PHYSICAL REVIEW A VOLUME 23, NUMBER 5 MAY 1981

Consequences of the renormalization group for the thermodynamics of fluids near the critical point

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(Received 12 January 1979; revised manuscript received 8 December 1980)

We have obtained expressions including corrections to scaling terms for a number of thermodynamic properties of fluids near the critical point by specializing the appropriate derivatives of the logarithm of the grand partition function to trajectories of experimental interest. Our justification for applying Wegner's general predictions, for the functional form of the free energy, to this thermodynamic potential is that it is the potential for a fluid most closely analogous to the Helmholtz free energy for the Ising model. It is found that the average of the coexisting densities, the so-called rectilinear diameter, is a nonlinear function of the temperature with a temperature derivative which diverges like the constant volume specific heat, at the critical point, with a system-dependent coefficient. The second-temperature derivative of the chemical potential, along either the coexistence curve or the critical isochore, is found to be nondivergent at the critical point and its value is the same above and below T_c. The corrections due to the irrelevant scaling fields are found to be as important as those due to higher-order terms in the expansion of the scaling fields around the critical point. Using the parametric representation of the linear model, we have been able to obtain expressions for the elements of the matrix relating relevant scaling fields and physical variables in linear form, in terms of experimentally measurable quantities.

I. INTRODUCTION

Even though it has been generally taken for granted that Ising-type systems and real simple fluids have the same critical exponents, it has been experimentally observed that the temperature range where this happens is very restricted. In fact, according to experiments by Hocken and Moldover[1] on SF_6, Xe, and CO_2, the intervals are as small as 10^{-5} in reduced temperature. When a single-term power-law expression is used to determine the exponents from experiments on fluids in a larger interval it is found that the best values for the exponents are somewhat higher than those predicted for Ising systems by high-temperature series expansions.[2] On the other hand, in a recent study, Valls and Hertz[3] conclude that fluids and Ising-like systems do not belong to the same universality class due to the fact that the odd terms, which must be included in the Ising Hamiltonian when used to characterize a fluid, may produce a new fixed point. However, Nicoll[4] points out through a global stability analysis, that the symmetric fixed point is strongly stable against odd perturbations, thus supporting the conjecture that fluids have the same universal critical behavior as symmetric Ising systems. These results may be taken to mean that, if indeed fluids and Ising-like systems belong to the same universality class, the expressions for the thermodynamic properties of fluids must contain additional terms if the real, and not the apparent, value for the exponents is to be extracted from data analysis.

The purpose of this work is to obtain series of correction terms to the simple power-law expressions for the properties of fluids along various trajectories in the thermodynamic phase plane. We shall do so by explicitly applying to fluids, the general predictions made by Wegner[5] on the functional form of the free energy near the critical point; such predictions are based on general arguments from the renormalization-group (RG) approach.

In Sec. II, we discuss the features of the proper fluid's thermodynamic potential to which Wegner's predictions are to be applied. This section begins with the remark that the Hamiltonian describing a fluid, subject to density fluctuations, has a similar structure to that of an Ising model in the presence of an external magnetic field. Thus, invoking the universality principle, we argue that the proper thermodynamic potential, to which RG predictions are to be applied, must be the logarithm of the grand partition function. Such potential will be assumed to possess symmetry properties which are not immediately apparent when it is written as an explicit function of the physical variables.

The general form for the thermodynamic properties, such as density, isothermal compressibility, and constant volume specific heat have been derived. However, due to the fact that the obtained expressions are lengthy, we only give, in Sec. III, a summary of the properties along trajectories of experimental interest such as the coexistence curve, the critical isochore, and the critical isotherm. The expressions for such properties are given as expansions in noninteger powers of the reduced temperature or density with coefficients that depend on system-dependent parameters contained in the thermodynamic potential. The explicit dependence will be given for some of the coefficients; for the others, the interested reader may see Ref. 6.

We are able to relate, in Sec. IV, some of the mentioned parameters to combinations of experimentally measurable quantities through the use of the parametric representation.[7] Others are perforce left undetermined, since very little is known about the parametric representation of Wegner's correction terms. Finally, in Sec. V, we summarize and conclude on our results.

II. PROPERTIES OF THE THERMODYNAMIC POTENTIAL

In order to apply the predictions from the RG approach to fluids, it is necessary to make a decision about which thermodynamic potential is the proper analog to that obtained from the canonical partition function for the Ising model, for which the method was designed in the first instance. To make such a decision, we note that the Ising model in a magnetic field is equivalent to a lattice gas (or fluid) with a variable number of particles in a fixed volume. Since the latter system is naturally described by the grand ensemble, the proper thermodynamic potential $\tilde{p}$ must be

$$\tilde{p}=pv/k_BT=\ln Z/N_0\,, \tag{2.1}$$

with Z the grand partition function, p the pressure, N_0 Avogadro's number and $v=V/N_0$ a fixed specific volume which turns out to be, in this case, the critical volume per particle v_c.

Thus, according to Wegner, $\tilde{p}$ is a generalized homogeneous function of the infinite, in principle, set of scaling fields. However, for practical purposes we shall restrict $\tilde{p}$ to depend on a set of five scaling fields. The reason for such restriction is that for systems undergoing a second-order phase transition, such as a simple fluid, there are three relevant scaling fields, but since our aim is to obtain the form of the correction terms, we shall also consider the two most import irrelevant scaling fields. The relevant scaling fields will be denoted by p_0, g_h, and g_E, the corresponding eigenvalues being d, $d\Delta/(2-\alpha)$ with $\Delta=\beta\delta$ and $d/(2-\alpha)$, respectively; d is the dimensionality of the system and β, δ, and α are the critical exponents describing the coexistence curve, the critical isotherm, and the constant volume specific heat singularity, respectively. We denote the irrelevant fields by g_A and g_S, the corresponding eigenvalues by $-d\Delta_A(2-\alpha)$, and $-d\Delta_S(2-\alpha)$, respectively. Theoretical expansions as well as high-temperature series expansions, for the three-dimensional Ising model, have an estimated value of $\Delta_S=0.49\pm0.01$.[8] In addition to a similar value for Δ_S, Wegner[9(a)] has found that $\Delta_A=0.5+\epsilon+O(\epsilon^2)$ with $\epsilon=4-d$. (It should be mentioned, however, that Nicoll and Zia[9(b)] have recently calculated Δ_A to order ϵ^2; their result indicates a poor convergence for the expansion and a value for Δ_A that could be anywhere between 0.5 and 1.5.) The scaling fields g_S and g_A are found to correspond to eigenvectors containing products of an even number beginning with four, and of an odd number beginning with five, of Ising variables, respectively.

Therefore, we assume that a reasonable description of a fluid may be obtained from a free energy $\tilde{p}$ given as

$$\tilde{p}=p_0+p_s(g_h,g_E,g_A,g_S)\,, \tag{2.2}$$

the sum of a regular part p_0 and a singular part p_s which is a generalized homogeneous function. The scaling function p_s is universal and dimensionless, as are the scaling fields p_0 and g. Since in the calculation of the grand partition function for a simple fluid with n particles and chemical potention μ, the effective Hamiltonian includes a factor $-\mu n$ the intensive variables are μ and T; then according to general RG predictions, the scaling fields are of the form

$$p_0(\tilde{\mu},t)=\tilde{p}_{00}+\tilde{p}_{10}\tilde{\mu}+\tilde{p}_{01}t+O(\tilde{\mu}^2,t^2)\,, \tag{2.3a}$$

$$g_h(\tilde{\mu},t)=\tilde{g}^h_{10}\tilde{\mu}+\tilde{g}^h_{01}t+O(\tilde{\mu}^2,t^2)\,, \tag{2.3b}$$

$$g_E(\tilde{\mu},t)=\tilde{g}^E_{10}\tilde{\mu}+\tilde{g}^E_{01}t+O(\tilde{\mu}^2,t^2)\,, \tag{2.3c}$$

$$g_k(\tilde{\mu},t)=\tilde{g}^k_{00}+\tilde{g}^k_{10}\tilde{\mu}+\tilde{g}^k_{01}t+O(\tilde{\mu},t^2)\,,\quad k=A,S \tag{2.3d}$$

where $\tilde{\mu}=(\mu-\mu_c)/\mu_c$ and $t=(T-T_c)/T_c$ are the reduced chemical potential and temperature difference, respectively. The coefficients in the preceding expansions are dimensionless system-dependent quantities some of which, at least, will be identified with combinations of measurable parameters in the course of this work. The relevant character of the scaling fields g_h and g_E has been already taken into account in setting the constant term in their expansion equal to zero so that they vanish at the critical point ($\tilde{\mu}=t=0$). It should be mentioned that the arguments of the grand partition function are μ/k_BT and $1/k_BT$ so that the above expansions should be in terms of such variables. However, $\mu/k_BT=(\mu_c/k_BT_c)(\tilde{\mu}+1)/(t+1)$ and $(k_BT)^{-1}=(k_BT_c)^{-1}/(t+1)$; since $\tilde{\mu}$ and t are very small in the critical region the scaling fields may be expanded as indicated.

The homogeneity property of p_s together with the form of the eigenvalues corresponding to g_h and g_E imply that the singular part will have different forms, each being appropriate to describe the fluid in a given section of the thermodynamic plane. If, in addition, we assume that p_s satisfies the following symmetry property:

$$p_s(g_h, g_E, g_A, g_S) = p_s(-g_h, g_E, -g_A, g_S)\,, \qquad (2.4)$$

then the combination of signs of the relevant scaling fields can be used to characterize the phase of the fluid. Thus,

$$p_s(g_h, g_E, g_A, g_S) = |g_E|^{2-\alpha} p_s(g_h |g_E|^{-\Delta}, \pm 1, g_A |g_E|^{\Delta_A}, g_S |g_E|^{\Delta_S})\,, \qquad (2.5a)$$

will be the appropriate form of p_s to describe the one-phase region ($g_E > 0$), if the (+) sign is used, or the two-phase region ($g_E < 0$), if the (–) sign is used, while

$$p_s(g_h, g_E, g_A, g_S) = |g_h|^{(2-\alpha)/\Delta} p_s(\pm 1, g_E |g_h|^{-1/\Delta}, g_A |g_h|^{\Delta_A/\Delta}, g_S |g_h|^{\Delta_S/\Delta})\,, \qquad (2.5b)$$

will be the appropriate form of p_s to describe the high-density phase ($g_h > 0$), if the (+) sign is used, or the low-density phase ($g_h < 0$), if the (–) sign is used. The case of an asymmetric singular part has been analyzed by Nicoll, Chang, Hankey, and Stanley.[10] It can be shown in this case that the chemical potential along the coexistence curve will have a second derivative which diverges as $|t|^{-(\alpha+\beta)}$, at the critical point, with a coefficient that is related to the asymmetry. So far, there is no experimental evidence[11] supporting such an anomaly.

Finally, we take into account that the scaling function may be expanded in integer powers of its arguments, the reduced scaling fields, about their zero value. Either of these will be expansions around the critical point ($g_h = g_E = 0$), since the reduced irrelevant scaling fields $g_k |g_E|^{\Delta_k}$ or $g_k |g_E|^{\Delta_k/\Delta} (k = A, S)$ vanish in that limit even though g_k may be nonzero. However, the forms of the expansion of the scaling function will depend strongly on the way the critical region is approached since $g_h |g_E|^{-\Delta}$ will vanish at the critical point if $g_h \rightarrow 0$ first, while $g_E |g_h|^{-1/\Delta}$ vanishes if $g_E \rightarrow 0$ first. Thus, the thermodynamic properties along the coexistence curve are obtained from

$$\tilde{p} = p_0(\tilde{\mu}, t) + |g_E|^{(2-\alpha)} \sum_{i,j,k} (g_h |g_E|^{-\Delta})^i (g_S |g_E|^{\Delta_S})^j \times (g_A |g_E|^{\Delta_A})^k P^{\pm(i)}_{jk}(0, -1)\,, \qquad (2.6)$$

where $P^{\pm(i)}_{jk}(0, -1)$ is the value, at the critical point, of the ith, jth, and kth derivatives of $p_s(g_h |g_E|^{-\Delta}, -1, g_A |g_E|^{\Delta_A}, g_S |g_E|^{\Delta_S})$ with respect to $g_h |g_E|^{-\Delta}$, $g_S |g_E|^{\Delta_S}$, and $g_A |g_E|^{\Delta_A}$, respectively. We have made explicit the fact that in the inhomogeneous region, the potential $\tilde{p}$ has discontinuous derivatives across the phase boundary so that Eq. (2.6) represents the expansion of two smooth functions which are to be used in describing the approach from the liquid (gas) phase when the +(–) sign is used. Of course, the expansion coefficients are not independent; in fact, the symmetry property (2.4) implies

$$P^{+(i)}_{jk}(0, -1) = (-1)^{i+k} P^{-(i)}_{jk}(0, -1)\,. \qquad (2.6)$$

However, thermodynamic properties in the one-phase region along the critical isochore are derived from

$$\tilde{p} = p_0(\tilde{\mu}, t) + |g_E|^{(2-\alpha)} \sum_{i,j,k} (g_h |g_E|^{-\Delta})^i (g_S |g_E|^{\Delta_S})^j \times (g_A |g_E|^{\Delta_A})^k P^i_{jk}(0, +1)\,, \qquad (2.7)$$

where $P^i_{jk}(0, +1)$ is the value, at the critical point, of the ith, jth, and kth derivatives of $p_s(g_h |g_E|^{-\Delta}, +1, g_A |g_E|^{\Delta_A}, g_S |g_E|^{\Delta_S})$ with respect to $g_h |g_E|^{-\Delta}$, $g_S |g_E|^{\Delta_S}$, and $g_A |g_E|^{\Delta_A}$, respectively. It should be noted that since $\tilde{p}$ has continuous derivatives everywhere in the homogeneous region, the symmetry property (2.4) implies that the coefficients with $i + k$ an odd integer are zero.

The thermodynamic properties along trajectories close to the critical isotherm, either from the high- (+) or low- (–) density side, are obtained from

$$\tilde{p} = p_0(\tilde{\mu}, t) + |g_h|^{(2-\alpha)/\Delta} \sum_{i,j,k} (g_E |g_h|^{-1/\Delta})^i (g_s |g_h|^{\Delta_S/\Delta})^j \times (g_A |g_h|^{\Delta_A/\Delta})^k Q^i_{jk}(\pm 1, 0)\,, \qquad (2.8)$$

where $Q^i_{jk}(\pm 1, 0)$ is the value at the critical point of ith, jth, and kth derivatives of $p_s(\pm 1, g_E |g_h|^{-1/\Delta}, g_A |g_h|^{\Delta_A/\Delta}, g_S |g_h|^{\Delta_S/\Delta})$ with respect to $g_E |g_h|^{-1/\Delta}$, $g_S |g_h|^{\Delta_S/\Delta}$, and $g_A |g_h|^{\Delta_A/\Delta}$, respectively. The symmetry property (2.4) implies that

$$Q^i_{jk}(+1, 0) = (-1)^k Q^i_{jk}(-1, 0)\,. \qquad (2.8')$$

III. THERMODYNAMIC PROPERTIES

Using the conditions for coexistence, contained in (2.4) and (2.5a) together with the fact that $\tilde{p}$ has a discontinuous first derivative across the phase boundary so that $P^{-(1)}_{00}(0, -1) \neq 0$, it can be found that the coexistence curve in the $g_h - g_E$ coordinate system is given by

$$g_h = -g_A |g_E|^{\Delta+\Delta_A} \sum_{i,j} C_{i,2j} (g_S |g_E|^{\Delta_S})^i (g_A |g_E|^{\Delta_A})^{2j}, \tag{3.1}$$

with the coefficients $C_{i,2j}$ universal quantities, since they are functions of $P^{-(n)}_{1,m}(0,-1)$. This equation implies that the coexistence curve is described by $g_h = 0$, as in ordinary scaling, when the irrelevant field are ignored. Moreover, if the contributions from such fields are not ignored, $g_h = 0$ is asymptotically tangent to the coexistence curve at the critical point, since $\Delta + \Delta_A > 1$, as in revised scaling but the reasons are not the same. In any case, (3.1) implies that $g_h = 0$ is asymptotically tangent to the coexistence curve and the departure from this curve depends on the antisymmetric irrelevant field. Substitution of the scaling fields in terms of the physical variables in the preceding equation yields an expression in $\tilde{\mu}$ and t, which may be solved for $\tilde{\mu}$ by iteration since $g^h_{10} \neq 0$, to obtain an equation for the *chemical potential along the coexistence curve*

$$\tilde{\mu}_0(t) \approx (\zeta_0 + \zeta_1 |t| + \zeta_2 |t|^{(\Delta-1)+\Delta_A} + \zeta_3 |t|^{(\Delta-1)+\Delta_A+\Delta_S} + \cdots)|t|, \tag{3.2}$$

where the coefficients in this expression depend on the system-dependent expansion coefficients for the scaling fields as follows:

$$\zeta_0 = -\tilde{g}^h_{01}/\tilde{g}^h_{10}, \tag{3.2a}$$

$$\zeta_1 = -[\tilde{g}^h_{20}(\tilde{g}^h_{01})^2 - \tilde{g}^h_{11}\tilde{g}^h_{10}\tilde{g}^h_{01} + \tilde{g}^h_{02}(\tilde{g}^h_{10})^2]/(\tilde{g}^h_{10})^3, \tag{3.2b}$$

so that the limiting slope at the critical point of the chemical potential along the coexistence curve is given by the ratio of the leading coefficients in the expansion of the relevant scaling field g_h, as should be expected.

The behavior along the coexistence curve of other thermodynamic quantitites is obtained by inserting the expressions describing g_h and the chemical potential along such a curve into the equation corresponding to the property of interest. Thus, for the *vapor pressure*, we get

$$p \approx \frac{k_B T_c}{v_c} (\tilde{p}_{00} + P_0 |t| + P_1 |t|^{2-\alpha} + P_2 |t|^2 + P_3 |t|^{2-\alpha+\Delta_S} + \cdots), \tag{3.3}$$

with

$$P_0 = \frac{(\tilde{p}_{00} + \tilde{p}_{01})\tilde{g}^h_{10} - \tilde{p}_{10}\tilde{g}^h_{01}}{\tilde{g}^h_{10}}, \tag{3.3a}$$

$$P_1 = \left| \frac{\tilde{g}^h_{10}\tilde{g}^E_{01} - \tilde{g}^E_{10}\tilde{g}^h_{01}}{\tilde{g}^h_{10}} \right|^{(2-\alpha)} P^{-(0)}_{00}(0,-1). \tag{3.3b}$$

It is possible to relate the coefficients $\tilde{p}_{00}$, $\tilde{p}_{10}$, and $\tilde{p}_{01}$ to "measurable quantities" since one of the first derivatives of $\tilde{p}$ is related to the density ρ, while the other is a function of the internal energy u and entropy s densities. Therefore, taking into account that the singular part as well as its first derivatives vanish at the critical point, we find

$$\tilde{p}_{00} = p_c v_c / k_B T_c, \tag{3.3c}$$

$$\tilde{p}_{10} = \mu_c \rho_c v_c / k_B T_c, \tag{3.3d}$$

$$\tilde{p}_{01} = \left(\frac{u_c - \mu_c \rho_c}{k_B T_c} \right) v_c = \left(\frac{s_c T_c - \rho_c}{k_B T_c} \right) v_c, \tag{3.3e}$$

with the subindex c denoting the critical point value of the corresponding variables. This means that the slope of the vapor pressure curve at the critical point is given by

$$\lim_{T \to T_c} \frac{dp}{dT} = \frac{p_c}{T_c} \left(1 + \frac{u_c - \mu_c \rho_c}{p_c} - \frac{\mu_c \rho_c}{p_c} \frac{\tilde{g}^h_{01}}{\tilde{g}^h_{10}} \right) = s_c - \frac{\mu_c p_c}{T_c} \frac{\tilde{g}^h_{01}}{\tilde{g}^h_{10}}. \tag{3.4}$$

Thus, the ratio of the leading coefficients in the expansion of g_h may be obtained from an experimentally accessible quantity, the limiting slope of the vapor pressure curve. However, the value of this ratio is not uniquely defined since of the three quantities, the internal energy density, the entropy density, and the chemical potential, two are undetermined up to an arbitrary constant, while the third is determined by the Gibbs-Duhem relation. However, if we make the choice $s_c = 0$ and $\mu_c = p_c/\rho_c$ then $u_c = 0$ and the ratio of the leading coefficients reduces to

$$\frac{\tilde{g}^h_{01}}{\tilde{g}^h_{10}} = -\frac{T_c}{p_c} \lim_{T \to T_c} \frac{dp}{dT}. \tag{3.5}$$

An expression for the *density along the two branches of the coexistence curve* is given by

$$\rho^{\pm} \approx \frac{k_B T_c}{p_c v_c} \rho_c (\tilde{p}_{10} \pm B'_0 |t|^{\beta} \pm B'_1 |t|^{\beta+\Delta_S} + D'_0 |t|^{\beta+\Delta-1} + D'_1 t \pm B'_2 |t|^{\beta+2\Delta_S} \pm B'_3 |t|^{\beta+1} + D'_2 |t|^{\beta+(\Delta-1)+\Delta_S} + D'_3 |t|^{\beta+\Delta_A} + \cdots), \tag{3.6}$$

where the +(–) sign is to be used for the liquid (vapor) phase and where the symmetry of $\tilde{p}$ has been already taken into account through the coefficients B'_i and D'_i. Thus, for the *difference of coexisting densities* we get

$$\frac{\rho_L - \rho_G}{2\rho_c} \approx (B_0 + B_1 |t|^{\Delta_S} + B_2 |t|^{2\Delta_S} + B_3 |t| + \cdots)|t|^{\beta}, \tag{3.7}$$

with

$$B_0 = \frac{k_B T_c}{p_c v_c} \tilde{g}^h_{10} \left| \frac{\tilde{g}^h_{10}\tilde{g}^E_{01} - \tilde{g}^E_{10}\tilde{g}^h_{01}}{\tilde{g}^h_{10}} \right|^{\beta} |P^{-(1)}_{00}(0,-1)|, \tag{3.7$'$}$$

while for the average of coexisting densities, the so-called *diameter of the coexistence curve*, we obtain

$$\frac{\rho_L+\rho_G}{2}\approx\rho_c+D_0|t|^{1-\alpha}+D_1|t| +D_2|t|^{1-\alpha+\Delta_S}+D_3|t|^{1-\alpha-(\Delta-1)+\Delta_A}+\cdots, \tag{3.8}$$

with

$$D_0=-\frac{k_BT_c}{p_cv_c}\rho_c\tilde{g}_{10}^E\left|\frac{\tilde{g}_{10}^h\tilde{g}_{01}^E-\tilde{g}_{10}^E\tilde{g}_{01}^h}{\tilde{g}_{10}^h}\right|^{1-\alpha} \times(2-\alpha)P_{00}^{-(0)}(0,-1). \tag{3.8$'$}$$

Therefore, if $\Delta_A>\Delta-1$ then average of coexisting densities will have a leading behavior of the form

$$\frac{\rho_L+\rho_G}{2}\approx\rho_c+D_0|t|^{1-\alpha}+\cdots, \tag{3.9}$$

so that the diameter has a nonanalytic behavior which is a consequence of the mixing of variables in the scaling field g_E, since the coefficient of the temperature-dependent term depends on g_{10}^E. This result is equivalent to that obtained by Rehr and Mermin[12] in their proposal of revised scaling, noting that their work is based on Widom's[13] original scaling proposal where g_{10}^E is identically zero, as is the case for ferromagnets. If, on the other hand, $\Delta_A=\Delta-1$ then

$$\frac{\rho_L+\rho_G}{2}\approx\rho_c+(D_0+D_3)|t|^{1-\alpha}+\cdots. \tag{3.9a}$$

The temperature derivative of the diameter will again be singular at the critical point, even if there is no mixing of $\tilde{\mu}$ and t in g_E, since the term D_3 in the amplitude of the divergence turns out to depend on the constant of the irrelevant field g_A. An equivalent result has been obtained by Green, Cooper, and Sengers[14(a)] in their attempt to extend the range of validity of ordinary scaling. In either case, at the critical point, the temperature derivative of the diameter has the same divergence as that of the constant volume specific heat. Contrary to this result, we find that if $\Delta_A<\Delta-1$ then

$$\frac{\rho_L+\rho_G}{2}\approx\rho_c+D_3|t|^{1-\alpha-(\Delta-1)+\Delta_A}+\cdots. \tag{3.9b}$$

The divergence of the temperature derivative of the diameter will be stronger than that of the specific heat. In all cases, we have assumed that $\Delta_S>\alpha\geqslant 0$.

On the other hand, even though the corrections from both, antisymmetric and symmetric, irrelevant fields are present, their relative importance is uncertain since the value of Δ_A is not known accurately. In fact, it has been already pointed out by Sengers[14(b)] that both contributions would be of the same order if $\Delta_A\simeq 1.0$ and therefore, both should be considered in data analysis.

It is worth mentioning that Sengers,[15] in a generalization of mean-field theory, has found a diameter behaving as

$$\frac{\rho_L+\rho_G}{2}\approx\rho_c+A|t|^{2\beta}+\cdots. \tag{3.9c}$$

However, contrary to the preceding results, Hubbard and Schofield[16] in their RG treatment of a fluid predict a rectilinear diameter. In such treatment the thermodynamic potential has the Ising symmetry, Eq. (2.4), but only when written as a function of the physical variables rather than as a function of the scaling fields; this means that in this treatment there is no mixing of the physical variables so that the real asymmetries in a fluid are neglected.

The *isothermal compressibility* along the coexistence curve is

$$(\rho^{\pm})^2K_T\approx\frac{k_BT_c}{p_c^2v_c}\rho_c^2(\Gamma_0'+\Gamma_1'|t|^{\Delta_S}\pm\Gamma_2'|t|^{\Delta-1} +\Gamma_3'|t|^{2\Delta_S}+\cdots)|t|^{-\gamma}. \tag{3.10}$$

The (+) and (–) signs are used to describe the liquid and gas phases, respectively with the first coefficient given as

$$\Gamma_0'=2(\tilde{g}_{10}^h)^2\left|\frac{\tilde{g}_{10}^h\tilde{g}_{01}^E-\tilde{g}_{10}^E\tilde{g}_{01}^h}{\tilde{g}_{10}^h}\right|^{-\gamma}P_{00}^{-(2)}(0,-1). \tag{3.10$'$}$$

Finally, for the *constant volume specific heat* along the coexistence curve, we get

$$C_v^{\pm}\approx k_B(A_1+A_0|t|^{\alpha}\pm A_2|t|^{\beta}+A_3|t|^{\Delta_S}+\cdots)|t|^{-\alpha} \tag{3.11}$$

with

$$A_1=\left|\frac{\tilde{g}_{10}^h\tilde{g}_{01}^E-\tilde{g}_{10}^E\tilde{g}_{01}^h}{\tilde{g}_{10}^h}\right|^{2-\alpha}\frac{2(1-\alpha)(2-\alpha)P_{00}^{-(0)}(0,-1)P_{00}^{-(2)}(0,-1)-[\beta P_{00}^{-(1)}(0,-1)]^2}{2P_{00}^{-(2)}(0,-1)}. \tag{3.11$'$}$$

This means that the constant volume specific heat has a discontinuity of size $2A_2|t|^{\beta-\alpha}$ across the phase boundary. However, the trajectory of interest in the two phase as far as C_v is concerned, is the critical isochore. Along the critical isochore in the two-phase region, the constant volume specific heat is found to be

$$C_v\approx k_B(A_1'+A_0|t|^{\alpha}+A_2'|t|^{\Delta_S}+\cdots)|t|^{-\alpha} \tag{3.12}$$

with

$$A_1' = \left| \frac{\tilde{g}^h_{10}\tilde{g}^E_{01} - \tilde{g}^E_{10}\tilde{g}^h_{01}}{\tilde{g}^h_{10}} \right|^{2-\alpha} (1-\alpha)(2-\alpha)P^{-(0)}_{00}(0,-1)\,, \tag{3.12'}$$

where we have taken into account that for most physical systems the critical isochore lies inside the heterogeneous region.

So far, we have derived expressions for the thermodynamic properties along the trajectory characterized by $g_h \sim g_A |g_E|^{\Delta+\Delta_A}$ with small negative g_E, which as it has been seen, is identified with the coexistence curve. We are now interested in the one-phase region where the path of experimental concern is the critical isochore. Taking into account that such curve is identified by $\rho = \rho_c$, it is possible to find that along such a path the following equation is satisfied:

$$g_h \sum_{i,j,k} (g_h|g_E|^{-\Delta})^{2i}(g_S|g_E|^{\Delta_S})^j(g_A|g_E|^{\Delta_A})^{2k}D^0_{ijk} = F(\tilde{\mu},t) - |g_E|^{\Delta} \sum_{i,j,k} (g_h|g_E|^{-\Delta})^{2i}(g_S|g_E|^{\Delta_S})^j(g_A|g_E|^{\Delta_A})^{2k} \times (D^1_{ijk}|g_E|^{\Delta-1} + D^2_{ijk}g_A|g_E|^{\Delta_A})\,, \tag{3.13}$$

where the coefficients D^0_{ijk}, D^1_{ijk}, and D^2_{ijk} depend on the expansion coefficients in Eq. (2.7) and we have explicitly taken into account that $P^{2i}_{j,2k+1}(0,+1)$ and $P^{2i+1}_{j,2k}(0,+1)$ are equal to zero. $F(\tilde{\mu},t)$ is a function which can be expanded in integer powers of $\tilde{\mu}$ and t with a vanishing constant term defined as

$$F(\tilde{\mu},t) = \frac{p_c v_c}{k_B(t+1)} - \frac{\partial p_0}{\partial \mu}\,. \tag{3.13'}$$

The solution to Eq. (3.13) will give us the function describing the critical isochore. Owing to the presence of $F(\tilde{\mu},t)$ the solution for g_h will not only be a function of the other scaling fields, as it is along the coexistence curve, but of $\tilde{\mu}$ and t as well. We note, however, that if this function were absent, the solution would be of the form

$$g_h = -\sum_{i,j,k,l} (J^0_{ijkl}|g_E|^{2\Delta-1} + J^1_{ijkl}|g_E|^{\Delta+\Delta_A}) \times |g_E|^{i+j(\Delta-1)+k\Delta_S+l\Delta_A}\,, \tag{3.14}$$

where the coefficients are functions having expansions in integer powers of $\tilde{\mu}$ and t, since they depend on the scaling fields and their derivatives, in particular,

$$J^0_{0000} = \frac{(2-\alpha)P^0_{00}(0,+1)\partial|g_E|/\partial\tilde{\mu}}{2P^2_{00}(0,+1)\partial g_h/\partial\tilde{\mu}} \tag{3.14a}$$

and

$$J^1_{0000} = \frac{P^1_{01}(0,+1)}{2P^2_{00}(0,+1)} g_A\,. \tag{3.14b}$$

This implies that in the absence of $F(\tilde{\mu},t)$, the leading term will be $|g_E|^{2\Delta-1}$ or $|g_E|^{\Delta+\Delta_A}$ depending upon whether $\Delta_A > \Delta - 1$ or $\Delta_A < \Delta - 1$, respectively. Thus, higher-order derivatives along the coexistence curve will differ from those along the critical isochore, even though both curves may have a common tangent at the critical point. In fact, if $\Delta_A > \Delta - 1$, the third derivatives will be different due to the mixing of $\tilde{\mu}$ and t in g_E. In any case, (3.13) implies that very near the critical point, $g_h = 0$ is asymptotically tangent to the critical isochore and the departure from this curve depends not only on the irrelevant fields, but also on the mixing of variables in g_E, as well as on the higher-order terms in p_0. Replacing the scaling fields by their expansions in (3.13) yields an equation whose solution for $\tilde{\mu}$ by iteration, gives us the *chemical potential along the critical isochore*

$$\tilde{\mu}_{cic}(t) \approx (\mathfrak{g}_0 + \mathfrak{g}_1 t + \mathfrak{g}_2|t|^{2(\Delta-1)} + \mathfrak{g}_3|t|^{2(\Delta-1)+\alpha} + \cdots)t\,, \tag{3.15}$$

with

$$\mathfrak{g}_0 = -\tilde{g}^h_{01}/\tilde{g}^h_{10} \tag{3.15a}$$

and

$$\mathfrak{g}_1 = -[\tilde{g}^h_{20}(\tilde{g}^h_{01})^2 - \tilde{g}^h_{11}\tilde{g}^h_{10}\tilde{g}^h_{01} + \tilde{g}^h_{02}(\tilde{g}^h_{10})^2]/(\tilde{g}^h_{10})^3\,. \tag{3.15b}$$

It is worth pointing out that $\mathfrak{g}_0 = \zeta_0$ and $\mathfrak{g}_1 = \zeta_1$ so that the coexistence curve and the critical isochore, as far as the chemical potential is concerned, have a common slope, as well as curvature, at the critical point.

The expression describing the pressure along the *critical isochore* in the one-phase region is found to be

$$p \approx \frac{k_B T_c}{v_c}(\tilde{p}_{00} + P_0' t + P_1'|t|^{2-\alpha} + P_2' t^2 + P_3'|t|^{1+2(\Delta-1)} + \cdots) \tag{3.16}$$

with

$$P_0' = \frac{(\tilde{p}_{00} + \tilde{p}_{01})\tilde{g}^h_{10} - \tilde{p}_{10}\tilde{g}^h_{01}}{\tilde{g}^h_{10}}\,, \tag{3.17a}$$

$$P_1' = \left| \frac{\tilde{g}^h_{10}\tilde{g}^E_{01} - \tilde{g}^E_{10}\tilde{g}^h_{01}}{\tilde{g}^h_{10}} \right|^{2-\alpha} P^0_{00}(0,+1)\,. \tag{3.17b}$$

We note from the above equations, for the chemical potential and the pressure along the critical isochore and the coexistence curve, that according to the Yang-Yang[17] relation

$$\frac{\rho C_v}{T} = \left(\frac{\partial^2 p}{\partial T^2}\right)_\rho - \rho\left(\frac{\partial^2 \mu}{\partial T^2}\right)_\rho\,.$$

The anomalous behavior in the specific heat is due to an anomaly in the second-temperature derivative of the pressure since the term $(\partial^2\mu/\partial T^2)$ is well behaved at the critical point.

The *isothermal compressibility* along the critical isochore in the one-phase region is given as

$$K_T \approx \frac{k_B T_c}{p_c^2 v_c}\left(\Gamma_0 + \Gamma_1 |t|^{\Delta_S} + \Gamma_2 |t|^{2\Delta_S} + \Gamma_3 |t|^{2(\Delta-1)} + \cdots\right)|t|^{-\gamma} \tag{3.18}$$

with

$$\Gamma_0 = 2(\tilde{g}_{10}^h)^2 \left| \frac{\tilde{g}_{10}^h \tilde{g}_{01}^E - \tilde{g}_{10}^E \tilde{g}_{01}^h}{\tilde{g}_{10}^h} \right|^{-\gamma} P_{00}^2(0,+1)\,. \tag{3.18$'$}$$

Finally, the *constant volume specific heat* along the critical isochore in the one-phase region will be

$$C_v \approx k_B(A_1'' + A_0 |t|^{\alpha} + A_2'' |t|^{\Delta_S} + \cdots)|t|^{-\alpha} \tag{3.19}$$

with

$$A_1'' = \left| \frac{\tilde{g}_{10}^h \tilde{g}_{01}^E - \tilde{g}_{10}^E \tilde{g}_{01}^h}{\tilde{g}_{10}^h} \right|^{2-\alpha} (2-\alpha)(1-\alpha) P_{00}^0(0,+1)\,. \tag{3.19$'$}$$

Since near the critical point $g_E > 0 (g_E < 0)$ may be identified with the one- (two-) phase region, the critical isotherm will be among those paths characterized by small $g_E |g_h|^{-1/\Delta}$. For such trajectories the appropriate form for $\tilde{p}$ is given by (2.8) so that its derivative with respect to $\tilde{\mu}$ will give us the density ρ. Therefore, if we set $t=0$ into the expansions for the scaling fields and then substitute these into Eq. (2.8) and the equation for ρ, we will obtain expressions parametrized by $\tilde{\mu}$ for the thermodynamic potential and the density along the critical isotherm. Thus, by eliminating $\tilde{\mu}$ from the resulting equations, we can obtain the form of the critical isotherm $p(\rho)$. That is, for the pressure along the critical isotherm, we find

$$p \approx \frac{k_B T_c}{v_c}\left(\tilde{p}_{00} \pm F_0 \left|\frac{\rho^{\pm} - \rho_c}{\rho_c}\right|^{\delta} + F_1 \left|\frac{\rho^{\pm} - \rho_c}{\rho_c}\right|^{\delta+1} \mp F_2 \left|\frac{\rho^{\pm} - \rho_c}{\rho_c}\right|^{(\Delta+\Delta_S)/\beta} + \cdots\right), \tag{3.20}$$

with

$$F_0 = \frac{\tilde{p}_{10}}{\tilde{g}_{10}^h}\left|\frac{p_c v_c}{k_B T_c}\, \frac{\Delta}{(\Delta+\beta)\tilde{g}_{10}^h Q_{00}^0(+1,0)}\right|^{\delta}. \tag{3.20$'$}$$

III. PARAMETRIC REPRESENTATION

The expressions we have derived allow us to relate the nonuniversal expansion coefficients for the scaling fields to experimentally measurable quantities just as the amplitudes and critical exponents are. However, in order to obtain these relations, we need to know the explicit form or the value of the universal expansion coefficients for the scaling function, either for a model or for a system in the same universality class as that for a fluid. There have been several forms proposed for the scaling function. Brezin, Wallace, and Wilson,[18] using RG techniques and the systematic ϵ expansion, have derived the equation of state for Ising-like systems and have established that at least to order ϵ^2 the results are the same as those predicted by Schofield, Litster, and Ho[7] (SLH) using the linear model of the parametric representation. Thus, to that order, the correct relations between the system-dependent parameters in the expansion of the scaling fields and purely experimental quantities may be obtained using the simplicity of the linear model to calculate the explicit form of the expansion coefficients for the scaling function.

In order to find the explicit form of the universal coefficients $P_{jk}^{\pm(i)}(0,\pm 1)$, in terms of experimentally measurable quantities, we shall parametrize the relevant scaling fields rather than the physical variables with the variables r, θ and use the linear model to determine $p_s(g_h, g_E, 0, 0)$. The irrelevant scaling fields will be ignored in the scaling function since very little information about their effect is known. As far as we know, only one attempt[19] to explicitly evaluate $P_{jk}^{\pm(i)}(0,\pm 1)$ with $j \neq 0$, $k=0$, has been made.

Let r be the distance from the critical point and θ the distance from some origin along a path of constant r; then the parametrization will be

$$g_h = r^{\Delta} h(\theta) \tag{4.1}$$

and

$$g_E = r t(\theta)\,, \tag{4.2}$$

where h and t are analytic functions of θ. This implies that the singular part $p_s(g_h, g_E, 0, 0)$ is of the form

$$p_s(g_h, g_E, 0, 0) = \left\{ \begin{array}{ll} r^{(2-\alpha)} |t(\theta)|^{2-\alpha} p_s(h(\theta)|t(\theta)|^{-\Delta}, \pm 1) & \quad (4.3\text{a}) \\ r^{(2-\alpha)} |h(\theta)|^{(2-\alpha)/\Delta} p_s(\pm 1, t(\theta)|h(\theta)|^{-1/\Delta}) & \quad (4.3\text{b}) \end{array} \right\} = r^{(2-\alpha)} p(\theta)\,,$$

where $p(\theta)$ is an analytic function which is determined from the solution to the differential equation

$$\frac{\partial p_s}{\partial g_h} = r^{\beta} m(\theta)\,. \tag{4.4}$$

and the function $m(\theta)$ is analytic.

For the linear model the functions $h(\theta)$, $t(\theta)$, and $m(\theta)$ are, to lowest order, given as

$$h(\theta) = \theta(1-\theta^2)\,, \tag{4.1$'$}$$

$$t(\theta)=1-b^2\theta^2\,, \tag{4.2a}$$

$$m(\theta)=\theta\,, \tag{4.4'}$$

respectively. The parameter b is a universal quantity and given by

$$b^2=\frac{\delta-3}{(\delta-1)(1-2\beta)}\,, \tag{4.2b}$$

for the restricted linear model. Thus, in this representation, the coexistence curve will be described by $\theta=\pm 1$ (+ for the liquid phase and − for the vapor phase). It should be pointed out that in the SLH parametric representation there are two system-dependent parameters, namely, a and k that appear in the equations for $h(\theta)$ and $m(\theta)$, respectively. Such parameters will appear in p_s making it nonuniversal, which is contrary to what we have assumed; we have therefore set $a=k=1$.

The solution to the differential equation (4.4), using the given forms for h, t, and m is

$$p(\theta)=\frac{2\Delta(b^2-1)}{2b^4(\Delta+\beta)}+\frac{(b^2-3)-2\Delta(b^2-2)}{2b^4(\Delta+\beta-1)}(1-b^2\theta^2)-\frac{2\Delta-3}{2b^4(\Delta+\beta-2)}(1-b^2\theta^2)^2 \tag{4.5}$$

assuming that $\alpha\neq 0$. Since the coefficients $P^{\pm(i)}_{jk}(0,\pm 1)$ are the derivatives evaluated at the critical point of the scaling function, we have

$$P^{-(0)}_{00}(0,-1)=\frac{(\Delta-3\beta)-b^2(\Delta+\beta)(1-2\beta)}{2b^4(\Delta+\beta)(\Delta+\beta-1)(\Delta+\beta-2)}\times|b^2-1|^{-(1-\alpha)}\,, \tag{4.6}$$

$$P^{-(1)}_{00}(0,-1)=|b^2-1|^{-\beta}\,, \tag{4.6a}$$

and

$$P^{-(2)}_{00}(0,-1)=\frac{1-(1-2\beta)b^2}{4(b^2-1)}\,|b^2-1|^{(\Delta-\beta)}\,. \tag{4.6b}$$

Inserting the latter expressions into the equations for B_0, D_0, and Γ_0' will give us three coupled equations whose solutions are

$$\tilde{g}^h_{10}=\frac{p_cv_c}{k_BT_c}B_0\left|\frac{1-(1-2\beta)b^2}{2(b^2-1)}\left(\frac{p_cv_c}{k_BT_c}\right)^2\frac{B_0^2}{\Gamma_0'}\right|^{-\beta/(2-\alpha)}\,, \tag{4.7}$$

$$\tilde{g}^E_{10}=\frac{p_cv_c}{k_BT_c}\frac{D_0}{\rho_c}\frac{2b^4\alpha(1-\alpha)}{(\Delta-3\beta)-b^2(\Delta+\beta)(1-2\beta)}\times\left|\frac{1-(1-2\beta)b^2}{2(b^2-1)}\left(\frac{p_cv_c}{k_BT_c}\right)^2\frac{B_0^2}{\Gamma_0'}\right|^{-(1-\alpha)/(2-\alpha)}\,, \tag{4.7a}$$

and

$$|\tilde{g}^h_{10}\tilde{g}^E_{01}-\tilde{g}^E_{10}\tilde{g}^h_{01}|=\frac{p_cv_c}{k_BT_c}(b^2-1)B_0\times\left|\frac{1-(1-2\beta)b^2}{2(b^2-1)}\left(\frac{p_cv_c}{k_BT_c}\right)^2\frac{B_0^2}{\Gamma_0'}\right|^{(1-\beta)/(2-\alpha)}\,. \tag{4.7b}$$

These equations together with (3.5) define the transformation to lowest order from physical variables to relevant scaling fields.

Finally, we can also identify the system-dependent parameters a, k appearing in the SLH parametric representation with combinations of the expansion coefficients for the scaling fields, by noting that the relations of the former parameters to measurable quantities are

$$\frac{\rho^{\pm}-\rho_c}{\rho_c}=\pm|b^2-1|^{-\beta}k|t|^{\beta}\,, \tag{4.8}$$

and

$$\left(\frac{\rho^{\pm}}{\rho_c}\right)^2K_Tp_c=\frac{k}{2a}[1-(1-2\beta)b^2]|b^2-1|^{\gamma-1}|t|^{-\gamma}\,, \tag{4.8'}$$

so that, the comparison of (4.8) and (4.8′) with (3.6) and (3.10) yields

$$k|b^2-1|^{-\beta}=B_0 \tag{4.9}$$

and

$$\frac{k}{2a}[1-(1-2\beta)b^2]|b^2-1|^{\gamma-1}=\frac{k_BT_c}{p_cv_c}\Gamma_0' \tag{4.9'}$$

which combined with Eqs. (4.7) will give equations whose solutions are

$$k=\frac{k_BT_c}{p_cv_c}\tilde{g}^h_{10}\left|\frac{\tilde{g}^h_{10}\tilde{g}^E_{01}-\tilde{g}^E_{10}\tilde{g}^h_{01}}{\tilde{g}^h_{10}}\right|^{\beta} \tag{4.10}$$

and

$$a=\frac{1}{\tilde{g}^h_{10}}\left|\frac{\tilde{g}^h_{10}\tilde{g}^E_{01}-\tilde{g}^E_{10}\tilde{g}^h_{01}}{\tilde{g}^h_{10}}\right|^{\Delta}\,. \tag{4.10'}$$

Thus, in this approach, the features of a system are implicitly contained in the scaling fields and they appear explicitly through the derivatives of the fields with respect to the physical variables.

V. SUMMARY AND CONCLUSIONS

Four assumptions have allowed us to obtain expressions containing correction to scaling terms and describing the thermodynamic behavior of simple fluids near the critical point. The assumptions, on which our derivations are based, are the following.

(i) The thermodynamic potential appropriate to describe the critical behavior of a simple fluid is that associated with the logarithm of the grand partition function.

(ii) This potential possesses the general properties given by Wegner using renormalization-group arguments.

(iii) A reasonable description of the fluid may be obtained by considering only the two most important irrelevant scaling fields in addition to the three relevant fields. Marginal scaling fields are absent in these systems.

(iv) The thermodynamic potential possesses Ising symmetry when written as a function of the scaling fields.

The derivation of the expressions for the thermodynamic properties has been specialized to trajectories of experimental interest leading to the critical point. Thus, along the coexistence curve, we find as follows: the *chemical potential*

$$\tilde{\mu}_0(t) \approx (\zeta_0 + \zeta_1 |t| + \zeta_2 |t|^{(\Delta-1)+\Delta_A} + \zeta_3 |t|^{(\Delta-1)+\Delta_A+\Delta_s} + \cdots)|t| ,$$

the *pressure*

$$p \approx (k_B T_c / v_c)(\tilde{p}_{00} + P_0 |t| + P_1 |t|^{2-\alpha} + P_2 |t|^2 + P_3 |t|^{2-\alpha+\Delta_s} + \cdots) ,$$

the *difference* of densities

$$(\rho_L - \rho_G)/2\rho_c \approx (B_0 + B_1 |t|^{\Delta_s} + B_2 |t|^{2\Delta_s} + B_3 |t| + \cdots)|t|^{\beta} ,$$

the *average* of densities

$$(\rho_L + \rho_G)/2 \approx \rho_c + D_0 |t|^{1-\alpha} + D_1 |t| + D_2 |t|^{1-\alpha+\Delta_s} + D_3 |t|^{1-\alpha-(\Delta-1)+\Delta_A} + \cdots ,$$

the *isothermal* compressibility

$$(\rho^{\pm})^2 K_T \approx (k_B T_c / p_c^2 v_c)\rho_c^2(\Gamma_0' + \Gamma_1' |t|^{\Delta_s} \pm \Gamma_2' |t|^{\Delta-1} + \Gamma_3' |t|^{2\Delta_s} + \cdots)|t|^{-\gamma} ,$$

and the constant volume specific heat

$$C_v^{\pm} \approx k_B(A_1 + A_0 |t|^{\alpha} \pm A_2 |t|^{\beta} + A_3 |t|^{\Delta_s} + \cdots)|t|^{-\alpha} .$$

Along the critical isochore, we find the chemical potential

$$\tilde{\mu}_{cic}(t) \approx (\mathscr{g}_0 + \mathscr{g}_1 t + \mathscr{g}_2 t^{2(\Delta-1)} + \mathscr{g}_3 t^{2(\Delta-1)+\alpha} + \cdots)t ,$$

the pressure

$$p \approx (k_B T_c / v_c)(\tilde{p}_{00} + P_0' t + P_1' |t|^{2-\alpha} + P_2' t^2 + P_3' |t|^{1+2(\Delta-1)} + \cdots) ,$$

the isothermal compressibility

$$K_T \approx (k_B T_c / p_c^2 v_c)(\Gamma_0 + \Gamma_1 |t|^{\Delta_s} + \Gamma_2 |t|^{2\Delta_s} + \Gamma_3 |t|^{2(\Delta-1)} + \cdots)|t|^{-\gamma} ,$$

the constant volume specific heat, in the *one-phase* region ($t > 0$)

$$C_v \approx k_B(A_1'' + A_0 |t|^{\alpha} + A_2'' |t|^{\Delta_s} + \cdots)|t|^{-\alpha} ,$$

and the constant volume specific heat, in the *two-phase* region ($t < 0$)

$$C_v \approx k_B(A_1' + A_0 |t|^{\alpha} + A_2' |t|^{\Delta_s} + \cdots)|t|^{-\alpha} .$$

Finally, along the critical isotherm, we find the pressure

$$p \approx (k_B T_c / v_c)(\tilde{p}_{00} \pm F_0 |\tilde{\rho}^{\pm}|^{\delta} + F_1 |\tilde{\rho}^{\pm}|^{\delta+1} \mp F_2 |\tilde{\rho}^{\pm}|^{(\Delta+\Delta_s)/\beta} + \cdots) ,$$

where $\tilde{\rho}^{\pm} = (\rho^{\pm} - \rho_c)/\rho_c$ is the reduced density and the +(−) sign is used to describe the approach from the high- (low-) density phase. The expressions for the coefficients in the preceding expansions in terms of the system-dependent parameters may be found in Ref. 6.

The expressions for the difference and the average of coexisting densities, as well as for the isothermal compressibility along the coexistence curve, have been used together with the universal ($a = k = 1$) parametric representation of the linear model to relate the system-dependent expansion coefficients in the scaling fields and experimentally measurable quantities. These relations are

$$\tilde{g}_{10}^{h} = \frac{p_c v_c}{k_B T_c} B_0 \left| \frac{1-(1-2\beta)b^2}{2(b^2-1)} \left(\frac{p_c v_c}{k_B T_c}\right)^2 \frac{B_0^2}{\Gamma_0'} \right|^{-\beta/(2-\alpha)} ,$$

$$\tilde{g}_{01}^{h} = -\tilde{g}_{10}^{h} \frac{T_c}{p_c} \lim_{T \to T_c} \frac{dp}{dT}$$

$$\tilde{g}_{10}^{E} = \frac{p_c v_c}{k_B T_c} \frac{D_0}{\rho_c} \frac{2b^4 \alpha(1-\alpha)}{(\Delta - 3\beta) - b^2(\Delta+\beta)(1-2\beta)} \left| \frac{1-(1-2\beta)b^2}{2(b^2-1)} \left(\frac{p_c v_c}{k_B T_c}\right)^2 \frac{B_0^2}{\Gamma_0'} \right|^{-(1-\alpha)/(2-\alpha)} ,$$

and

$$\left|\tilde{g}_{10}^{h}\tilde{g}_{01}^{E}-\tilde{g}_{10}^{E}\tilde{g}_{01}^{h}\right|=\frac{p_c v_c}{k_B T_c}(b^2-1)B_0\left|\frac{1-(1-2\beta)b^2}{2(b^2-1)}\left(\frac{p_c v_c}{k_B T_c}\right)^2\frac{B_0^2}{\Gamma_0'}\right|^{(1-\beta)/(2-\alpha)}.$$

The four assumptions, as well as the form of the derived expressions, allow us to conclude the following.

(a) RG selects the dependent variable, as well as the set of independent variables, from the set of intensive variables associated to a simple fluid.

(b) RG predicts the existence of a curvilinear coordinate system which is unique, except for two arbitrary constants. This coordinate system is spanned by the relevant scaling fields and its origin is located at the critical point. In the curvilinear system, the surface described by the singular part of the potential looks alike for all systems in the same universality class. The transformation from physical variables to scaling fields involves system-dependent quantities which can be measured experimentally.

(c) The diameter of the coexistence curve is nonrectilinear. The nonlinearity is such that the temperature derivative of the diameter diverges at the critical point like the constant volume specific heat. However, this type of behavior is not expected to be exhibited experimentally in all fluids since the coefficient of the singular term is not universal and may be below observability for some systems.

(d) The second derivative of the chemical potential with respect to temperature, along either the coexistence curve or the critical isochore, is nonsingular at the critical point. This derivative is the same at the critical point, when the approach is either from above or from below T_c.

(e) The corrections to single power-law expressions, due to the irrelevant scaling fields are as important as those due to the nonlinear terms in the expansions of the scaling fields in terms of the physical intensive variables.

ACKNOWLEDGMENT

M.L.K. wishes to thank Professor J. V. Sengers for valuable suggestions in the proofreading of this paper.

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