

Phenomenology of first-order phase transitions

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(Received 11 December 1980)

A phenomenological description of first-order phase transitions is proposed in terms of the solution of a certain linear, first-order, partial differential equation suggested by Fisher. In the asymptotic region of the critical point, the coefficient functions of the equation are uniquely determined by the scaling laws. The imposition of the further requirement that the phase boundary coincide with a characteristic curve of this equation is shown to lead to solutions that can reproduce the singular behavior—for example, the density and entropy discontinuities for the case of the liquid-gas transition—along the entire vapor-pressure curve. The important role played by the characteristic curves is stressed and confirmed for the special case of the ideal, d -dimensional, Bose gas. New relations involving discontinuities in the second derivatives of the thermodynamic functions are derived and shown to be useful in obtaining the coefficient functions near the phase boundary. Details are presented for the case of ferromagnetic and ferroelectric systems and include a comparison with experiment.

I. INTRODUCTION

A few years ago, Fisher^{1,2} proposed a new way to approximate the singular behavior of thermodynamic functions in the region around a multicritical point. In this method, which is a multivariable generalization of the “ $D \log$ ” Padé technique,³ the critical behavior of the system is approximated by the appropriate solution of a certain linear, first-order, partial differential equation with polynomial coefficients, the multicritical point itself being defined by the simultaneous vanishing of those polynomial coefficients which multiply the derivatives of the thermodynamic function. As a point of interest, Fisher called attention to the fact that in the asymptotic region of the singular point, this partial differential equation bears a strong resemblance to equations of the “scaling” type, familiar in renormalization-group analyses of critical behavior.⁴

The purpose of the present work is to show that, in a slightly modified form, Fisher’s equation also lends itself to a phenomenological description of first-order phase transitions, in a region near the phase boundary. For the case of the liquid-gas transition of a one-component system, for example, the proposed phenomenology is intended to be applicable in the low-temperature region around the vapor-pressure curve, and to extend upward to that around the critical point and beyond. That the thermodynamic behavior of the system at the critical point itself can be correctly described by this method was shown by Fisher.² Hence, to obtain a phenomenology applicable throughout the larger region including that around the vapor-pressure curve, it is necessary to

establish that the equation also has solutions which have the appropriate discontinuous derivatives along the phase boundary. As will be seen in Sec. III, this feature is easily achieved but requires a further assumption. The assumption that we choose here involves the coefficient functions and restricts their form so that one of the characteristic curves of the equation coincides with the vapor-pressure curve. That this somewhat unusual assumption is not entirely random will be seen in Sec. II where the ideal Bose gas is considered from the present point of view.

The critical point, which is the only point of the vapor-pressure curve associated with long-range thermal fluctuations and thus with infinite values for the specific heats, the isothermal compressibility, etc., will be seen to play a central role in our considerations. It constrains, in significant measure, the allowable forms of the coefficient functions in the equation and exerts a strong influence on the geometrical properties of the characteristic curves and of their associated solutions. Of particular interest is the fact that the analyticity requirements that we impose on these coefficient functions are not compatible with different values for the critical exponents of corresponding quantities above and below T_c . If, for example, experiment were to show that any critical exponents, say γ and γ' for the isothermal compressibility above and below T_c , respectively, were different, then the phenomenology as here proposed would require significant modification.

Another distinctive feature of the proposed phenomenology is associated with the fact that the solutions of the underlying partial differential equation involve, in general, an undetermined function of

a single variable. As a consequence, all formulas for thermodynamic functions obtained by its usage are incomplete and generally require additional data for a full specification. In the asymptotic neighborhood of the critical point, this incompleteness is not unexpected and is naturally identifiable with the scaling function. The fact that outside of the critical region the solutions also involve an undetermined function is not as readily interpretable. Nevertheless, the existence of undetermined functions in the solutions of the equation seems to be an inherent part of our scheme, and may be responsible in large measure for the "washing out" of details that makes the proposed phenomenology possible at all.

The details of the phenomenology are presented in Sec. III and follow an introductory discussion of some of the underlying ideas in terms of the ideal Bose gas in Sec. II. Section IV contains details of the key arguments regarding the discontinuities in the derivatives of the thermodynamic functions. The problem of determining the coefficient functions is considered in Sec. V, where it is shown how this can be achieved in terms of a knowledge of the discontinuities of the second derivatives of the Gibbs function along the vapor-pressure curve. Finally, in Sec. VI we apply this method to ferromagnetic and ferroelectric systems and are able to make a direct comparison with experimental curves for the spontaneous magnetization and the spontaneous polarization for particular materials.

II. IDEAL BOSE GAS

To introduce some of the main concepts underlying the proposed phenomenology in this section we consider a formulation of the ideal Bose-Einstein gas in terms of Fisher's partial differential equation.

Consider a physical system whose thermodynamic description involves two independent variables. Let us recall that for this case, Fisher's equation has the form

$$Q(x,y) \frac{\partial F}{\partial x} + R(x,y) \frac{\partial F}{\partial y} = P(x,y) F, \quad (1)$$

where x and y are the two independent variables, $F \equiv F(x,y)$ is the sought-for approximation for a thermodynamic function, and where Q , R , and P are appropriate polynomials in x and y , to be determined. The multicritical point is defined by the simultaneous vanishing of Q and R ; that is, by the condition $Q = R = 0$. It is generally convenient to assume that the multicritical point is at the origin at $x = y = 0$.

By contrast to the linear form of Eq. (1), the characteristic equations associated with Eq. (1) are in general nonlinear. They are defined by the system of ordinary differential equations.

$$\frac{dx}{ds} = Q(x,y); \quad \frac{dy}{ds} = R(x,y); \quad \frac{dF}{ds} = P(x,y)F, \quad (2)$$

with s a suitable parameter. Given any initial point with coordinates (x_0, y_0, F_0) , then in terms of running parameter s , the solution of Eq. (2) defines a characteristic curve, $(x(s), y(s), F(s))$ in the space with coordinate axes xyF . For future reference it is convenient to recast the first two of Eqs. (2) into the simpler form

$$\frac{dy}{dx} = \frac{R(x,y)}{Q(x,y)}, \quad (3)$$

whose solutions are the projections of the characteristics into the xy plane.

Consider now the ideal Bose gas. It is well known that if the temperature of a fixed amount of this gas is lowered isobarically (or isochorically) then at a certain temperature $T_c(P)$ [or $T_c(n)$] the gas particles find it more favorable to condense into the ground state. Macroscopically, this manifests itself in a phase transition with phase boundary along the curve $T = T_c(P)$ [or $T_c(n)$]. Figure 1 shows schematically some of the isotherms of the Bose gas which is known to have discontinuities in the second derivative ($\partial^2 P / \partial n^2$) along the phase boundary (the dotted curve). The physical significance of this plot is that if along a given isotherm the density $n = 1/V$ is increased to values of $n > n_0(T)$, where $n_0(T)$ corresponds to the dotted line, then the added particles go into the ground state and do not contribute to the gas pressure P .

The thermodynamics of the ideal Bose gas can be calculated in the conventional way^{5,6} from

$$P = -\frac{kT}{V} \sum_q \ln(1 - ze^{-\beta\epsilon_q}), \quad (4)$$

$$n = \frac{1}{V} \sum_q \frac{z}{e^{\beta\epsilon_q} - z}, \quad (5)$$

where P , n , and V are the gas pressure, density, and

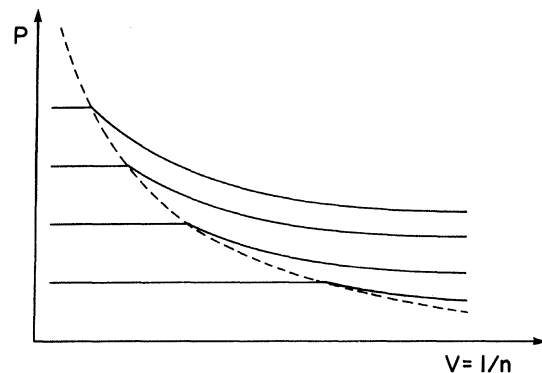


FIG. 1. Schematic of the isotherms for the ideal Bose-Einstein gas. The dotted curve represents the phase boundary.

volume, respectively, k is Boltzmann's constant, $\beta = 1/kT$, and z , the fugacity, is related to the chemical potential μ by $\mu = kT \ln z$. We assume that the single-particle kinetic energy is $\hbar^2 q^2/2m$ and that in the thermodynamic limit, sums may be replaced by integrals in the usual way⁶

$$\sum_q \rightarrow \frac{V}{(2\pi)^d} \int d^d q, \quad (6)$$

where the exponent " d " signifies the dimension of the system. Since there is no Bose Einstein condensation for dimension $d \leq 2$, it is of particular interest to carry along the parameter d in order to see how this fact manifests itself in the present formulation.

To obtain, for the Bose gas, an equation of the Fisher form in Eq. (1), imagine eliminating the fugacity z between the two formulas in Eqs. (4) and (5) to obtain an explicit formula for the surface $P \equiv P(n, T)$. If we make use of Eq. (6) it is straightforward to verify that this formula for $P(n, T)$ satisfies the equation

$$\left(\frac{2}{d+2} \right) T \frac{\partial P}{\partial T} + \left(\frac{d}{d+2} \right) n \frac{\partial P}{\partial n} = P \quad (7)$$

exactly! As anticipated, this is precisely of the Fisher form in Eq. (1), with T and n being here the independent variables and with the polynomials Q , R , and P having the very simple forms implied in Eq. (7). In principle, the surface $P(n, T)$ can be obtained directly by solving Eq. (7) subject to appropriate boundary conditions.

That the similarity in form between Eqs. (7) and (1) is not coincidental can be verified by deriving, for the ideal Bose gas, the corresponding equations for other thermodynamic quantities. Thus with T and n the independent variables, as in Eq. (7), it is easy to confirm relations such as

$$T \frac{\partial A}{\partial T} + \left(\frac{d}{2} \right) n \frac{\partial A}{\partial n} = A, \quad (8)$$

$$T \frac{\partial S}{\partial T} + \left(\frac{d}{2} \right) n \frac{\partial S}{\partial n} = 0, \quad (9)$$

$$T \frac{\partial C_V}{\partial T} + \left(\frac{d}{2} \right) n \frac{\partial C_V}{\partial n} = 0, \quad (10)$$

with A the Helmholtz potential, S the entropy and $C_V = T(\partial S/\partial T)_V$ the specific heat at constant volume. It should be noted that these three relations are not independent. For the derivative with respect to T of Eq. (8) yields Eq. (9) and similarly Eq. (10) can be derived from Eq. (9) by use of the definition of C_V .

In the same way, with P and T as independent variables, we can easily show that for the ideal Bose gas

we have relationships such as:

$$T \frac{\partial G}{\partial T} + \left(1 + \frac{d}{2} \right) P \frac{\partial G}{\partial P} = G, \quad (11)$$

$$T \frac{\partial E}{\partial T} + \left(1 + \frac{d}{2} \right) P \frac{\partial E}{\partial P} = E, \quad (12)$$

$$T \frac{\partial C_P}{\partial T} + \left(1 + \frac{d}{2} \right) P \frac{\partial C_P}{\partial P} = 0, \quad (13)$$

each of which is also of the form in Eq. (1). Here, $G \equiv NkT \ln z$ is the Gibbs function, E is the energy, and C_P is the specific heat at constant pressure. As for the above case with (n, T) the independent variables, these relations are not independent. Thus Eq. (13) follows from Eq. (12) by differentiation with respect to T . Moreover, Eq. (11) can also be obtained directly from Eq. (8) by carrying out the appropriate Legendre transformation. It should also be emphasized that each of Eqs. (7)–(13) is valid on both sides of the phase boundary. Thus since $(\partial P/\partial n)_T = 0$ in the region of the condensed phase, to the left of the dashed curve in Fig. 1, it follows from Eq. (7) that consistent with known results⁵ in this region, $P = CT^{(1+d/2)}$ with C a known constant.

A very important feature of the above partial differential equations follows by comparison with Eq. (3) and noting that the projections into the nT plane of the characteristic equations of each of Eqs. (7)–(10) [or equally of each of Eqs. (11)–(13)] are identical. Substitution into Eq. (3), we obtain for the characteristic equation of, say, Eq. (7)

$$\frac{dn}{dT} = \frac{n}{T} \left(\frac{d}{2} \right), \quad (14)$$

and this integrates to

$$n = CT^{d/2}, \quad (15)$$

with C a positive constant of integration. Of particular interest is the fact that the phase boundary for the ideal Bose gas is precisely one of the curves in Eq. (15). It corresponds to the choice of $C = C_0$ where

$$C_0 = (2\pi mk/h^2)^{d/2} \xi(d/2). \quad (16)$$

As noted in Sec. I, it is just this feature, namely, that the phase boundary coincide with one of the characteristics, that we find essential for our treatment of a real gas. The characteristics and the phase boundary in the PT plane, are $P = CT^{(1+d/2)}$ and can be obtained in a similar way by use of Eqs. (11)–(13). These are only of passing interest here and will no longer be referred to.

Figure 2 shows schematically some of the characteristics in Eq. (15), in the nT plane. Part (a) depicts the situation for $d > 2$ and part (b) for $d < 2$. Since both n and T are inherently positive, the characteris-

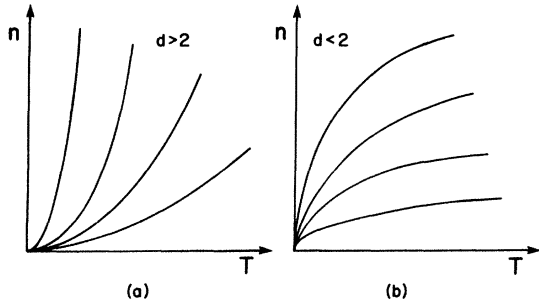


FIG. 2. Some of the characteristic curves of the ideal Bose gas in the nT plane for dimension $d > 2$. (a) and $d < 2$. (b).

tics are, as shown, confined to the positive quadrant of the nT plane. Particularly noteworthy is the fact that each characteristic is associated with a constant-entropy process. For reference to Eq. (9) shows that its most general solution is

$$S = f(n/T^{d/2}) \quad (17)$$

with f an arbitrary (differentiable) function. Thus, as the system traverses along the characteristic, $n = CT^{d/2}$, its entropy does not change. Equivalently, this can be described by the statement that maximum entropy changes are associated with traversals along the orthogonal trajectories of the characteristics; that is along the concentric ellipses of eccentricity $[1 - (2/d)]^{1/2}$ for $d > 2$, or $[1 - (d/2)]^{1/2}$ for $d \leq 2$.

Also of interest for our more general discussion in the ensuing sections are the solutions of the partial differential equations (7)–(10). As typical, consider Eq. (7). By direct substitution, it can be confirmed that its solution is of the form

$$P(n, T) = T^{(1+d/2)} f(n/T^{d/2}) \quad (18)$$

where f is an undetermined function. For the particular case of the Bose gas, this undetermined function can, in principle, be uniquely determined by use of Eqs. (4) and (5). For from the latter we find by use of Eq. (6)

$$P(T, z) = T^{(1+d/2)} h_1(z), \quad n(T, z) = T^{d/2} h_2(z) \quad ,$$

with h_1 and h_2 known⁵ functions. The explicit formula for f in Eq. (18) is then easily calculated to be $f(x) = h_1(h_2^{-1}(x))$ with h_2^{-1} the inverse of h_2 . In other words, since we have available the explicit forms in Eqs. (4)–(6) we can obtain a unique result with f in Eq. (18) known. By contrast, and this is the important point, if we begin only with the partial differential equation (7), we again obtain Eq. (18) but with f now *undetermined*. Thus a formulation in terms of an equation such as in Eq. (1) may be effective in describing some of the essential features of a first-order phase transition only by virtue of being

able to gloss over some of the details included in the undetermined function f .

Another point of interest associated with the above analysis has to do with the fact that even though Eq. (7), say, may describe a physical system correctly, it does not necessarily follow that its solution must of necessity have discontinuous derivatives along a characteristic. Nor indeed that the system undergoes a phase transition at all! For as we know, the phenomenon of Bose-Einstein condensation for the ideal gas takes place only in dimension $d > 2$. Yet the formulas above fail to make any significant distinction between the cases $d \gtrless 2$.

In connection with this last point it is of interest to note that an analysis of the above type but for the ideal *Fermi-Dirac* gas shows that each of the Eqs. (7)–(13) is also valid for this system of Fermions! And yet we know that for the ideal Fermi gas there is no phase transition in any dimension. The explanation, as above, is that the use of, say, Eq. (7) to describe the thermodynamic behavior of a system does not necessarily mean that it must undergo a phase transition. But only that if it does, then the phase boundary must lie along a characteristic.

Although not directly germane to the present discussion, it is also of interest to point out that the ideal Boltzmann gas is also described correctly by Eqs. (7)–(13)! Thus, each of the partial differential Eqs. (7)–(13) is applicable to each of the three types—Bose-Einstein, Fermi-Dirac, and Boltzmann—of physically significant ideal gases. The difference between these gases manifests itself only insofar as the undetermined functions which appears in the solution of these equations are different.

III. GENERAL FORMALISM

With the above discussion as background, in this section we detail the proposed phenomenology as specialized to the case of the liquid gas transition of a one-component system.

A. Preliminaries

Figure 3 shows schematically a part of the phase diagram for a single component substance such as water or CO_2 . The point C , associated with the critical values T_c and P_c is the critical point and lies at the upper end of the vapor-pressure curve tC . At the lower end, is the triple point, t , where the gaseous, liquid, and solid phases of the substance all coexist. The region inside the close dashed curve represents that region of the PT plane of primary interest here. Included in this region is that around the critical point and on both sides of the vapor-pressure curve but above and excluding the triple point.

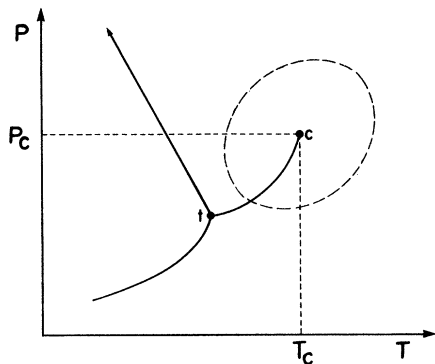


FIG. 3. Schematic of the phase diagram for a single component substance. The region inside the closed dashed curve is the focus of interest.

To simplify the notation, let us select an origin at the critical point, C , and define the variables t and p to be, respectively, the dimensionless temperature and the pressure relative to the point C by the formulas $t = (T_c - T)/T_c$ and $p = (P_c - P)/P_c$. Note that both t and p are positive for points below and to the left of the critical point in Fig. 3 and in particular that both are positive all along the vapor-pressure curve except for the point C itself.

It is convenient to describe the thermodynamic behavior of the liquid-gas transition by use of the Gibbs function, $G(t, p)$. The alternative of a formulation in terms of the Helmholtz potential $A(T, V)$ is also of interest but will not be detailed here. The latter formulation is not quite as straightforward due in part to the fact that the singular behavior around the coexistence curve manifests itself as a discontinuity in the *second* derivatives of A while for $G(t, p)$ the singular behavior along the vapor-pressure curve shows up as a discontinuity in the first derivative.

Figure 4 shows schematically the Gibbs surface $G(t, p)$ as a function of the relative temperature and pressure t and p , respectively. The heavy line on the surface represents the values of G along the vapor-pressure curve across which the first derivatives⁷ $G_t = S$ and $G_p = -V$ are discontinuous. Geometrically, this line corresponds to a crease on the surface. The projection of this crease down into the tp plane is also shown, and is the vapor-pressure curve itself; this time with its end point C at the origin. We assume that the equation $p = h(t)$ for the vapor-pressure curve is a given quantity. As is well known, near the critical point, $h(t)$ has the form⁸ $h(t) = p_0 t + Ct^{\beta\delta}$ with p_0 the slope at $t=0$, C a constant and with $\beta \cong 0.32$ the critical exponent for the coexistence curve and with $\delta \cong 4.5$ the exponent for the critical isotherm.⁹

For later reference, let us summarize some of the

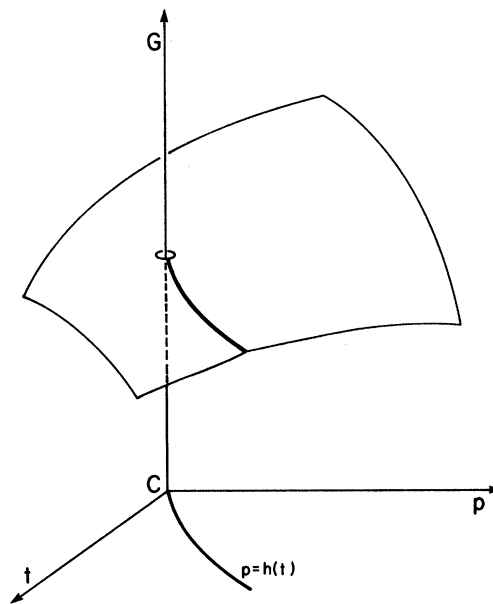


FIG. 4. Geometrical structure of the Gibbs surface $G(t, p)$ near the vapor-pressure curve. The heavy solid line on the surface represents a crease whose projection into the tp plane is the vapor-pressure curve. The critical point is at the origin.

properties of the Gibbs function in Fig. 4. First G is continuous and must be singularity-free everywhere except at the critical point and along the vapor-pressure curve. The nature of the singularity at C is known and generally believed to satisfy scaling^{10,11} and thus to be describable by a generalized homogeneous function.¹² Along the vapor-pressure curve, there are discontinuities in the derivatives of G : $\Delta S = S_L - S_G$ and $\Delta V = V_L - V_G$ where, for example, S_L is the entropy of the substance in the liquid phase, and is thus the limit of G_t as the vapor pressure is approached from the liquid side. The slope dh/dt of the vapor-pressure curve is related to these discontinuities by the Clausius-Clapeyron equation

$$\frac{dh}{dt} = \frac{\Delta S}{\Delta V} \quad (19)$$

We shall presume that these quantities $h(t)$, ΔS , and ΔV are known along the entire vapor-pressure curve and related in accordance with Eq. (19) at each point.

B. Phenomenology

Following Fisher, we assume that in the region around the vapor-pressure curve, that is inside the closed dashed curve in Fig. 3, the Gibbs surface $G(t, p)$ can be found among the solutions of the par-

tial differential equation

$$u \frac{\partial G}{\partial t} + v \frac{\partial G}{\partial p} = G + A_0 \quad (20)$$

Here t and p are defined above and u and v are appropriate *analytic* functions of t and p . The quantity A_0 , which is not present in Fisher's Eq. (1) represents an analytic background term. Thus, we generalize Fisher's formulation by allowing for the presence of $A_0(t,p)$ and by not restricting the coefficients u and v to be ratios of polynomials. Our requirements on u and v are simply that they be Taylor expandable in each variable and that in addition they satisfy certain other conditions as described below.

First, as discussed in connection with the ideal Bose gas, we impose on $u \equiv u(t,p)$ and $v \equiv v(t,p)$ the condition that one of the characteristic curves of Eq. (20) must coincide with the vapor-pressure curve $p = h(t)$. Reference to Eq. (3) shows that this condition is satisfied provided u and v are related by

$$\frac{dh}{dt} = \frac{v(t, h(t))}{u(t, h(t))} \quad (21)$$

This is a very important constraint and restricts the forms of u and v but only near the vapor-pressure curve.

The second important condition to be imposed on u and v arises from the fact that, consistent with experiment, in the asymptotic region of the critical point, Eq. (20) must have solutions which exhibit scaling. As will be confirmed below, a sufficient condition for this is that both of the coefficients u and v vanish at the origin:

$$u(0,0) = v(0,0) = 0 \quad (22)$$

Reference to the original Eq. (20), or its associated characteristic equations

$$\frac{dt}{ds} = u(t,p); \quad \frac{dp}{ds} = v(t,p); \quad \frac{dF}{ds} = F + A_0(t,p) \quad (23)$$

shows that the condition in Eq. (22) makes the origin a singular point of the equation. This is exemplified in Fig. 5 which shows that the slopes dp/dt of the characteristics are indeterminate at the origin. By contrast, the characteristics through any points, other than this singular point, are unique.

Besides the condition in Eq. (22), experiments of liquid-gas critical behavior^{9,12} require that in the asymptotic region of the critical point, u and v have the form

$$u = \frac{1}{\beta(\delta+1)} t; \quad v = \frac{\delta}{\delta+1} p + \frac{p_0(1-\beta\delta)}{\beta(\delta+1)} t \quad (24)$$

with p_0 the slope of the vapor-pressure curve at the critical point and with β and δ precisely the critical exponents referred to above. For substitution into Eq. (21) shows that consistent with our expectations

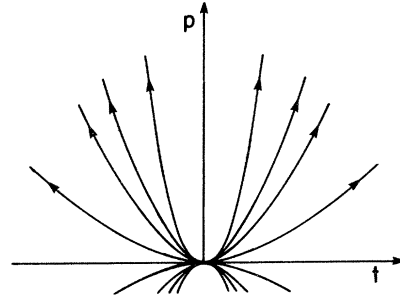


FIG. 5. Schematic of the projections of the characteristics of Eq. (20) into the pt plane. Because of Eq. (22), the origin $(0,0)$ is a singular point. For simplicity the parameter p_0 has been assumed to be zero. See Ref. 15.

$h(t) - p_0 t \cong t^{\beta\delta}$. Further, if we use the forms for u and v from Eq. (24) in Eq. (20) we find² that the latter has (up to addition of the, here inconsequential, background term A) precisely the correct scaling form $G = t^{\beta(\delta+1)} f((p - p_0 t)/t^{\beta\delta})$ with f an undetermined scaling function.

To recapitulate, Eq. (20) with the analytic functions u and v constrained by Eqs. (21), (22), and (24) comprise the essential framework on which we propose to erect a phenomenology of first-order phase transitions. Our main task remaining is to show that Eq. (20) admits solutions with appropriate discontinuous derivatives along the vapor-pressure curve. This will be our goal in Sec. IV.

However, before going into this, there are several features of this formulation which deserve comment, at least in a preliminary way.

As stated above, in the asymptotic region of the critical point, where the forms in Eq. (24) are applicable, it is easily verified that the solutions of Eq. (20) can be expressed in the scaling form

$$G(t,p) = t^{\beta(\delta+1)} f((p - p_0 t)/t^{\beta\delta}) + A(t,p) \quad (25)$$

with $A(t,p)$ an appropriate analytic function and with f an arbitrary function of the indicated variable. More generally, we find that this feature, namely, that the solutions of Eq. (20) can be separated into a sum of a singular term involving an undetermined function and an analytic background term, is not restricted to the asymptotic region. By use of theorem III in the Appendix it is easy to confirm that this feature carries over to the entire region of interest including the points of the vapor-pressure curve. Moreover, as will become clear in Sec. IV, the undetermined function in terms of which the solution to Eq. (20) is expressed, need not be the same in each of the four quadrants. That is, although there is no particular reason to expect that the undetermined function will be different in different quadrants, we

emphasize that this is not mandated in our formulation. It is possible to satisfy the physical condition that the Gibbs function and each of its derivatives be continuous across the t and the p axes without this constraint. Note, however, that because u and v are analytic, the analytic background function, for example, $A(t, p)$ in Eq. (25) must be the same in each quadrant. We shall return to this matter again in Sec. IV.

An extremely important point that comes up in this connection is the following. Even though the forms of the undetermined scaling function, for example, f in Eq. (25), can vary from one quadrant to the next (within limits as discussed in Sec. IV), the parameters β and δ appearing in this solution *cannot*. This follows, since the asymptotic forms for u and v are uniquely fixed in Eq. (24), and these two functions are analytic and thus must have exactly the same form in *all four quadrants*. We cannot have one formula for u and v in one quadrant and a different one in another without violating the analyticity assumption above. It follows that if experiment were to show that the critical exponents for the specific heat C_p , or for the isothermal compressibility K_T , were different above and below the critical point, then the proposed phenomenology would *not work*. Thus, a necessary condition for the validity of the formulation here proposed is that the critical exponents for C_p , K_T , etc., are the same above and below T_c .

Finally, it should be mentioned that we have implicitly assumed in all of the above that the corrections to scaling predicted by Wegner,¹³ and subsequently confirmed experimentally⁹ will not significantly affect the situation outside of the asymptotic region. Should such "confluent" singularities play an important role, say along the vapor-pressure curve, then it will be necessary to modify Eq. (24) or possibly to alter the structure of Eq. (20) itself.

IV. SINGULARITY ALONG THE VAPOR-PRESSURE CURVE

In this section we consider the problem of obtaining, for Eq. (20), solutions with discontinuous derivatives. Specifically, we shall establish the existence of solutions that are singularity-free everywhere, except along the vapor-pressure curve, and that there they can be selected to have discontinuities corresponding to values for ΔS and ΔV given by the experimental latent heat and coexistence curves, respectively. Our discussion relies on the mathematical theorems listed in the Appendix but includes details of the crucial arguments.¹⁴

As noted above, the characteristic curves associated with Eq. (20) play an extremely important role in the analysis of this equation. Accordingly, before presenting the analysis itself it is worthwhile to digress

briefly to describe some of the key properties of these characteristics.

Let us first note that since u , v , and A_0 are each analytic, it follows from Eqs. (23) for the characteristics, that through any fixed initial point (t_0, p_0, G_0) there exists, in general, one and only one characteristic curve. The only exceptions to this are the points along the G axis for which according to Eq. (22), u and v vanish simultaneously so that the slope dp/dt is not uniquely determined for these. Figure 5 shows schematically some of the projections of these characteristics down into the tp plane.¹⁵ The similarity between these curves and the corresponding ideal Bose-gas characteristics in Fig. 2(a) should be noted. In the present case, however, the independent variables t and p are not restricted to positive values so that now there are characteristic curves in each of the four quadrants.

It is possible to make the case that the characteristics are important not only for purposes of analyzing the solutions of Eq. (20) but also because they may have a direct physical significance. For the ideal Bose gas this is clear since according to Eq. (17) the characteristics are precisely the isentropes. For the case of an interacting gas, the potential importance of the characteristics was first emphasized by Benguigui.¹⁶ This author pointed out that in the asymptotic region of the critical point where the form in Eq. (25) is applicable, the derivatives of the Gibbs function (i.e., V, S, C_p , etc.) along the characteristics $p - p_0 t = C_1 t^{\beta\delta}$ vary simply as a power of t or equivalently of p . For example, it is easy to confirm from Eq. (25) that along a given characteristic we have $V - V_c = C_1 t^\beta$ with C_1 a constant coefficient depending only on the particular characteristic selected. Furthermore analyses such as those of Ho and Litster,¹⁷ of Levelt Sengers *et al.*,¹⁸ and Green *et al.*¹⁹—which produce scaling functions in the form of measured curves—are direct experimental confirmation for the physical importance of characteristic curves.

Returning now to the analysis of Eq. (20), we shall establish that this equation has solutions with discontinuous derivatives along the vapor-pressure curve by actually showing that through each of its characteristics there are infinitely many solutions. Then from the fact that we have selected the vapor-pressure curve to be the projection into the tp plane, [Eq. (21)], of a characteristic, it follows that we can easily find solutions continuous everywhere but with the necessary discontinuous derivatives along the phase boundary.

Consider in Fig. 6 an arbitrary space curve C and let C_0 represent its projection down into the tp plane. Let the curve C be representable in terms of a parameter τ by means of the three functions $(t_0(\tau), p_0(\tau), G_0(\tau))$ so that as τ varies, the point specified by the coordinates $(t_0(\tau), p_0(\tau), G_0(\tau))$ traces out the space curve C .

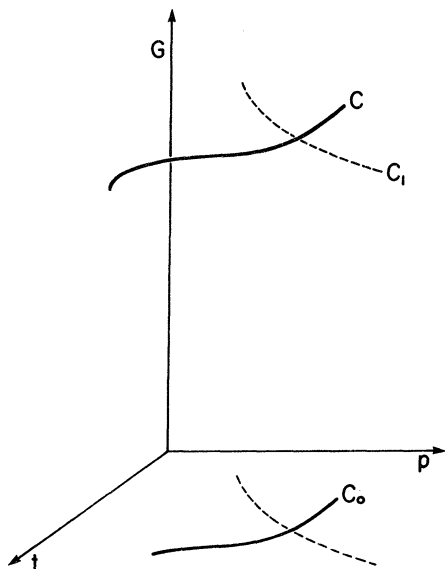


FIG. 6. C represents an arbitrary space curve and C_1 a curve that intersects it. C_0 and the dashed curve in the tp plane are the projections of C and C_1 , respectively, onto this plane.

Imagine now solving the characteristic Eqs. (23) to obtain the characteristics that go through *each* of the points of the curve C . These characteristics will, in general, depend on two variables s and τ , and with the important exception noted below, will collectively define a surface $G(t, p)$ that solves Eq. (20). Geometrically, we can think of this surface as being swept out sequentially by the characteristics that emanate from the various points of C in Fig. 6.

To see in detail how such a surface $G(t, p)$ can be generated, consider the solutions of the characteristic Eqs. (23):

$$t = t(s, \tau); \quad p = p(s, \tau); \quad G = G(s, \tau), \quad (26)$$

with $t(0, \tau) = t_0(\tau)$, etc. A formula for the associated solution surface, $G(t, p)$, can be obtained, in principle, by solving the first two of Eqs. (26) backwards to obtain $s = s(t, p)$ and $\tau = \tau(t, p)$ as functions of t and p and substituting into the third. The result is the desired function $G(t, p)$ which, on the one hand, solves Eq. (20) and on the other contains the given space curve C . As confirmed by theorem 4 in the Appendix, provided these steps can actually be carried out, we obtain a unique surface $G(t, p)$ in this way.

The crucial step in carrying out this procedure involves our ability to solve the first two of Eqs. (26) backwards to express both s and τ in terms of t and p . The condition for this is well known and is that the Jacobian $J(s, \tau)$ of the transformation, defined

by

$$J(s, \tau) = t_s p_\tau - p_s t_\tau \quad (27)$$

(with $t_s = \partial t / \partial s$, etc.) does not vanish. Making use of this we can conclude—consistent with theorem 4 in the Appendix—that provided $J \neq 0$ along C , there is one and only one solution of Eq. (20) that contains the curve C . This is analogous to the situation for a first order, ordinary differential equation for which a unique solution follows from the specification of the unknown function at a single point. Here, for the two-independent-variable case, it is necessary to specify the unknown function along a space curve.

The condition $J \neq 0$ along C —or equivalently along C_0 , since u and v depend only on t and p in our case—has simple geometrical meaning. For if along C we set $J(0, t) = 0$, we have

$$t_\tau p_s = t_s p_\tau, \quad (s = 0)$$

and it follows from the first two of Eqs. (23) that the characteristic through each point of C_0 is parallel to the tangent p_τ / t_τ at that point. Hence it must coincide with C_0 . Or in other words, C_0 must itself be the projection into the tp plane of a characteristic curve.²⁰ More formally, since at fixed τ , $p_s = dp/ds$ and $t_s = dt/ds$, making use of Eq. (23) we may rewrite the relation immediately above in the form

$$\frac{t_\tau}{p_\tau} = \frac{t_s}{p_s} = \frac{dt}{dp} \quad (s = 0), \quad (28)$$

which shows that C_0 is characteristic. Hence, the procedure leading to Eq. (26) will yield a unique solution of Eq. (20) containing a given curve C only provided that C or equivalently C_0 is *not* a characteristic curve.

It is now a simple matter to show that if C is indeed characteristic then there are an infinity of solutions of Eq. (20) that contain C . For if as shown in Fig. 6 by the dashed curve, we draw an arbitrary curve C_1 ($\neq C$) through an arbitrary but fixed point of C , then since C_1 cannot be characteristic (since C is presumed to be) it follows from the discussion of the preceding paragraph that there exists a unique solution through C_1 . But by theorem 1 of the Appendix this same solution must also contain C ! Clearly we can draw an infinite number of curves through the intersection of C_1 and C and for each of these, the solution of Eq. (20) containing this curve must also contain C . Hence it follows that through any given characteristic curve there are an infinite number of solutions of Eq. (20).

In particular, therefore, since we have forced one of the characteristic curves of Eq. (20) to coincide with the vapor-pressure curve [Eq. (21)], it follows that there are an infinity of solutions of Eq. (20) that contain the phase boundary of the physical system. Thus on crossing the vapor-pressure curve if we

transfer from one of these solutions to another, it is possible to obtain a solution to Eq. (20) that is both continuous everywhere and at the same time has the appropriate discontinuous first derivatives along the vapor-pressure curve. In a sense, this procedure is simply the famous Maxwell construction but in the context of Eq. (20).

V. DISCONTINUITIES IN HIGHER DERIVATIVES

One advantage of the present formulation of first-order phase transitions is that it is possible to derive new relations among thermodynamic quantities simply by differentiating Eq. (20). Relations obtained in this way are of particular interest here since by their usage we can obtain information on the coefficient function u and v along the *entire* vapor-pressure curve.

For orientation purposes, it is useful to consider first the problem of how the Clausius-Clapeyron Eq. (19) comes out in the present formulation. To this end, consider Eq. (20) in the limits as a fixed point $(t, h(t))$ of the vapor-pressure curve is approached from the liquid (+) side and from the gaseous (-) side. Introducing the symbols ΔG_l and ΔG_p for the respective differences $(G_l^+ - G_l^-)$ and $(G_p^+ - G_p^-)$, we find by subtracting these two limiting forms of Eq. (20) the result

$$u \Delta G_l + v \Delta G_p = 0, \quad (29)$$

where $u = u(t, h(t))$, $v = v(t, h(t))$ are here evaluated at the fixed point of the vapor-pressure curve. Also used in obtaining this relation are the facts that u , v , and A_0 are analytic and thus, *ipso facto* continuous across the vapor-pressure curve, and that the Gibbs function G , although not itself analytic, is nevertheless continuous across the same curve. Note that the analytic background function A_0 has cancelled out in Eq. (29).

As is well known, the Clausius Clapeyron equation for a first-order transition follows from the continuity of G along the phase boundary. Hence it should not be surprising that it also follows from Eq. (29) when we make use of $\Delta S = \Delta G_l$ and $\Delta V = -\Delta G_p$ and our hypothesis that the vapor-pressure curve is a characteristic, and hence satisfies Eq. (21). Indeed, solving Eq. (29) for the ratio v/u and equating this to dh/dt in accordance with Eq. (21) we find that the Clausius Clapeyron Eq. (19) results. Equivalently, we can think of the constraint in Eq. (21), namely that the vapor-pressure curve coincide with a characteristic curve, as being mandated by Eqs. (19) and (29).

This same method can also be used to obtain new relations involving the second derivatives of G . This time, we first differentiate Eq. (20) with respect to t and then a second time with respect to p with the

result:

$$u G_{ll} + v G_{pl} = (1 - u_l) G_l - v_l G_p + A_{0l}, \quad (30)$$

$$u G_{lp} + v G_{pp} = -u_p G_l + (1 - v_p) G_p + A_{0p}.$$

Continuing as in the preceding paragraph, we now take the limits of each of these relations as a fixed point of the vapor-pressure curve is approached from the (+) and (-) sides. Taking the respective differences, as above, we obtain on using the facts that u , v , and A_0 as well as all of their derivatives are continuous across the vapor-pressure curve, that

$$u \Delta G_{ll} + v \Delta G_{pl} = (1 - u_l) \Delta G_l - v_l \Delta G_p, \quad (31)$$

$$u \Delta G_{lp} + v \Delta G_{pp} = -u \Delta G_l + (1 - v_p) \Delta G_p,$$

where u , v , and their derivatives are to be evaluated at the given point of the vapor-pressure curve. In more familiar terms. Eqs. (31) may be written in the form

$$-u T \Delta C_p + v \Delta(V \alpha_p) = (1 - u_l) \Delta S + v_l \Delta V, \quad (32)$$

$$u \Delta(V \alpha_p) - v \Delta(V K_T) = -u_p \Delta S - (1 - v_p) \Delta V,$$

where C_p , α_p , and K_T are, respectively, the specific heat at constant pressure, the coefficient of thermal expansion, and the isothermal compressibility, all evaluated at the fixed point of the vapor-pressure curve. In principle, a knowledge of the discontinuities of C_p , α_p , K_T , V , and S along the vapor-pressure curve yields these two relations involving as unknowns only the coefficients u , v , and their derivatives. Thus we can obtain information about u and v in a region around the entire vapor-pressure curve.

It is interesting to note the similarity between Eqs. (32) and a similar one obtained by Griffiths²¹ involving the discontinuity in C_v across the coexistence curve for a *second-order* phase transition. Griffith's formula was derived by use of the appropriate Ehrenfest relation and since he did not need to rely on the validity of Eq. (20), as we have here, is of more general validity than are Eqs. (31). In this connection, it is also of interest to note that for the case of second-order transition for which $\Delta G_l = \Delta G_p = 0$, Eqs. (31) assume the simpler form

$$u \Delta G_{ll} + v \Delta G_{pl} = 0, \quad u \Delta G_{lp} + v \Delta G_{pp} = 0. \quad (33)$$

It is then easy to confirm in the same way as above [see the discussion immediately following Eq. (29)] that these relations are equivalent to the two Ehrenfest relations for a second-order phase transition! The fact that Eqs. (33) can indeed be satisfied without both u and v vanishing identically also follows from these two Ehrenfest relations which show that the determinant of the coefficients in Eqs. (33)

must vanish:

$$(\Delta G_u)(\Delta G_{pp}) - (\Delta G_{up})^2 = 0 .$$

To summarize then, the relations in Eqs. (32), and corresponding ones involving discontinuities in the third and possibly higher derivatives, are useful from the present point of view for a number of reasons. First, they are independent of the analytic background term A_0 and hence are useful even without a knowledge of this function. Secondly, they are applicable along the *entire* vapor-pressure curve and hence can be conveniently used without the difficulties generally associated with measurements in the laboratory made right at the critical point. Third, a knowledge of the discontinuities in the second derivatives of G yields direct information about the forms of u and v . That is, just as the Clausius Clapeyron Eq. (19) gives us partial information about the shape of the vapor-pressure curve, and thus about the ratio v/u via Eq. (21), the relations in Eqs. (32) give us information on the *derivatives* of u and v and thus information about u and v *near* the vapor-pressure curve. Additional knowledge of u and v is, in principle, obtainable by the generalization of Eqs. (32) to higher derivatives.

A straightforward application of this procedure can be given in the asymptotic region of the critical point by use of the solution in Eq. (25). Assuming that the form for G in this relation is given and accurately summarizes experiment, we may calculate by its usage the discontinuities in the various derivatives of the Gibbs function G along the phase boundary ($p = p_0 t + C_0 t^{\beta\delta}$ with C_0 known). Substituting these results into Eqs. (31), we obtain relations involving u and v along the phase boundary. It is then easy to show—or at least to confirm—that u and v are given by

$$u = \frac{1}{\beta(\delta+1)} t; \quad v = C_0 \frac{\delta}{(\delta+1)} t^{\beta\delta} + \frac{p_0}{\beta(\delta+1)} t ,$$

which is precisely Eq. (24) evaluated along the phase boundary.

An application of this procedure but not confined to the critical region will be considered in the next section.

VI. SPONTANEOUS MAGNETIZATION AND POLARIZATION

As an application of the procedure suggested in the preceding section, let us consider the case of a ferromagnetic system, whose thermodynamic behavior is described by the two independent variables, H and t where H is the magnetic field and $t = (T_C - T)/T_C$ with T_C , the Curie temperature. For negative values of t , the system is paramagnetic, while for $t > 0$, it ex-

hibits a spontaneous magnetization $M_0 = M_0(t)$. This transition is very similar²² to the liquid-gas transition considered above, but is somewhat less complex owing to the system's symmetry under magnetic field reversal. This has the consequence that the Gibbs function $G(t, H)$ must be an even function of H in order that magnetization $M(t, H) \equiv -G_H$, change sign with the magnetic field. The discontinuity in the first derivative of G determines the spontaneous magnetization in accordance with the formula

$$\lim_{H \rightarrow \pm 0} M(t, H) = \pm M_0(t) . \quad (34)$$

In geometric terms, if we think of the p axis in Fig. 4 as the H axis, and the vapor-pressure curve there as coinciding with the t axis ($H = 0$), then the surface in this figure can be thought of as representing the Gibbs function $G(t, H)$.

The starting point for the analysis is an appropriately modified Eq. (20)

$$u \frac{\partial G}{\partial t} + v \frac{\partial G}{\partial H} = G + A_0 , \quad (35)$$

with u , v , and A_0 analytic functions, now of t and H . To satisfy the above noted symmetry requirements according to which $G(t, H)$ must be even in H , it is easy to see that it is necessary for $u(t, H)$ to be an even and $v(t, H)$ an odd function of H . Moreover, since v is also analytic, it follows that $v(t, 0) = 0 = v_t(t, 0)$. This is consistent with the condition in Eq. (21),

$$\frac{dH}{dt} = \frac{v(t, 0)}{u(t, 0)} = 0 ,$$

and confirms that the phase boundary $H = 0$, coincides with a characteristic curve in this case. As is well known, the condition $dH/dt = 0$ when used in conjunction with the Clausius Clapeyron Eq. (19) means that no latent heat is associated with the transition.

Proceeding now from Eq. (35), we find as in the derivation of Eq. (31)

$$\begin{aligned} u \Delta G_{tt} + v \Delta G_{Ht} &= (1 - u_t) \Delta G_t - v_t \Delta G_H , \\ u \Delta G_{tH} + v \Delta G_{HH} &= -u_H \Delta G_t + (1 - v_H) \Delta G_H , \end{aligned} \quad (36)$$

where all quantities are evaluated along the phase boundary $H = 0$. Because of the symmetry available, in the present ferromagnetic case, these two relations simplify considerably. As noted above, both v and v_t must vanish at $H = 0$ and since no latent heat is associated with the transition, so must the terms involving ΔG_t . Moreover, according to Eq. (34), $\Delta G_{Ht} = -2M_0(t)$ and brief reflection shows that $\Delta G_{HH} = -2dM_0/dt$. Substituting these facts into Eq. (36) we find that the first of these reduces to $\Delta G_{tt} = 0$. This is consistent with the experimental fact²³ that

the specific heat C_H of a ferromagnet is continuous across the line $H=0$. The second of Eqs. (36), however, yields something new. For the substitution of the above $H=0$ values for v , ΔG_t , etc., into Eq. (36) yields the relation

$$\frac{dM_0}{dt} = M_0(t) \frac{(1-v_H)}{u}; \quad (H=0) \quad (37)$$

It follows from this formula that, except for a constant of integration, the shape of the spontaneous magnetization curve is completely determined by the values of u and v_H along the phase boundary. And conversely, given an experimental curve for $M_0(t)$, we can use Eq. (37) to deduce information about the functions u and v in the immediate neighborhood of this boundary.

As a first check on Eq. (37), consider the asymptotic region at the critical point where u and v have the form²⁴

$$u = \frac{1}{\beta(\delta+1)}t; \quad v = \frac{\delta}{\delta+1}H \quad (38)$$

Substituting these into Eq. (37), we obtain

$$\frac{dM_0}{dt} = \beta \frac{M_0}{t}$$

and this is consistent with the well-known experimental fact $M \sim t^\beta$ in the critical region.

Let us now attempt to extend this argument away from the critical region by modifying appropriately the forms for u and v in Eqs. (38). If we make use of the analyticity requirements that have been imposed on these two functions, such modifications are, in, "first order" unique and lead one to the formulas

$$u = \frac{1}{\beta(\delta+1)}t(1+at); \quad v = \frac{\delta}{\delta+1}H(1+bt) \quad (39)$$

where a and b are constants to be determined by experiment. Substituting into Eq. (37) and integrating we obtain

$$M_0(t) = K \frac{t^\beta}{(1+at)^{\beta\xi}} \quad (40)$$

where the parameter ξ is defined by $\xi - 1 = b\delta/a$ and K is a positive constant of integration. Note the interesting fact that the parameter "a" appears both in the factor $(1+at)$ in the denominator in Eq. (40) as well as in the exponent $\beta\xi$ of this factor.

To make practical usage of Eq. (40) it is necessary to obtain numerical values for the two parameters a and b . This could be achieved, in principle, by simply making a comparison—at small t where the forms for u and v in Eq. (39) are expected to be valid—with experimental curves for $M_0(t)$. With the parameters a and b then at hand, we could utilize Eqs. (35) and (39) to obtain a formula for the Gibbs functions $G(t,H)$ valid in an extended region around the criti-

cal point. Regardless of the values obtained for a and b in this way, this formula for $G(t,H)$ would be consistent with experiment in the asymptotic region at the critical point.

However, rather than following this approach here, let us consider briefly the possibility of obtaining the parameters a and b by assuming that Eq. (40) can be extended all the way down to $t = -T_C$; that is to, $T=0$. To this end, we recall that near $T=0$, Bloch's spin-wave theory²⁵ predicts $M_0(T) - 1 \cong T^{3/2}$. Brief reflection shows that it is *not* possible for Eq. (40) to agree with this limiting behavior for any choice of the constants a and b . If, however, we assume, that $b = 1/\delta$, then we find from Eq. (40) that for small T , $(M_0 - 1) \sim T^2$ and this also agrees—although not nearly as well—with the experimental points not too close to $T=0$. Substituting this value $b = 1/\delta$, we find, on normalizing M_0 to unity at $T=0$, that Eq. (40) assumes the form

$$M_0(T) = \frac{(1 - T/T_C)^\beta}{(1 - T/\xi T_C)^{\beta\xi}} \quad (41)$$

with T_C the Curie point and with ξ , the only remaining free parameter, constrained to be larger than unity. As noted above, the parameter ξ , appears both in the factor $(1 - T/\xi T_C)$ as well as in the exponent $\beta\xi$ of this factor.

A detailed study of Eq. (41) shows that its form is rather insensitive to the choice for the parameter ξ in the range $3 \leq \xi \leq 12$. Figure 7 shows a graph of Eq. (41) for the values $\xi = 10$, $\beta = 0.33$ and also includes for comparison some experimental data²⁶ for Ni. The insert in the same figure shows some experimental points of nickel on an expanded and thus more sensitive scale and includes for comparison also, graphs for: Eq. (41), the spin-wave theory, an empirical T^2 curve, and the classical Weiss theory.²³ In comparing these curves it should be borne in mind that Eq. (41) is intended to be a representation of experiment only in the region right around the critical point at $T = T_C$. Thus, it may well be fortuitous that the present results compare favorably with the other curves in the figure outside of the critical region.

As a second application of the procedure suggested in the preceding section, let us consider the case of a ferroelectric material.²⁷ Of particular interest to us is the curve for the spontaneous polarization as a function of temperature, analogous to the curve for the spontaneous magnetization in Fig. 7. However, rather than attempting to produce here curves for ferroelectrics whose polarization curves are similar to the magnetization curves in Fig. 7 it is somewhat more instructive to consider the unusual polarization curve for Rochelle salt ($\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$). This material which was the first known ferroelectric²⁷ actually has two Curie temperatures, one at about 24 °C and the other at -18 °C. Figure 8 shows some experimental points²⁸ for the spontaneous polarization of

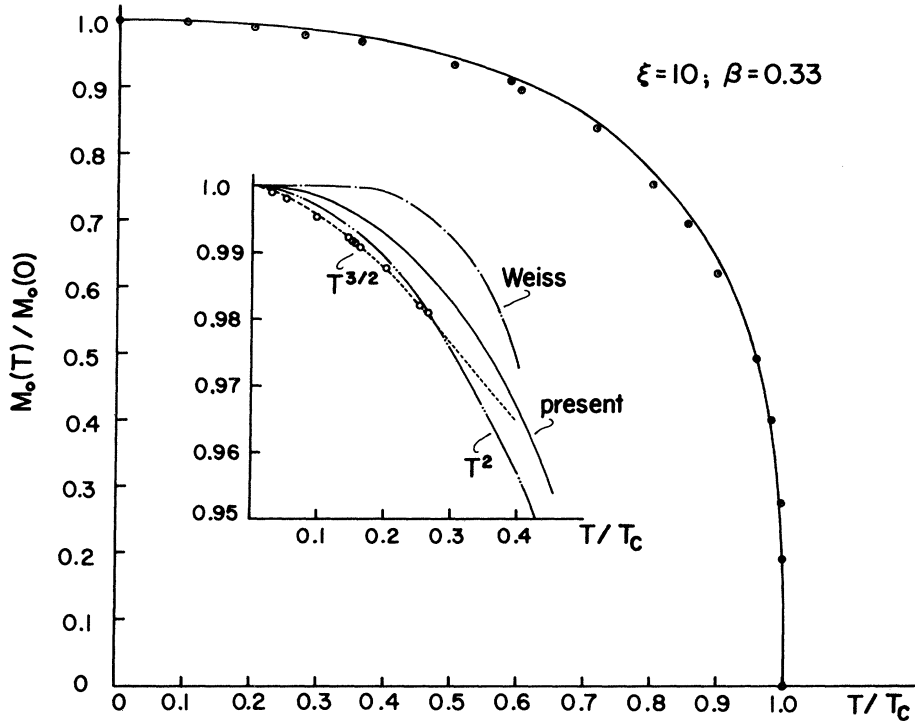


FIG. 7. Graph of Eq. (41) for the parameter values $\beta=0.33$ and $\xi=10$. The experimental points are for nickel (Ref. 26) and the insert shows a comparison with the spin-wave theory, an empirical T^2 fit and the classical Weiss theory.

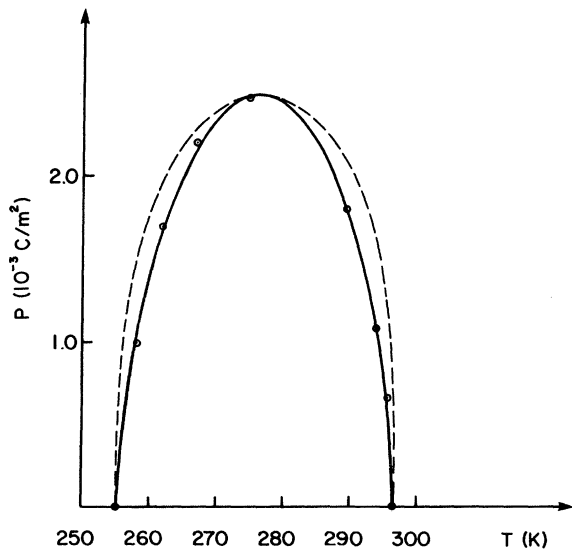


FIG. 8. The spontaneous polarization of Rochelle salt as given by Eq. (43) with $\eta=1.05, \beta=0.60$ (the solid curve) and with $\eta=1.05, \beta=0.33$ (the dashed curve). The experimental points are taken from Ref. 38.

this material.

Making use of the same symmetry arguments as used above for the ferromagnetic case, we can obtain formulas similar to Eqs. (37)–(40) and conclude that the spontaneous polarization P is given by

$$P = K \frac{t^\beta}{(1 + at)^{\beta\xi}} \quad (42)$$

In this formula $\xi = 1 + b\delta/a$ and the constants a and b , as in Eq. (39), are to be determined by experiment. As before, K is a constant of integration.

To make practical use of this formula in Eq. (42) it is necessary to select appropriate value for the constants K, a, b, ξ , and β . Obviously, in order that Eq. (42) be consistent with the existence of two Curie points, we need to select the parameters a and ξ to be negative. Hence, defining $\eta = -\xi$, we may reexpress Eq. (42) in the form

$$P = C (T_1 - T)^\beta (T - T_2)^{\beta\eta} \quad (43)$$

where C is a constant determined by the scale on the left in Fig. 8, $T_1 \approx 297 \text{ K}$, is the temperature of the upper Curie point and $T_2 \approx 255 \text{ K}$ is the temperature of the lower Curie point. In terms of the original parameters, for example, $a = -(T_1 - T_2)^{-1}$. Finally,

to determine a value for η , we use the easily verifiable fact that the maximum of the curve for P in Eq. (43) occurs at $T = T_{\max}$, where

$$T_{\max} = T_2 + \eta(T_1 - T_2)/(\eta + 1) . \quad (44)$$

Hence, comparison with the experimental points which indicate that the maximum of P occurs about midway between the two Curie points, we deduce that $\eta \cong 1$.

Empirically, we find that the experimental values for the spontaneous polarization of Rochelle salt can be fairly well represented by the choice

$$\eta = 1.05; \quad \beta = 0.60 . \quad (45)$$

The solid curve in Fig. 8 is the graph of Eq. (43) with this choice for the parameters. For comparison, we also show by the dashed curve, the graph of Eq. (43) with the parameter values $\eta = 1.05$, $\beta = 0.33$. The constant C is selected in both cases so that the maximum coincides with the experimental maximum. It should be noted that the values $\beta = 0.5$ and $\eta = 1.0$ are not ruled out by the experimental points.

Finally, it is interesting to note the relationship that, according to Eq. (44), seems to exist between the "critical" exponents β and $\eta\beta$ at the two Curie points and the maximum in the polarization curve. It should be recalled in this connection, however, that the relations in Eqs. (43) and (44) are based on the assumption implied in Eq. (39) and the latter has only a restricted range of validity.

VII. CONCLUDING REMARKS

In conclusion, let us consider several items which relate to this proposal.

First, the agreement with experiment for the magnetization curve in Fig. 7, as well as that for the spontaneous polarization of Rochelle salt in Fig. 8, seems to indicate that the simple forms for u and v in Eq. (39) may already be a reasonable approximation to the correct forms for these functions. This was certainly not foreseen by the author and may well turn out to be fortuitous! In any event, making use of data, such as that in Figs. 7 and 8, we are able to obtain what seem to be reasonable estimates for the parameters a and b in Eqs. (39). Armed with this knowledge we can then specify u and v in Eq. (39) and then use these in Eq. (35) to calculate the Gibbs function. For the ferromagnetic system, for example, we find in this way

$$G(t, H) = \left(\frac{t}{1 + at} \right)^{\beta(\delta+1)} f(H/[t(1 + at)^\lambda]^{\beta\delta}) + A , \quad (46)$$

with $\lambda = (b - a)/a$ and with A an appropriate analytic background term. In other words, by simply inputting the data from the magnetization curves, we can obtain a formula for the Gibbs function that is valid in a region around the phase boundary. Note, however, that much of the information obtained in this way is restrictive in that the formula for $G(t, H)$ in Eq. (46) involves an undetermined function f as well as the analytic background term A .

A second item of interest deals with the question of the uniqueness of the form of Eq. (20), or equivalently of Eq. (35). As soon as one agrees to go to a phenomenology of first-order phase transitions *via* the partial-differential-equation route, there are a maze of possibilities that can and should be explored. The one selected here in Eq. (20) is distinguished in this sense mainly by the fact that it is linear, and first order and therefore presumably the simplest member of this class. A possible "first-order" modification of Eq. (30) might be to replace " G " on the right-hand side by an analytic function, say $W(G)$. The resultant nonlinearization of Eq. (20) would not change, in a substantial way, much of the material presented above. The main alterations would be: (1) to make it awkward to separate G , as in Eqs. (25) and (46) into a singular term and an analytic background term; and (2) to modify the right-hand sides of Eqs. (30)–(32) by the replacement of G_i by $W'G_i$ and G_p by $W'G_p$ where W' is the derivative of W . Of these, the latter is the less serious, for it would correspond mainly to a modification in the forms for u and v in the region around the vapor-pressure curve.

A third item of interest comes up in connection with a possible alternate formulation of Eq. (20) in terms of the Helmholtz potential, $A(T, V)$ or one of its derivatives, say the pressure $P(T, V)$. The projection of the curve corresponding to the crease in Fig. 4 would in this case be that part to the coexistence curve in the first quadrant. Brief reflection shows that to specify the entire coexistence curve it would be necessary now to join together—through the origin—two characteristics from adjacent quadrants. This possibility is thus more complex than the Gibbs-function approach described here but may well be worth exploring.

Finally, it may be worth commenting on the possible generalizations of Eq. (20) to the case where additional independent variables are relevant for a description of the physical system. As pointed out by Fisher,² the extension to higher dimensions of relations such as that in Eq. (20) is straightforward and relatively free of ambiguity. In the present case, we would simply add to the left-hand side of Eq. (20) a term, say $w(t, p, x)G_x$, where x would be a third independent variable—for example, the concentration of a component in a mixture—and where now u , v , w , A_0 , and G would each depend on the three vari-

ables t , p , and x . Of considerable interest in this connection is the phase boundary, across which the first derivatives of G would be discontinuous. Here, this surface would be a two-dimensional one in the space spanned by the Cartesian t , p , and x axes. A preliminary study of this equation, shows that an analysis of the type in Sec. IV, can be carried out as easily with three independent variables as with two. We find that the phase-boundary surface obtained this way is the solution of an equation of precisely the form in Eq. (20).

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the hospitality extended to the author by Professor Joachim Appel and Professor Heinrich von Geramb and their colleagues at the University of Hamburg, where this work was begun. The author is particularly grateful to Professor Hartwig Schmidt of the I. Institut für Theoretische Physik for several informative discussions on the subject of this paper. Also, I am indebted to my Purdue colleagues, Professor Nick Giordano and Professor Gary Grest and to Professor Michael E. Fisher for critical readings of the manuscript and for several helpful suggestions.

APPENDIX

In this Appendix, we state without proof,¹⁴ a number of theorems regarding the solutions of the partial differential Eq. (20) and its associated characteristic curves as determined by Eqs. (23). Where appropriate, we specialize to the case of present in-

terest for which $u(t,p)$ and $v(t,p)$ are analytic in t and p , independent of G , and where u and v both vanish at the origin $t=0$, $p=0$. Further, we shall be concerned only with solutions which have derivatives of all orders everywhere with the possible exception of an isolated point or an isolated line.

Theorem 1: If a solution surface $G(t,p)$ of Eq. (20) has a point in common with one of the characteristics of Eqs. (23), then this characteristic curve lies in its entirety on the surface $G(t,p)$.

Theorem 2: If two solution surface $G_1(t,p)$ and $G_2(t,p)$ have a point in common—i.e., $G_1(t_0,p_0) = G_2(t_0,p_0) = G_0$ for a given (t_0,p_0) —then they must intersect along the unique characteristic curve through the point (t_0,p_0,G_0) .

Note 1: This theorem is not valid for the case that equality of G_1 and G_2 occurs at the point $t_0=0=p_0$. For at this unique singular point of the equation there does not exist a unique characteristic curve.

Note 2: This theorem is a direct consequence of the preceding one.

Theorem 3: If $G_0(t,p)$ is a particular integral of Eq. (20) and if $h(t,p)$ is a solution of the associated homogeneous equation $u(\partial h/\partial t) + v(\partial h/\partial p) = 0$ then if $G(t,p) = G_0(t,p) + h(t,p)$, then as $h(t,p)$ runs through all the solutions of its equation, $G(t,p)$ will run through all the solutions of Eq. (20).

Theorem 4: Let C (Fig. 6) be an arbitrary space curve and C_0 its projection down into the tp plane. Then there exists one and only one solution of Eq. (20) that contains the curve C provided its projection C_0 is not a characteristic curve—i.e., is not a solution of Eq. (23). If C_0 is a characteristic curve, then there are infinitely many solutions of Eq. (20) that contain C .

¹M. E. Fisher, *Physica* (Utrecht) **86–88B**, 590 (1977). See, also Michael E. Fisher and Helen Au-Yang, *J. Phys. A* **12**, 1677 (1979); **13**, 1517 (1980).

²Michael E. Fisher, in *Proceedings of the Symposium in Honor of E. W. Montroll's 60th Birthday* (Plenum, New York, 1978). The author is indebted to Professor David Mukamel for pointing out this work to him and for a helpful conversation on the subject of this paper.

³*The Padé Approximation in Theoretical Physics*, edited by G. A. Baker and J. L. Gammel (Academic, New York, 1970).

⁴Michael E. Fisher, *Rev. Mod. Phys.* **46**, 597 (1974); Kenneth G. Wilson and J. Kogut, *Phys. Rep.* **12**, 75 (1974).

⁵See, for example, L. D. Landau and E. M. Lifshitz, *Statistical Physics*, 3rd ed. (Pergamon, New York, 1980), Part I, Chap. 5.

⁶For an alternate approach to the following analysis, see Martin J. Cooper and Melville S. Green, *Phys. Rev.* **176**, 302 (1968).

⁷We shall frequently use the shorthand G_t in place of the more usual $\partial G/\partial t$. Note that because of our definitions for the quantities t and p : $G_t = T_c G_T$; $G_p = -P_c G_P$, etc.

⁸Robert G. Griffiths and John C. Wheeler, *Phys. Rev. A* **2**, 1047 (1970). We follow here the arguments of these authors consistent with which the appropriate scaling variable is $(p - p_0 t)/t^{p_0}$. For ferromagnetic systems the parameter analogous to p_0 is zero.

⁹J. M. H. Levelt Sengers and J. V. Sengers, *Phys. Rev. A* **12**, 2622 (1975). See also, F. W. Balfour, J. V. Sengers, M. R. Moldover, and J. M. H. Levelt Sengers, *Phys. Rev. Lett.* **65A**, 223 (1978) for more recent values.

¹⁰B. Widom, *J. Chem. Phys.* **43**, 3898, 3829 (1965).

¹¹L. P. Kadanoff, *Physics* **2**, 263 (1966). See also, Kadanoff *et al.*, *Rev. Mod. Phys.* **39**, 395 (1967).

¹²See, for example, H. Eugene Stanley, *Phase Transitions and Critical Phenomena* (Oxford University Press, New York, 1971), Chaps. 11 and 12.

¹³F. Wegner, *Phys. Rev. B* **2**, 4529 (1972).

¹⁴See, for example, R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Wiley-Interscience, New York, 1962), Vol. II, Chap. 2.

¹⁵In Fig. 5, we have for simplicity assumed $p_0=0$ and used the fact that in the asymptotic region of the critical point

Eqs. (20), (23), and (24) imply that these characteristic curves have the form $|p - p_0 t| = C |t|^{\beta\delta}$ with $1 < \beta\delta < 2$ and with C a constant.

¹⁶L. Benguigui, *Physica (Utrecht)* **64**, 189 (1973). We here translate this author's arguments from the ferromagnetic case to that of the liquid-gas transition.

¹⁷J. T. Ho and J. D. Litster, *Phys. Rev. Lett.* **20**, 603 (1969). For more recent measurements, see A. T. Aldred, P. de V. duPlessis, and G. H. Lander, *J. Magn. Magn. Mater.* **20**, 236 (1980).

¹⁸J. M. H. Levelt Sengers, W. L. Green, and J. V. Sengers, *J. Phys. Chem. Ref. Data* **5**, 1 (1976).

¹⁹M. S. Green, M. Vicentini-Missini, and J. M. H. Levelt Sengers, *Phys. Rev. Lett.* **18**, 1113 (1967).

²⁰The other possibility, that it is an envelope of the characteristics (Ref. 14) is not possible in the present case.

²¹Robert R. Griffiths, *Phys. Rev.* **43**, 1958 (1965).

²²For a fuller discussion of this similarity see Ref. 12.

²³E. Kneller, *Ferromagnetism* (Springer-Verlag, Berlin, 1962), p. 147ff.

²⁴By contrast to the case of the liquid-gas transition for which it was necessary to introduce the parameter p_0 for the slope of the vapor-pressure curve at the critical point [see Eq. (24)], here we know the slope to be zero thus leading to the simpler form for v in Eqs. (38).

²⁵F. Bloch, *Z. Phys.* **61**, 206 (1930); **74**, 295 (1932). See also, F. J. Dyson, *Phys. Rev.* **102**, 1217 and 1230 (1956).

²⁶M. Fallot, *Ann. Phys. (Paris)* **6**, 305 (1936); P. Weiss and R. Forrer, *ibid.* **5**, 153 (1926).

²⁷For a recent review, see M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon, Oxford, 1977).

²⁸J. Hablützel, *Helv. Phys. Acta.* **8**, 498 (1935); **12**, 489 (1939).