}{\partial x^\mu \partial x^\nu} \, , \tag{4.31}$$

where the comma notation ",α" denotes partial differentiation with respect to x^α. Now evaluate the coefficients at x_0; the solution is

$$P\left[\begin{array}{c|c} x & x_0 \\ t & 0 \end{array}\right] = c \left[\frac{1}{2\pi t}\right]^{n/2} \sqrt{g} \exp\left[\left[\frac{1}{2} g^{\mu\nu}{}_{,\mu\nu} - K^\mu{}_{,\mu}\right] t\right] \exp\left[-\frac{1}{2t} g_{\mu\nu}(\Delta x^\mu + g^{\mu\xi}{}_{,\xi} t - K^\mu t)(\Delta x^\nu + g^{\nu\xi}{}_{,\xi} t - K^\nu t)\right] , \tag{4.32}$$

where c is a constant. Such a solution has been discussed, for example, by Wehner and Wolfer (1983a). It also reduces to the Gaussian approximation of the classical theory in the thermodynamic limit $t \to 0$. This solution, however, suffers from the problem that it does not preserve normalization, because of the presence of the first exponential term.

Methods for finding approximate solutions to the Fokker-Planck equation are well known and are dealt with in the literature [see Wehner and Wolfer (1983a) for references]. The approximations are not unique, however, because there are several ways of approximating derivatives by finite differences (Graham, 1977a). Improving upon Eq. (4.29), making it more accurate, and going to the limit of infinitesimal time interval leads to the path-integral solution of the diffusion equation (Graham, 1977a, 1977b; Grabert and Green, 1979; Dekker, 1979, 1980, 1981; Langouche, Roekaerts, and Tirapegui, 1980; Takahashi and Watanabe, 1981). These approaches lead to Riemannian geometry. But the path-integral method is difficult and more than is needed here. It suffices that for very small times the solution is Gaussian, and that deviations from this approximation result from derivatives of the metric and because of nonzero drift K^α. All approximate solutions support these points.

C. Fluctuations at volumes of the order of the thermodynamic curvature

1. General absence of "ideal coordinates"

As t increases, the Gaussian approximation equation (4.30) eventually fails for typical fluctuations. There are two ways this can happen. The first is that fluctuations become so large that the metric elements can no longer be treated as constants evaluated at the initial point x_0. The second is for the drift terms proportional to t in the argument of the exponential in Eq. (4.29) to become too large to ignore.

For any t and any reservoir state x_0, it is possible to find coordinate systems such that either or both of these problems are present; the upper limit on t such that the Gaussian theory is *valid in all* coordinate systems is zero. The fundamental question is whether we can find an upper limit on t such that the classical thermodynamic fluctuation theory *must fail in all* coordinate systems for all larger t's.

The first impression might be that transformation rules (4.26) and (4.27) can always be solved to find an ideal coordinate system where the drift vector K^α is globally zero and where the metric elements $g_{\alpha\beta}$ are globally constant. However, this turns out not to be the case, as we now argue.

Two methods for attempting to construct an ideal coordinate system suggest themselves. The first begins with a transformation to a class of coordinate systems where $K^\alpha=0$,[39] followed by a transformation to coordinates within this class to make $g_{\alpha\beta}$ globally constant. The second method reverses the order of these operations.

The first method is unlikely to work. Given that we have found a coordinate system with $K^\alpha=0$, we may maintain this equality with a linear transformation. However, such a transformation with Eq. (4.26) will not result in constant $g_{\alpha\beta}$, unless we were so fortunate that the initial transformation made them constant. Another try is to choose some nonlinear transformation that leaves the second term on the right side of Eq. (4.27) zero and brings the metric elements to constants. However, as we shall demonstrate, it is not generally possible to do even the latter, much less both.

Though this argument establishes that an ideal coordinate system is unlikely to exist for a given thermodynamic system, it fails to offer any limiting value for t beyond which the classical theory must fail for typical fluctuations, no matter what the coordinate system. For this we must look in detail at the second procedure of first attempting to make the metric elements constant.

2. Equivalent metrics

Geometrically, the question of whether we may find, for a given metric $g_{\alpha\beta}(x)$, a new coordinate system with globally constant metric elements was of much interest to mathematicians in the last century; see Kline (1972) for a discussion of these historical issues. A more general question was eventually answered by Riemann (1861): Given a coordinate system x with line element

$$dl^2=g_{\mu\nu}(x)dx^\mu dx^\nu\ , \tag{4.33}$$

is it possible to find another coordinate system $x'=x'(x)$ with *given* metric elements $g'_{\alpha\beta}(x')$?[40] A key restriction is that the coordinate transformation $x'(x)$ must preserve the distance between every pair of neighboring points[41]:

$$g_{\mu\nu}(x)dx^\mu dx^\nu=g'_{\mu\nu}(x')dx'^\mu dx'^\nu\ . \tag{4.34}$$

Riemann showed that this is possible if and only if a certain indexed quantity, called the Riemann tensor, transforms as a fourth-rank tensor.

Modern differential geometry provides some very elegant treatments of Riemannian geometry, and we refer the interested reader to the literature (see, e.g., Spivak, 1970a, 1970b, 1975a, 1975b, 1975c; Weinberg, 1972; Misner, Thorne, and Wheeler, 1973). These treatments start with language and axioms whose immediate connection to the problem at hand is not transparent, and much of which is not essential for the purposes of this review. We shall deviate from the modern presentations and use a more direct one in the spirit of Riemann's original derivation. Most of the manipulations we make are standard (see, e.g., Weinberg, 1972). What is somewhat unconventional in this treatment is the context of the Taylor-series solution.

The metric relation (4.34) may be expressed in the form of a first-order partial differential equation for $x'(x)$:

$$g_{\alpha\beta}(x)=\frac{\partial x'^\mu}{\partial x^\alpha}\frac{\partial x'^\nu}{\partial x^\beta}g'_{\mu\nu}(x')\ . \tag{4.35}$$

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[39] Such coordinates certainly exist, e.g., the standard densities.

[40] As a sample problem, consider the plane. In Cartesian coordinates, the metric elements consist of the identity matrix $g_{\alpha\beta}(x)=\delta_{\alpha\beta}$. Take $g'_{11}(x')=1$, $g'_{12}(x')=0$, and $g'_{22}(x')=x_1'^2$. The corresponding transformation is to polar coordinates defined by $x_1=x'_1\cos x'_2$ and $x_2=x'_1\sin x'_2$. However, such problems may be solved only under very special circumstances, as we shall see.

[41] In Sec. III this corresponds to the statement that small entropy differences between two neighboring states are independent of the coordinates.

The dependence of both sets of symmetric metric elements on their coordinates is assumed to be known. One may observe that there is likely to be a problem finding a solution $x'(x)$, since there are $n(n+1)/2$ independent equations, but only n functions to adjust to satisfy these equations. Such an overdetermination forces a set of consistency relations that must be satisfied as well. Our basic procedure will be to assume that there is a solution, and then to have the conditions required to make this assumption self-consistent emerge naturally.

Consider some point x_0 in the space of states and write

$$x'^{\alpha}(x)=x'^{\alpha}_0+x'^{\alpha}{}_{,\mu}\Delta x^{\mu}+\frac{1}{2!}x'^{\alpha}{}_{,\mu\nu}\Delta x^{\mu}\Delta x^{\nu}+\frac{1}{3!}x'^{\alpha}{}_{,\mu\nu\xi}\Delta x^{\mu}\Delta x^{\nu}\Delta x^{\xi}+\cdots , \tag{4.36}$$

where $\Delta x^{\alpha}=x^{\alpha}-x^{\alpha}_0$ and where all the derivative coefficients on the right-hand side are evaluated at x_0. These derivatives can be determined by repeated differentiation of Eq. (4.35) and the solution of relatively simple algebraic equations. The value of x'_0 may be set arbitrarily.

The mechanical solution procedure for the derivatives has the potential problem that the resulting series coefficients might not all have commuting lower indices; such invariance under index exchange is essential, since the order of partial differentiation must be irrelevant. In our discussion, we shall start with the first derivatives and then work our way up. The job is somewhat simplified, since at each new derivative, we need consider only the exchange of the two final indices. The others commute already from the work at the lower-order derivatives.

The first set of algebraic equations is the partial differential equation (4.35) itself, evaluated at the point x_0:

$$g_{\alpha\beta}=x'^{\mu}{}_{,\alpha}x'^{\nu}{}_{,\beta}g'_{\mu\nu} . \tag{4.37}$$

We say that g and g' are congruent matrices at x_0 (Eves, 1966), which is certainly required for the transformation to exist. It may be shown that if one of the two matrices is symmetric, then the other one must be symmetric as well. Of key importance in the construction of locally Cartesian coordinates is the theorem (Eves, 1966) that any symmetric positive-definite matrix is congruent to the identity matrix.

Differentiating Eq. (4.35) with respect to x_{γ} yields

$$g_{\alpha\beta,\gamma}=\frac{\partial x'^{\mu}}{\partial x^{\alpha}}\frac{\partial x'^{\nu}}{\partial x^{\beta}}\frac{\partial x'^{\xi}}{\partial x^{\gamma}}g'_{\mu\nu,\xi}+\frac{\partial x'^{\mu}}{\partial x^{\beta}}\frac{\partial^2 x'^{\nu}}{\partial x^{\alpha}\partial x^{\gamma}}g'_{\mu\nu}+\frac{\partial x'^{\mu}}{\partial x^{\alpha}}\frac{\partial^2 x'^{\nu}}{\partial x^{\beta}\partial x^{\gamma}}g'_{\mu\nu} , \tag{4.38}$$

where the derivatives of $g_{\mu\nu}$ and $g'_{\mu\nu}$ are with respect to their respective natural variables x and x'. To solve for the second derivatives $x'^{\alpha}{}_{,\beta\gamma}$, it is helpful to introduce the Christoffel symbols

$$\Gamma^{\alpha}{}_{\beta\gamma}\equiv\frac{1}{2}g^{\mu\alpha}(g_{\mu\beta,\gamma}+g_{\mu\gamma,\beta}-g_{\beta\gamma,\mu}) , \tag{4.39}$$

symmetric in their lower two indices,

$$\Gamma^{\alpha}{}_{\beta\gamma}=\Gamma^{\alpha}{}_{\gamma\beta} . \tag{4.40}$$

There is a corresponding definition in x' coordinates. Some algebra with the indexed quantities and Eq. (4.26) yield

$$\frac{\partial^2 x'^{\alpha}}{\partial x^{\beta}\partial x^{\gamma}}=\Gamma^{\mu}_{\beta\gamma}\frac{\partial x'^{\alpha}}{\partial x^{\mu}}-\Gamma'^{\alpha}{}_{\mu\nu}\frac{\partial x'^{\mu}}{\partial x^{\gamma}}\frac{\partial x'^{\nu}}{\partial x^{\beta}} . \tag{4.41}$$

Because of the symmetry of the Christoffel symbols, the right-hand side of the equation is invariant with respect to an exchange of β and γ, as required. Evaluation at x_0 yields the second-order Taylor-series coefficients $x'^{\alpha}{}_{,\beta\gamma}$ directly.

Now differentiate Eq. (4.41) with respect to x^{δ}:

$$\begin{aligned}\frac{\partial^3 x'^{\alpha}}{\partial x^{\beta}\partial x^{\gamma}\partial x^{\delta}}=&-\Gamma^{\mu}{}_{\beta\delta}\Gamma'^{\alpha}{}_{\nu\xi}\frac{\partial x'^{\nu}}{\partial x^{\gamma}}\frac{\partial x'^{\xi}}{\partial x^{\mu}}-\Gamma^{\mu}{}_{\beta\gamma}\Gamma'^{\alpha}{}_{\nu\xi}\frac{\partial x'^{\nu}}{\partial x^{\delta}}\frac{\partial x'^{\xi}}{\partial x^{\mu}}-\Gamma^{\mu}{}_{\gamma\delta}\Gamma'^{\alpha}{}_{\nu\xi}\frac{\partial x'^{\nu}}{\partial x^{\mu}}+\Gamma'^{\mu}{}_{\nu\xi}\Gamma'^{\alpha}{}_{\mu o}\frac{\partial x'^{\nu}}{\partial x^{\delta}}\frac{\partial x'^{\xi}}{\partial x^{\gamma}}\frac{\partial x'^{o}}{\partial x^{\beta}}\\&+\Gamma'^{\mu}{}_{\nu\xi}\Gamma'^{\alpha}{}_{\mu o}\frac{\partial x'^{\nu}}{\partial x^{\delta}}\frac{\partial x'^{\xi}}{\partial x^{\beta}}\frac{\partial x'^{o}}{\partial x^{\gamma}}+\Gamma^{\mu}{}_{\beta\gamma}\Gamma^{\nu}{}_{\mu\delta}\frac{\partial x'^{\alpha}}{\partial x^{\nu}}+\Gamma^{\mu}{}_{\beta\gamma,\delta}\frac{\partial x'^{\alpha}}{\partial x^{\mu}}-\Gamma'^{\alpha}{}_{\mu\nu,\xi}\frac{\partial x'^{\mu}}{\partial x^{\gamma}}\frac{\partial x'^{\nu}}{\partial x^{\beta}}\frac{\partial x'^{\xi}}{\partial x^{\delta}} ,\end{aligned} \tag{4.42}$$

where the second derivatives were eliminated by substituting the known values Eq. (4.41). These third derivatives are already symmetric under an exchange of β and γ, but not necessarily with respect to an exchange of γ and δ. Require

$$x'^{\alpha}{}_{,\beta\gamma\delta}-x'^{\alpha}{}_{,\beta\delta\gamma}=0 . \tag{4.43}$$

A straightforward calculation shows that this obtains if and only if the four indexed quantity

$$R^{\alpha}{}_{\beta\gamma\delta}=\Gamma^{\alpha}{}_{\beta\gamma,\delta}-\Gamma^{\alpha}{}_{\beta\delta,\gamma}+\Gamma^{\mu}{}_{\beta\gamma}\Gamma^{\alpha}{}_{\mu\delta}-\Gamma^{\mu}{}_{\beta\delta}\Gamma^{\alpha}{}_{\mu\gamma} \tag{4.44}$$

(with a corresponding definition in primed coordinates) transforms as a fourth-rank tensor:

$$R^{\alpha}{}_{\beta\gamma\delta}=\frac{\partial x^{\alpha}}{\partial x'^{\mu}}\frac{\partial x'^{\nu}}{\partial x^{\beta}}\frac{\partial x'^{\xi}}{\partial x^{\gamma}}\frac{\partial x'^{o}}{\partial x^{\delta}}R'^{\mu}{}_{\nu\xi o} . \tag{4.45}$$

$R^{\alpha}{}_{\beta\gamma\delta}$ is called the Riemann curvature tensor, and its tensor transformation rule is the consistency relation we have sought.

The proof is now essentially complete, because the fourth-order coefficients $x'^{\alpha}{}_{,\beta\gamma\delta\varepsilon}$ must have commuting last two indices, since both δ and ε originate from the differentiation of a single expression. The same is true for the higher-order coefficients.

The requirement equation (4.45) is a necessary condition for the existence of a solution to the partial differential equation (4.35). It allows the construction of a Taylor-series solution. That it is a sufficient condition, however, is not obvious, since there is no guarantee that the Taylor series will actually converge. We shall not take up this issue here, but will be content to have motivated naturally the choice of Riemannian curvature. Those interested in how to prove convergence of Taylor-series solutions to general partial differential equations should consult, for example, Garabedian (1964).

According to Kline (1972), Riemann, using a special construction, proved that Eq. (4.45) is a sufficient condition for the case with zero curvature. Christoffel later proved it in general with a similar construction.

3. Properties of the Riemannian curvature tensor

Let us pause to state some readily proved properties of the Riemann curvature tensor. From Eq. (4.44),

$$R^{\alpha}{}_{\beta\gamma\delta}=-R^{\alpha}{}_{\beta\delta\gamma} \tag{4.46}$$

and

$$R^{\alpha}{}_{\beta\gamma\delta}+R^{\alpha}{}_{\gamma\delta\beta}+R^{\alpha}{}_{\delta\beta\gamma}=0 \ . \tag{4.47}$$

Of value is the tensor with four covariant indices,

$$R_{\alpha\beta\gamma\delta}=g_{\alpha\mu}R^{\mu}{}_{\beta\gamma\delta} \ . \tag{4.48}$$

Straightforward calculation with Eq. (4.39), Eq. (4.44), and the readily proved identities

$$g_{\alpha\mu}g^{\mu\beta}{}_{,\gamma}=-g_{\alpha\mu,\gamma}g^{\mu\beta} \tag{4.49}$$

and

$$g_{\alpha\beta,\gamma}=g_{\alpha\mu}\Gamma^{\mu}{}_{\beta\gamma}+g_{\beta\mu}\Gamma^{\mu}{}_{\alpha\gamma} \tag{4.50}$$

demonstrates that (Weinberg, 1972, p. 141)

$$R_{\alpha\beta\gamma\delta}=R_{\gamma\delta\alpha\beta} \ , \tag{4.51}$$

$$R_{\alpha\beta\gamma\delta}=-R_{\beta\alpha\gamma\delta}=-R_{\alpha\beta\delta\gamma}=R_{\beta\alpha\delta\gamma} \ , \tag{4.52}$$

and

$$R_{\alpha\beta\gamma\delta}+R_{\alpha\gamma\delta\beta}+R_{\alpha\delta\beta\gamma}=0 \ . \tag{4.53}$$

Define, as well, the second-rank Ricci tensor[42]

$$R_{\alpha\beta}=R^{\mu}{}_{\alpha\mu\beta} \ , \tag{4.54}$$

which we may write as

$$R_{\alpha\beta}=g^{\mu\nu}R_{\mu\alpha\nu\beta} \ . \tag{4.55}$$

The symmetry property equation (4.51) establishes that the Ricci tensor is symmetric. Finally, define the Riemannian curvature scalar:

$$R=g^{\mu\nu}R_{\mu\nu} \ . \tag{4.56}$$

The value of R at any point is independent of the choice of coordinate system; it is a scalar.

There are a number of possible sign conventions. We could as well have defined $R^{\alpha}{}_{\beta\gamma\delta}$ in Eq. (4.44) with a minus sign. Or, in defining the Ricci tensor, we could contract on the final lower index; the result differs by a minus sign. (Contraction on the first lower index yields zero.) We have used the sign convention of Weinberg (1972), which yields a negative curvature scalar R for standard spheres with positive-definite metrics. It also yields a negative thermodynamic curvature near the critical point. Misner, Thorne, and Wheeler (1973) have given a comprehensive summary of sign conventions in various texts. Of course, authors are free to use any sign convention, but they should certainly make clear which they have picked.

4. Riemann normal coordinates

Let us return to the problem that necessitated these derivations, that of finding coordinates where the metric elements are globally constant. If the metric elements are constant in some coordinate system, all components of the curvature must be zero, as is clear from definition (4.44) of the curvature. But, by the tensor transformation equation (4.45), if the curvature is zero in one coordinate system, then it must be zero in all coordinate systems. Thus the vanishing of the Riemann tensor is a necessary condition for the existence of a coordinate system where the metric elements are constant. It is also a sufficient condition, since a vanishing Riemannian curvature allows us to satisfy the consistency equation (4.45) with a constant metric.[43]

As we shall see in Sec. VI, the single-component ideal gas has zero thermodynamic curvature. Conceivably, then, the classical thermodynamic fluctuation theory could work all the way down to atomic volumes. Indeed, statistical mechanical calculation of the fluctuations supports such a point of view (Ruppeiner, 1983b).

But the typical case corresponds to nonzero curvature. Here the question is, How far may we move away from the point x_0 and still have the geometry behave reasonably close to that of a flat surface? To address this, we first find coordinates $x'(x)$ as close as possible to Cartesian coordinates in the neighborhood of the point x_0.

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[42] Equation (4.23) can be used to prove that the contraction of a tensor, defined in footnote 22 in Sec. III, formed by summing an upper and a lower index is a tensor, but with rank reduced by 2.

[43] All these results are valid only locally. There is no implication for the overall topology. For example, a cylinder has zero Riemannian curvature, but it is certainly not topologically equivalent to the plane.

With no essential loss of generality, we take $x'_0=0$.

The first condition we wish to impose is that, at x'_0, the metric elements be locally Cartesian:

$$g'_{\alpha\beta}=\delta_{\alpha\beta} \ . \tag{4.57}$$

This may be accomplished simply by solving the algebraic equations (4.37) for the first derivatives $x'^{\alpha}{}_{,\beta}$. There are more unknowns than equations, and the extra degrees of freedom allow a choice of orientation of the coordinate system.

Next, try to set as many derivatives of $g'_{\alpha\beta}(x)$ to zero at x_0 as possible. We begin with the first derivatives and simply take

$$\Gamma'^{\alpha}{}_{\beta\gamma}=0 \ , \tag{4.58}$$

which yields with Eq. (4.41) the second-derivative coefficients

$$x'^{\alpha}{}_{,\beta\gamma}=\Gamma^{\mu}{}_{\beta\gamma}x'^{\alpha}{}_{,\mu} \ . \tag{4.59}$$

The second derivatives of $g'_{\alpha\beta}(x)$, however, may not all be set to zero, because doing so would result in zero curvature, which we assumed not to be the case. This marks the end of the process of setting derivatives of the metric elements to zero.

We may, however, effect some further improvement by examining geodesics. As a first step, note that since we can make the first derivatives of $g'_{\alpha\beta}$ vanish, we have

$$R'^{\alpha}{}_{\beta\gamma\delta}=\Gamma'^{\alpha}{}_{\beta\gamma,\delta}-\Gamma'^{\alpha}{}_{\beta\delta,\gamma} \ , \tag{4.60}$$

where the left-hand side is known at this stage by the tensor transformation rule for the curvature equation (4.45). The first derivatives of the Christoffel symbols can clearly be chosen in such a way as to satisfy this consistency relation. However, the choice is not unique, since we may add any indexed quantity symmetric in γ and δ to the first derivatives of the Christoffel symbols and not change the difference in Eq. (4.60).

The particular choice

$$\Gamma'^{\alpha}{}_{\beta\gamma,\delta}=\frac{1}{3}(R'^{\alpha}{}_{\beta\gamma\delta}+R'^{\alpha}{}_{\gamma\beta\delta}) \tag{4.61}$$

satisfies Eq. (4.60), as we may readily verify using Eqs. (4.46) and (4.47). Substituting back into Eq. (4.42) would now yield the coefficients $x^{\alpha}{}_{,\beta\gamma\delta}$. These coordinates are called *Riemann normal coordinates.* As shown below, they are the closest possible to locally Cartesian coordinates. Higher-derivative coefficients are not unique.

We here and henceforth drop the prime superscript, since the original coordinate system will no longer be used in this section.

A basic construction in Riemannian geometry is the geodesic, paths of shortest distance between pairs of neighboring points. The length of a path $x(\lambda)$ is given by

$$\int\left[g_{\mu\nu}\frac{dx^{\mu}}{d\lambda}\frac{dx^{\nu}}{d\lambda}\right]^{1/2}d\lambda \ , \tag{4.62}$$

where λ is taken to be the arclength of the curve. A straightforward exercise in the calculus of variations (Misner, Thorne, and Wheeler, 1973) establishes that geodesics are solutions to the geodesic equation:

$$\frac{d^2x^{\alpha}}{d\lambda^2}+\Gamma^{\alpha}{}_{\mu\nu}\frac{dx^{\mu}}{d\lambda}\frac{dx^{\nu}}{d\lambda}=0 \ . \tag{4.63}$$

Without any loss of generality, we may choose $x_0=0$ and measure λ from this point. Geodesic curves passing through $x_0=0$ may be written as a Taylor series:

$$x^{\alpha}=b^{\alpha}\lambda+\frac{1}{2!}c^{\alpha}\lambda^2+\frac{1}{3!}d^{\alpha}\lambda^3+O(\lambda^4) \ . \tag{4.64}$$

The expansion of the Christoffel symbols is

$$\Gamma^{\alpha}{}_{\mu\nu}(x)=\Gamma^{\alpha}{}_{\mu\nu}+\Gamma^{\alpha}{}_{\mu\nu,\xi}b^{\xi}\lambda+O(\lambda^2) \ . \tag{4.65}$$

Substituting these series into the geodesic equation in Riemann normal coordinates and equating like powers of λ, we find that c^{α} vanishes, since the Christoffel symbols vanish, and d^{α} vanishes by the antisymmetry of the Riemann tensor in its last two indices. We have

$$x^{\alpha}=b^{\alpha}\lambda+O(\lambda^4) \ . \tag{4.66}$$

In a curved space, this equation is the closest we can come to that of a flat space.

5. Regime of validity of the classical thermodynamic fluctuation theory

We now have all of the tools needed to estimate how far we may move from the point x_0 so that the geometry still looks reasonably flat. We work in two dimensions, where a convenient measure of deviation from flatness is the circumference of a circle with small radius r and centered at $x_0=0$. The circle is the locus of all points on the geodesics starting from x_0 with the parameter $\lambda=r$.

Useful is the expansion of the metric elements:

$$g_{\alpha\beta}=\delta_{\alpha\beta}+\frac{1}{2}g_{\alpha\beta,\mu\nu}b^{\mu}b^{\nu}\lambda^2+O(\lambda^3) \ . \tag{4.67}$$

It also helps to express the direction cosines parametrically:

$$b^1=\cos\theta \text{ and } b^2=\sin\theta \ , \tag{4.68}$$

where θ ranges from 0 to 2π. In Riemann normal coordinates, Eq. (4.50) leads to

$$g_{\alpha\beta,\gamma\delta}=\frac{1}{3}(R_{\alpha\gamma\beta\delta}+R_{\beta\gamma\alpha\delta}) \ . \tag{4.69}$$

Of use, as well, is the readily proved relation for the Riemann curvature scalar,

$$R=\frac{2R_{1212}}{g} \ , \tag{4.70}$$

which follows from the symmetry relations of the Riemann tensor, and which *holds in any coordinate system.*

The circumference of the circle is

$$C=\int_{\theta=0}^{2\pi}\left[g_{\mu\nu}\frac{dx^{\mu}}{d\theta}\frac{dx^{\nu}}{d\theta}\right]^{1/2}d\theta\ . \tag{4.71}$$

Substituting the metric expansion and the parametric expressions for b^{α}, and doing a somewhat laborious computation, yields

$$C=2\pi r+\frac{\pi}{6}Rr^3+O(r^4)\ , \tag{4.72}$$

the formula of Bertrand and Puiseux (Spivak, 1970b). Note that it is essential in the calculation that Eq. (4.66) hold to $O(\lambda^4)$.

Let us add some remarks about units. First, in the thermodynamic Riemannian geometry, the square of the distance has units of inverse volume, since the argument of the exponential function in Eq. (3.12) must be dimensionless. With Eq. (4.72), this clearly shows that the scalar curvature R must have units of volume. This results as well from the long formula (4.56), regardless of the dimension n of the thermodynamic state space.

We are now in a position to estimate how large typical fluctuations may become so that the state space still appears locally reasonably flat. We require that the first term on the right-hand side of Eq. (4.72) dominate the second. This is obtained if

$$r^2\ll\frac{12}{|R|}\ . \tag{4.73}$$

However, from Eq. (3.12) for fluctuations, we observe that the typical fluctuation has distance

$$r^2\approx\frac{2}{V}\ . \tag{4.74}$$

To be in the regime where the classical theory provides a good approximation to the fluctuations requires then that

$$V\gg\frac{1}{6}|R|\ . \tag{4.75}$$

Hence $|R|$ sets the limiting lower volume for the classical theory. Certainly, it cannot hold for smaller volumes, no mater how we choose the coordinate system. Of course, in any particular case, it is possible that the classical theory could fail at a *larger* volume because of the drift K^{α}, which is connected with the additivity of the standard extensive parameters. Since K^{α} does not transform as a tensor, it is harder to make a general statement about its effect on the limiting volume. There does not appear to have been any investigation of the role of K^{α} in any specific case.

In any event, Eq. (4.75) certainly offers a lower bound for the volume of the validity of the classical thermodynamic fluctuation theory. In Sec. II we argued that, physically, this theory must fail at length scales of the order of the correlation volume, where regarding the environment of the subsystem as uniform is no longer adequate. This leads us to interpret $|R|$ as the correlation volume:

$$R=\kappa_2\xi^d\ , \tag{4.76}$$

where κ_2 is a constant with absolute value of order unity. This interpretation is supported by calculations, as we shall see in Sec. VI.

Little has been reported in higher dimensions. Perhaps calculations of this type will reveal similar properties about the physical meaning of the thermodynamic curvature. Indeed, in the path-integral approach (Ruppeiner, 1983b), the quantity R appears no matter what the dimension. It is worth pointing out, however, that in two dimensions R provides complete information about the curvature at any particular point, since, by Eq. (4.70) and the symmetries of the Riemann tensor equations (4.51)–(4.53), all the components of $R_{\alpha\beta\gamma\delta}$ may be constructed knowing R. Hence any two-dimensional thermodynamic curvature theory must be based on R. The same is not true in higher dimensions.

Diósi and Lukács (1985b, 1986) took a somewhat different direction in estimating the volume at which the classical theory breaks down. Working in standard density coordinates, they calculated the next-order terms $[O(t^2)]$ in the second fluctuation moments. They found these terms to be related to the second derivatives of the metric elements and attributed them to "spatial correlations." Furthermore, they interpreted as the correlation volume the volume at which these correction terms equal the leading ones. There is a different volume for every pair of fluctuating variables, and Diósi and Lukács (1985b) explicitly evaluated the maximum one.

Diósi and Lukács (1985b) worked out the examples of the ideal gas and the gas of photons. For the ideal gas, their correlation volume was on the order of the specific volume occupied by a single molecule, a sensible result, since this volume certainly signifies the scale at which a thermodynamic description must fail. For the photon gas, which has zero Riemann curvature because its geometry is one dimensional, they obtained a volume on the order of the wavelength of the peak of the blackbody curve. This is, again, a physically appealing result, and the volume is of the same order as that found by Einstein (1904) in which the volume where energy fluctuations are of the same order as the energy. Near the critical point, their volume was estimated to be on the order of the correlation volume.

If the calculation were made in Riemann normal coordinates, the method used by these authors would likely lead to the same basic estimate as Eq. (4.75), since in these coordinates the second derivatives of the metric elements are simply related to the curvature scalar through Eq. (4.69).

Diósi and Lukács (1986) inverted their logic and began by assuming the existence of two different length scales in a dilute gas. When worked backwards, this assumption yields an equation of state of the van der Waals type.

D. Fluctuations at volumes less than the order of the thermodynamic curvature

In this section, we discuss thermodynamic fluctuation theory at volumes less than the correlation volume of

A_{V_0}. It seems clear that fluctuations in this regime must behave quite differently from those at large volumes, since translational invariance fails. Present evidence indicates, however, that Markovicity remains reliable (Ruppeiner, 1986), offering at least the possibility for a thermodynamic theory in this volume regime.

We begin by arguing that translational invariance breaks down. Translational invariance includes the assertion that the intensive quantities, including the metric elements, are the same as those of an infinite system with the same mechanical parameters. It is well known, however, from the modern theory of critical phenomena, that to produce the thermodynamics in the thermodynamic limit near the critical point requires contributions from many scales of length, all the way up to the correlation length (Wilson, 1979). In subsystems, however, length scales larger than the system size do not exist. This is not a problem for large subsystems; but for subsystems smaller than the correlation volume, this exclusion surely affects the thermodynamics.

The properties of the pair-correlation function allow a more detailed argument. Consider an infinite ferromagnetic Ising lattice A_{V_0} of arbitrary dimensionality, with spin at the ith lattice site $\sigma_i = \pm 1$ and with an interaction Hamiltonian

$$H = -\sum_{i,j \varepsilon A_{V_0}} J_{ij}\sigma_i\sigma_j - h \sum_{i \varepsilon A_{V_0}} \sigma_i \ , \tag{4.77}$$

where

$$J_{ij} \geq 0 \tag{4.78}$$

for all i and j. Let A_V be a subsystem of A_{V_0}, and consider the set of all microstates of A_V with energy per volume and magnetization per volume each falling into some very small range. This set is called a subsystem microcanonical ensemble. As time advances, A_V will fluctuate through various microstates, and occasionally into the small interval of interest. By definition, for any microstate of A_V,

$$m = \frac{1}{V} \sum_{i \varepsilon A_V} \sigma_i \ . \tag{4.79}$$

For convenience, we take the small range of the magnetization to be centered on $m = 0$. Then

$$0 = \langle m^2 \rangle = \frac{1}{V^2} \sum_{i,j \varepsilon A_V} \langle \sigma_i \sigma_j \rangle \ , \tag{4.80}$$

where the average is taken over only the states of interest, and the interval size has been set to zero, for simplicity of discussion. In the thermodynamic limit $V \rightarrow \infty$, the argument of the summation $\langle \sigma_i \sigma_j \rangle$ becomes the pair-correlation function, which, for the ferromagnetic Ising model, may rigorously be proven to be positive for all i and j (Griffiths, 1972).

This cannot hold, however, for the finite subsystem. Since the diagonal elements $i = j$ all contribute $+1$, some of the terms in the sum equation (4.80) must clearly be negative. This finding clashes with the hypothesis of translational invariance, which asserts that $\langle \sigma_i \sigma_j \rangle$ is independent of V. Translational invariance fails at volumes of the order of the correlation volume.[44]

Ruppeiner (1985a, 1986) explored this point with computer simulations on the two-dimensional Ising model and found such negative parts of $\langle \sigma_i \sigma_j \rangle$ for subsystems. Ruppeiner (1986) also found a breakdown of translational invariance in the purely thermodynamic internal energy.

A replacement principle for translational invariance probably must include not only a dependence on the size and shape of A_V, but on its position within A_{V_0} (if the outer system is not infinite in volume). Whether general statements, independent of the microscopic details, are possible is unclear.

For an example of the type of hypothesis we are seeking, but without Markovicity, Bruce (1981) stated a scaling type postulate for order parameter fluctuation probabilities near the critical point. More recently Bruce and Wilding (1992) examined both energy and density fluctuations near the liquid-gas critical point using idea from finite size scaling theory and the concept of field mixing.

Rice and Chang (1974) anticipated several of the physical ideas in this section with statistical mechanical arguments. They argued that in the pure fluid the thermodynamic expression for density fluctuations

$$\left\langle \left[\frac{\Delta\rho}{\rho} \right]^2 \right\rangle = \frac{k_B T k_T}{V} \ , \tag{4.81}$$

where k_T is the isothermal compressibility, should work all the way down to microscopic volumes in the ideal gas, but near the critical point must fail at volumes of the order of the correlation volume. Moreover, they suggested that at volumes less than the correlation volume, this thermodynamic expression could still work, but with a different value for k_T, one associated with the local thermodynamic state.

Rice and Chang (1974) also made a statistical mechanical argument for the inverse proportionality between the singular part of the free energy and the correlation volume equation (2.51). They derived exponent scaling relations.

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[44] Technically, the argument about negative parts of the correlation function applies also in the thermodynamic limit $V \rightarrow \infty$. Here, however, $\langle m^2 \rangle$ is zero without negative parts to the correlation function, since the denominator of the right-hand side of Eq. (4.80) diverges as the square of V, whereas the sum of the terms near the diagonal of the numerator, the only significant ones for short-range interactions, diverges only as V. Another way to look at this is that the negative parts may be distributed over an infinite number of spins, not available to a finite subsystem.

E. Geodesic length

A natural question in Riemannian geometry is the physical meaning of geodesics, curves between two points of locally minimum distance. For nearby thermodynamic states, the square of the lengths of the geodesics gives the probability of a fluctuation between the states. But this does not appear to generalize to larger separations between thermodynamic states. Indeed, a curved space might even allow more than a single geodesic connecting a given pair of states.

An interesting attempt at a physical interpretation for geodesics was given by Diósi, Lukács, and Rácz (1989), who used geodesics as a basis for classifying thermodynamic states into different "phases." The basic physical motivation was the difficulty posed by the termination of the liquid-gas phase-separation curve at the critical point to the task of differentiating between liquid and gas states. These authors defined two thermodynamic states as belonging to the same "phase" if they can be connected by a smooth geodesic. They explicitly computed the geodesics for the van der Waals model and found four distinct regimes.

We point out, however, that at the boundaries between these phases there are no discontinuities in the thermodynamic functions; so the distinct regimes found by these authors do not correspond to phases in the Ehrenfest sense. Their definition also fails to be transitive; namely, if states A and B are in the same phase and states B and C are in the same phase, then it does not necessarily follow that states A and C are in the same phase.

F. Weinhold's geometry

An interesting inner product on classical thermodynamic phase space was proposed by Weinhold (1975a, 1975b, 1975c, 1975d, 1976a, 1976b). It, and requirements of mathematical consistency, allowed for a geometric representation of the basic laws of standard equilibrium thermodynamics.

Weinhold worked in the energy representation, where we denote the full (extended) set of $n+1$ extensive variables of the subsystem by $Y_e=(S,N^1,\ldots,V,\ldots,N^r)$.[45] These variables are identical to the extended set X_e of extensive variables in the entropy representation, except in the first slot where the entropy rather than the internal energy appears. The last variable is the fixed subsystem scale, which might be the volume. The corresponding conjugate intensive parameters

$$P_e^\alpha=\frac{\partial U}{\partial Y_e^\alpha} \tag{4.82}$$

are $P_e=(T,\mu^1,\ldots,-p,\ldots,\mu^r)$. By the Gibbs-Duhem relation (Callen 1985), any one of the P_e^α's may be expressed in terms of the others. The dependent P_e^α is usually chosen to be the last one, which is conjugate to the fixed subsystem scale.

Differentials of thermodynamic functions may be represented by vectors in a vector space. As a set of basis vectors, the n independent dP_e^α's will serve, since

$$df=\sum_{\mu=0}^{n-1}\frac{\partial f}{\partial P_e^\mu}dP_e^\mu \tag{4.83}$$

for any thermodynamic function f. Weinhold's (1975a, 1975b, 1975c, 1975d, 1976a, 1976b) contribution was to assign an inner product:

$$(dP_e^\alpha|dP_e^\beta)=\frac{\partial^2 U}{\partial Y_e^\alpha\partial Y_e^\beta} \tag{4.84}$$

between pairs of basis vectors. This inner product is clearly commutative. In addition, Weinhold imposed the requirement that it be bilinear:

$$(dP_e^\alpha|a dP_e^\beta+b dP_e^\gamma)=a(dP_e^\alpha|dP_e^\beta)+b(dP_e^\alpha|dP_e^\gamma)\ , \tag{4.85}$$

for any values of the constants a and b, with a similar relation for the left-hand slot. These relations and Eq. (4.83) enable us to write the inner product of any pair of vectors.

One is free, of course, to assign any inner product to thermodynamic phase space. But to make it interesting, there must be some physical motivation. Weinhold's idea was to represent the second law of thermodynamics with a positive-definite inner product. One may prove that (Mrugała, 1984; Salamon, Nulton, and Ihrig, 1984)[46]

$$\sum_{\mu,\nu=0}^{n-1}\frac{\partial^2 U}{\partial Y_e^\mu\partial Y_e^\nu}dY_e^\mu dY_e^\nu=-T\sum_{\mu,\nu=0}^{n-1}\frac{\partial^2 S}{\partial X_e^\mu\partial X_e^\nu}dX_e^\mu dX_e^\nu\ . \tag{4.86}$$

By the argument in Sec. III.B, the right-hand side is a positive-definite quadratic form. Therefore the left-hand side of Eq. (4.86) is also positive definite, and this suffices to prove (Eves, 1966) that the matrix in Eq. (4.84) is positive definite.

We then have

$$(dP_e^\alpha|dP_e^\alpha)\geq 0 \tag{4.87}$$

and

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[45] The notation here differs from Weinhold's.

[46] When the volume is the fixed scale, this follows from equating Eqs. (3.26) and (3.30). The extension to the general case is immediate.

$$(dP_e^\alpha|dP_e^\alpha)(dP_e^\beta|dP_e^\beta)-(dP_e^\alpha|dP_e^\beta)^2\geq 0\ . \tag{4.88}$$

In addition, other inequalities may be constructed with relations (3.20)–(3.24). These inequalities are expressions of the second law of thermodynamics. Weinhold provided a number of examples of calculations with his geometry.

Weinhold's geometry could equally well have been formulated in the entropy representation (Ruppeiner, 1979), since his inner product may be multiplied by any positive function without changing the inequalities. Because of applications in fluctuation theory and thermodynamics in finite time, it is nowadays more fashionable to use the entropy representation.

We may formally turn Weinhold's inner product into a true Riemannian metric of the type in this review, as Eq. (4.86) shows. However, such a geometry appears to have no physical meaning in the context of purely equilibrium thermodynamics.[47] Though Weinhold (1976b) did remark on the possibility of a Riemannian metric in thermodynamics, this does not seem to have been his basic intent. For a true thermodynamic Riemannian geometry, we must add fluctuations or finite-time processes.

G. Embedding of thermodynamic manifolds in higher-dimensional flat spaces

The introduction of a Riemannian metric based on the second derivatives of either the entropy or the energy gave rise at one point to a dispute concerning embeddings of the corresponding n-dimensional thermodynamic manifolds in $(n+1)$-dimensional Euclidean spaces (Gilmore, 1984, 1985; Horn, 1985; Ruppeiner, 1985b). The dispute has since been resolved (Andresen, Berry, Gilmore, Ihrig, and Salamon 1988). The key point is that there is neither an explicit nor an implicit assumption in the introduction of the thermodynamic metric that the corresponding thermodynamic state space can be embedded in a higher-dimensional Euclidean metric space.[48,49] Berry (1988) has given a brief review of the controversy and its resolution. He discussed three types of Riemannian metrics in thermodynamic state space, including an account of their uses and limitations.

Examples of thermodynamic manifolds embedded in higher-dimensional flat spaces are the Gibbs-type representations, which show energy or entropy surfaces graphed in a flat space with $n+1$ extensive quantities as axes. Gilmore (1984) has shown, from thermodynamic convexity, that all Gaussian sectional curvatures of such manifolds are positive.

However, the curvature need not be positive for the purely intrinsic Riemannian thermodynamic geometries. Ruppeiner (1985b) found an example satisfying thermodynamic stability and possessing either positive or negative curvature with the adjusting of some parameters. Curvature with both signs was also found by Ruppeiner and Chance (1990) in the Takahashi gas and by Janyszek and Mrugała (1990a) in the ideal quantum gases. These findings clearly demonstrate that there is no connection between the Riemannian geometry of this review and that of the embedded Gibbs spaces.

There are, nevertheless, some interesting questions related to embeddings. Andresen, Berry, Ihrig, and Salamon (1988) proved that a thermodynamic Riemannian metric of the form used here cannot be induced on an equation-of-state surface from a Euclidean metric in an ambient $(n+1)$-dimensional Gibbs space of all extensive state variables. But it can be induced if the ambient space is assumed to have a curved Riemannian metric,

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[47] Consider the following quote from Tisza (1961): "Neither the elementary, nor the Riemannian theory of curvature can be applied in Gibbs space, in which no physically meaningful metric form is definable." If one extends beyond the purely equilibrium theory, it is, of course, a different story.

[48] Imprecise semantics can contribute to misunderstanding. Gauss (1827) showed that on two-dimensional surfaces embedded in three-dimensional Euclidean spaces, a scalar surface quantity called the Gaussian curvature can be computed knowing only the metric on the embedded surface in terms of a pair of surface coordinates. The Gaussian curvature is proportional to the Riemannian curvature scalar on the surface ($K=-R/2$), which in the Riemannian geometry requires no higher-dimensional embedding space for either its definition or its computation. Though the Gaussian curvature may formally be computed from the metric in exactly the same manner as the Riemannian curvature, it is semantically superior to refer to the thermodynamic curvature as "Riemannian curvature," and not as "Gaussian curvature." The latter term, used by Ruppeiner (1979, 1981), implies (but certainly does not require) a flat three-dimensional embedding space.

[49] In dealing with thermodynamic metric geometry, care should be taken to fix one of the extensive variables as the constant system scale. The metric geometry of the type here should not be formulated with full extended lists of variables such as X_e or Y_e. If the scale is not fixed, but included as one of the variable parameters, a metric with zero determinant results, and the geometry is singular. Physically, this corresponds to the fact that a fluctuation in the volume at fixed particle and energy densities does not change the entropy.

which is, however, not unique. Such a geometry was considered by Gilmore (1984).

A question that Andresen, Berry, Ihrig, and Salamon (1988b) did not address is whether or not we may find some "lift function" $f(x)$, not necessarily one of the usual thermodynamic parameters, such that the $(n+1)$-dimensional space with axes $[x,f(x)]$ has a Euclidean metric which induces the proper Riemannian metric on the graph of $f(x)$. Constructions of this type are common in general relativity, to allow, for example, the visualization of spacetime near black holes (Misner, Thorne, and Wheeler, 1973, p. 614). Though such structures are unlikely to exist in general in thermodynamics, there may be specific examples in which this could lend insight.

H. Information theoretic approaches

Substantial efforts have been made to place thermodynamic fluctuation theory within the broader context of information theory. For a review of the classic work in this area, see Tisza and Quay (1963). More recent work has been done following up Rao's (1945) concept of relative information in mathematical statistics (Ingarden, 1976, 1981, 1987; Ingarden *et al.*, 1979; Ingarden and Janyszek, 1982; Ingarden, Janyszek, Kossakowski, and Kawaguchi, 1982; Ingarden, Kawaguchi, and Sato, 1982; Salamon, Nulton, and Berry, 1985). For an extended discussion of the general topic of information theory and Riemannian geometry, see Amari (1985). Campbell (1985) has also discussed Riemannian geometry in information theory. For a recent introduction to information theory in statistical mechanics, see Grandy (1987). Information theory is used in many branches of science and technology. Moreover, it gives a direct and strong support for the fluctuation interpretation of the metric and curvature.

A significant contribution in this area has been the use of contact structures, introduced by Hermann (1973), who suggested that these are very natural in thermodynamics. Contact structures have been connected to the Riemannian geometry of thermodynamics (Mrugala, 1984; Janyszek, 1986a, 1986b; Janyszek and Mrugala, 1989a; Mrugala *et al.*, 1990). The starting point here is the statistical mechanical partition function. The Riemannian geometric structure is induced from a $(2n+1)$-dimensional space with a metric related to that in Eq. (3.26).

Another interesting idea in the broader context is that of "statistical distance" in quantum mechanics (Wooters, 1981). This involves a Riemannian metric of the same kind as that used here. Though it was presented in the context of quantum mechanics, it has seen use in the thermodynamic type of geometries as well (Salamon *et al.*, 1985; Feldmann *et al.*, 1986).

I. Finite-time thermodynamics

A major application of the Riemannian thermodynamic metric has been in finite-time thermodynamics. This subject is too large to review here, and we refer the reader to the literature for details (Salamon *et al.*, 1980; Salamon and Berry, 1983; Andresen *et al.*, 1984).

Finite-time thermodynamics deals with limits to the control of thermodynamic processes. In standard thermodynamics, a key tool for dealing with such processes is the notion of reversible processes. These take place infinitely slowly, so that the system is never out of equilibrium with its environment. The total entropy remains constant, and there is no loss of ability to convert heat into work. Such reversible processes are then compared with the net effect of real processes to assess the extent of losses.

Real processes, however, of necessity take place in a finite time, and the entropy of the universe consequently must increase, even if these processes are controlled to minimize the amount of entropy production. In finite-time thermodynamics, the physical problem is this: given the total time within which the process must be completed, along which path in thermodynamic phase space should it proceed to minimize the increase in entropy? Salamon and Berry (1983) proved that the dissipated availability is given by the square of the thermodynamic length times a mean relaxation time and divided by the total time of the process. Making the connection between optimal processes and those which minimize thermodynamic length was expanded upon by Nulton, Salamon, Andresen, and Anmin (1985). These notions have also been applied within the context of simulated annealing (Nulton and Salamon, 1988; Ruppeiner, 1988; Salamon *et al.*, 1988; Ruppeiner *et al.*, 1991).

J. Other results on metric geometries of thermodynamics

In this section we discuss some other issues of metric geometry in thermodynamics, a subject which certainly extends beyond fluctuations.

Best known in thermodynamics are affine geometries, geometries with no metric. These have seen application in the state space representation originated by Gibbs to illustrate, among other things, the phases of matter. Tisza (1961) emphasized that though the n-dimensional Gibbs geometry has no well-defined notion of distance in the sense of Riemann (in the purely equilibrium theory!), it nevertheless has a well-defined curvature with respect to the flat $(n+1)$-dimensional embedding space. This curvature, quite different from that featured in this review, has fixed sign, because of the convexity of the thermodynamic potentials. The mathematics of the underlying geometry was developed by Pick and Blaschke (Blaschke, 1923).

Buchdahl (1966) used a Euclidean metric in thermodynamics:

$$(\Delta l)^2=\sum_{\mu=0}^{r}(\Delta x^{\mu})^2 \; . \tag{4.89}$$

This rule for distance permits the notion of the "thermodynamic neighborhood" of a thermodynamic state. We may object, however, to assigning any quantitative physical meaning to such a metric, since the distance between two thermodynamic states will depend on the choice of the coordinate system. Hence perhaps this distance reveals more about the person who chose the coordinates than about the properties of the system of interest!

Peterson (1979) has drawn an analogy between thermodynamics and classical mechanics and has demonstrated that both can be based on a symplectic structure.

Provost and Vallee (1980) applied Riemannian geometry to the structure of quantum mechanics and discussed some issue of the curvature. They connected the curvature to the dispersion of the wave packet.

Diósi *et al.* (1984) used the geometry in this review to make a geometric interpretation of the renormalization-group theory of the critical point. The scaling laws are shown to follow from the assumption of a conformal Killing symmetry in the metric.

Schlögl (1985) related the thermodynamic metric to the scheme of bit-number cumulants.

Sieniutycz and Salamon (1986) applied notions of covariance to the extended nonequilibrium thermodynamics of lumped systems. This program was continued by Sieniutycz and Berry (1989), who wrote down a Lagrangian density leading to the components of the energy-momentum tensor and corresponding conservation laws. Sieniutycz and Berry (1991) applied these ideas to a thermodynamics with fluxes included as thermodynamic parameters, and worked out the thermodynamic Riemannian curvature.

Lukács and Martinás (1986) proved that the postulates of equilibrium thermodynamics (Callen, 1960) do not specify the entropy uniquely. Only the Riemannian structure of the thermodynamic state space is uniquely determined.

Caianiello and Noce (1988) have discussed the Riemannian geometry of thermodynamics within the context of the thermodynamic uncertainty relations.

Sieniutycz and Salamon (1990) have reviewed topics related to thermodynamic fluctuation theory, including a Riemannian metric, within a broader context containing general nonequilibrium theories, and the connection of those topics with extremum principles.

Janyszek and Mrugala (1990b) discussed both Riemannian and Finslerian geometry in thermodynamic fluctuation theory. In particular, they introduced a Finsler-type metric for nonequilibrium thermodynamics.

Pevzner (1991) applied projective differential geometry to the Riemannian metric structure. He calculated various forms of the Gaussian curvature in multicomponent ideal gases.

Obata, Hara, and Endo (1992) applied Riemannian geometry to Uhlenbeck-Ornstein processes and to a random walk.

Krommes and Hu (1993) discussed Riemannian geometry in thermodynamics to examine the proper thermodynamic variables to choose in expressing Onsager reciprocity in irreversible thermodynamics.

V. EXAMPLES

This section presents examples of fluctuations, mostly in simple spin systems whose thermodynamics are known. These are then compared with exact calculations from statistical mechanics.

A. Paramagnet

The first example illustrates that the covariant thermodynamic fluctuation theory not only offers qualitatively new ideas, but quantitative improvements in the simplest of problems.

Consider a subsystem A_N of N noninteracting spins in an environment of an infinite number of identical spins, characterized by a temperature T and an external magnetic field h. Each spin is allowed to be in one of two microstates, up or down, denoted for the ith spin by $\sigma_i=+1$ or -1, respectively. A specification of the values of all σ_i's of A_N denotes the microstate of the subsystem.

Statistical mechanics (Ma, 1985) gives the probability of finding some particular microstate as

$$\frac{1}{Z}\exp\left[-\frac{H}{T}\right], \tag{5.1}$$

where the Hamiltonian is

$$H=-h\sum_{i=1}^{N}\sigma_i\ , \tag{5.2}$$

and the partition function

$$Z=2^N\cosh^N\left[\frac{h}{T}\right]. \tag{5.3}$$

In this example, and the next one, we have set $k_B=1$.

All of the thermodynamics follows from the free energy per spin[50]

$$\omega(T,h)=-\frac{T}{N}\ln Z=-T\ln\left[2\cosh\left[\frac{h}{T}\right]\right]. \tag{5.4}$$

The magnetization for the environment A_{N_0} ($N_0\to\infty$) is

$$m_0=-\left[\frac{\partial\omega}{\partial h}\right]_T=\tanh\left[\frac{h}{T}\right], \tag{5.5}$$

and the entropy per spin, written as a function of the magnetization, is

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[50] Quantities "per spin" for a magnetic system are effectively the same as those "per volume" for fluid systems, since the spins are fixed in place.

$$s(m)=-\left[\frac{\partial\omega}{\partial T}\right]_h=\ln[2\sqrt{1/(1-m^2)}]-(\tanh^{-1}m)m\ . \tag{5.6}$$

Since we may write the entropy as a function just of the magnetization, the Riemannian geometry of this system is one dimensional.

The metric element follows [by Table II, and the magnetic-fluid-analogy equation (3.61)] from differentiating $s(m)$ twice:

$$g=\left[\frac{1}{1-m^2}\right]\ . \tag{5.7}$$

The drift K is zero in these coordinates. Hence, by Eqs. (2.22) and Eq. (4.3), the fluctuation equation is

$$\frac{\partial P}{\partial t}=\frac{1}{2}\frac{\partial^2}{\partial m^2}[(1-m^2)P]\ , \tag{5.8}$$

with $t=1/N$. This equation is subject to the initial condition

$$P_{t\to 0}(m\,|\,m_0)=\delta(m-m_0)\ , \tag{5.9}$$

and boundary conditions at $m=\pm 1$ which preserve normalization:

$$\frac{\partial}{\partial m}(g^{-1}P)=0\ . \tag{5.10}$$

At the boundaries, g^{-1} is zero; so by the reasoning in Sec. II.E, $\langle m\rangle$ will also remain constant, as expected for a standard extensive parameter. Note further that since the derivative of g^{-1} is not zero at the boundary, Eq. (5.10) requires the boundary condition $P=0$, which is used here.

Consider now the numerical solution to Eq. (5.8) for the case $m_0=0.5$. In place of a delta-function initial condition, we use a Gaussian distribution equation (2.9) for $N=50$:

$$P_N(m\,|\,m_0)=\left[\frac{N}{2\pi(1-m_0^2)}\right]^{1/2}\exp\left[-\frac{N(m-m_0)^2}{2(1-m_0^2)}\right]\ . \tag{5.11}$$

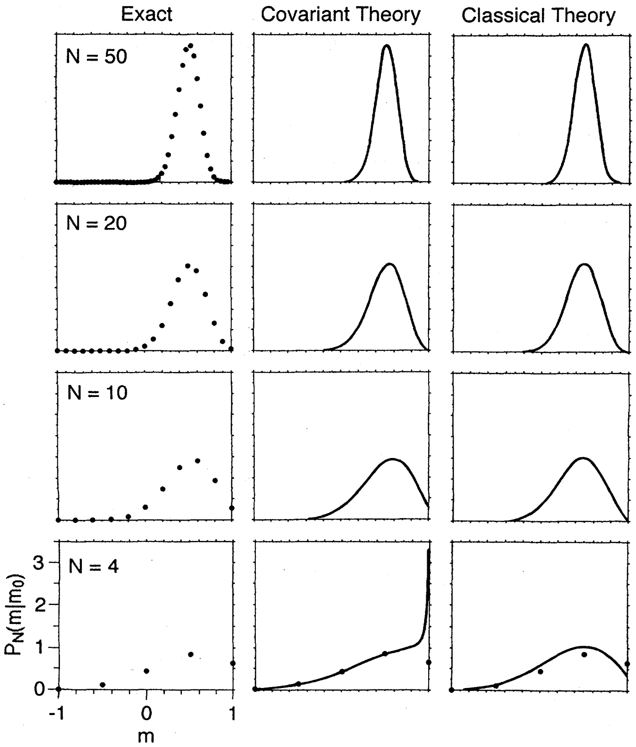

FIG. 9. Fluctuation probability density for the paramagnet computed for four subsystem volumes three different ways: (1) exactly, with the binomial distribution; (2) with the covariant thermodynamic fluctuation theory; and (3) with the full thermodynamic fluctuation theory. The covariant theory yields quantitatively better results than the classical thermodynamic fluctuation theory, as is shown explicitly for $N=4$. The covariant theory, but not the classical theory, mimics the rise at the edges into a limiting delta-function-like behavior.

Results for the covariant and consistent thermodynamic fluctuation theory are shown in column 2 of Fig. 9. As t increases, the curve broadens as fluctuations in m grow. There is a sharp rise in P near $m=+1$ as the curve tries to mimic the true bimodal distribution for the single spin.

For comparison, the fluctuation probability distribution may be evaluated exactly with elementary probability theory, which yields the binomial distribution (Reif, 1965)

$$P_N(m\,|\,m_0)=\frac{N!}{[N(m+1)/2]![N(m-1)/2]!}\left[\frac{1+m_0}{2}\right]^{N(m+1)/2}\left[\frac{1-m_0}{2}\right]^{N(m-1)/2}\ . \tag{5.12}$$

Results are shown in the first column of Fig. 9.

We may sow that the classical thermodynamic fluctuation theory establishes

$$\Delta S_0=N\left[-\frac{ds(m)}{dm}\bigg|_{m=m_0}(m-m_0)+s(m)-s(m_0)\right] \tag{5.13}$$

and

$$P_N(m\,|\,m_0)dm=C\exp(\Delta S_0)dm\ , \tag{5.14}$$

where C is a normalization constant which may be determined from numerical integration of the probability density. Results of this theory are shown in column 3 of Fig. 9. In addition, we point out that, according to Greene and Callen (1951), these results are the same as would be obtained with the canonical ensemble with finite V.

The covariant theory agrees better with the exact results than the classical thermodynamic fluctuation theory. Note that neither the full classical thermodynamic fluctuation theory nor its Gaussian approximation attempts to model the sharp rise in the probability distribution at the end points. Note as well that the covariant theory conserves $\langle m \rangle$, whereas the full classical theory does not. This was verified in the calculations.

B. One-dimensional Ising model

Ruppeiner (1983a) numerically solved the covariant thermodynamic fluctuation equation for the one-dimensional Ising model. The form of the equation was, however, slightly different from that used here in that the *covariant* drift, rather than the drift in the standard densities, was set to zero everywhere. The rationale for such a choice was to avoid restrictions specific to particular coordinates. However, explicit conditions imposed in certain coordinates do not break general covariance; and requiring conservation laws, as first suggested by Diósi and Lukács (1985a), seems very natural. The same is done in general relativity, which is certainly covariant (Misner, Thorne, and Wheeler, 1973).

The 1D Ising model consists of a set of spins as above, but arranged in a line, and each spin interacting with its nearest neighbor, as described by the Hamiltonian

$$H=-J\sum_{i=1}^{\infty}\sigma_i\sigma_{i+1}-h\sum_{i=1}^{\infty}\sigma_i\ , \tag{5.15}$$

where J is the coupling constant. In the ferromagnetic case, adjacent spins tend to align with each other, and J is positive. In the antiferromagnetic case, adjacent spins tend to disalign, and J is negative. It is a straightforward calculation in statistical mechanics (Thompson, 1972) to show that the thermodynamic potential is

$$\phi(x,y)=\ln[e^{x}\cosh y+(e^{2x}\sinh^2 y+e^{-2x})^{1/2}]\ , \tag{5.16}$$

where $x=J/T$, and $y=-h/T$. The metric elements are now straightforward to work out in F coordinates by using the line element in Eq. (3.32) and the magnetic-fluid-analogy equation (3.61).

The comparison procedure (Ruppeiner, 1983a) used $T/J=0.8$ and $h=0$. The probability of the fluctuation in the magnetization of the subsystem of spins was then computed as a function of subsystem size in three different ways: (1) exactly,[51] (2) with the covariant thermodynamic fluctuation theory, and (3) using the full Einstein thermodynamic fluctuation theory. Results are shown in Fig. 10.

The covariant theory yields results superior to the full classical one, even at very large volumes. At small volumes, it predicts the upturn of the magnetization at the edges, which occurs when the spins essentially lock into place with one another either up or down. This happens at subsystem sizes of the order of the correlation length, in this case 6.6 lattice sites (Ruppeiner, 1983a).

To repeat the calculation with exactly the same thermodynamic covariant fluctuation equation as that used here would likely yield even better results, since it explicitly includes the conservation laws.

C. Ideal gas

Fluctuations in the ideal gas were worked out by Ruppeiner (1983b). The classical theory was found to work very well down to volumes of the order of a single molecule (10% deviation at the level of five molecules), as ex-

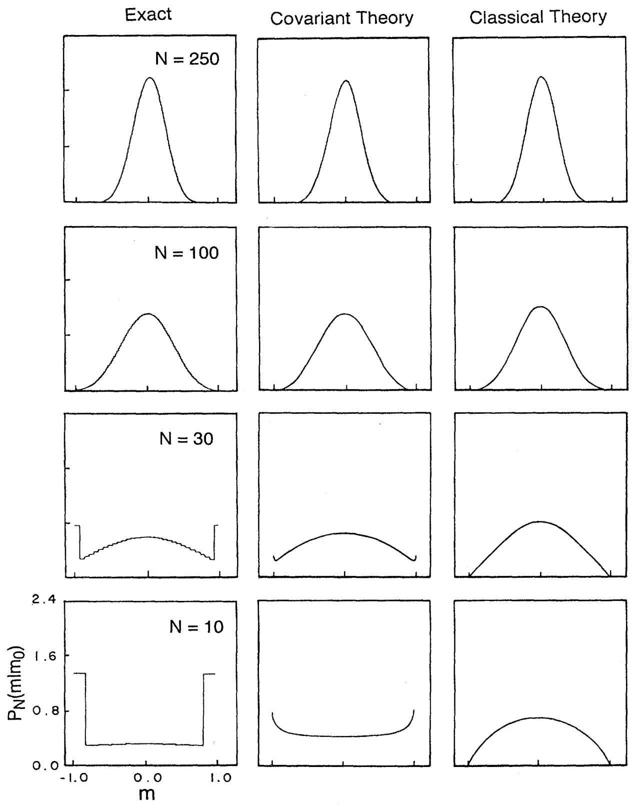

FIG. 10. Fluctuation probability density for the ferromagnetic 1D Ising model computed for four subsystem volumes three different ways: (1) exactly, with statistical mechanics; (2) with the covariant thermodynamic fluctuation theory; and (3) with the full thermodynamic fluctuation theory. The covariant theory yields quantitatively better results generally. In particular, it attempts to mimic the rise at the edges into a limiting delta-function-like behavior.

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[51] The exact calculation was performed beginning with the grand canonical distribution in the thermodynamic limit. Using this, the probability of finding some value m of the magnetization of the finite A_N may be calculated by summing the probabilities of all the microstates in the system in the thermodynamic limit that have value m for the magnetization of the finite A_N. This is a somewhat unusual way to calculate in statistical mechanics. It has been done, for example, by Bruce and co-workers in a number of dimensions (see, e.g., Bruce, 1981).

pected, since the curvature is zero. The covariant theory shows some slight improvement over the classical theory.

VI. THERMODYNAMIC RIEMANNIAN CURVATURE

In this section, we present a three-part discussion of the thermodynamic curvature. The first part reviews calculations of the curvature from the known thermodynamics of several models. An earlier, less detailed review of some of this work was given by Ruppeiner (1990). The second part covers the stability interpretation of the thermodynamic curvature (Janyszek and Mrugała, 1989b). The third part discusses a theory of critical phenomena based on thermodynamic curvature.

A. Thermodynamic curvature for known models

It is natural to calculate the thermodynamic curvature for models whose thermodynamics is known exactly. This has been done by several authors, though not always with the interpretation for thermodynamic curvature featured in this review.

We repeat that, by the rules of Riemannian geometry, the value of the thermodynamic curvature for any particular thermodynamic state is independent of the coordinate system in which it is calculated. The choice of coordinates is one entirely of convenience. This point is essential, since we desire to endow the curvature with an intrinsic physical meaning.

1. Single-component ideal gas

A simple and fundamental example is the single-component ideal gas. Here the constituent molecules are all identical and interact only very weakly with one another. They are allowed, however, to have *internal* energy levels.

The Helmholtz free energy per volume

$$f = u - Ts \tag{6.1}$$

is

$$f(T,\rho) = \rho k_B T \ln\rho + \rho k_B f(T) , \tag{6.2}$$

where $\rho = N/V$ is the density, and where $f(T)$ is some function of the temperature with negative second derivative, to assure a positive-definite heat capacity (Landau and Lifshitz, 1977). We have

$$s = -\left[\frac{\partial f}{\partial T}\right]_\rho \tag{6.3}$$

and

$$\mu = \left[\frac{\partial f}{\partial \rho}\right]_T . \tag{6.4}$$

This yields, with the line element equation (3.38),

$$(\Delta l)^2 = -\frac{\rho f''(T)}{T}(\Delta T)^2 + \frac{1}{\rho}(\Delta\rho)^2 . \tag{6.5}$$

It is instructive to demonstrate (Ruppeiner, 1979) that the curvature is zero simply by making a coordinate transformation to Euclidean coordinates. Define

$$t = \int_{T_0}^{T} \sqrt{-f''(T)/T}\, dT , \tag{6.6}$$

where T_0 is an arbitrary positive constant, and define

$$x^1 = \sqrt{2\rho}\,[\cos(\tfrac{1}{2}t) + \sin(\tfrac{1}{2}t)] \tag{6.7}$$

and

$$x^2 = \sqrt{2\rho}\,[\cos(\tfrac{1}{2}t) - \sin(\tfrac{1}{2}t)] . \tag{6.8}$$

Straightforward computation verifies that

$$(\Delta l)^2 = (\Delta x^1)^2 + (\Delta x^2)^2 , \tag{6.9}$$

which is a locally Euclidean line element. This is sufficient to prove that the ideal gas has zero Riemannian curvature.[52]

Zero curvature was obtained by Ruppeiner (1979) and, independently for a similar metric, by Ingarden *et al.* (1979). It is a very appealing result, clearly linking thermodynamic curvature with interactions. Zero curvature is not essential to make this connection, however. A curvature on the order of the specific volume per molecule would serve as well, and is actually more typical.

Zero curvature also follows from the original metric equation (6.5) using the equation for the Riemannian curvature. For a diagonal metric,

$$(\Delta l)^2 = g_{11}(\Delta x^1)^2 + g_{22}(\Delta x^2)^2 , \tag{6.10}$$

we may readily verify from Eq. (4.70) that the Riemannian curvature scalar is

$$R = \frac{1}{\sqrt{g}}\left[\frac{\partial}{\partial x^1}\left[\frac{1}{\sqrt{g}}\frac{\partial g_{22}}{\partial x^1}\right] + \frac{\partial}{\partial x^2}\left[\frac{1}{\sqrt{g}}\frac{\partial g_{11}}{\partial x^2}\right]\right] . \tag{6.11}$$

Substitution of the line element equation (6.5) immediately yields zero thermodynamic curvature.[53] Despite zero curvature, however, the topology of this Riemannian geometry is not that of the plane (Ruppeiner, 1983b; Nulton and Salamon, 1985), but resembles more a helical structure.

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[52] The curvature for the ideal gas with the particle number rather than the volume as the fixed scale is also zero (Nulton and Salamon, 1985).

[53] When the metric is not diagonal, and of the form

$$(\Delta l)^2 = g_{11}(\Delta x^1)^2 + 2g_{12}\Delta x^1 \Delta x^2 + g_{22}(\Delta x^2)^2 ,$$

it is straightforward to verify from Eq. (4.70) that the Riemannian curvature scalar is (Sokolnikoff, 1964)

$$R = -\frac{1}{\sqrt{g}}\left[\frac{\partial}{\partial x^1}\left[\frac{g_{12}}{g_{11}\sqrt{g}}\frac{\partial g_{11}}{\partial x^2} - \frac{1}{\sqrt{g}}\frac{\partial g_{22}}{\partial x^1}\right] + \frac{\partial}{\partial x^2}\left[\frac{2}{\sqrt{g}}\frac{\partial g_{12}}{\partial x^2} - \frac{1}{\sqrt{g}}\frac{\partial g_{11}}{\partial x^2} - \frac{g_{12}}{g_{11}\sqrt{g}}\frac{\partial g_{11}}{\partial x^1}\right]\right] .$$

2. Ideal paramagnet

Analogous to the monatomic ideal gas is the ideal paramagnet of noninteracting magnetic spins. It is characterized by the equation of state

$$m=f\left[\frac{h}{T}\right], \tag{6.12}$$

where f is some function with positive first derivative (Kittel 1958). This equation of state leads to the theorem

$$\left[\frac{\partial u}{\partial h}\right]_T=0\,. \tag{6.13}$$

The line element in (T,m) coordinates is, from Eq. (3.38) and the magnetic-fluid-analogy equation (3.61),

$$(\Delta l)^2=g_{TT}(\Delta T)^2+g_{mm}(\Delta m)^2\,, \tag{6.14}$$

where

$$g_{TT}=\frac{1}{k_BT}\left[\frac{\partial s}{\partial T}\right]_m, \tag{6.15}$$

and

$$g_{mm}=\frac{1}{k_BT}\left[\frac{\partial h}{\partial m}\right]_T. \tag{6.16}$$

The magnetic equation of state, (6.12), now yields

$$\left[\frac{\partial g_{mm}}{\partial T}\right]_m=0\,, \tag{6.17}$$

and the theorem equation (6.13) yields

$$\left[\frac{\partial g_{TT}}{\partial m}\right]_T=0\,. \tag{6.18}$$

Substituting into the equation for the thermodynamic curvature, (6.11), shows that the thermodynamic curvature is zero for the ideal paramagnet, provided the metric element

$$g_{TT}\neq 0\,. \tag{6.19}$$

If the zero obtains, as is the case if neither the spins nor the underlying lattice possesses internal energy levels, the geometry is singular and effectively one dimensional. This technically has zero curvature as well, since in one dimension we may always find a Euclidean coordinate system.

This example was worked out by Janyszek and Mrugała (1989b), who made several of these points.

3. Multicomponent ideal gas

The thermodynamic curvature of the multicomponent ideal gas is also straightforward to work out (Ruppeiner and Davis, 1990). The Helmholtz free energy per volume is

$$f(T,a^1,a^2,\ldots,a^r)=\sum_{i=1}^{r}a^ik_BT\ln a^i+\sum_{i=1}^{r}a^ik_Bf_i(T)\,, \tag{6.20}$$

where the $f_i(T)$'s are functions of the temperature whose second derivatives are negative to ensure a positive-definite heat capacity (Landau and Lifshitz, 1977). Using the free energy in the metric equation (3.38) yields a diagonal line element

$$(\Delta l)^2=\left[\sum_{i=1}^{r}a^ih_i(T)\right](\Delta T)^2+\sum_{i=1}^{r}\frac{1}{a^i}(\Delta a^i)^2\,, \tag{6.21}$$

where

$$h_i(T)=-\frac{f_i''(T)}{T}>0\,. \tag{6.22}$$

Because of the simplicity of the metric, many of the elements of the curvature tensor vanish, or have the same functional form. Accordingly, it is fairly direct to show with Eq. (4.56) that

$$R=\frac{\sum_{i=1}^{r}h_i(T)\sum_{j=1}^{r}a^jh_j(T)-\sum_{i=1}^{r}a^i[h_i(T)]^2}{2\left[\sum_{i=1}^{r}a^ih_i(T)\right]^2}\,. \tag{6.23}$$

If all of the $h_i(T)$'s are the same, as would be the case were all the constituents of the mixture monoatomic, Eq. (6.23) will reduce to

$$R=\frac{(r-1)}{2\rho}\,, \tag{6.24}$$

where

$$\rho=\sum_{i=1}^{r}a^i \tag{6.25}$$

is the total number density. This is a surprisingly simple result, depending neither on the temperature nor on the relative densities of the component gases. For the single-component ideal gas, $r=1$, and R is zero, as was found above.

The curvature in Eq. (6.24) is on the order of the volume where there is just a single particle present, at which a thermodynamic description must certainly fail. Indeed, Ruppeiner (1983b) explicitly showed that for a single-component ideal gas, the classical thermodynamic fluctuation theory works reasonably well even for volumes containing only a few particles. But for smaller volumes, it breaks down. These results for the thermodynamic curvature are therefore consistent with expectations that such curvature gives the volume where the classical theory breaks down. However, the computation linking curvature to a limiting volume in Sec. IV.C.5 has only been done for $n=2$, and the general significance of curvature in higher dimensions is largely unexplored. So this physical interpretation is perhaps premature.

It has been shown (Ruppeiner and Davis, 1990) that

Eq. (6.24) provides at least a rough estimate for Eq. (6.23) even for general $h_i(T)$'s.

The result (6.24) linking the curvature to the molecular volume seems surprising at first, since molecular properties appear to emerge from a purely thermodynamic calculation, when the thermodynamics has no basic constant with the units of length. The resolution to this apparent paradox is simple: the thermodynamics put into the calculation at first, Eq. (6.20), already contains atomic properties through Boltzmann's constant k_B. The theory of fluctuations, expressed in Eq. (3.1), contains this same constant, which connects thermodynamics with atomic properties. Compagner (1989) has described what happens to thermodynamics in the limit $k_B \to 0$. One consequence of this limit is that thermodynamic fluctuations in the ideal gas disappear at all length scales.

4. Ideal quantum gases

Janyszek and Mrugała (1990a; see also Janyszek, 1986b) worked out the thermodynamic curvature for ideal Fermi and Bose gases. They used the notation of Pathria (1972). The thermodynamic potential

$$\phi\left[\frac{1}{T},-\frac{\mu}{T}\right]=k_B(2S+1)\lambda^{-3}f_{\pm}\left[\frac{5}{2},\eta\right], \tag{6.26}$$

where

$$\lambda=\frac{h}{\sqrt{2\pi m k_B T}} \tag{6.27}$$

is the thermal wavelength,

$$\eta=e^{\mu/(k_B T)}, \tag{6.28}$$

$$f_{\pm}(l,\eta)=\frac{1}{\Gamma(l)}\int_{x=0}^{\infty}\frac{x^{l-1}dx}{\eta^{-1}e^{x}\pm 1}, \tag{6.29}$$

h is Planck's constant, m is the particle mass, S is the particle spin, and $\Gamma(l)$ is the gamma function.[54] The $+$ sign corresponds to the Fermi gas, and the $-$ sign to the Bose gas.

The metric elements are

$$g_{\alpha\beta}=\frac{1}{k_B}\phi_{,\alpha\beta} \tag{6.30}$$

in $F=(1/T,-\mu/T)$ coordinates; see Table II. Janyszek and Mrugała (1989b) demonstrated that if the metric elements may be written purely as the second derivatives of a certain thermodynamic potential, then the thermodynamic curvature may be written in terms of second and third derivatives[55]:

$$R=\frac{k_B}{2}\frac{\begin{vmatrix}\phi_{,11} & \phi_{,12} & \phi_{,22}\\ \phi_{,111} & \phi_{,112} & \phi_{,122}\\ \phi_{,112} & \phi_{,122} & \phi_{,222}\end{vmatrix}}{\begin{vmatrix}\phi_{,11} & \phi_{,12}\\ \phi_{,12} & \phi_{,22}\end{vmatrix}^2}. \tag{6.31}$$

This relationship follows from Eq. (4.70) for the thermodynamic curvature. It appears, at first, somewhat surprising, since generally the curvature depends on the second derivatives of the metric elements. Hence one would expect it to involve fourth derivatives of the potential. But fourth derivatives cancel when the calculation is performed with a metric of the form Eq. (6.30). Gilmore (1984) has also made this point.

Working out the thermodynamic curvature is now a straightforward exercise of evaluating the derivatives:

$$R=-5\lambda^3(2S+1)^{-1}\frac{[f_{\pm}^2(\tfrac{3}{2},\eta)f_{\pm}(\tfrac{1}{2},\eta)-2f_{\pm}(\tfrac{5}{2},\eta)f_{\pm}^2(\tfrac{1}{2},\eta)+f_{\pm}(\tfrac{5}{2},\eta)f_{\pm}(\tfrac{3}{2},\eta)f_{\pm}(-\tfrac{1}{2},\eta)]}{[5f_{\pm}(\tfrac{5}{2},\eta)f_{\pm}(\tfrac{1}{2},\eta)-3f_{\pm}^2(\tfrac{3}{2},\eta)]^2}. \tag{6.32}$$

Janyszek and Mrugała (1990a) reported that for the ideal Fermi gas, R is always positive (in the sign convention of this review), whereas for the ideal Bose gas, it is always negative and diverges strongly as the temperature approaches

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[54] This expression is from Janyszek and Mrugała (1990a) and follows from Landau and Lifshitz [1977, Eq. (55.6)]. To make the transformation from the Landau-Lifshitz (1977) expression to the one used here, note that their $\Omega=-TV\phi$.

[55] These authors used a curvature sign convention the opposite of that used here.

zero.[56] This limit is related to the Bose-Einstein phase transition, which has some analogies with the liquid-vapor phase transition (Pathria, 1972). In both the Fermi and Bose gases, the curvature goes to zero in the limit of the ideal gas.

The possible relationship between the curvature and the correlation volume in this system has not been explored.

5. Takahashi gas

An elementary one-dimensional model of hard rods is the Takahashi gas (Takahashi, 1942; Gürsey, 1950). The rods are impenetrable, and each has length b. There is an attractive square-well potential between adjacent rods:

$$\psi(r)=\begin{cases}\infty, & 0\le r<b\ ,\\ -\varepsilon, & b\le r<2b\ ,\\ 0, & 2b\le r\ ,\end{cases} \tag{6.33}$$

where r is the distance between the centers of the neighboring rods.

For this system, the correlation function is defined as

$$G(r)=\left[\frac{\rho(r)-\rho}{\rho}\right], \tag{6.34}$$

where $\rho(r)$ is the average density at a distance r from some particular rod. A method for finding the correlation function for one-dimensional continuum systems with nearest-neighbor interactions was worked out by Salsburg, Zwanzig, and Kirkwood (1953). For large r, $G(r)$ follows the form of Ornstein and Zernike (Fisher and Widom, 1969):

$$G(r)=\frac{A\exp(-k_1 r)\cos(k_2 r)}{r^{-(d-1)/2}}, \tag{6.35}$$

where A, k_1, and k_2 are all functions of the temperature T and the pressure p. The correlation length $\xi=1/k_1$ gives the range of the envelope of the exponentially decaying envelope of $G(r)$.

Fisher and Widom (1969) examined a correlation function expansion for this system and looked for the term with the longest-ranged exponentially decaying envelope. They showed that there is a locus in the (T,p) plane over which the asymptotic decay of the correlation function crosses from monotonic to oscillatory. In the diffuse gaslike phase, the attractive part of the interaction dominates, and the correlation function decay is monotonic. As one increases the density, at a given low temperature, the long-range part of $G(r)$ becomes oscillatory, as the smallest value of k_1 in the correlation function expansion has corresponding $k_2\neq 0$. This signals that the hard-core repulsive part of the potential has become dominant.

As the system is compressed from low density at fixed low temperature, it undergoes an abrupt pseudo-phase transition from a gaslike phase to a liquidlike phase in which most of the rods remain within each other's potential wells. This resembles an "anomalous first-order phase transition" in which the pressure changes discontinuously, but the density remains fixed (Milton and Fisher, 1983; Fisher and Milton, 1986; Ruppeiner, 1991a). The density corresponding to this transition varies little with the temperature. Indeed, Fisher and Milton (1986) have argued that the laws of thermodynamics require that the density remain thus "fixed" in true phase transitions of this type. Of course a one-dimensional system with finite potential cannot have a true phase transition, but the change in p is nevertheless very abrupt and approaches a true discontinuity as $T\to 0$.

The calculation of the thermodynamic metric poses a special problem for the Takahashi gas, because the only thermodynamic potential that may readily be expressed in terms of its natural variables is the Gibbs free energy:

$$\Phi(T,p,N)=-NT\ln J\left[\frac{p}{T}\right], \tag{6.36}$$

where

$$sJ(s)=\exp\left[\frac{\varepsilon}{T}\right]\exp(-bs)\times\left\{1-\left[1-\exp\left[-\frac{\varepsilon}{T}\right]\right]\exp(-bs)\right\}, \tag{6.37}$$

and k_B has been set to unity. The difficulty with the metric calculation is that all three variables in the Gibbs free energy are allowed to fluctuate, with the condition of the fixed volume appearing as an implicit constraint. The details were worked out by Ruppeiner and Chance (1990).

The thermodynamic curvature is shown in Fig. 11. We use the Gaussian curvature

$$\xi_G\equiv -R/2\ . \tag{6.38}$$

The theory in Sec. IV does not give the constant of proportionality between curvature and the correlation volume, except that its absolute value should be of order unity. For reasons that are not precisely understood, ξ_G is in *excellent* agreement with the correlation length in a number of one-dimensional models, including this one in the gaslike regime, as Fig. 11 clearly shows. Here, the correlation function decay is monotonic.

The curvature at the pseudo-phase transition (corresponding to $\rho^{-1}=3b/2$) is seen to have a narrow negative spike, whose origin is not as yet explained.

In the liquidlike phase, where the correlation function decay is oscillatory, ξ_G is on the order of a rod length.

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[56] Robinson (1951) discussed how to evaluate the functions $f_{\pm}(l,\eta)$ by series, especially necessary for negative l's, when the integral does not converge. There are two small errors in Eqs. (4.17) and (4.21) of Janyszek and Mrugała (1990a): the prefactor 20 should be a 5, and the final $f_{1/2}(\eta)$ in the numerator of Eq. (4.21) should be $f_{-1/2}(\eta)$.

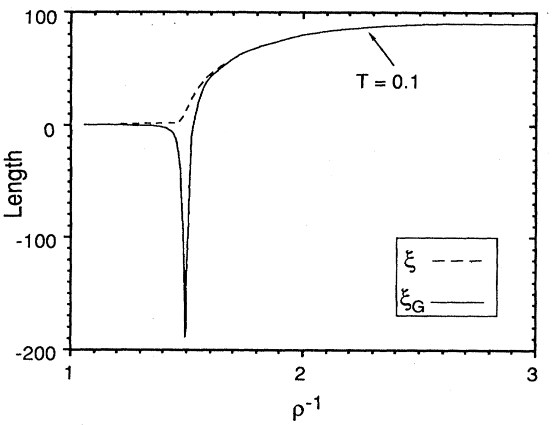

FIG. 11. Correlation length ξ and the thermodynamic Gaussian curvature ξ_G as functions of ρ^{-1} for $T=0.1$ for the Takahashi gas with $\varepsilon=b=1$. Agreement between ξ and ξ_G is excellent in the gaslike phase with ρ^{-1} larger than about 3/2. The curvature ξ_G is seen to possess a narrow negative spike at the pseudo-phase transition $\rho^{-1}=3/2$. In the liquidlike phase, ξ_G is on the order of a rod length.

While the detailed statistical mechanics of fluctuations in the liquidlike phase of this model does not appear to have been worked out, we would expect that, as in the ideal gas, classical thermodynamic fluctuation theory works in the liquidlike phase down to length scales on the order of a rod length. Therefore small curvatures are no surprise.

The thermodynamic curvature was calculated for the thermodynamics not including the kinetic energy. If the kinetic-energy term is included, the results are more difficult to interpret, particularly at small pressures (Ruppeiner and Chance, 1990).

Fisher and Widom (1969) found that, at any given low temperature, the crossover from monotonic to oscillatory occurs at a clearly *higher* density than the pseudo-phase transition. This would appear to conflict with the thermodynamic Riemannian curvature where the crossover from one type of behavior to another happens *at* the pseudo-phase transition. But Fisher and Widom (1969) compared only the *ranges* of the exponentially decaying envelopes of the leading monotonic and oscillatory terms in the correlation function expansion; they did not examine the *amplitudes* of these terms.

Ruppeiner and Chance (1990) noted that the amplitude of the leading monotonic term in the correlation function expansion vanishes at the pseudo-phase transition as $T\rightarrow 0$, and argued that physically the crossover of the correlation function decay happens effectively at the pseudo-phase transition, consistent with the thermodynamic curvature. This resolves the apparent discrepancy. Ruppeiner (1991a) found similar behavior in a triangular potential $\psi(r)$.

6. One-dimensional Ising model

The one-dimensional Ising model has a relatively simple thermodynamics. Its thermodynamic curvature was first worked out numerically by Ruppeiner (1981). A simple and exact expression for R was later found by Janyszek and Mrugała (1989b), who started with the known expression, Eq. (5.16), for the thermodynamic potential, and worked out the metric elements with Eq. (3.32) and the magnetic-fluid-analogy equation (3.61). Equation (6.31) now yields the remarkably simple result (Janyszek and Mrugała, 1989b)

$$-R=\cosh y(\sinh^2 y+e^{-4x})^{-1/2}+1\ , \tag{6.39}$$

consistent with the results of Ruppeiner (1981). Though Ruppeiner's (1981) metric in (T,m) coordinates was diagonal, Eq. (3.32) has the advantage that the metric elements are derivatives of the natural thermodynamic potential.

Ruppeiner (1981) also evaluated the correlation length and found that for the ferromagnetic case $J>0$, where the correlation function decay is monotonic, the thermodynamic Gaussian curvature ξ_G is in excellent agreement with the correlation length, never deviating by more than a single lattice constant. For the antiferromagnetic case $J<0$, the correlation function decay is oscillatory, with a wavelength of the order of the lattice spacing, and ξ_G is always on the order of the separation distance between adjacent spins.

Though the results for the ferromagnetic case $J>0$ are convincing, the ones for the antiferromagnetic case $J<0$ are not clear cut. Let us discuss this, beginning with the statistical mechanics. The introduction of staggered spins and magnetic field,

$$\sigma_i'=(-1)^i\sigma_i\ , \tag{6.40}$$

$$h_i'=(-1)^i h\ , \tag{6.41}$$

and the transformation

$$J'=-J>0\ , \tag{6.42}$$

leads to the Hamiltonian

$$H=-J'\sum_{i=1}^{\infty}\sigma_i'\sigma_{i+1}'-\sum_{i=1}^{\infty}h_i'\sigma_i'\ , \tag{6.43}$$

precisely the same as that for the ferromagnetic $J>0$. Hence, with the staggered quantities, we get the same thermodynamic curvature and correlation length as with $J>0$, and correspondingly good agreement between them.

With unstaggered quantities, Ruppeiner (1983b) noted that for $h=0$ the spins essentially lock into place with one another in a single microstate, with alternating spins, at a length corresponding to the correlation length ξ for the envelope of the oscillatory correlation function. The correlation length ξ diverges as $T\rightarrow 0$. Therefore ξ sets a lower limit on the volume at which thermodynamics may reasonably be applied, and thermodynamic curvatures on the order of a lattice spacing have little physical significance.

Janyszek and Mrugała (1989b) interpreted the results for this model in terms of "stability" (see Sec. VI.B), saying that the $J<0$ case is more stable than the $J>0$ case.

Another viewpoint, however, is to note that the magnetic field h is not the variable conjugate to the "order parameter" in antiferromagnets, which is the staggered magnetization, and that the curvature for $J<0$ was worked out with the "wrong" thermodynamics. As noted above, the use of a staggered magnetization and field leads to the same curvature as the $J>0$ case.

7. Critical point

Perhaps the most significant thermodynamic curvature results so far have been found near the critical point.

Let us begin by describing simple phase transitions and the critical point. The language of magnetic systems is used, but it is easily changed to that of fluid systems (Stanley, 1971; Fisher, 1983). We denote the temperature of the critical point by T_c. It is useful to define the reduced temperature

$$t=\frac{T-T_c}{T_c} . \tag{6.44}$$

The magnetization is m, which acts as the "order parameter." We also define the conjugate "ordering field" h. The order parameter has the property that in zero ordering field, it is zero above T_c and nonzero below it. Figure 12 shows a sketch of the phase diagram for a simple magnetic system near its critical point. Table III gives the notation for critical phenomena, which is reasonably standard.

Thermodynamic quantities behave as power laws near the critical point. These power laws are characterized by critical exponents and critical amplitudes. For example, the specific heat at constant field for $h=0$ is

$$C_h=-\frac{1}{T_c}\frac{\partial^2\omega}{\partial t^2}=A^{\pm}|t|^{-\alpha} , \tag{6.45}$$

where the + and − superscripts on the critical amplitude $A^{\pm}$ refer to the sign of t.[57] Generally, A^+ differs from A^-. A factor of T has been set to the critical temperature, since we are very close to the critical point.

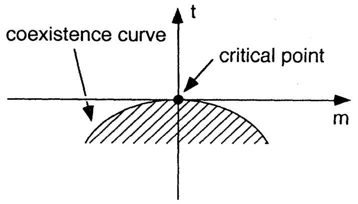

FIG. 12. Schematic of (t,m) space. It shows the critical point, which corresponds to the point of highest temperature at which the system shows zero magnetization in zero magnetic field. At lesser temperatures the system spontaneously magnetizes in one of two directions.

TABLE III. Basic notation for critical phenomena.

$C_h(=-\omega_{,tt}/T_c)=A^+t^{-\alpha}$	$t>0$	$h=0$
$C_h=A^-(-t)^{-\alpha}$	$t<0$	$h=0$
$h=Dm\|m\|^{\delta-1}$	$t=0$	
$h=m\|m\|^{\delta-1}h(x)$		$m\neq 0$
$m(=-\omega_{,h})=B(-t)^{\beta}$	$t<0$	$h=0$
$t=\frac{T-T_c}{T_c}$		
$x=t\|m\|^{-1/\beta}$		$m\neq 0$
$z=h\|t\|^{-\beta\delta}$	$t\neq 0$	
$\xi=\xi_0^+t^{-\nu}$	$t>0$	$h=0$
$\xi=\xi_0^-(-t)^{-\nu}$	$t<0$	$h=0$
$\omega(t,h)=\|t\|^{2-\alpha}Y(z)$	$t\neq 0$	
$\chi_t(=-\omega_{,hh})=\Gamma^+t^{-\gamma}$	$t>0$	$h=0$
$\chi_t=\Gamma^-(-t)^{-\gamma}$	$t<0$	$h=0$

As another example, consider the isothermal susceptibility for $h=0$:

$$\chi_t=-\frac{\partial^2\omega}{\partial h^2}=\Gamma^{\pm}|t|^{-\gamma} . \tag{6.46}$$

Yet another example is the spontaneous magnetization curve for $h=0$ and $t<0$:

$$m=-\frac{\partial\omega}{\partial h}=\pm B(-t)^{\beta} . \tag{6.47}$$

There is also a relation on the critical isotherm $t=0$:

$$h=Dm|m|^{\delta-1} . \tag{6.48}$$

These power laws appear even in "classical" theories, such as that of van der Waals, for which the critical exponents have values $\alpha=0, \beta=1/2, \gamma=1$, and $\delta=3$ (Fisher, 1983). Generally speaking, the behavior at the critical point is nonanalytic. Namely, the free energy cannot be expanded in a Taylor series, and the critical exponents are neither integers nor simple fractions.

An essential ingredient in the modern picture of critical phenomena is scaling, namely, the hypothesis that the free energy per volume near the critical point is a generalized homogeneous function of its arguments (Widom, 1965; Kadanoff, 1966; Stanley, 1971; Fisher, 1983):

$$\omega(t,h)=n_1|t|^{\beta(\delta+1)}Y(n_2h|t|^{-\beta\delta}) , \tag{6.49}$$

where $Y(\ )$ is a function of one variable and n_1 and n_2 are constants. (These constants are not needed for the statement of scaling, but are needed for the statement of universality below.) It is straightforward to verify that this assumption implies that only two of the critical exponents are independent of each other; there exists a class of scaling equations among them. For example,

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[57] In most treatments of critical phenomena, the free energy ω is denoted by f, a symbol which has another meaning in this review; "f" was used as well by Ruppeiner (1991b, 1993).

$\gamma=\beta(\delta-1)$ and $2-\alpha=\beta(\delta+1)$.

Note, this free energy per volume is only that connected with critical phenomena, the nonanalytic singular part. There is, in addition, a regular background part, which plays only a weak role in the critical properties and which we do not consider further here.

Another essential ingredient in critical phenomena is universality, which asserts that the critical exponents and the function $Y(\,)$ are the same within given "universality classes," differentiated by their spatial and the order-parameter dimensionalities. For example, all pure fluids are in the same universality class, that of the three-dimensional Ising model. The constants n_1 and n_2 are material dependent and differentiate between systems in the same universality classes.

In addition, there is the hyperscaling relation (Widom, 1974), which relates the correlation volume ξ^d to $\omega(t,h)$. The basic idea is that the (extensive) free energy associated with fluctuations at volumes of the order of ξ^d is $k_B T_C$. The free energy is equated to the singular part of the (extensive) free energy near the critical point and, therefore, to the singular part of the free energy *per volume,*

$$\omega(t,h)=\kappa_1 \frac{k_B T_C}{\xi^d} , \tag{6.50}$$

where κ_1 is a dimensionless constant of order minus unity. Equation (6.50) is equivalent to Eq. (2.51), by Eq. (3.43) with the replacement $T\rightarrow T_C$. It is a simple exercise to show that Eq. (6.50) leads to the exponent relation

$$d\nu=2-\alpha , \tag{6.51}$$

where ν is the correlation length exponent; see Table III.

"Two-scale factor universality" (Stauffer *et al.*, 1972) includes the above statements about scaling, universality, and the correlation volume and adds one more. It can be written as four independent statements: (1) $\omega(t,h)$ is a generalized homogeneous function of its arguments; (2) the function $Y(\,)$ is universal up to the two material-dependent constants n_1 and n_2, one for the function and the other for its argument; (3) $\omega(t,h)$ is proportional to the inverse of the correlation volume; and (4) κ_1 is a universal constant.

The thermodynamic metric is given by Eq. (3.41); and very near the critical point, T in the prefactor may be regarded as a constant and

$$g_{\alpha\beta}=-\frac{1}{k_B T_C}\omega_{,\alpha\beta} , \tag{6.52}$$

in coordinates (t,h). Equation (6.31), with an extra factor of $-T_C$, now allows us to calculate the curvature by using a series expansion of the function $Y(\,)$ for small values of its argument. For $h=0$,

$$R=\frac{(\beta\delta-1)(\delta-1)k_B T_C}{(\beta\delta+\beta-1)(1+\delta)Y(0)}t^{\alpha-2} . \tag{6.53}$$

To get this expression, it was assumed that the order parameter $m=-\omega_{,h}$ in zero field is zero, and hence $Y'(0)=0$. This means that it is valid only for $t>0$. This result was obtained by Ruppeiner (1990) and, in a more roundabout manner, by Ruppeiner (1979).

By Eq. (6.51) we see that the thermodynamic curvature diverges at the critical point in the same way as the correlation volume (Ruppeiner, 1979). In addition, the specific heat is

$$C_h=-\frac{(2-\alpha)(1-\alpha)Y(0)t^{-\alpha}}{T_C} . \tag{6.54}$$

Since the specific heat must be positive, and since α is typically near zero (Fisher, 1983), we see that $Y(0)$ must be negative. Therefore, with typical values of the critical exponents, R must be negative. The quantity

$$RC_h t^2=-\beta(\delta-1)(\beta\delta-1)k_B \tag{6.55}$$

is a universal constant, consistent with the prediction of two-scale factor universality (Stauffer *et al.*, 1972). This means that both the amplitude of the curvature and its exponent are the same as those of the correlation volume.

The relation between the correlation length and the curvature will be explored further in Sec. VI.C.

8. van der Waals model

Also straightforward to calculate is the thermodynamic curvature for the van der Waals model, which Janyszek (1990) worked out for closed systems. Ruppeiner (1990) gave some discussion of this model for open systems, and the discussion is extended here.

The Helmholtz free energy per volume of the van der Waals model is

$$f(T,\rho)=\rho k_B T \ln\left[\frac{\rho}{\rho_0}\right]+\rho k_B e(T) -\rho k_B T\ln(1-b\rho)-ak_B\rho^2 , \tag{6.56}$$

where $e(T)$ is a function of T with a negative second derivative, and a, b, and ρ_0 are constants (Landau and Lifshitz, 1977). For a gas with constant heat capacity per molecule c_v (dimensionless and of order unity, e.g., 3/2 for the monatomic ideal gas),

$$e(T)=-c_v T\ln\left[\frac{T}{T_0}\right]+\varepsilon_0 , \tag{6.57}$$

where T_0 and ε_0 are constants. From Eq. (3.38) we see that the metric is diagonal, with metric elements

$$g_{TT}=\frac{\rho c_v}{T^2} \tag{6.58}$$

and

$$g_{\rho\rho}=\frac{1}{\rho(1-b\rho)^2}-\frac{2a}{T} . \tag{6.59}$$

The curvature may be worked out with Eq. (6.11):

$$R=\{-(1-b\rho)[-2a^2\rho+6a^2b\rho^2-6a^2b^2\rho^3+2a^2b^3\rho^4+2aT -ac_vT-2ab\rho T+3abc_v\rho T-3ab^2c_v\rho^2T+ab^3c_v\rho^3T+bc_vT^2]\}[c_v(-2a\rho+4ab\rho^2-2ab^2\rho^3+T)^2]^{-1}\,. \tag{6.60}$$

Of interest is the thermodynamic curvature near the critical point, which is characterized by having both the metric element $g_{\rho\rho}$ and its first derivative with respect to ρ be zero. It has parameters (Landau and Lifshitz, 1977)

$$T_c=\frac{8a}{27b} \text{ and } \rho_c=\frac{1}{3b}\,. \tag{6.61}$$

Using Eq. (6.60) for the thermodynamic curvature, and substituting the critical density ρ_C and the reduced temperature t, yields, to leading order in t,

$$R=-\frac{3b}{2c_v}t^{-2}\,. \tag{6.62}$$

The specific-heat exponent $\alpha=0$; so R has the same critical exponent as the correlation volume, by the scaling relation (6.51). The amplitude is on the order of the molecular volume. The same is true of the correlation volume amplitude ξ_0^d (Sengers and Levelt Sengers, 1978).

Very near the critical point, the specific heat is

$$C_\rho=-T_C\frac{\partial^2 f}{\partial T^2}=\frac{c_v k_B}{3b}\,, \tag{6.63}$$

and the combination

$$RC_\rho t^2=-\frac{1}{2}k_B\,, \tag{6.64}$$

to leading order in t. This is in agreement with the result from the two-scale factor universality equation (6.55), with the classical exponents $\beta=1/2$ and $\delta=3$.

Janyszek and Mrugała (1989b) worked out another mean-field-theory model, the Curie-Weiss model, with similar results.

One may wonder what the curvature does at first-order phase transitions. The answer for the van der Waals gas is—nothing special. By Eq. (6.60), the curvature diverges only when the denominator goes to zero, which it does at the critical point and along the spinodal curve. Focusing on its effect on correlation length, Widom (1974) argued that the correlation length remains at about the thickness of the interface between the two phases. This thickness is finite except at the critical point.

9. Other cases

Casas-Vazquez and Jou (1985) evaluated the Riemannian curvature scalar of the ideal gas using the formalism of extended irreversible thermodynamics, including a heat current as an additional thermodynamic parameter. This treatment required a three-dimensional Riemannian manifold. These authors used the particle number rather than the volume as the fixed subsystem size parameter. The use of closed rather than open subsystems makes a physical interpretation of thermodynamic curvature in terms of this review unclear, and the authors did not attempt it.

Mijatovic, Veselinovic, and Trencevski (1987) evaluated the geometry in the paramagnetic ideal gas, which is represented by a three-dimensional Riemannian geometry. These authors, however, used the "energy form" of the metric, which differs from the one used here by a multiplicative factor inversely proportional to the temperature. They also used the particle number as the fixed scale.

Sieniutycz and Berry (1991) also worked out the thermodynamic curvature in a formalism of extended irreversible thermodynamics. They related their results to those of Casas-Vazquez and Jou (1985).

B. Stability interpretation of the thermodynamic curvature

Janyszek and Mrugała (1989b) offered an alternative interpretation of the thermodynamic curvature. They suggested that R is a measure of the stability. Namely, the larger the R (in the sign convention used here), the more stable the system. This interpretation was partially motivated by the results for the 1D Ising model, where the magnetization in the ferromagnetic case has large fluctuations at low temperatures and zero field, but corresponding states for the antiferromagnetic case have small fluctuations. Hence, in the former case, large groups of spins flop back and forth, and it is in this sense less stable.

Also compelling is the work by these authors on the boson and fermion ideal gases, discussed in Sec. VI.A.4. These fundamentally different systems have thermodynamic curvature with opposite signs. For the Bose gas, R is negative, and for the Fermi gas it is positive, indicating that the Bose gas, with the effectively attractive interactions, is the less stable.

The stability interpretation is certainly intellectually appealing and offers a direct interpretation of the sign of the Riemannian curvature, which the interpretation featured here has not. There are, however, some questions the stability interpretation has not yet addressed. It has not offered an interpretation for the units of the thermodynamic curvature. Nor has it explained why the amplitude and the critical exponent of the thermodynamic curvature are those of the correlation length. It also lacks a statistical foundation, so it is unclear why it should offer a measure of stability in some new distinct way.

In addition, Janyszek (1990) has postulated that the sign of the thermodynamic curvature shall always be the same for any system near the critical point. This postulate places a restriction on the values of the critical exponents:

$$\gamma > \alpha \, , \tag{6.65}$$

in accordance with what is presently known. This suggests the viewpoint that the first law of thermodynamics makes a statement about the first derivatives of the entropy; the second law, the second derivatives; and the curvature, a statement about the third derivatives.[58] A statement about the third derivatives of the entropy is certainly in the spirit of the geometric equation (2.52), but the postulate about the sign of the curvature is less restrictive and does not explicitly involve fluctuations.

C. Riemannian geometric theory of critical phenomena

Here we shall summarize the Riemannian geometric theory of critical phenomena (Ruppeiner, 1990, 1991b, 1993).

Again, Eq. (2.52) gives the connection between the thermodynamic curvature and the free energy:

$$R = -\kappa \frac{k_B}{\phi} \, , \tag{6.66}$$

where κ is a dimensionless constant of order unity.[59] More frequently encountered in the literature of critical phenomena is the thermodynamic potential $\omega(t,h)$. By Eq. (3.43)

$$R = \kappa \frac{k_B T_C}{\omega} \, , \tag{6.67}$$

where we have set $T = T_C$, an approximation that suffices for the asymptotic critical properties, but not if we are interested in corrections to this, a subject not pursued here.

The metric is given by Eq. (6.52), and the curvature follows from Eq. (6.31):

$$-\frac{\begin{vmatrix} \omega_{,tt} & \omega_{,th} & \omega_{,hh} \\ \omega_{,ttt} & \omega_{,tth} & \omega_{,thh} \\ \omega_{,tth} & \omega_{,thh} & \omega_{,hhh} \end{vmatrix}}{2 \begin{vmatrix} \omega_{,tt} & \omega_{,th} \\ \omega_{,th} & \omega_{,hh} \end{vmatrix}^2} = \frac{\kappa}{\omega} \, . \tag{6.68}$$

Expanding the determinants yields

$$\begin{aligned}(&\omega_{,tt}\omega_{,thh}\omega_{,thh} - \omega_{,th}\omega_{,thh}\omega_{,tth} - \omega_{,tt}\omega_{,hhh}\omega_{,tth} \\ &+ \omega_{,hh}\omega_{,tth}\omega_{,tth} + \omega_{,th}\omega_{,hhh}\omega_{,ttt} - \omega_{,hh}\omega_{,thh}\omega_{,ttt}) \\ &\times [2(\omega_{,tt}\omega_{,hh} - \omega_{,th}\omega_{,th})^2]^{-1} = \frac{\kappa}{\omega} \, . \end{aligned} \tag{6.69}$$

The geometric equation may be reduced to a third-order nonlinear ordinary differential equation (Ruppeiner, 1991b) by the substitution

$$\omega(t,h) = |t|^a Y(z) \, , \tag{6.70}$$

where

$$z = h|t|^{-b} \, . \tag{6.71}$$

The function $Y(z)$ has different branches for $t > 0$ and $t < 0$ which join smoothly at $t = 0$. This substitution equation is exactly the scaling form of the free-energy equation (6.49). The constants a and b are free parameters in the theory and are related to the usual critical exponents by a comparison with Eq. (6.49):

$$a = 2 - \alpha = \beta(\delta + 1) \tag{6.72}$$

and

$$b = \beta\delta \, . \tag{6.73}$$

The resulting ordinary differential equation is of the form

$$Y^{(3)}(z) = F_\kappa[z, Y(z), Y'(z), Y''(z)] \, , \tag{6.74}$$

where the function F_κ is a ratio of polynomials too lengthy to write out here. The terms quadratic in $Y^{(3)}(z)$ in Eq. (6.69) cancel. It may be shown (Ruppeiner, 1991b) that the solution of the differential equation is regular at $z = 0$ and $t > 0$ if and only if

$$\kappa = \frac{(b-1)(2b-a)}{a(a-1)} \, , \tag{6.75}$$

the value used henceforth.

A third-order differential equation in the form of Eq. (6.74) can be solved uniquely in the neighborhood of any nonsingular point, provided exactly three constants of integration are given (Ince, 1956). These constants of integration are connected with the following three conditions, the first two of which are readily proved from the geometric equation: (1) if $Y(z)$ is a solution, then $n_1 Y(z)$ is a solution; (2) if $Y(z)$ is a solution, then $Y(n_2 z)$ is a solution. The third integration constant is connected with the following standard assumption: (3) the order pa-

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[58] This viewpoint was expressed to me by H. Janyszek and R. Mrugała.

[59] The negative sign is introduced to have κ be positive, as in Ruppeiner (1990, 1991b). Both the dimensionless constants κ_1 and κ_2 are negative in systems like the pure fluid. Near the critical point, ϕ is positive and R is negative. In the earlier references the geometric equation was expressed in terms of $\omega(= -T\phi)$, which was denoted by the symbol "f," since that is standard usage in the literature of critical phenomena. In this review, the symbol "f" is reserved for the Helmholtz free energy (see Table I).

rameter $m=-\omega_{,h}$ is zero in zero field h at temperatures above the critical temperature.

Conditions (1) and (2) are exactly consistent with the prediction of two-scale factor universality. The constants n_1 and n_2 are equivalent to the scaling factors in Eq. (6.49). It can be shown that condition (3) results, with the geometric equation, in a free energy that is an even function of h. The case of asymmetric solutions will be discussed below.

A convenient test case is offered by the mean-field-theory exponents (Fisher, 1983) $\beta=1/2$ and $\delta=3$. The free energy resulting from the geometric equation is found to be analytic everywhere in the one-phase region (Ruppeiner, 1991b) and results in *exactly*

$$h=d_1 mt+d_2 m^3 , \tag{6.76}$$

where d_1 and d_2 are constants. This corresponds to the well-known mean-field-theory equation of state (Kadanoff *et al.*, 1967). In addition, the specific heat may be found with the geometric equation, and the universal ratio of specific-heat amplitudes $A^+/A^-=1/4$ is exactly that found by Brezin *et al.* (1974) with renormalization-group theory for mean-field theory.

A more physically meaningful case is the 3D ferromagnetic Ising model, with critical exponents near $\beta=5/16$ and $\delta=5$ (Liu and Fisher, 1989). With these values for the critical exponents, a solution to the geometric equation may again be worked out with the same basic procedure as that followed for the mean-field-theory exponents (Ruppeiner, 1991b). Qualitatively, the free energy looks similar to that of the mean-field-theory exponents, but with one major difference. The solution curve intersects a line of singularities, which results in a discontinuity in the second derivatives of the free energy along a curve above the critical temperature. Ruppeiner (1991b) chose the smoothest solution possible.

We might take the view that the discontinuity is a feature of the theory which should be sought in the analysis of experimental data, since it is not ruled out by any general principle of thermodynamics or statistical mechanics (Griffiths, 1967). If it existed, it would show up as a discontinuity of the order of 5% in the isothermal compressibility along a supercritical curve intersecting the critical point. Ruppeiner (1992) has concluded that present pure-fluid pressure volume temperature data are not sufficient to rule it out.

However, in light of present theoretical understanding of the critical point, such a nonanalyticity seems unlikely in real systems. It is believed that the critical properties fall into universality classes according to the spatial and order-parameter dimensionalities. The pure fluid falls into the same universality class as the three-dimensional Ising model, whose free energy is certainly analytic everywhere except the critical point and the phase boundary (Ruelle, 1969). Hence a more realistic attitude to take with respect to the discontinuity is that it is perhaps an undesirable feature of the theory, which one should work to correct. One possible explanation is that either t or h does not correspond to the true physical reduced temperature or ordering field, and that a transformation of coordinates to the true physical ones would remove the singularity.

Compare now the predicted results for the 3D Ising exponents with known results. It is conventional to use the Griffiths (1967) form of the equation of state:

$$h=m|m|^{\delta-1}h(x) , \tag{6.77}$$

where

$$x=t|m|^{-1/\beta} . \tag{6.78}$$

Define, as well, the related constants

$$h_0=h(x)|_{x=0}=D \tag{6.79}$$

and

$$x_0=-x|_{h=0,t<0}=B^{-1/\beta} . \tag{6.80}$$

Figure 13(a) shows $h(x)/h_0$ as a function of $(x+x_0)/x_0$ computed from the geometric equation (Ruppeiner, 1991b); it depends only on the values of the critical exponents and is hence universal. A universal curve in these variables is in accordance with expectations from scaling and universality. Figure 13(b) shows the known 3D Ising curve (Domb, 1974). The agreement is close, within about 10% over the full range.

Another important example is the pure fluid. To make the translation between magnetic systems and fluid systems, we use

$$m\rightarrow(\rho-\rho_C)/\rho_C \tag{6.81}$$

and

$$h\rightarrow[\mu-\mu(T)/\mu_C] , \tag{6.82}$$

where ρ_C and μ_C are the critical density and critical chemical potential, respectively, and $\mu(T)$ is the chemical potential along the critical isochore and coexistence curve. The pure fluid was historically analyzed using critical exponents near $\beta=0.35$ and $\delta=4.45$ (Levelt Sengers, 1974).[60] The pure-fluid exponents lead to a solution that is qualitatively similar to that for the 3D Ising exponents, including a discontinuous second derivative of the free energy. Figure 14 shows the theory compared with experiment in four pure fluids. The match is evidently very good and could certainly be improved by varying the critical exponents to produce the best fit.

In real physical problems, the free energy is not typically an even function of h. In the modern theory of critical phenomena, this is generally handled with the mixing-of-coordinates scheme of Rehr and Mermin (1973):

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[60] More recent measurements and analyses of fluid data (Pittman *et al.*, 1979; Albright *et al.*, 1987) indicate that very near the critical point the pure fluid exponents become those of the 3D Ising model, as expected from universality.

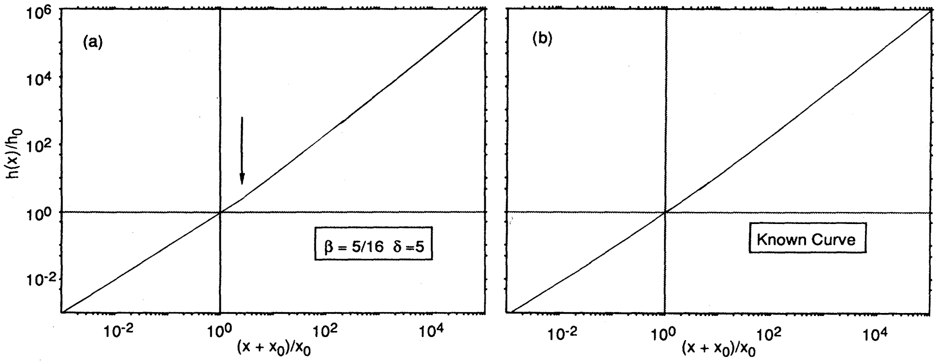

FIG. 13. Quantity $h(x)/h_0$ as a function of $(x+x_0)/x_0$ computed two different ways: (a) from the geometric equation with $\beta=5/16$ and $\delta=5$; and (b) from the known results for the 3D Ising model (Domb, 1974). The down-pointing arrow in (a) corresponds to the place where the geometric equation curve suffers a discontinuity in the slope. The Ising curve shows no such discontinuity. The curves are in good agreement with each other, within about 10% over the full range shown.

$$u=c_1t+c_2h \tag{6.83}$$

and

$$v=c_3t+c_4h\ , \tag{6.84}$$

where u and v are the new thermodynamic parameters, and the coefficients c_1, c_2, c_3, and c_4 are constant.

The mixing of coordinates has been demonstrated to be consistent with the Riemannian geometric theory of critical phenomena (Ruppeiner, 1993). Furthermore, with the scaled form of the free energy and the assumption of universality, this appears to be the only scheme for introducing into the theory an asymmetry that does not have a singularity in the free energy near the critical isochore.

These results merely scratch the surface of the problems in the theory of critical phenomena. A question of obvious importance is the possibility of including a logarithmic term in the solution of the geometric equation. Such a term dominates the critical-point specific heat in, for example, the two-dimensional Ising model (Onsager, 1944). Another issue of interest is how to include nonsingular "background" terms in the free energy. Such a question would be of particular interest for cases with negative heat-capacity exponents α. A problem of a somewhat higher order of difficulty is that of including more thermodynamic variables, as needed, for example, near tricritical points. This raises the whole question of the proper form of the geometric equation in this case, since Eq. (6.66) does not necessarily generalize to higher dimensions. These considerations may also reveal how to deal with the issue of "corrections to scaling," which emerges if we are interested in deviations from the asymptotic critical behavior.

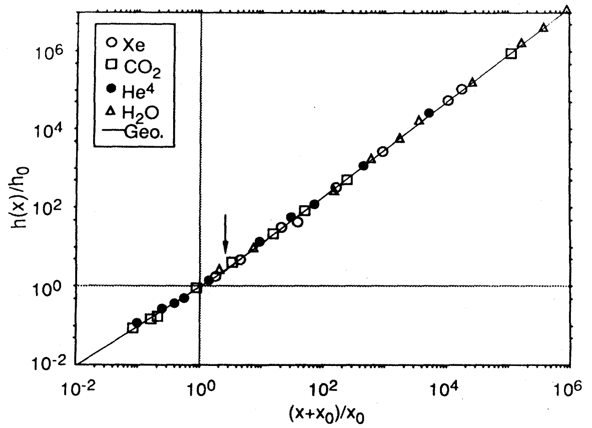

FIG. 14. Quantity $h(x)/h_0$ as a function of $(x+x_0)/x_0$ computed from the geometric equation with $\beta=0.35$ and $\delta=4.45$ and determined from experiment in four pure fluids (Levelt Sengers, 1974). The down-pointing arrow indicates the discontinuity in the slope of the geometric equation curve. The match between theory and experiment is very good.

Donato and Valenti (1994) examined the general properties of the geometric equation. They treated a general class of third-order hyperbolic nonlinear partial differential equations in two variables, with solutions in some sense as well behaved as possible. Namely, discontinuities in the derivatives never evolve into shocks. Not yet resolved, however, are such fundamental issues as what general boundary conditions are required to specify a unique solution and make it a "well-posed problem" (Garabedian, 1964).

We may inquire into other possible forms for the connection between the thermodynamic curvature and the free energy. A more general equation is

$$R+\alpha_1+\frac{\alpha_2}{R}+\frac{\alpha_3}{R^2}+\cdots$$
$$=-\frac{\kappa k_B}{\phi}+\beta_1+\beta_2\phi+\beta_3\phi^2+\cdots\ . \tag{6.85}$$

The constants $\alpha_1\ldots\beta_1\ldots$ must be formed from quantities with units of length. This means that they are unlikely to have universal values, because there are no universal constants in thermodynamics or statistical mechanics with

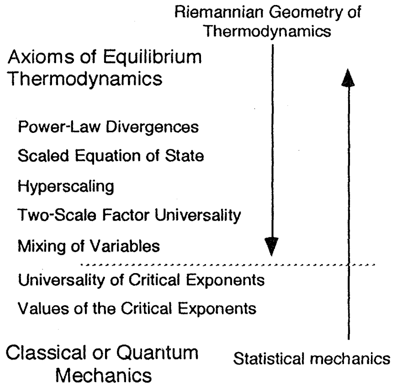

FIG. 15. Basic context of the Riemannian geometric theory of critical phenomena. The top of the diagram represents macroscopic, and the bottom microscopic. Statistical mechanics, augmented by renormalization-group theory, may be used to "build up" from the microscopic to deduce information about the macroscopic. In contrast, the covariant thermodynamic fluctuation theory "builds down" from the macroscopic using Riemannian geometry. Microscopic details enter the theory through the values of the critical exponents.

the units of length. Nonuniversal quantities, such as the critical density, would have to be considered. Thus the form of this more general equation would not be expected to be universal. This is an unexplored area.

This theory forms a logical completion of the structure developed in this review, where we "build down" from the thermodynamic limit to extract information about finite subsystems. This is the inverse of the process in statistical mechanics, where we "build up" from the microscopic to get at the macroscopic (see Fig. 15). The basic philosophy is perhaps not too different from that expressed by Mandelbrot (1956): "Since, therefore, the kinetic foundations of thermodynamics are not sufficient in the absence of further hypotheses of randomness, are they still quite necessary in the presence of such hypotheses? Or else, could not one 'short-circuit' the atoms, by centering upon any element of randomness... ."

VII. CONCLUSIONS

This review has examined several aspects of thermodynamic fluctuation theory, with emphasis on the explicit inclusion of the concepts of covariance and consistency. These are naturally developed using the language of Riemannian geometry.

The covariant thermodynamic fluctuation theory has the same form in all coordinate systems and conserves energy and mole numbers at all subsystem volumes. In addition, it may be applied consistently to fluctuations within subsystems. Coupled with these concepts is an extension of the basic structure of thermodynamic fluctuation theory beyond the classical one of a subsystem in contact with an infinite uniform reservoir. Used here is a hierarchy of concentric subsystems, each of which samples only the thermodynamic state of the subsystem immediately larger than itself. Tests on known models reveal qualitative improvements over the classical theory.

This theory has microscopic foundations. These make it clear that the basic rules for fluctuations at volumes less than the correlation volume must be fundamentally different from those near the thermodynamic limit. They are yet to be completely discovered. However, present evidence suggests that the principle of Markovicity offers at least a foundation for a thermodynamic theory at such volumes.

Of special interest is the Riemannian thermodynamic curvature, which gives a lower bound for the volume where the classical theory based on the assumption of a uniform environment may work. Physically, there are good reasons to believe that near the critical point this volume should be the correlation volume, and straightforward evaluation of the curvature in several models confirms this. The combination of the interpretation of the thermodynamic curvature with a simple postulate of critical phenomena yields a purely thermodynamic theory of critical phenomena. It is consistent with several aspects of the modern theory of critical phenomena.

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