

# Critical-point thermodynamics of fluids without hole-particle symmetry

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We have examined an infinite class of fluids which exhibit a liquid-vapor critical point, with regard to corrections to thermodynamic scaling of critical phenomena. These "penetrable-sphere models" possess an underlying bilateral symmetry in their equivalent binary fluid mixture versions. After postulating a suitable scaling for these mixtures, we show that the transcription to the penetrable-sphere models produces a generalization of the conventional pure-fluid scaled equation of state. Some leading corrections to the scaled form of thermodynamic properties are derived and tabulated. These corrections are presented in a form that makes no explicit reference to their modelistic source, so in fact they may apply to real substances.

## I. INTRODUCTION

It has been proposed<sup>1-5</sup> that the equation of state of the lattice gas model<sup>6</sup> in the one-phase region near its critical point, is of the form

$$\mu(\rho, T) - \mu(\rho_c, T) = (\rho - \rho_c) |\rho - \rho_c|^{\delta-1} \times h_1[(T - T_c)/|\rho - \rho_c|^{1/\beta}], \quad (1.1)$$

where  $\mu(\rho, T)$  is the chemical potential as a function of the number density  $\rho$  and the temperature  $T$ , with  $\rho_c$  and  $T_c$  the critical density and critical temperature;  $\delta$  and  $\beta$  are two critical-point exponents; and where  $h_1$  is some function only of the ratio of  $T - T_c$  to  $|\rho - \rho_c|^{1/\beta}$ , as shown. It has been subsequently found that the equation of state of a real fluid near its critical point can be represented in the form (1.1) with considerable accuracy.<sup>7-10</sup>

If Eq. (1.1) is to be a correct asymptotic form, it is essential<sup>1</sup> that  $\mu(\rho_c, T)$ , the chemical potential on the critical isochore, be analytic in  $T$  in the neighborhood of  $T = T_c$ . Models are now known<sup>11-13</sup> in which that condition is violated. In those models  $\mu(\rho_c, T)$  in the two-phase region is still analytic in  $T$  at  $T = T_c$ , but  $\mu(\rho_c, T)$  in the one-phase region is a different, and singular, function of  $T$ . The failure of  $\mu(\rho_c, T)$  to be a single function of  $T$  analytic at  $T_c$  is related to the lack in those models of the hole-particle symmetry of the lattice gas and to the associated failure of the law of rectilinear diameters.<sup>11-14</sup> It is now generally believed<sup>11,14,15</sup> that in real fluids, too, hole-particle symmetry is absent, the law of rectilinear diameters fails, and  $\mu(\rho_c, T)$  is not a single function of  $T$  analytic at  $T = T_c$ . Such effects are being actively sought in experiment<sup>16</sup>; but because Eq. (1.1), with its implicit assumption of hole-particle symmetry and analyticity of  $\mu(\rho_c, T)$ , does hold quite accurately, deviations from lattice-gas symmetry in real fluids are slight at most and will be difficult to establish. But in anticipation of those deviations being ultimately found, and to provide some guide as to how they may be sought, it is im-

portant to find a generalization of Eq. (1.1) that is no longer dependent on the lattice-gas symmetry. The object of this paper, ultimately realized in Sec. III, is to propose such a generalization and to study some of its implications.

A program of this kind was first undertaken by Green, Cooper, and Levelt Sengers.<sup>17</sup> Our approach differs considerably from theirs, and the corresponding results of the two approaches differ in some respects, though in many instances (especially if comparison is made with the later works in Ref. 17) they are the same. The procedure of Green, Cooper, and Levelt Sengers is not only directed only toward evaluating the effects of deviations from lattice-gas symmetry, but is intended also to yield the leading terms among those corrections to the asymptotic formula (1.1) that are present even in the lattice-gas model. The present paper has only the former object. The corrections to Eq. (1.1) that may become important outside the asymptotic regime, when  $|T - T_c|$  or  $|\rho - \rho_c|$  is not small, are not known with certainty even in the lattice gas, though for that case their form has been conjectured by Domb.<sup>18</sup> Where it is possible to compare our correction terms, which account for the deviation from lattice-gas symmetry, with those of Domb, we verify that ours are the larger; so that, if Domb's estimates and the present theory are both correct, the leading corrections to Eq. (1.1) in real fluids will prove to be those that are due to deviations from hole-particle symmetry and that have, therefore, no counterpart in the lattice gas.

The basis of our analysis, as it is ultimately developed in Sec. III, is the assumption that the form of Eq. (1.1) remains correct even when the lattice-gas symmetry is lacking, provided that the three quantities  $\mu(\rho_c, T)$ ,  $T - T_c$ , and  $\rho = \rho_c$  are replaced by three others, chosen so that in terms of them the fluid has thermodynamic symmetries closely analogous to those which the lattice gas has in terms of the original variables. The possibility of the existence of such symmetry variables in real fluids is suggested in the first place by the penetrable-sphere model<sup>11</sup> and by Mermin's models<sup>12,13</sup>; but we shall show

in Sec. II that the transcription and symmetry rules first found in the penetrable-sphere model apply equally well to a very much larger class of model fluids, which includes one derived from the binary mixture of Gaussian molecules.<sup>19-21</sup>

In all these cases there is found to exist a *line of symmetry* (see Fig. 1), with the property that for any thermodynamic state on one side of the line there is a conjugate state on the other side in which the thermodynamic functions of the fluid are related by a simple (though model-dependent) transformation to those in the original state. In the two-phase region the line of symmetry coincides with the locus of the midpoints of the diameters of the coexistence curve, that is, with the locus of states in which the density  $\rho$  is the arithmetic mean  $\frac{1}{2}(\rho_1 + \rho_g)$  of the densities  $\rho_1$  and  $\rho_g$  of coexistent liquid and vapor. In all known cases the chemical potential on the line of symmetry (hence, in particular, in the two-phase region) is an analytic function of  $T$  in the neighborhood of  $T = T_c$ . The lattice gas also has such a line of symmetry; but because conjugate states in the lattice gas are those related by the simple particle-hole transformation, the line of symmetry is there just the critical isochore,  $\rho = \rho_c$ ; whereas more generally, as shown in Fig. 1, the line of symmetry in the  $T, \rho$  plane is more complex. In each of the models of the class discussed in Sec. II, and in each of Mermin's models,<sup>12,13</sup> the density on the line of symmetry, as a function of the temperature, has a singularity at  $T = T_c$  that is like that in the energy,

$$|\rho - \rho_c| \sim |T - T_c|^{1-\alpha} \quad (\text{line of symmetry}), \quad (1.2)$$

where  $\alpha$  is the index of the divergence of the constant-volume specific heat. Because in the two-phase region the line of symmetry coincides with the diameter of the coexistence curve, (1.2) implies the failure of the law of rectilinear diameters. (It fails also in the model of Hemmer and Stell,<sup>14</sup> which is of a quite different kind.)

The whole of the development in Sec. III presupposes the existence of a line of symmetry with the properties just described. If in a real fluid the chemical potential in the two-phase region is analytic in  $T$  at  $T = T_c$ , then an operational definition of the line of symmetry in the  $T, \rho$  plane is that it is the coexistence-curve diameter in the two-phase region and, in the one-phase region, is the curve on which the chemical potential is the *same* analytic function of  $T$  as it is in the two-phase region. So far as it is now possible to tell from experiment,<sup>9,22,23</sup> the chemical potential in the two-phase region is indeed analytic in the temperature at the critical point. Should it ultimately prove to be singular it will mean that the equation of state to be proposed in Sec. III applies at most only to model systems with special symmetries; while for real fluids, instead of  $\mu(\rho, T)$  some other thermodynamic function, perhaps a combination of chemical potential and pressure that

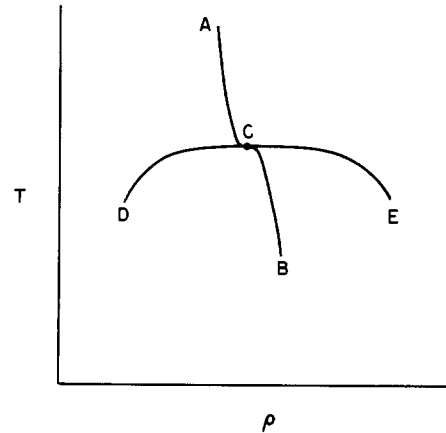


FIG. 1. Line of symmetry (ACB) and coexistence curve (DCE) in the temperature-density plane. The critical point is at C. The portion CB of the line of symmetry is also the locus of midpoints of the coexistence curve diameters, defined by  $\rho = \frac{1}{2}(\rho_1 + \rho_g)$ .

in the two-phase region is analytic in  $T$  at  $T = T_c$ , would have been the appropriate quantity in terms of which to express the equation of state.

## II. GENERAL TRANSCRIPTION AND SYMMETRY RELATIONS

In order to provide a concrete basis for justification of our generalized scaling formalism, we now consider an infinite class of binary fluid mixture models. These mixtures will be related in turn to equivalent pure fluids, which we shall collectively call "penetrable-sphere models." The two constituents of the starting mixtures (denoted by 1 and 2, with respective molecular numbers  $N_1$  and  $N_2$ ) interact only in unlike molecular pairs. The components then are separately ideal gases, but in the mixture the total potential energy  $U(N_1 | N_2)$  will have the form

$$U(N_1 | N_2) = \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} u(|\mathbf{r}_i - \mathbf{s}_j|), \quad (2.1)$$

in which positions  $\mathbf{r}_i$  and  $\mathbf{s}_j$  refer, respectively, to molecules of types 1 and 2.

We shall require  $u$  to be nonnegative:

$$u(x) \geq 0 \quad (x \geq 0), \quad (2.2)$$

for otherwise the mixture would be subject to catastrophic collapse in the conventional infinite system limit. In addition it is mandatory to require an integrability condition; for all  $B > 0$  we therefore demand

$$\int_0^\infty x^{d-1} \min[B, u(x)] dx < \infty \quad (2.3)$$

(the dimensionality  $d$  need not be restricted to 3).

Under conditions of sufficiently high density or low temperature,  $U$  can produce phase separation of the two components, and the resulting critical solution point forms the major object of attention here.

The mixture grand partition function has the following form:

$$\begin{aligned} Z_G(y_1, y_2, \beta_m) &= \exp(\beta_m p_m V) \\ &= \sum_{N_1, N_2} (y_1^{N_1} y_2^{N_2} / N_1! N_2!) \\ &\times \int d\mathbf{r}_1 \cdots \int d\mathbf{s}_{N_2} \exp[-\beta_m U(N_1 | N_2)], \\ \beta_m &= 1/kT_m, \end{aligned} \tag{2.4}$$

where the  $y_1$  and  $y_2$  are absolute activities,  $V$  is the system volume, and the mixture temperature and pressure are denoted by  $T_m$  and  $p_m$ . The two species of molecules are mechanically identical, so the mixture possesses an obvious symmetry relation,

$$p_m(y_1, y_2, \beta_m) = p_m(y_2, y_1, \beta_m). \tag{2.5}$$

This component interchange symmetry is analogous to (but not trivially isomorphous with) the Ising model spin reversal symmetry.

Owing to the simple structure of  $U$ , shown in Eq. (2.1), the integrals over positions of all component 2 molecules may immediately be carried out in  $Z_G$  to give

$$\begin{aligned} \exp(\beta_m p_m V) &= \sum_{N_1} (y_1^{N_1} / N_1!) \int d\mathbf{r}_1 \cdots d\mathbf{r}_{N_1} \\ &\times \exp[y_2 W(\mathbf{r}_1 \cdots \mathbf{r}_{N_1}, \beta_m)], \end{aligned} \tag{2.6}$$

where

$$W(\mathbf{r}_1 \cdots \mathbf{r}_{N_1}, \beta_m) = \int d\mathbf{s} \exp[-\beta_m \sum_{i=1}^{N_1} u(|\mathbf{s} - \mathbf{r}_i|)] \tag{2.7}$$

is an effective volume available to a particle of species 2 when those of species 1 have fixed locations.

If positions  $\mathbf{r}_1 \cdots \mathbf{r}_{N_1}$  were widely dispersed relative to the range of  $u$ ,  $W$  would differ from the geometric volume  $V$  by  $N_1$  localized decrements  $v_0$ ,

$$W \rightarrow V - N_1 v_0(\beta_m),$$

$$v_0(\beta_m) = - \int d\mathbf{s} \{ \exp[-\beta_m u(|\mathbf{s} - \mathbf{r}|)] - 1 \}. \tag{2.8}$$

This observation motivates writing Eq. (2.6) in an alternative way,

$$\begin{aligned} \exp[(\beta_m p_m - y_2) V] &= \sum_{N_1} (1/N_1!) \{ y_1 \exp[-y_2 v_0(\beta_m)] \}^{N_1} \\ &\times \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_{N_1} \exp\{ y_2 [W(1 \cdots N_1, \beta_m) \\ &\quad - V + N_1 v_0(\beta_m)] \}. \end{aligned} \tag{2.9}$$

The last result may be cast into the form of a grand partition function for a pure fluid, at inverse temperature  $\beta_0 = 1/kT$ , by adjusting  $y_2$  to the value,

$$y_2 = \beta_0 \epsilon / v_0(\beta_m), \tag{2.10}$$

where  $\epsilon$  is an arbitrary positive constant. By that

means Eq. (2.9) adopts the form

$$\begin{aligned} \exp(\beta_0 p V) &= \sum_{N_1} (y^{N_1} / N_1!) \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_{N_1} \\ &\times \exp[-\beta_0 \Phi(1 \cdots N_1)]. \end{aligned} \tag{2.11}$$

In terms of the mixture model quantities, the pure-fluid pressure, activity, and potential energy have been identified as follows:

$$p = (\beta_m p_m - y_2) / \beta_0; \tag{2.12}$$

$$y = y_1 \exp[-y_2 v_0(\beta_m)]; \tag{2.13}$$

$$\begin{aligned} \Phi(\mathbf{r}_1 \cdots \mathbf{r}_{N_1}) &= [\epsilon / v_0(\beta_m)] [V - N_1 v_0(\beta_m) \\ &\quad - W(\mathbf{r}_1 \cdots \mathbf{r}_{N_1}, \beta_m)]. \end{aligned} \tag{2.14}$$

Although variations in  $\epsilon$  merely change the energy scale for  $\Phi$ , different choices for the temperature parameter  $\beta_m$  for the underlying mixture yield fundamentally distinct potentials  $\Phi$ .

We can write  $\Phi$  as the following integral:

$$\begin{aligned} \Phi(\mathbf{r}_1 \cdots \mathbf{r}_{N_1}) &= \frac{\epsilon}{v_0} \int d\mathbf{s} [1 - \sum_{i=1}^{N_1} \Delta_i - \prod_{i=1}^{N_1} (1 - \Delta_i)], \end{aligned} \tag{2.15}$$

where

$$\Delta_i(\mathbf{s}) = 1 - \exp[-\beta_m u(|\mathbf{s} - \mathbf{r}_i|)]. \tag{2.16}$$

On account of the nonnegativity of  $u$ , Eq. (2.2), we have

$$0 \leq \Delta_i \leq 1. \tag{2.17}$$

Notice that

$$(1 - \Delta_a)(1 - \Delta_b) = 1 - \Delta_a - \Delta_b + \Delta_a \Delta_b \geq 1 - \Delta_a - \Delta_b, \tag{2.18}$$

if the  $\Delta$ 's satisfy condition (2.17). Then at least for  $N_1 = 1, 2$  the integrand in Eq. (2.15) is never positive. Suppose for some integer  $M \geq 1$  it has been established that

$$1 - \Delta \equiv \prod_{i=1}^M (1 - \Delta_i) \geq 1 - \sum_{i=1}^M \Delta_i, \tag{2.19}$$

where of course  $0 \leq \Delta \leq 1$ . Then

$$\begin{aligned} \prod_{i=1}^{M+1} (1 - \Delta_i) &= (1 - \Delta)(1 - \Delta_{M+1}) \\ &\geq 1 - \Delta - \Delta_{M+1}, \\ &= 1 - \sum_{i=1}^{M+1} \Delta_i. \end{aligned} \tag{2.20}$$

Hence by induction Eq. (2.19) must be true for all  $M \geq 1$ . The integrand in Eq. (2.15) therefore is never positive, so

$$\Phi(\mathbf{r}_1 \cdots \mathbf{r}_{N_1}) \leq 0 \tag{2.21}$$

for every pure-fluid model derivable from our symmetric mixtures.

In order to most conveniently discuss the pure-fluid

thermodynamic properties, we introduce the following dimensionless quantities:

$$\begin{aligned} z &= v_0 y && \text{(activity),} \\ \rho &= \langle N_1 \rangle v_0 / V && \text{(density),} \\ \theta &= \epsilon \beta_0 = \epsilon / kT && \text{(inverse temperature),} \\ \phi &= v_0 \langle \Phi \rangle / V \epsilon && \text{(potential energy density),} \\ \pi &= \beta_0 p v_0 && \text{(pressure).} \end{aligned} \quad (2.22)$$

The mixture symmetry relation (2.5) connects pairs of points  $(y_1, y_2, \beta_m)$  and  $(y_2, y_1, \beta_m)$  that map into another pair  $(z, \theta)$  and  $(z', \theta')$  for the pure fluid. By virtue of transcription relations (2.10) and (2.13), these conjugate points for the pure fluid satisfy the thermodynamic identity

$$\theta' = z \exp(\theta). \quad (2.23)$$

Furthermore, Eqs. (2.5) and (2.12) require

$$\pi' + \theta' = \pi + \theta. \quad (2.24)$$

After taking the logarithm of both sides of Eq. (2.9) and then differentiating with respect to  $y_2$ , a third conjugate thermodynamic identity results,

$$\rho' = \theta(1 - \phi - \rho). \quad (2.25)$$

Obviously Eqs. (2.23) and (2.25) must remain valid under interchange of primed variables for unprimed ones.

The bilateral symmetry line  $y_1 = y_2$  in the mixture maps into the pure fluid locus,

$$z = \theta \exp(-\theta). \quad (2.26)$$

Above the critical temperature for the pure fluid, this relation describes a single curve in the  $\rho, T$  plane which intersects the critical point (see Fig. 1). Below the critical temperature, however, Eq. (2.26) generates all points on or within the coexistence curve; in particular coexisting phases of the pure fluid have

$$\begin{aligned} \theta' &= \theta, \\ \rho &= \rho_g \quad \text{(vapor phase),} \\ \rho' &= \rho_l \quad \text{(liquid phase).} \end{aligned} \quad (2.27)$$

Clearly the chemical potential is analytic in  $\theta$  along the entire locus (2.26).

Out of the infinite set of pure-fluid models which can be generated by mixture interactions of type (2.1), only two have thus far received special attention:

(a) The specific penetrable-sphere model introduced by Widom and Rowlinson<sup>11</sup> selects  $u$  to be the rigid sphere interaction,

$$\begin{aligned} u(x) &= +\infty, && (0 \leq x < \sigma) \\ &= 0, && (\sigma \leq x). \end{aligned} \quad (2.28)$$

The elementary volume  $v_0$  will equal the content of the spherical exclusion region in  $d$  dimensions:

$$v_0 = 2\pi^{d/2} \sigma^d / d\Gamma(\frac{1}{2}d), \quad (2.29)$$

independently of the choice for  $\beta_m$ . The potential  $\Phi$  then measures the total overlap volume of the  $N_1$  exclusion spheres.

(b) The Gaussian mixture model<sup>19,20</sup> trades the clean geometric directness of model (a) for cluster integral simplicity by requiring for all positive  $x$ ,

$$u(x) = -u_0 \ln[1 - \exp(-\alpha x^2)], \quad (2.30)$$

where  $u_0$  and  $\alpha$  are positive constants. Then when  $\beta_m$  is chosen equal to  $u_0^{-1}$ , the Mayer  $f$  function becomes a Gaussian,

$$\exp[-\beta_m u(x)] - 1 = -\exp(-\alpha x^2), \quad (2.31)$$

and for that unique temperature the cluster integrals may be computed (irrespective of topological complexity) by quadratic-form diagonalization. Although this artifice fixes  $\beta_m$ , the pure fluid temperature parameter  $\beta_0$  (i.e.,  $\theta$ ) is still free to vary.

In view of the fact that thermodynamic scaling provides an accurate description of the symmetrical Ising ferromagnet near its critical point, and leads in turn to the lattice gas statement (1.1), it is appealing to suppose that scaling might also apply to our symmetric mixture models. That hypothesis has in fact been tested for the Gaussian mixture,<sup>20</sup> and appears to be valid, with a set of exponents that are distinctly "nonclassical" in three dimensions. We have therefore proceeded on the plausible assumption that thermodynamic scaling applies to all mixture models obeying Eqs. (2.1)–(2.3).

A possible format in which to express the scaling property for the mixtures is the following:

$$\ln \left( \frac{y_1}{y_2} \right) = (\rho_1 - \rho_2) | \rho_1 - \rho_2 |^{\delta-1} h_m \left( \frac{\ln(y_1 y_2 / y_c^2)}{| \rho_1 - \rho_2 |^{1/\beta}} \right), \quad (2.32)$$

where  $\rho_\alpha = \langle N_\alpha \rangle v_0 / V$ , and  $y_c$  is the common value of  $y_1$  and  $y_2$  at the critical point. The general transformation from mixture to pure fluid carries this manifestly symmetrical relationship into one which is unsymmetrical in the pure-fluid (penetrable sphere) version. The basic aim of this paper is investigation of new terms that arise under this symmetry-warping transcription, which carries the specific statement (2.32) into

$$\ln \left( \frac{\theta'}{\theta} \right) = (\rho - \rho') | \rho - \rho' |^{\delta-1} h_m \left( \frac{\ln(\theta\theta'/\theta_c^2)}{| \rho - \rho' |^{1/\beta}} \right). \quad (2.33)$$

In the next section we in fact propose and study an equation of state of the form of Eq. (2.33) as the generalization of Eq. (1.1) that is appropriate for this whole class of penetrable-sphere models.

### III. EQUATION OF STATE IN THE NEIGHBORHOOD OF THE CRITICAL POINT

We now consider a generalization of Eq. (1.1) that, so far as possible, preserves its form, yet differs from it in this important respect: It is no longer assumed that on the line of symmetry (on which the chemical potential is an analytic function of the temperature) the density is simply the constant  $\rho_c$ , but instead the density on the line of symmetry is allowed to be a singular function of the temperature, as in Eq. (1.2).

If  $\mu(\rho, T)$  is again the chemical potential of the fluid at density  $\rho$  and temperature  $T$ , and if the analytic function  $M(T)$  is the chemical potential on the line of symmetry at the same temperature  $T$ , then for all the models with a line of symmetry given by Eq. (2.26) we have

$$[\mu(\rho, T) - M(T)]/kT = \ln(z/\theta e^{-\theta}) = \ln(\theta'/\theta), \quad (3.1)$$

where, as in the preceding section,  $z$  and  $\theta$  are the activity and reciprocal temperature in the thermodynamic state  $\rho, T$  and  $\theta'$  is the reciprocal temperature in the conjugate state. If at the same time  $\rho'$  is, as before, the density in the conjugate state, then the appropriate generalization of Eq. (1.1) for this whole class of models, in the one-phase region, is

$$\ln(\theta'/\theta) = (\rho - \rho') |\rho - \rho'|^{\beta-1} h[t(\theta, \theta') / |\rho - \rho'|^{1/\beta}], \quad (3.2)$$

where  $t(\theta, \theta')$  is any symmetric function of  $\theta, \theta'$  such that  $t(\theta, \theta) \equiv 1/\theta - 1/\theta_c$ . Notice that this slightly modifies Eq. (2.33).

On the interchange of the primed and unprimed variables, that is, under the transformation from any one thermodynamic state to its conjugate state, both sides of Eq. (3.2) simply change sign, so the proposed relation is invariant to that transformation. This is analogous to the way in which the particle-hole symmetry of the lattice gas is reflected in Eq. (1.1), both sides of which change sign when  $\rho$  is replaced by the conjugate  $\rho' = 2\rho_c - \rho$ ; because of the particle-hole symmetry  $\mu(\rho, T) + \mu(2\rho_c - \rho, T) = 2\mu(\rho_c, T)$ .

Because in the lattice gas the density on the line of symmetry,  $\rho_{1s}$ , is just the critical density,  $\rho_c$ , the variable  $\rho - \rho_c$  that appears in Eq. (1.1) is both  $\rho - \rho_{1s}$  and  $\frac{1}{2}(\rho - \rho')$ . In the generalization from Eq. (1.1) to Eq. (3.2) these are no longer equivalent, and it is important that  $\frac{1}{2}(\rho - \rho')$  rather than  $\rho - \rho_{1s}$  be chosen to play the role previously played by  $\rho - \rho_c$ . Had  $\rho - \rho_c$  in Eq. (1.1) been replaced instead by  $\rho - \rho_{1s}$ , then on account of Eqs. (1.2) and (3.1) the thermodynamic function  $\mu(\rho, T)$  would thereby have been made to be singular along the whole of the critical isotherm in the one-phase region. No such spurious singularities appear when  $\rho - \rho_c$  is replaced by  $\frac{1}{2}(\rho - \rho')$ , for  $\rho'$ , unlike  $\rho_{1s}$ , is just another thermodynamic function—typically, as in

Eq. (2.25), it is  $\theta(1 - \phi - \rho)$ , with  $\phi$  the potential energy density in the state  $\rho, \theta$ —and is therefore, like  $\mu(\rho, T)$ , analytic at all points in the one-phase region.

That the left-hand side of Eq. (3.2) differs by the factor  $1/kT$  from being the strict analog of the left-hand side of Eq. (1.1), is of no consequence. Because

$$T^{-1} = \frac{[1 - (T - T_c)/T_c + \dots]}{T_c},$$

the left-hand side of Eq. (1.1) could equally well have been taken to be  $[\mu(\rho, T) - \mu(\rho_c, T)]/kT$  without altering its asymptotic properties or the asymptotic properties of any of the thermodynamic functions derived from it. Similarly, any function  $t$  in Eq. (3.2) that satisfies the conditions stated for it is in that same sense equivalent to any other, and it is a matter of indifference which is chosen. For technical reasons that will become clear later it is convenient to choose

$$t(\theta, \theta') = 1/(\theta\theta')^{1/2} - 1/\theta_c \quad (3.3)$$

but this choice has no fundamental significance.

When  $\rho - \rho_c$  in Eq. (1.1) was replaced by  $\frac{1}{2}(\rho - \rho')$ , the resulting factors  $2^{-\beta}$  in the coefficient multiplying the function  $h_l$  and  $2^{1/\beta}$  in the argument of that function were simply made part of the definition of the new function  $h$  in Eq. (3.2). Except for such scale factors, the functions  $h$  in Eq. (3.2) and  $h_l$  in (1.1) might well be the same. One must in any event require the same properties of  $h$  in Eq. (3.2) that are required of the analogous function in the lattice gas.<sup>1,5</sup> (i)  $h(\zeta)$  is an analytic function of  $\zeta$  in the neighborhood of  $\zeta = 0$ . This is necessary again to avoid spurious singularities at the critical isotherm in the one-phase region. (ii)  $h(0) \neq 0$ , so that the critical isotherm is of algebraic degree  $\delta$ . (iii)  $\zeta^{-\beta(\delta-1)}h(\zeta)$  is an analytic function of  $\zeta^{-2\beta}$  near  $\zeta^{-2\beta} = 0$ , when  $\zeta > 0$ . This is necessary to avoid spurious singularities at the line of symmetry  $\rho = \rho'$  in the one-phase region. (iv)  $\zeta^{-\beta(\delta-1)}h(\zeta)$  has a nonvanishing limit as  $\zeta \rightarrow +\infty$ . This makes  $\mu(\rho, T) - M(T)$  proportional to  $\rho - \rho'$  in the neighborhood of the line of symmetry and so leads to a finite, nonvanishing compressibility there for all temperatures  $T > T_c$ . Two further conditions, (v) and (vi), concern the behavior of  $h$  at the boundary of the two-phase region. The critical-point exponent  $\beta$  is defined to be such that the algebraic degree of the coexistence curve in the temperature-density plane is  $1/\beta$ , so that as the critical point is approached the coexistence curve in the temperature-density plane is asymptotically of the form  $-t = a |\rho - \rho'|^{1/\beta}$ , with  $\rho$  and  $\rho'$  then the densities  $\rho_l$  and  $\rho_g$  of coexisting liquid and vapor, with  $t(\theta, \theta')$  then just  $1/\theta - 1/\theta_c$ , and with  $a$  some positive constant. Then: (v)  $h(-a) = 0$ , so that  $\theta' = \theta$  and  $\mu(\rho, T) = M(T)$  at the coexistence curve. (vi) The derivative  $h'(-a)$  exists, so that the compressibility in the one-phase region remains finite as the coexistence curve is approached at any point other than the critical point.

TABLE I. Consequences of proposed equation of state. The functions  $M(T)$  and  $Q(T)$  are analytic at  $T = T_c$  but are not otherwise specified. The quantities  $A_{\pm}, B, C, D, E, F_{\pm}, G, H_{\pm}, I_{\pm}, J_{\pm}, K_{\pm}, L, N, O_{\pm}, R_{\pm}, S_{\pm}, U_{\pm}, W_{\pm}, X_{\pm}$  are constants, the subscript  $\pm$  specifying either of two values according as  $T > T_c$  (subscript +) or  $T < T_c$  (subscript -), except in the case of  $F_{\pm}$ , where the subscripts specify either of two values according as  $\rho > \rho_c$  or  $\rho < \rho_c$ .

	On the critical isochore	On the line of symmetry	At the coexistence curve	On the critical isotherm
$\mu$	$M(T) + A_{\pm}(T - T_c)^{\gamma+1-\alpha} + \dots$ ( $A_{-} = 0$ )	$M(T)$	$M(T)$	$\mu_c + (\rho - \rho_c)   \rho - \rho_c  ^{\beta-1} [B + C(\rho - \rho_c) \times   \rho - \rho_c  ^{\beta-1/\beta-1} + \dots]$
$(\partial\mu/\partial\rho)_T = (\rho^2\chi)^{-1}$	$D(T - T_c)^{\gamma} + \dots$ ( $T > T_c$ )	$D(T - T_c)^{\gamma} + \dots$ ( $T > T_c$ )	$E(T_c - T)^{\gamma} [1 + F_{\pm}(T_c - T)^{\gamma+1+\theta} + \dots]$ in the one-phase region ( $F_{-} = -F_{+}$ )	
$(\partial^2\mu/\partial\rho^2)_T$	$G(T - T_c)^{2\gamma-1} + \dots$ ( $T > T_c$ )			
$p$	$Q(T) +  T - T_c ^{\beta-\alpha} \times [H_{\pm} + I_{\pm}  T - T_c ^{\gamma-1} + \dots]$ ( $I_{-} = 0, H_{-} = J_{-}$ )	$Q(T) +  T - T_c ^{\beta-\alpha} \times [J_{\pm} + K_{\pm}(T - T_c) + \dots]$ ( $J_{-} = H_{-}$ )	$Q(T) +  T - T_c ^{\beta-\alpha} \times [J_{-} + K_{-}(T - T_c) + \dots]$ ( $J_{-} = H_{-}$ )	$p_c + (\rho - \rho_c)   \rho - \rho_c  ^{\beta-1} \times [L + N(\rho - \rho_c) + \dots]$
$C_v$	$ T - T_c ^{-\alpha} [O_{\pm} + R_{\pm}  T - T_c ^{\alpha} + S_{\pm}  T - T_c ^{\beta-\alpha} + \dots]$ ( $S_{\pm} = 0$ )	$ T - T_c ^{-\alpha} [U_{\pm} + W_{\pm}  T - T_c ^{\alpha} + X_{\pm}  T - T_c ^{\beta-\alpha} + \dots]$		

The logical status of Eq. (3.2) with respect to the class of models discussed in Sec. II is the same as that of Eq. (1.1) with respect to the lattice gas, viz., that of a well-motivated conjecture, supported by experience, with no known contradictions. Equation (1.1), as already mentioned, has proven useful also in the interpretation of the properties of real fluids. Similarly, the hope is that the present results, though most narrowly construed only as a description of the penetrable-sphere models, may also prove useful in applications to real fluids. Some such generalization of Eq. (1.1) will in any event be required if or when  $\mu(\rho_c, T)$  and the coexistence curve diameter, are found to be singular. That Eq. (3.2) may be more generally applicable than was at first intended is indicated by the fact that, if Eq. (1.1) is assumed to be correct for the lattice gas, then  $\mu - M(T)$  for Mermin's bar model<sup>12</sup> has the asymptotic form given by Eq. (3.2), even though the bar model is not one of the class of penetrable-sphere models.<sup>24</sup> However, Eq. (3.2) is probably still too model dependent to be universal; it is in any case not in a convenient form for applications to real fluids, because as it stands it requires a knowledge of the thermodynamic functions both in the given state and in its conjugate state. But the consequences of Eq. (3.2), as they are derived below, are ultimately stated in a form that makes no explicit reference to the models in which they originated, so those results may be directly applicable to any fluid with a line of symmetry, including real fluids if these prove to have one.

The origin and status of Eq. (3.2) having now been explained, the remainder of this section is devoted to an examination of its consequences. The chemical potential  $\mu$ , the derivatives  $(\partial\mu/\partial\rho)_T$  and  $(\partial^2\mu/\partial\rho^2)_T$  (the first of which is equal to  $1/\rho^2\chi$ , where  $\chi$  is the isothermal compressibility), the pressure  $p$ , and the constant-volume heat capacity  $C_v$ , as obtained from Eqs. (1.2), (3.2), and (3.3), are evaluated along one or more paths that pass through the critical point: the critical isochore, the line of symmetry, the coexistence curve, or the critical isotherm. Each function so evaluated is expressed as a leading term (or terms) plus correction terms, the leading terms being the same as in the lattice gas and the correction terms accounting for such deviations from lattice-gas symmetry as the nonanalyticity of  $\mu(\rho_c, T)$  and the failure of the law of rectilinear diameters. An exception is  $(\partial\mu/\partial\rho)_T$  on the critical isochore and on the line of symmetry, which is obtained for a purpose other than that of illustrating deviations from lattice-gas symmetry, and for which only the leading term is found.

The results are in Table I. There follows here, for each of the five thermodynamic functions in turn, an outline of the derivation of the entries in Table I and remarks on their significance.

A.  $\mu$

It is being assumed that there is a line of symmetry on which the chemical potential is a function  $M(T)$

analytic at  $T_c$ , so the second and third entries for  $\mu$  in Table I are just  $M(T)$ , and  $A_- = 0$ . The remaining entries for  $\mu$  are calculated from Eqs. (3.1)–(3.3) with  $\rho'$  and  $\theta'$  assumed given by Eqs. (2.25) and (2.23), but the results are then expressed in a language that makes no explicit reference to any model.

On the critical isochore in the one-phase region ( $T > T_c$ ), the potential energy density  $\phi$  is assumed to be of the form  $\phi_c +$  terms of order  $(T - T_c)^{1-\alpha}$ , where  $\phi_c$  is the value of  $\phi$  at the critical point and  $\alpha$  is the index of the divergence of  $C_v$ ; and explicit use is made of property (iv) of the function  $h$ . On the critical isotherm  $\phi$  is found from the thermodynamic identity  $(\partial\phi/\partial\theta)_\rho = (\partial \ln z / \partial \theta)_\rho$ , and explicit use is made of property (ii) of the function  $h$ .

It is found that on the one-phase portion of the critical isochore, near the critical point,  $\mu - M(T)$  is of order  $(T - T_c)^{1-\alpha+\beta(\delta-1)}$ . But in Sec. III.B, below,  $(\partial\mu/\partial\rho)_T$  is found to vanish as  $(T - T_c)^{\beta(\delta-1)}$ , so that Eq. (3.2), like the earlier Eq. (1.1), entails the exponent relation  $\gamma = \beta(\delta - 1)$ , where  $\gamma$  is the index of the divergence of  $\chi$ . Thus, the correction term in  $\mu$  on the critical isochore may be expressed as  $(T - T_c)^{\gamma+1-\alpha}$ , and it is so entered in Table I. This result was already obtained for the penetrable-sphere model much more simply,<sup>11</sup> and it is rederived here only to verify the consistency of the present theory.

In the lattice gas,  $\mu$  is analytic on the critical isochore, so  $A_\pm(T - T_c)^{\gamma+1-\alpha}$  is the first example of a term that has no counterpart in the lattice gas and that begins to account for derivations from particle-hole symmetry. As remarked earlier,<sup>11</sup> this correction to  $\mu$  on the critical isochore does not affect its continuity at the critical point nor that of its first two temperature derivatives, so it is hardly conceivable that it will ever be seen in experiment with any certainty. It is in fact characteristic of all the predicted deviations from lattice-gas symmetry that they will be very difficult to establish experimentally.

In the expression for  $\mu$  on the critical isotherm, as entered in Table I, the correction term that appears in the brackets is of order  $|\rho - \rho_c|^{\delta-1/\beta}$ , which is roughly of order  $(\rho - \rho_c)^2$ . It will be found in Sec. III.D, below, that the corresponding correction term in the expression for  $p$  on the critical isotherm is of order  $(\rho - \rho_c)$ . This significant difference between  $\mu$  and  $p$  is due to its having been  $\mu$  rather than  $p$  that was, in the first place, imagined to be analytic on some line of symmetry, and therefore to its having been  $\mu$  rather than  $p$  that was directly given in the basic equation of state Eq. (3.2). The term of order  $|\rho - \rho_c|^{\delta-1/\beta}$  in the brackets agrees with the corresponding term as given by Green, Cooper, and Levelt Sengers. It is of lower order (i.e., larger) than the term of order  $|\rho - \rho_c|^{1/\beta}$ , roughly of order  $|\rho - \rho_c|^3$ , which appears in the analogous place in Domb's estimate<sup>18</sup> of the corrections in the lattice gas that arise from being outside the final asymptotic

region around the critical point; so this is the first indication that the corrections due to deviations from particle-hole symmetry are the more important. This is true also in two dimensions, where  $\delta - 1/\beta = 7$  while  $1/\beta = 8$ .

### B. $(\partial\mu/\partial\rho)_T$

This density derivative follows from the same basic equations that yielded  $\mu$ . It may be evaluated on those portions of the critical isochore and the line of symmetry that are in the one-phase region, by making explicit reference to properties (iii) and (iv) of the function  $h$ . Only the leading terms in  $(\partial\mu/\partial\rho)_T$  are found in those cases; for the purpose of finding  $(\partial\mu/\partial\rho)_T$  there is only to verify that it is of order  $(T - T_c)^{\beta(\delta-1)}$ . Thus, as explained in III.A, one may conclude from the definition of the exponent  $\gamma$  that  $\gamma = \beta(\delta - 1)$ , and  $(T - T_c)^{\beta(\delta-1)}$  may thereafter be called  $(T - T_c)^\gamma$  in Table I. It is of interest that the same coefficient  $D$  (see Table I) appears both on the critical isochore and on the line of symmetry. To evaluate  $(\partial\mu/\partial\rho)_T$  at the coexistence curve (approached through the one-phase region), which is the remaining entry in the second line of the table, requires recognition of properties (v) and (vi) of  $h$ . The correction term, represented by  $F_\pm(T_c - T)^{\gamma-1+\beta}$  in the brackets, is of interest for two reasons. First, it is essentially equivalent to the observation of Mermin and Rehr<sup>25</sup> that as the critical point is approached the difference between the isothermal compressibility  $\chi$  in the liquid and vapor phases diverges proportionally to  $(T_c - T)^{-1+\beta}$ . Second,  $(T_c - T)^{\gamma-1+\beta}$ , because of the expected exponent relation  $\alpha + 2\beta + \gamma = 2$  which is verified in III.E below, is larger than  $(T_c - T)$ ; so this provides another example of a deviation from particle-hole symmetry leading to a more important correction than the one that Domb<sup>18</sup> estimates to be present in the lattice gas.

### C. $(\partial^2\mu/\partial\rho^2)_T$

This second density derivative, evaluated on the critical isochore in the one-phase region, is of interest because it vanishes in the lattice gas. Thus, even the leading term is now associated with a deviation from particle-hole symmetry. The result quoted in Table I is equivalent to one first found by Swift<sup>26</sup> using Kadanoﬀ's operator calculus<sup>27,28</sup> together with an assumption about the form of the density operator that was motivated by one of the models<sup>13</sup> in which particle-hole symmetry is lacking. The coincidence in the results of the two calculations verifies the mutual consistency of the quite different sets of ideas that underlie them.

### D. $p$

The basic idea behind the calculation of  $p$ , and thence also of  $C_v$  in III.E below, is the following.

At a fixed value of the product  $\theta\theta'$ , we have from

Eq. (2.23),

$$(1+\theta^{-1})d\theta+d \ln z=0 \quad (\theta\theta' \text{ fixed}). \quad (3.4)$$

But with  $\pi$  again the dimensionless pressure-to-temperature ratio, as in Sec. II, we have by thermodynamic identity

$$d(\pi+\theta)=(1-\phi)d\theta+\rho d \ln z, \quad (3.5)$$

so from Eqs. (2.25) and (3.4),

$$d(\pi+\theta)=-\left(\rho-\rho'\right) d \ln \theta \quad (\theta\theta' \text{ fixed}). \quad (3.6)$$

At the same time, from Eqs. (2.23) and (3.4),

$$d \ln (\theta' / \theta)=-2 d \ln \theta \quad (\theta\theta' \text{ fixed}). \quad (3.7)$$

Then from Eqs. (3.6) and (3.7) there follows

$$\left(\frac{\partial(\pi+\theta)}{\partial(\rho-\rho')}\right)_{\theta\theta'}=\frac{1}{2}\left(\rho-\rho'\right)\left(\frac{\partial \ln (\theta' / \theta)}{\partial(\rho-\rho')}\right)_{\theta\theta'}, \quad (3.8)$$

which holds for the whole class of models discussed in Sec. II. It is the existence of the relation (3.8) that dictates (3.3) as the convenient choice for the function  $t(\theta, \theta')$ . Equation (3.8) is to the equation of state (3.2) as the simpler identity  $(\partial p / \partial \rho)_T=\rho(\partial \mu / \partial \rho)_T$  is to the lattice-gas equation (1.1); the same technique previously used<sup>1</sup> to obtain  $p$  from Eq. (1.1) may now be used to obtain  $\pi+\theta$  from Eq. (3.2).

The result is that if  $(\pi+\theta)_{1s}$  means  $\pi+\theta$  evaluated as a function of  $t=1 /(\theta\theta')^{1/2}-1 / \theta_c$  on the line of symmetry, then

$$\pi+\theta=(\pi+\theta)_{1s}+\beta \int_{1-\rho-\rho'|^{-1/\beta}}^{a /|t|} y^{-\beta(\delta+1)-1} g(t y) d y+A t^{\beta(\delta+1)} \mathbf{1}(t), \quad (3.9)$$

where the function  $g$  is related to the function  $h$  in the equation of state by

$$g(\zeta)=\frac{1}{2} \delta h(\zeta)-(2 \beta)^{-1} \zeta h'(\zeta), \quad (3.10)$$

where  $A$  is the constant

$$A=\beta \int_a^{\infty} \zeta^{-\beta(\delta+1)-1} g(\zeta) d \zeta, \quad (3.11)$$

and where  $\mathbf{1}(t)$  is the unit step function, equal to 1 when  $t>0$  and 0 when  $t<0$ . By property (i) of  $h$ , the function  $g(\zeta)$  defined by (3.10) has a power series expansion,

$$g(\zeta)=g_0+g_1 \zeta+g_2 \zeta^2+\cdots \quad (3.12)$$

Because  $\pi+\theta$  must be analytic in  $t$  at  $t=0$  for all fixed  $\rho-\rho'$  other than  $\rho-\rho'=0$ , the singular part of  $(\pi+\theta)_{1s}$  may be explicitly isolated from (3.9) and expressed in terms of the coefficients  $g_n$ ,

$$\begin{aligned} (\pi+\theta)_{1s} &= \omega(t)+\left(-A \mathbf{1}(t)-\frac{\beta}{a^{\beta(\delta+1)}}\right. \\ &\times \sum_{n=0}^{\infty} \frac{g_n}{n-\beta(\delta+1)}(\pm a)^n\left.)\right| t|^{\beta(\delta+1)}, \quad (3.13) \end{aligned}$$

where  $\omega(t)$ , the nonsingular part of  $(\pi+\theta)_{1s}$ , is analytic at  $t=0$ , where  $\pm$  means  $+$  when  $t>0$  and  $-$  when  $t<0$ , and where the formula is subject to the usual modification<sup>1</sup> in the event that  $\beta(\delta+1)=2$  (which corresponds to a logarithmic divergence of  $C_v$ ). In these terms, Eq. (3.9) may be re-expressed as

$$(\pi+\theta)=\omega(t)-\beta \sum_{n=0}^{\infty} \frac{g_n}{n-\beta(\delta+1)} t^n|\rho-\rho'|^{-[n-\beta(\delta+1)] / \beta}, \quad (3.14)$$

which is the more convenient form near  $t=0$  and near the critical isotherm, although the original Eq. (3.9), with (3.13), is the more convenient near the line of symmetry  $\rho-\rho'$ , and near the critical isochore.

With  $\theta'$  and  $\rho'$  assumed given by Eqs. (2.23) and (2.25), and with  $\mu$  (hence also  $z$ ) already known on the critical isotherm,  $\pi$  (hence also  $p$ ) on the critical isotherm may be calculated from Eq. (3.14). The result is entered in Table I. The difference between the form of the correction term in  $p$  and that of the corresponding term in  $\mu$  has already been commented upon. It should be observed that the quoted form of  $p$  is an inevitable consequence of that of  $\mu$  simply because of the thermodynamic identity  $(\partial \pi / \partial \rho)_\theta=\rho(\partial \ln z / \partial \rho)_\theta$ , so it is not necessary that  $p$  on the critical isotherm be obtained via Eq. (3.14), but obtaining it by that route provides a useful test of consistency.

$C_v$  is later seen to diverge as  $|T-T_c|^{\beta(\delta+1)-2}$ , so we have the expected exponent relation  $\beta(\delta+1)=2-\alpha$ . Where the exponent  $\beta(\delta+1)$  appears it may then be replaced by the more familiar  $2-\alpha$ , and that has been done in the remaining entries for  $p$  in Table I. The pressure on the line of symmetry, as given in the table, is an immediate consequence of Eq. (3.13). The pressure at the coexistence curve, as well as on that portion of the critical isochore that lies in the two-phase region, is the same as the pressure on the line of symmetry  $T<T_c$ .

The behavior of  $p$  on the critical isochore when  $T>T_c$  follows from Eqs. (3.9) and (3.13) and from the already known behavior of  $\mu$ . (The latter is relevant because  $z$  appears in  $\theta'$  and therefore in  $t$ .) In the resulting expression for  $p$  we do not have in the brackets any correction term of order  $|T-T_c|^{1-\alpha-\beta}$ , though such a term is found in the work cited in Ref. 17. It is pointed out by Rehr<sup>29</sup> that that term disappears when, as here, it is assumed that there is a line of symmetry.

### E. $C_v$

Thermodynamically,  $C_v$  is intimately connected to  $p$  in a number of ways. For the model systems of Sec. II it may be shown that

$$\frac{d^2 \pi}{d \theta^2}=\frac{\left(c_v-\rho\right)}{\theta^2}+\frac{\left(d \rho / d \theta\right)^2}{\rho^2 \chi} \quad (\text { on line of symmetry }) \quad (3.15)$$



and

$$d^2\pi/d\theta^2 = (c_v - \rho)/\theta^2 \quad (\text{in two-phase region}), \quad (3.16)$$

where the appropriate dimensionless variables, like those defined in Sec. II, are being used, and where in particular  $c_v$  is a dimensionless form of the heat capacity per unit volume  $C_v/V$ .

$C_v$  on the critical isochore in the two-phase region follows from Eqs. (3.16) and (1.2), and from the properties of  $\pi$  as determined in III.D, above. The result is entered in Table I. Note that  $S_- = 0$ , so that on the two-phase portion of the critical isochore there is in the brackets no analog of the term  $X_{\pm} |T - T_c|^{1-\alpha}$  subsequently found there for  $C_v$  on the line of symmetry.

It is convenient to next find  $C_v$  on the line of symmetry, before completing the evaluation of  $C_v$  on the critical isochore by extending the calculation to the one-phase region. The compressibility  $\chi$  in the one-phase region diverges so rapidly as the critical point is approached that the second term on the right-hand side of Eq. (3.15), despite the diverging value of  $d\rho/d\theta$  on the line of symmetry that is implied by Eq. (1.2), proves not to contribute to  $C_v$  to within the accuracy with which the latter is ultimately quoted. It is also to be recognized that  $C_v$  is essentially  $Vc_v$ , and that according to Eq. (1.2) the volume  $V$  of the fluid on the line of symmetry differs from its volume  $V_c$  at the critical point by an amount that is proportional to  $|T - T_c|^{1-\alpha}$ . Then  $C_v$  on the line of symmetry follows from Eqs. (3.15) and (1.2), and from the properties of  $\pi$  as determined in III.D, above. The result is given in Table I.

The remaining entry in the table, which is  $C_v$  on the one-phase portion of the critical isochore, may now also be found. If  $C_v'$  and  $C_v''$  are, respectively, the values of  $C_v$  on the line of symmetry and on the critical isochore, both at the same temperature  $T > T_c$ , and if  $V'$  and  $V''$  are the corresponding values of  $V$ , then

$$C_v'' \sim C_v' + (\partial C_v / \partial V)_T (V'' - V'), \quad (3.17)$$

where  $(\partial C_v / \partial V)_T$ , which by thermodynamic identity is also  $T(\partial^2 p / \partial T^2)_V$ , may be imagined evaluated on the critical isochore at the temperature  $T$ . But  $\partial^2 p / \partial T^2)_V$  on the critical isochore is known from III.D, above;  $C_v'$  has just been calculated; and  $V'' - V'$  is known from (1.2) to be of order  $(T - T_c)^{1-\alpha}$ . Thus,  $C_v''$ , which is  $C_v$  on the critical isochore at  $T > T_c$ , may now be evaluated. The result is in the table. The argument given here, taken alone, would have left open the possibility of a term  $S_+ |T - T_c|^{1-\alpha}$  in the brackets, but more detailed calculation<sup>29</sup> shows that the terms of that magnitude that come from the two terms on the right-hand side of (3.17) cancel exactly, so that  $S_+$ , like  $S_-$ , is 0. As seen above, the reason such terms are present on the line of symmetry is that  $C_v$  is essentially  $V$  times the simpler heat capacity per unit volume  $c_v$ , and it is just

that factor  $V$  which contributes the extra correction term. But on the critical isochore  $V$  is constant, so no correction term comes from this source.

In all these calculations the leading term in  $C_v$  first appears as a term proportional to  $|T - T_c|^{\beta(\delta+1)-2}$ ; but then, as mentioned in the earlier discussion of  $p$ , this very fact allows  $2 - \beta(\delta+1)$  to be identified as the specific heat exponent  $\alpha$ , and to be so called in the table. [Because it was previously verified that  $\beta(\delta-1) = \gamma$ , this also entails the relation  $\alpha + 2\beta + \gamma = 2$ , as was anticipated earlier.]

The terms proportional to  $|T - T_c|^\alpha$  that appear inside the brackets, when combined with the factor  $|T - T_c|^{-\alpha}$  outside, yield constants, which are then just part of the analytic background in  $C_v$ . The next terms in the brackets, proportional to  $|T - T_c|^{1-\alpha}$ , yield the first singular corrections. For  $C_v$  on the critical isochore, just as for  $p$  on the critical isochore, Green *et al.*<sup>17</sup> have in the brackets a term proportional to  $|T - T_c|^{1-\alpha-\beta}$  of which we have no counterpart. Such a term would in any case be smaller than  $|T - T_c|^\alpha$ .

#### IV. DISCUSSION

The foregoing considerations raise several fundamental issues that demand further attention, both from experimental and theoretical points of view.

(a) Although the types of asymmetries suggested by this and related work have not yet been visible in experiments on real fluids, we feel the search should vigorously be pursued. To be sure, there are discrepancies between the corrections suggested by the various theoretical approaches. But all agree that the rectilinear diameter hypothesis should break down, and they agree that the breakdown should entail a "1- $\alpha$ " singularity. This aspect then remains one of the best candidates for test of hole-particle symmetry absence in real fluids.

Specifically, it might be advantageous to make careful optical measurements vs  $T_c - T$  of the interface height in a sealed cell containing an average density precisely equal to  $\rho_c$ . The conventional rectilinear diameter law would have this height vary as  $(T_c - T)^{1-\beta}$ , and increase as  $T$  approaches  $T_c$  from below. The extended scaling approach advocated here however requires that sufficiently close to  $T_c$  the interface position should vary as  $(T_c - T)^{1-\alpha-\beta}$ , while also increasing with  $T$ . The distinction may well be experimentally visible.<sup>30</sup>

(b) In spite of the fact that the thermodynamic scaling hypothesis seems plausible for the entire class of mixtures discussed in Sec. II, direct support is available only from the Gaussian mixture. Although indirect support is also offered by success of scaling for the Ising model (in its binary alloy guise), one would like a further more direct test. A likely possibility seems to be the binary mixtures for which unlike-pair repulsive interactions describe oriented squares ( $d=2$ ) or cubes ( $d=3$ ).<sup>31</sup> These models do not possess the rotational

symmetry of  $U(N_1|N_2)$  in Eq. (2.1), but like the Gaussian mixture their cluster integrals can be reduced to elementary form regardless of topological complexity. Standard series analysis could then be used to test for those critical exponent relations which are required by scaling.

(c) One of the most intriguing theoretical questions that remains is the analyticity at  $T_c$  of the coexistence chemical potential, as a function of  $T$ . That all known models imply analyticity may merely reflect the fact that they possess an internal symmetry in some version (spin reversal for the Ising model, component interchange for our mixtures). Therefore we stress the desirability of expending effort either to find a new model which violates chemical potential analyticity, or

to discover a deep reason why analyticity is universally to be expected.

(d) Finally, we remark that corrections to the strict scaling behavior for molecular distribution functions<sup>2</sup> could also be examined using the same strategy that has been employed here for thermodynamic behavior. One would initially assume that scaling applied to the distribution functions of the binary mixture, invoking the symmetry as justification, and then analyze asymmetries generated by the transcription to the single-component penetrable-sphere fluid.

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