

## Equation of State in the Neighborhood of the Critical Point

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A specific form is proposed for the equation of state of a fluid near its critical point. A function  $\Phi(x, y)$  is introduced, with  $x$  a measure of the temperature and  $y$  of the density. Fluids obeying an equation of state of van der Waals type ("classical" fluids) are characterized by  $\Phi$  being a constant. It is suggested that in a real fluid  $\Phi(x, y)$  is a homogeneous function of  $x$  and  $y$ , with a positive degree of homogeneity (Sec. 2). This leads to a nonclassical compressibility, the behavior of which is determined by the degree of homogeneity of  $\Phi$  (Sec. 3). A previously derived relation connecting the degree of the critical isotherm, the degree of the coexistence curve, and the compressibility index, again follows, this time without the restrictive assumption of effective isochore linearity (Sec. 4). The locus in the temperature-density plane of the points of inflection in the pressure-density isotherms, as determined experimentally by Habgood and Schneider, is accounted for (Sec. 5). It is shown that if a certain combination of the compressibility and coexistence curve indices is an integer, then the constant-volume specific heat on the critical isochore has a logarithmic singularity at the critical temperature with, in general, a superimposed finite discontinuity (Sec. 6).

## 1. INTRODUCTION

It is generally recognized that a fluid in the neighborhood of its critical point differs in many important respects from the "classical" fluid which obeys an equation of state of van der Waals type. Near the critical point of a real fluid, the densities of the coexisting phases, the shape of the critical isotherm, the rate of divergence of the compressibility, and the nature of the singularity in the constant-volume specific heat, are all nonclassical.

The purpose of the present work is to suggest a specific form that the equation of state might have, consistent with the full range of nonclassical behavior as now known. A function  $\Phi$  is introduced which is a function of two variables, one a measure of the density of the system and the other a measure of the temperature. The classical theory is characterized by  $\Phi$  being a constant. It is suggested that, by contrast, a real fluid of finite dimensionality is characterized by  $\Phi$  being a homogeneous function of its variables, with a positive degree of homogeneity. It is just this assumption which leads to the nonclassical compressibility and specific heat.

Two of the most interesting results of the theory are: (i) If a certain combination of the exponents which determine the behavior of the compressibility and the coexistence curve, happens to be an integer, then the constant-volume specific heat along the critical isochore has a logarithmic singularity at the critical point with, in general, a superimposed finite discontinuity. (ii) A puzzling and hitherto unexplained experimental result obtained by Habgood and Schneider,<sup>1</sup> concerning the locus of the points of inflection in the pressure-density isotherms, is now accounted for.

<sup>1</sup>H. W. Habgood and W. G. Schneider, Can. J. Chem. **32**, 98 (1954).

## 2. PROPOSED EQUATION OF STATE

Let  $\mu(\rho, T)$  be the chemical potential (Gibbs function per unit mass), as a function of the mass density  $\rho$  and temperature  $T$ , in a one-component fluid; and let  $\rho_c, T_c$  be the density and temperature at the critical point. Let  $M(T)$  be the chemical potential along the

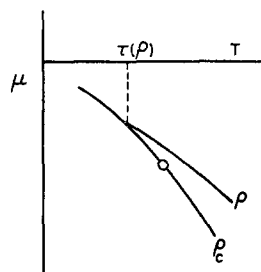


FIG. 1. The critical isochore ( $\rho_c$ ) and a general isochore ( $\rho$ ) in the  $\mu, T$  plane. They intersect at the temperature  $\tau(\rho)$ . The circle marks the critical point.

critical isochore,  $\rho = \rho_c$ , so that

$$\mu(\rho_c, T) = M(T).$$

The critical isochore  $M(T)$  in the  $\mu, T$  plane, and one general isochore, are shown schematically in Fig. 1. The general isochore corresponding to density  $\rho$  intersects the critical isochore at the temperature  $\tau(\rho)$ , where

$$T = \tau(\rho)$$

is the equation of the coexistence curve in the  $T, \rho$  plane shown in Fig. 2.

All the classical theories, of van der Waals type, agree that in a homogeneous fluid phase in the immediate neighborhood of the critical point  $\mu$  is given as a function of  $\rho$  and  $T$  by

$$\mu(\rho, T) - M(T) = (\rho - \rho_c)[T - \tau(\rho)]\Phi, \quad (1)$$

with  $\Phi$  a constant. They agree, further, that the coexistence curve is parabolic, that is, that  $\tau(\rho)$  is given near the critical point by

$$T_c - \tau(\rho) = a |\rho - \rho_c|^d, \quad (2)$$

with  $a$  a constant, and with  $d=2$ .

It is a consequence of Eq. (1) that  $\mu$  reduces to  $M(T)$  both when  $\rho = \rho_c$ , that is, on the critical isochore, and when  $T = \tau(\rho)$ , that is, at the coexistence curve. These are necessary features of any correct equation of state, and simply express in analytical form the content of Fig. 1. That  $\Phi$  is asymptotically constant as the critical point is approached is, however, a feature of the classical theories alone, and is not a necessary property of the equation of state. It is the constancy of  $\Phi$  which yields the classical compressibility, quite independently of whether the coexistence curve is classical, with  $d=2$  in Eq. (2), or nonclassical, with  $d \neq 2$ ; for it follows from Eqs. (1) and (2) that if  $\Phi$  is constant, then

$$\begin{aligned} (\partial\mu/\partial\rho)_T &= (T - T_c)\Phi, & \text{at } \rho = \rho_c, \\ (\partial\mu/\partial\rho)_T &= (T_c - T)\Phi d, & \text{at } T = \tau(\rho). \end{aligned}$$

Because

$$(\partial\mu/\partial\rho)_T = \rho^{-1}(\partial p/\partial\rho)_T = (\rho^2\kappa)^{-1}, \quad (3)$$

with  $p$  the pressure and  $\kappa$  the isothermal compressibility, the preceding relations imply that  $\kappa$  becomes infinite proportionally to  $|T - T_c|^{-1}$  as the critical point is approached either along the critical isochore, with  $T$  approaching  $T_c$  from above, or along the coexistence curve, with  $T$  approaching  $T_c$  from below. But in reality the compressibility behaves nonclassically<sup>2</sup> and becomes infinite proportionally to  $|T - T_c|^{-f}$ , with  $f > 1$ .

Thus, in constructing a more general equation of state, the form of Eq. (1) is to be retained, but  $\Phi$  may not be assumed constant. Likewise, the form of Eq. (2) is to be retained, but  $d$  may not be assumed equal to 2. As the critical point is approached, coexistence curves do in reality have the asymptotic form implied by

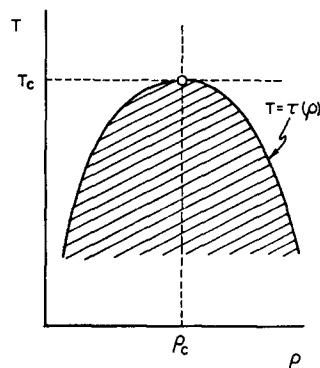
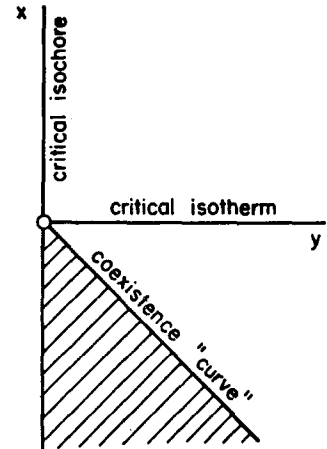


FIG. 2. The coexistence curve  $T = \tau(\rho)$  in the  $T, \rho$  plane. The two-phase region is shaded. The dashed lines are the critical isochore (vertical) and the critical isotherm (horizontal). The circle marks the critical point.

<sup>2</sup> J. W. Essam and M. E. Fisher, J. Chem. Phys. **38**, 802 (1963).

FIG. 3. The critical isochore, critical isotherm, and coexistence "curve" in the  $x, y$  plane. The two-phase region is shaded. The critical point is at the origin, marked by a circle.



Eq. (2), with  $a$  constant, but they are of algebraic degree  $d$  greater than 2.

It is convenient to measure the temperature  $T$  by the variable

$$x = T - T_c \quad (4)$$

and the density  $\rho$  by the variable

$$y = T_c - \tau(\rho), \quad (5)$$

and then to suppose that  $\Phi$  is a function of  $x$  and  $y$ ,

$$\Phi = \Phi(x, y).$$

To be sure, because of Eq. (2), the variable  $y$  does not define the density uniquely, but is instead an even function of  $\rho - \rho_c$ , so that the density is a two-valued function of  $y$ . But from Eqs. (1), (4) and (5), the equation of state in the one-phase region near the critical point becomes

$$\mu(\rho, T) - M(T) = (\rho - \rho_c)(x + y)\Phi(x, y). \quad (6)$$

Then  $y$  being an even function of  $\rho - \rho_c$  implies that at fixed temperature  $\mu(\rho, T) - M(T)$  is an odd function of  $\rho - \rho_c$ . In the lattice gas model of a fluid,<sup>3</sup>  $\mu(\rho, T) - M(T)$  for fixed  $T$  is indeed an odd function of  $\rho - \rho_c$  everywhere; and it is virtually certain that this symmetry property is also characteristic of a real fluid near its critical point. Thus, it is in any case necessary to suppose that  $\Phi$  is an even function of  $\rho - \rho_c$ , so there is no loss of generality in taking it to be a function of  $y$ .

The ranges of the variables  $x$  and  $y$  are shown in Fig. 3. The critical point is at the origin,  $x = y = 0$ . Because the coexistence curve in Fig. 2 has its maximum at  $T = T_c$  it follows that  $y$ , as defined in Eq. (5), is always positive. The two-phase region in Fig. 2 is defined by  $T < \tau(\rho)$ , that is, by  $x + y < 0$  in the  $x, y$  plane, and is the shaded region in Fig. 3. The whole of Fig. 3 represents a transformation of Fig. 2, obtained by folding the  $T, \rho$  plane in half along the critical

<sup>3</sup> T. D. Lee and C. N. Yang, Phys. Rev. **87**, 410 (1952).

isochore, translating the critical point to the origin, and then redefining the density variable so that the coexistence curve becomes the straight line  $x+y=0$ . The critical isochore remains a vertical straight line, coinciding with the  $x$  axis ( $y=0$ ) in the  $x, y$  plane; while the critical isotherm remains a horizontal straight line, coinciding with the positive  $y$  axis ( $x=0$ ).

It is now suggested that the behavior of a fluid in the neighborhood of its critical point may be comprehended in the single statement that  $\Phi$  is a homogeneous function of its variables. The remaining sections of this paper are concerned with the systematic derivation of the consequences of this conjecture.<sup>4</sup>

If the supposed degree of homogeneity is called  $f-1$ , then what is being conjectured is that

$$\begin{aligned}\Phi(x, y) &= y^{f-1}\Phi(x/y, 1) \\ &= x^{f-1}\Phi(1, y/x) \quad \text{if } x > 0 \\ &= (-x)^{f-1}\Phi(-1, y/-x) \quad \text{if } x < 0.\end{aligned}\quad (7)$$

Though the homogeneity of  $\Phi$  is only asserted to hold asymptotically as the critical point is approached, and though the entire theory is limited to the immediate neighborhood of the critical point, it is clear from Eqs. (7) that infinite ranges of the arguments of  $\Phi$  are nevertheless relevant, and that the behavior of  $\Phi$  may be quite different according as the critical point is approached with  $x/y \sim -1, \infty$ , or a finite number greater than  $-1$ . This complexity is not present in the classical case, where  $\Phi$  is a constant.

The one-phase region, where Eq. (6) applies, is the portion left unshaded in Figs. 2 and 3. At any point in the interior of this region  $\mu(\rho, T) - M(T)$  is assumed to be a regular function of both  $\rho$  and  $T$ . A typical point in the interior of the one-phase region is the point  $x=0, y=1$  on the critical isotherm. The function  $\Phi(x, 1)$  is therefore assumed to be regular in  $x$  and to admit a power series expansion

$$\Phi(x, 1) = \phi_0 + \phi_1 x + \phi_2 x^2 + \phi_3 x^3 + \dots \quad (8)$$

Another point in the interior of the one-phase region is the point  $x=1, y=0$  on the critical isochore. The function  $(1+y)\Phi(1, y)$  is therefore assumed to be regular in  $y^{2/d}$  and to admit a power series expansion<sup>5</sup>

$$(1+y)\Phi(1, y) = c_0 + c_1 y^{2/d} + c_2 y^{4/d} + \dots \quad (9)$$

At the boundary of the one-phase region, that is, at the coexistence curve,  $\mu(\rho, T) - M(T)$  may indeed

<sup>4</sup> After this article was submitted it was called to the author's attention that E. Helfand, in a paper presented at the March, 1965 meeting of the American Physical Society at Kansas City, proposed particular cases of Eq. (6) to account for nonclassical behavior near the critical point; and that R. B. Griffiths subsequently showed that Helfand's equation of state implied a logarithmic specific heat singularity, as is found in Sec. 6 of the present paper.

<sup>5</sup> This formulation of the behavior of  $\Phi$  at the critical isochore arose from remarks made by R. B. Griffiths (private communication) and by the referee of this paper, to both of whom the author is indebted.

be singular, but there is no question about the existence there of  $\Phi$  and of its derivatives of low order. Let the subscript 1 on  $\Phi$  indicate differentiation with respect to its first argument. Then, in fact, the strongest assumptions it is later found necessary to make about the behavior of  $\Phi$  on the coexistence curve are that  $\Phi(-1, 1)$  exists, and that

$$\lim_{x+y \rightarrow 0} (x+y)\Phi_1(x/y, 1) = 0,$$

which says that, should the derivative of  $\Phi(x, y)$  with respect to  $x$  fail to exist at the coexistence curve, that derivative at least does not approach infinity as rapidly as  $x+y$  approaches zero, as the coexistence curve is approached.

No regularity assumption of any kind is made about the behavior of  $\Phi(x, y)$  at the origin, that is, at the critical point itself.

Finally, it is to be understood that what is meant by  $\Phi$  is the function in Eq. (6) that determines the behavior of  $\mu$  in the one-phase region. This function may or may not have a meaningful analytic extension into the two-phase region, depending on whether it is analytic at the typical point  $-1, 1$  on the coexistence curve in the  $x, y$  plane. In the classical case, where it is a constant,  $\Phi$  does of course have such a continuation, and then Eq. (6) is taken to be not only the equation of state in the region of single-phase stability but also the equation of state of a homogeneous metastable phase with  $x+y < 0$ . In both classical and real fluids, however, the stable states of the system are described by

$$\mu(\rho, T) - M(T) = (\rho - \rho_c)(x+y)\Psi(x, y),$$

where

$$\begin{aligned}\Psi(x, y) &\equiv \Phi(x, y), & x+y > 0, \\ \Psi(x, y) &\equiv 0, & x+y < 0.\end{aligned}\quad (10)$$

The point here, though, is that it is not  $\Phi$ , but  $\Psi$ , which is undefined at the coexistence curve;  $\Phi(-1, 1)$  has a perfectly definite value.

### 3. COMPRESSIBILITY

The coexistence curve is assumed to be given by Eq. (2) and the equation of state by Eq. (6), with  $\Phi(x, y)$  homogeneous of degree  $f-1$ . Then it follows that

(i) on the critical isochore ( $y=0, x>0$ ),

$$(\partial\mu/\partial\rho)_T = \Phi(1, 0)x^f; \quad (11)$$

(ii) on the critical isotherm ( $x=0$ ),

$$(\partial\mu/\partial\rho)_T = (1+fd)\Phi(0, 1)y^f; \quad (12)$$

(iii) at the coexistence curve ( $x+y=0$ ),

$$(\partial\mu/\partial\rho)_T = d\Phi(-1, 1)y^f = d\Phi(-1, 1)(-x)^f. \quad (13)$$

From Eq. (3), and the definition of  $x$  in Eq. (4), it is seen that the compressibility becomes infinite pro-

portionally to  $|T - T_c|^{-f}$  as the critical point is approached along either the critical isochore or the coexistence curve. With  $f > 1$ , that is, with the degree of homogeneity  $f - 1$  assumed positive, this is just the nonclassical behavior of the compressibility which is found in systems of finite dimensionality.<sup>2</sup> In a classical fluid  $\Phi$  is a constant, so that  $f = 1$ ; while the coexistence curve is parabolic, with  $d = 2$ ; then Eqs. (11), (12), (13) reduce to  $(\partial\mu/\partial\rho)_T = \Phi x$ ,  $3\Phi y$ ,  $2\Phi y = -2\Phi x$ , respectively, which are the correct results in that case.

It is a necessary consequence of the assumed homogeneity of  $\Phi$  that the same exponent  $f$  appears in both Eqs. (11) and (13), that is, that the compressibility diverges equally rapidly above and below the critical point. This is in accord with the known behavior of the compressibility in the two-dimensional lattice gas<sup>2</sup> as well as in classical fluids, but it may not be generally correct. There is some evidence that in the three-dimensional lattice gas the  $f$  which characterizes the compressibility along the critical isochore, and the  $f$  which characterizes the compressibility at the coexistence curve, are slightly different, being very close to  $5/4$  in the first case and perhaps as large as  $21/16$  in the second.<sup>2,6</sup> The homogeneity hypothesis could be easily altered to accommodate unequal  $f$ 's, but then  $\Phi$  would have to be known fairly explicitly before the consequences of Eq. (6) could be derived. The point of the present work is that many of the properties of a fluid may be derived explicitly without a knowledge of  $\Phi$ , provided only that it is a homogeneous function, so this hypothesis is retained throughout.

#### 4. CRITICAL ISOTHERM

From Eq. (6), and the assumed homogeneity of  $\Phi$ , the equation of the critical isotherm ( $x = 0$ ) in the  $\mu, \rho$  plane is

$$\mu - \mu_c = \Phi(0, 1)(\rho - \rho_c)y^f, \quad (14)$$

where  $\mu_c = M(T_c)$  is the chemical potential at the critical point, and where  $y$  is expressible in terms of  $\rho - \rho_c$  through Eqs. (2) and (5). Equation (14) is the integrated form of the result already obtained in Eq. (12). Because the coexistence curve is itself of degree  $d$ , it follows that the algebraic degree  $g$  of the critical isotherm is<sup>7</sup>

$$g = 1 + fd. \quad (15)$$

Because of Eq. (3), this is also the degree of the pressure-density critical isotherm at the critical point.

The relation in Eq. (15) was previously derived<sup>8</sup> under an assumption of effective isochore linearity in the  $p, T$  plane. The analog of that assumption in the  $\mu, T$  plane, from which Eq. (15) is again derivable, is

that close to the critical point,

$$(\partial\mu/\partial T)_\rho - dM/dT$$

at any given density has the same value at the coexistence curve as it does at the critical isotherm. If, near the critical point, the  $\mu, T$  isochores were effectively linear in the temperature interval  $\tau(\rho) \leq T \leq T_c$  then, indeed,  $(\partial\mu/\partial T)_\rho$  and  $dM/dT$ , and therefore also the difference between them, would be constant, so the earlier argument<sup>8</sup> could be applied and would provide an alternative derivation of Eq. (15).

However, if the homogeneity of  $\Phi$  is granted, then the hypothesis of isochore linearity may be tested. One finds that at the coexistence curve,

$$(\partial\mu/\partial T)_\rho - dM/dT = \Phi(-1, 1)(\rho - \rho_c)y^{f-1},$$

while at the critical isotherm,

$$(\partial\mu/\partial T)_\rho - dM/dT = [\Phi(0, 1) + \Phi_1(0, 1)](\rho - \rho_c)y^{f-1}.$$

But, in general,

$$\Phi(-1, 1) \neq \Phi(0, 1) + \Phi_1(0, 1),$$

so the hypothesis of isochore linearity is false. The earlier theory<sup>8</sup> of the critical isotherm is, therefore, unnecessarily restrictive, and while it gives the correct degree  $g$ , it leads to the wrong coefficient in Eq. (14). In classical fluids  $\Phi$  is constant, so the derivative  $\Phi_1$  vanishes and  $\Phi(-1, 1) \equiv \Phi(0, 1)$ . In that case, then, the earlier theory is fully correct.

#### 5. LOCUS $(\partial^2 p/\partial \rho^2)_T = 0$ IN THE $T, \rho$ PLANE

From their experimentally determined  $p(\rho, T)$  for xenon, Habgood and Schneider<sup>1</sup> located the points of inflection in a number of the  $p, \rho$  isotherms. They plotted the density and temperature at which these points of inflection occur, and obtained thereby a number of experimentally determined points on the locus  $(\partial^2 p/\partial \rho^2)_T = 0$  in the  $T, \rho$  plane. These data are reproduced in Fig. 4. Because of the flatness that characterizes a point of inflection, the density at which the isotherm has its inflection is very difficult to determine accurately, and this accounts for the substantial scatter of the plotted data. The straight line in Fig. 4 is the rectilinear diameter of the coexistence curve, which was also shown by Habgood and Schneider, and they pointed out that the experimentally determined locus  $(\partial^2 p/\partial \rho^2)_T = 0$  is clearly not a smooth extension of the rectilinear diameter. It is equally obvious that this locus is not asymptotic to the critical isochore at the critical point; yet one or the other of these two lines might reasonably have been expected to coincide with the locus in question, at least asymptotically at the critical point. The point of the present analysis, however, is to show that the locus is *not* linear at the critical point, but rather that it has vanishing slope there,

<sup>6</sup> D. S. Gaunt, M. E. Fisher, M. F. Sykes, and J. W. Essam, *Phys. Rev. Letters* **13**, 713 (1964).

<sup>7</sup> In the widely used notation of Fisher,  $g, f, d$  are called  $\delta, \gamma', 1/\beta$ , respectively.

<sup>8</sup> B. Widom, *J. Chem. Phys.* **41**, 1633 (1964).

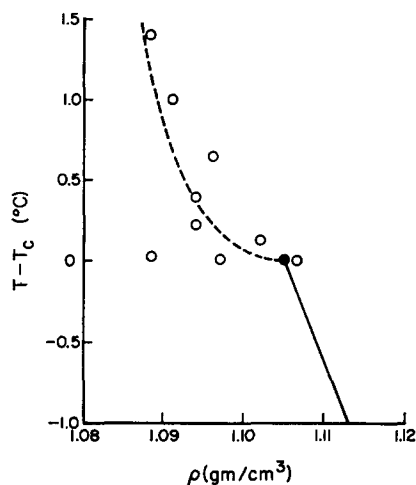


FIG. 4. The locus  $(\partial^2 p / \partial \rho^2)_T = 0$  in the  $T, \rho$  plane of xenon. The open circles are points on the locus which were determined experimentally by Habgood and Schneider. The dashed curve has vanishing slope at the critical point (filled circle), and is drawn to give a reasonable fit to the data. The present theory requires the locus to be such a curve, confined to the quadrant  $\rho \leq \rho_c$ ,  $T \geq T_c$ . The solid line is the coexistence curve's rectilinear diameter, as drawn by Habgood and Schneider.

like the dashed curve in Fig. 4, which obviously accounts for the data.

Because of Eq. (3), the locus  $(\partial^2 p / \partial \rho^2)_T = 0$  is the same as the locus

$$\rho(\partial^2 \mu / \partial \rho^2)_T + (\partial \mu / \partial \rho)_T = 0. \quad (16)$$

However,  $(\partial \mu / \partial \rho)_T$  is always positive, so the locus in question must be confined to a region in which  $(\partial^2 \mu / \partial \rho^2)_T$  is negative. In the neighborhood of the critical point, as was already mentioned,  $\mu(\rho, T) - M(T)$  is an odd function of  $\rho - \rho_c$ , so that  $(\partial^2 \mu / \partial \rho^2)_T$  vanishes on the critical isochore; and it is also known that this is a local *minimum*, and not a maximum, in  $(\partial \mu / \partial \rho)_T$ . Thus,  $(\partial^2 \mu / \partial \rho^2)_T$  is positive when  $\rho > \rho_c$  and negative when  $\rho < \rho_c$ . Therefore, the locus sought is confined entirely to  $\rho \leq \rho_c$ , which accounts for the first obvious property of the data in Fig. 4.

As the critical point is approached, the locus defined by Eq. (16) may be found from Eqs. (2), (6), and (9), and the assumed homogeneity of  $\Phi$ , to be asymptotic to the curve

$$x = (6c_1/c_0)^{d/2} (1 - \rho/\rho_c)^{-d/2} y. \quad (17)$$

From the definitions of  $x$  and  $y$  in Eqs. (4) and (5), it follows that this curve is of algebraic degree  $d/2$  in the  $T, \rho$  plane, so with the coexistence curve known to be approximately cubic, the locus of  $(\partial^2 p / \partial \rho^2)_T = 0$  is approximately of degree  $\frac{3}{2}$ , as shown schematically by the dashed curve in Fig. 4. Only in a classical fluid, where the coexistence curve is parabolic, would the locus in question be linear.

It also follows from Eq. (6), and from the homogeneity of  $\Phi$ , that as the critical point is approached

along the locus defined by Eq. (17),

$$(\partial \mu / \partial \rho)_T \sim \Phi(1, 0) x^f.$$

Comparing this with Eq. (11), one sees that the compressibility along the locus  $(\partial^2 p / \partial \rho^2)_T = 0$  is asymptotically the same as the compressibility along the critical isochore. Thus, a  $p, \rho$  isotherm is so flat near the critical point that it has essentially the same slope at its point of inflection as it does at  $\rho = \rho_c$ , even though the density at the point of inflection is substantially displaced from the critical density, by an amount proportional to  $(T - T_c)^{2/d}$ .

## 6. PRESSURE, AND CONSTANT-VOLUME SPECIFIC HEAT, ON THE CRITICAL ISOCHORE

From Eqs. (6) and (8), and the assumed homogeneity of  $\Phi$ ,

$$\mu(\rho, T) - M(T) = (\rho - \rho_c)(x + y) \sum_{n=0}^{\infty} \phi_n y^{d-1-n} x^n, \quad (18)$$

where the constant coefficients  $\phi_n$  are derivatives of  $\Phi$  with respect to the temperature at the critical isotherm,

$$\begin{aligned} \phi_0 &= \Phi(0, 1), \\ \phi_1 &= \Phi_1(0, 1), \\ \phi_2 &= \frac{1}{2} \Phi_{11}(0, 1), \text{ etc.} \end{aligned} \quad (19)$$

According to Eq. (18), at any fixed density  $\mu(\rho, T) - M(T)$  is regular at  $T = T_c$ , which is the assumption that led to Eq. (8) in the first place. The coefficient of  $x^n$  in Eq. (18) is not itself a regular function of the density at  $\rho = \rho_c$ , so there is no suggestion that  $\mu(\rho, T) - M(T)$  is regular at the critical point, but only at the critical isotherm *away* from the critical point. Such points on the critical isotherm, of which  $x = 0, y = 1$  is representative, lie in the interior of the one-phase region, where  $\mu(\rho, T)$  is surely free of singularities. Therefore, with  $\mu(\rho, T) - M(T)$  assumed nonsingular, and  $\mu(\rho, T)$  surely nonsingular, at  $T = T_c$  for any fixed  $\rho \neq \rho_c$ , it follows that  $M(T)$  is being assumed nonsingular at  $T = T_c$ .

That the chemical potential along the critical isochore,  $M(T)$ , has no singularity at  $T = T_c$ , is in accord with the known behavior of the lattice gas model.<sup>3,9</sup> Nothing is independently known, either theoretically or experimentally, about the analytic nature of  $M(T)$  at  $T = T_c$  in a real continuum fluid. Should it ever be discovered that  $M$  is singular at the critical temperature, then the hypothesis that  $\Phi(x, 1)$  is regular at  $x = 0$ , from which Eq. (8) follows, would have to be abandoned in treating a real continuum fluid, and the theory presented in the remainder of this section would then apply to the lattice gas models alone.

Suppose now that  $\pi(T)$  is the pressure along the critical isochore,

$$p(\rho_c, T) = \pi(T).$$

<sup>9</sup> C. N. Yang and C. P. Yang, Phys. Rev. Letters **13**, 303 (1964).

Below the critical temperature  $\pi(T)$  is the equilibrium vapor pressure, so it is also the pressure at the coexistence curve at the temperature  $T$ , just as  $M(T)$ , in addition to being the chemical potential on the critical isochore, is also the chemical potential at the coexistence curve. But, whereas  $M(T)$  is presumed regular at  $T=T_c$ , the function  $\pi(T)$  is known to be singular at the critical temperature.<sup>9</sup> Both  $\pi$  and  $d\pi/dT$  exist and are continuous at  $T=T_c$ , but  $d^2\pi/dT^2$  is discontinuous at  $T=T_c$  in a classical fluid, has a symmetrical logarithmic infinity there in the two-dimensional lattice gas,<sup>10</sup> and also has infinite singularities there, the precise natures of which have not yet been fully ascertained, in the three-dimensional lattice gas and in a real continuum fluid.<sup>11</sup> Because

$$d\mu = -\sigma dT + \rho^{-1} d\rho,$$

where  $\sigma$  is the entropy per unit mass, it follows that

$$d^2M/dT^2 = (-s/T) + (\rho_c^{-1} d^2\pi/dT^2),$$

where  $s$  is the constant-volume specific heat (heat capacity per unit mass) on the critical isochore.<sup>9</sup> Then with  $M(T)$  entirely free of singularities, whatever singularity is present in  $d^2\pi/dT^2$  is simultaneously present in the specific heat, and vice versa.

Define a new thermodynamic function  $Y$  by

$$Y(\rho, T) = \rho[\mu(\rho, T) - M(T)] - [\rho(\rho, T) - \pi(T)], \quad (20)$$

and note that  $Y$  vanishes both on the critical isochore and at the coexistence curve, that is, along the entire boundary of the unshaded region in Fig. 3. Also, because of Eq. (3),

$$(\partial Y/\partial \rho)_T = \mu(\rho, T) - M(T),$$

so from Eqs. (2) and (4)–(6) the function  $Y(\rho, T)$  is given everywhere in the one-phase region  $x+y>0$  by

$$da^{2/d}Y = \int_{-x\mathbf{1}(-x)}^{\mathbf{v}} \eta^{2/d-1}(x+\eta)\Phi(x, \eta)d\eta, \quad (21)$$

where  $\mathbf{1}$  is the unit step function, equal to 0 when its argument is negative and 1 when its argument is positive. The path of integration is a line of constant  $x$  in the  $x, y$  plane, with  $\eta$  the varying value of  $y$ ; it starts at the boundary of the unshaded region, that is, at the critical isochore ( $y=0$ ) when  $x>0$  but at the coexistence curve ( $y=-x$ ) when  $x<0$ ; and it extends to a general value of  $y$  in the one-phase region. The constant factor  $da^{2/d}$  is made up of the two parameters  $a, d$  that characterize the coexistence curve according to Eq. (2), while the degree  $d$  of the coexistence curve appears again in the integrand, in the exponent of  $\eta$ .

Thus, the function  $Y$  defined in Eq. (20) is, through Eq. (21), derivable from the basic homogeneous function  $\Phi$  in the equation of state. If the right-hand side of Eq. (21) is now expanded about  $x=0$  for any fixed, positive  $y$ , one expects terms of two distinct types. Firstly, there would be a power series in  $x$ , with coefficients that are functions of  $y$  singular at  $y=0$ ; this being an expansion like that on the right-hand side of Eq. (18), and arising from that part of  $Y$  which, for given  $\rho$ , is nonsingular at  $T=T_c$ . The function  $-\rho(\rho, T)$ , like  $\mu(\rho, T)$ , is surely regular in the one-phase region, and would be contained in its entirety in this series. Secondly, there would be one or more terms, independent of  $y$ , which are singular at  $x=0$ ; these arising from the singularity in  $\pi(T)$ , and being such that their second derivatives are discontinuous, or infinite, or both, at  $x=0$ .

The expansion just described may be found explicitly. The assumed homogeneity of  $\Phi$  makes the integral in Eq. (21) a generalized hypergeometric function with analytical properties very similar to that of an ordinary hypergeometric function. The detailed form of the expansion depends on whether  $f+2/d$  is, or is not, exactly equal to an integer. In the present physical context,<sup>2,12,13</sup>

$$1 < f+2/d \leq 2;$$

so that, if  $f+2/d$  equals an integer at all, then the integer is 2, as in a classical fluid and in a two-dimensional lattice gas.

#### i. $f+2/d=2$

The expansion in this case is

$$da^{2/d}Y = \sum_{n=0}^{\infty} * \frac{\phi_{n-1} + \phi_n}{2-n} y^{2-n} x^n + [Q_{\pm} + (\phi_1 + \phi_2) \ln(y/|x|)] x^2, \quad (22)$$

where the asterisk on the summation sign means that the term  $n=2$  is omitted, and where  $\phi_{-1} \equiv 0$ , all the other constant  $\phi_n$  being as defined in Eqs. (8) and (19). The quantity  $Q_{\pm}$  is one constant,  $Q_+$ , when  $x>0$ , and a different constant,  $Q_-$ , when  $x<0$ , these constants being given by

$$Q_+ = -\frac{3}{2}\phi_0 - \phi_1 + \int_1^{\infty} \left\{ (\eta+1) \left[ \Phi(\eta^{-1}, 1) - \phi_0 - \frac{\phi_1}{\eta} \right] - \frac{\phi_2}{\eta} \right\} d\eta + \int_0^1 (\eta+1) \Phi(\eta^{-1}, 1) d\eta, \quad (23)$$

$$Q_- = \frac{1}{2}\phi_0 + \phi_1 + \int_1^{\infty} \left\{ (\eta-1) \left[ \Phi(-\eta^{-1}, 1) - \phi_0 + \frac{\phi_1}{\eta} \right] - \frac{\phi_2}{\eta} \right\} d\eta. \quad (24)$$

All the integrals are convergent.

<sup>10</sup> L. Onsager, Phys. Rev. **65**, 117 (1944).

<sup>11</sup> M. E. Fisher, Phys. Rev. **136**, A1599 (1964).

<sup>12</sup> B. Widom, J. Chem. Phys. **37**, 2703 (1962).

<sup>13</sup> G. S. Rushbrooke, J. Chem. Phys. **39**, 842 (1963).

The power series in the first line on the right-hand side of Eq. (22), and the term  $(\phi_1 + \phi_2)x^2 \ln y$  in the second line, are to be ascribed to those part of  $Y$  that are regular at  $x=0$  for fixed, positive  $y$ . The remaining terms in the second line,

$$[Q_{\pm} - (\phi_1 + \phi_2) \ln |x|]x^2,$$

are independent of the density, and are to be ascribed to the singular part of  $\pi(T)$ . Their second derivative yields the singularity in the constant-volume specific heat on the critical isochore. This singularity is seen to be a *symmetrical logarithmic infinity*, with a *superimposed finite discontinuity*.

The only known examples in which it is certain that  $f+2/d=2$  are the classical fluid and the two-dimensional lattice gas. In the classical fluid  $\Phi$  is a constant, so  $\phi_1 = \phi_2 = 0$ ; that is, the coefficient of the singular  $\ln |x|$  term vanishes, and only the finite discontinuity remains as the specific-heat singularity. That the specific-heat singularity in that case is just a finite discontinuity, is well known.

In the two-dimensional lattice gas the singularity is known<sup>10</sup> to be just the symmetrical logarithmic infinity, *without* the superimposed finite discontinuity. In that case, therefore, it is quite certain that the basic (but unknown) homogeneous function  $\Phi$  in the equation of state satisfies a special symmetry condition leading to the equality of  $Q_+$ , given by Eq. (23), and  $Q_-$ , given by Eq. (24). The condition which  $\Phi$  must satisfy for this to be the case is most simply expressed, not in terms of  $\Phi$  itself, but in terms of the related function  $\Psi$  defined in Eq. (10). The condition for  $Q_+ = Q_-$  is then

$$\int_0^{\infty} [(1+\eta)\Psi(\eta^{-1}, 1) + (1-\eta)\Psi(-\eta^{-1}, 1) - 2(\phi_0 + \phi_1)]d\eta = 0.$$

The integral is convergent. The integrand is an even function of  $\eta$ , so the integral may be extended from  $-\infty$  to  $\infty$ . The function  $\Psi(x, y)$  is undefined at  $x+y=0$ , but at just such a point in the range of integration, the factor by which  $\Psi$  is multiplied vanishes.

From the present point of view, the fact that the singularity in the specific heat is a symmetrical logarithmic infinity with a superimposed finite discontinuity, is a universally occurring consequence of  $f+2/d=2$ . The logarithmic term is missing in a classical fluid only because of the "accidental" vanishing of its coefficient, while the finite discontinuity is missing in the two-dimensional lattice gas only because of an "accidental" symmetry in the function  $\Phi$ . This leads one to conjecture that the symmetrical logarithmic infinity with superimposed finite discontinuity that characterizes the specific heat of helium at its lambda point,<sup>14</sup> may have something equivalent to Eq. (21) as its mathematical origin.

<sup>14</sup> W. M. Fairbank, M. J. Buckingham, and C. F. Kellers, Bull. Am. Phys. Soc. (II) 2, 183 (1957).

## ii. $1 < f+2/d < 2$

The expansion in this case is

$$da^{2/d}Y = \sum_{n=0}^{\infty} \frac{\phi_{n-1} + \phi_n}{f+2/d-n} y^{f+2/d-n} x^n + R_{\pm} |x|^{f+2/d}, \quad (25)$$

where again  $\phi_{-1} \equiv 0$ . The quantity  $R_{\pm}$  is one constant,  $R_+$ , when  $x > 0$ , and a different constant,  $R_-$ , when  $x < 0$ , these constants being given by

$$R_+ = -\frac{\phi_0}{f+2/d} - \frac{\phi_0 + \phi_1}{f+2/d-1} - \frac{\phi_1 + \phi_2}{f+2/d-2} + \int_1^{\infty} \eta^{f+2/d-2} \left\{ (\eta+1) \left[ \Phi(\eta^{-1}, 1) - \phi_0 - \frac{\phi_1}{\eta} \right] - \frac{\phi_2}{\eta} \right\} d\eta + \int_0^1 \eta^{f+2/d-2} (\eta+1) \Phi(\eta^{-1}, 1) d\eta, \quad (26)$$

$$R_- = -\frac{\phi_0}{f+2/d} + \frac{\phi_0 + \phi_1}{f+2/d-1} - \frac{\phi_1 + \phi_2}{f+2/d-2} + \int_1^{\infty} \eta^{f+2/d-2} \left\{ (\eta-1) \left[ \Phi(-\eta^{-1}, 1) - \phi_0 + \frac{\phi_1}{\eta} \right] - \frac{\phi_2}{\eta} \right\} d\eta. \quad (27)$$

All the integrals are convergent.

The power series in Eq. (25) is to be ascribed to those parts of  $Y$  that are regular at  $x=0$  for fixed, positive  $y$ . The remaining term,

$$R_{\pm} |x|^{f+2/d},$$

is independent of the density, and is to be ascribed to the singular part of  $\pi(T)$ . Its second derivative yields the singularity in the constant-volume specific heat on the critical isochore. This singularity is seen to be an *unsymmetrical inverse-power infinity*, the power in question being  $2 - (f+2/d)$ . It may happen that the singularity in the specific heat is accidentally symmetrical about the critical temperature, that is, that  $\Phi$  is such as to make  $R_+$  in Eq. (26) equal to  $R_-$  in Eq. (27).

If  $\alpha$  is the power of  $|x|^{-1}$  with which the specific heat on the critical isochore diverges at  $x=0$ , and if one agrees formally to let  $\alpha=0$  correspond to the case of a logarithmic infinity, or finite discontinuity, or both, then the results of both Cases (i) and (ii) may be summarized by

$$f+2/d+\alpha=2. \quad (28)$$

One also, in this theory, necessarily finds the same  $\alpha$  characterizing the specific heat singularity above the critical temperature as below it.

If  $C_v$  is the constant-volume heat capacity and  $\Delta C_v$  is the discontinuity in  $C_v$  that accompanies the crossing of the coexistence curve, at the temperature  $T$ , from the one-phase region to the two-phase region; and if  $\alpha^*$  is the power of  $(T_c - T)^{-1}$  with which  $\Delta C_v$  diverges

as  $T$  approaches  $T_c$ ; then, necessarily,<sup>12</sup>

$$f + 2/d + \alpha^* = 2.$$

Therefore, from Eq. (28),  $\alpha = \alpha^*$ , that is, in the present theory the specific heat on the critical isochore, and  $\Delta C_v$ , are characterized by the same divergence index. Equation (28) is also characteristic of Fisher's model,<sup>2</sup> and it corresponds to the Rushbrooke inequality<sup>13</sup> holding as an equality. From Eqs. (15) and (28) it follows that in the present theory the Griffiths inequality<sup>15</sup> also holds as an equality.

That it is the same  $\alpha$  which determines the divergence of the specific heat both above and below the critical temperature, is a necessary consequence of the assumed homogeneity of  $\Phi$ . This is similar to the circumstance observed in Sec. 3, where the homogeneity of  $\Phi$  required that the compressibility index  $f$  be the same above and below the critical temperature. Just as there is some

evidence<sup>2,6</sup> that the two  $f$ 's may, in reality, differ slightly in three-dimensional systems, so also there is some evidence<sup>11</sup> that in three-dimensional systems the two  $\alpha$ 's may differ slightly. However, there is no suggestion that either  $\alpha$  is far from 0; so Case (i), with its logarithmic singularity and superimposed discontinuity probably always provides an adequate description of the behavior of the specific heat at the critical point.

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<sup>15</sup> R. B. Griffiths, Phys. Rev. Letters **14**, 623 (1965).

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## Influence of Electric and Magnetic Fields on the Molecular Alignment in the Liquid Crystal Anisal-*p*-aminoazobenzene\*

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The molecular alignment has been studied for anisal-*p*-aminoazobenzene in the presence of external magnetic and ac electric fields. Measurements of the dielectric loss at a microwave frequency of 24 kMc/sec were used to indicate the extent of the molecular alignment. For the external fields parallel to each other, the degree of molecular alignment which could be obtained for a 370 kc/sec electric field was the same as that which could be produced by a magnetic field. For the magnetic and electric fields perpendicular to each other, the ratio of  $E/H$  corresponding to a random orientation of the molecules in the plane of  $E$  and  $H$  was obtained. As the magnetic field was changed from 500 to 3000 G the ratio of  $E/H$  remained constant within the limits of experimental error. The value obtained for  $E/H$  could not be explained by assuming that the processes responsible for the molecular alignment were associated with only the anisotropy in the dielectric constant and the permeability.

### INTRODUCTION

PREVIOUS work<sup>1</sup> has indicated that the degree of molecular alignment which could be produced by an electric field in a liquid crystal with positive dielectric anisotropy was comparable to that produced by a magnetic field. The primary object of this work is to make a more accurate comparison between electric and magnetic fields for producing molecular alignment and to investigate the molecular alignment when the magnetic and electric fields are at right angles to each

other. Previous work<sup>1</sup> on anisal-*p*-aminoazobenzene involved coaxial and ordinary waveguide cells so that external magnetic and electric fields could not act simultaneously.

Fredericksz and Zwetkoff<sup>2</sup> investigated some liquid crystals in the presence of external magnetic and electric fields acting simultaneously. They studied *p*-azoxyanisole, *p*-acetoxybenzalazin, dibenzalbenzidin, and anisilidenbenzidin. Using optical techniques they were able to compare the effectiveness of electric and magnetic fields in producing molecular alignment.

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<sup>1</sup> E. F. Carr, J. Chem. Phys. **42**, 738 (1965).

<sup>2</sup> V. Fredericksz and V. Zwetkoff, Acta Physicochim. URSS **3**, 895 (1935).