Riemannian geometric approach to critical points: General theory

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The postulate that *the thermodynamic Riemannian curvature scalar is inversely proportional to the free energy* is generalized to cases with more than two independent thermodynamic variables. In the appropriate thermodynamic coordinates, the resulting partial differential equation has as a solution a free energy in the form of a generalized homogeneous function. In addition, linear transformations of the variables leave the functional form of the solution unchanged. These findings are consistent with expectations from scaling and universality. Analyzed in some detail are ''corrections to scaling,'' where one ''irrelevant'' variable is added to a ''relevant'' ordering field and the temperature. The ratio of the corrections to scaling amplitudes is computed for the heat capacity and the susceptibility along the critical isochore. Two solution branches result, in the form of exact equations in terms of the critical exponents. The first solution branch is in good agreement with other calculations of this universal ratio. With three variables, our scaled equation of state is not determined uniquely in terms of just a single set of critical exponents. How this relates to the modern theory of critical phenomena is discussed. [S1063-651X(98)10505-6]

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INTRODUCTION

Purely thermodynamic theories of critical points date back to van der Waals [1], whose celebrated equation of state yielded a liquid-gas phase transition and critical point. Landau [2] generalized this approach in the form of classical or mean-field theories, which are based on the assumption that the free energy is analytic at the critical point.

Despite the effectiveness of mean-field theories, they do not agree with experiment, differing, for example, in the values of the critical exponents. Widom [3] suggested that the basic structure of mean-field theory be extended by means of nonclassical critical exponents and the assumption that the free energy is a generalized homogeneous function of its arguments. This scaling hypothesis and the further assumption of universality form the foundations of the modern theory of the critical point [4]. This structure is supported by statistical-mechanical models and renormalization-group theory.

Phase transitions and critical phenomena may also be approached thermodynamically by Riemannian geometry, with a metric related to thermodynamic fluctuations [5–7]. For the case of *two* independent thermodynamic variables, it has been postulated that *the Riemannian curvature scalar is proportional to the inverse of the free energy*. Since this curvature may be written in terms of the third and lower derivatives of the free energy, this postulate leads to a third-order partial differential equation (PDE) for the free energy. A generalized homogeneous function of its arguments is a solution and specifying the values of the critical exponents results in a full scaled equation of state.

In this paper I generalize the curvature postulate to cases with more thermodynamic variables, corresponding to Riemannian geometries with dimension larger than 2. It is demonstrated that, with the proper variables, a solution for the free energy in arbitrary dimension is a generalized homogeneous function, consistent with expectations from the modern theory of critical phenomena. It is also demonstrated that linear transformations of these variables leave the functional form of the solution unchanged.

In addition, I examine in some detail a problem involving three-dimensional Riemannian geometries, in which we have a temperature and two ordering fields, one ''relevant'' and the other ''irrelevant'' [4]. The latter leads to corrections to the usual asymptotic critical properties. Using series expansions in powers of small fields, I compute the corrections to the scaling amplitude ratio of the heat capacity to the susceptibility. Two solution branches result, each an exact formula in terms of the critical exponents. One of the two solution branches yields numbers in good agreement with known results. Discussion is also given of the lack of uniqueness of our resulting scaled equation of state and how this relates to the modern theory of critical phenomena.

I. INTRODUCTION TO THE RIEMANNIAN GEOMETRY OF THERMODYNAMICS

For the Riemannian geometry of thermodynamics, I use the notation of Ref. [7], based roughly on that of Callen [8]. The initial discussion is pitched in terms of fluid mixtures, but the formalism is readily generalized to include magnetic systems, a language I turn to in Sec. IV.

For a general, open, r-component fluid mixture system with fixed volume V, denote by

$$X=(U,N^1,N^2,\ldots,N^r) \tag{1}$$

the standard extensive quantities in the entropy representation. Here U is the internal energy and $N^1,N^2,\ldots,N^r$ are the mole numbers of the chemical species. The volume V is omitted from the parameter list since its value does not fluctuate. It, rather than one of the mole numbers, is picked as the fixed system scale because we are interested in intrinsic properties of fluids and certainly do not wish to impose artificial boundaries to impede the flow of the constituents. The volume is the only choice of system scale involving no arti-

TABLE I. Notation for important quantities.

Notation	Meaning
$F=(1/T,-\mu^1/T,\ldots,-\mu^r/T)$	intensive parameters in the entropy representation
R	Riemannian curvature scalar
T	temperature
T_C	critical temperature
Y	scaled equation of state
a	standard densities in the entropy representation
a,b,c	critical exponents
$d[i,j]$	free-energy series coefficients
$g_{\alpha\beta}$	metric elements
h	relevant ordering field
k_B	Boltzmann's constant
m	order parameter
$n=r+1$	thermodynamic dimension
o	irrelevant ordering field
p	pressure
$q=o/\|t\|^c$	irrelevant scaling variable
r	number of fluid components
s	entropy per volume
$t=1-T_C/T$	reduced temperature
$z=h/\|t\|^b$	relevant scaling variable
κ	dimensionless universal constant
μ^i	chemical potential of the ith species
$\phi(F)=s-\Sigma_{\mu=0}^r F^\mu a^\mu \ \ (=p/T)$	free energy

ficial internal boundaries. The dimension of the thermodynamic state space is $n=r+1$. Frequently used notation is given in Table I.

Denote by the n-tuple

$$a=\frac{X}{V} \tag{2}$$

the extensive quantities per volume and by

$$F=\left(\frac{1}{T},-\frac{\mu^1}{T},-\frac{\mu^2}{T},\ldots,-\frac{\mu^r}{T}\right) \tag{3}$$

the conjugate intensive quantities, where T is the temperature and $\mu^1,\mu^2,\ldots,\mu^r$ are the chemical potentials of the r chemical species. The free energy per volume appropriate to the F coordinates is denoted by

$$\phi(F)=s-\sum_{\mu=0}^{r}F^\mu a^\mu\left(=\frac{p}{T}\right), \tag{4}$$

where s is the entropy per volume and the superscript μ (which ranges from 0 to r) denotes which variable in the parameter list. I add that the choice of independent variables F, together with the choice of p/T as the dependent free energy, is routinely made in the analysis of near-critical point fluid data [9].

Set now the context of the fluctuation theory. Consider a finite, open subsystem A_V of an infinite system A_{V_0} in thermodynamic equilibrium. The subsystem A_V has fixed volume V, but the rest of its thermodynamic parameters F fluctuate as particles and energy flow randomly across the boundary. The large A_{V_0} has volume V_0 (tending to infinity) and fixed thermodynamic state F_0. According to the classic thermodynamic fluctuation theory [2], the probability of finding F in a small differential element $dF^0dF^1\cdots dF^r$ is (in the Gaussian approximation)

$$\begin{aligned}P_V(F|F_0)&dF^0dF^1\cdots dF^r\\&=\left(\frac{V}{2\pi}\right)^{n/2}\exp\left\{-\frac{V}{2}\sum_{\mu,\nu=0}^{r}g_{\mu\nu}\Delta F^\mu\Delta F^\nu\right\}\\&\quad\times\sqrt{g}\,dF^0dF^1\cdots dF^r,\end{aligned} \tag{5}$$

where $\Delta F^\alpha=F^\alpha-F_0^\alpha$, the "metric elements"

$$g_{\alpha\beta}=\frac{1}{k_B}\frac{\partial^2\phi}{\partial F^\alpha\partial F^\beta}, \tag{6}$$

$$g=\det(g_{\alpha\beta}), \tag{7}$$

and k_B is Boltzmann's constant. The metric elements are evaluated in the state of maximum entropy, which corresponds to $F=F_0$.

The quadratic form

$$(\Delta l)^2=g_{\mu\nu}\Delta F^\mu\Delta F^\nu \tag{8}$$

constitutes a positive-definite Riemannian thermodynamic metric on the n-dimensional thermodynamic state space [7]. Here and henceforth summation over repeated indices from 0 to r is understood. Physically, the interpretation for distance between two thermodynamic states is clear from Eq. (5): *The* *larger the distance between two thermodynamic states, the less the probability of a fluctuation between them.*

This basic geometry has also seen other applications. Weinhold originally used an inner product based on second derivatives of the energy to simplify certain thermodynamic computations [10]. Andresen, Salamon, and Berry [11] have used this geometry in the context of finite-time thermodynamics, where the line element represents the entropy dissipated during an irreversible process.

I add that to go from a fluid system to a magnetic one generally requires only that we replace chemical potentials with magnetic fields and densities by magnetizations. A discussion of this analogy is given by Kittel [12] in a general context and by Fisher [13] in the context of the critical point.

II. RIEMANNIAN GEOMETRIC THEORY OF THE CRITICAL POINT

Of primary interest is the fourth-rank thermodynamic Riemannian curvature tensor, which follows from the metric:

$$R^{\alpha}{}_{\beta\gamma\delta}=\Gamma^{\alpha}{}_{\beta\gamma,\delta}-\Gamma^{\alpha}{}_{\beta\delta,\gamma}+\Gamma^{\mu}{}_{\beta\gamma}\Gamma^{\alpha}{}_{\mu\delta}-\Gamma^{\mu}{}_{\beta\delta}\Gamma^{\alpha}{}_{\mu\gamma}, \quad (9)$$

where the Christoffel symbols

$$\Gamma^{\alpha}{}_{\beta\gamma}=\tfrac{1}{2}g^{\mu\alpha}(g_{\mu\beta,\gamma}+g_{\mu\gamma,\beta}-g_{\beta\gamma,\mu}) \quad (10)$$

and $g^{\alpha\beta}$ denotes the inverse of the metric tensor $g_{\alpha\beta}$. The comma notation $,\alpha$ in the subscript indicates differentiation with respect to the thermodynamic coordinate F^{α}. Associated with the Riemannian curvature are the Ricci curvature

$$R_{\alpha\beta}=R^{\mu}{}_{\alpha\mu\beta} \quad (11)$$

and the Riemannian curvature scalar

$$R=g^{\mu\nu}R_{\mu\nu}. \quad (12)$$

I follow the curvature sign convention of Weinberg [14]. I note that with our metric, R will have units of volume, in all dimensions.

For *two* thermodynamic variables the basic postulate in this geometry of thermodynamics is the geometric equation [5–7]

$$R=-\kappa\,\frac{k_B}{\phi}, \quad (13)$$

where κ is a universal dimensionless constant of order unity. The word ''universal'' is used in the sense of the modern theory of critical phenomena, which I take here to mean depends only on the critical exponents, which get introduced in the solution process [15]. The free energy per volume ϕ includes just the singular part, that associated with critical point fluctuations. It goes to zero at the critical point where it becomes infinitely easy to produce fluctuations. Picking this singular part out in the solution process is generally straightforward.

The original argument for this postulate consisted of dual components. First is the finding that R is a measure of the effective intermolecular interaction strength, specifically, the correlation volume ξ^d. For example, R is zero in the ideal gas and diverges as ξ^d near the critical point [16]. Second is the statement of hyperscaling [17] that the inverse of the free energy is proportional to ξ^d. Combining these components leads immediately to Eq. (13).

The extent to which these two parts of the argument generalize to higher thermodynamic dimensions is, *a priori*, not clear. Notice, for example, that in two dimensions there is only one independent component of the Riemann tensor and all information basically resides in the scalar R [14]. This makes it easy to pick it out as the essential part of the Riemann curvature. However, such is not the case in higher dimensions and a fundamentally different approach is called for to arrive at a physical law. I will bypass the dual arguments above entirely.

For guidance, I set down three principles a correct theory should obey: (i) It should be covariant, (ii) it should contain in some natural way the known theory in two dimensions, and (iii) any constant appearing in the theory should be universal, admitting a multiplicity of solutions.

Let us discuss these principles, starting with covariance. By covariance, I mean that once the theory has been formulated, the results computed with it do not depend on the coordinate system picked to calculate in. For example, a given thermodynamic state has specific values of its physical parameters, such as pressure, entropy, or internal energy, regardless of the coordinates we use. The rules of Riemannian geometry are designed specifically to force the proper transformation of physical quantities under a change of coordinates. For example, Eq. (12) for R will transform as a scalar.

The geometric equation (13) in two dimensions is not written in a way that manifests covariance since ϕ on the right-hand side of the equation is the natural free energy specific to the set of coordinates F. This is partly due to our early, and necessary, singling out of the volume as a special coordinate. However, when a free energy is picked, it inevitably comes with a natural set of thermodynamic coordinates. The reason for picking $\phi(F)$ was discussed in some detail in Ref. [7]. Although the arguments are not very rigorous, they are a productive way to move us forward. To have the right-hand side of the equation consistent with the left, we are obliged to transform ϕ as a scalar.

Having stressed covariance, let me say that it certainly does not prevent us from finding special coordinates where things are in one way or another simplified. The F coordinates allow us to write the metric as the second derivatives of $\phi(F)$. This allows proof of some special theorems, as we will see.

The second guiding principle, that the theory should reduce in some natural way to the known theory in two dimensions, is a call for simplicity. The statement of a successful theory should transcend dimensionality. It should not be necessary to reinvent it every time a thermodynamic variable is added.

The third principle, calling for universal constants, represents a desire for a class of solutions for every value of the constants. It is motivated by universality in the modern theory of critical phenomena, where, for example, many fluid systems reside in the same universality class. This principle rules out all theories where the constants are not dimensionless. This is because neither statistical mechanics nor the theory of critical points has universal constants with units other than k_B.

Clearly, the simple equation (13) satisfies all three of our principles. I will adopt it in generality, after examining a few unsatisfactory possibilities. Among proposed theories that do not work consider

$$R^2 = -\kappa \frac{k_B}{\phi}, \tag{14}$$

$$R^{\mu\nu} R_{\mu\nu} = -\kappa \frac{k_B}{\phi}, \tag{15}$$

and

$$R^{\mu\nu} \phi_{,\mu\nu} = -\kappa k_B. \tag{16}$$

Each violates the second principle, in failing to reduce naturally to the known two-dimensional case. The first two also fail to satisfy the third principle since their constant κ's have units of volume raised to some power and such constants cannot be universal. The third proposed theory is not covariant since the second derivatives of scalar functions do not transform as tensors. This problem could, however, be fixed by taking the covariant derivative of ϕ, but this does not solve the inconsistency with the second principle.

Consider also a proposed theory of the form

$$g^{\mu\nu} \Gamma^{\xi}{}_{\mu\nu} \phi_{,\xi} = \kappa, \tag{17}$$

which has a left-hand side not manifestly covariant since the Christoffel symbols do not transform as the components of a tensor [14]. Indeed, it is not possible to form a tensor from quantities formed from first derivatives of the metric, hence the emphasis on curvature. One might argue for a theory like Eq. (17) by saying that this form is intended to hold only in some specific coordinate system and then demand that both sides of the equation transform as a scalar. However, although such arguments are plausible for the free energy, they become increasingly unlikely for derivatives of this quantity. The adopted equation (13) seems to be the simplest postulate and the best.

III. GENERALIZED HOMOGENEOUS FUNCTION SOLUTIONS

We may readily work out an expression for R valid in arbitrary dimension n. By Eq. (12),

$$R = \tfrac{1}{4} g^{\mu\nu} g^{\xi o} g^{\pi\rho} (g_{\mu\nu,\xi} g_{o\pi,\rho} - g_{\mu o,\rho} g_{\nu\xi,\pi}). \tag{18}$$

The metric identity

$$g^{\alpha\beta}{}_{,\gamma} = -g^{\alpha\mu} g^{\beta\nu} g_{\mu\nu,\gamma} \tag{19}$$

was useful in this calculation. The second derivatives of the metric elements (fourth derivatives of ϕ) cancel. I emphasize that this *form* of the curvature scalar obtains only with the special form of the metric given in Eq. (6) and is not coordinate invariant.

We may rewrite Eq. (18) as

$$R = \frac{1}{4g^3} G^{\mu\nu} G^{\xi o} G^{\pi\rho} (g_{\mu\nu,\xi} g_{o\pi,\rho} - g_{\mu o,\rho} g_{\nu\xi,\pi}), \tag{20}$$

where $G^{\alpha\beta}$ is the cofactor of $g_{\alpha\beta}$, in terms of which [18]

$$g^{\alpha\beta} = \frac{G^{\alpha\beta}}{g}. \tag{21}$$

This expression demonstrates some points that prove important. Consider some specific index value α. From the properties of the determinants g and $G^{\alpha\beta}$, one may see that each term in the numerator and the denominator of Eq. (20) contains exactly six derivatives of ϕ with respect to F^α [19]. In addition, each term in the numerator has $3n-1$ factors of ϕ and each term in the denominator has $3n$ factors of ϕ.

These observations allow us to prove two theorems of central importance. Define first the variables $z^1,\ldots,z^r$ by

$$z^i = \frac{F^i}{|F^0|^{\phi_i}}, \tag{22}$$

where $\phi_1,\ldots,\phi_r$ are arbitrary, constant ‘‘critical exponents.’’ Also define ϕ_0 to be a constant critical exponent. We have the following.

Theorem 1. The functional form

$$\phi(F) = |F^0|^{\phi_0} Y(z^1, z^2, \ldots, z^r) \tag{23}$$

satisfies the geometric equation in the sense that the substitution of this form reduces the geometric equation to a partial differential equation for the function Y in terms of the reduced list of variables $z^1,\ldots,z^r$.

The proof of this theorem is straightforward and results since all factors of F^0 will cancel out on substituting this form into the geometric equation, as a consequence of the properties noted above of the determinants. Also correct is the following.

Theorem 2. If the function $\phi(F) = |F^0|^{\phi_0} Y(z^1, z^2, \ldots, z^r)$ satisfies the geometric equation, then so does the function

$$\phi(F) = |\lambda_0 F^0|^{\phi_0} Y(\lambda_1 z^1, \lambda_2 z^2, \ldots, \lambda_r z^r) \tag{24}$$

for all values of the constants $\lambda_0, \lambda_1, \ldots, \lambda_r$.

The proof again follows from the properties of the determinants in Eq. (20). We may multiply each F^α in the geometric equation by a corresponding factor of λ_α without changing the form of the equation. That the form of the geometric equation is unchanged by the transformation $F^\alpha \to \lambda_\alpha F^\alpha$ (no summation intended) establishes the theorem. Both these theorems were proved previously in two dimensions [5]. Here we see that they hold more generally.

Theorem 1 embodies the concept of scaling in the theory of critical phenomena. It leads to the usual equalities among critical exponents, as well as various ways of plotting experimental data for a given fluid so that they fall on the same curve. Theorem 2 embodies the concept of the universality of the function Y. For each function Y, there is a class of different fluids with members differentiated by values of the multiplicative constants λ_α. Scaling is then a statement about the *function* $\phi(F)$, whereas universality is a statement about what is allowed by the *machinery* that gives us $\phi(F)$, in this case a PDE.

I will confine our study to functions of this form. Whether or not they are unique solutions to the geometric equation is unresolved mathematically, but in the absence of proof to the contrary, the possibility of other solutions must certainly be admitted. It might then be thought that scaling and universality have merely been built into the theory, but this is not the case. They are allowed by the special form of the geometric equation and this constitutes a strong positive result.

Let us prove another theorem of general validity. Consider a linear transformation of the standard intensive variables

$$F'^{\alpha} = c^{\alpha} + \sum_{\mu=0}^{r} c^{\alpha}_{\mu} F^{\mu}, \tag{25}$$

where the c's are all constants. We may write the metric elements in the F' coordinates using the general tensor transformation rule [14]

$$g'_{\alpha\beta} = \frac{\partial F^{\mu}}{\partial F'^{\alpha}} \frac{\partial F^{\nu}}{\partial F'^{\beta}} g_{\mu\nu}. \tag{26}$$

Since the partial derivatives of the coordinates are constants, this leads, with Eq. (6) for $g_{\alpha\beta}$, immediately to

$$g'_{\alpha\beta} = \frac{1}{k_B} \frac{\partial^2 \phi}{\partial F'^{\alpha} \partial F'^{\beta}}. \tag{27}$$

We see that the form of the metric elements is exactly the same in F' coordinates as in F coordinates. Hence the forms of the curvature scalar R and the partial differential geometric equation are exactly the same in the two coordinate systems. This implies the following.

Theorem 3. If $\phi(F^0, F^1, \ldots, F^r)$ is a solution to the geometric equation, then $\phi(F'^0, F'^1, \ldots, F'^r)$ will also be a solution, with the same function ϕ. Furthermore, Theorems 1 and 2 hold as well with the new variables.

This mixing of variables was suggested by Rehr and Mermin [20]. It is used routinely in the analysis of fluid data [21].

I mention on the side that one implicit, though not essential, idea in this approach is that R should in some sense be the correlation volume. This certainly appears to be the case in two dimensions, but, to my knowledge, the only reported test of this possibility beyond two dimensions was by the present author and Davis [22]. We worked out R for the ideal gas in arbitrary dimension and found that it is small, on the order of the intermolecular distance. This is certainly consistent with what is expected with a correlation volume interpretation.

IV. SOLUTION IN THREE DIMENSIONS AND CORRECTIONS TO SCALING

Turn now to a physical application, corrections to scaling contributed by an extra independent variable near the critical point. Let us set the context with Fisher's review [4], using the language of magnetic systems. The free energy is allowed to depend on three variables, the reduced temperature t, defined below, a magnetic ordering field h conjugate to the order parameter, and a thermodynamic field o coupling only weakly to the critical properties. The fields h and o are regarded as proportional to F^1 and F^2 or to some linear combination of these fields, as in Eq. (25), so the metric has the

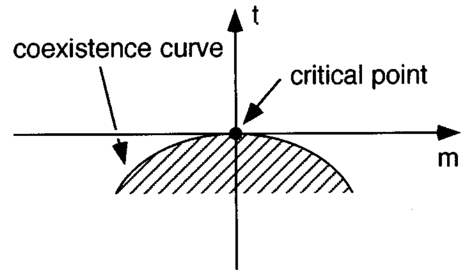

FIG. 1. Schematic of (t,m) space. It shows the critical point, which corresponds to the point of highest temperature at which the system shows zero magnetization m in the zero ordering field h. At lesser temperatures the system spontaneously magnetizes in one of two directions along the coexistence curve $(h=0)$.

form given in Eq. (27). As we will see, the variable t is also linearly related to the F^{α}'s. Therefore, the theorems of Sec. III all apply in the coordinate system (t,h,o).

We may write

$$\phi(t,h,o) = |t|^a Y(z,q), \tag{28}$$

where

$$z = \frac{h}{|t|^b}, \tag{29}$$

$$q = \frac{o}{|t|^c}, \tag{30}$$

and a, b, and c will denote in this section our three constant critical exponents [23]. I take $a>1$, $b>0$, and $c<0$. The case with $c>0$, where o is also "relevant," is beyond the scope of this paper. The reduced temperature t is defined as

$$t = 1 - \frac{T_C}{T}, \tag{31}$$

with T_C being the critical temperature. As emphasized by Fisher [4], this definition agrees with the more traditional definition $(T-T_C)/T_C$ up to analytic corrections of order t^2. Note, by Theorem 3, that we could have T_C/T depend linearly on h and o if we desired. This accommodates a structure where T_C varies with the ordering fields.

Clearly, as $t \to 0$, the effect of a changing h on the function Y grows, while that of a changing o diminishes to insignificance. Hence we call h *relevant* to the asymptotic critical properties and o *irrelevant.* Define the order parameter associated with h as

$$m = \phi_{,h}. \tag{32}$$

In the Ising or the Curie-Weiss model, m is the magnetization per spin. We take the function Y to be an even function of h and z. For $o \to 0$ and typical values of the critical exponents a and b, we get the familiar critical properties; see Fig. 1. Of interest in corrections to scaling is how the asymptotic behavior gets modified as we go away from the critical point.

Much studied in the theory of the critical point are universal ratios of critical amplitudes. Let me work out an important one in corrections to scaling. A series for the free energy for small q and z may be written as

$$\phi = t^a \sum_{i=0}^{\infty} \sum_{\substack{j=0 \\ \Delta j=2}}^{\infty} d[i,j] q^i z^j. \tag{33}$$

From here on out, I take $t>0$ and have no more need for the absolute value sign on t. The first few terms in the series are

$$\phi = d[0,0]t^a + d[0,2]t^{a-2b}h^2 + d[1,0]t^{a+|c|}o + d[1,2]t^{a-2b+|c|}oh^2 + \cdots . \tag{34}$$

For $h=0$, the heat capacity is corrected to leading order as

$$\phi_{,tt} = a(a-1)d[0,0]t^{a-2}(1 + a_c o t^{|c|} + \cdots), \tag{35}$$

with the correction amplitude

$$a_c = \frac{(a+|c|)(a+|c|-1)d[1,0]}{a(a-1)d[0,0]}. \tag{36}$$

The susceptibility is

$$\phi_{,hh} = 2d[0,2]t^{a-2b}(1 + a_\chi o t^{|c|} + \cdots), \tag{37}$$

with

$$a_\chi = \frac{d[1,2]}{d[0,2]}. \tag{38}$$

The ratio

$$\frac{a_c}{a_\chi} = \frac{(a+|c|)(a+|c|-1)d[1,0]d[0,2]}{a(a-1)d[0,0]d[1,2]} \tag{39}$$

is expected to be universal [24].

Let us now return to the geometric equation. Partial differential equations generally have a multiplicity of solutions depending on boundary conditions and assumptions about regularity. The PDE appearing here has, to my knowledge, not been investigated beyond two dimensions [25] and its general properties are not known. The search for a solution must then rest at this point on some plausible limiting assumptions: (i) The free energy is a generalized homogeneous function of its arguments; (ii) the function $Y(q,z)$ is regular at $q=z=0$; (iii) the two ''boundary'' functions $Y(0,z)$ and $Y(q,0)$ result from the solution of the geometric equation in two dimensions, with the first function symmetric in z $[Y(0,z)=Y(0,-z)]$, but the second not symmetric in q; and (iv) the solution satisfies thermodynamic stability at $q=z=0$.

The first assumption is the natural form of the solution, as I have discussed. The second assumption seems at least a plausible first try since in the modern theory of critical phenomena the free energy is expected to be regular except at phase boundaries. The third assumption stipulates boundary conditions; that these assume neither too much nor too little is, *a priori*, not clear. That these work will be revealed by the solution process. I take our critical point to be even in the magnetic field h, but not in the irrelevant scaling field o. As we will see, alternatives to this last point are not mathematically attractive.

The fourth assumption, of thermodynamic stability, is connected with the fact that the entropy is a maximum in equilibrium [2]. This implies that the quadratic form in Eq. (8) must be positive-definite. Necessary and sufficient conditions for this are [26]

$$g_{00} > 0, \tag{40}$$

$$\begin{vmatrix} g_{00} & g_{01} \\ g_{10} & g_{11} \end{vmatrix} > 0, \tag{41}$$

and

$$\begin{vmatrix} g_{00} & g_{01} & g_{02} \\ g_{10} & g_{11} & g_{12} \\ g_{20} & g_{21} & g_{22} \end{vmatrix} > 0. \tag{42}$$

Since the geometric equation is symmetric in h, a symmetric boundary condition $Y(0,z)$ must result in a full solution symmetric in z. The series (33) then applies and thermodynamic stability in (t,h,o) coordinates requires

$$d[0,0], d[0,2], d[2,0] > 0 \tag{43}$$

and

$$2a(a-1)d[0,0]d[2,0] > (a-c)^2 d[1,0]^2. \tag{44}$$

Turn now to the solution of the geometric equation with two variables, which is covered in some detail in the Appendix. It is found that we can pick the four coefficients $d[0,0]$, $d[1,0]$, $d[2,0]$, and $d[0,2]$ arbitrarily subject only to thermodynamic stability. The geometric equation in two dimensions will then determine all of the other boundary coefficients $d[i,0]$ and $d[0,j]$ uniquely. I interpret $d[0,0]$, $d[2,0]$, and $d[0,2]$ as scaling constants and $d[1,0]$ as an asymmetry constant.

Return now to the solution of the full three-dimensional Riemannian geometry. I first calculate the thermodynamic Riemannian curvature scalar with Eq. (20). We have

$$R = \frac{\phi_{,th}\phi_{,th}\phi_{,tt}\phi_{,hoo}\phi_{,hoo} - \phi_{,hh}\phi_{,tt}\phi_{,tt}\phi_{,hoo}\phi_{,hoo} + \cdots}{2[-\phi_{,to}\phi_{,to}\phi_{,hh} + 2\phi_{,ho}\phi_{,to}\phi_{,th} + \cdots]^2}, \tag{45}$$

where a factor of g has canceled in the numerator and denominator. This expression is too large to show in totality because there are 122 terms in the numerator and 5 terms in the square brackets in the denominator. Clearly, a computer program for doing symbolic mathematics is highly desirable, if not essential, for doing such lengthy calculations [27].

To compute the constant κ, I use a basic methodology similar to that in two dimensions described in the Appendix. Calculate a series for $R\phi$ to zeroth order in z and q. Then exploit the postulated independence of κ on the series coefficients $d[i,j]$. The six coefficients that appear in the zeroth-order series for $R\phi$ are $d[0,0]$, $d[1,0]$, $d[2,0]$, $d[0,2]$, $d[3,0]$, and $d[1,2]$. The first four coefficients may be freely set, $d[3,0]$ follows from the method of the Appendix, and

$d[1,2]$ follows from the method laid out below. If we were to set $d[1,0]$ to zero, then both boundary functions would be even in their arguments. Since the geometric equation is an even function of both its arguments, its solution would then likewise be an even function and $d[1,2]$ would be zero. In the limits $d[1,0]\to 0$ and $d[1,2]\to 0$, a somewhat laborious computation yields the universal expression

$$\kappa=\frac{4a-4b-4c-4bc-a^2+4b^2+4c^2}{2(a-1)a}, \tag{46}$$

regardless of the values of the remaining coefficients.

Let us illustrate this solution process with the mean-field theory exponents $a=2$, $b=\frac{3}{2}$, and $c=0$. Substituting the series (33) into the expression for the curvature (45) yields

$$\begin{aligned}R\phi=&(4d[0,0]d[0,2]d[1,0]^3d[1,2]+d[0,0]^2d[1,0]^2d[1,2]^2+d[0,0]d[0,2]^2d[1,0]^2d[2,0]\\&-7d[0,0]^2d[0,2]d[1,0]d[1,2]d[2,0]-d[0,0]^3d[1,2]^2d[2,0]-7d[0,0]^2d[0,2]^2d[2,0]^2\\&+6d[0,0]^2d[0,2]^2d[1,0]d[3,0]+3d[0,0]^3d[0,2]d[1,2]d[3,0])/\{4d[0,2]^2\\&\times(-d[1,0]^2+d[0,0]d[2,0])^2\}+O(z,q).\end{aligned} \tag{47}$$

In the limits $d[1,0]\to 0$ and $d[1,2]\to 0$, we get $\kappa=\frac{7}{4}$, regardless of the values of the other coefficients. This value is consistent with Eq. (46). Having determined κ, we may now set $d[0,0]$, $d[1,0]$, $d[2,0]$, and $d[0,2]$ as we like, use the method of the Appendix to find $d[3,0]$, and all of the other boundary coefficients, and solve the zeroth-order term in Eq. (47) $(=-\kappa)$ for $d[1,2]$.

Clearly the value of $d[1,2]$ will not be unique since it follows from the solution to a quadratic equation. I offer no method in this paper to decide which of these two roots for $d[1,2]$ is physically appropriate other than comparisons with what is known from other calculations. We may show that, generally

$$d[1,2]=(\text{universal constant})_{\pm}\,\frac{d[1,0]d[0,2]}{d[0,0]}, \tag{48}$$

with the universal constant having two solution branches, denoted by the $\pm$ sign. The roots to the quadratic equation are real for all values of the critical exponents. Substituting into Eq. (39) then yields two solution branches for the corrections to scaling amplitude ratio:

$$\frac{a_c}{a_\chi}=\frac{a+|c|-1}{2+a-2b+2|c|} \tag{49a}$$

$$=\frac{a+|c|-1}{a-2b}. \tag{49b}$$

These ratios are entirely independent of the series coefficients $d[i,j]$. They are hence universal.

We now turn to comparisons with results from the modern theory of critical phenomena. Here it is believed that the order parameter and spatial dimensionalities determine all of the critical properties [4]. The three variable solution to the geometric equation in this section is restricted to an order parameter dimensionality of unity; the order parameter m is a scalar. However, the spatial dimensionality is allowed to vary and enters the theory through the values of the critical exponents.

Aharony and Ahlers [28] have worked out expressions for the corrections to scaling amplitudes and for the critical exponents. For the mean-field theory exponents (four spatial dimensions) $a=2$, $b=\frac{3}{2}$, and $c=0$, they obtained $a_c/a_\chi=+1$. Equations (49a) and (49b) yield $a_c/a_\chi=+1$ and -1, respectively. The first value is in agreement with the known value. For this reason, I will pick the first solution branch [Eq. (49a)] as the true physical one. Written in the language of Fisher [4] (see also Ref. [23]) it reads

$$\frac{a_c}{a_\chi}=\frac{1-\alpha+\theta}{4-\alpha-2\Delta+2\theta}. \tag{50}$$

I offer no physical interpretation for the second solution branch.

Let us turn to the three-dimensional (3D) Ising model exponents, which have values near $a=\frac{15}{8}$ and $b=\frac{25}{16}$ [29]. The corrections to scaling exponent has value near $c=-\frac{1}{2}$ and the known $a_c/a_\chi=0.9\pm 0.1$ [30]. For these exponent values, Eq. (49a) yields $a_c/a_\chi=\frac{11}{14}=0.79$, in agreement with the known value.

Once we have picked one of the two values for $d[1,2]$, the rest of the series coefficients $d[i,j]$ follow uniquely from this algorithm.

1. $i=1$.
2. Begin the outer loop. Write the series for $Y(q,z)$ to orders q^{i+3} and z^{i+3}.
3. With this series, compute the series for $R\phi$ to orders q^i and z^i.
4. $j=0$.
5. Begin the inner loop. From the series for $R\phi$, pick the coefficient of the term $q^{i-j}z^j$.
6. Set this coefficient to zero and solve algebraically for the coefficient $d[i-j+1,j+2]$.
7. $j=j+2$.
8. Repeat the inner loop at step 5 until j exceeds i.
9. $i=i+1$.
10. Repeat the outer loop at step 2 as long as desired.

This algorithm is very direct and simple. The algebraic equation in step 6 has the coefficient $d[i-j+1,j+2]$ expressed linearly in terms of coefficients that have been previously determined in the solution process. The procedure may be repeated as long as desired, but it becomes increas-

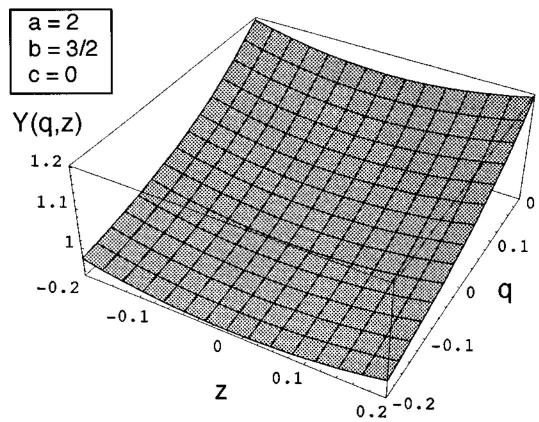

FIG. 2. Graph of $Y(q,z)$ as a function of q and z for the mean-field theory exponents, $d[0,0]=d[0,2]=d[2,0]=1$ and $d[1,0]=\frac{1}{2}$, and with the principle physical root for $d[1,2]$ corresponding to Eq. (49a). The function is smoothly behaved on the square shown. Thermodynamic stability is also satisfied.

ingly time consuming as i increases due to the difficulty of computing the series in step 3. My limit in this research was $i=7$.

Figure 2 shows the scaled free energy $Y(q,z)$ for the mean-field theory exponents with initial series coefficients $d[0,0]=d[0,2]=d[2,0]=1$ and $d[1,0]=\frac{1}{2}$. Of the two solution branches for $d[1,2]$ I picked the one in Eq. (49a). The boundary function $Y(0,z)$ is analytic in the whole range $z=\pm\infty$ [5]. The solution curve for the boundary function $Y(q,0)$ is shown in Fig. 3. It has infinities in the first and second derivatives of Y near $q=0.76$ and -1.46. In Fig. 2, I have held well back from these limiting values. The full function $Y(q,z)$ is well behaved on the displayed square and satisfies thermodynamic stability. For fixed q, it is a minimum for $z=0$. For fixed z, ϕ increases monotonically with q. I also computed $Y(q,z)$ on this square for the other root

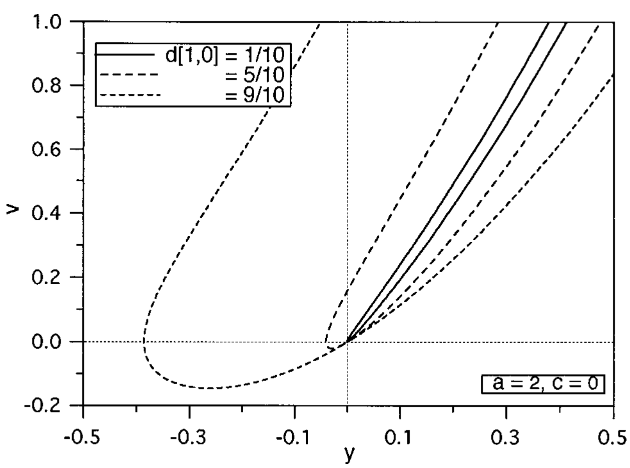

FIG. 3. Family of solution trajectories in (y,v) space with $d[0,0]=d[2,0]=1$ and various values of $d[1,0]$ for the critical exponents $a=2$ and $c=0$. The limit of thermodynamic stability corresponds to $|d[1,0]|=1$. Trajectories start from the origin $(q=0)$ and move into the first quadrant for $q>0$ and into the third quadrant for $q<0$. All the physical trajectories eventually head for $(y,v)\rightarrow(\infty,\infty)$ in the first quadrant, but with $|q|$ remaining finite.

for $d[1,2]$, corresponding to Eq. (49b), and found no essential qualitative difference that would lead me to prefer one root or another.

The function $Y(q,z)$ found here is not universal in the sense in this paper of depending only on a single set of critical exponents and three scaling constants. This is because, in addition to the scaling constants $d[0,0]$, $d[0,2]$, and $d[2,0]$, $Y(q,z)$ depends on the asymmetry parameter $d[1,0]$. In the light of the modern theory of critical phenomena, this additional dependence is perhaps not surprising. Let me quote from Privman, Hohenberg, and Aharony [24]: ''Critical exponents emerge from the 'local' properties of the [renormalization-group] flow in the immediate vicinity of each fixed point, and they can be calculated from the linearized recursion relations. On the other hand, the scaling functions are properties of the complete 'global' (nonlinear) [renormalization-group] flow away from the fixed point under consideration, along 'relevant' trajectories in the parameter space (leading to other fixed points or to infinity)....'' This entire issue is clearly deserving of further study, but this is beyond the scope of this paper.

Having explored one type of solution to the geometric equation in three dimensions, I now turn to some less favorable possibilities. Specifically, the following two questions are addressed. First, one of the boundary functions, but not the other, has been picked to be symmetric in its variable. However, may they both be symmetric, or neither? Second, the boundary functions have been determined by solving the geometric equation in two dimensions. Is doing so mathematically necessary, or could we pick all of the boundary coefficients freely?

Consider the possibility of boundary conditions that are symmetric in *both* q and z. I tried this for the pair of exponent sets discussed above, using the method of the Appendix to solve for the boundary coefficients, with $d[1,0]=0$. For both exponent sets, the series solution method leads to either inconsistent algebraic equations or complex roots. Hence, at least for these exponent sets, I reject the completely symmetric solution as inconsistent with the geometric equation.

The case with neither boundary solution even in its argument (i.e., $d[0,1]\neq 0$) results in considerable algebraic complication. It also lacks interest because there seems to be no good physical interpretation for either boundary solution in this case. Hence I do not consider it further here.

Let us now turn to the issue of the freedom available in choosing the boundary coefficients. First, if we choose $d[3,0]$ freely, rather than with the method of the Appendix, then Eq. (48) would not obtain and the corrections to scaling amplitude ratio in Eq. (49) would not be universal. This issue aside, I tried an entirely free set of boundary coefficients for the pair of exponents values (a,b,c) discussed above. One of the boundary coefficient sets corresponds to a symmetric function and the other does not. No mathematical inconsistencies were encountered in the solution process. However, despite being mathematically viable, free boundary conditions are not physically very interesting because universality in no sense obtains.

CONCLUSION

In conclusion, I have extended the basic postulate that the thermodynamic Riemannian curvature scalar is proportional to the inverse of the free energy to an arbitrary number of dimensions. The resulting partial differential equation has as a solution a generalized homogeneous function, in all dimensions. Such a form is expected from the modern theory of critical phenomena and it embodies scaling and universality. A linear mixing of the standard intensive variables in the entropy representation, in conjunction with a given functional form of the free energy, is also allowed as a solution in all dimensions. Such a mixing of variables is routinely used in the modern theory of critical phenomena. In addition, I have worked out the ratio of the corrections to scaling amplitude for the heat capacity and the susceptibility on the critical isochore. Two solution branches result in the form of exact equations in terms of the critical exponents. One of the solution branches is in good agreement with what was previously known.

Left unresolved are questions centering around the uniqueness of the solution. The series coefficient $d[1,0]$ in three dimensions is not a scaling constant, so the absence of some preferred value for it means that our equation of state is not yet universal. (Note that this does not affect calculated values of the ratio a_c/a_χ). An additional ambiguity consists of the two solution branches for the series coefficient $d[1,2]$. Generally, a lack of uniqueness is not unexpected in the context of the modern theory of critical phenomena since the scaled equation of state could depend on more than a single critical fixed point. To make further progress on this problem probably requires a full solution scheme for the partial differential equation, one that goes beyond the relatively limited series here. In any case, additional ideas are called for. Despite unresolved issues, I feel that the results presented here represent a clear and significant advance towards computing equations of state from thermodynamics with the Riemannian geometric method.

APPENDIX: SOLUTIONS IN TWO DIMENSIONS

This appendix discusses solutions to the two-dimensional geometric equation, essential because such solutions constitute the boundary conditions for the three-dimensional problem. Such solutions have been discussed previously [5,6], so only a brief review is provided. Emphasis is on solutions not symmetric about the zero ordering field since these have been less discussed. Hence the focus is on the variable o, its critical exponent c, and the function $Y(q)=Y(0,q)$.

The geometric equation in two dimensions may be written [7]

$$\frac{\begin{vmatrix} \phi_{,tt} & \phi_{,to} & \phi_{,oo} \\ \phi_{,ttt} & \phi_{,tto} & \phi_{,too} \\ \phi_{,tto} & \phi_{,too} & \phi_{,ooo} \end{vmatrix}}{2\begin{vmatrix} \phi_{,tt} & \phi_{,to} \\ \phi_{,to} & \phi_{,oo} \end{vmatrix}^2} = -\frac{\kappa}{\phi}. \tag{A1}$$

Substitution of a scaling form

$$\phi=|t|^a Y(q), \tag{A2}$$

where

$$q=o|t|^{-c}, \tag{A3}$$

reduces this PDE to an ordinary third-order differential equation for $Y(q)$ by Theorem 1.

Of primary interest are series solutions

$$Y(q)=\sum_{i=0}^{\infty} d[i,0]q^i. \tag{A4}$$

The first three coefficients $d[0,0]$, $d[1,0]$, and $d[2,0]$ may be set freely, subject only to thermodynamic stability [Eqs. (43) and (44)]. Before the remaining coefficients can be solved for, we must evaluate the constant κ in Eq. (A1). By our basic principle for a correct theory, its value depends only on the critical exponents a and c and in no way on the series coefficients $d[i,0]$. In particular, this means that κ should have whatever value it has in the limit $d[1,0]\to 0$, where

$$\kappa=\frac{(c-1)(2c-a)}{a(a-1)}, \tag{A5}$$

regardless of the values of the other coefficients. This expression results as well from the requirement that the solution be regular at $q=0$ for symmetric solutions produced by setting $d[1,0]=0$ [5,6].

Let us illustrate with $a=2$ and $c=0$. The basic method consists of computing a series for $R\phi$ to successively higher powers of q. By the geometric equation (A1), only the zeroth-order term differs from zero; this allows the unique determination of all of the coefficients $d[i,0]$ for $i>3$. Substituting a third-order series for ϕ yields

$$\begin{aligned} R\phi = {} & d[0,0](d[1,0]^2 d[2,0]-4d[0,0]d[2,0]^2 \\ & +3d[0,0]d[1,0]d[3,0])/4(d[1,0]^2-d[0,0]d[2,0])^2 \\ & +O(q). \end{aligned} \tag{A6}$$

In the limit $d[1,0]\to 0$, the first term on the right-hand side goes to -1, no matter what the values of the other coefficients, and $\kappa=1$, consistent with Eq. (A5).

At this point, the first three coefficients may be set freely and $d[3,0]$ follows on setting the zeroth-order term in Eq. (A6) to $-\kappa$. Successively higher-order series expansions of $R\phi$ now determine uniquely as many of the remaining coefficients as desired. For the particular choices $d[0,0]=d[2,0]=1$ and $d[1,0]=\frac{1}{2}$, the series is

$$\begin{aligned} Y(q) = {} & 1+\frac{q}{2}+q^2+q^3+\frac{23q^4}{16}+\frac{277q^5}{160} \\ & +\frac{737q^6}{320}+\frac{2623q^7}{896}+\cdots . \end{aligned} \tag{A7}$$

Consider some additional points about the first three series coefficients. By Theorem 2, Y and q may each be multiplied by constants and the result will remain a solution to the geometric equation. In Ref. [5] I took these scaling constants to be $d[0,0]$ and $d[2,0]$. In this paper I take them both to be 1, with no loss of generality [31]. The coefficient $d[1,0]$, however, does not represent a scaling constant and in Ref. [6] it was found that it must be set to zero to reproduce the usual critical point behavior. However, there appears to be no reason to require this asymmetry coefficient $d[1,0]$ to be zero in connection with the boundary conditions. In fact, I show in Sec. IV that to get a mathematically consistent solution to the geometric equation in three dimensions, we cannot set $d[1,0]$ to zero. Other than this, and thermodynamic stability, I bring forth no restrictions on $d[1,0]$.

Not essential in our series solution method, but instructive nonetheless, are full solutions to the geometric equation in two dimensions [5]. To do this, return to Eq. (A1) and make the change of variables

$$x=\ln|q|, \tag{A8}$$

$$w=\ln(Y), \tag{A9}$$

$$y=\frac{dw}{dx}=\frac{q}{Y}\,Y', \tag{A10}$$

and

$$v=\frac{d^2w}{dx^2}=\left[\frac{qY'}{Y}+\frac{q^2Y''}{Y}-\frac{q^2(Y')^2}{Y^2}\right]. \tag{A11}$$

The third-order differential equation for $Y(q)$ now reduces to a pair of coupled first-order differential equations

$$\frac{dv}{dx}=f(y,v) \tag{A12}$$

and

$$\frac{dy}{dx}=v, \tag{A13}$$

where $f(y,v)$ is a ratio of polynomials in y and v. The solutions to these coupled equations are parametrized trajectories in (y,v) space.

By our general assumptions, it is implicit that $q=0$ represents a point on the solution trajectory. The additional assumptions of analyticity, thermodynamic stability, and the transformation equations (A10) and (A11) then imply that $q=0$ corresponds to the *origin* in (y,v) space. The transformation equations further imply that, regardless of the values of the critical exponents, if $d[1,0]=0$ the solution trajectory starts from the origin with slope 2 and if $d[1,0]\neq 0$ it starts with slope 1. The discontinuity in the limit $d[1,0]\to 0$ was discussed in Ref. [6] and was connected with the preference for symmetric solutions with relevant scaling fields.

The constant multipliers $d[0,0]$ and $d[2,0]$ for Y and q do not affect the solution trajectories $v=v(y)$, but the trajectories do depend on $d[1,0]$. As an example, consider again the case $a=2$ and $c=0$, where

$$f(y,v)=-2y(1+y)^2+v(3+4y). \tag{A14}$$

Essential in the numerical solution process are singular points and curves. In this case $f(y,v)$ is analytic everywhere, so the only singular points to the differential equations (A12) and (A13) correspond to $f(y,v)$ and v both zero. This happens at only two points, both on the y axis: $(-1,0)$ and $(0,0)$. The former point turns out not to be relevant since the physical trajectories (those that satisfy thermodynamic stability at

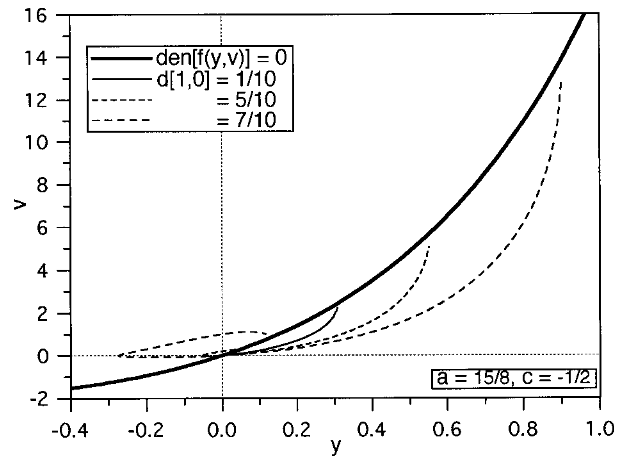

FIG. 4. Family of solution trajectories in (y,v) space with $d[0,0]=d[2,0]=1$ and various values of $d[1,0]$ for the critical exponents $a=\frac{15}{8}$ and $c=-\frac{1}{2}$. The limit of thermodynamic stability corresponds to $|d[1,0]|=0.7627$. Solutions start from the origin $(q=0)$ and move into the first quadrant for $q>0$ and into the third quadrant for $q<0$. All the physical trajectories eventually hit the curve of singularities where the denominator $f(y,v)=0$ and where the third derivative of Y diverges, but with $|q|$ remaining finite.

the origin) starting at the origin do not go there. The latter is a singular point for all critical exponents and corresponds to the simple coordinate singularity at $q=0$ in Eq. (A8). There is no nonanalytic behavior in the thermodynamic properties at the origin. The series (A7) is used to start the numerical solution from the origin $(q=0)$.

Figure 3 shows a family of solution trajectories with different values of $d[1,0]$, all in a range allowed by thermodynamic stability $|d[1,0]|<1$. As q increases from zero, trajectories move into the first quadrant. As q decreases from zero, trajectories move initially into the third quadrant. Regardless of starting direction, all physical trajectories eventually go to infinity in the first quadrant, $(y,v)\to(\infty,\infty)$, but with finite $|q|$. Changing the sign of $d[1,0]$ has the same effect as changing the sign of q and adds nothing new to Fig. 3. Any possible physical nature of these solutions is unclear since these critical exponents by themselves do not seem to correspond to those of any known physical system.

Another pair of exponent values of interest is $a=\frac{15}{8}$ and $c=-\frac{1}{2}$, where (with $d[1,0]=\frac{1}{2}$)

$$Y(q)=1+\frac{q}{2}+q^2+\frac{488\,623q^3}{264\,600}+\frac{105\,351\,151q^4}{24\,131\,520}+\cdots, \tag{A15}$$

and

$$\begin{aligned}f(y,v)=(&-132\,300v^2+20\,160v^3+848\,925vy\\&+739\,200v^2y-507\,150y^2+1\,413\,300vy^2\\&-105\,984v^2y^2-2\,009\,280y^3-553\,968vy^3\\&-2\,453\,824y^4-232\,128vy^4-918\,528y^5\\&-105\,984y^6)/[105(-420v+2415y+192vy\\&+1364y^2+192y^3)].\end{aligned} \tag{A16}$$

This particular $f(y,v)$ is more complicated than the one in Eq. (A14) by virtue of a denominator that is zero along a curve in (y,v) space. This curve of singularities, shown in Fig. 4, results in a new class of singular solutions. Figure 4 also shows a family of solution trajectories with several values of $d[1,0]$ (we require $|d[1,0]|<\sqrt{210}/19$, by thermodynamic stability). The solution trajectories eventually all encounter the curve of singularities where the third derivative of Y diverges. One way to avoid this nonanalyticity would be to have the curve of singularities crossed by a curve of zero numerator of $f(y,v)$, resulting in a cancellation of singularities. However, there are no such crossings, other than at the origin, and one point on the negative y axis. The latter is not physically relevant. Again, any physical significance of these critical exponents by themselves is unclear. Complete solutions for the boundary functions $Y(0,z)$ for the exponent values $(a,b)=(2,\frac{3}{2})$ and $(\frac{15}{8}, \frac{25}{16})$ are given in Ref. [5] and will not be restated here.

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