Asymmetric free energy from Riemannian geometry

George Ruppeiner
Division of Natural Sciences, New College of the University of South Florida, Sarasota, Florida 34243
(Received 10 February 1992; revised manuscript received 21 September 1992)

It is shown how to include free energies not symmetric in the ordering field in a recent Riemannian geometric theory of critical phenomena [G. Ruppeiner, Phys. Rev. A **44**, 3583 (1991)]. A mixing of coordinates scheme, as is conventionally used to deal with asymmetry, is proved to be consistent with the geometric theory. Furthermore, with scaled forms of the free energy and the assumption of universality, this appears to be the only scheme for including asymmetry in this theory which does not introduce a singularity near the critical isochore.

PACS number(s): 05.70.−a, 02.40.−k, 05.40.+j, 64.10.+h

I recently introduced a thermodynamic theory of critical phenomena based on Riemannian geometry [1]. The resulting singular part of the scaled free energy near the critical point is generally in good agreement with known results for simple critical points. As input one need only supply the values of the critical exponents. The solution process of Ref. [1], however, was limited to free energies symmetric in the ordering field. But asymmetric free energies appear to have physical importance as well (e.g., the pure fluid), and the Riemannian geometric theory should address this. In this paper I prove that a mixing of coordinates scheme, as is conventionally used to deal with asymmetry [2], is consistent with this theory. Furthermore, I show that with scaled forms of the free energy and the assumption of universality this appears to be the only scheme for including asymmetry in this theory which does not introduce a singularity near the critical isochore.

The Riemannian metric here originated from the thermodynamic theory of fluctuations and is constructed from the second derivatives of the free energy. The resulting theory of critical phenomena is based on this hypothesis: *The Riemannian curvature scalar is proportional to the inverse of the free energy.* Though my method should generalize, I consider only the case of systems with a single-order parameter m, with conjugate ordering field h, and a reduced temperature

$$t=\frac{(T-T_C)}{T_C}\ , \tag{1}$$

where T_C is the critical temperature [3].

Introduce now the notation of fluctuations and Riemannian geometry. Consider a finite, open subsystem A' of an infinite system A. A' has fixed volume V'. Denote the thermodynamic state of A by $a=(a_1,a_2)=(t,h)$ and the corresponding thermodynamic state of A' by $a'=(t',h')$. The Gaussian approximation to the classical thermodynamic fluctuation theory asserts that the probability of finding the thermodynamic state of A' between a' and $a'+da'$ is [4,5]

$$P(a,a')da'_1da'_2=\left[\frac{V'}{2\pi}\right]\exp\left[-\frac{V'}{2}\sum_{\mu,\nu=1}^{2}g_{\mu\nu}(a)\Delta a'_\mu\Delta a'_\nu\right]\times\sqrt{g(a)}\,da'_1da'_2\ , \tag{2}$$

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

$$g_{\mu\nu}(a)=-\frac{1}{k_BT_C}\frac{\partial^2 f}{\partial a_\mu\partial a_\nu}=-\frac{1}{k_BT_C}f_{,\mu\nu}\ , \tag{3}$$

$$g(a)=\det[g_{\mu\nu}(a)]\ , \tag{4}$$

and k_B is Boltzmann's constant. The comma notation in Eq. (3) denotes partial differentiation of the free energy per volume $f(t,h)$.

The quadratic form

$$(\Delta l)^2=\sum_{\mu,\nu=1}^{2}g_{\mu\nu}(a)\Delta a'_\mu\Delta a'_\nu \tag{5}$$

constitutes a positive-definite Riemannian metric on the two-dimensional thermodynamic state space of points with coordinates (t,h) [6]. Physically, the interpretation for distance between two thermodynamic states is clear from Eq. (2): the less probable a fluctuation between two states, the further apart they are.

The metric defines the Riemannian curvature tensor in terms of derivatives of the free energy. It was argued in Ref. [1] that the Riemannian curvature scalar R is proportional to the inverse of the free energy per volume very near the critical point:

$$R=\kappa\frac{k_BT_C}{f}\ . \tag{6}$$

This geometric equation may be written as a third-order nonlinear partial differential equation [1],

$$\frac{\begin{vmatrix} f_{,tt} & f_{,th} & f_{,hh}\\ f_{,ttt} & f_{,tth} & f_{,thh}\\ f_{,tth} & f_{,thh} & f_{,hhh}\end{vmatrix}}{\begin{vmatrix} f_{,tt} & f_{,th}\\ f_{,ht} & f_{,hh}\end{vmatrix}^2}=-\frac{2\kappa}{f}\ , \tag{7}$$

where I have here used a determinant notation originated by Janyszek and Mrugala [7] for the thermodynamic curvature.

Consider now a linear transformation of variables,

$$u = c_{11}t + c_{12}h \ , \tag{8a}$$

$$v = c_{21}t + c_{22}h \ , \tag{8b}$$

where the c_{ij}'s are constants, with nonzero determinant. By straightforward computation,

$$\begin{vmatrix} f_{,tt} & f_{,th} \\ f_{,ht} & f_{,hh} \end{vmatrix} = (c_{11}c_{22} - c_{12}c_{21})^2 \begin{vmatrix} f_{,uu} & f_{,uv} \\ f_{,vu} & f_{,vv} \end{vmatrix} \tag{9}$$

and

$$\begin{vmatrix} f_{,tt} & f_{,th} & f_{,hh} \\ f_{,ttt} & f_{,tth} & f_{,thh} \\ f_{,tth} & f_{,thh} & f_{,hhh} \end{vmatrix} = (c_{11}c_{22} - c_{12}c_{21})^4 \times \begin{vmatrix} f_{,uu} & f_{,uv} & f_{,vv} \\ f_{,uuu} & f_{,uuv} & f_{,uvv} \\ f_{,uuv} & f_{,uvv} & f_{,vvv} \end{vmatrix} . \tag{10}$$

This proves the theorem that the form of the geometric equation Eq. (7) is invariant under a linear transformation of independent variables [8].

This theorem implies that if $f(t,h)$ is a solution to the geometric equation in (t,h) coordinates, then so is $f(c_{11}t + c_{12}h, c_{21}t + c_{22}h)$. To see this, substitute $f(c_{11}t + c_{12}h, c_{21}t + c_{22}h)$ into the geometric equation in (t,h) coordinates. Then transform the surrounding equation to (u,v) coordinates, which, by the theorem, may be done simply with the substitution $t \to u$ and $h \to v$. Finally, transform the arguments of the function f to u and v by Eqs. (8). The form of the resulting equation is formally identical to the original one, so $f(u,v)$ remains a solution.

To complete this discussion of invariance, consider a more general coordinate mixing which includes the free energy:

$$u = c_{11}t + c_{12}h + c_{13}f(t,h) \ , \tag{11a}$$

$$v = c_{21}t + c_{22}h + c_{23}f(t,h) \ , \tag{11b}$$

$$w(u,v) = c_{31}t + c_{32}h + c_{33}f(t,h) \ , \tag{11c}$$

where the coefficients c_{ij} are constants, with nonzero determinant. I examined the matrices

$$c = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 1 & 1 & 1 \end{bmatrix} , \quad \begin{bmatrix} 1 & 0 & 1 \\ 0 & 1 & 1 \\ 0 & 0 & 1 \end{bmatrix} , \quad \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} . \tag{12}$$

None yielded an additional invariance in the sense that the resulting partial differential equation for $w(u,v)$ has the same form as Eq. (7) for $f(t,h)$.

Let us reflect on the physical meaning of the invariance under the coordinate change Eqs. (8). In the context of physical applications, there are generally three possible types of transformations of the geometric equation allowed within a specific universality class: (1) those which describe a given thermodynamic system in terms of a new set of thermodynamic variables, (2) those which apply a given set of thermodynamic variables to a new thermodynamic system, and (3) a combination of these two transformations. A transformation of the first type usually changes the form of the geometric equation, but leaves the boundary conditions effectively the same (consistent with the original ones). A transformation of the second type leaves the geometric equation unchanged, but new boundary conditions are invoked.

These three types of transformations are physically quite different from each other. Since the invariance theorem could be applied to any one of these transformations, it is at this point just mathematical manipulation, which takes on physical significance only if the context is specified. The interesting case in this paper are transformations that occur in connection with scaling and universality where the free energy has the form

$$f(t,h) = |t|^a Y(z) \ . \tag{13}$$

Here

$$z = h|t|^{-b} \ , \tag{14}$$

a and b are the constant critical exponents, and $Y(z)$ is some function. It was shown in Ref. [1] that such a form of the free energy simplifies the geometric equation to a third-order nonlinear ordinary differential equation (ODE) for $Y(z)$, which I shall elaborate on below.

In addition to specifying the form of the free energy for a given system, scaling and universality deal with how given thermodynamic quantities transform under a change of thermodynamic systems within a particular universality class, and this corresponds to coordinate transformations of type (2). Restricted by the scaling form Eq. (13), there are three ways to bring about a coordinate transformation of type (2). The first is to drop Eq. (14) for the relation between z, t, and h, but leave the function Y the same. The second is to stay with Eq. (14), but change the functional form of Y. The third is to change both the argument and the functional form of Y.

For the first case, we may use the invariance theorem above to construct an asymmetric solution to the geometric equation by a two-step procedure. First, solve it in coordinates (t,h) where f is symmetric in the ordering field $[f(t,h) = f(t,-h)]$, by, for example, the method of Ref. [1]. Next, substitute the coordinate transformation Eqs. (8). The result is

$$f(t,h) = |c_{11}t + c_{12}h|^a Y \left[\frac{(c_{21}t + c_{22}h)}{|c_{11}t + c_{12}h|^b} \right] , \tag{15}$$

which remains a solution. The change in boundary conditions is reflected through the constants c_{ij}. The general notion in critical phenomena of such a scheme of mixed coordinates to extend scaling and universality to deal with asymmetry is well known, and seems to be accepted [2,9]. Its prediction of a deviation from the law of rectilinear diameters has been experimentally verified [10,11].

Consider now the second possibility, changing the function Y, leaving the dependence between z, t, and h

fixed by Eq. (14). I shall argue that this does not appear to yield an acceptable solution since it leads to a singularity near the critical isochore, as I now show.

Substitution of Eq. (13) reduces the geometric equation Eq. (7) to a third-order nonlinear ODE for $Y(z)$ [1],

$$Y^{(3)}(z)=\frac{p_n(\kappa,z,Y,Y',Y'')}{p_d(z,Y,Y',Y'')}, \quad (16)$$

where the numerator and denominator on the right-hand side are polynomial functions of their arguments. This equation is too lengthy to write out here for general a and b, but the Appendix shows it for the mean-field theory (MFT) exponents $a=2$ and $b=\frac{3}{2}$.

Assuming that $Y(z)$ is analytic at $z=0$, it admits a Taylor series:

$$Y(z)=y_0+y_1z+y_2z^2+y_3z^3+\cdots . \quad (17)$$

Because $Y(z)$ is a solution to a third-order ODE, it has three free constants of integration, which I take as y_0, y_1, and y_2. In Ref. [1], a symmetric solution was obtained by setting $y_1=0$. But consider what happens with $y_1\neq 0$.

First, note that the solution to the ODE (16) is regular at $z=0$ unless the denominator $p_d(z,Y,Y',Y'')$ is zero there. Substituting the series for $Y(z)$ leads to

$$p_d(0,Y(0),Y'(0),Y''(0))=(a-1)a(a-b)(b-1)y_0^2y_1 , \quad (18)$$

which shows that, barring fortuitous values of the critical exponents, or the unphysical choice $y_0=0$, the denominator is not zero at $z=0$ if $y_1\neq 0$. Hence, a Taylor-series solution method is guaranteed to converge in some neighborhood of $z=0$.

The case with $y_1=0$ has zero denominator at $z=0$, and the only way to get a locally regular solution is to require that the numerator be zero as well. This obtains regardless of y_0 and y_2 if [1]

$$\kappa=\frac{(b-1)(2b-a)}{a(a-1)} . \quad (19)$$

This value results in a cancellation of a single factor of z on the right-hand side of Eq. (16), and a regular solution at $z=0$.

Turning back to the case with $y_1\neq 0$, we must pick a value for κ, which is not now set by a regularity requirement at $z=0$. There are three basic options: (1) regard κ to be universal and given by Eq (19); (2) allow κ to vary with y_0, y_1, and y_2, but go to the expression Eq. (19) in the limit $y_1\to 0$; (3) require no consistency with Eq. (19).

Let us explore the first option, which is clearly preferable since it is not thought that the issue of symmetry is relevant for determining the universality class. Also, the solution process which lead to the value of κ in Eq. (19) resulted in a good symmetric free energy; in particular, the scaled equation of state obtained for the MFT exponents was exactly what was expected [1]

Start by choosing $y_0=y_2=-1$ [12]. The construction of a series solution in terms of y_1 is now immediate. Table I shows the first few series coefficients for the MFT exponents. As may be seen, in the limit $y_1\to 0$ the coefficients computed with $y_1\neq 0$ do not converge to those computed with $y_1=0$. This behavior is representative of that for other values of a and b, including the three-dimensional (3D) Ising exponents $a=\frac{15}{8}$ and $b=\frac{25}{16}$. The reason for this qualitative difference is clear; for $y_1=0$ the cancellation of z's brings the coefficients y_i down one order on the right-hand side of Eq. (16), resulting in a different set of recurrence relations in the series solution. Physically, a slight asymmetry should be nearly indistinguishable from the symmetric case; therefore one of the solutions here must be unphysical, probably the one with $y_1\neq 0$.

For $y_1>0$ the series coefficients are all negative for i not too small, provided $|y_1|$ is not too large, and have alternating sign for $y_1<0$. This means that the closest singular point for $Y(z)$ should lie on the real z axis, positive for $y_1>0$ and negative for $y_1<0$. Assuming that $Y(z)$ has a nearest singularity on the real axis at z_0 of the form

$$Y(z)\approx A(z-z_0)^g , \quad (20)$$

TABLE I. The first seven series coefficients computed for the MFT exponents $a=2$ and $b=\frac{3}{2}$ for both the symmetric and asymmetric solution schemes, with κ given by Eq. (19). In the limit $y_1\to 0$ the later series coefficients do not approach the former except for $i=0,1,2,3$, and, indeed, diverge for $i\geq 5$.

i	y_i $(y_1=0)$	y_i $(y_1\neq 0)$
0	-1	-1
1	0	y_1
2	-1	-1
3	0	$\frac{-28y_1^2+y_1^4}{96y_1}$
4	$\frac{1}{12}$	$\frac{-448y_1-132y_1^3+7y_1^5}{1536y_1}$
5	0	$\frac{-73\,728-8224y_1^2-1700y_1^4+117y_1^6}{61\,440y_1}$
6	$-\frac{1}{36}$	$\frac{-3\,538\,944-992\,768y_1^2+35\,232y_1^4-11\,364y_1^6+689y_1^8}{737\,280y_1^2}$

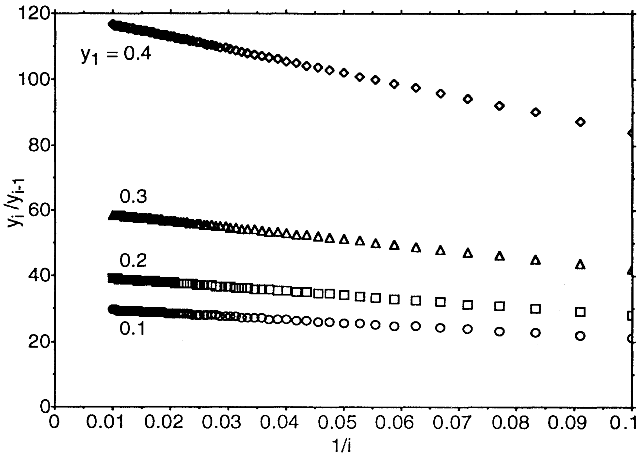

FIG. 1. The coefficient ratios y_i/y_{i-1} as a function of $1/i$ for several values of y_1. The graphs are linear, supporting the contention that there is a singularity in $Y(z)$ of the form $A(z-z_0)^g$ at z_0.

where A and g are constants, we expect the ratio of series coefficients for large values of the index i to be linear in $1/i$:

$$\frac{y_i}{y_{i-1}} = -\left[\frac{g+1}{z_0}\right]\frac{1}{i} + \frac{1}{z_0}, \tag{21}$$

if either $g < -1$ or g is noninteger [3]. Figure 1 shows that the series coefficients for the 3D Ising exponents obey such a relation for a range of values of y_1. Table II gives z_0 and g for several y_1. It may be seen that for both MFT and 3D Ising exponents there is a singularity on the real z axis which approaches $z=0$ as y_1 gets smaller [13]. Such a singularity is physically undesirable, however, particularly for the MFT exponents which result from models whose underlying assumption is that the free energy is regular at the critical point. Hence, this method for including asymmetry appears to be inferior to the mixing of coordinates scheme.

One may attempt to remove the discontinuity in the limit $y_1 \to 0$ by adjusting κ (and possibly a and b) to produce the cancellation of z's for all values of y_1. This requires setting the denominator p_d in Eq. (18) to zero at $z=0$ for all y_1. However, this is clearly impossible for anything but a few special values of a and b, values which cannot go smoothly to either the MFT or the 3D Ising exponents in the limit $y_1 \to 0$. Another possibility, beyond the scope of this paper, is to abandon entirely the solution in Ref. [1] and adjust κ and the critical exponents to remove the singularity at z_0. This might possibly produce an acceptable solution, but probably one quite different from that of Ref. [1].

The third possible way of constructing an asymmetric solution, varying both the function Y and its argument, does not seem to offer much chance of success either because of the problem with the singularity in Y.

In conclusion, the main result of this paper is the proof that a mixing of coordinates scheme, as is conventionally used, is consistent with the Riemannian geometric theory of critical phenomena. Furthermore, this appears to be the most plausible scheme for dealing with asymmetry with this theory, since the natural alternative leads to a singularity near the critical isochore. Stronger, but beyond the scope of this paper, would be uniqueness theorems both for the scaling form of free energy very near the critical point, and for the uniqueness of the transformation Eq. (8) for leaving the geometric equation invariant.

TABLE II. Values of z_0 and g for several y_1. Convergence as more terms were added to the series was too slow using the ratio method Eq. (21), so these values were calculated using Padé approximants. The values for z_0 are precise, within a digit in the least significant place; the g's are harder to calculate, and not quite as certain.

	y_1	z_0	g
MFT	0.4	0.048 093	2.50
	0.3	0.036 588	2.50
	0.2	0.024 686	2.49
	0.1	0.012 452	2.36
	0.06	0.007 489	2.21
3D Ising	0.4	0.032 605	2.50
	0.3	0.024 659	2.49
	0.2	0.016 552	2.43
	0.1	0.008 317	2.25
	0.06	0.004 996	2.12

I thank M. E. Fisher and J. J. Rehr for useful correspondence.

APPENDIX

Equation (A1) is the result of substituting the scaling form of the free energy Eq. (13) into the geometric equation Eq. (7) for the MFT exponents. For other values of the critical exponents a and b, the equation looks similar.

$$\begin{aligned} Y^{(3)}(z) = [(&2\kappa Y'^4 + YY'^2Y'' - 32\kappa YY'^2Y'' + 12\kappa zY'^3Y'' - 32Y^2Y''^2 + 128\kappa Y^2Y''^2 \\ &+ 24zYY'Y''^2 - 96\kappa zYY'Y''^2 + 18\kappa z^2Y'^2Y''^2 - 9z^2YY''^3)][Y(8YY' - 9zY'^2 + 24zYY'' - 9z^2Y'Y'')]^{-1}. \end{aligned} \tag{A1}$$

[1] G. Ruppeiner, Phys. Rev. A **44**, 3583 (1991).

[2] J. J. Rehr and N. D. Mermin, Phys. Rev. A **8**, 472 (1973).

[3] Though I use the language and notation of magnetic systems, it is easily adapted to that of the pure fluid; see, e.g., M. E. Fisher, Rep. Prog. Phys. **30**, 615 (1967).

[4] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, New York, 1977).

[5] There has been some recent discussion about the meaning of thermodynamic "fields," such as the temperature, for fluctuating subsysttems [H. Feshbach, Phys. Today **40** (11), 9 (1987); C. Kittel, *ibid.* **41** (5), 93 (1988); B. B. Mandelbrot, *ibid.* **42** (1), 71 (1989)]. My viewpoint is that of Ref. [4], where equations of state are used to assign values to fields in terms of mechanical parameters, such as energy, mole numbers, or magnetization. Though this interpretation sheds little insight into the physical interpretation of the fluctuating fields, it does seem to be used by a majority of the textbooks on the subject. For an interesting statistical interpretation, see the article by Mandelbrot, who, however, has to leave the domain of traditional thermodynamics to establish his points. I should add that one can regard thermodynamic fluctuation theory purely as a theory of the mechanical parameters, with no essential need to interpret physically other parameters. In Riemannian geometry, the choice of coordinates is one only of convenience; the theory could be worked out with the explicitly physical mechanical parameters with the same physical results, though the free energy $f(t,h)$ would be awkward to handle in these coordinates.

[6] G. Ruppeiner, Phys. Rev. A **20**, 1608 (1979); **24**, 488 (1981).

[7] H. Janyszek and R. Mrugala, Phys. Rev. A **39**, 6515 (1989).

[8] The thermodynamic curvature R and the free energy f are certainly invariant under any change of coordinates; they are functions of state. However, the form of the geometric equation is invariant necessarily only under a linear change of coordinates. Including additive constant terms in the transformation equations Eq. (8) would work as well, but this leads to no particular advantage since we want the thermodynamic fields to go to zero at the critical point.

[9] Reference [2] considered also higher-order terms in the coordinate transformation Eqs. (8). These appear to be beyond the reach of the geometric theory. Analysis of experimental data, however, does not appear to require nonlinear terms; see, e.g., P. C. Albright, T. J. Edwards, Z. Y. Chen, and J. V. Sengers, J. Chem. Phys. **87**, 1717 (1987).

[10] R. Goldstein, A. Parola, N. W. Ashcroft, M. W. Pestak, M. H. W. Chan, J. R. de Bruyn, and D. A Balzarini, Phys. Rev. Lett. **58**, 41 (1987).

[11] Note that we may certainly introduce asymmetry in the order parameter with an asymmetric coordinate transformation of type (1). A relevant physical example occurs in the pure fluid, where the coexistence curve looks nearly symmetric when represented in density coordinates, but asymmetric when expressed in terms of the molar volume [J. M. H. Levelt Sengers, Physica **73**, 73 (1974)]. The theory here certainly supports such transformations.

[12] As was discussed in Ref. [1], if $Y(z)$ is a solution to the geometric equation, then so is $n_1 Y(n_2 z)$, where n_1 and n_2 are constants. Hence, two of the three required integration constants merely set the scale of z and $Y(z)$ and do not otherwise affect the basic character of the solution. Hence, fixing y_0 and y_2 (to negative values, by thermodynamic stability) and varying y_1 should reveal all of the interesting behavior for small y_1 near $z=0$.

[13] The critical isochore is the curve along which the order parameter $m=-f_{,h}=0$. Padé analysis of its series reveals that, for the values of y_1 shown in Table II, the critical isochore lies within about 1% of z_0, and may possibly coincide with z_0.