

## Thermodynamic Functions for Fluids and Ferromagnets near the Critical Point\*

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Modifications to the classical analysis of equilibrium thermodynamic properties near the liquid-vapor critical point are proposed in order to allow for infinite singularities in  $C_v$ , nonclassical behavior of the coexistence curve, etc. A requirement that all thermodynamic functions for the homogeneous fluid be analytic is retained and turns out to be necessary in order to justify Maxwell's prescription for modifying the Van der Waals equation of state. A corresponding analysis is presented for ferromagnets near the Curie point. Widom's proposed "homogeneous" equation of state is discussed with special attention to requirements of thermodynamic stability. Several examples of such homogeneous functions are constructed, including cases where the critical indices agree (very nearly, at least) with current estimates for two- and three-dimensional Ising models.

### I. INTRODUCTION

FOR many years the Van der Waals and Weiss molecular-field equations of state have been prototypes for a "classical" thermodynamic discussion of the critical point of a liquid-vapor transition, and the Curie point of a (slightly idealized) ferromagnet, respectively. This classical analysis has come under attack from two sides.<sup>1</sup> On the one hand, experimental work of increasing precision—including, but not limited to, heat-capacity measurements<sup>2</sup>—suggests that "anomalies" near the critical point not present in the classical treatment may be the rule rather than the exception in pure materials. On the other hand, recent theoretical work has shown that the classical results arise in many statistical models where the range of attractive forces is permitted to become infinite,<sup>3</sup> whereas for several models with (presumably more realistic) finite-range forces, the scant evidence<sup>1,4</sup> presently available suggests "anomalies" similar to those found in nature.<sup>5</sup> The logarithmic heat-capacity singularity in two-dimensional Ising ferromagnets is well known.<sup>6</sup> Although exact results are not available for more realistic three-dimensional Ising

models, the powerful methods of series extrapolation<sup>7</sup>—which may, with some justification, be called "numerical" experiments—have provided suggestive, if not conclusive, evidence for similar "anomalies" in these systems, as also in the three-dimensional Heisenberg ferromagnet.<sup>8</sup>

Thus, some extensions or changes in the classical thermodynamic analysis seem necessary. But on what assumptions should a new approach be based? Section II provides our answer to this question in a set of rules or hypotheses for the behavior of thermodynamic variables near the critical point. While making no claim to originality—most of the rules have been stated explicitly or used implicitly by other workers—we feel that a concise, detailed statement of principles will help avoid confusion and show explicitly in what respect the "new" and "classical" approaches differ.

As an interesting sideline we examine, in Appendix B, the Maxwell construction applied to the Van der Waals equation of state in light of the criteria in Sec. II. This construction is justified, from our point of view, not on the basis of the usual "equal area" or "double tangent construction" arguments, but only because of a very strong assumption of analytic behavior for the thermodynamic variables of the homogeneous fluid.

In Sec. III we consider a specific class of "homogeneous" functions proposed by Widom<sup>9</sup> and the conditions they must satisfy to conform with the criteria of Sec. II. They may in some sense be the simplest extensions of the classical functions. At least it is interesting that analogous or identical functional forms, or specific examples of such functions, have been proposed independently by Helfand<sup>10</sup> (two-dimensional Ising model); Domb and Hunter<sup>11</sup> (magnets); Patashinskii and

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<sup>1</sup> For a summary and reference to much of the pertinent experimental and theoretical work, see M. E. Fisher, *J. Math. Phys.* **5**, 944 (1964), and his article in *Lectures in Theoretical Physics*, edited by W. E. Brittin (University of Colorado Press, Boulder, Colorado, 1965), Vol. VII C, p. 1; C. Domb and A. R. Miedema, *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1964), Vol. IV, p. 296.

<sup>2</sup> Recent work includes measurements by A. V. Voronel', V. G. Gorbunova, Yu. R. Chashkin, and V. V. Shchekochikhina, *Zh. Eksperim. i Teor. Fiz.* **50**, 897 (1966) [English transl.: *Soviet Phys.—JETP* **23**, 597 (1966)] on nitrogen; and A. R. Miedema, R. F. Wielinga, and W. J. Huiskamp, *Phys. Letters* **17**, 87 (1965) on the ferromagnet  $\text{CuK}_2\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ .

<sup>3</sup> G. A. Baker, Jr., *Phys. Rev.* **122**, 1477 (1961); E. Helfand, *J. Math. Phys.* **5**, 127 (1964); M. Kac, G. E. Uhlenbeck, and P. C. Hemmer, *ibid.* **4**, 216 (1963); J. L. Lebowitz and O. Penrose, *ibid.* **7**, 98 (1966); E. Lieb, *ibid.* **7**, 1016 (1966).

<sup>4</sup> Unfortunately, most of the standard approximation schemes become unreliable near the critical point. See M. E. Fisher, Ref. 1.

<sup>5</sup> An important exception is the spherical model discussed by T. H. Berlin and M. Kac, *Phys. Rev.* **86**, 821 (1952). Reasons for the exceptional behavior have been discussed by J. S. Langer, *ibid.* **137**, A1531 (1965).

<sup>6</sup> L. Onsager, *Phys. Rev.* **65**, 117 (1944).

<sup>7</sup> C. Domb, *Advan. Phys.* **9**, 149 (1960); M. E. Fisher, *J. Math. Phys.* **4**, 278 (1963).

<sup>8</sup> G. A. Baker, Jr., H. E. Gilbert, J. Eve, and G. S. Rushbrooke, *Phys. Letters* **20**, 146 (1966); **22**, 269 (1966).

<sup>9</sup> B. Widom, *J. Chem. Phys.* **43**, 3898 (1965).

<sup>10</sup> E. Helfand, paper presented at a meeting of the American Physical Society, March, 1965 (unpublished).

<sup>11</sup> C. Domb and D. L. Hunter, *Proc. Phys. Soc. (London)* **86**, 1147 (1965).

Pokrovskii<sup>12</sup> (magnets); Azbel', Voronel', and Giterman<sup>13</sup> (fluids); and possibly others of whose work the author is unaware. The homogeneous functions are in a sense "derived" in Refs. 11, 12, and in a paper by Kadanoff<sup>14</sup> (whose assumption of unequal values for critical indices above and below  $T_c$  appears to be thermodynamically inconsistent—see Appendix A). They are implicit in a model used by Essam and Fisher.<sup>15</sup> The essential similarity of all these proposals is discussed in Appendix A. [Note added in proof. Recently J. S. Kouvel and D. S. Rodbell [Phys. Rev. Letters **18**, 215 (1967); J. Appl. Phys. **38**, 979 (1967)] have used homogeneous functions to fit experimental magnetization data above the Curie points of  $\text{CrO}_2$  and Ni. M. S. Green, M. Vicentni-Missoni, and J. M. H. Levelt-Sengers [Phys. Rev. Letters (to be published)] have analyzed data for the equation of state of several fluids in terms of homogeneous functions. D. L. Elwell and H. Meyer [Bull. Am. Phys. Soc. **12**, 95 (1967); and (private communication)] have a similar analysis for their data for  $\text{He}^3$ .]

Our own formulation (Sec. III) rests heavily on the work of Widom, but differs in the fact that we use notation appropriate to magnets rather than fluids. We prefer to use "magnetic language" because Widom's proposal assumes a symmetry only approximately fulfilled in real fluids but exact for magnets, and also because when comparing results with "experiment" we use known or estimated values for Ising models. Though these values may be stated either in "lattice-gas" or "magnetic" language, the latter is most common in the literature.

Actual examples of functions for several values of the critical indices are found in Sec. IV. The reader who wishes to use these as first approximations for fluid systems is referred to Appendix A for the appropriate thermodynamic isomorphism.

It should be clear that the purely thermodynamic approach employed in this paper cannot in and of itself tell us the behavior of various functions near the critical point. Rather, it provides correlations among data obtained from experiments, or from statistical calculations, and checks on their consistency. The value of thermodynamics for checking consistency has already been demonstrated.<sup>16,17</sup>

The functions discussed below may be of value for

<sup>12</sup> A. Z. Patashinskii and V. L. Pokrovskii, Zh. Eksperim. i Teor. Fiz. **50**, 439 (1966) [English transl.: Soviet Phys.—JETP **23**, 292 (1966)].

<sup>13</sup> (a) M. Ya. Azbel', A. V. Voronel', and M. Sh. Giterman, Zh. Eksperim. i Teor. Fiz. **46**, 673 (1964) [English transl.: Soviet Phys.—JETP **19**, 457 (1964)]. This paper is, unfortunately, too brief, and some important quantities are left undefined. The authors' intentions become clearer in the more extensive article, (b) M. Sh. Giterman, Zh. Fiz. Khim. **39**, 989 (1965) [English transl.: Russian J. Phys. Chem. **39**, 522 (1965)].

<sup>14</sup> L. P. Kadanoff, Physics **2**, 263 (1966).

<sup>15</sup> J. W. Essam and M. E. Fisher, J. Chem. Phys. **38**, 802 (1963).

<sup>16</sup> G. S. Rushbrooke, J. Chem. Phys. **39**, 842 (1963); R. B. Griffiths, Phys. Rev. Letters **14**, 623 (1965).

<sup>17</sup> R. B. Griffiths, J. Chem. Phys. **43**, 1958 (1965).

interpolation between different experimental or theoretical results. This purpose is best fulfilled if the functions themselves are not taken too seriously. In particular, singularities in the complex plane are chosen for convenience and not because of any fundamental significance. We have sought to find concrete examples of thermodynamically consistent and (in the sense of Sec. II) analytic functions possessing nonclassical singularities near the critical point; we cannot, and do not, claim they are exact for any real or model systems. In the final analysis, the advance in our theoretical understanding of the critical point awaits further developments in statistical mechanics.

## II. REQUIREMENTS ON THERMODYNAMIC FUNCTIONS NEAR THE CRITICAL POINT

### A. Fluids

The equilibrium thermodynamic properties of a pure single-component fluid are completely determined<sup>18</sup> by a knowledge of the Helmholtz free energy per unit volume  $a(\rho, T)$  as a function of density  $\rho$  and temperature  $T$ . In particular, the chemical potential  $\mu$  and entropy per unit volume  $s$  are given by

$$\mu = (\partial a / \partial \rho)_T, \quad s = -(\partial a / \partial T)_\rho. \quad (1)$$

For an arbitrary function  $a$  these derivatives may not exist, so our first hypothesis is:

C1. The functions  $a$ ,  $\mu$ , and  $s$  exist and are continuous functions of  $\rho$  and  $T$  everywhere in the vicinity of the critical point.

Near the critical point the  $\rho, T$  plane may be divided into two regions by a continuous curve, which we shall call the "phase boundary," shown schematically in Fig. 1. Below this curve we have the inhomogeneous or two-phase region where both liquid and vapor phases are present in equilibrium, and  $\rho$  denotes the average density of fluid in the container. Above this curve lies the homogeneous or one-phase region.

In the two-phase (inhomogeneous) region, the free energy will be the sum of the free energies of the liquid and vapor phases present, plus corrections due to surfaces separating the two phases and at the container walls. Provided the container is not too small, the surface free energies are negligible, so we have:

C2. For fixed  $T$ ,  $a$  is a linear function of  $\rho$  in the two-phase region.

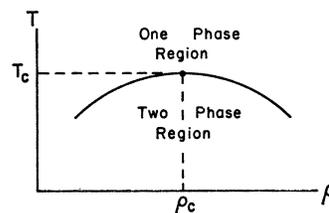


FIG. 1. Phase boundary in the  $\rho, T$  plane near the critical point of a fluid.

<sup>18</sup> See, for example, H. B. Callen, *Thermodynamics* (John Wiley & Sons, Inc., New York, 1960), Chap. 5.

Note that we are excluding from consideration metastable states;  $a(\rho, T)$  is the single-valued function for the equilibrium state, whether homogeneous or inhomogeneous. As far as we know, C1 and C2 are universally assumed in analyzing the liquid-vapor phase transition; did they not hold, one would be dealing with a different type of transition. Their content is not trivial, however. For example, the equality of pressure  $p = \mu\rho - a$  in the liquid and vapor phases, and also the equality of  $\mu$ , follows at once from C1 and C2.

The next two "convexity" conditions express the stability of the fluid.

C3. For fixed  $T$ ,  $a(\rho, T)$  is a convex-downwards function of  $\rho$ ; that is,  $\mu$  is monotone nondecreasing in  $\rho$  at constant  $T$ .

C4. For fixed  $\rho$ ,  $a(\rho, T)$  is a convex-upwards function of  $T$ ; that is,  $s$  is monotone nondecreasing in  $T$  at constant  $\rho$ .

Stated in more familiar terms, C3 means that the isothermal compressibility is never negative, and C4 the same for the constant-volume heat capacity. We prefer to express stability in terms of convex functions<sup>19</sup> since there is then no possible ambiguity in regions where phase transitions take place. Not only do C3 and C4 follow from the usual thermodynamic arguments, but rigorous proofs exist that the conditions are satisfied for a large class of fairly realistic statistical models.<sup>20</sup>

The final two hypotheses, unlike those already discussed, follow neither from thermodynamic requirements nor (excluding special cases) from statistical calculations and merely reflect the usual aesthetic desire in theoretical science to use functions "as smooth as possible."

C5. The phase boundary (Fig. 1)  $T(\rho)$  is a convex-upwards analytic function of  $\rho$  in the vicinity of the critical point except, perhaps, at  $\rho = \rho_c$ , the unique point where  $T(\rho)$  achieves its maximum.

C6. The free energy  $a(\rho, T)$  is an analytic function of both arguments together everywhere in the vicinity of the critical point, except on the phase boundary.

It may be well to indicate explicitly what is meant by C6. Given any  $(\rho_o, T_o)$  not on the phase boundary, the series

$$a(\rho, T) = \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} a_{jk} (\rho - \rho_o)^j (T - T_o)^k \quad (2)$$

converges for  $|\rho - \rho_o|$  and  $|T - T_o|$  smaller than some positive constants  $\epsilon_\rho$  and  $\epsilon_T$ , respectively, which will depend on  $\rho_o$  and  $T_o$ .

The "analyticity" requirements C5 and C6 represent very strong assumptions and one may well ask how they, and especially C6, differ from the "classical" analysis as

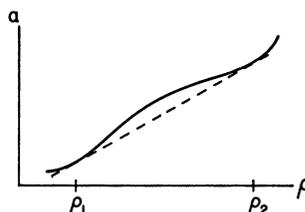


FIG. 2. Double tangent construction. The solid curve shows the prototype free energy  $\tilde{a}(\rho)$  at fixed temperature. The equilibrium free energy  $a$  for  $\rho$  between  $\rho_1$  and  $\rho_2$  is given by the dotted straight line tangent to  $\tilde{a}(\rho)$  at these two densities.

exemplified, for instance, in Rowlinson's treatment.<sup>21</sup> In the latter one constructs a prototype function  $\tilde{a}(\rho, T)$  analytic *everywhere* in the  $\rho, T$  plane near the critical point, but not satisfying C3. The equilibrium  $a(\rho, T)$  is obtained from  $\tilde{a}$  by a "double tangent" construction, illustrated in Fig. 2, in which that portion of  $\tilde{a}$  which lies in the two-phase region is replaced by a function linear in  $\rho$  (at constant  $T$ ). This is equivalent to the well-known "Maxwell construction."

Thus, the classical analysis adds a condition of analyticity of  $\tilde{a}$  (in the two-phase region) which does not explicitly appear in the equilibrium function  $a$ . By contrast, one very practical method of constructing functions satisfying C5 and C6 is to find a prototype function  $\tilde{a}(\rho, T)$  analytic except for branch points and the like in the two-phase region, and then apply the double tangent construction, thus "concealing" the singularities. This additional flexibility in choice of functions appears to be just what we need in order to obtain logarithmic heat capacity singularities at the critical point, etc.

From the thermodynamic viewpoint, the above analysis works equally well using the Helmholtz free energy per mole  $A(v, T)$ , where  $v$  is the molar volume, in place of  $a(\rho, T)$ . One has

$$p = -(\partial A / \partial v)_T; \quad S = -(\partial A / \partial T)_v, \quad (3)$$

where  $S$  is the molar entropy. In hypotheses C1-C6,  $a$  should be replaced by  $A$ ,  $s$  by  $S$ ,  $\rho$  by  $v$ , and  $\mu$  by  $-p$ . There seems no reason to prefer the analysis using  $a$  to that using  $A$ , except that the phase boundary for simple fluids shows more (though by no means complete) symmetry about  $\rho = \rho_c$  in the  $\rho, T$  plane than about  $v = v_c$  in the  $v, T$  plane, where the subscript  $c$  denotes the critical value. For lattice gases<sup>22</sup> it turns out that  $a$  is closely related to the corresponding magnetic free energy, which we discuss next.

## B. Magnets

Let  $A(T, M)$  be the free energy<sup>23</sup> per mole with the properties

$$H = (\partial A / \partial M)_T; \quad S = -(\partial A / \partial T)_M, \quad (4)$$

<sup>21</sup> J. S. Rowlinson, *Liquids and Liquid Mixtures* (Butterworth Scientific Publications, London, 1959), Chap. 3.

<sup>22</sup> T. D. Lee and C. N. Yang, *Phys. Rev.* **87**, 410 (1952).

<sup>23</sup> Unfortunately there seems to be no uniform terminology for magnetic free energies;  $A$  is that free energy for which the relations (4) are satisfied.

<sup>19</sup> An approach equivalent to that used by Gibbs in 1873: *The Collected Works of J. Willard Gibbs* (Yale University Press, New Haven, 1948), pp. 33-54.

<sup>20</sup> D. Ruelle, *Helv. Phys. Acta* **36**, 183 (1963); **36**, 789 (1963); M. E. Fisher, *Arch. Ratl. Mech. Anal.* **17**, 377 (1964).

where we have chosen a particular direction for the external magnetic field  $H$ , and  $M$  is the component of magnetization along that direction. Demagnetizing effects will henceforth be neglected. The reader may suppose either that a long, thin sample is being considered, with  $M$  and  $H$  parallel to the sample axis, or that the long-range part of the dipolar interaction has been "turned off," as in the usual Heisenberg and Ising model ferromagnets.

The curve of spontaneous magnetization  $M_s$  in the  $M, T$  plane near the critical point is shown schematically in Fig. 3. Beneath this phase boundary curve is the "two-phase" or inhomogeneous region in which the sample consists of domains pointed in opposite directions, and above this curve lies the homogeneous or "one-phase" region.

The hypotheses below correspond to C1–C6 in the case of a fluid (part *A*) with the addition of an important symmetry: Time reversal invariance of the Hamiltonian in the absence of a magnetic field means that  $A$  is an even function of  $M$ .

CM1.  $A, H$ , and  $S$  exist and are continuous functions of  $M$  and  $T$  everywhere in the vicinity of the critical (Curie) point ( $M=0$  and  $T=T_c$ ). For fixed  $T$ ,  $H$  is odd and  $A$  and  $S$  are even functions of  $M$ .

CM2. In the two-phase region,  $H$  vanishes and thus, for fixed  $T$ ,  $A$  is constant, independent of  $M$ .

CM3. For fixed  $T$ ,  $A(M, T)$  is convex-downwards in  $M$ , that is,  $H$  is a monotone nondecreasing function of  $M$ .

CM4. For fixed  $M$ ,  $A(M, T)$  is convex-upwards in  $T$ , that is,  $S$  is a monotone nondecreasing function of  $T$ .

CM5. The phase boundary or spontaneous magnetization curve  $T(M)$  is symmetric about  $M=0$ , convex upwards near the critical point, and an analytic function of  $M$  except, perhaps, at  $M=0$ .

CM6.  $A(M, T)$  is an analytic function of both arguments together [compare Eq. (2)] in the vicinity of the critical point except on the phase boundary.

The convexity conditions CM3 and CM4 which correspond, respectively, to the positivity of the constant temperature susceptibility

$$\chi = (\partial M / \partial H)_T \quad (5)$$

and the heat capacity at constant magnetization, rest on less secure grounds than the corresponding conditions for fluids. Diamagnetism does, after all, occur in nature. It can be proved that the conditions are satisfied in the usual Heisenberg and Ising-model ferromagnets.<sup>24</sup>

### C. Equation of State

All the equilibrium thermodynamic variables are determined if  $A(M, T)$  is given. However, a knowledge of the equation of state  $H(M, T)$  together with the phase boundary curve is almost as good near the critical point

<sup>24</sup> R. B. Griffiths, *J. Math. Phys.* **5**, 1215 (1965); *Phys. Rev.* **152**, 240 (1966), Appendix A.

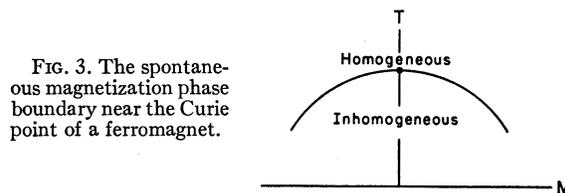


FIG. 3. The spontaneous magnetization phase boundary near the Curie point of a ferromagnet.

if we are only interested in investigating the singularities of thermodynamic variables in this region. Thus, choose some  $M_1 < 0$  near the edge of the region we wish to consider (Fig. 3) and write

$$A(M, T) = A(M_1, T) + \int_{M_1}^M H(M, T) dM. \quad (6)$$

For fixed  $M_1$ ,  $A(M_1, T)$  is an analytic function of temperature by CM6 (provided  $T$  is not too much less than  $T_c$ ), so that  $A$  is determined from  $H$  up to an additive analytic function which cannot influence the form of any singularities.

Hence, one procedure for constructing thermodynamic functions with different sorts of singularities is to search for a suitable  $H(M, T)$ . Certain difficulties in checking conditions CM1–CM6 are, however, more acute in this scheme than if one constructs  $A(M, T)$  directly. Suppose, for example, that  $H(M, T)$  is an analytic function in the one-phase region. If  $T$  is less than  $T_c$  and  $M > 0$  lies on the opposite side of the two-phase region from  $M_1$ , can one be sure that  $A(M, T)$  defined in (6) will join smoothly with  $A(M, T)$  for  $T > T_c$  and define a single analytic function?

An affirmative answer to this question for magnetic systems follows from symmetry considerations, but the analogous problem for fluids, given an equation of state  $\mu(\rho, T)$  or  $p(v, T)$ , is nontrivial. A concrete example, the Van der Waals equation of state, is discussed in Appendix B. It turns out that one can specify a location for the horizontal portion of the isotherm which differs from Maxwell's proposal, and every condition C1 to C6 is satisfied *except* for C6. From this point of view, the Maxwell construction is justified only by a requirement of analyticity.

## III. HOMOGENEOUS FUNCTIONS FOR MAGNETIC SYSTEMS

### A. Notation

In the vicinity of the critical point,  $T = T_c$  and  $M = 0$ , various thermodynamic functions are assumed to have (as a first approximation) the form given in Table I, with

$$t = (T - T_c) / T_c \quad (7)$$

a dimensionless parameter measuring the deviation of temperature from its critical value, and  $M$  the magnetization divided by its saturation value (i.e.,  $M$  becomes one as  $H$  approaches infinity). The critical indices  $\alpha$ ,

TABLE I. Notation for thermodynamic functions for a ferromagnet near the critical point.

Normalized temperature	$t = (T - T_c)/T_c$
Spontaneous magnetization	$M_s \simeq B(-t)^\beta$ for $t < 0$
Heat capacity for $M=0$ : <sup>a</sup>	$C_M \simeq (A'/\alpha')[(-t)^{-\alpha'} - 1]$ for $t < 0$ $\simeq -A' \ln(-t)$ for $\alpha' = 0, t < 0$ $C_M \simeq (A/\alpha)[t^{-\alpha} - 1]$ for $t > 0$ $\simeq -A \ln t$ for $\alpha = 0, t > 0$ $D = \lim_{t \rightarrow 0^+} [C_M(t) - C_M(-t)]$
Critical isotherm:	$H \simeq \Delta M^\delta$ for $t = 0, M > 0$
Isothermal susceptibility <sup>b</sup>	$\chi \simeq \Gamma t^{-\gamma}$ for $t > 0$ $\simeq \Gamma'(-t)^{-\gamma'}$ for $t < 0$

<sup>a</sup> Equal to the heat capacity  $C_H$  for  $H = 0$ .

<sup>b</sup>  $(\partial M / \partial H)_T$  in the limit  $H \rightarrow 0^+$ .

$\alpha', \beta$ , etc., are those used by Fisher<sup>1</sup>; for multiplicative factors we use the corresponding Greek capitals. The special form adopted for  $C_{M=0}$  deserves comment. Since for  $t > 0$ ,

$$\lim_{\alpha \rightarrow 0} \alpha^{-1} [t^{-\alpha} - 1] = -\ln t, \quad (8)$$

the case of a logarithmic heat capacity is included by setting  $\alpha = 0$ . Both in thermal and numerical experiments it seems difficult to distinguish a logarithmic singularity from a small positive value of  $\alpha$  or  $\alpha'$ . We hope the form used in Table I makes  $A$  and  $A'$  slightly less sensitive to this uncertainty. The constants  $\beta$  and  $\delta$  are always assumed to be greater than zero in the following analysis ( $\beta$  cannot exceed 1 without contradicting CM5) and  $\alpha$  is restricted by (19) in part C.

### B. Equation of State

In the one-phase region we assume  $H$  is given by

$$H(M, T) = M |M|^{\delta-1} h(t |M|^{-1/\beta}), \quad (9)$$

where  $h(x)$  is some as yet undetermined function of the

TABLE II. Exponents and coefficients for homogeneous functions.<sup>a</sup>

$\gamma = \gamma' = \beta(\delta - 1)$	$\Delta = h(0)$
$\alpha = \alpha' = 2 - \beta(\delta + 1)$	$\Gamma = \lim_{x \rightarrow \infty} x^\gamma / h(x)$
$B = x_0^{-\beta}$	$\Gamma' = \beta x_0^{\gamma-1} / h'(-x_0)$
$\alpha > 0:$	$A = \alpha \beta T_c^{-1} \int_0^\infty h''(y) y^{\alpha-1} dy$
	$A' = \alpha \beta T_c^{-1} \left\{ \int_{-x_0}^0 h''(y)  y ^{\alpha-1} dy + x_0^{\alpha-1} h'(-x_0) \right\}$
$\alpha = 0:$	$A = A' = \beta T_c^{-1} h''(0)$
	$D = \beta T_c^{-1} \left\{ \frac{-h'(-x_0)}{x_0} + P \int_{-x_0}^\infty \frac{h''(y)}{y} dy \right\}^b$

<sup>a</sup> There are many alternative ways of expressing  $A$  and  $A'$  for  $\alpha > 0$  and  $D$  for  $\alpha = 0$ ; the ones shown here are those we have found most convenient in practice.

<sup>b</sup>  $P$  denotes the Cauchy principal value of the integral.

real variable

$$x = t |M|^{-1/\beta}. \quad (10)$$

By construction,  $H$  changes sign when  $M$  is replaced by  $-M$ , so all the symmetry requirements of Sec. IIB are satisfied. The function (9) is Widom's proposal<sup>9</sup> in a disguised form (see Appendix A), and he has shown that it leads to the relations among critical indices shown in Table II.

The fact that  $H$  vanishes on the phase boundary (conditions CM1, 2), is analytic everywhere else (CM6), and non-negative for  $M \geq 0$  (CM1, 3) leads to some obvious requirements on  $h$ :

H1. Define

$$x_0 = B^{-1/\beta} \quad (11)$$

(with  $B$  and  $\beta$  from Table I). For  $-x_0 < x < \infty$ ,  $h(x)$  is a real, positive, analytic function of  $x$ , and  $h(-x_0)$ , the limit of  $h(x)$  as  $x \rightarrow (-x_0)$ , vanishes.

Condition H1 insures the analytic behavior of  $H$  everywhere in the one-phase region apart from the line  $M = 0, T > T_c$ , which we shall now consider. For  $t > 0$  we have, by CM6, a series

$$H(M, T) = \sum_{n=1}^{\infty} f_n(t) M^{2n-1}, \quad (12)$$

which converges for  $|M|$  less than some  $M_0(t) > 0$ . Let us equate (9) and (12) for  $M > 0$ , replacing  $M$  by  $(t/x)^\beta$  in accord with (10):

$$H = t^{\beta\delta} x^{-\beta\delta} h(x) = \sum_{n=1}^{\infty} f_n(t) t^{(2n-1)\beta} x^{\beta(1-2n)}, \quad (13)$$

where the series on the right converges, in general, only if  $M$  is sufficiently small for a given  $t > 0$ , that is, provided  $x$  is sufficiently large. Since  $t^{-\beta\delta} H$  is a function of  $x$  alone, it is evident that in (13) we must have

$$f_n(t) = \eta_n t^{\beta(1+\delta-2n)} \quad (14)$$

and the following condition applies to  $h(x)$ :

H2. For some finite constant  $R$ ,  $h(x)$  possesses a series expansion

$$h(x) = \sum_{n=1}^{\infty} \eta_n x^{\beta(\delta+1-2n)}, \quad (15)$$

which converges for all  $x$  in the range  $R < x < \infty$ .

Note that the series (15) must be convergent, not merely asymptotic. Condition H2 implies that (12) converges for

$$|M| < (t/R)^\beta, \quad (16)$$

thus insuring the analyticity of  $H(M, T)$  at  $M = 0, T > T_c$ .

The function  $f_1(t)$  in (12) is just the inverse of the "high-temperature" ( $T > T_c$ ) zero-field susceptibility, and by (14) supplies the values of  $\gamma$  and  $\Gamma$  given in Table II. The inverse susceptibility is given in

general by

$$\chi^{-1} = (\partial H / \partial M)_t = M^{\delta-1} [\delta h(x) - \beta^{-1} x h'(x)], \quad (17)$$

and upon letting  $x$  approach  $-x_0$  one obtains  $\gamma'$  and  $\Gamma'$  as shown in Table II. The convexity condition CM3 is equivalent to requiring that  $\chi^{-1}$  be non-negative; thus,

H3. For  $-x_0 < x < \infty$ ,  $h(x)$  satisfies

$$\beta \delta h(x) \geq x h'(x). \quad (18)$$

The second convexity condition, CM4, poses a more difficult problem which we shall discuss in Sec. III D.

### C. The Free Energy

We restrict our discussion to  $\alpha$  (Tables I and II) in the range

$$0 \leq \alpha < 1, \quad (19)$$

where the upper limit serves to insure the continuity of  $S$  (condition CM1). For convenience the cases  $\alpha > 0$  and  $\alpha = 0$  are considered separately.

(a) For  $\alpha > 0$  assume  $A$  has the form

$$A(M, T) = A_o(T) + |M|^{\delta+1} a(t|M|^{-1/\beta}) \quad (20)$$

in the one-phase region, with  $A_o(T)$  an analytic function of the temperature, and  $a(x)$  satisfying the differential equation [compare Eqs. (4) and (9)]:

$$-x a'(x) + (2 - \alpha) a(x) = \beta h(x). \quad (21)$$

The homogeneous equation ( $h=0$ ) has the general solution of a constant times  $|x|^{2-\alpha}$ . Thus, the solution to (21) which is analytic near  $x=0$  is unique. It may be written in the form

$$a(x) = \beta \left\{ \frac{h_0}{2-\alpha} + \frac{h_1 x}{1-\alpha} - x |x|^{1-\alpha} \int_0^x \frac{g_2(y)}{|y|^{3-\alpha}} dy \right\}, \quad (22)$$

where we have used the series expansion convergent near  $x=0$ ,

$$h(x) = \sum_{j=0}^{\infty} h_j x^j \quad (23)$$

and for  $k$  an integer,  $g_k$  is defined by

$$g_k(x) = \sum_{j=k}^{\infty} h_j x^j. \quad (24)$$

In fact, (22) defines a function analytic for all  $x$  in the interval  $-x_0 < x < \infty$  [analyticity near  $x=0$  is easily checked by inserting the power-series expansion (24) for  $g_2$  and integrating term by term]. Another solution to (21), valid for  $x > 0$ , is

$$a(x) = C x^{2-\alpha} + \beta x^{2-\alpha} \int_x^{\infty} h(y) y^{\alpha-3} dy. \quad (25)$$

For  $x > R$  we may substitute (15) in the integrand and

integrate term by term, to obtain

$$a(x) = C x^{2-\alpha} + \frac{1}{2} \sum_{n=1}^{\infty} n^{-1} \eta_n x^{2-\alpha-2\beta n}, \quad (26)$$

with the series convergent for  $R < x < \infty$ . Consequently, we have

$$A(M, T) = A_o(T) + C t^{2-\alpha} + \frac{1}{2} \sum_{n=1}^{\infty} n^{-1} \eta_n t^{2-\alpha-2\beta n} M^{2n}, \quad (27)$$

with the series converging for  $M$  satisfying (16). The analyticity of  $A(M, T)$  in the one-phase region is thus assured. The constant  $C$  must be chosen so that (25) and (22) are identical. It is the coefficient of the dominant term in  $a(x)$  for large  $x$ :

$$C = -\beta \int_0^{\infty} g_2(y) y^{\alpha-3} dy. \quad (28)$$

In the two-phase region,  $A$  is a function of  $T$  alone, equal to its value on the phase boundary:

$$A(M, T) = A_o(T) + a(-x_0) \cdot (-t/x_0)^{2-\alpha}. \quad (29)$$

(b) For  $\alpha = 0$ , in which case  $\beta(\delta+1) = 2$ , assume  $A$  has the form

$$A(M, T) = A_o(T) + |M|^{\delta+1} a_o(t|M|^{-1/\beta}) + h_2 t^2 \ln |M| \quad (30)$$

in the one-phase region, with  $a_o$  satisfying a differential equation analogous to (21):

$$-x a_o'(x) + 2 a_o(x) = \beta [h(x) - h_2 x^2]. \quad (31)$$

The general solution to (31),

$$a_o(x) = \beta \left\{ \frac{1}{2} h_0 + h_1 x + F x^2 - x^2 \int_0^x g_3(y) y^{-3} dy \right\}, \quad (32)$$

in which  $F$  is an undetermined constant, is evidently an analytic function for  $-x_0 < x < \infty$ . A series expansion convergent for  $x > R$ ,

$$a_o(x) = \beta h_2 x^2 \ln x + \beta G x^2 + \frac{1}{2} \sum_{n=1}^{\infty} n^{-1} \eta_n x^{2-2\beta n}, \quad (33)$$

may be obtained from a second solution to (31):

$$a_o(x) = \beta \left\{ h_2 x^2 \ln x + G x^2 + x^2 \int_x^{\infty} h(y) y^{-3} dy \right\}, \quad (34)$$

valid for  $x > 0$ , with  $G$  another undetermined constant. From (30) and (33) we obtain the series [convergent for  $M$  satisfying (16)]:

$$A(M, T) = A_o(T) + \beta h_2 t^2 \ln t + \beta G t^2 + \frac{1}{2} \sum_{n=1}^{\infty} n^{-1} \eta_n t^{2-2\beta n} M^{2n}. \quad (35)$$

It is clear from (35) that  $G$  is not uniquely determined, since  $\ell^2$  is analytic and  $A_o(T)$  has not been specified. However,  $F$  and  $G$  are related by

$$F = G + \int_0^\infty \frac{dy}{y} \left[ \frac{g_2(y)}{y^2} - \frac{h_2}{1+y} \right] \quad (36)$$

if (32) and (34) represent the same function. [Equation (36) comes from replacing  $h(y)$  by  $h_1 + h_2 y + g_2(y)$  in (34) and comparing the result with (32) in the limit  $x \rightarrow 0$ .]

In the two-phase region  $A$  is given by

$$A(M, T) = A_o(T) + \beta h_2 \ell^2 \ln(-t/x_o) + a_o(-x_o)(t/x_o)^2. \quad (37)$$

#### D. Positivity of the Heat Capacity $C_M$

After discussing the free energy in part C we are now in a position to examine the second convexity condition CM4. Direct computation shows that  $S$  as a function of  $T$  is continuous across the phase boundary and that

$$C_M = T(\partial S / \partial T)_M \quad (38)$$

decreases discontinuously by an amount

$$(T/T_o^2)\beta h'(-x_o)(-t)^{-\alpha x_o \alpha - 1} \quad (39)$$

as the temperature increases. [One can compute (39) using (20), (29), (21), and the fact that  $h(-x_o) = 0$ , or the analogous equations for  $\alpha = 0$ . A more rapid procedure is to employ the analog of Eq. (56) of Ref. 17 for magnetic systems.] As  $h'(-x_o)$  is non-negative by (18), (39) is positive; that is, the heat capacity is always less on the one-phase (upper) side of the phase boundary than on the two-phase side. Thus to check CM4 it is sufficient (and necessary) to show that  $C_M$  is non-negative in the one-phase region near the critical point.

Given  $H(M, T)$ ,  $C_M$  is only determined within an additive, analytic function of the temperature

$$C_o(T) = -T(\partial^2 A_o(T) / \partial T^2)_M, \quad (40)$$

which we can always adjust to make  $C_M$  positive unless the second temperature derivative of  $A_o(T) - A(M, T)$  diverges to minus infinity. It is this "catastrophe" which we must avoid. Again the cases  $\alpha > 0$  and  $\alpha = 0$  should be considered separately.

(a) For  $\alpha > 0$ , the expression (for the one-phase region)

$$C_M(M, T) = C_o(T) - (T/T_o^2) |M|^{-\alpha a''} (t |M|^{-1/\beta}) \quad (41)$$

clearly indicates a catastrophe as  $M$  approaches zero unless for all  $x$  in the range  $-x_o < x < \infty$

$$a''(x) \leq 0. \quad (42)$$

The necessary and sufficient condition (42) is hard to translate into any simple condition on  $h(x)$ . A condition we have found useful in constructing functions is the following:

H4a. For  $\alpha > 0$ , a condition sufficient (but not necessary) to insure that CM4 will not be violated is

$$h''(x) \geq 0 \quad (43)$$

for  $-x_o < x < \infty$ .

That this condition suffices is clear from the relation

$$(\partial C_M / \partial M)_T = -T(\partial^2 H / \partial T^2)_M, \quad (44a)$$

which, combined with (9) and (43), implies that  $C_M$  decreases as  $|M|$  increases at constant  $T$ . Any divergence, therefore, will be to  $+\infty$ , not  $-\infty$ .

(b) For  $\alpha = 0$  we have (in the one-phase region)

$$C_M(M, T) = C_o(T) - (T/T_o^2) [a_o''(t |M|^{-1/\beta}) + 2h_2 \ln |M|]. \quad (44b)$$

It is clear immediately that  $h_2 = \frac{1}{2} h''(0)$  must be non-negative to avoid a logarithmic divergence to  $-\infty$  as  $|M| \rightarrow 0$ . However, this is almost all we need require:

H4b. For  $\alpha = 0$  the necessary and sufficient conditions to insure CM4 are that

$$h''(0) \geq 0 \quad (45)$$

and that  $h'(x)$  be bounded from above as  $x \rightarrow -x_o$ .

The proof that H4b corresponds to the condition CM4 will be found in Appendix C. Clearly it is much weaker than the condition H4a.

#### IV. EXAMPLES OF HOMOGENEOUS FUNCTIONS

Some examples of functions  $h(x)$  satisfying conditions H1, 2, 3 of Sec. III B and H4a or H4b of Sec. III D are presented below. In general, conditions H1, 3, and 4 must be checked for any particular choice of adjustable parameters. Of course, if  $h(x)$  satisfies these conditions, the same is true of  $\mu h(\nu x)$  with  $\mu$  and  $\nu$  positive constants ( $x_o$  depends on  $\nu$ ). The equation of state corresponding to any  $h(x)$  may be found from Eq. (9) or, for fluids, (A1) or (A2) of Appendix A.

Table III contains values of  $B$ ,  $\Gamma$ ,  $\Gamma'$ ,  $T_o A$ ,  $T_o A'$ , and  $T_o$  for a two-dimensional square and a body-centered cubic Ising lattice with nearest-neighbor interactions. It is commonly assumed that the critical indices  $\alpha$ ,  $\beta$ , etc., depend only on dimensionality, whereas the coefficients  $A$ ,  $B$ , etc., depend as well on the specific type of lattice. Values for the coefficients were obtained from Fisher's tabulation<sup>25</sup> (his notation and ours do not coincide) with energies expressed in units of the exchange constant  $J$  (the interaction energy between nearest neighbors is  $\mp J$  depending on whether the spins are parallel or antiparallel), temperatures in units of  $J/k$ , heat capacity per spin in units of  $k$ , magnetization as a fraction of its saturation value  $M_o$ , and magnetic field  $H$  in units of  $J/M_o$ . This amounts to replacing  $J$ ,  $k$ , and  $Nm^2$  with 1 in Fisher's tabulation. Values for the bcc lattice were derived from series expansions assuming  $\alpha = \alpha' = 0$  (logarithmic heat capacity),  $\beta = 5/16$ ,

<sup>25</sup> M. E. Fisher, J. Math. Phys. 4, 278 (1963).

TABLE III. Critical-point coefficients for Ising models.

Lattice:	B	$\Gamma$	$\Gamma'$	$T_c A$	$T_c A'$	$T_c$
Square	1.222	0.424	0.0115	1.122	1.122	2.27
Body-centered cubic	1.49	0.156	0.030	1.35	$\simeq 4.0$	6.35

and  $\gamma = \gamma' = 5/4$ . There is some evidence<sup>26,27</sup> that  $\alpha$  and  $\alpha'$  may have small positive values and  $\gamma'$  may be closer to 21/16 than 5/4.

**Example 1.**  $\beta = \frac{1}{2}$ ,  $\delta = 3$ ,  $\gamma = 1$ ,  $\alpha = 0$

The critical indices are identical with those for the Weiss molecular-field (or Van der Waals) model. Our main interest is in the case where  $C_M$  has a logarithmic divergence; i.e.,  $h''(0) > 0$ . For large  $x$ , the expansion (15) has terms of the form  $x$ , 1,  $x^{-1}$ ,  $x^{-2}$ ,  $\dots$ , which suggests

$$h(x) = \mathcal{P}_{n+1}(x)/\mathcal{Q}_n(x), \quad (46)$$

where  $\mathcal{P}_{n+1}$  and  $\mathcal{Q}_n$  are polynomials of degree  $n+1$  and  $n$ , respectively. The proposal of Azbel', Voronel', and Giterman<sup>13</sup> is of this form with  $n=2$  (see Appendix A). Perhaps the simplest interesting example is

$$h(x) = (x+b)(x+c)(x+d)^{-1}, \quad (47)$$

which fulfills H1–H4 with  $x_0 = b$  provided

$$0 < b \leq c \leq d \quad (48)$$

and has a logarithmic heat-capacity singularity for  $c < d$ .

Another possible functional form<sup>28</sup> is

$$h(x) = x + b + c \operatorname{Re}[i + dx^2]^{1/2}, \quad (49)$$

where Re stands for "real part." Conditions H1–H4 are satisfied, for example, with  $b=0$ ,  $c=0.91$ ,  $d=1$ .

**Example 2.**  $\beta = 1/8$ ,  $\delta = 15$ ,  $\gamma = 7/4$ ,  $\alpha = 0$

These indices are appropriate for a two-dimensional Ising model.<sup>1</sup> Equation (15) yields for large  $x$  an expansion with terms  $x^{7/4}$ ,  $x^{3/2}$ ,  $x^{5/4}$ ,  $x$ ,  $x^{3/4}$ ,  $\dots$  which suggests, in analogy with (46), an expression of the form

$$h(x) = [\mathcal{P}_{n+1}(x)/\mathcal{Q}_n(x)]^{7/4} \quad (50)$$

or perhaps

$$h(x) = \mathcal{Q}_1(x)[\mathcal{P}_2(x)]^{3/8} \quad (51)$$

(the form proposed by Helfand<sup>10</sup>) among many possibilities. The quantity  $D$  (Table II) is easily evaluated for the function

$$h(x) = cb(x+b^4)^{7/4} + db^2(x+b^4)^{3/2} + fb^3(x+b^4)^{5/4} + gb^4(x+b^4), \quad (52)$$

which satisfies conditions H1–4 and yields the values for  $A$ ,  $A'$ ,  $B$ ,  $\Gamma$ ,  $\Gamma'$  (also  $D=0$ ) given in Table III for the

<sup>26</sup> D. S. Gaunt, M. E. Fisher, M. F. Sykes, and J. W. Essam, Phys. Rev. Letters **13**, 713 (1964).

<sup>27</sup> G. A. Baker, Jr., and D. S. Gaunt, Phys. Rev. **155**, 545 (1967).

<sup>28</sup> R. B. Griffiths, Phys. Rev. Letters **16**, 787 (1966).

square lattice, provided that

$$\begin{aligned} b &= 0.699, \quad c = 3.52, \quad d = 6.54, \\ f &= -1.75, \quad g = 16.2. \end{aligned} \quad (53)$$

However, values of  $(\partial^{2m-1}M/\partial H^{2m-1})_T$  evaluated at  $H=0$ ,  $T > T_c$  are in rather poor agreement with series estimates<sup>11,29</sup> for  $m \geq 2$  if the constants in (53) are employed, so it is doubtful if (52) represents a reasonable interpolation formula despite its relative simplicity. The unpleasant divergence of second- and higher-order derivatives of (52) at  $x = -x_0 = -b^4$  can be remedied by replacing the first term by  $(x+b^4)(x+\tilde{b}^4)^{3/4}$ ,  $\tilde{b} > b$ , and similarly modifying the second and third terms. We have not investigated this modification numerically.

**Example 3.**  $\beta = 1/3$ ,  $\delta = 5$ ,  $\gamma = 4/3$ ,  $\alpha = 0$

This case is of some interest since many simple fluids and also certain ferro- (and antiferro-) magnets appear to have values of  $\beta$  near  $\frac{1}{3}$ .<sup>1,30</sup> Experimental values of  $\delta$  appear<sup>31</sup> to be less than 5; on the other hand,  $\gamma \simeq 1\frac{1}{3}$  is observed for certain ferromagnets.<sup>1,31,32</sup>

Unlike the two cases previously considered,  $1/\beta$  is not an even integer and thus the phase boundary  $T(M)$  is not analytic at  $M=0$ . The series (15) has terms of the form  $x^{4/3}$ ,  $x^{2/3}$ , 1,  $x^{-2/3}$ ,  $\dots$ . Since the expansion of  $(x+b)^{4/3}$  for large  $x$  contains a term behaving as  $x^{1/3}$ , it is clear that analogs of the functions (50) and (52) will not suffice. An easy way out of the difficulty is to use the real part of certain complex functions. Thus, for example, if

$$q(z) = \mathcal{P}_{n+2}(z)/\mathcal{Q}_n(z) \quad (54)$$

is a rational function, then

$$h(x) = \operatorname{Re}q[(x+ib)^{2/3}], \quad (55)$$

or a sum of similar functions, has the required form for large  $x$ . A particular example is

$$h(x) = \operatorname{Re}[(x+ib)^{4/3} + c(x+id)^{2/3} + f]. \quad (56)$$

For the values  $b=c=d=1$  and  $f=1.59$  this function satisfies H1–H4 with  $x_0=1$  and yields a logarithmic divergence in the heat capacity.

**Example 4.**  $\beta = 5/16$ ,  $\delta = 5$ ,  $\gamma = 5/4$ ,  $\alpha = 1/8$

The values for  $\beta$  and  $\gamma$  are based on series expansions for three-dimensional Ising models,<sup>7</sup> and the value of  $\delta$  is very close to the series estimate.<sup>26</sup> The expansion (15) has terms proportional to  $x^{5/4}$ ,  $x^{5/8}$ , 1,  $x^{-5/8}$ , etc., so a simple expression such as  $(x+b)^{5/4}$  cannot be used.

<sup>29</sup> C. Domb (private communication).

<sup>30</sup> P. Heller and G. Benedek, Phys. Rev. Letters **14**, 71 (1965); **8**, 428 (1962).

<sup>31</sup> J. S. Kouvel and M. E. Fisher, Phys. Rev. **136**, A1626 (1964); C. D. Graham, Jr., J. Appl. Phys. **36**, 1135 (1965).

<sup>32</sup> S. Aarj, J. Appl. Phys. **36**, 1136 (1965); J. E. Noakes, N. E. Tornberg, and A. Arrott, *ibid.* **37**, 1264 (1966); L. Passell, K. Blinowski, T. Brun, and P. Nielsen, Phys. Rev. **139**, A1866 (1965).

Consider the expression

$$\sum_{p=1}^5 (x+e_p)^r, \quad (57)$$

with

$$e_p = \exp 2\pi i p/5 \quad (58)$$

the five fifth roots of one. If  $r$  is  $5/4$  or  $5/8$  or  $-5/8$ , etc., (57) has an expansion for large  $x$  of the form (15) with, however, only every eighth  $\eta_n$  different from zero. With  $q(z)$  given in (54),

$$h(x) = \sum_{p=1}^5 q[(cx+e_p)^{5/8}] \quad (59)$$

satisfies condition H2.

We have not actually evaluated  $h(x)$  for  $q$  a rational function, but have considered a polynomial

$$q(z) = 0.942z^2 + 0.385z + 0.430 \\ + 0.019z^{-1} + 0.009z^{-2} + 0.009z^{-3}. \quad (60)$$

The coefficients (setting the last two or three equal to zero would make no essential difference) together with the choice  $c=1.25$  in (59) are chosen to yield the values of  $B$ ,  $\Gamma$ , and  $\Gamma'$  for the bcc lattice given in Table III, and so that  $h(x)$  satisfies conditions H1, H3, and H4a. The values 0.40 and 1.14 for  $T_c A$  and  $T_c A'$ , respectively, were obtained by numerical integration and are substantially less than those given in Table III. Different functional forms or perhaps different constants in (60) could no doubt reduce this discrepancy. It may be doubted whether the results would be significant, since values in Table III were computed assuming  $\alpha = \alpha' = 0$  (logarithmic heat capacity), not  $\frac{1}{8}$ .

#### Example 5. $\beta = 5/16$ , $\delta = 26/5$ , $\gamma = 21/16$ , $\alpha = 1/16$

The indices are close to the series estimates for three-dimensional Ising models and differ but little from those in Example 4. We shall show that no additional difficulties arise when  $\delta$  is not an odd integer as classical theory requires. The expansion (15) contains terms proportional to  $x^{21/16}$ ,  $x^{11/16}$ ,  $x^{1/16}$ ,  $x^{-9/16}$ , etc., with exponents larger by  $\frac{1}{16}$  than those in Example 4. With

$$q(z) = z^{1/10} [\mathcal{O}_{n+2}(z)/\mathcal{Q}_n(z)], \quad (61)$$

Eq. (59) yields  $h(x)$  satisfying H2. We have for simplicity examined

$$q(z) = 0.386z^{21/16} + 0.386z^{11/16} + 0.370z^{1/16} \\ + 0.008z^{-9/16} + 0.004z^{-19/16} + 0.004z^{-25/16} \quad (62)$$

(setting the last two or three coefficients equal to zero would make little difference) which with  $c=2.50$  yields  $B$ ,  $\Gamma$ , and  $\Gamma'$  for the bcc lattice as given in Table III. Values of  $T_c A$  and  $T_c A'$ , 0.88 and 1.19, respectively, still do not coincide with those in Table III, though there is a small (probably accidental) improvement over Example 4.

#### General Values of $\beta$

The above examples indicate a method which can in principle be used to generate  $h(x)$  with the required analytic properties whenever

$$2\beta = m/j \quad (63)$$

is a rational fraction,  $m$  and  $j$  integers.

If  $m$  is odd, define

$$e_p = e^{2\pi i p/m}. \quad (64)$$

The expansion for large  $x$  of

$$\sum_{p=1}^m (cx+e_p)^\eta \quad (65)$$

contains terms of the form  $x^\eta$ ,  $x^{\eta-m}$ ,  $x^{\eta-2m}$ , etc.; and provided that

$$\eta = \beta(\delta + 1 - 2k) \quad (66)$$

for some integer  $k \geq 1$ , the expansion is of the form (15). The function  $h(x)$  may be expressed as a sum of terms of the form (65) for different values of  $\eta$  given by (66), and of course  $c$  may depend on  $\eta$ .

When  $m$  is even,  $e_{m/2}$  is  $-1$  and (65) in general has a singularity at  $x=1/c$ . To get around this difficulty, replace (64) by

$$e_p = \exp[2\pi i(p - \frac{1}{2})/m] \quad (67)$$

and use the modified definition in (65). This procedure was followed in Example 3.

Apart from its inability to handle irrational  $\beta$ , the method here outlined proves cumbersome when  $m$  is large. Even for  $\beta = \frac{5}{16}$  ( $m=5$ ) the functions are inconvenient without an electronic computer. In actual applications it may prove sensible to replace analyticity by a weaker condition—perhaps continuity of a sufficient number of derivatives of the thermodynamic functions. Of course, there may very well be better ways of generating analytic functions than that suggested above.

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#### APPENDIX A. RELATION BETWEEN DIFFERENT PROPOSALS FOR THE EQUATION OF STATE

##### 1. Isomorphisms between "Magnetic" and "Fluid" Equations of State

There are two simple, but nonequivalent, ways of going from (9) to an equation of state for a fluid. The first is to replace  $M$  by  $\Delta\rho = \rho - \rho_c$ , the deviation of density from its critical value, and  $H$  by  $\mu - \mu_o(T)$ , where  $\mu_o(T)$  is the value of the chemical potential for  $\rho = \rho_c$ . One thus obtains

$$\mu(\rho, T) - \mu_o(T) = \Delta\rho |\Delta\rho|^{\delta-1} h(t |\Delta\rho|^{-1/\beta}), \quad (A1)$$

with  $t$  defined in (7). In addition,  $C_M$  for the magnetic system is replaced by  $\rho C_v$ , where  $C_v$  is the specific heat at constant volume (heat capacity per mole if  $\rho$  is measured in moles per unit volume). Equation (A1) predicts, among other things, a coexistence curve symmetric about  $\rho = \rho_c$ , which is only approximately true for real fluids. This isomorphism is the one commonly used in statistical calculations involving "lattice gases."

The second isomorphism is to replace  $M$  by  $\Delta v = v - v_o$ , the deviation of specific volume from its critical value, and  $H$  by  $p_o(T) - p$ , where  $p_o(T)$  is the pressure along the critical isochore (the vapor pressure for  $T < T_c$ ). The equation of state becomes

$$p_o(T) - p = \Delta v |\Delta v|^{\delta-1} h(t |\Delta v|^{-1/\beta}) \quad (\text{A2})$$

and  $C_M$  in the magnetic system is replaced by  $C_v$ . The symmetry of the coexistence curve about  $v_c$  predicted by (A2) is in somewhat worse agreement with experiment than the aforementioned symmetry about  $\rho_c$ .

The analyticity requirement C6 of Sec. II requires  $\mu_o(T)$  to be an analytic function of  $T$  including  $T = T_c$  if (A1) is adopted, and the same for  $p_o(T)$  if (A2) is adopted.

## 2. The Scheme of Widom

Widom's<sup>9</sup> fundamental equation (6) has the form

$$\mu(\rho, T) - \mu_o(T) = \Delta \rho (x + y) \Phi(x, y), \quad (\text{A3})$$

where  $\mu_o$  is the same as Widom's  $M$ , and

$$x = T - T_c = T_c t, \quad (\text{A4})$$

$$y = C |\Delta \rho|^{1/\beta}. \quad (\text{A5})$$

The constant  $C$  need not concern us. Since by Widom's Eq. (7),

$$\Phi(x, y) = y^{\gamma-1} \Phi(x/y, 1), \quad (\text{A6})$$

using our notation for critical indices we may write [note that  $\gamma$  is  $\beta(\delta-1)$ ]:

$$\mu(\rho, T) - \mu_o(T) \propto \Delta \rho |\Delta \rho|^{\delta-1} g(x/y), \quad (\text{A7})$$

where

$$g(x/y) = g[(T_c/C)t |\Delta \rho|^{-1/\beta}] = (1 + x/y) \Phi(x/y, 1) \quad (\text{A8})$$

differs from  $h$  in (A1) only by a scaling factor and constant of proportionality.

## 3. The Scheme of Domb and Hunter

For small values of field and temperatures near  $T_c$ , the quantity  $\tau$  used by these authors<sup>11</sup> is proportional to  $H$ . To conform with our notation,  $x$  in their Eq. (12) should be replaced by  $M$ ,  $(1-t)$  by  $t/T_c$  (assuming  $T \simeq T_c$ ), and  $\Delta$  by  $2\beta\delta$ , with the result

$$H \propto M t^{\beta(\delta-1)} G(T_c^{2\beta} M^2 t^{-2\beta}) \\ = M |M|^{\delta-1} h(t |M|^{-1/\beta}), \quad (\text{A9})$$

provided

$$h(x) = x^{\beta(\delta-1)} G(T_c^{2\beta} x^{-2\beta}) \quad (\text{A10})$$

for  $x > 0$ . Their discussion of the transition from  $T > T_c$  to  $T < T_c$  for positive  $M$  is incomplete, and their conclusion that on the critical isotherm the dependence of  $H$  on  $M$  cannot be described by a power law is, we believe, erroneous (see Sec. IV, Example 5).

## 4. The Scheme of Patashinskii and Pokrovskii

If one differentiates Patashinskii and Pokrovskii's<sup>12</sup> equation (3.1) with respect to  $H$  [see also their Eq. (3.4)], the result, brought into conformity with our notation through replacing  $\tau$  by  $t$ ,  $\alpha a$  by  $\beta(\delta+1)$ ,  $\alpha\beta$  by  $2\beta$ , and  $M$  by  $MV$ , is

$$M = -2kT_c H t^{-\beta(\delta-1)} f'(H^2 t^{-2\beta\delta}). \quad (\text{A11})$$

Introducing the variables

$$u = M t^{-\beta}, \quad v = H t^{-\beta\delta} \quad (\text{A12})$$

permits us to rewrite (A11) as

$$u = -2kT_c v f'(v^2), \quad (\text{A13})$$

which may, at least in principle, be solved for  $v$  in the form

$$v = uG(T_c^{2\beta} u^2). \quad (\text{A14})$$

But this is just the functional form of Domb and Hunter, (A9) above.

## 5. The Scheme of Azbel', Voronel', and Giterman

These authors<sup>13</sup> are concerned with the case  $\beta = \frac{1}{2}$ ,  $\delta = 3$ ,  $\alpha = 0$  with a logarithmic singularity in  $C_v$  (compare Sec. IV, Example 1). Giterman<sup>13b</sup> has also considered the lowest-order corrections due to the lack of symmetry of the coexistence curve in the  $v, T$  plane. If these corrections are omitted [ $C = K = 0$  in Eq. (6) of Ref. 13b] one obtains

$$p - p_o(T) = -a_o t \Delta v - a_1 \Delta v^3 \\ - \frac{a_3 t^2 \Delta v [t + (a_4 + a_5) \Delta v^2]}{(t + a_4 \Delta v^2)^2 + a_5 \Delta v^4}, \quad (\text{A15})$$

with  $\Delta v = v - v_c$  and the  $a_j$  (our notation) adjustable constants. [The result (A15) is obtained by adding Eq. (6) of Ref. 13b (with  $C = K = 0$ ) to  $-\partial F/\partial v$  from Eq. (4) of Ref. 13a, discarding the undefined  $F_{\text{reg}}$  and  $\chi(t, v)$  in the latter.] It is easily verified that (A15) has the form

$$p_o(T) - p = \Delta v^3 h(t \Delta v^{-2}) \quad (\text{A16})$$

corresponding to (A2).

## 6. The Scheme of Kadanoff

Upon replacing  $\epsilon$  by  $t$ ,  $h$  by  $H$ , and  $(s-\psi)v$  by  $\beta\delta$ , one obtains Kadanoff's<sup>14</sup> Eq. (18) in the form

$$f(t, H) = t^{2-\alpha} F(t^{\beta\delta}/H), \quad t > 0 \\ = |t|^{2-\alpha} F'(|t|^{\beta\delta}/H), \quad t < 0, \quad (\text{A17})$$

where  $f$  is the singular part of the free energy per atom (that is, the part yielding the dominant singularities in the thermodynamic functions near the critical point), and  $F$  and  $F'$  are two different functions (the prime does not denote a derivative). An expression similar to (A11) is obtained after some manipulation if one takes the partial derivative of (A17) with respect to  $H$ .

Equation (A17) apparently permits different values for the critical indices for  $T > T_c$  and  $T < T_c$ , but this liberty is, in fact, ruled out on grounds of thermodynamic consistency. For  $T > T_c$  define  $\Phi$  by

$$F(x) = x^{-(2-\alpha)/\beta\delta} \Phi(x^{1/\beta\delta}) \quad (\text{A18})$$

and for  $T < T_c$  an analogous  $\Phi'$  using  $F'$ ,  $\alpha'$ , etc. Then (A17) becomes

$$\begin{aligned} f(t, H) &= H^{(2-\alpha)/\beta\delta} \Phi(tH^{-1/\beta\delta}), & t > 0 \\ &= H^{(2-\alpha')/(\beta\delta)'} \Phi'(|t|H^{-1/(\beta\delta)'}), & t < 0. \end{aligned} \quad (\text{A19})$$

Continuity of the free energy along the critical isotherm  $t=0$  implies that

$$(2-\alpha)/\beta\delta = (2-\alpha')/(\beta\delta)'. \quad (\text{A20})$$

If in addition one supposes the entropy, proportional to  $-\partial f/\partial t$ , is continuous at  $t=0$  (otherwise one would have a first-order phase transition), then (A19) yields

$$\beta\delta = (\beta\delta)' \quad (\text{A21})$$

as well. The argument for equality assumes, of course, that both  $\Phi(x)$  and its first derivative do not vanish at  $x=0$ .

## APPENDIX B. MAXWELL CONSTRUCTION AND THE VAN DER WAALS EQUATION OF STATE

The well-known Van der Waals equation of state

$$(\tilde{p} + a/v^2)(v-b) = RT \quad (\text{B1})$$

possesses regions where  $(\partial\tilde{p}/\partial v)_T$  is positive provided  $T$  is less than  $T_c = 8a/(27Rb)$ , as illustrated schematically in Fig. 4. Maxwell<sup>33</sup> proposed that the pressure  $p$  corre-

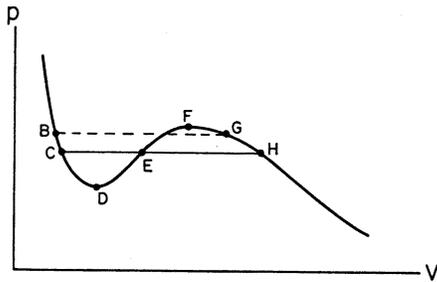


FIG. 4. Schematic drawing of a Van der Waals isotherm below the critical temperature together with different possibilities for the equilibrium isotherm.

<sup>33</sup> *The Scientific Papers of James Clerk Maxwell* (Dover Publications, Inc., New York, 1890), Vol. II, p. 425.

sponding to the physical equilibrium state be defined by

$$\begin{aligned} p &= \tilde{p} \quad \text{for } v \leq v_C, \quad v \geq v_H \\ &= \tilde{p}_C = \tilde{p}_H \quad \text{for } v_C \leq v \leq v_H \end{aligned} \quad (\text{B2})$$

(for  $T \geq T_c$ ,  $p$  coincides with  $\tilde{p}$ ), where the subscripts refer to the corresponding points in Fig. 4. The points  $C$  and  $H$  on the  $\tilde{p}$  isotherm correspond to the same pressure and are also chosen so that

$$(v_H - v_C)\tilde{p}_C = \int_{v_C}^{v_H} \tilde{p}(v, T) dv \quad (\text{B3})$$

is satisfied, the "equal area rule."

An equivalent procedure is to find a function  $\tilde{A}$  satisfying

$$\tilde{p} = -(\partial\tilde{A}/\partial v)_T. \quad (\text{B4})$$

Integration of (B1) yields

$$\tilde{A}(v, T) = A_o(T) + a/v - RT \ln(v-b), \quad (\text{B5})$$

with  $A_o(T)$  an undetermined function of temperature. The double tangent construction (compare Fig. 2) applied to  $\tilde{A}$  as a function of  $v$  at fixed  $T$  yields the convex-downwards function  $A(v, T)$  from which  $p$  in (B2) may be obtained via Eq. (3). Of course,  $A$  and  $\tilde{A}$  coincide for  $T \geq T_c$ .

Both procedures make use of a portion of the original  $\tilde{p}$  isotherm—the segment CDEFH in Fig. 4—which is later discarded, at least when discussing equilibrium properties. The first employs it explicitly in (B3), the second implicitly in order to obtain (B5) from (B4).

In contrast, our "nonclassical" hypotheses in Sec. II A involve only the equilibrium thermodynamic variables, and it is interesting to ask whether they also provide a basis for Maxwell's rule. The answer is "yes" provided one invokes the full force of the analyticity requirement C6.

Thus, consider the alternate construction shown by the dotted line in Fig. 4 and corresponding to a pressure

$$\begin{aligned} p^* &= \tilde{p} \quad \text{for } v \leq v_B, \quad v \geq v_G \\ &= \tilde{p}_B = \tilde{p}_G \quad \text{for } v_B \leq v \leq v_G \end{aligned} \quad (\text{B6})$$

(for  $T > T_c$ ,  $p^*$  coincides with  $\tilde{p}$ ), where we have chosen points  $B$  and  $G$  with the same pressure, necessarily lying between  $p_D$  and  $p_F$ , but not satisfying (B3). We now construct the corresponding  $A^*$  in a manner analogous to Eq. (6), that is, by direct integration of  $p^*(v, T)$  at constant temperature. The result may be written as

$$\begin{aligned} A^*(v, T) &= \tilde{A}(v, T) \quad \text{for } v \geq v_G(T) \\ &= \tilde{A}(v, T) + Q(T) \quad \text{for } v \leq v_B(T) \end{aligned} \quad (\text{B7})$$

if for  $v_B \leq v \leq v_G$ ,  $A^*$  is obtained by linear interpolation between its values at the end points of this interval. The quantity  $Q$  is just the area of the region in Fig. 4 bounded by the horizontal lines  $BG$  and  $CH$ , and the curved lines  $BC$  and  $GH$ ; positive for  $p_B > p_C$  and

negative for  $p_B < p_C$ . For  $T > T_c$ , we shall assume  $A^*$  and  $\bar{A}$  are identical.

By choosing  $v_B$  and  $v_G$  as smooth functions of the temperature it is easy to satisfy conditions C1–C4 of Sec. II. The analyticity conditions C5 and C6 are more stringent, and the latter is uniquely satisfied by the Maxwell construction (B3). This may be seen as follows. In order that  $A^*(v, T)$  be an analytic function of temperature in the one-phase region, it is clearly necessary that  $A_o(T)$  in (B5) be analytic. Now consider some  $v_1$  greater than  $b$  and less than  $v_C$ . For  $T > T_c$ ,  $A^*(v_1, T)$  and  $\bar{A}(v_1, T)$  coincide. By hypothesis C6 we may continue  $A^*(v_1, T)$  analytically to values of  $T < T_c$ , provided we remain in the one phase region. But the unique analytic continuation of  $A^*$  is just  $\bar{A}$ , and hence  $Q(T)$  in (B7) must vanish. That is,  $B$  coincides with  $C$  and  $G$  with  $H$ .

Expressed in different terms, any attempt to place the horizontal part of the isotherm at a position where (B3) is not satisfied leads inevitably to some sort of phase transition in the one-phase region. This transition may be made very "weak" by the correct choice of  $p_B(T)$ . In fact one may have a function  $A^*$  infinitely differentiable (though not analytic) in the one-phase region, and still have isotherms which do not satisfy Maxwell's prescription in the two-phase region. Note, however, that apart from requirements of analyticity and provided one only considers functions for equilibrium states, there is no thermodynamic inconsistency in using a rule other than Maxwell's for modifying the Van der Waals equation of state. *Note added in proof.* The nonuniqueness of Maxwell's procedure has also been pointed out by G. D. Kahl [Phys. Rev. **155**, 78 (1967)]. Similar remarks apply to the generalization of Maxwell's procedure by Landau and Lifschitz,<sup>34</sup> which has been used in some recent discussions of the critical point.<sup>35</sup>

#### APPENDIX C. THE SECOND CONVEXITY CONDITION CM4 AND $h(x)$ FOR $\alpha = 0$

Equation (44) [note that  $C_o(T)$  is an analytic but otherwise arbitrary function] shows that a necessary

<sup>34</sup>L. D. Landau and E. M. Lifschitz, *Statistical Physics* (Pergamon Press, Ltd., London, 1958), pp. 264 ff.

<sup>35</sup>L. Tisza and C. E. Chase, Phys. Rev. Letters **15**, 4 (1965); L. Mistura and D. Sette, *ibid.* **16**, 268 (1965); R. E. Barieau, J. Chem. Phys. **45**, 3175 (1966).

and sufficient condition for a positive  $C_M$  in the one-phase region is

$$a_o''(t|M|^{-1/\beta}) + 2h_2 \ln|M| \leq K, \quad (C1)$$

where  $K$  is some positive constant independent of  $M$  and  $t$ .

First consider the interval

$$-x_o + \epsilon \leq x = t|M|^{-1/\beta} \leq 2R, \quad (C2)$$

where  $\epsilon$  is a positive constant, and (33) is assumed convergent for  $R < x < \infty$ . From the analyticity of  $a_o(x)$  for  $-x_o < x < \infty$ , it follows that  $a_o''(x)$  is bounded on the interval (C2), and  $h_2 \geq 0$  suffices to guarantee (C1) for the corresponding region in the  $M, T$  plane.

For the interval

$$2R \leq x < \infty, \quad (C3)$$

the left side of (C1) may, with the help of (33), be expressed as

$$\beta[2h_2 \ln t + 3h_2 + 2G] + \sum_{n=1}^{\infty} n^{-1}(1-\beta n)(1-2\beta n)\eta_n y^n, \quad (C4)$$

with

$$y = M^2 t^{-2\beta} \leq (2R)^{-2\beta}. \quad (C5)$$

Since the series in (35), of the form

$$\frac{1}{2} t^2 \sum_{n=1}^{\infty} n^{-1} \eta_n y^n \quad (C6)$$

converges for  $y < R^{-2\beta}$  [equivalent to (16)], it is easily shown that the series in (C4) is bounded for  $y$  satisfying (C5). Details are left to the reader. Once again  $h_2 \geq 0$  suffices to guarantee (C1).

The problem of what happens as  $x$  approaches  $-x_o$  still remains. By hypothesis H1 of Sec. III B,  $h(x)$  goes continuously to zero. Equation (32) shows that  $a_o(x)$  approaches a finite constant. These facts together with (31) imply that  $a_o'(x)$  also approaches a finite constant. Upon differentiating (31) once with respect to  $x$  we conclude that:  $a_o''(x)$  is bounded from above as  $x \rightarrow -x_o$  if and only if the same is true for  $h'(x)$ . And this is precisely the second condition in H4b.