Riemannian geometric theory of critical phenomena

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By combining the hypothesis that the thermodynamic curvature is the correlation volume with the hypothesis that the free energy is the inverse of the correlation volume, I propose that the thermodynamic curvature is proportional to the inverse of the free energy near the critical point. This hypothesis leads to a partial differential geometric equation for the free energy which a generalized homogeneous function reduces to a third-order nonlinear ordinary differential equation whose solution is consistent with two-scale factor universality. The resulting scaled equation of state is, overall, in very good agreement with mean-field theory, the three-dimensional Ising model, and experiment for the pure fluid. Universal ratios among the critical amplitudes are also in good agreement with known values. For the non-mean-field theory exponents, the solution considered here is not analytic in the whole one-phase region; the second derivative of the free energy suffers a discontinuity.

I. INTRODUCTION

Thermodynamics is generally done in the limit of infinite system size, where collective macroscopic laws govern [1,2]. These laws of equilibrium thermodynamics may be connected to microscopic mechanics with statistical mechanics [3]. In its rigorous version [4], statistical mechanics offers a proof of a number of properties in the thermodynamic limit for several general classes of microscopic models.

Less clear is the application of thermodynamics to finite systems, to problems such as fluctuations. Despite a lack of rigor, however, rules such as Einstein's thermodynamic fluctuation theory [3,5] have become well established and connected, at least heuristically, to statistical mechanics. Thermodynamic fluctuation theory is written in terms of thermodynamic properties and its expression does not rest on any microscopic model. Many treatments of thermodynamics include fluctuation theory in the domain of thermodynamics [1,2]. Lewis [6] has argued that this inclusion is logically necessary.

More complicated is the case near the critical point where fluctuations reach macroscopic proportions and where new thermodynamic rules appear, such as power-law divergences, the scaled form of the free energy, and universality. These rules may be connected to microscopic mechanics by renormalization-group theory [7], which, though not rigorous either, lends insight and computational power.

Since many of the rules of critical phenomena are general statements about thermodynamic behavior, one may inquire as to what extent they might follow from some sort of unifying thermodynamic principle. In this paper I discuss this question in the context of a thermodynamic hypothesis that follows from combining the results of a Riemannian geometric theory of thermodynamic fluctuations with a well-known relation between the singular part of the free energy and the correlation length. This hypothesis is: *the thermodynamic Riemannian curvature is proportional to the inverse of the free energy.*

The hypothesis takes the form of a partial differential equation for the free energy. I show that a generalized homogeneous function reduces this equation to a third-order nonlinear ordinary differential equation whose solution yields a free energy in agreement with two-scale factor universality. In addition, the resulting scaled equation of state is in good agreement with mean-field theory (MFT), the three-dimensional (3D) Ising model, and with experiment in the pure fluid. The universal critical amplitude ratios also agree well with what is known. As input into the solution it is necessary to supply only the values of the critical exponents.

For the non-MFT exponents the solution to the geometric equation is found to be nonanalytic in the one-phase region. This requires an additional assumption; I assume that the solution is generally as smooth as possible, and, specifically, is smooth on the critical isochore in the one-phase region. These assumptions limit the nonanalyticity to a single point where the second derivative of the free energy suffers a discontinuity. Such a point of nonanalyticity is at odds with usual beliefs. For example, it has been proved rigorously that the Ising model has no nonanalyticities away from the coexistence curve [4]. This issue is discussed.

In this paper I start by summarizing the relevant concepts in critical phenomena. Then, the geometric equation is stated and its solution discussed for a number of systems. Though the method should generalize, I consider here only systems with ordinary critical points, characterized by a single order parameter. I confine myself to power-law divergences with a positive heat-capacity exponent. In addition, I consider only the behavior very close to the critical point and do not include "corrections to scaling."

II. THEORY

In this section I present the relevant theoretical structures. First, I summarize some fundamental concepts in the modern theory of critical phenomena, both to set the context and to introduce notation. Second, I describe the Riemannian geometry of thermodynamics, with particular emphasis on the thermodynamic Riemannian curvature scalar. Third, I discuss the resulting partial differential equation for the free energy.

A. Critical phenomena

I consider the case of systems with a reduced temperature

$$t=\frac{T-T_C}{T_C}\ , \tag{2.1}$$

where T_C is the critical temperature, and a single order parameter m, with conjugate ordering field h. Near the critical point, thermodynamic quantities behave as power laws characterized by critical exponents and critical amplitudes; see Table I. The critical exponents are related to one another by scaling relations, which leave only two exponents independent. These scaling relations can be deduced from the assumption that the singular part of the free energy per volume can be written as a generalized homogeneous function:

$$f(\lambda^{a_t}t,\lambda^{a_h}h)=\lambda f(t,h)\ , \tag{2.2}$$

where a_t and a_h are critical exponents and λ is a positive constant [8–10]. Setting $\lambda=|t|^{-1/a_t}$ and using standard values for the critical exponents leads to

$$f(t,h)=n_1|t|^{2-\alpha}Y(n_2h|t|^{-\beta\delta})\ , \tag{2.3}$$

where I have introduced two constant scaling factors n_1 and n_2. The function Y has two branches, one for $t>0$ and the other for $t<0$.

An essential quantity in critical phenomena is the correlation length ξ, which gives the range of the pair-correlation function [10]. It is the characteristic size of organized fluctuations near the critical point. The correlation volume ξ^d, where d is the spatial dimension, is related to the free energy per volume through an additional

TABLE I. The basic notation for critical phenomena. The scaling hypothesis predicts that $\alpha=\alpha'$ and $\gamma=\gamma'$. The comma notation indicates partial differentiation.

$t=\dfrac{T-T_C}{T_C}$		
$m(=-f_{,h})=B(-t)^{\beta}$	$t<0$	$h=0$
$\chi(=-f_{,hh})=\Gamma t^{-\gamma}$	$t>0$	$h=0$
$\chi=\Gamma'(-t)^{-\gamma'}$	$t<0$	$h=0$
$C_h(=-f_{,tt})=At^{-\alpha}$	$t>0$	$h=0$
$C_h=A'(-t)^{-\alpha'}$	$t<0$	$h=0$
$h=Dm\|m\|^{\delta-1}$	$t=0$	
$z=h\|t\|^{-\beta\delta}$	$t\neq0$	
$f(t,h)=\|t\|^{2-\alpha}Y(z)$	$t\neq0$	
$\tilde{z}=t\|h\|^{-1/\beta\delta}$		$h\neq0$
$f(t,h)=\|h\|^{1+1/\delta}\tilde{Y}(\tilde{z})$		$h\neq0$
$x=t\|m\|^{-1/\beta}$		$m\neq0$
$h=m\|m\|^{\delta-1}h(x)$		$m\neq0$

hypothesis of critical phenomena. The basic idea [11] is that the (extensive) free energy associated with fluctuations at volumes of the order of ξ^d is k_BT_C, where k_B is the Boltzmann constant. This free energy is equated to the singular part of the (extensive) free energy near the critical point and, therefore, the singular part of the free energy *per volume*

$$f(t,h)=\kappa_1\frac{k_BT_C}{\xi^d}\ , \tag{2.4}$$

where κ_1 is a dimensionless constant of order minus unity.

"Two-scale factor universality" [12] includes the above statements about scaling and the correlation volume and adds two more. It can be written as four independent statements: (1) $f(t,h)$ is a generalized homogeneous function of its arguments; (2) Y is universal up to the two material-dependent constants n_1 and n_2; (3) $f(t,h)$ is proportional to the inverse of the correlation volume; and (4) κ_1 is a universal constant. "Universal" means the same for any system in a given universality class characterized by the spatial- and order-parameter dimensions [10].

B. Geometry of thermodynamics

Turn now to the Riemannian geometry of thermodynamic fluctuations [13], which was recently reviewed [14]. The discussion begins with a summary of thermodynamic fluctuation theory. Consider a finite, open subsystem A' of an infinite thermodynamic fluid or magnetic 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 [3]

$$P(a,a')da'_1da'_2 =\left[\frac{V'}{2\pi}\right]\exp\left[-\frac{V'}{2}\sum_{\mu,\nu=1}^{2}g_{\mu\nu}(a)\Delta a'_\mu\Delta a'_\nu\right]\times\sqrt{g(a)}da'_1da'_2\ , \tag{2.5}$$

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

$$g_{\mu\nu}(a)=-\frac{1}{k_BT_C}\frac{\partial^2 f}{\partial a_\mu\partial a_\nu}=-\frac{1}{k_BT_C}f_{,\mu\nu}\ , \tag{2.6}$$

and

$$g(a)=\det[g_{\mu\nu}(a)]\ . \tag{2.7}$$

The comma notation in Eq. (2.6) denotes partial differentiation of $f(t,h)$. (I have replaced a factor of $1/T$ in front of the second derivatives of f by $1/T_C$, since it is assumed the system is very near the critical point.)

The quadratic form in Eq. (2.5),

$$(\Delta l)^2=\sum_{\mu,\nu=1}^{2}g_{\mu\nu}(a)\Delta a'_\mu\Delta a'_\nu\ , \tag{2.8}$$

constitutes a positive definite Riemannian metric on the two-dimensional thermodynamic state space of points with coordinates (t,h) [13]. Physically, the interpretation for distance between two thermodynamic states is clear from Eq. (2.5): the less probable a fluctuation between two states, the further apart they are. Note also that the quantity

$$\sqrt{g(a)}da_1'da_2' \tag{2.9}$$

is the Riemannian thermodynamic-state space-volume element [13–15].

The metric defines the fourth-rank Riemannian curvature tensor $\underline{R}$ in terms of derivatives of the free energy. The complete contraction of $\underline{R}$, the Riemannian curvature scalar R, has units of real space volume for the metric here, regardless of the dimension of the thermodynamic-state space [16]. It has been found to be zero for the monocomponent ideal gas [13,17], and to diverge in the same way as the correlation volume ξ^d near the critical point of pure fluid or ferromagnetic systems [13].

The metric and its curvature have been placed in the context of a covariant thermodynamic fluctuation theory that was proposed as the correct way to extend thermodynamic fluctuation theory beyond the Gaussian approximation [16,18]. This theory, in the path-integral form [16], predicts that the absolute value of the curvature scalar R is the volume where classical thermodynamic fluctuation theory breaks down. Near critical points, the breakdown volume is physically expected to be the correlation volume ξ^d. Therefore

$$R=\kappa_2\xi^d , \tag{2.10}$$

where κ_2 is a dimensionless constant, with absolute value of order unity, related to how ξ^d is defined. The constant κ_2 should be trivially universal if the definition of ξ^d is consistent between materials.

The sign of the Riemannian curvature scalar depends on the choice of sign convention. With the sign convention in this paper [19], the thermodynamic curvature is negative near the critical point for all the cases considered in this paper. I add that Janyszek [20] has suggested that, for a given sign convention, the thermodynamic curvature must have the same sign for all systems in the critical regime. This hypothesis places constraints on the values of the critical exponents which are in accord with what is observed.

C. Geometric equation

Combining the hypothesis connecting the free energy and the correlation volume Eq. (2.4) with the hypothesis connecting the curvature and the correlation volume Eq. (2.10) yields

$$R(t,h)=\kappa\frac{k_BT_C}{f(t,h)} , \tag{2.11}$$

where

$$\kappa=\kappa_1\kappa_2 . \tag{2.12}$$

In words, this geometric equation states: *the thermodynamic curvature is proportional to the inverse of the free energy*. As will be seen in the solution process near the critical point, k_BT_C cancels out and κ is a universal constant.

By a standard formula for the Riemannian curvature scalar in terms of the metric elements, and the thermodynamic metric Eq. (2.6), one can show that the geometric equation is [21]

$$\frac{(f_{,tt}f_{,thh}f_{,thh}-f_{,th}f_{,thh}f_{,tth}-f_{,tt}f_{,hhh}f_{,tth}+f_{,hh}f_{,tth}f_{,tth}+f_{,th}f_{,hhh}f_{,ttt}-f_{,hh}f_{,thh}f_{,ttt})}{2(f_{,tt}f_{,hh}-f_{,th}f_{,th})^2}=\frac{\kappa}{f} . \tag{2.13}$$

Because of the form of the metric elements the fourth derivatives of f cancel in calculating the curvature; this has been emphasized by Janyszek and Mrugała [22]. Gilmore has also made this point [23]. Of interest is the solution of this partial differential equation near $f=0$, which corresponds to the critical point.

In the hypothesis connecting the free energy to the correlation volume it is only the singular part of the free energy that is relevant. However, in most previous treatments of the thermodynamic curvature it was the total free energy that was used. With one exception [24], however, the presence of an additive background term was not very important. By an elementary examination of the Taylor series, one may demonstrate that, if $f(t,h)$ is an even function of h, $\alpha>0$, and $\beta\delta>1$, then the singular part of the free energy Eq. (2.3) will dominate a regular background free energy in every term of the Taylor series in the expression for the thermodynamic curvature. Therefore, the background term is irrelevant very near the critical point in the cases considered in this paper.

III. SOLUTION METHOD

In this section I discuss the method of solution of the geometric equation. The method starts on the critical isochore in the one-phase region, proceeds to the critical isotherm, and ends on the coexistence curve.

A. Reduction to an ordinary differential equation

Guided by what is known about critical phenomena, I try as a solution to Eq. (2.13) a generalized homogeneous function:

$$f(t,h)=|t|^aY(h|t|^{-b}) , \tag{3.1}$$

where a and b are constants that the geometric equation does not determine. Each group of terms in the numerator and denominator on the left hand side of Eq. (2.13) contains the same total number of derivatives with respect to both t and h, four. This, coupled with the absence of explicit factors of t and h, results in the reduction of the geometric equation to a third-order nonlinear ordinary differential equation for $Y(z)$ in the independent variable

$$z=h|t|^{-b}: \tag{3.2}$$

$$Y^{(3)}(z)=F_k[z,Y(z),Y'(z),Y''(z)] , \tag{3.3}$$

where, because of its length, F_κ, a ratio of polynomials, is not written out explicitly here [25]. The third derivative $Y^{(3)}(z)$ appears linearly in the geometric equation, so F_κ is unique. This differential equation consists of two branches, one for $t>0$ and the other for $t<0$, which must be joined at the critical isotherm $t=0$. Table II shows the notation used for the differential equations.

A third-order differential equation in the form of Eq. (3.3) can be solved uniquely in the neighborhood of any nonsingular point provided exactly three constants of integration are given [26]. These constants of integration are connected with the following three conditions. The first two 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. Here, n_1 and n_2 are constants. The third constant is connected with the following standard assumption: (3) the order parameter $m=-f_{,h}$ is zero in zero field at a temperature above the critical temperature.

Conditions (1) and (2) are exactly consistent with the prediction of two-scale factor universality. In addition, they imply that the geometric equation is a scale invariant differential equation, which means that its order can be reduced by an appropriate change of variables [27]. This is done below. It can be shown that condition (3) results, with the geometric equation, in a free energy that is an even function of h.

TABLE II. Notation used in the course of the solution of the differential equations. The x here differs from the one in the scaled equation of state in Table I and $f(y,v)$ differs from the free energy $f(t,h)$. Comparing Eqs. (2.3) and (3.1) provides the link between the standard critical exponents and those used in conjunction with solving the differential equation: $a=\beta(\delta+1)=(2-\alpha)$ and $b=\beta\delta$.

$z=h\|t\|^{-b}$	$t\neq 0$
$f(t,h)=\|t\|^{a}Y(z)$	$t\neq 0$
$a=\beta(\delta+1)=2-\alpha$	
$b=\beta\delta$	
$x=\ln(z)$	$t\neq 0,\ h\neq 0$
$w=\ln(-Y)$	$Y\neq 0$
$y=dw/dx$	
$v=dy/dx$	
$\frac{dv}{dx}=f(y,v)$	
$\tilde{z}=t\|h\|^{-1/b}$	$h\neq 0$
$f(t,h)=\|h\|^{a/b}\tilde{Y}(\tilde{z})$	$h\neq 0$

B. Series solution on the critical isochore ($z=0$, $t>0$)

I consider first the behavior of Eq. (3.3) near the critical isochore $z=0$, $t>0$, where I will assume that $Y(z)$ is regular. The geometric equation certainly does not require this assumption, and my reason for it is that rigorous treatments of statistical mechanics [4] as well as experiments have shown this to be true in a number of cases. Since m is zero in zero field for $t>0$, I am interested in a solution with $Y'(0)=0$. However, the denominator of F_κ is zero if z and $Y'(0)$ are both zero. To avoid a diverging $Y^{(3)}(z)$ as $z\to 0$ it is necessary that the numerator of F_κ be zero as well in this limit. This obtains, independent of $Y(0)$ and $Y''(0)$, if and only if the constant in the geometric equation

$$\kappa=\frac{(b-1)(2b-a)}{a(a-1)} . \tag{3.4}$$

With this choice of κ, which I make in the remainder of this paper, F_κ is regular on the critical isochore, where it goes to zero. Note that κ depends only on the critical exponents and is hence universal. This implies that κ_1 is universal as well, in accord with another prediction of two-scale factor universality. I solve, hence, the differential equation:

$$Y^{(3)}(z)=F[z,Y(z),Y'(z),Y''(z)] . \tag{3.5}$$

I shall display F explicitly for the MFT exponents below.

I shall construct a Taylor-series solution

$$Y(z)=\sum_{n=0}^{\infty} y_{2n}z^{2n} , \tag{3.6}$$

to Eq. (3.5) about $z=0$. It can be proved that $y_1=0$ forces all the odd coefficients to be zero; this corresponds to an even function solution. Thermodynamic stability requires $y_0<0$ and $y_2<0$; otherwise, y_0 and y_2 can be picked freely and are simply related to the scaling constants n_1 and n_2. I shall pick convenient values for y_0 and y_2 and match experiment as necessary by scaling Y and z appropriately.

C. Numerical solution to the critical isotherm ($z\to\infty$)

Very helpful in carrying the solution from the critical isochore ($z=0$, $t>0$) to the critical isotherm ($z\to\infty$) is the change of variables:

$$x=\ln(z) \tag{3.7}$$

and

$$w=\ln(-Y) . \tag{3.8}$$

Define also

$$y=\frac{dw}{dx}=\frac{z}{Y}Y' \tag{3.9}$$

and

$$v=\frac{d^2w}{dx^2}=\left[\frac{zY'}{Y}+\frac{z^2Y''}{Y}-\frac{z^2(Y')^2}{Y^2}\right] . \tag{3.10}$$

This coordinate transformation is well behaved except for $z=0$, $z\to\infty$, $Y=0$, and $Y\to\infty$. The case $z=0$ is handled with the Taylor series in the preceding section. The critical isotherm $z\to\infty$ is handled by computing limits as described below. Y is never found to be zero, but it approaches $-\infty$ as $z\to\infty$. This is also handled with the limiting procedure below.

This change of variables is useful for two reasons. First, both z and $Y(z)$ vary over many orders of magnitude in cases of interest. The more gradually varying x and $w(x)$ are more manageable, particularly in numerical solution schemes. Second, and more important, it is straightforward to show that this change of variables reduces the geometric equation Eq. (3.5) to a second-order autonomous differential equation:

$$\frac{d^2y}{dx^2}=f(y,v)\ , \tag{3.11}$$

where $f(y,v)$ is shown explicitly in two examples below [and should not be confused with the free energy $f(t,h)$].

This second-order differential equation may be expressed as two coupled first-order autonomous differential equations:

$$\frac{dv}{dx}=f(y,v) \tag{3.12}$$

and

$$\frac{dy}{dx}=v\ , \tag{3.13}$$

which may be solved for $y=y(x)$ and $v=v(x)$ given appropriate initial conditions, computed with the series Eq. (3.6). In addition, the auxiliary differential equation

$$\frac{dw}{dx}=y \tag{3.14}$$

may be integrated to obtain $w=w(x)$ given $y(x)$ and the initial condition. This solution scheme yields the values of (x,w,y,v) along the entire trajectory; these may be converted to (z,Y,Y',Y'') by inverting the transformation equations (3.7)–(3.10).

It is straightforward to show that $(z,Y,Y',Y'')=(0,-1,0,-2)$ on the critical isochore corresponds to $(x,w,y,v)=(-\infty,0,0,0)$. Therefore, the solution trajectory in the (y,v) plane starts at the origin. It is also straightforward to demonstrate that the scaling factors n_1 and n_2 contribute additive terms to x and w, but have no effect on y and v. Hence, the solution trajectory $v=v(y)$ in the (y,v) plane is independent of n_1 and n_2.

On the critical isotherm ($t=0$), the fact that $f(t,h)$ is a generalized homogeneous function leads to

$$f(t,h)=|h|^{a/b}\tilde{Y}(\tilde{z})\ , \tag{3.15}$$

where

$$\tilde{z}=t|h|^{-1/b}\ . \tag{3.16}$$

Since $f(t,h)$ is assumed symmetric in h, we can without loss of generality take $h>0$ and $z>0$. Equating Eqs. (3.1) and (3.15) and taking derivatives with respect to $\tilde{z}$ yields (with positive z and $\tilde{z}$)

$$\tilde{z}=z^{-1/b}\ , \tag{3.17}$$

$$\tilde{Y}(\tilde{z})=\frac{Y(z)}{z^{a/b}}\ , \tag{3.18}$$

$$\tilde{Y}'(\tilde{z})=\frac{d\tilde{Y}}{d\tilde{z}}=\frac{aY(z)-bzY'(z)}{z^{(a-1)/b}}\ , \tag{3.19}$$

and

$$\tilde{Y}''(\tilde{z})=\frac{d^2\tilde{Y}}{d\tilde{z}^2}=\frac{-aY(z)+a^2Y(z)+bzY'(z)-2abzY'(z)+b^2zY'(z)+b^2z^2Y''(z)}{z^{(a-2)/b}}\ . \tag{3.20}$$

D. Series solution on the critical isotherm ($t=0$)

Substituting the form of the free energy Eq. (3.15) into the geometric equation (2.13) yields a third-order nonlinear differential equation for $\tilde{Y}(\tilde{z})$ in terms of $\tilde{z}$:

$$\tilde{Y}^{(3)}(\tilde{z})=\tilde{F}[\tilde{z},\tilde{Y}(\tilde{z}),\tilde{Y}'(\tilde{z}),\tilde{Y}''(\tilde{z})]\ , \tag{3.21}$$

where $\tilde{F}$ is a ratio of polynomials. This differential equation can be solved in the neighborhood of the critical isotherm with the Taylor-series method about $\tilde{z}=0$:

$$\tilde{Y}(\tilde{z})=\sum_{n=0}^{\infty}\tilde{y}_n\tilde{z}^n\ . \tag{3.22}$$

The first three coefficients, which follow from Eqs. (3.17)–(3.20) by taking limits $z\to\infty$, together with the geometric equation suffice to determine all of the other coefficients.

E. Numerical solution to the coexistence curve ($z=0$, $t<0$)

The critical isotherm series can be used to generate initial conditions for Eq. (3.11) for the start of the solution process to the coexistence curve. This involves decreasing z and x, and hence requires a negative step size Δx in the numerical solution scheme. One may readily verify that the critical amplitudes on the coexistence curve are

$$A'=-a(a-1)Y_-(0)\ , \tag{3.23}$$

$$B=-Y'_-(0)\ , \tag{3.24}$$

and

TABLE III. Limiting values for several variables.

	z	Y	Y'	Y''	x	w	y	v	v/y
$h=0,\ t>0$	0	-1	0	-2	$-\infty$	0	0	0	2
$t=0,\ h>0$	$+\infty$	$-\infty$	$-\infty$	0	$+\infty$	$+\infty$	$1+1/\delta$	0	0
$h=0,\ t<0$	0	$-A'/[(2-\alpha)(1-\alpha)]$	$-B$	$-\Gamma'$	$-\infty$	$\ln\{A'/[(2-\alpha)(1-\alpha)]\}$	0	0	1

$$\Gamma' = -Y''_{-}(0)\ . \tag{3.25}$$

The minus subscript on Y refers to the branch $t<0$. The critical isotherm amplitude

$$D = \left[-\tilde{Y}(0)\left[1+\frac{1}{\delta}\right]\right]^{-\delta} . \tag{3.26}$$

The ranges of the variables used here are given in Table III.

Of considerable interest is the Griffiths form of the equation of state [28]:

$$h = m|m|^{\delta-1}h(x)\ , \tag{3.27}$$

where

$$x = t|m|^{-1/\beta}\ . \tag{3.28}$$

(Note, this x should be distinguished from the one used in connection with the differential equation in Table II.) It is straightforward to show that

$$h(x) = |z|\ |Y'(z)|^{-\delta} \tag{3.29}$$

and

$$x = \mathrm{sgn}(t)|Y'(z)|^{-1/\beta}\ , \tag{3.30}$$

where sgn(t) is the sign of t. Define as well the standard constants

$$h_0 = h(x)|_{x=0} = D\ , \tag{3.31}$$

$$x_0 = -x|_{h=0,t<0} = B^{-1/\beta}\ . \tag{3.32}$$

IV. RESULTS

In this section I present results. I start with the mean-field theory exponents, proceed to the 3D Ising exponents, and conclude briefly with the pure fluid exponents. The considerations in this section lead to further statements about the regularity of the solution.

A. Mean-field theory

An important approach in critical phenomena consists of mean-field theory which results, essentially, from ignoring fluctuations [10]. MFT has power-law divergences governed by the "classical" exponents ($\beta=\frac{1}{2}$ and $\delta=3$). The equation of state is of the form

$$h = c_1 mt + c_2 m^3\ , \tag{4.1}$$

where c_1 and c_2 are system-dependent constants. One frequently sees higher powers of m, but they are usually neglected, since m is small near the critical point. Since the solution of the MFT is well known, and since it is relatively simple to treat with my method, it offers a good starting point. In addition, much of what is learned can be applied to more complicated cases.

For the MFT exponents, $a=2$, $b=\frac{3}{2}$, and $\kappa=\frac{1}{4}$. For these values the differential equation for $Y(z)$ is

$$Y^{(3)} = \frac{Y'^4 - 14YY'^2Y'' + 6zY'^3Y'' + 9z^2Y'^2Y''^2 - 18Yz^2Y''^3}{16Y^2Y' - 18YzY'^2 + 48Y^2zY'' - 18Yz^2Y'Y''}\ . \tag{4.2}$$

The function $Y(z)$ can be expanded in a Taylor series about $z=0$ for $t>0$:

$$Y(z) = \sum_{n=0}^{\infty} y_{2n} z^{2n}\ , \tag{4.3}$$

where the y_{2n}'s are constants. Substituting this series into Eq. (4.2), and using the convenient values $y_0=-1$ and $y_2=-1$ as the starting point in a recursive solution scheme, yields a linear algebraic equation corresponding to each power of z:

$$\begin{aligned} &O[z^0]:\ 0=0\ ,\\ &O[z^1]:\ 24y_4 = 2 \Longrightarrow y_4 = \tfrac{1}{12}\ ,\\ &O[z^2]:\ 0=0\ ,\\ &O[z^3]:\ 120y_6 = -\tfrac{10}{3} \Longrightarrow y_6 = -\tfrac{1}{36}\ ,\\ &O[z^4]:\ \cdots\ , \end{aligned} \tag{4.4}$$

This procedure can be used to uniquely determine all of the series coefficients. The result is

$$Y(z) = -1 - z^2 + \frac{z^4}{12} - \frac{z^6}{36} + \frac{z^8}{72} - \frac{11z^{10}}{1296} + \frac{91z^{12}}{15552} + \cdots\ . \tag{4.5}$$

Calculating the series for the order parameter with this equation and inverting it for h yields the classic MFT equation of state:

$$h = \tfrac{1}{2}mt + \tfrac{1}{48}m^3\ . \tag{4.6}$$

I have done this calculation up to $O(z^{80})$, and never found a term in the expansion for h beyond the third order in m. Indeed, a change of variables reveals this to be an exact solution of the geometric equation. This solution serves as a useful test of numerical solution schemes.

For the MFT exponents, Eq. (3.12) becomes

$$\frac{dv}{dx}=f(y,v)=\frac{144v^2-18v^3-192vy-144v^2y+64y^2+352vy^2+9v^2y^2-160y^3-204vy^3+148y^4+36vy^4-60y^5+9y^6}{48v-32y-18vy+48y^2-18y^3} \tag{4.7}$$

and

$$\frac{dy}{dx}=v \ . \tag{4.8}$$

By standard existence and uniqueness theorems [29], this pair of differential equations possess a unique solution passing through any point (x,y,v) provided that $f(y,v)$ is sufficiently smooth at that point and provided that $f(y,v)$ and v are not both zero. Smoothness obtains unless the denominator of $f(y,v)$ is zero. Points at which $f(y,v)$ and v are both zero are called singular points, and they have considerable influence over the solution trajectories. Necessary, but not sufficient, conditions that a point be a singular point is that it be on the y axis and that the numerator of $f(y,v)$ is zero. The location of the curve of zeros of the denominator and the three points on the y axis, (0,0), $(\frac{4}{3},0)$, and (2,0), where the numerator of $f(y,v)$ is zero, are indicated in Fig. 1.

For autonomous differential equations, the dependence of y on v is entirely independent of x because we can write

$$\frac{dv}{dy}=\frac{f(y,v)}{v} \ , \tag{4.9}$$

which involves only y and v. This makes the solution trajectories in (y,v) space, also shown in Fig. 1, very revealing.

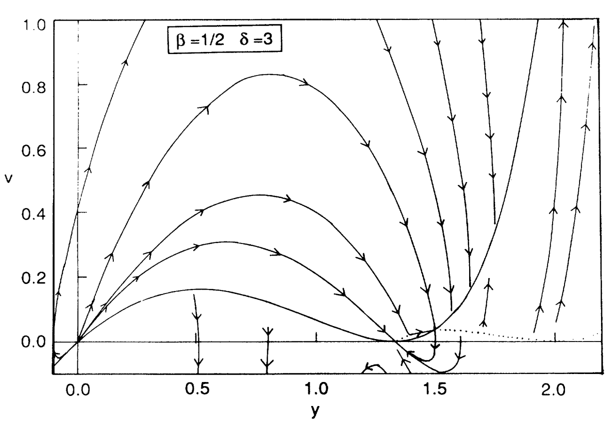

FIG. 1. The curves with arrows are (mostly unphysical) solution trajectories to Eqs. (4.7) and (4.8). The solid curve without arrows passing through the origin is the locus of zeros of the denominator of $f(y,v)$, where existence and uniqueness theorems break down. There are three points on the y axis where the numerator of $f(y,v)$ is zero: (0,0), $(\frac{4}{3},0)$, and (2,0). The critical isochore and coexistence curve corresponds to the origin, and the point $(\frac{4}{3},0)$ corresponds to the critical isotherm. The dotted curve corresponds to a curve of zero numerator; it intersects the line of zeros of the denominator at the point (1.497 474, 0.034 507), which some trajectories, including the physical one, use to bridge the curve of zeros of the denominator.

The standard approach to a singular point $(y_0,0)$ starts by linearizing the differential equation in the neighborhood of that point [29]:

$$\frac{dv}{dx}=a_1(y-y_0)+a_2v \ , \tag{4.10}$$

and

$$\frac{dy}{dx}=v \ , \tag{4.11}$$

where a_1 and a_2 are constant Taylor-series coefficients. Trying a solution to these linear differential equations of the form

$$y(x)-y_0=re^{\lambda x} \tag{4.12}$$

and

$$v(x)=se^{\lambda x} \ , \tag{4.13}$$

where λ, r, and s are constants, leads to a characteristic equation for λ

$$\lambda^2-a_2\lambda-a_1=0 \tag{4.14}$$

as a necessary condition that there are nonzero solutions for r and s.

Let us look at the three singular points individually.

1. Singular point at (0,0)

Though the numerator of $f(y,v)$ is zero at (0,0), so is the denominator, and a Taylor series is not possible. Since the numerator and the denominator of $f(y,v)$ have no common factors, the curve of zeros of the numerator and zeros of the denominator do not coincide. Therefore, $f(y,v)$ is infinite along the curve of zero denominator and the limit of $f(y,v)$ as the origin is approached along this curve does not exist. One may readily show, however, that the substitution in $f(y,v)$ of a straight line with slope c,

$$v=cy \ , \tag{4.15}$$

results in a cancellation of y's. The function $f(y,cy)$ is now regular at the origin, provided that $c\neq\frac{2}{3}$, which corresponds to a line through the origin tangent to the curve of zero denominator. A first-order Taylor series yields

$$f(y,v)=-2y+3v \ . \tag{4.16}$$

Since the physical solution trajectories are asymptotically straight near the origin with $c\neq\frac{2}{3}$, this is the relevant expression, and we can apply the analysis for singular points.

At this point

$$\lambda = 1,2\ , \tag{4.17}$$

$$y(x) = b_1 e^x + b_2 e^{2x}\ , \tag{4.18}$$

and

$$v(x) = b_1 e^x + 2b_2 e^{2x}\ , \tag{4.19}$$

where b_1 and b_2 are arbitrary constants. Since the roots λ are real, positive, and unequal, this point corresponds to an unstable singular point from which trajectories emerge as x increases from negative infinity [29]. Near the origin ($x \to -\infty$) the solution trajectories are straight lines with slope $v/y = 1$ if b_1 is not zero and slope 2 if b_1 is zero.

2. *Singular point at* $(\frac{4}{3}, 0)$

Here the denominator as well as the numerator of $f(y,v)$ is zero, and the limit of $f(y,v)$ does not exist for essentially the same reason as at the origin. Substituting a straight line

$$v = c(y - \tfrac{4}{3}) \tag{4.20}$$

into $f(y,v)$ results in the cancellation of a factor of $(y - \frac{4}{3})$, and the ratio of polynomials

$$f[y, c(y - \tfrac{4}{3})]$$

is regular in the neighborhood of this point if $c \neq 0$, which is the slope of a line tangent to the curve of zero denominator. A first-order Taylor series leads to

$$f(y,v) = \frac{8}{27c}(y - \tfrac{4}{3}) - \tfrac{4}{3}v\ . \tag{4.21}$$

This expression reveals that $f(y,v)$ goes to zero if this point is approached along a straight line with nonzero slope, as the physically interesting solution trajectory does. Therefore, this point is a singular point. However, this case is more complicated than the form of Eq. (4.10), since the series coefficient a_1 depends on c. I will not attempt a full analysis here, but rather will proceed with numerical methods.

3. *Singular point at (2,0)*

At this point, the denominator of $f(y,v)$ is not zero, and $f(y,v)$ admits a Taylor series:

$$f(y,v) = 2v\ , \tag{4.22}$$

which results in

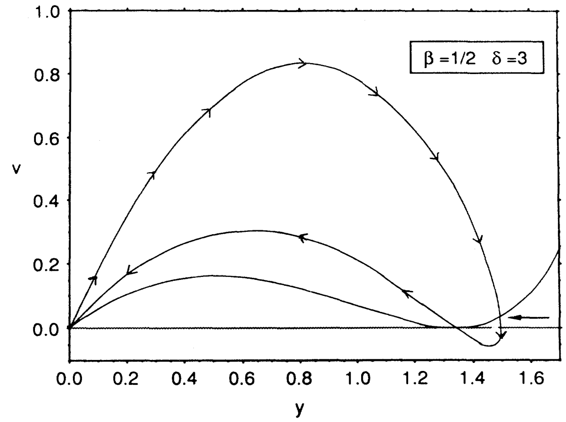

FIG. 2. Trajectory (curve with arrows) followed by MFT as it traverses from the critical isochore to the coexistence curve. The trajectory starts at the origin with slope 2 and crosses the singular curve at a bridge point (1.497 474, 0.034 507), indicated with a horizontal arrow, where the numerator of $f(y,v)$ is also zero. It then approaches the singular point $(\frac{4}{3},0)$, the critical isotherm, which is crossed using the series Eq. (3.22), and goes back to the origin (with negative step size Δx), reaching limiting slope 1.

$$\lambda = 0 \text{ or } 2\ . \tag{4.23}$$

This is an indeterminate case because of the zero root [29]. However, this singular point plays no role, since the physically interesting trajectory does not go near it.

The numerical solution process is standard. I used the fourth-order Runge-Kutta method [30]. Figure 2 shows the complete trajectory from the critical isochore to the coexistence curve. Initial conditions were computed with the series Eq. (4.5), with $z = 0.01$ and a series up to $O(z^{20})$. The trajectory starts at the origin with slope 2, as expected from Table III, and crosses the curve of zero denominator of $f(y,v)$ at a "bridge" point (1.497 474, 0.034 507), where the numerator is zero as well and where the solution trajectory appears to cross without any discontinuity. It then crosses the y axis and turns back to the singular point at $(\frac{4}{3},0)$, which corresponds to the critical isotherm, which it approaches increasingly slowly as $x \to \infty$.

Figure 3 shows $f(y,v)$ as a function of z in a range including the bridge point. As can be seen, there are no anomalies for the MFT exponents because the zero of the numerator of $f(y,v)$ cancels the singularity caused by the zero in the denominator. The MFT solution is regular in the entire range from the critical isochore to the coexistence curve.

For the MFT exponents, Eq. (3.21) is

$$\tilde{Y}^{(3)} = \frac{-\{[(\tilde{Y}')^2 - 2\tilde{Y}\tilde{Y}''][4(\tilde{Y}')^2 - 2\tilde{Y}\tilde{Y}'' - 4\tilde{z}\tilde{Y}'\tilde{Y}'' + \tilde{z}^2(\tilde{Y}'')^2]\}}{2\tilde{Y}[2\tilde{Y}\tilde{Y}' - 3\tilde{z}(\tilde{Y}')^2 + 2\tilde{Y}\tilde{z}\tilde{Y}'' + \tilde{z}^2\tilde{Y}'\tilde{Y}'']}\ . \tag{4.24}$$

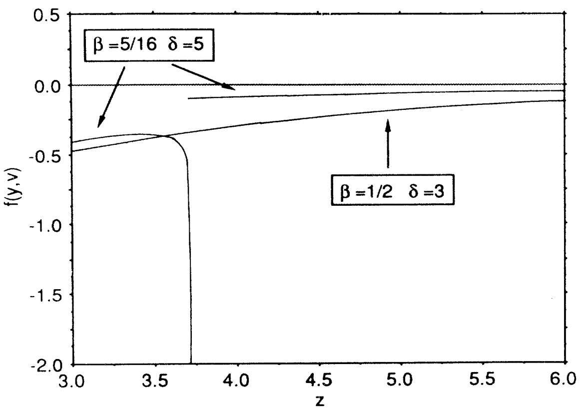

FIG. 3. The function $f(y,v)$ along the physical solution trajectory as a function of z for both the MFT exponents and the 3D Ising exponents in a range including the intersection with the curve of zero denominator of $f(y,v)$, which occurs at $z=4.8931$ for the MFT exponents and $z=3.7193$ for the 3D Ising exponents. The curve for the MFT exponents shows no anomaly because it intersects the singular curve at a bridge point where the numerator of $f(y,v)$ is zero as well. For the 3D Ising exponents, the solution curve misses the bridge point and $f(y,v)$ diverges to $-\infty$ at the intersection point.

A Taylor-series Eq. (3.22) solution method yields a unique solution given the first three coefficients. During the computation the series coefficients $\tilde{y}_0, \tilde{y}_1$, and $\tilde{y}_2$ were computed with the limits in Eqs. (3.17)–(3.20).

This series allows a computation of the initial values of (z, Y, Y', Y'') for the solution to the coexistence curve. It proceeds with negative Δx. Limiting values for the critical amplitudes on the coexistence curve were computed with Eqs. (3.23)–(3.25). Table IV shows A', B, and Γ' as a function of $|\Delta x|$. Convergence to the known exact values is seen to be excellent.

B. 3D Ising exponents

Turn now to the 3D Ising exponents $\beta=\frac{5}{16}$ and $\delta=5$ [31], which correspond to $a=\frac{15}{8}$ and $b=\frac{25}{16}$. The series for $Y(z)$ in small powers of z for $t>0$ is

$$Y(z)=-1-z^2+\frac{29z^4}{189}-\frac{37\,697z^6}{535\,815}+\frac{13\,681\,733z^8}{303\,807\,105}-\cdots, \quad (4.25)$$

where I have again taken $y_0=y_2=-1$. Initial conditions for the numerical solution to the critical isotherm were computed with this series to $O(z^{20})$ with $z=0.01$.

For these exponents, see Eq. (4.26),

$$\frac{dv}{dx}=f(y,v)=(26\,460v^2-4725v^3-38\,808vy-30\,030v^2y+14\,112y^2+83\,244vy^2+4050v^2y^2-41\,664y^3 -57\,810vy^3+45\,872y^4+12\,825vy^4-22\,320y^5+4050y^6) \times(8820v-7056y-4725vy+11\,550y^2-4725y^3)^{-1}, \quad (4.26)$$

and, again,

$$\frac{dy}{dx}=v\ . \quad (4.27)$$

The curve along which the denominator of $f(y,v)$ is zero is shown in Fig. 4. The bridging point where the numerator is zero as well is $(y,v)=(1.311\,953, 0.017\,8747)$. There are also three singular points on the y axis where the numerator of $f(y,v)$ is zero, discussed below.

1. *Singular point at (0,0)*

Though the numerator of $f(y,v)$ is zero at this point, so is the denominator, and the limit of $f(y,v)$ does not exist, basically for the same reason as at the origin for MFT. Here again, the substitution of a straight line into $f(y,v)$ results in a cancellation of a factor of y. The resulting function is regular at the origin if $c\neq\frac{4}{5}$. A first-order Taylor series leads to the same expression as MFT:

$$f(y,v)=-2y+3v\ , \quad (4.28)$$

which yields

$$\lambda=1,2\ , \quad (4.29)$$

and diverging solutions of the form Eqs. (4.18) and (4.19).

2. *Singular point at* $(\frac{6}{5},0)$

Here both the numerator and the denominator of $f(y,v)$ are zero and a Taylor series does not exist. However, the behavior is very similar to that for MFT, and I proceed in analogous fashion.

TABLE IV. Limiting values for MFT for three critical amplitudes on the coexistence curve as a function of $|\Delta x|$. For comparison, I show the exact values for B and Γ' calculated with Eq. (4.6). The exact value for A' is not known.

$\|\Delta x\|$	A'	B	Γ'
0.010 00	8.106 93	4.964 38	1.013 36
0.003 00	8.031 90	4.918 47	1.003 99
0.001 00	8.010 45	4.905 34	1.001 31
0.000 30	8.003 02	4.900 78	1.000 38
0.000 10	8.000 88	4.899 48	1.000 11
0.000 03	8.000 13	4.899 01	1.000 02
Exact:	8.000 00(?)	4.898 98	1.000 00

3. Singular point at $(\frac{14}{9},0)$

This point has the same essential character as the analogous point in MFT. However, the physically interesting trajectory does not go near it.

The trajectories in (y,v) space for the 3D Ising exponents look qualitatively similar to those for MFT shown in Fig. 1, and will not be reproduced in detail. The major difference is that the physical solution trajectory from $z=0$ to $z\rightarrow\infty$ intersects the line of zero denominator of $f(y,v)$ at a point other than the "bridging" point. Figure 5 shows an enlargement of the intersection point where existence and uniqueness theorems break down and special measures are called for.

Griffiths [28] proposed a set of thermodynamic postulates for critical phenomena. His postulate C6 states: "The free energy $a(\rho,T)$ is an analytic function of both arguments together everywhere in the vicinity of the critical point, except on the phase boundary." Griffiths points out that the rationale for this hypothesis follows "neither from thermodynamic requirements nor (excluding special cases) from statistical calculations and merely reflect the usual aesthetic desire in theoretical science to use functions 'as smooth as possible.'" It has been proved rigorously, however, with statistical mechanics in a number of dimensions that the Ising model has no nonanalyticities of any kind except on the coexistence curve [4]. This result provides strong support for the hypothesis of Griffiths.

It is clear that the solution considered here to the geometric equation for the 3D Ising exponents cannot be smooth in accord with the hypothesis of Griffiths. I will, however, still use this hypothesis for guidance, and seek the smoothest solution possible. The first try is to assume that the solution trajectory $y=y(v)$ simply continues across the curve of zero denominator. In this case all the variables (x,w,y,v) can be kept continuous, and only the derivative of v with respect to x suffers an infinity. However, this attempt does not work because $f(y,v)$ changes sign and becomes positive below the curve, forcing trajectories to move up and to the right, away from the critical isotherm. This region of positive $f(y,v)$ is indicated in Fig. 5 and must be jumped, forcing v to be discontinuous.

One may observe that if the solution trajectory is simply continued from the y axis directly below the intersection point, then it not only goes on to the critical isotherm, but x, w, y, and dy/dv may be kept continuous.

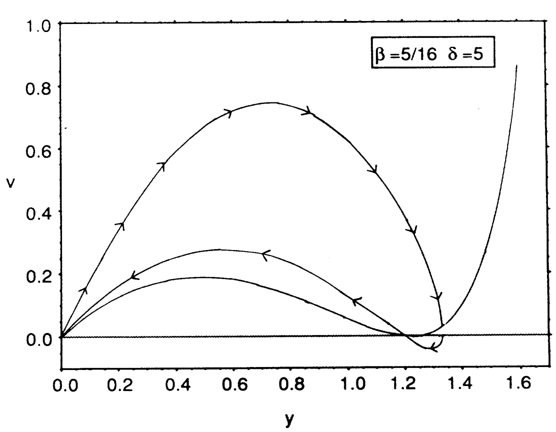

FIG. 4. The curve without the arrows corresponds to the curve along which the denominator of $f(y,v)$ is zero. It has a bridging point at (1.311 953,0.017 8747), where the numerator is zero as well. The curve with arrows is the solution trajectory for the 3D Ising exponents. The solution curve misses the bridging point, and this results in a discontinuous solution.

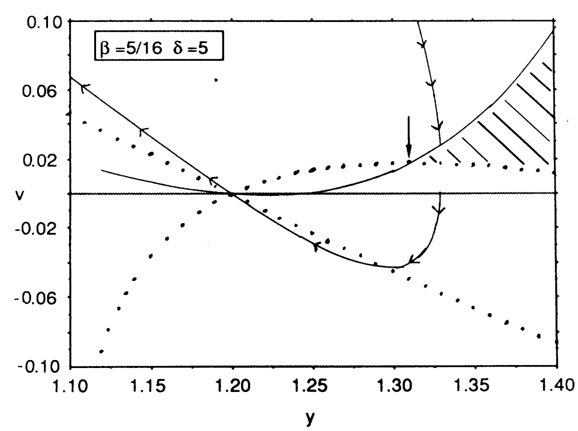

FIG. 5. An enlargement of the region near the bridging point. The dotted curves are curves of zero numerator of $f(y,v)$. The solid curve without arrows is the curve along which the denominator of $f(y,v)$ is zero. It dips slightly below the y axis to the right of the singular point at $(\frac{6}{5},0)$. The bridge point is indicated with a down arrow. The cross-hatched region corresponds to a region of positive $f(y,v)$, where trajectories move upwards and to the right. This region must be jumped in order to approach the critical isotherm at $(\frac{6}{5},0)$ from below, as is the case for MFT. The solution curve corresponds to continuous x, w, y, dy/dv, and discontinuous v.

TABLE V. Universal critical amplitude ratios for the MFT and 3D Ising model [31,33] compared with the values computed with the geometric equation. Generally, the agreement for the ratios that do not involve the heat capacity is very good. I show also the calculated universal amplitude ratios for the critical exponents frequently used for the pure fluid [35], but do not compare with experimental ratios, since there is considerable uncertainly in them.

System	Γ/Γ'	A/A'	$R_x=\Gamma D B^{\delta-1}$	$R_C=AB^{-2}\Gamma$
MFT (exact)	2		1	
Geo ($\beta=\frac{1}{2}$, $\delta=3$)	1.999 96	0.249 996	1.000 04	0.166 665
3D Ising (series)	4.95±0.15	0.523±0.009	1.67±0.11	0.559±0.01
Geo ($\beta=\frac{5}{16}$, $\delta=5$)	4.964 54	0.401 89	1.583 77	0.247 234
Geo ($\beta=0.35$, $\delta=4.45$)	3.910 28	0.384 40	1.391 30	0.235 51

One could keep the first three of these variables continuous by jumping vertically to any point below the region of positive $f(y,v)$. It is true also that a range of positions eventually lead to the critical isotherm. However, the only jumping point that, in addition, keeps dy/dv continuous is the y axis. Since I seek the smoothest solution, I pick this jumping point for continuing the solution. Figures 4 and 5 show a solution trajectory in accord with this assumption.

The remaining solution procedure goes the same way as for the MFT exponents, and I shall omit the details. Of much interest are universal ratios among the critical amplitudes [32]. Results are shown in Table V. My numbers for MFT agree with the exact ones [33] to a level approaching a small fraction of a percent, which gives some indication of the general accuracy of the method. For the 3D Ising exponents, the agreement of the ratios not involving the heat capacity with the known 3D Ising values [31,33] is also very good. The agreement with the known values involving the heat capacity is not as good, but in light of the disagreement about analyticity, some discrepancy is not surprising.

Consider now the equation of state in the form Eq. (3.27). Figure 6(a) shows $h(x)/h_0$ as a function of $(x+x_0)/x_0$ for the geometric equation; it depends only on the values of the critical exponents. The discontinuity in the variable v shows up as a discontinuous slope at the place indicated. Figure 6(b) shows the known 3D Ising curve [34]. The agreement is very close, within about 10% over the full range. The primary difference is that the known curve looks a little "rounder" than that of the geometric equation because of the presence of a kink in the latter.

C. Pure fluid

Another important system is the pure fluid, which has been experimentally found to have critical exponents

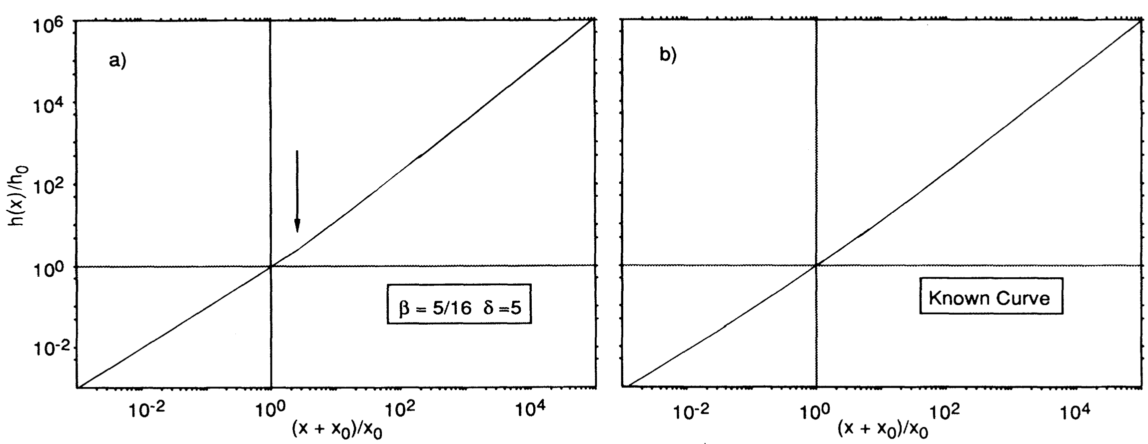

FIG. 6. This figure shows $h(x)/h_0$ as functions of $(x+x_0)/x_0$ computed from the geometric equation with $\beta=\frac{5}{16}$ and $\delta=5$, and from the known results for the 3D Ising model. The down pointing arrow in (a) corresponds to the place where the curve suffers a discontinuity in the slope. The curves are in good agreement with one another, within about 10% over the full range tested.

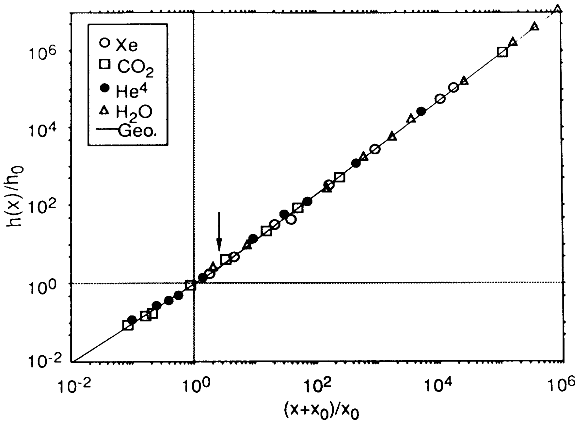

FIG. 7. This figure shows $h(x)/h_0$ as functions of $(x+x_0)/x_0$ computed from the geometric equation with $\beta=0.35$ and $\delta=4.45$, and from experiment in four pure fluids [35,36]. The down-pointing arrow corresponds to the place where the geometric equation curve suffers a discontinuity in the slope. The match between theory and experiment is very good.

$\beta=0.35$ and $\delta=4.45$ [35,36]. The pure fluid exponents lead to a solution that is qualitatively similar to that of the 3D Ising exponents, including a discontinuous second derivative of the free energy. Figure 7 shows $h(x)/h_0$ as a function of $(x+x_0)/x_0$. The figure includes data points from experiments in four pure fluids [35]. The match between theory and experiment is very good. The agreement could be improved even further by varying the critical exponents to produce the best fit.

V. CONCLUSION

In conclusion, I have proposed a thermodynamic hypothesis from which several rules of critical phenomena follow: *the thermodynamic curvature is proportional to the inverse of the free energy.* This hypothesis may be expressed in terms of a partial differential equation that has many solutions corresponding to different boundary conditions and to different assumptions about regularity.

I examined in this paper just one specific type of solution. I demonstrated that a free energy of the form of a generalized homogeneous function of its arguments reduces the geometric equation to a third-order nonlinear ordinary differential equation. Furthermore, this free energy is predicted to be universal up to two material-dependent constants (assuming that the critical exponents are universal), consistent with two-scale factor universality. The only required inputs are the critical exponents. I solved this differential equation explicitly for the exponents corresponding to the mean-field theory, the 3D Ising model, and the pure fluid. Both the resulting equations of state and the universal critical amplitude ratios are generally in good agreement with what is known by other means.

To obtain solutions, I made two regularity assumptions, neither of which is required by the geometric equation. The first is that the free energy is regular on the critical isochore $h=0$ for $t>0$. The second assumption concerns a point of singularity in the solution for both the 3D Ising exponents and the pure fluid exponents. Here the equation does not have a unique solution, and I picked the smoothest one possible. Clearly, in light of proofs from rigorous statistical mechanics, the existence of a point of nonanalyticity raises questions about a theory that otherwise produces very good results. Whether or not this is a feature that will disappear with another type of solution, or whether nonanalyticity is an inevitable feature of this approach, is unclear. I emphasize, however, that my method is thermodynamic. Hence, the presence of nonanalyticity, should it prove to be inevitable, constitutes a disagreement with the results of rigorous statistical mechanics but not any internal inconsistency.

ACKNOWLEDGMENTS

I thank M. E. Fisher for useful correspondence, and in particular for suggesting that the MFT exponents and the 3D Ising exponents constitute good test cases and for clarifying the position of statistical mechanics on analyticity. I also thank H. Meyer for sending tabulations of He^3 data that gave considerable insight into the properties of fluids near the critical point.

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