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Critical Points in Multicomponent Systems

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The thermodynamics of critical points in multicomponent systems, more generally systems with more than two independent variables (including binary fluid mixtures, the helium λ transition, order-disorder transitions in alloys, and antiferromagnetism) are discussed from a unified geometrical point of view, in analogy with one-component (liquid-vapor and simple-ferromagnetic) systems. It is shown that, from a few simple postulates, the qualitative behavior near the critical point of quantities such as compressibilities, susceptibilities, and heat capacities, with different choices of the variables held fixed, can be easily predicted. A number of seemingly exceptional cases (such as critical azeotropy), which arise when critical or coexistence surfaces bear an "accidental" geometrical relationship with the thermodynamic coordinate axes, are explained in terms of the same postulates. The predicted results are compared with several theoretical models and experimental data for a variety of systems.

I. INTRODUCTION

Our understanding of phenomena near the critical points of pure fluids and simple ferromagnets has increased considerably during the last decade.[1] The widespread adoption and experimental measurement of nonclassical critical-point exponents, the observation of specific-heat "anomalies" the proposal and (to a degree) experimental vindication of scaling laws, the observation and at least tentative explanations of unexpected anomalies in transport coefficients, are among the more notable examples. It is natural to enquire how these advances may be extended to more complex physical systems in which a single critical point is replaced by a critical line or surface, etc. Examples include critical mixing and liquid-vapor critical points in multicomponent fluids; λ transitions in solids (including the Néel transition in antiferromagnets); and the normal-superfluid transition in liquid helium, including He^3-He^4 mixtures.

In this paper, we shall exhibit a very natural and consistent way to extend results for equilibrium thermodynamic properties near simple critical points to more complex cases. Our approach is geometrical in character and depends heavily on a proper choice of independent thermodynamic variables. In particular, we find it most convenient to use "intensive" rather than "extensive" thermodynamic variables (the notions are made more precise in Sec. II), in contrast to the work of Tisza,[2] which is (so far as we know) the most general and systematic work to date on phase transitions and critical points in multicomponent systems. Among the large number of topics which can properly be discussed under the heading of critical points in multicomponent systems, we shall focus our attention on the divergences of thermodynamic derivatives such as heat capacities, thermal-expansion coefficients, and susceptibilities near critical points (lines, surfaces, etc.), since these serve to illustrate rather well our geometrical point of view and are directly relevant to a large class of experimental measurements. Our primary concern is with qualitative rather than quantitative aspects of these divergences, and in this sense, the present paper can only be regarded as a very preliminary effort in understanding the phenomena of interest.

An outline of the paper is as follows. Some notational conventions and terminology, along with some very general comments on phase transitions in multicomponent systems are found in Sec. II. The reader who intends to read any part of Secs. III–V would be well advised to first examine Sec. II, since our terminology (for reasons there explained) is not standard, and abbreviations are then introduced which are employed throughout the remainder of the paper. Section III is a discussion of simple critical points in fluids and ferromagnets from a particular geometrical point of view which is easy to generalize to the multicomponent case considered in Sec. IV. Section IV contains, first, a series of postulates which determine the general character of divergence of thermodynamic derivatives near critical surfaces; second, a number of thermodynamic formulas useful for relating specific derivatives to the general postulates; and third, some comments on the relation between these postulates and rigorous bounds for thermodynamic quantities which we derived in an earlier paper.[3] Applications to a number of systems are given in Sec. V where the explicit consequences of our postulates are worked out for a number of systems – simple critical points, critical points in multicomponent fluids, antiferromagnets in a magnetic field, order-disorder in β brass, the λ transition in He^4 and He^3-He^4 mixtures – and comparison is made with experimental results. A summary of our conclusions together with remarks on where further work is needed constitutes Sec. VI.

II. THERMODYNAMIC VARIABLES AND PHASE EQUILIBRIUM

The customary division of thermodynamic variables into "intensive" and "extensive" is a very important one, though the reasons for this division are seldom clearly stated, and the terms themselves can be misleading. One knows, for example, that temperature T belongs in the first category and entropy in the second. But what about entropy per mole s, a quantity which remains unchanged upon the combination to two identical systems (and consequent doubling of extensive variables)? We shall use the term "density" for such a variable (a more precise definition of density is given below), which though in one sense intensive plays quite a different role in thermodynamic equations than temperature and pressure p, which we shall refer to as "fields."[4] Other examples of fields are the chemical potentials of different components in fluid mixtures, and magnetic and electric fields in paramagnets and dielectrics, respectively.

The fields (in contrast with densities) have the property that they take on identical values in two phases which are in thermodynamic equilibrium with each other. A system with n independent thermodynamic variables ($n=2$ for a pure fluid) may be characterized by $n+1$ fields $h_0, h_1, \ldots, h_n$ with one of these, say h_0, regarded as a function of the rest. The dependent field, for which we use the symbol ϕ, will be called the "potential." With this particular choice of independent and dependent variables, the n densities ρ_j are defined by

$$\rho_j = -\frac{\partial\phi}{\partial h_j} \quad . \tag{2.1}$$

For the thermodynamic systems we wish to consider, it is always possible to choose the potential as a concave function of the other fields, and the statement that ϕ is a concave function of all the h_j together comprehends all the requirements of thermodynamic stability.

The choice of variables is certainly not unique. For example, if we introduce $h_1', \ldots, h_n'$ through

$$h_j' = \sum_{k=1}^{n} T_{jk} h_k + t_j \quad , \tag{2.2}$$

with T_{jk} and t_j real constants, the determinant of T_{jk} nonzero, and a new potential

$$\Phi(h_1', \ldots, h_n') = h_0' = \phi(h_1, \ldots, h_n) + \sum_{k=1}^{n} \epsilon_k h_k \quad , \tag{2.3}$$

with the ϵ_k a set of real numbers, this new set of variables will serve equally well, and of course there will be a new set of densities

$$\rho_j' = -\frac{\partial\Phi}{\partial h_j'} \quad . \tag{2.4}$$

Alternatively, it is often possible to interchange dependent and independent variables. Thus, if $h_0 = \phi$ is a monotone increasing function of h_1 for all values of $h_2, \ldots, h_n$, then h_1 may be expressed as a function of $h_0, h_2, \ldots, h_n$, and the appropriate potential is

$$\chi(h_0, h_2, \ldots, h_n) = -h_1 \quad , \tag{2.5}$$

(the minus sign yields a concave, rather than convex, function of the independent arguments) with, of course, a corresponding set of densities defined in analogy with (2.1).

Finally, note that if one of the independent fields h_1, for example, takes on only positive values (for instance, $h_1 = T$), one can define another set of fields

$$g_1 = 1/h_1, \quad g_j = h_j/h_1 \qquad \text{for } j \geq 2 \quad , \tag{2.6}$$

and the corresponding potential

$$g_o = \Psi(g_1, \ldots, g_n) = g_1\phi(1/g_1, g_2/g_1, \ldots, g_n/g_1) \quad , \tag{2.7}$$

with, of course, still another set of densities. The concavity of Ψ as a function of the g_j in (2.7), as also of χ and Φ in (2.5) and (2.3), is guaranteed by the concavity of ϕ.

For example, in a two-component fluid mixture, we could let $h_o = -p$, $h_1 = \mu_1$ (chemical potential of first component), $h_2 = \mu_2$, $h_3 = T$. Then ρ_1 and ρ_2 as defined by (2.1) are the ordinary molar densities per unit volume of the two components and ρ_3 is the entropy per unit volume. An alternative choice of variables is used in Sec. V B.

If two phases a and b are in equilibrium, each field must have the same value in both phases:

$$h_j^{(a)} = h_j^{(b)}, \quad j = 0, 1, \ldots, n \tag{2.8}$$

and this, in general, defines in the space of the n-independent fields (the "field space") a hypersurface of dimension $n-1$. Provided at least one of the densities is a discontinuous function of the fields at this hypersurface – that is, possesses two different values upon approaching a point on the surface from the side of phase a or of phase b

– we shall say that hypersurface is a coexistence surface (CXS) or a first-order phase-transition surface.

Such a hypersurface may terminate in the field space in a variety of ways, some of which are the following.

(i) A field may reach the limit of its definition. Thus, if μ_j is the chemical potential of the jth component, $\mu_j \rightarrow -\infty$ yields a system with $(n-1)$-independent variables in which component j is absent. Quite frequently, the $(n-1)$-dimensional CXS terminates in an $(n-2)$-dimensional CXS in the new field space.

(ii) The CXS may intersect another CXS in a triple "line" (hypersurface of dimension $n-2$) at which three phases are in equilibrium.

(iii) The CXS may pass into another hypersurface which continues to separate two phases but which has the property that all densities are continuous at the hypersurface. One then has a "higher-order" phase transition; in many cases, such a surface turns out to be a critical surface [see (iv)] in a suitably augmented field space.

(iv) The CXS may terminate in a line (hypersurface of dimension $n-2$) of critical points, which we call the critical surface (CRS) with the property that discontinuities in densities across the CXS go continuously to zero upon approaching the CRS in such fashion that at the CRS there is no longer any distinction between the previously separated phases. The existence of a CRS implies that there is a path in the field space extending from one side of the CXS to the other, looping around the CRS, along which all thermodynamic variables are completely smooth functions exhibiting no phase transitions.

The geometrical notion basic to our analysis is the following. Suppose that we have a CXS terminating in a CRS; choose a particular point Y on the CRS and consider the two-dimensional plane passing through this point parallel to two of the field axes, for instance h_1 and h_2. In general, the intersection of the CXS with this plane will be a coexistence line and this line will terminate in the intersection of the CRS with this plane, that is, in a critical point. (The geometry is most easily visualized for $n=3$ when CXS and CRS are of dimension two and one, respectively). We then expect the critical behavior in this plane, given by ϕ as a function of h_1 and h_2 (the other $h_j, j \geqslant 3$ remaining fixed) to be very similar to that found at a simple fluid or ferromagnetic critical point, at least if one excludes the rather special case in which the plane is parallel or almost parallel to the CXS at the point Y. Nor do we expect this conclusion to be qualitatively altered if some new set of variables $h_1', h_2', \ldots, h_n'$, linear combinations of the original variables, is introduced. It is crucial, however, that the variables be fields; the same conclusion is almost certainly not correct when fields are replaced by densities as independent variables.

The above idea has been used by Fisher[5] in a particular case for discussing renormalization of critical-point exponents, and he gives some reasons for regarding it as not implausible. However, it must still be regarded as a postulate in need of further confirmation both by statistical calculations and experimental measurements.

The notion of a line or plane parallel to some (in general curved) surface at a particular point plays an important role in the development of Secs. III and IV. We shall frequently use the abbreviations PCXS and PCRS for "parallel to the coexistence (hyper) surface" and "parallel to the critical (hyper) surface," respectively, including the cases where the CXS (or CRS) is a one-dimensional line.

III. CRITICAL POINTS IN ONE-COMPONENT SYSTEMS

Before discussing multicomponent systems, we wish to review certain properties, by now fairly well established,[1] of the liquid-vapor phase transition in a pure fluid. Let the two independent fields be $-p$ and T. The coexistence curve terminating in a critical point is shown in Fig. 1.

The natural choice for dependent variable is the chemical potential μ, with the corresponding densities, volume per mole and entropy per mole, given by

$$v = \frac{\partial \mu}{\partial p}, \quad s = -\frac{\partial \mu}{\partial T} . \tag{3.1}$$

As is well known, both the isothermal compressibility

$$K_T = -v^{-1}\left(\frac{\partial v}{\partial p}\right)_T \tag{3.2}$$

and the heat capacity at constant pressure

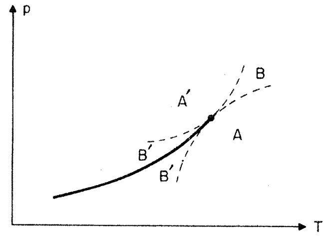

FIG. 1. Liquid-vapor coexistence curve (solid line) and critical point for a pure fluid. The dotted lines are an aid in visualizing how regions in the pT plane near the critical point are mapped into corresponding regions in vT plane (Fig. 2) – see text.

$$C_p = T\left(\frac{\partial s}{\partial T}\right)_p \tag{3.3}$$

diverge to infinity in the vicinity of the critical point. It is not often emphasized, however, that the form of this divergence depends on the route by which one approaches the critical point. In other words, if the approach is along the critical isochore with $T > T_c$ – to a first approximation, along a linear extension of the coexistance curve in the pT plane – the divergence is of the form

$$C_p \sim K_T \sim (T - T_c)^{-\gamma} \sim (p - p_c)^{-\gamma} \ , \tag{3.4}$$

with the index γ typically about 1.2–1.3 (1.0 in the van der Waals equation). A similar divergence occurs upon approaching the critical point for $T < T_c$ along either side of the coexistence curve. The corresponding index γ' is harder to estimate but is believed to be about the same as γ. We shall call these "γ divergences." On the other hand, along the critical isotherm, one has an ϵ divergence

$$K_T \sim |p - p_c|^{-\epsilon} \ , \tag{3.5}$$

with $\epsilon = 1 - 1/\delta$ in the customary notation,[1b] lying in the range 0.75–0.8 ($\frac{2}{3}$ for a van der Waals gas).

The divergences are clearly different in the two cases. With γ divergences, the path of approach is asymptotically parallel to the coexistence curve, whereas the ϵ divergence is along a path approaching the critical point at an angle to the coexistence curve.

Indeed, it seems to us that when considering divergences at the critical point, the only direction in the field space which is, so to speak, singled out by the nature of the phase transition itself is a direction parallel to the coexistence curve. In support of this we note that (i) in a space spanned by two variables p and T with different units there is no natural way to define orthogonality, and (ii) the stability requirement that μ be a concave function of p and T remains invariant under linear transformations of variables (including rotations) – that is, if μ is concave in the original variables, it is concave in the new variables, and vice versa.

Consequently, it is our expectation that both K_T and C_p will exhibit an ϵ divergence upon approaching the critical point along any line which is not asymptotically parallel to the coexistence curve; e. g., along the critical isobar one, would expect

$$C_p \sim K_T \sim |T - T_c|^{-\epsilon} \ . \tag{3.6}$$

There is, of course, no unique way of specifying "distance" from the critical point in some general direction in the pT plane. Either $|p - p_c|$ or $|T - T_c|$ may be used, or $[(T-T_c)^2 + (p - p_c)^2]^{1/2}$ if some dimensionless units are adopted for T and p. Of course, on a curve asymptotically parallel to the critical isotherm one should, clearly, use $|p - p_c|$ not $|T - T_c|$. It is possible that the index ϵ will depend on whether one approaches the critical point from the side A or A′ shown in Fig. 1. At present, there is no definite experimental evidence for such a difference, but we do not wish to rule out the possibility.

To emphasize the importance of the notion of "parallel to the coexistence curve" in Fig. 1, let us consider the situation when p is replaced by v, its conjugate density. The situation is shown in Fig. 2. The coexistence curve has two branches corresponding to two values of v (liquid and vapor) which may be in equilibrium at the same temperature. In the vT plane, we find the following result, which, though obvious after some reflection on the matter, has often been overlooked. The regions marked A and A′ in Fig. 1, which include (asymptotically) all approaches to the critical point making an angle with the coexistence curve, reduce in Fig. 2 to narrow wedges surrounding the critical isotherm, while B and B′ in Fig. 2, which seemingly include almost all approaches to the critical point in the vT plane, are in turn but narrow wedges in the pT plane of Fig. 1. This is a purely geometrical effect associated with Legendre transformations of variables and is of course related to the large compressibility near the critical point which means that small changes in p lead to large changes in v. It shows why "asymptotically parallel" to the coexistence curve in the pT plane is rather easily achieved in practice by fixing v or making it a slowly varying function of temperature. (Analogous results would be obtained, of course, by fixing the entropy.)

One cannot make a completely precise definition of asymptotically parallel without a more detailed knowledge of the equation of state. In the case of a scaling-law equation of state,[6] the condition is that deviations from a line drawn through the critical point parallel to the coexistence curve at this point

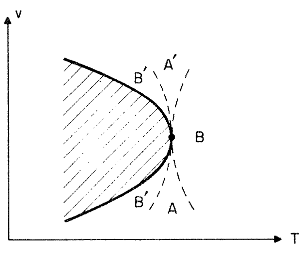

FIG. 2. Liquid-vapor coexistence curve (solid line) and critical point for a pure fluid. The two-phase region is crosshatched, and the dotted lines correspond to those in Fig. 1.

must be smaller than a constant times $|T - T_c|^{\Delta}$, with $\Delta = \beta\delta$, in the customary notation[1b] between 1.3 and 1.7 (1.5 for the van der Waals equation).

In addition to C_p and K_T, quantities which we shall say are *strongly divergent* at the critical point, there are other quantities – the best known is the heat capacity at constant volume C_v – which in the classical van der Waals theory remain finite at the critical point, but according to the more recent experimental and theoretical studies[1] may be expected to diverge, though in a less pronounced fashion than K_T. We shall refer to these as *weak divergences*. Along a path asymptotically parallel to the coexistence curve, the divergence is as $(T-T_c)^{-\alpha}$ or $(T_c-T)^{-\alpha'}$ (for $T > T_c$, $T < T_c$, respectively) with α, typically, between 0 and 0.2; we shall call these α divergences. A logarithmic divergence corresponds to $\alpha = 0$. On a curve making an angle with the coexistence curve, the divergence is as $|T-T_c|^{-\xi}$ or $|p-p_c|^{-\xi}$, thus, a ξ divergence. There is no customary notation for this last index, but in the case of a scaling-law equation of state, it has the value $\alpha/\beta\delta$.

Both strong and weak divergences are included in the determinant $D(p, T)$ of the matrix

$$\begin{bmatrix} \dfrac{-\partial^2\mu}{\partial p^2} & \dfrac{-\partial^2\mu}{\partial p \partial T} \\ \dfrac{-\partial^2\mu}{\partial p \partial T} & \dfrac{-\partial^2\mu}{\partial T^2} \end{bmatrix} \tag{3.7}$$

of second derivatives of μ. Since we have

$$D(p, T) = vK_T C_v/T = vK_s C_p/T \tag{3.8}$$

(K_s is the adiabatic compressibility), we may say that $D(p, T)$ diverges "strongly times weakly" with the precise exponent ($\alpha + \gamma$ or $\xi + \epsilon$) depending on the path along which the critical point is approached.

What is the geometrical distinction between quantities which diverge weakly and those which diverge strongly at the critical point? We note that K_T and C_p are essentially second derivatives of μ in directions parallel to the p axis and T axis, respectively, in the pT plane, directions not parallel to the coexistence curve at the critical point. It would, therefore, not be surprising to find that the second derivative of μ in a direction parallel to the coexistence curve diverges weakly at the critical point. Consider $d^2\mu/dT^2$ along a straight line of slope dp/dT in the pT plane. The thermodynamic identity

$$-\frac{d^2\mu}{dT^2} = \frac{C_v}{T} + vK_T\left[\frac{dp}{dT} - \left(\frac{\partial p}{\partial T}\right)_v\right]^2 , \tag{3.9}$$

which is a special case of (4.10) below, can be analyzed in the context of a scaling-law equation of state to show that if dp/dT is the slope of the coexistence curve at the critical point, the second term on the right-hand side is no more than weakly divergent, so that $-d^2\mu/dT^2$ diverges weakly, whereas, for any other value of dp/dT, the second term is eventually proportional to K_T, resulting in a strong divergence.

Another point of view comes from noting that, with a suitable choice of dimensionless units for the p and T axes, $D(p, T)$ is simply the product of the eigenvalues of the matrix (3.7). On the basis of the experimental behavior of C_v and K_T and the fact that $(\partial p/\partial T)_v$ and $(\partial p/\partial T)_s$ tend to a constant at the critical point, it is easy to show that one of these eigenvalues diverges weakly and one strongly upon approaching the critical point, and the corresponding eigenvectors become, respectively, parallel and perpendicular to the coexistence curve.

Along the coexistence curve itself, the densities v and s are discontinuous from one side of the curve to the other. The difference in specific volumes Δv between vapor and liquid approaches zero as $(T_c-T)^{\beta}$, and the discontinuity Δs vanishes with the same power law (from the Clausius-Clapeyron equation and noting that the slope of the coexistence curve dp/dT is finite at the critical point). Typically, β lies between 0.33 and 0.4 ($\frac{1}{2}$) in the van der Waals equation). Note that both v and s are first derivatives of μ in a direction not parallel to the coexistence curve at the critical point, and that either $p_c - p$ or $T_c - T$ will serve as a suitable measure of distance from the critical point along the coexistence curve.

Whereas the geometrical characterization of thermodynamics at the critical point is largely independent of coordinate axes, the prediction for the behavior of specific derivatives may be altered when one of the coordinate axes is parallel to the coexistence curve at the critical point. A well-known example is the Ising ferromagnet[7] with magnetic field H serving, together with T, as one of the independent fields, and a potential ϕ such that entropy S and magnetization M are given by

$$S = \left(\frac{\partial\phi}{\partial T}\right)_H , \qquad M = \left(\frac{\partial\phi}{\partial H}\right)_T . \tag{3.10}$$

The coexistence curve is a portion of, and hence parallel to, the T axis. Consequently, one expects C_H, involving a second derivative of ϕ parallel to the coexistence curve, to diverge weakly at the critical point (in contrast to C_p for a fluid), while the susceptibility

$$\chi_T = \left(\frac{\partial M}{\partial H}\right)_T , \tag{3.11}$$

involving a second derivative of ϕ at an angle perpendicular to the coexistence curve, should diverge strongly (in analogy with K_T). The determinant of the matrix of second derivatives $D(H, T)$, since it is invariant under rotations and other unimodular transformations, is unaffected by the fact that T axis and coexistence curve are parallel, so it should be strongly times weakly divergent. Since we have

$$D(H, T) = \chi_T C_M / T = \chi_S C_H / T \quad , \tag{3.12}$$

we expect C_M to be weakly and χ_S to be strongly divergent. All these expectations are confirmed, at least to a degree, by calculations, and certainly hold for a scaling equation of state which seems, at present, to represent the thermodynamic properties of Ising ferromagnets at least moderately well.[8] In addition, for $H = 0$ and $T > T_c$, we have

$$C_H = C_M \, , \quad \chi_S = \chi_T \quad , \tag{3.13}$$

which shows that on this line in particular the two heat capacities must diverge in identical fashion, and likewise, the two susceptibilities.

Another effect of the special orientation of the coordinate axes is that the difference in entropy (first derivative of ϕ parallel to the coexistence curve) across the coexistence curve is zero, while the discontinuity in M vanishes as $(T_c - T)^\beta$. One cannot, of course, use H to measure distance from the critical point along the coexistence curve.

IV. CRITICAL POINTS IN MULTICOMPONENT SYSTEMS

A. General Description

Consider a thermodynamic system described by $n+1$ fields $h_o, h_1, \ldots, h_n$, with the potential $\phi = h_o$, a concave function of the n-independent fields $h_1, h_2, \ldots, h_n$. Suppose there is a CXS, a hypersurface of dimension $n-1$, terminating in CRS of dimension $n-2$. When A is a subset of $h_1, h_2, \ldots, h_n$ containing m elements, we define $D(A)$ as the determinant of the $m \times m$ matrix

$$\frac{-\partial^2 \phi}{\partial h_k \, \partial h_l} \, , \tag{4.1}$$

with the h's drawn from A and assigned some arbitrary order. Concavity of ϕ implies that none of the $D(A)$ are ever negative. In particular, if A is the single element $\{h_i\}$, then

$$D(h_i) = \frac{-\partial^2 \phi}{\partial h_i^2} \tag{4.2}$$

is minus the second derivative of ϕ along this coordinate axis. In analogy with the single-component case discussed in Sec. III, it seems plausible to suggest that in general $D(h_i)$ diverges strongly upon approaching a point on the CRS, unless h_i is parallel to the CXS (PCXS) at the point in question. In that event, $D(h_i)$ should diverge weakly. However, a third possibility remains which is not present in single-component systems: that h_i is parallel to the CRS (PCRS) in addition to PCXS at the point of interest. Various model calculations suggest that in this case $D(h_i)$ will be finite at the CRS.

We next consider what to expect when A contains a number of elements – say, $h_1, h_2, \ldots, h_m$. The determinant is invariant under unimodular linear transformations of the $h_1, h_2, \ldots, h_m$, which shows that it is not a function of the direction of any particular h_j, but rather of the m-dimensional linear manifold $\mathcal{A}$ of vectors which are linear combinations of the members of A. From considerations of the dimensionality of the CXS and CRS it is apparent that at a given point on the CRS we can in general choose a basis $h_1', h_2', \ldots, h_m'$ for $\mathcal{A}$ with the property that h_1' is not PCXS, h_2' is PCXS but not PCRS, and h_j' for $3 \leq j \leq m$ are all PCRS. This suggests (we are exhibiting an intuitive geometrical idea behind our postulate, not constructing a proof) that in the general case, if A contains at least two members, $D(A)$ will be strongly times weakly divergent when approaching the CRS. Exceptions will occur in cases where, for example, $\mathcal{A}$ lacks a vector PCXS. The various cases are catalogued in the following postulates:

(a) If $\mathcal{A}$ contains a vector not PCXS, and also a vector PCXS but not PCRS, $D(A)$ is strongly times weakly divergent.

(b) If $\mathcal{A}$ contains a vector not PCXS, but no vector which is both PCXS and PCRS, than $D(A)$ is strongly divergent.

(c) If $\mathcal{A}$ contains a vector not PCRS, but all vectors in α are PCSX, then $D(A)$ diverges weakly.

(d) If all vectors in $\mathcal{A}$ are PCRS, then $D(A)$ remains finite.

These four postulates may be summarized in terms of the answers to the two questions: (i) Does $\mathcal{A}$ possess a vector not PCXS? (ii) Does $\mathcal{A}$ possess a vector PCXS but not PCRS? The character of the divergence in the four possible cases is given by Table I.

In addition, we make the following two postulates:

(e) The character of the divergence or nondivergence of $D(A)/D(B)$, where A, B are two subsets of $h_1, \ldots, h_n$, is determined by the appropriate divi-

TABLE I. Character of the divergence in four cases.

Question	(ii)[a] yes		(ii)[d] no
(i)[b] yes	strong × weak	1	strong
(i)[b] no	weak		finite

[a] Refers to Question ii in text.

[b] Refers to Question i in text.

sion; if $D(A)$ is strongly times weakly divergent and $D(B)$ is weakly divergent, then $D(A)/D(B)$ is strongly divergent, whereas, if $D(B)$ is strongly divergent, then $D(A)/D(B)$ is weakly divergent. If $D(A)$ and $D(B)$ have the same degree of divergence, then $D(A)/D(B)$ approaches a constant. Other cases are determined in analogous fashion.

(f) Since the postulates (a)–(e) are geometrical in character, they should be equally valid under any of the transformations of fields mentioned in Sec. II in connection with Eq. (2.2) and the discussion which follows it. In particular, they should apply when A is a subset of $h_1', \ldots, h_n'$, where h' coordinates are obtained from the h coordinates by a nonsingular linear transformation. This means that $D(h_i')$ for any h_i' PCRS should be finite at the CRS and for h_i', PCXS but not PCRS, should be weakly divergent, etc. Therefore, we shall regard postulates (a)–(e) as applying equally to the $h_1', \ldots, h_n'$ as well as to the original $h_1, \ldots, h_n$.

An alternative point of view closely related to the above is to consider eigenvalues and eigenvectors of the symmetric matrix (4.1). In the general case, we expect that upon approaching some point on the CRS, $m-2$ of the eigenvectors become PCRS and the corresponding eigenvalues are finite, while one eigenvector becomes PCXS while not PCRS with weakly diverging eigenvalue, and one eigenvector not PCXS is associated with a strongly divergent eigenvalue. Although there is a close intuitive connection between the properties of eigenvectors and eigenvalues just mentioned, the divergences of second derivatives of ϕ taken in various directions, and postulates (a)–(d), the formal relationship involves certain mathematical subtleties we have not investigated in detail. The postulates as stated seem the most convenient for predicting the behavior of specific thermodynamic functions.

We next wish to make the terms strong and weak divergence somewhat more explicit. Consider the variation of $D(A)$ along a line L passing through a point $Y=\{h_1^0, h_2^0, \ldots, h_n^0\}$ on the CRS. Let y denote some measure of distance from Y along L – for example, $|h_j-h_j^0|$ provided the line is not asymptotically perpendicular to the h_j axis near Y, or perhaps $[\sum_j(h_j-h_j^0)^2]^{1/2}$. Whether $D(A)$ has a strong or weak divergence depends on the relationship of the CRS or CXS to the manifold $\mathfrak{A}$ at Y, whereas the orientation of L determines whether a strong divergence, for example, is of the γ or ϵ type. If L is not asymptotically PCXS, the strong divergence is of the form $y^{-\epsilon}$, and the weak divergence is of the form $y^{-\zeta}$, whereas if L is asymptotically PCXS but not PCRS, the strong divergence is of the form $y^{-\gamma}$, and the weak divergence is of the form $y^{-\alpha}$. We exclude the case where L is asymptotically PCRS, since the form of divergence will depend on the rate of approach to the CRS. Given this rate of approach it is, of course, possible (with reasonable assumptions) to calculate the form of divergence. A particular case has been considered by Fisher,[5] who has shown that in some cases holding an appropriate density fixed leads to curves asymptotically PCRS which "renormalizes" certain exponents.

Just as in the one-component case, various densities will be discontinuous across the CXS in multicomponent systems, and the discontinuities for different ρ_j are related by analogs of the Clausius-Clapeyron equation. When one of the h_j axes is asymptotically PCXS near the CRS, the corresponding ρ_j will have exceptional behavior; entropy for the ferromagnet, (Sec. III) and composition for an azeotrope (Sec. V) are examples. If we exclude the case just mentioned, $\Delta\rho_j$ along a curve L lying in the CXS will go to zero as y^β, where y is a suitable measure of distance from the CRS (see discussion in previous paragraph), provided, of course, that L is not asymptotically PCRS. A curve asymptotically PCRS requires special discussion. (Fisher's renormalized β is such a case.)

B. Thermodynamic Relations

We now investigate the implications of our postulates (a)–(f) for certain thermodynamic derivatives near critical points. For convenience, the following notation is used for partial derivatives. The independent variables are $h_1, h_2, \ldots, h_n$ except that h_k is replaced by its conjugate density ρ_k, if ρ_k appears as a subscript to, or in the denominator of, the derivative. For example,

$$\left(\frac{\partial\rho_1}{\partial h_1}\right)_{\rho_3\rho_4}$$

means a derivative with $h_2, \rho_3, \rho_4, h_5, h_6, \ldots, h_n$ held constant.

The derivative of a density ρ_j with respect to its conjugate field h_j, when the other fields are held fixed, is

$$\frac{\partial\rho_j}{\partial h_j}=-\frac{\partial^2\phi}{\partial h_j^2}=D(h_j)\ , \tag{4.3}$$

whereas, if certain other densities are held fixed, we obtain, assuming j, k, l all distinct,

$$\left(\frac{\partial\rho_k}{\partial h_k}\right)_{\rho_j}=\frac{\partial(\rho_k,\rho_j)}{\partial(h_k,\rho_j)}=\frac{\partial(\rho_k,\rho_j)}{\partial(h_k,h_j)}\bigg/\frac{\partial(h_k,\rho_j)}{\partial(h_k,h_j)}$$

$$=\frac{D(h_k,h_j)}{D(h_j)}\ , \tag{4.4}$$

$$\left(\frac{\partial\rho_l}{\partial h_l}\right)_{\rho_j\rho_k}=\frac{\partial(\rho_l,\rho_k,\rho_j)}{\partial(h_l,\rho_k,\rho_j)}=\frac{\partial(\rho_l,\rho_k,\rho_j)}{\partial(h_l,h_k,h_j)}\bigg/\frac{\partial(h_l,\rho_k,\rho_j)}{\partial(h_l,h_k,h_j)}$$

$$=\frac{D(h_l, h_k, h_j)}{D(h_k, h_j)} \quad , \tag{4.5}$$

by straightforward manipulation of Jacobians (see, e.g., Callen[9] or Tisza[10]), and analogous formulas, if additional densities are held fixed. Postulates (a)–(e) determine the behavior of the right-hand terms in (4.3)–(4.5). For example, in the general case where the coordinate axes $h_1\, h_2, \ldots, h_n$ bear no special relation to the CXS or CRS, $D(h_j)$ diverges strongly upon approaching the CRS by postulate (b), while $D(h_k, h_j)$ and $D(h_l, h_k, h_j)$ diverge strongly times weakly by postulate (a). Consequently, $\partial\rho_j/\partial h_j$ diverges strongly, whereas, by employing postulate (e), $(\partial\rho_k/\partial h_k)_{\rho_j}$ diverges weakly, and $(\partial\rho_l/\partial h_l)_{\rho_j\rho_k}$ approaches a constant. The modification of these results when the $h_1, \ldots, h_n$ bear some special relation to the CXS or CRS, is also easily determined by combining (4.3)–(4.5) with postulates (a)–(e). Specific examples are considered in Sec. V.

Information about the divergence of the off-diagonal derivative $j \neq k$

$$\frac{\partial\rho_j}{\partial h_k} = -\frac{\partial^2\phi}{\partial h_k\, \partial h_j} = \frac{\partial\rho_k}{\partial h_j} \tag{4.6}$$

may be obtained by considering the determinant

$$D(h_j, h_k) = D(h_j)\, D(h_k) - \left(\frac{\partial\rho_j}{\partial h_k}\right)^2 \quad . \tag{4.7}$$

If both $D(h_j)$ and $D(h_k)$ diverge strongly, the same must be true of $|(\partial\rho_j/\partial h_k)|$, since $D(h_j, h_k)$ can diverge at most strongly times weakly. However, if one of the pair $D(h_j)$, $D(h_k)$ diverges strongly and the other weakly, the strongly times weakly divergence of $D(h_j, h_k)$ implies that $(\partial\rho_j/\partial h_k)^2$ is at most strongly times weakly divergent. There are several other possibilities and we shall not attempt a complete catalog.

It is worth noting that similar reasoning can be employed with one or more densities held fixed. For example, with j, k, l all distinct, the equation

$$\left(\frac{\partial\rho_j}{\partial h_j}\right)_{\rho_l} \left(\frac{\partial\rho_k}{\partial h_k}\right)_{\rho_l} - \left(\frac{\partial\rho_j}{\partial h_k}\right)_{\rho_l}^2 = \begin{vmatrix} \left(\dfrac{\partial\rho_j}{\partial h_j}\right)_{\rho_l} & \left(\dfrac{\partial\rho_j}{\partial h_k}\right)_{\rho_l} \\ \left(\dfrac{\partial\rho_k}{\partial h_j}\right)_{\rho_l} & \left(\dfrac{\partial\rho_k}{\partial h_k}\right)_{\rho_l} \end{vmatrix}$$

$$= \frac{\partial(\rho_j, \rho_k, \rho_l)}{\partial(h_j, h_k, \rho_l)} = \frac{\partial(\rho_j, \rho_k, \rho_l)}{\partial(h_j, h_k, h_l)} \bigg/ \frac{\partial(h_j, h_k, \rho_l)}{\partial(h_j, h_k, h_l)}$$

$$= \frac{D(h_j, h_k, h_l)}{D(h_l)} \tag{4.8}$$

combined with (4.4) permits us to infer some properties of $(\partial\rho_j/\partial h_k)_{\rho_l}$ from a knowledge of the behavior of the various D's.

The above predictions for off-diagonal derivatives can be improved in certain cases, and the sign of divergence (to plus or minus infinity) and rate of divergence relative to certain diagonal derivatives can be expressed in terms of geometrical properties of the CXS and CRS. For this purpose, and also because of their intrinsic interest, we shall next consider derivatives of the type $(\partial h_2/\partial h_1)_{\rho_2}$ and $(\partial h_2/\partial h_1)_{\rho_2\rho_3}$. Their behavior upon approaching the CRS is determined by the two formulas (4.10) and (4.11), obtained as follows.

The second derivative of ϕ, with respect to h_1 along a direction in $h_1, \cdots, h_n$ space specified by the vector $\vec{V}$ with components 1, V_2, $V_3, \ldots, V_n$, is given by the quadratic form

$$-\frac{d^2\phi}{dh_1^2} = \sum_{i=1}^{n} \sum_{j=1}^{n} - \frac{\partial^2\phi}{\partial h_i\, \partial h_j} \frac{dh_1}{dh_1} \frac{dh_1}{dh_1} \quad , \tag{4.9}$$

where $dh_j/dh_1 = V_j$ is the derivative of h_j with respect to h_1 in the direction specified by $\vec{V}$ (and $dh_1/dh_1 = 1$).

This quadratic form can be brought into diagonal form by a unimodular transformation of the sort proposed by Tisza.[10] When $\vec{V}$ lies in the $h_1 h_2$ plane ($V_j = 0$ for $j \geqslant 3$), the result is

$$-\frac{d^2\phi}{dh_1^2} = \left(\frac{\partial\rho_1}{\partial h_1}\right)_{\rho_2} + \frac{\partial\rho_2}{\partial h_2}\left[\frac{dh_2}{dh_1} - \left(\frac{\partial h_2}{\partial h_1}\right)_{\rho_2}\right]^2$$

$$= \frac{D(h_1, h_2)}{D(h_2)} + D(h_2)\left[\frac{dh_2}{dh_1} - \left(\frac{\partial h_2}{\partial h_1}\right)_{\rho_2}\right]^2 \quad , \tag{4.10}$$

while for $\vec{V}$ lying in the $h_1\, h_2\, h_3$ manifold ($V_j = 0$ for $j \geqslant 4$), the result is

$$-\frac{d^2\phi}{dh_1^2} = \left(\frac{\partial\rho_1}{\partial h_1}\right)_{\rho_2\rho_3} + \left(\frac{\partial\rho_2}{\partial h_2}\right)_{\rho_3}\left[\frac{dh_2}{dh_1} - \left(\frac{\partial h_2}{\partial h_1}\right)_{\rho_2\rho_3}\right]^2$$

$$+ \frac{\partial\rho_3}{\partial h_3}\left[\frac{dh_3}{dh_1} - \left(\frac{\partial h_3}{\partial h_1}\right)_{\rho_3} - \left(\frac{\partial h_3}{\partial h_2}\right)_{\rho_3} \frac{dh_2}{dh_1}\right]^2$$

$$= \frac{D(h_1, h_2, h_3)}{D(h_2, h_3)} + \frac{D(h_2, h_3)}{D(h_3)}\left[\frac{dh_2}{dh_1} - \left(\frac{\partial h_2}{\partial h_1}\right)_{\rho_2\rho_3}\right]^2$$

$$+ D(h_3)\left[\frac{dh_3}{dh_1} - \left(\frac{\partial h_3}{\partial h_1}\right)_{\rho_3} - \left(\frac{\partial h_3}{\partial h_2}\right)_{\rho_2} \frac{dh_2}{dh_1}\right]^2 \quad . \tag{4.11}$$

Note that in both (4.10) and (4.11), each term on the right-hand side is non-negative. Details of this diagonalization are found in the Appendix.

The evaluation of $(\partial h_2/\partial h_1)_{\rho_2}$ in the general case proceeds as follows. Consider a plane of constant $h_3, \ldots, h_n$, which intersects the CXS in a curve X, and the CRS at a point r at which $D(h_2)$ diverges strongly, i.e., where the h_2 axis is not PCXS (and consequently not parallel to X). Let the vector $\vec{V}$ which enters the quadratic form (4.9) be parallel to X at r. By postulates (c) and (f), the left-hand side of (4.10) diverges weakly near r, and thus both positive terms on the right-hand side diverge at most weakly. The strong divergence of $D(h_2)$ means that

$$\left(\frac{\partial h_2}{\partial h_1}\right)_{\rho_3} \to \frac{dh_2}{dh_1}\bigg|_{\mathrm{CXS},\, h_3, \ldots, h_n} \tag{4.12}$$

upon approaching r, where note that by construction, the right-hand side is the derivative dh_2/dh_1 along X at r, that is, along the intersection of the CXS with the plane of constant $h_3, \ldots, h_n$. A system with only two independent fields in which the coexistence curve is not parallel to the h_2 axis at the critical point (see applications in Sec. V A) is contained in the above argument as a special case.

The evaluation of $(\partial h_2/\partial h_1)_{\rho_2\rho_3}$ requires (4.11). Choose a three-dimensional hyperplane of constant $h_4, \ldots, h_n$ which intersects the CXS and CRS in a coexistence surface $\bar{X}$ and a critical line R. Choose on R a point r at which the conditions of postulate (a) imply that $D(h_2, h_3)$ diverges strongly-times-weakly (consequently R is not parallel to the h_2h_3 plane at r). Let $\vec{V}$ be parallel to R at r. By postulates (d) and (f), the left-hand side of (4.11) does not diverge near r, and hence the same must be true of all three positive terms on the right-hand side. Since $D(h_2, h_3)/D(h_3)$ diverges (at least weakly), we conclude that, upon approaching the point r,

$$\left(\frac{\partial h_2}{\partial h_1}\right)_{\rho_2\rho_3} \to \frac{dh_2}{dh_1}\bigg|_{\mathrm{CRS},\, h_4, \ldots, h_n} \tag{4.13a}$$

and, upon interchanging subscripts 2 and 3 in the above argument,

$$\left(\frac{\partial h_3}{\partial h_1}\right)_{\rho_2\rho_3} \to \frac{dh_3}{dh_1}\bigg|_{\mathrm{CRS},\, h_4 \cdots h_n} \tag{4.13b}$$

By construction, the right-hand terms in Eqs. (4.13) are derivatives along the critical line R, the intersection of the CRS with the hyperplane of constant $h_4, \ldots, h_n$. A system with only three independent fields in which the $h_2\, h_3$ plane is parallel to neither coexistence surface nor critical line at r (applications in Sec. V B) is contained in the above argument as a special case.

Equations (4.12) and (4.13) immediately provide information about derivatives of densities with respect to other densities through the Maxwell relations

$$-\left(\frac{\partial \rho_1}{\partial \rho_2}\right)_{h_1 h_3 \cdots} = \left(\frac{\partial h_2}{\partial h_1}\right)_{\rho_2 h_3 \cdots} \to \frac{dh_2}{dh_1}\bigg|_{\mathrm{CXS},\, h_3 \cdots},$$

$$-\left(\frac{\partial \rho_1}{\partial \rho_2}\right)_{h_1 \rho_3 h_4 \cdots} = \left(\frac{\partial h_2}{\partial h_1}\right)_{\rho_2 \rho_3 h_4 \cdots} \to \frac{dh_2}{dh_1}\bigg|_{\mathrm{CRS},\, h_4 \cdots}, \tag{4.14}$$

etc.

They are also useful in determining the limiting ratio diagonal and off-diagonal derivatives. For example, we have

$$\left(\frac{\partial \rho_2}{\partial h_1}\right) \Big/ \left(\frac{\partial \rho_2}{\partial h_2}\right) = -\left(\frac{\partial h_2}{\partial \rho_1}\right)_{\rho_2} \Big/ \left(\frac{\partial h_1}{\partial \rho_1}\right)_{\rho_2}$$

$$= -\left(\frac{\partial h_2}{\partial h_1}\right)_{\rho_2} \to -\frac{dh_2}{dh_1}\bigg|_{\mathrm{CXS}\, h_3 \cdots h_n}, \tag{4.15}$$

provided the conditions used in deriving (4.12) are satisfied, and

$$\left(\frac{\partial \rho_2}{\partial h_1}\right)_{\rho_3} \Big/ \left(\frac{\partial \rho_2}{\partial h_2}\right)_{\rho_3} = -\left(\frac{\partial h_2}{\partial \rho_1}\right)_{\rho_2\rho_3} \Big/ \left(\frac{\partial h_1}{\partial \rho_1}\right)_{\rho_2\rho_3}$$

$$= -\left(\frac{\partial h_2}{\partial h_1}\right)_{\rho_2\rho_3} \to -\frac{dh_2}{dh_1}\bigg|_{\mathrm{CRS}\, h_4 \cdots h_n}, \tag{4.16}$$

when conditions in the derivation of (4.13) are satisfied. Thus, in the general case when the CXS and CRS bear no special relationship to the coordinate axes, we expect that $\partial\rho_2/\partial h_1$ will diverge strongly with its sign given by (4.15); that $(\partial h_2/\partial\rho_1)_{\rho_2}$ will go to zero weakly {that is, that $[(\partial h_2/\partial\rho_1)_{\rho_2}]^{-1}$ will diverge weakly}, that $(\partial\rho_2/\partial h_1)_{\rho_3}$ will diverge weakly, and that $(\partial h_2/\partial\rho_1)_{\rho_2\rho_3}$ will remain finite and nonzero approaching the CRS.

From (4.15) and (4.16), we may obtain ratios of certain diagonal derivatives. Thus, the ratio

$$\left(\frac{\partial \rho_1}{\partial h_1}\right)_{\rho_2} \Big/ \left(\frac{\partial \rho_2}{\partial h_2}\right)_{\rho_1} = \frac{D(h_1)}{D(h_2)} = \left(\frac{\partial \rho_1}{\partial h_1}\right) \Big/ \left(\frac{\partial \rho_2}{\partial h_2}\right)$$

$$= \left(\frac{\partial \rho_1}{\partial h_2}\right)\left(\frac{\partial h_2}{\partial h_1}\right)_{\rho_2} \Big/ \left(\frac{\partial \rho_2}{\partial h_1}\right)\left(\frac{\partial h_1}{\partial h_2}\right)_{\rho_1}$$

$$= \left(\frac{\partial h_2}{\partial h_1}\right)_{\rho_2} \Big/ \left(\frac{\partial h_1}{\partial h_2}\right)_{\rho_1} \to \left(\frac{dh_2}{dh_1}\right)^2 \Bigg|_{\mathrm{CXS},\, h_3 \ldots h_n} , \qquad (4.17)$$

tends to the square of the slope of the CXS at the CRS. The first equality is a consequence of (4.4) and the final limit invokes (4.12), both in the form given there and with h_1 and h_2 interchanged. The limiting ratio $D(h_1)/D(h_2)$ is correctly given by (4.17) whenever $D(h_2)$ diverges strongly. The derivation as given requires strong divergence of $D(h_1)$, but should this not diverge strongly, the derivative dh_2/dh_1 is zero by our postulates, and the ratio $D(h_1)/D(h_2)$ obviously approaches the same limit.

By an entirely analogous argument utilizing (4.16), we find

$$\frac{D(h_1, h_3)}{D(h_2, h_3)} = \left(\frac{\partial \rho_1}{\partial h_1}\right)_{\rho_3} \Big/ \left(\frac{\partial \rho_2}{\partial h_2}\right)_{\rho_3}$$

$$= \left(\frac{\partial \rho_1}{\partial h_1}\right)_{\rho_2 \rho_3} \Big/ \left(\frac{\partial \rho_2}{\partial h_2}\right)_{\rho_1 \rho_3} \to \left(\frac{dh_2}{dh_1}\right)^2 \Bigg|_{\mathrm{CRS},\, h_4 \ldots h_n} , \qquad (4.18)$$

provided that $D(h_2, h_3)$ diverges strongly times weakly.

C. Relation to Rigorous Bounds

Consider the intersection of the CRS with a hyperplane obtained by fixing the values of all the independent fields except for h_j, h_k, and h_l. This intersection is, in general, a curve along which the following inequality, derived in an earlier paper,[3] will be valid:

$$\frac{D(h_j, h_k, h_l)}{D(h_k, h_l)} = \left(\frac{\partial \rho_j}{\partial h_j}\right)_{\rho_k \rho_l}$$

$$\leqslant \frac{d\rho_j}{dh_j} + \frac{d\rho_k}{dh_j}\frac{dh_k}{dh_j} + \frac{d\rho_l}{dh_j}\frac{dh_l}{dh_j} . \qquad (4.19)$$

The total derivatives on the right-hand side are taken along the curve in question. In the general case where CXS and CRS bear no special relation to the coordinate axes, these total derivatives should be finite (almost everywhere), while postulates (a) and (e) predict that the left-hand side will be finite.

The difference between right- and left-hand sides of (4.19) is

$$\left(\frac{\partial h_k}{\partial \rho_k}\right)_{\rho_l} \left(\frac{d\rho_k}{dh_j}\right)^2 + \left(\frac{\partial h_l}{\partial \rho_l}\right)_{\rho_k} \left(\frac{d\rho_l}{dh_j}\right)^2$$

$$+ \left[\left(\frac{\partial h_l}{\partial \rho_k}\right)_{\rho_l} + \left(\frac{\partial h_k}{\partial \rho_l}\right)_{\rho_k}\right] \frac{d\rho_k}{dh_j}\frac{d\rho_l}{dh_j} . \qquad (4.20)$$

If the total derivatives are finite, postulates (a)–(e), together with Eqs. (4.4) and (4.15), imply that this quantity will (again in the general case) vanish at the CRS. Consequently, the bound (4.19) is, in general, the best possible at the CRS, with left- and right-hand sides equal. Note that this equality with two densities held fixed will not, in general, hold true for the corresponding inequalities when three or more densities are held fixed, even at the CRS.

Another application of bounds of the form (4.19) lends additional support to our postulates. Tisza[10] has pointed out that the determinant $D(h_1 \cdots h_n)$ may be written

$$D(h_1 \cdots h_n) = \frac{D(h_1 \cdots h_n)}{D(h_1 \cdots h_{n-1})}\frac{D(h_1 \cdots h_{n-1})}{D(h_1 \cdots h_{n-2})} \cdots$$

$$\times [D(h_1, h_2)/D(h_1)] D(h_1) , \qquad (4.21)$$

where

$$\frac{D(h_1 \cdots h_j)}{D(h_1 \cdots h_{j-1})} = \left(\frac{\partial \rho_j}{\partial h_j}\right)_{\rho_1 \cdots \rho_{j-1}} . \qquad (4.22)$$

The inequalities of which (4.19) is a particular case indicate that the terms in (4.22) for $j \geqslant 3$ are (in general) bounded on the CRS. This supports postulate (a) that the divergence of $D(h_1 \cdots h_n)$ is at most strong times weak [for $D(h_1)$ and $D(h_1, h_2)/D(h_1)$], respectively, rather than for example, strong times weak times some still weaker divergence.

V. APPLICATIONS

A. One-Component Systems

To illustrate the use of postulates (a)–(f) and the associated thermodynamic formulas, let us use them to derive the results previously pointed out in Sec. III, as well as certain results not mentioned there.

1. *Pure Fluid*

If we let $\phi = \mu$, $h_1 = -p$, $h_2 = T$, $\rho_1 = v = V/N$, $\rho_2 = s = S/N$, then

$$D(p) = vK_T = -\frac{\partial^2 \mu}{\partial p^2}, \quad D(T) = \frac{1}{T} C_p = -\frac{\partial^2 \mu}{\partial T^2} ,$$

$$D(p, T) = \frac{\partial^2 \mu}{\partial p^2}\frac{\partial^2 \mu}{\partial T^2} - \left(\frac{\partial^2 \mu}{\partial p \, \partial T}\right)^2 . \qquad (5.1)$$

By postulate (a) (note that PCRS is excluded in the present instance since the critical surface is a point), $D(p, T)$ is strongly-times-weakly divergent; whereas, if the CXS is not parallel to the p or T axes at the critical point, $D(p)$ and $D(T)$ will be strongly divergent by postulate (b). This in turn implies that

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{C_v}{T} = \frac{D(p,T)}{D(p)}$$

and (5. 2)

$$\left(\frac{\partial v}{\partial p}\right)_s = vK_s = \frac{D(p,T)}{D(T)}$$

are both weakly divergent at the critical point. The off-diagonal derivatives are expressed in terms of the diagonal derivatives and the slope of the coexistence curve as described in Sec. IV B. For example, the ratio

$$-\left(\frac{\partial v}{\partial T}\right)_p \Big/ \left(\frac{\partial v}{\partial p}\right)_T = \left(\frac{\partial p}{\partial s}\right)_v \Big/ \left(\frac{\partial T}{\partial s}\right)_v$$

$$= \left(\frac{\partial p}{\partial T}\right)_v \to \frac{dp}{dT}\bigg|_{\text{CXS}} \tag{5. 3}$$

approaches the slope of the vapor-pressure curve at the critical point. Thus, the thermal-expansion coefficient $\alpha = v^{-1}(\partial v/\partial T)_p$ will diverge strongly, and $-(\partial T/\partial v)_s = (\partial p/\partial s)_v$ will go to zero weakly at the critical point. The ratio of the heat capacity to the compressibility is found from (4. 17) to be

$$\frac{C_p}{TvK_T} = \frac{C_v}{TvK_s} \to \left(\frac{dP}{dT}\bigg|_{\text{CXS}}\right)^2 . \tag{5. 4}$$

We remark that Eqs. (5. 3) and (5. 4) imply that, sufficiently close to the critical point, a knowledge of any two out of the three quantities C_p, K_T, α permits one to calculate the third, and also the slope of the vapor-pressure curve at the critical point.

2. *Ferromagnets*

We use the notation in the latter part of Sec. III. Note that for experimental applications, H should be the internal field differing from the externally applied magnetic field by a demagnetization correction or, equivalently, the data should be corrected to the case where both H and M are parallel to the axis of a long thin needle-shaped specimen. Since PCRS is again excluded, and since the CXS occurs at $H = 0$, our postulates predict that $D(H, T)$, $D(H)$, and $D(T)$ should diverge strongly times weakly, strongly, and weakly, respectively. Thus, the susceptibilities

$$\chi_T = D(H)\ , \quad \chi_S = D(H,T)/D(T) \tag{5. 5}$$

should diverge strongly, and the heat capacities

$$C_H/T = D(T)\ , \quad C_M/T = D(H,T)/D(H) \tag{5. 6}$$

should diverge weakly. The relation

$$D(H,T) = D(H)D(T) - \left(\frac{\partial M}{\partial T}\right)_H^2 \tag{5. 7}$$

implies that $[(\partial M/\partial T)_H]^2$ diverges *at most* strongly times weakly. Along the coexistence curve this implies $(T_c - T)^{2\beta-2}$ is asymptotically not larger than $(T_c - T)^{-\alpha'-\gamma'}$, a result guaranteed by the Rushbrooke inequality.[11] On the other hand, at $H = 0$ and $T > T_c$, $(\partial M/\partial T)_H$ vanishes identically. Another derivative of possible experimental interest

$$\left[\left(\frac{\partial T}{\partial H}\right)_S\right]^2 = \left[\left(\frac{\partial M}{\partial T}\right)_H \Big/ \left(\frac{\partial S}{\partial T}\right)_H\right]^2 \tag{5. 8}$$

has, according to the preceding discussion, at most a strong/weak divergence.

It is found experimentally[12] in some ferromagnets that the zero-field heat capacity, while achieving large values near the Curie point, appears on close examination to have a finite rounded peak at sufficiently high-temperature resolution, rather than the weak divergence predicted by postulate (c). The reason for this rounding is at present a subject of some dispute. In some cases, it may be the effect of impurities and crystalline defects and in others an intrinsic property of the appropriate statistical model for an ideal crystal. One may take at least two attitudes towards this deviation from our predictions. The first is to say that as long as the critical region is examined on a scale coarse enough so that rounding of heat capacity does not appear, our predictions remain unaltered. The other is to replace "weak" in our postulates by "nondivergent" and work out the appropriate consequences using the machinery of Sec. IV B. A similar problem arises in the case of antiferromagnets (see Sec. V C).

B. Two-Component Fluid

For a binary fluid, let $n_1 n_2$ be the mole numbers and μ_1 and μ_2 the chemical potentials of the two components. If we let

$$\Delta = \mu_1 - \mu_2\ , \tag{5. 9}$$

and choose the dependent potential to be

$$\phi(\Delta, p, T) = \mu_2\ , \tag{5. 10}$$

then

$$x = \frac{n_1}{n_1+n_2} = -\left(\frac{\partial \phi}{\partial \Delta}\right)_{p,T}\ , \quad v = \frac{V}{n_1+n_2} = \left(\frac{\partial \phi}{\partial p}\right)_{\Delta,T}\ ,$$
$$s = \frac{S}{n_1+n_2} = -\left(\frac{\partial \phi}{\partial T}\right)_{\Delta,p}\ , \tag{5. 11}$$

are the conjugate densities. The CXS is a two-dimensional surface and the CRS is a one-dimensional curve.

Let us first consider the general case when the p, T, Δ axes bear no special relationship to the CXS or CRS at the point of interest on the CRS. Then, by postulate (b), we expect that

$$D(T)=\left(\frac{\partial s}{\partial T}\right)_{p\Delta}=\frac{C_{p\Delta}}{T}\ , \quad D(p)=-\left(\frac{\partial v}{\partial p}\right)_{T\Delta}=vK_{T,\Delta}\ , \quad D(\Delta)=\left(\frac{\partial x}{\partial \Delta}\right)_{pT}\ , \tag{5.12}$$

will be strongly divergent. Derivatives of this sort are of interest in understanding the intensity of light scattering near the critical line. Experimental convenience usually dictates that direct measurements of thermodynamic properties be made at constant x rather than constant Δ. According to postulates (a) and (e), quantities such as

$$vK_{Tx}=-\left(\frac{\partial v}{\partial p}\right)_{Tx}=\frac{D(p,\Delta)}{D(\Delta)}\ , \quad \frac{C_{px}}{T}=\left(\frac{\partial s}{\partial T}\right)_{px}=\frac{D(T,\Delta)}{D(\Delta)}\ , \tag{5.13}$$

should diverge weakly at the CRS while derivatives with two densities held fixed, such as

$$vK_{sx}=-\left(\frac{\partial v}{\partial p}\right)_{sx}=\frac{D(p,T,\Delta)}{D(T,\Delta)}\ , \quad \frac{C_{vx}}{T}=\left(\frac{\partial s}{\partial T}\right)_{vx}=\frac{D(p,T,\Delta)}{D(p,\Delta)}\ , \tag{5.14}$$

should not diverge at all, in agreement with previous arguments by Rice[13] and the authors[3] (see also Sec. IV C). Off-diagonal derivatives will diverge in the same manner as the corresponding diagonal derivatives in the general case. For example,

$$\left(\frac{\partial v}{\partial \Delta}\right)_{Tp}=\left(\frac{\partial x}{\partial p}\right)_{T\Delta} \tag{5.15}$$

should diverge strongly, whereas

$$v\alpha_x=\left(\frac{\partial v}{\partial p}\right)_{px} \tag{5.16}$$

should diverge only weakly.

According to Eq. (4.19) and the following discussion, the (finite) values of C_{vx} and K_{sx} on the critical curve can be expressed in terms of total derivatives taken along the curve

$$\frac{C_{vx}}{T}=\frac{ds}{dT}-\frac{dp}{dT}\frac{dv}{dT}+\frac{d\Delta}{dT}\frac{dx}{dT}\ , \tag{5.17a}$$

$$vK_{sx}=\frac{ds}{dp}\frac{dT}{dp}-\frac{dv}{dp}+\frac{d\Delta}{dp}\frac{dx}{dp}\ . \tag{5.17b}$$

Note that term by term, the ratio of the right-hand side of (5.17a) to the right-hand side of (5.17b) is $(dp/dT)^2$, and thus we have

$$\frac{C_{vx}}{TvK_{sx}}=\left(\frac{dp}{dT}\right)^2\bigg|_{\text{CRS}}\ . \tag{5.18}$$

This result can also be obtained from Eqs. (4.13), which guarantee, in the general case, that derivatives such as

$$\left(\frac{\partial p}{\partial T}\right)_{vx}\to\frac{dp}{dT}\bigg|_{\text{CRS}}\ , \quad \left(\frac{\partial T}{\partial p}\right)_{sx}\to\frac{dT}{dp}\bigg|_{\text{CRS}}\ , \quad \left(\frac{\partial \Delta}{\partial T}\right)_{vx}\to\frac{d\Delta}{dT}\bigg|_{\text{CRS}}\ , \tag{5.19}$$

tend to the corresponding total derivatives along the critical line. Consequently, we have

$$\frac{C_{px}}{vTK_{Tx}}=\frac{C_{vx}}{vTK_{sx}}=\left(\frac{\partial p}{\partial T}\right)_{vx}\bigg/\left(\frac{\partial T}{\partial p}\right)_{sx}\to\left(\frac{dp}{dT}\right)^2\bigg|_{\text{CRS}}\ , \tag{5.20}$$

and also

$$\frac{C_{px}}{Tv\alpha_x}=\left(\frac{\partial T}{\partial p}\right)_{sx}^{-1}\to\frac{dp}{dT}\bigg|_{\text{CRS}}\ , \tag{5.21a}$$

$$\frac{\alpha_x}{K_{Tx}}=\left(\frac{\partial p}{\partial T}\right)_{vx}\to\frac{dp}{dT}\bigg|_{\text{CRS}}\ , \tag{5.21b}$$

so that a knowledge of any two of α_x, K_{Tx}, C_{px} sufficiently close to the critical line determines the remaining one as well as the value of dp/dT along the critical line.

These predictions can be compared with a variety of decorated lattice-gas models of binary fluids investigated by Widom,[14] by Clark,[15] and by Neece.[16] We have verified that postulates (a) – (d) hold in these models (using p/T as dependent potential, and $1/T$, μ_1/T, and μ_2/T as independent fields) near the appropriate critical lines.

Several exceptions to the general case are of interest. One of these is when the critical temperature passes through a maximum or minimum as a function of x, and hence of Δ (this occurs, for example, in CO_2-H_2O,[17] Ne-Ar,[18] N_2+NH_3, and CH_4-NH_3[19]) at some point r on the critical curve, while the CXS itself bears no particular relationship to the coordinate axes at r. As the critical curve is parallel to the $p\Delta$ plane at r, $D(p,\Delta)$ diverges strongly rather than strongly times weakly, by postulate (b), while the divergence of the other D's is the same as in the general case described above. Consequently, K_{Tx} should remain finite and C_{vx} diverge weakly upon approaching r. In the decorated lattice-gas model investigated by Clark,[15] the critical temperature passes through a maximum and our predictions are verified in detail. An even more common phenomenon is the occurrence of a maximum or minimum in the critical pressure as a function of concentration (as in several binary organic mixtures[17,19]: CH_4-C_2H_6, CH_4-nC_3H_8, CH_3OH-C_2H_6, C_2H_6-nC_3H_7OH, etc.), and the reader may verify that our postulates lead to K_{sx} diverging weakly and a nondivergent C_{px} near such a point.

A particularly interesting exception to the general case is provided by critical azeotropy in a binary mixture, when the azeotropic line intersects the critical curve (illustrated in Fig. 3) at a point r. An azeotropic point is one in which the composition is the same in the liquid and vapor phase. Equivalently, it is a point at which the vapor pressure passes through an extremum in x at constant T, and the boiling temperature passes through an extremum in x at constant p. Consequently, it is a point at which the CXS is parallel to the Δ axis. Critical azeotropy occurs in a number of systems, including[19] CO_2-C_2H_6, CO_2-C_2H_4, C_2H_6-C_2H_2, and HCl-$(CH_3)_2O$. In general, the critical pressure and temperature will not pass through extrema at r, though systems which exhibit critical azeotropy generally also have an extremum in critical temperature (at some other point on the critical curve). Thus, we expect that $D(\Delta)$ will diverge only weakly at r, whereas the other D's have the same character as in the general case. This means that both K_{Tx} and C_{px} should diverge strongly (as in the pure fluid), but C_{vx} should still remain finite (unlike the pure fluid, and unlike a suggestion found in our previous paper[3]).

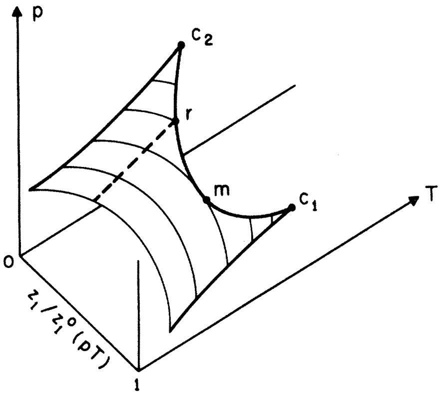

FIG. 3. Schematic representation of the coexistence surface of a binary fluid mixture exhibiting critical azeotropy. [We have used $z_1/z_1^0(T, p)$, the value of the activity of component 1 $(z_1 = e^{u_1/kT})$ divided by its value in the pure fluid at the same T and p, rather than Δ in this figure, so that the coexistence curves of the pure components can be shown. The geometry will be essentially unaffected in the interior of the diagram]. The point r is the critical azeotrope. It is the intersection of the critical curve c_1mrc_2 with the line of azeotropes (dashed curve). m is the minimum critical temperature usually associated with positive critical azeotropy. The points c_1 and c_2 are the critical points of components 1 and 2, respectively. At r, the CXS is parallel to the z_1/z_1^0 axis and, therefore, to the Δ axis.

Experiments on real fluid mixtures which can be compared with the foregoing predictions are, unfortunately, relatively few. Light-scattering measurements exhibit the expected strong divergences.[20] There are also heat-capacity measurements on binary mixtures by Voronel' and co-workers. A C_{vx} measurement for air[21] shows a much less pronounced spike than analogous measurements in pure N_2,[22] measurements of C_{px} in methanol-cyclohexane[23] at the critical solution point exhibit a weak divergence analogous to that of C_v in a pure fluid, and C_{vx} at the azeotropic critical point of a CO_2-C_2H_6 mixture[24] also exhibits a weak divergence. The first two results are in agreement with our predictions and the third is in disagreement. There are reasons to suspect, however, that neither the confirmations nor disagreement should at present be taken too seriously.

Consider first the measurement of C_{vx} in air (regarded, to a first approximation, as an O_2-N_2 mixture). As indicated in Sec. IV C, the maximum value of C_{vx} at the critical point of such a mixture should be equal to the rigorous upper bound we derived earlier. While the actual value of the bound is hard to obtain because of lack of information about the chemical potentials along the critical curve, very rough estimates show that it could be quite large, substantially larger than the largest values of C_v which Voronel' and co-workers observed[22] in pure N_2. Another way of stating this is that while our theory predicts *in principle* a finite value of C_{vx}, it may turn out that the rate of variation of T with Δ along the critical line is so small that *in practice* the situation all along the critical line resembles the one discussed above in which the critical temperature passes through an extremum and C_{vx} diverges weakly. The difference between a weak divergence and a sharp cusp may be extremely difficult to observe in practice (see our discussion in Sec. V D of the liquid-helium λ transition, where an analogous situation occurs) with the temperature resolution, etc., currently available. This is one reason we do not regard the (apparent) weak divergence of C_{vx} at the azeotropic critical point of CO_2-C_2H_6 as necessarily contradicting our hypotheses, even though we are unable at present to make even a rough guess of the upper bound to C_{vx} in this system.

There is, however, still another reason why the results of Voronel' and co-workers should be treated with some caution. As pointed out by Edwards, Lipa, and Buckingham,[25] severe corrections to C_v occur in the case of a pure fluid due to density gradients induced by the gravitational field, and these have not been properly considered in the experiments of Voronel' *et al.* It is not at all clear that stirring the fluid serves to compensate for these gravitational effects. In the case of nonazeotropic mixtures near a critical line, the total compressibility K_{Tx} will diverge only weakly, but the gravitational field then results in strong concentration gradients in equilibrium, and again the result of stirring is not too clear.

In conclusion, it may be worth remarking that discontinuities in x and v on a binary mixture CXS are found, in both theoretical models and experimental measurements, to exhibit precisely the behavior described at the end of Sec. IV A. For example, composition and density discontinuities vanish near critical points in close analogy to density discontinuities in a pure fluid.[1c,26] An azeotropic mixture is, of course, an exception, precisely because x is the conjugate density to Δ, and the CXS is parallel to the Δ axis at an azeotropic point.

C. Antiferromagnetism

Antiferromagnetism[27] is one of several order-disorder transitions in solids which, at first glance, does not seem to fit the categories of Sec. IV. The reason is that there is no physically realizable field conjugate to the sublattice magnetization (per unit volume) ψ, which in the simple antiferromagnet is the analog of ordinary magnetization M in a ferromagnet. Nonetheless, for conceptual purposes, it is very useful to formally introduce a field η, a magnetic field which points in opposite directions on the two magnetic sublattices, conjugate to ψ. The potential ϕ is a function of η, the ordinary magnetic field H (same direction on both sublattices), and T with

$$\psi = \frac{-\partial\phi}{\partial\eta}, \quad M = \frac{-\partial\phi}{\partial H}, \quad S = \frac{-\partial\phi}{\partial T}. \tag{5.22}$$

We shall want to assume H is the internal field corrected for demagnetizing effects, and both H and η are along the axis of easy sublattice magnetization.

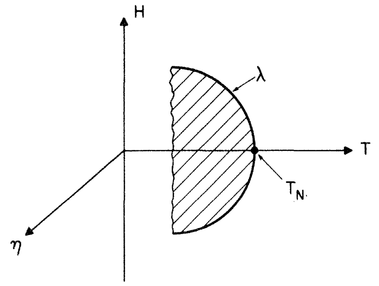

FIG. 4. Coexistence surface (cross hatched) and the critical line λ for a simple ferromagnet near the Néel point.

Near the Néel temperature T_N the CXS for this system, shown schematically in Fig. 4, lies in the $\eta = 0$ plane and terminates in a CRS labeled λ in the figure. Experiments can only be carried out at $\eta = 0$, and the curve λ is commonly called a phase boundary, separating the antiferromagnetically ordered region (cross hatched) from the paramagnetic region, and the transition between these two regions is called a second-order or λ transition. However it is more natural, considering the analogy with other systems, to refer to λ as a line of critical points. If this is done, the behavior of various thermodynamic derivatives can be predicted in terms of our postulates. We shall not concern ourselves with the additional complications which arise at lower temperatures and/or larger fields associated with spin flopping.

Let us first consider the behavior at $H = 0$. The susceptibility $\partial\psi/\partial\eta = D(\eta)$ should diverge strongly at the Néel temperature according to postulate (b), and though it is not directly observable, neutron-scattering measurements of the pair-correlation function give strong evidence that such a divergence takes place.[28] Nuclear magnetic resonance measurements[29] indicate a spontaneous sublattice magnetization ψ varying as $(T_N - T)^\beta$ near the Néel point, with $\beta \approx \frac{1}{3}$. The weak divergence of $C_H = TD(T)$ is supported by direct measurements,[29] as is the fact that $\chi = \partial M/\partial H = D(H)$ achieves a finite constant, in accordance with postulates (c) and (d), respectively.

For $H \neq 0$, the curve λ is parallel to neither the H nor the T axis, and consequently we predict that both C_H and χ should diverge weakly. The behavior of the former is similar to what is found at $H = 0$,[30] while magnetization curves support the presence of large, if not infinite, values of χ at λ.[31,32]

It is of some interest to apply (4.10), choosing $h_1 = H$, $h_2 = T$, and $\vec{V}$ parallel to the curve λ at some point in the plane $\eta = 0$, so that the left-hand side of (4.10) is finite. The divergence of $D(T)$ upon approaching λ means that $(\partial T/\partial H)_s$ approaches dT/dH along the curve λ. In other words, adiabatic curves of T versus H should cross λ tangentially, which seems to be the case experimentally.[31] In analogy with (4.15) we obtain the "Pippard relations" (note $\partial S/\partial H = \partial M/\partial T$)[33]

$$\left(\frac{\partial S}{\partial H}\right)_T \bigg/ \left(\frac{\partial S}{\partial T}\right)_H \to -\left(\frac{dT}{dH}\right)_\lambda ,$$
$$\left(\frac{\partial M}{\partial H}\right)_T \bigg/ \left(\frac{\partial M}{\partial T}\right)_H \to -\left(\frac{dT}{dH}\right)_\lambda , \tag{5.23}$$

results which hold upon approaching the λ curve from higher or from lower temperatures.

Again, as in the case of ferromagnets (see Sec.

V A), there is evidence that in many cases the predicted weak divergence is not a genuine divergence, but that a "rounding" of C_H and χ occurs in a small interval near the CRS.[32,34] Nonetheless, our hypotheses yield a fairly good qualitative picture in agreement with observed behavior. While the adiabats may not cross λ precisely tangentially, they are very close, and χ is certainly quite large (for $T < T_N$), both in the antiferromagnetic and paramagnetic regions near λ – results which are in contradiction with molecular field calculations.[35]

D. λ Transition in Liquid Helium

Just as in the case of antiferromagnetism (Sec. V C), we find it convenient in discussing the λ transition in helium[36] to introduce a nonphysical field η conjugate to the superfluid order parameter ψ.[37] For our purposes the phase of ψ is unimportant; we shall choose both it and η real. The potential ϕ is such that

$$\psi = \frac{-\partial\phi}{\partial\eta}, \quad v = \frac{\partial\phi}{\partial p}, \quad s = \frac{-\partial\phi}{\partial T} \quad . \tag{5.24}$$

The CXS is that portion of the pT plane, $\eta = 0$, where superfluid He II occurs, and the λ line is, in our terminology, a line of critical points. Our postulates predict that near the λ line $D(p)$ and $D(T)$, and thus K_T and C_p, should diverge weakly. If in (4.10) we let $h_1 = -p$ and $h_2 = T$ and evaluate the left-hand side in a direction parallel to the λ line (with $\eta = 0$) at some point, we conclude that

$$\left(\frac{\partial T}{\partial p}\right)_s \to \left(\frac{dT}{dp}\right)_\lambda \quad , \tag{5.25}$$

and, interchanging the role of h_1 and h_2, that $(\partial T/\partial p)_v$ reaches the same limit. The Pippard relations[33]

$$\frac{Tv\alpha}{C_p} \to \left(\frac{dT}{dp}\right)_\lambda \quad , \tag{5.26a}$$

$$\frac{K_T}{\alpha} \to \left(\frac{dT}{dp}\right)_\lambda \tag{5.26b}$$

are consequences of (4.15). None of the above results are at all new; they can be found, for example in the work of Buckingham and Fairband.[38] We state them merely to show that this transition is one among many which agree with our postulates. It may be worth noting that near the intersection of the λ line and the vapor-pressure curve, $(dT/dp)_\lambda$ is so small that in applying our postulates to the practical experimental situation it is best to regard the critical (λ) line as parallel to the p axis. We then predict no divergence for $D(p) \propto K_T$ and a weak divergence for $C_v \propto D(p, T)/D(p)$, results which are in good accord with experiments performed with currently available temperature resolution.[39]

Superfluidity also occurs in mixtures[40] of He^3 and He^4. The independent fields may be chosen as η, T, $-p$, and $\Delta = \mu_3 - \mu_4$, the difference of the chemical potentials of He$_3$ and He$_4$, with potential $\phi = \mu_4$, and with conjugate densities ψ, s, v, and $x = n_3/(n_3 + n_4)$ (compare with Sec. V B). Again, the only region experimentally accessible is $\eta = 0$, and the CXS lies in the $\eta = 0$ hyperplane. The CXS terminates in a two-dimensional CRS, the surface (in T, p, Δ space) of λ transitions between the superfluid and normal phases. (At lower temperatures, the superfluid-normal transition is first order rather than λ-like; we shall not discuss this case.) There is no evidence that the CRS bears any particular relation to the coordinate axes except as $\Delta \to -\infty$, pure He^4, where it is parallel to the Δ axis. Excluding this case, we have $D(T)$, $D(p)$, $D(\Delta)$, $D(T, p)$, $D(T, \Delta)$, $D(p, \Delta)$, and $D(T, p, \Delta)$, all weakly divergent. This implies that $C_{px} = TD(T, \Delta)/D(\Delta)$ and $K_{Tx} = vD(p, \Delta)/D(\Delta)$ should be finite at the CRS, a conclusion we obtained earlier by means of rigorous bounds.[3] The former prediction appears to agree with experiment at least for p near the vapor pressure.[41] The quantity $(\partial x/\partial\Delta)_{Tp} = D(\Delta)$ should diverge weakly, and this divergence may be accessible to light-scattering experiments. There is a plausible argument (we shall not give the details) which suggests that this weak divergence should also be apparent in that curves of vapor pressure as a function of x for fixed T should cross the λ line (in the xT plane) with zero slope on both sides, in contradiction to classical theory which predicts a change in slope.[40]

E. β Brass

The situation here is somewhat analogous to that described in antiferromagnetism. At temperatures of about 740 °K an order-disorder transition takes place in β brass involving the sublattice ordering of copper and zinc atoms.[42] As in the case of antiferromagnetism, it is useful to introduce a field η (in addition to T, $-p$, $\Delta = \mu_{\text{Zn}} - \mu_{\text{Cu}}$) which couples to a sublattice order parameter ψ, which may be taken as the excess mole fraction of zinc on the first sublattice over that on the second. The potential

$$\phi(T, -p, \Delta, \eta) = \mu_{\text{Cu}} \tag{5.27}$$

is chosen so that

$$-\frac{\partial\phi}{\partial T} = s \quad , \quad \frac{\partial\phi}{\partial p} = v \quad ,$$
$$-\frac{\partial\phi}{\partial\Delta} = x = \frac{n_{\text{Zn}}}{n_{\text{Zn}} + n_{\text{Cu}}} \quad , \quad -\frac{\partial\phi}{\partial\eta} = \psi \quad . \tag{5.28}$$

The only physically accessible region is the (three-dimensional) $\eta = 0$ hyperplane, and the CXS of the order-disorder transition (also three dimensional) lies in this hyperplane, and ends in a two-dimensional CRS in p, T, Δ space.

Because the $pT\Delta$ manifold contains the CXS, postulate (b) predicts that

$$\left(\frac{\partial\psi}{\partial\eta}\right)_{pT\Delta} = D(\eta) \qquad (5.29)$$

should diverge strongly at the CRS. Although it is not directly measurable, neutron scattering measurements,[43] as in the case of antiferromagnetism, suggest strongly that such a divergence takes place. They also indicate a spontaneous sublattice ordering which vanishes at the CRS in the manner predicted by our theory. In contrast, however, to an antiferromagnet in which the H axis is PCRS at the Néel point, we know of no evidence that the CRS in β brass bears any special relationship to the T, p, or Δ axes. Accordingly, by postulate (c),

$$D(T),\quad D(p),\quad D(\Delta),\quad D(T,p),\quad D(T,\Delta),$$
$$D(p,\Delta),\quad D(p,T,\Delta)$$

should all diverge weakly. As a consequence, both

$$C_{px} = \frac{TD(T,\Delta)}{D(\Delta)} \quad \text{and} \quad C_{vx} = \frac{TD(T,p,\Delta)}{D(p,\Delta)}$$

should remain finite at the CRS (which can also be concluded from rigorous bounds presented earlier[3]), as should K_{Tx}, K_{sx}, α, and α_x. (See Sec. V B for definitions.) Experiments[44] on the heat capacity of β brass with $x = 0.475$ indicate that both C_{px} and C_{vx} rise sharply in the immediate vicinity of the CRS in a manner similar to a weak divergence. In particular, the values C_{vx} along a line of constant p and x appear to be in good numerical agreement with series estimates for the heat capacity of the three-dimensional Ising model over a range of $|T_c - T/T_c|$ between 10^{-1} and 10^{-5}.[45] From the values quoted in Ref. 44 of $d\rho/dT$, dv/dp, dp/dT along a line of constant x on the CRS, we obtain a value of $\sim 25R$ for the upper bound to C_{vx}, whereas the largest value observed experimentally for C_{vx} at $(T_c - T)/T_c \approx 10^{-5}$ is about $6R$.

The situation is similar to that described in our discussion of bounds to C_{vx} in Sec. V B; because our bound for C_{vx} is much larger than the largest value yet seen experimentally, there is no contradiction between our prediction of a finite value of C_{vx} on the CRS and the apparent divergence seen experimentally. The latter is so slow that it may never be possible actually to observe the maximum. It is plausible that this near divergence of C_{vx} is associated with the CRS being nearly parallel to both the p and Δ axes so that the weak divergence of $D(p, \Delta)$ is almost absent. There may be other points on the CRS where the bound on C_{vx} is smaller and the absence of a weak divergence could be checked experimentally, and an experimental determination of the shape of the CRS would be of interest.

VI. CONCLUSION

We have shown how the thermodynamic properties of a wide variety of physical systems near their respective critical points including the so-called λ transitions may be understood qualitatively from a unified point of view. This point of view is geometrical in character and attention is focused on the fields (intensive) rather than densities (extensive) as appropriate thermodynamic variables. Nonclassical behavior of various thermodynamic derivatives is easily introduced through a small number of postulates, and the consequences for a wide variety of cases is then a relatively straightforward application of thermodynamic formulas. Exceptional cases like azeotropy are shown to be due to accidental relations between coordinate axes and coexistence and critical surfaces, rather than exceptional behavior of the surfaces themselves or of the thermodynamic potential near these surfaces. We believe that similar geometrical considerations are of value in suggesting a natural extension of scaling laws to more complex systems and may also prove useful in discussion of dynamic phenomena near critical points.

There are also ways in which the theory we have developed is incomplete and preliminary. Obviously, there is a particular need for *quantitative* evaluation of certain properties near critical lines in order to estimate whether our predictions of divergence refer to a physically accessible region of observation or to an asymptotic region which can only be checked mathematically in some model calculations. Measurements or calculations of chemical potentials along critical lines in binary fluid mixtures would be extremely helpful in this connection. Further thought needs to be given to the characterization of quantities which, for one reason or another, do not diverge near the critical surface – they may nonetheless have rather interesting properties. The cases when weak divergences are not real divergences but "round out" on a sufficiently fine scale of measurement deserve additional discussion (some preliminary thoughts on the matter occur in Secs. V A and V C). Despite these deficiencies, we believe that our ideas provide a point of view in essential agreement with current experimental results and theoretical ideas, and that although further developments may modify some details in our postulates, the geometrical approach we have adopted is basically sound.

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APPENDIX: DIAGONALIZATION OF $-\partial^2\phi/\partial h_i\,\partial h_j$

Equations (4.10) and (4.11) are of the form

$$\sum_{i=1}^{n}\sum_{j=1}^{n}\Phi_{ij}x_i x_j=\sum_{k=1}^{n}\hat{\Phi}_{kk}Y_k^2\ , \tag{A1}$$

with

$$\Phi_{ij}=-\frac{\partial^2\phi}{\partial h_i\,\partial h_j}\ ,\quad \hat{\Phi}_{kk}=\left(\frac{\partial\rho_k}{\partial h_k}\right)_{\rho_{k+1}\cdots\rho_n}\ . \tag{A2}$$

The diagonalization of the quadratic form (A1) in the form specified by (A2) may be carried out by means of a unimodular transformation of the sort described by Tisza.[10] The diagonalization is accomplished by the matrix M, with the properties

$$\begin{aligned}\hat{\Phi}_{kl}=\hat{\Phi}_{kk}\,\delta_{kl}&=\sum_{i=1}^{n}\sum_{j=1}^{n}\Phi_{ij}M_{ik}M_{jl}\ ,\\ Y_k&=\sum_{i=1}^{n}x_i\,(M^{-1})_{ki}\ .\end{aligned} \tag{A3}$$

When, as in the case of Eq. (4.10), $X_j=0$ for $j>2$, the reader will easily verify that M and its inverse are

$$M=\begin{bmatrix}1 & 0\\ \left(\dfrac{\partial h_2}{\partial h_1}\right)_{\rho_2} & 1\end{bmatrix}\ ,\quad M^{-1}=\begin{bmatrix}1 & 0\\ -\left(\dfrac{\partial h_2}{\partial h_1}\right)_{\rho_2} & 1\end{bmatrix}\ . \tag{A4}$$

In the general case, the matrix M is

$$M=\begin{pmatrix}1 & 0 & 0 & \cdots & 0\\ \left(\dfrac{\partial h_2}{\partial h_1}\right)_{\rho_2\cdots\rho_n} & 1 & 0 & \cdots & 0\\ \left(\dfrac{\partial h_3}{\partial h_1}\right)_{\rho_2\cdots\rho_n} & \left(\dfrac{\partial h_3}{\partial h_2}\right)_{\rho_3\cdots\rho_n} & 1 & \cdots & 0\\ \vdots & & & \ddots & \\ \vdots & & & 1 & 0\\ \left(\dfrac{\partial h_n}{\partial h_1}\right)_{\rho_2\cdots\rho_n} & \left(\dfrac{\partial h_n}{\partial h_2}\right)_{\rho_3\cdots\rho_n} & \cdots & \left(\dfrac{\partial h_n}{\partial h_{n-1}}\right)_{\rho_n} & 1\end{pmatrix}, \tag{A5}$$

with inverse

$$M^{-1}=\begin{pmatrix}1 & 0 & 0 & \cdots & 0\\ -\left(\dfrac{\partial h_2}{\partial h_1}\right)_{\rho_2\cdots\rho_n} & 1 & 0 & \cdots & 0\\ -\left(\dfrac{\partial h_3}{\partial h_1}\right)_{\rho_3\cdots\rho_n} & -\left(\dfrac{\partial h_3}{\partial h_2}\right)_{\rho_3\cdots\rho_n} & 1 & \cdots & 0\\ \vdots & \vdots & & \ddots & \\ \vdots & \vdots & \vdots & 1 & 0\\ -\left(\dfrac{\partial h_n}{\partial h_1}\right)_{\rho_n} & -\left(\dfrac{\partial h_n}{\partial h_2}\right)_{\rho_n} & \cdots & -\left(\dfrac{\partial h_n}{\partial h_{n-1}}\right)_{\rho_n} & 1\end{pmatrix}. \tag{A6}$$

Equation (4.10) is obtained when $n=2$ and $X_1=1$, $X_2=dh_2/dh_1$; Eq. (4.11) is obtained when $n=3$ and $X_1=1$, $X_2=dh_2/dh_1$, $X_3=dh_3/dh_1$, as the reader will easily verify by applying the chain rule of differentiation and the Maxwell relations. Extension of Eqs. (4.10) and (4.11) to higher values of n is straightforward.

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