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Thermodynamic Bounds on Constant-Volume Heat Capacities and Adiabatic Compressibilities*

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A rigorous upper bound for the heat capacity at constant volume C_V is used to provide an alternative derivation of a result due to Rice: A locus of points of infinite C_V is in general incompatible with thermodynamic stability. An analogous upper bound is obtained for the adiabatic compressibility. The bounds are extended to multicomponent stystems, where they suggest that C_V should not diverge along a continuous line of critical points or plait points. They make plausible the absence of an infinite heat capacity in a certain class of "decorated" Ising models (including Syozi's model for a dilute ferromagnet) and in the spherical model. Possible implications for fluids or ferromagnets containing impurities are briefly discussed.

I. INTRODUCTION

THERE is by now good evidence that the constant-volume heat capacity C_V diverges to infinity near the critical point in certain lattice-gas models,[1] in a manner which seems to be reflected in the more careful experimental measurements on real fluids.[2] In addition to the exact results for two-dimensional Ising lattices, for which a logarithmic divergence is found in the soluble cases,[3] series expansion methods for three-dimensional Ising models suggest an analogous, or slightly sharper, divergence.[4]

By contrast, there are a variety of "decorated" Ising lattices whose properties can, by a suitable transformation, be derived from those of the "undecorated lattice," in which C_V, or its Ising-model analog, exhibits a sharp but finite cusp at the phase transition point.[5,6] The spherical model,[7] as is well known, possesses a finite heat capacity at its critical point. Clark[8] has investigated a soluble "lattice gas" model of a multicomponent system, and finds that along the locus of plait points C_V (with mole fractions held constant) is generally finite.

We intend to show that the aforementioned "exceptions" to an infinite heat capacity at a critical point are by no means accidental, but reflect specific features of the models involved and in fact a finite heat capacity is to be expected on grounds related to thermodynamic stability. Rice[9] has pointed out that a locus of points of infinite C_V in a compressible solid should lead to a mechanical instability resulting in a first-order phase transition (and, incidentally, reducing C_V to a finite value). Some first-order phase transitions in solids seem explicable in terms of an "incipient" infinity in C_V.[10] Our approach to the problem is similar to that of Rice, but we argue in reverse. We assume that the stability requirements are satisfied and deduce an upper bound for C_V which will in general be finite, or at least not divergent along a continuous curve. An analogous bound on the adiabatic compressibility is obtained by invoking thermal in place of mechanical stability.

In Sec. II the aforementioned bounds are derived for simple fluids and model paramagnets. A generalization to multicomponent systems will be found in Sec. III, while Sec. IV contains applications to various models and physical situations.

II. ONE-COMPONENT SYSTEMS

Consider a region in the volume V, temperature T plane in which entropy S and pressure p are continuous functions, together with their first partial derivatives with respect to V and T. Their total temperature derivatives along some differentiable curve $V(T)$ are

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[1] For a review of Ising model calculations see M. E. Fisher, in *Lectures in Theoretical Physics*, edited by W. E. Brittin (University of Colorado Press, Boulder, Colo., 1965), Vol. VII C, p. 1; Rept. Progr. Phys. **30**, 615 (1967).

[2] Recent papers include A. V. Voronel, V. G. Snigirev, and Yu. R. Chashkin, Zh. Eksperim. i Teor. Fiz. **48**, 981 (1965) [English transl.: Soviet Phys.—JETP **21**, 653 (1965)]; A. V. Voronel, V. G. Gorbunova, Yu. R. Chashkin, and V. V. Shchekochikhina, *ibid.* **50**, 897 (1966) [English transl.: *ibid.* **23**, 597 (1966)]; A. V. Voronel and Yu. R. Chashkin, *ibid.* **51**, 394 (1966) [English transl.: *ibid.* **24**, 263 (1967)]; M. R. Moldover and W. A. Little, Phys. Rev. Letters **15**, 54 (1965).

[3] L. Onsager, Phys. Rev. **65**, 117 (1944); see also Ref. 1.

[4] G. A. Baker, Jr., and D. S. Gaunt, Phys. Rev. **155**, 545 (1967); D. S. Gaunt, Proc. Phys. Soc. (London) **92**, 150 (1967); C. Domb, Discussions Faraday Soc. **43**, 85 (1967).

[5] I. Syozi, Progr. Theoret. Phys. (Kyoto) **34**, 189 (1965); I. Syozi and S. Miyazima, *ibid.* **36**, 1083 (1966); J. W. Essam and H. Garelick, Proc. Phys. Soc. (London) **92**, 136 (1967).

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[8] R. K. Clark, J. Chem. Phys. **48**, 741 (1968).

[9] O. K. Rice, J. Chem. Phys. **22**, 1535 (1954).

[10] C. W. Garland and R. Renard, J. Chem. Phys. **44**, 1120 (1966); **44**, 1125 (1966); **44**, 1130 (1966); C. Domb, Proc. Phys. Soc. (London) **88**, 260 (1966).

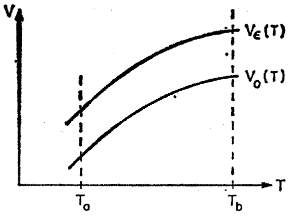

FIG. 1. Curves in the volume-temperature plane illustrating Eqs. (2.7) and (2.8).

given by

$$S'=\frac{dS}{dT}=\left(\frac{\partial S}{\partial T}\right)_V+\left(\frac{\partial S}{\partial V}\right)_T V', \tag{2.1}$$

$$p'=\frac{dp}{dT}=\left(\frac{\partial p}{\partial T}\right)_V+\left(\frac{\partial p}{\partial V}\right)_T V', \tag{2.2}$$

provided that $V'=dV/dT$ is finite. (We shall use primes to denote total temperature derivatives.) The Maxwell relation

$$(\partial p/\partial T)_V=(\partial S/\partial V)_T \tag{2.3}$$

combined with (2.1) and (2.2) yields

$$S'-p'V'=(\partial S/\partial T)_V-(\partial p/\partial V)_T(V')^2. \tag{2.4}$$

Thermodynamic stability implies that

$$-(\partial p/\partial V)_T\geq 0 \tag{2.5}$$

and hence

$$S'-p'V'\geq C_V/T=(\partial S/\partial T)_V. \tag{2.6}$$

Next consider a phase-transition curve in the V-T plane, by which we mean a curve at whose points the Helmholtz free energy has some nonanalytic behavior (for example, the coexistence curve for a liquid-vapor system). It is not *a priori* obvious that (2.6) will be applicable along such a curve, since some of the assumptions of continuity involved in its derivation may be violated. We may, however, adopt the following approach: Suppose $V_0(T)$ is a portion of a phase-transition curve which is twice continuously differentiable in some range $T_a\leq T\leq T_b$. For $\epsilon>0$ define a family of curves (Fig. 1)

$$V_\epsilon(T)=V_0(T)+\epsilon \tag{2.7}$$

along which we shall assume that (2.6) holds, at least when ϵ is sufficiently small. With ϵ fixed, let a and b denote the points $[V_\epsilon(T_a), T_a]$ and $[V_\epsilon(T_b), T_b]$, respectively. Integration of (2.6) along the curve $V_\epsilon(T)$ yields

$$\begin{aligned}\int_a^b S'dT-\int_a^b p'V'dT &= S(b)-S(a)-[p(b)V_0'(T_b)-p(a)V_0'(T_a)]\\ &\quad+\int_a^b pV_0''(T)dT\geq\int_a^b (C_V/T)dT,\end{aligned} \tag{2.8}$$

where we have used integration by parts to eliminate p'. Under the rather weak assumption that S and p are bounded throughout the region of immediate interest to us, including the curve $V_0(T)$, it is evident that the left side of (2.8) provides a finite upper bound, independent of ϵ, for the integral of C_V along any of these curves. In particular it rules out the possibility that C_V "diverges everywhere along $V_0(T)$" if the statement in quotation marks is taken to mean that given any $K>0$, and any temperature in the interval $T_a\leq T\leq T_b$, one can find an $\epsilon_K(T)>0$ such that within the range $V_0(T)<V<V_0(T)+\epsilon_K(T)$, C_V is not less than K. Our argument works *mutatis mutandis* in the region $V<V_0(T)$. Note also that a bound analogous to (2.8) and applicable near a twice-continuously differentiable phase boundary curve $p_0(T)$ in the p-T plane may be obtained from (2.6) by a similar technique. A "divergence" of C_V (in the sense used above) along a finite portion of such a curve is thus ruled out.

We expect that in most cases encountered in practice (2.6) is applicable along a phase-boundary curve itself, in the sense that the quantities involved possess finite limits as one approaches the curve. (The limits may be different on different sides of the curve.) As long as S', p', and V' are finite, so is C_V, but at certain isolated points on the curve one or more of these quantities may become infinite. Such an infinity must of course be an "integrable" singularity, since apart from very pathological model systems one always expects finite changes in S, p, and V along a finite portion of the phase-boundary curve.

The inequality (2.6) places an upper bound on the derivative of an extensive thermodynamic variable (entropy) with respect to the corresponding intensive variable (temperature) while holding another extensive variable (volume) fixed. We are thus led to expect an analogous upper bound for the adiabatic compressibility

$$K_S=-V^{-1}(\partial V/\partial p)_S. \tag{2.9}$$

The bound may be obtained as follows: Along a differentiable curve $S(p)$ in the entropy-pressure plane we have

$$-\frac{dV}{dp}=-\left(\frac{\partial V}{\partial p}\right)_S-\left(\frac{\partial V}{\partial S}\right)_p\frac{dS}{dp}, \tag{2.10}$$

$$\frac{dT}{dp}=\left(\frac{\partial T}{\partial p}\right)_S+\left(\frac{\partial T}{\partial S}\right)_p\frac{dS}{dp}. \tag{2.11}$$

With the help of the Maxwell relation

$$(\partial V/\partial S)_p=(\partial T/\partial p)_S, \tag{2.12}$$

and noting that

$$(\partial T/\partial S)_p=T/C_p\geq 0, \tag{2.13}$$

we arrive at the analog of (2.6):

$$-dV/dp+(dS/dp)(dT/dp)\geq VK_S. \tag{2.14}$$

On the basis of this inequality we would not, for example, expect K_S to diverge along a finite length of a twice continuously differentiable phase-transition curve $T_0(p)$.

By similar methods one can obtain upper bounds on the derivative of an intensive quantity while holding another intensive variable fixed; for example, $(\partial T/\partial S)_p$. The resulting *lower* bounds on heat capacity at constant pressure and isothermal compressibility do not at present seem to be of much interest in analyzing phase transitions.

Essential to the derivation of (2.6) and (2.14) are the conditions of mechanical and thermal stability, (2.5) and (2.13), which in turn correspond to convexity properties of various free energies. There are other systems in which the analogous inequalities are not quite as obviously related to stability. For example, in the Heisenberg and Ising model paramagnets (see Appendix) one can introduce a potential $A(T,M)$ with the properties

$$H=(\partial A/\partial M)_T\,,\quad S=-(\partial A/\partial T)_M \tag{2.15}$$

$$(\partial H/\partial M)_T=(\partial^2 A/\partial M^2)_T\geq 0\,, \tag{2.16}$$

where M is the magnetization and H is the external field. By replacing V by M and p by $-H$, one can repeat the entire argument from (2.1) to (2.6) in order to obtain

$$S'+H'M'\geq(\partial S/\partial T)_M=C_M/T\,, \tag{2.17}$$

where the prime denotes a total temperature derivative along a differentiable curve $M(T)$.

Presumably such an inequality is also valid for "real" paramagnets, including ferro- and antiferromagnets, provided that one neglects magnetomechanical coupling. (Otherwise the strain components in a crystal must be introduced as additional thermodynamic variables.) However, the condition (2.16) does not hold for diamagnetic materials, which shows that it does not have the same generality as (2.5).

The inequality which corresponds to (2.14) is

$$\frac{dM}{dH}+\frac{dS}{dH}\frac{dT}{dH}\geq\left(\frac{\partial M}{\partial H}\right)_S=\chi_S. \tag{2.18}$$

Its derivation is parallel to (2.10)–(2.12), with (2.13) replaced by (see Appendix)

$$(\partial T/\partial S)_H=T/C_H\geq 0\,. \tag{2.19}$$

III. MULTICOMPONENT SYSTEMS

We shall derive generalizations of (2.6) and (2.14) appropriate to multicomponent fluids. Analogous results are possible for other systems with more than two thermodynamic variables; for example, magnetic solids with non-negligible magnetomechanical effects. Consider a system containing $n_1, n_2,\cdots,n_m$ moles of components $1,2,\cdots,m$, respectively. If $F(T,V,n_1,\cdots,n_m)$ is the Helmholtz free energy, the chemical potential μ_j for the jth species is given by

$$\mu_j=\partial F/\partial n_j\,, \tag{3.1}$$

while the entropy is

$$S=-\partial F/\partial T. \tag{3.2}$$

In writing partial derivatives we shall assume the quantities held constant are among the arguments of F given above. For simplicity, we adopt the formal conventions

$$V=n_0\,,\quad -p=\mu_0=\partial F/\partial n_0. \tag{3.3}$$

Let

$$\Gamma=\{n_0(T),n_1(T),\cdots,n_m(T)\}$$

be a differentiable curve in the multidimensional variable space; we denote total temperature derivatives along this curve by a prime. Provided that the requisite derivatives exist and are continuous, we may write

$$S'=\partial S/\partial T+\sum_{j=0}^{m}\left(\frac{\partial S}{\partial n_j}\right)n_j'\,, \tag{3.4}$$

$$\mu_j'=\partial\mu_j/\partial T+\sum_k\left(\frac{\partial\mu_j}{\partial n_k}\right)n_k'. \tag{3.5}$$

The Maxwell relations [see (3.1) and (3.2)]

$$\partial S/\partial n_j=-\partial\mu_j/\partial T \tag{3.6}$$

enable us to combine (3.4) and (3.5) in the form

$$S'=\frac{\partial S}{\partial T}-\sum_j\mu_j'n_j'+\sum_j\sum_k n_j'n_k'\frac{\partial\mu_j}{\partial n_k}. \tag{3.7}$$

The Helmholtz free energy is a minimum at equilibrium for a system at a fixed temperature,[11] and hence its second variation should be non-negative;

$$\delta^2F=\sum_{jk}\frac{\partial^2F}{\partial n_j\partial n_k}\delta n_j\delta n_k=\sum_{jk}\frac{\partial\mu_j}{\partial n_k}\delta n_j\delta n_k\geq 0\,, \tag{3.8}$$

or, in other words, $\partial\mu_j/\partial n_k$ is the jk component of a symmetric positive matrix, a matrix with no negative eigenvalues. This is equivalent to the statement that F is a convex function of the $m+1$ independent extensive variables. We see that the final term in (3.7) is non-negative; by dropping it we obtain the desired inequality

$$S'+\sum_{j=0}^{m}\mu_j'n_j'\geq\left(\frac{\partial S}{\partial T}\right)_{V,n_i}=\frac{C_V}{T}. \tag{3.9}$$

Note that C_V is a heat capacity at constant volume *and* constant mole number for every species.

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[11] See, e.g., H. Callen, *Thermodynamics* (John Wiley & Sons, Inc., New York, 1960), Chap. 6.

Provided that the various derivatives possess finite limits as one approaches a phase-boundary curve, which in general will lie on a phase-boundary hypersurface, (3.9) is applicable along such a curve. A more cautious procedure is to assume that the curve Γ is twice continuously differentiable, and that (3.9) holds on a family of curves for $\epsilon > 0$.

$$\Gamma_\epsilon = \{n_0(T)+\epsilon\sigma_0, n_1(T)+\epsilon\sigma_1, \cdots, n_m(T)+\epsilon\sigma_m\}, \tag{3.10}$$

where the σ_j are constants. Integration along one such curve from $T=T_a$ (the point a) to $T=T_b$ (the point b) yields

$$S(b)-S(a)+\sum_j[\mu_j(b)n_j'(T_b)-\mu_j(a)n_j'(T_a)] \\ -\sum_j\int_a^b \mu_j n_j''(T)dT \geq \int_a^b \frac{C_V}{T}dT. \tag{3.11}$$

The left side is finite in the limit $\epsilon \rightarrow 0$, provided that the entropy and all chemical potentials are bounded. Thus from (3.11) or (3.9) one expects that C_V will not diverge along a finite length of the curve Γ. A word of caution is in order as to the type of curve Γ to which these arguments apply. Since in this section we have permitted all the extensive arguments of F to vary, one can obviously obtain a locus of infinite C_V by finding a single point $(T,V,n_1,\cdots)$ where C_V is infinite, and then generating a curve by increasing all the extensive variables by the same factor, the temperature remaining constant. Since the n_j' do not exist in this case, our considerations do not apply.

Let us next consider the heat capacity of a multicomponent system in which certain intensive variables are held constant. Let $G(T,n_0,\cdots n_q,\mu_{q+1},\cdots\mu_m)$ be the appropriate "free energy" for which

$$\begin{aligned} \mu_j &= \partial G/\partial n_j, & j&=0,1,\cdots,q \\ n_i &= -\partial G/\partial \mu_i, & i&=q+1,q+2,\cdots,m \\ S &= -\partial G/\partial T. \end{aligned} \tag{3.12}$$

The quantities held constant in partial derivatives are among the arguments of G. We shall assume that one of the n_l, not necessarily n_0, is equal to V, and the corresponding μ_l is equal to $-p$.

Consider a hyperplane in the space of variables obtained by setting all the μ_i for $q+1 \leq i \leq m$ equal to fixed constants. Along a differentiable curve

$$\Gamma = \{n_0(T), n_1(T), \cdots, n_q(T)\} \tag{3.13}$$

lying *within* this hyperplane we may express the total temperature derivatives of S and μ_j for $0 \leq j \leq q$ by means of (3.4) and (3.5), provided it is understood that the upper limit on the summations is q, not m. Both (3.6) and (3.7) are valid when both j and k lie between 0 and q and, with the same restriction, (3.8) holds with F replaced by G. Thus we obtain the desired result:

$$S'+\sum_{j=0}^{q}\mu_j'n_j' \geq \left(\frac{\partial S}{\partial T}\right)_{n_0\cdots n_q\mu_{q+1}\cdots\mu_m} \tag{3.14}$$

It must be emphasized that $\mu_{q+1}, \mu_{q+2}, \cdots, \mu_m$ are all *strictly constant* along the curve Γ to which the derivatives on the left side of (3.14) refer, and there is no such restriction in (3.9). The chemical potentials μ_k for $k>q$ are thus in a sense redundant; they are held constant on both sides of the inequality (3.14), which does not, therefore, represent much of an advance over (3.9). Nonetheless, it seems that (3.14) may be valuable in certain applications. In particular, if we let $p=-\mu_m$, that is, include pressure among the "redundant" variables, then (3.14) gives a bound on the heat capacity at constant pressure C_p along a curve for which p has a fixed value.

The generalization of (2.14) to multicomponent systems may be carried out in close analogy with (3.1)–(3.9). Let $H(p,S,n_1,\cdots,n_m)$ be the enthalpy for a system containing $n_1, n_2, \cdots, n_m$ moles of components $1, 2, \cdots, m$. We may write

$$V=\partial H/\partial p, \tag{3.15}$$

$$\mu_j=\partial H/\partial n_j, \tag{3.16}$$

where (3.16) holds also for $j=0$ if we employ the convention

$$n_0=S, \quad \mu_0=T. \tag{3.17}$$

The quantities held constant in taking partial derivatives are always among the arguments of H given above.

Let

$$\Delta=\{S(p),n_1(p),\cdots,n_m(p)\}$$

be a differentiable curve in our variable space, and let a prime denote the total *pressure* derivative (not temperature) along this curve. With suitable continuity conditions, we may write

$$V'=\frac{\partial V}{\partial p}+\sum_{j=0}^{m}\left(\frac{\partial V}{\partial n_j}\right)n_j', \tag{3.18}$$

$$\mu_j'=\frac{\partial \mu_j}{\partial p}+\sum_k\left(\frac{\partial \mu_j}{\partial n_k}\right)n_k', \tag{3.19}$$

which, combined with the aid of the Maxwell relations [see (3.15) and (3.16)]

$$\partial V/\partial n_j=\partial\mu_j/\partial p, \tag{3.20}$$

yield the result

$$-V'+\sum_j\mu_j'n_j'=-\frac{\partial V}{\partial p}+\sum_{jk}n_j'n_k'\frac{\partial\mu_j}{\partial n_k}. \tag{3.21}$$

The second variation of H at constant pressure is non-negative and we conclude, in analogy with (3.8), that the last term in (3.21) is non-negative. Thus

$$-\frac{dV}{dp}+\sum_{j=0}^{m}\frac{d\mu_j}{dp}\frac{dn_j}{dp}\geq-\left(\frac{\partial V}{\partial p}\right)_{S,n_i}=VK_S, \quad (3.22)$$

and the analog of (3.14) may also be obtained without difficulty.

IV. APPLICATIONS

A. λ Transition in Liquid Helium

Since dp/dT is finite for the λ transition curve separating normal and superfluid phases in pure He^4, we would expect C_V to be finite even if (as is often assumed) C_p becomes infinite. This result is well known; for instance, the analysis of Buckingham and Fairbank[12] suggests that (2.5), and consequently (2.6), become equalities on the λ line. However, the maximum value of C_V is so large (at least for pressures near the vapor pressure) that it appears to be experimentally inaccessible.[13]

In He^3-He^4 mixtures the composition provides an additional variable, so that the boundary separating superfluid and normal phases is a surface rather than a line. The intersection of this surface with a plane of constant pressure is a line along which we may apply the results of Sec. III. In particular, if pressure is considered a redundant variable, say, equal to μ_m, then (3.14) provides an upper bound on C_{px}, the heat capacity at constant pressure and composition. We would not, therefore, expect this heat capacity to diverge along a finite section of the phase-transition line in a constant pressure plane, though it might diverge at special points such as the limit of composition corresponding to pure He^4. Rice[14] has already pointed out that one should expect C_{px} to be finite, and has made the interesting suggestion—which is neither required nor ruled out by thermodynamics alone—that C_{px} might diverge at the temperature below which the second-order transition separating the normal and superfluid becomes first-order.[15]

B. Plait Points and Critical Points

A pure fluid has a unique liquid-vapor critical point in the p-T or n-T plane ($n=N/V$ is the density). In a binary mixture, on the other hand, the composition provides an additional variable, and one finds, in general, a locus of critical points in the n_1-n_2-T or p-x-T space [$x=N_1/(N_1+N_2)$].

In the simplest case, where the liquids are completely miscible, this locus may be a smooth curve joining the liquid-vapor critical points of the pure components[16] along which the results of Sec. III should apply. We therefore expect that $C_{V,x}$ and $K_{S,x}$ will not diverge along a finite portion of such a curve. Experiments on air and impure N_2 suggest that $C_{V,x}$ has a finite cusp along the critical-point curve of the system N_2-O_2.[17] [*Note added in proof.* J. S. Rowlinson has pointed out to us that the intersection of an azeotropic line with the critical-point curve provides a unique point on the curve which is an excellent candidate for an infinite C_V, since the behavior of an azeotrope is in many ways analogous to that of a pure fluid.]

In addition to the liquid-vapor critical-point curve, a two-component solution can have a liquid miscibility gap with a locus of consolute points at which two liquid phases in equilibrium become identical. These consolute points lie on a curve in n_1-n_2-T space, which may or may not intersect the liquid-vapor critical-point curve.[18] (If these curves do intersect, then the distinction between liquid-vapor and liquid-liquid equilibrium may cease to be meaningful.) In either case, provided that the curve $\{n_1(T), n_2(T)\}$ is twice differentiable, the results of Sec. III should apply, and so we expect that $C_{V,x}$ and $K_{S,x}$ will again be finite, except possibly at isolated points on the curve.

This conclusion is particularly interesting, because the usual Ising magnet or lattice-gas model can also be interpreted as a model of a binary liquid mixture with a miscibility gap,[1] and, when so interpreted, it predicts an *infinite* $C_{V,x}$ at the consolute point. When used as a model of a binary liquid mixture, however, the ordinary lattice-gas model does *not* include density as a variable, since every site of the lattice is occupied by a molecule of one species or the other. As a consequence, there is a unique critical point instead of a curve, and an infinity in $C_{V,x}$ at this point is not ruled out by our considerations.

On the other hand, a decorated lattice model of a binary mixture in which density *does* play a role has recently been investigated by Widom,[19] and extended by Clark[8] and by Neece.[20] This model is closely related to that of Syozi, discussed in Sec. IV C. Clark finds a miscibility gap in n_1-n_2-T space with a consolute-point curve (or plait-point curve) which passes through a maximum temperature. He finds that $C_{V,x}$ has a finite cusp at every consolute point except the one at the maximum temperature, for which $n_2'(T)=\infty$, and at which C_V diverges. This, of course, agrees precisely with the results of Sec. III. In a similar model investigated

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[12] M. J. Buckingham and W. M. Fairbank, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Co., Amsterdam, 1961), Vol. III, p. 80.

[13] K. C. Lee and R. D. Puff, Phys. Rev. **158**, 170 (1967); O. K. Rice, *ibid.* **153**, 275 (1967).

[14] O. K. Rice, Phys. Rev. Letters **19**, 295 (1967).

[15] E. H. Graf, D. M. Lee, and J. D. Reppy, Phys. Rev. Letters **19**, 417 (1967).

[16] John E. Ricci, *The Phase Rule and Heterogeneous Equilibrium* (D. Van Nostrand, Inc., New York, 1951), p. 56.

[17] Yu. R. Chaskin, V. G. Gorbunova, and A. V. Voronel, Zh. Eksperim. i Teor. Fiz. **49**, 433 (1965) [English transl.: Soviet Phys.—JETP **22**, 304 (1966)].

[18] See Ref. 16, Chap. 8; also J. S. Rowlinson, *Liquids and Liquid Mixtures* (Butterworths Scientific Publications, Ltd., London, 1959), Sec. 6.9.

[19] B. Widom, J. Chem. Phys. **46**, 3324 (1967).

[20] G. Neece, J. Chem. Phys. **47**, 4112 (1967).

by Clark and Neece,[21] the curve of consolute points has, as a natural end point, the consolute point obtained from the ordinary lattice gas, mentioned above. Here also, $C_{V,x}$ has a finite cusp at all the consolute points except the limiting one.

On the basis of our analysis in Sec. III, this behavior, at least insofar as C_V remains finite along (most of) the consolute-point curve, should be a quite general feature in multicomponent systems, and is not specifically related to the decorated lattice models. Thus we can with confidence rule out a locus of infinite $C_{V,x}$ in another model investigated by Wheeler,[22] even though the exact behavior of C_V is not known and would probably be very difficult to obtain.

Experimental measurements of the heat capacities of binary mixtures near the consolute point have been made, but are not sufficiently accurate to distinguish between a weak divergence and a finite cusp.[23] What is measured in practice is the heat capacity of a sealed tube containing the immiscible liquids in the presence of vapor, in the neighborhood of the liquid-liquid consolute point. The presence of vapor places an additional constraint on the system, and singles out a *unique* consolute point which is, in fact, an endpoint of the consolute-point curve. Because of this uniqueness, our results do not exclude the possibility of a divergent $C_{V,x}$ at this point. Although the measurement is made at constant volume, presumably the heat capacity measured is closer to $C_{p,x}$ of the liquids alone than to $C_{V,x}$ of the liquids alone, because the vapor pressure of the liquids does not change too rapidly. The measurement of a constant-volume heat capacity of a liquid mixture with no vapor present will be difficult experimentally because $(\partial p/\partial T)_{V,x}$ is large for liquids.

In a three-component solution there is still another composition variable, and the locus of critical points becomes, in general, a surface. In discussing the behavior of three-component systems, it is customary to consider the intersection of this surface with one of constant pressure, producing a curve in the x_1x_2T space, called the plait-point curve, along which the results of Sec. III apply. Since the pressure is strictly constant, we expect $C_{p,x}$ and $K_{T,x}$ as well as $C_{V,x}$ and $K_{S,x}$ to be finite along these curves. There do not yet exist accurate determinations of heat capacities or compressibilities near the plait-point curve for three-component solutions.

Both in the three-component case, above, and in two-component systems in which the consolute-point and critical-point curves intersect, it frequently happens that the critical locus passes through a maximum or minimum temperature.[18,24] When this happens, the bounds on C_V and/or C_p diverge, and, in analogy with Clark's results, we expect that C_V (and/or C_p) may diverge at this point.

In view of the interest in critical-point behavior in pure fluids, we would like to point out that the "infinite" heat capacities which are suggested by recent experiments should, in principle at least, become finite upon the addition of impurities to a sample. One assumes that a constant volume-and-composition heat capacity is being measured, and, since the impurity concentration is a new variable (or a new set of variables), there will be a curve (or surface) of critical points along which the results of Sec. III apply. Whether or not this is important in practice depends on the magnitude of the bound (3.9) in particular cases, and we have not attempted to make any estimates. A number of experimental problems such as the time required to reach equilibrium, presence of gravitational fields, and finite temperature resolution of the apparatus will serve to "round off" a heat-capacity spike and may well be more important than impurities for measurements made to date.

C. Dilute Ferromagnets

Certain modifications of the Ising model are known to lead to finite heat capacities at a point where the model undergoes a second-order phase transition. Let us consider Syozi's model of a dilute ferromagnet, a particular case of a decorated Ising model. For our purposes the details are unimportant; we need only note that in addition to ordinary Ising spins, Syozi introduces on special sites additional operators σ_i which can take the value 0, interpreted as an "unoccupied" site, in addition to the values ±1 (understood as a site "occupied" with an "ordinary" Ising spin). The total number of special sites which are occupied is given by

$$\mathcal{P}=\sum_i \sigma_i^2. \tag{4.1}$$

If $\mathcal{H}_0$ is the Hamiltonian, a free energy $F(T,\mu)$ may be defined through the relation

$$e^{-\beta F}=\mathrm{Tr}\{\exp[-\beta(\mathcal{H}_0-\mu\mathcal{P})]\}, \tag{4.2}$$

where Tr stands for trace, and μ is a chemical potential (Syozi uses the symbol ξ for $\beta\mu$) which is adjusted, as the temperature varies, to hold the thermal average of $\mathcal{P}$ fixed. The model possesses a critical point at which the heat capacity (in zero magnetic field) possesses a finite cusp. In the limit of 100% occupancy of the special sites, the heat capacity diverges to infinity.

We have here a situation very analogous to the constant-magnetization heat capacity in (2.17). By a Legendre transformation on F one obtains another free energy $A(T,\mathcal{P})$ with the properties (see Appendix)

$$S=-(\partial A/\partial T)_{\mathcal{P}},\quad \mu=(\partial A/\partial\mathcal{P})_T, \tag{4.3}$$

$$(\partial\mu/\partial\mathcal{P})_T\geq 0. \tag{4.4}$$

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[21] R. K. Clark and G. Neece, J. Chem. Phys. (to be published).

[22] J. C. Wheeler (to be published).

[23] H. Schmidt, G. Jura, and J. H. Hildebrand, J. Phys. Chem. **63**, 297 (1959); Kh. Amirkhanov, I. G. Gurvich, and É. M. Matizen, Dokl. Akad. Nauk (SSSR) **100**, 735 (1955).

[24] See Ref. 16, Chap. 10.

The obvious analogy with (2.15) and (2.16) allows us to write down the analog of (2.17) immediately:

$$\frac{dS}{dT}+\frac{d\mu}{dT}\frac{d\mathcal{P}}{dT}\geq\frac{C_{\mathcal{P}}}{T}. \tag{4.5}$$

Explicit calculation shows that the locus of critical points in the $\mathcal{P}$-T plane is a smooth curve with $d\mathcal{P}/dT$ finite or zero, so that along this curve we expect $C_{\mathcal{P}}$ to remain finite, in agreement with Syozi's result, apart from the special point where $\mathcal{P}$ achieves its maximum (and $\mu\rightarrow\infty$, so that a singularity is not surprising).

Our thermodynamic arguments make possible reasonable inferences about the behavior of analogous models for which closed-form solutions are not now available. If one made *every* site in an Ising model a "special" site, rather than just the decorated sites, one would again expect a finite heat capacity apart from 100% occupancy. There is no similar restriction on the heat capacity at constant μ (rather than $\mathcal{P}$), and in Syozi's model one finds that this diverges.

Brout[25] has pointed out that a physically more realistic model of a dilute ferromagnet is one in which the vacant sites are fixed in position, or "frozen in," since the processes leading to relocation of atoms in magnetic crystals are comparatively slow. Syozi's model differs from Brout's in that while the average concentration of occupied sites is fixed, the detailed features of the distribution may depend on temperature; e.g., the locations of occupied sites are correlated in a way which depends on temperature. We are unable to apply our results to Brout's model since we have no reason to believe that the free energy as a function of concentration has the required convexity properties. One might hope to make Syozi's model closer to Brout's by the device of introducing additional chemical potentials to regulate the pair correlations and higher-order correlations between occupied sites. As long as the number of such potentials remains finite, one can use our results in Sec. III to place bounds on the heat capacity at constant $\mathcal{P}$ and constant correlations. However, Brout's model is obtained in a strict sense only after introducing an infinite number of such potentials, which makes our argument inapplicable. (It does *not* imply that Brout's model would necessarily show an infinite capacity, but the question is left open.)

D. Spherical Model

In the spherical model[7] the "spins" σ_i may vary continuously from $-\infty$ to $+\infty$. In addition to the Hamiltonian

$$\mathcal{H}=-\sum_{i<j}J_{ij}\sigma_i\sigma_j, \tag{4.6}$$

a "spherical constraint" is introduced by requiring that

$$\mathcal{N}=\sum_i\sigma_i^2 \tag{4.7}$$

be a constant independent of temperature. (It is customary to let $\mathcal{N}=N$, the number of lattice sites.) We shall require that the thermal average $\langle\mathcal{N}\rangle$, which we shall also denote by $\mathcal{N}$, be constant, that is, we shall employ the "mean spherical model," which appears to give the same thermodynamic results as the "ordinary" spherical model.[26]

Let the free energy $F(T,\mu)$ be defined through the equation

$$e^{-\beta F}=\int d\sigma_1\int d\sigma_2\cdots\int d\sigma_N\exp[-\beta(\mathcal{H}-\mu\mathcal{N})]. \tag{4.8}$$

By a Legendre transformation one introduces

$$A(T,\mathcal{N})=F+\mu\mathcal{N} \tag{4.9}$$

with precisely the properties given in (4.3) and (4.4), but with $\mathcal{P}$ replaced by $\mathcal{N}$. The result which corresponds to (4.5) is

$$\frac{dS}{dT}+\frac{d\mu}{dT}\frac{d\mathcal{N}}{dT}\geq\frac{C_{\mathcal{N}}}{T}.$$

Since $C_{\mathcal{N}}$ is always "the heat capacity" computed for this model, we naturally expect it to be bounded if the phase-boundary curve, or locus of critical points, is well behaved in the $\mathcal{N}$-T plane. (It is a straight line with finite slope.)

Our argument is applicable not only in the usual spherical model, where the result of a finite heat capacity is known by explicit calculation, but also to Langer's modified spherical model[27] in which an additional interaction term serves to remedy some of the "unphysical" features of the ordinary spherical model. Langer was unable to work out the details of this model near its critical point, but our thermodynamic argument indicates that the heat capacity almost certainly remains finite, as long as the spherical constraint is maintained.

E. Thompson's Decorated Ising Models

Thompson[6] has calculated the properties of a decorated two-dimensional Ising model in which, in addition to ordinary Ising spins, continuum spins similar to those in the spherical model are placed on special sites. He found that (a) if each continuum spin has a normal distribution, the heat capacity of the entire system has a logarithmic divergence, like that of the standard Ising model. If, however, (b) the continuum spins satisfy a spherical constraint [see (4.7)], the heat

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[25] R. Brout, Phys. Rev. **115**, 824 (1959).

[26] H. W. Lewis and G. H. Wannier, Phys. Rev. **88**, 682 (1952); C. C. Yan and G. H. Wannier, J. Math. Phys. **6**, 1833 (1965).

[27] J. S. Langer, Phys. Rev. **137**, A1531 (1965).

capacity has a finite cusp at the critical point. It is clear from the discussion in Sec. IV D that our thermodynamic reasoning would supply an upper bound for the heat capacity in (b), and we would expect it to be finite apart from very special circumstances. There is no analogous constraint in (a), and thus nothing in our arguments which would rule out an infinite singularity.

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APPENDIX: STABILITY CONDITIONS FROM STATISTICAL CALCULATIONS

Let $\mathcal{H}$ be the Hamiltonian of a system and $\mathfrak{M}$ the operator corresponding to some extensive variable. We define a free energy $F(T,\mu)$ through the relation

$$e^{-\beta F}=\mathrm{Tr}[\exp-\beta(\mathcal{H}-\mu\mathfrak{M})], \tag{A1}$$

where $\beta=1/kT$ is the inverse temperature, and Tr denotes either the quantum-mechanical trace or the classical phase space integral. The entropy is given by

$$S=-(\partial F/\partial T)_\mu, \tag{A2}$$

while differentiation inside the trace yields

$$\langle\mathfrak{M}\rangle=\frac{\mathrm{Tr}[\mathfrak{M}e^{-\beta\mathcal{G}}]}{\mathrm{Tr}[e^{-\beta\mathcal{G}}]}=-\left(\frac{\partial F}{\partial\mu}\right)_T. \tag{A3}$$

The angular brackets $\langle\ \rangle$ denote the customary thermal average, and we employ the abbreviation

$$\mathcal{G}=\mathcal{H}-\mu\mathfrak{M}. \tag{A4}$$

Theorem: For positive temperatures, F is a convex-upwards, or concave, function of μ and T. That is, the matrix of second partial derivatives is negative or, given any real numbers x, y, then

$$x^2\frac{\partial^2F}{\partial T^2}+2xy\frac{\partial^2F}{\partial T\partial\mu}+y^2\frac{\partial^2F}{\partial\mu^2}\leq 0. \tag{A5}$$

When $\mathcal{H}$ and $\mathfrak{M}$ commute—this includes the examples discussed in the body of the paper—one may verify the theorem by differentiating inside the trace in (A1) and showing that the quadratic form is equal to

$$-\beta\langle[k\beta x(\mathcal{G}-\langle\mathcal{G}\rangle)+y(\mathfrak{M}-\langle\mathfrak{M}\rangle)]^2\rangle, \tag{A6}$$

which, since it is minus the average of the square of a real quantity (or a Hermitian operator), cannot be positive. The theorem also holds when $\mathfrak{M}$ and $\mathcal{H}$ do not commute, though the proof is more difficult.[28] For our present purposes we need only the results obtained from setting first x and then y equal to zero in (A5). (We shall use $\mathfrak{M}$ in place of $\langle\mathfrak{M}\rangle$.)

$$(\partial\mathfrak{M}/\partial\mu)_T=-(\partial^2F/\partial\mu^2)_T\geq 0, \tag{A7}$$

$$(\partial S/\partial T)_\mu=-(\partial^2F/\partial T^2)_\mu\geq 0. \tag{A8}$$

In general, one expects these to hold as strict inequalities unless μ or T achieves one of its limiting values ($\pm\infty$, 0 or $+\infty$, respectively), or possibly at a phase transition. One can introduce additional potentials by Legendre transformations; for example,

$$A(T,\mathfrak{M})=F+\mu\mathfrak{M} \tag{A9}$$

has the properties

$$S=-(\partial A/\partial T)_{\mathfrak{M}},\quad \mu=(\partial A/\partial\mathfrak{M})_T. \tag{A10}$$

Note that the arguments leading to (A7) and (A8) do not depend on whether $\mathfrak{M}$ is the magnetization and μ the magnetic field, in which case (A7) and (A8) correspond to (2.16) and (2.19), respectively, or $\mathfrak{M}$ is the concentration $\mathcal{P}$ in Syozi's model [compare (A1) and (4.2)] or $\mathfrak{M}$ is the parameter $\mathfrak{N}$ in the spherical model [see (4.8)]. In all cases, the inequality (A7) permits us to place an upper bound on the heat capacity.

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[28] D. Ruelle, Helv. Phys. Acta **36**, 789 (1963); R. B. Griffiths, J. Math. Phys. **5**, 1215 (1964).