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Scaling equation of state derived from the pseudospinodal

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Starting from the concept of the pseudospinodal, the authors derive an explicit expression for the scaling equation of state applicable to liquid-gas [and universality class (3,1)] systems. The advantages of this equation over other phenomenological equations are: it has no adjustable, unphysical parameters; it is valid in the metastable region; and it can simultaneously predict PVT data and the critical amplitude ratio for specific heat. The equation also fits PVT data as well as other phenomenological equations, is easy to use, and accurately predicts other critical amplitude ratios. It is argued that the success of this equation supports the usefulness of the pseudospinodal, which has been questioned by certain theoretical considerations.

I. INTRODUCTION

The concept of the spinodal was first introduced by van der Waals, and represents the limit of metastability of the one-phase state in the two-phase region. Benedek[1] used this concept to describe data off the critical isochore by assuming that various thermodynamic and transport properties diverge relative to a pseudospinodal temperature with the same power-law dependence as they exhibit along the critical isochore when the critical temperature is approached. This concept of the pseudospinodal has been discussed clearly by Chu, Schoenes, and Fisher.[2] Whether it is useful or not is still an open question: some theoretical considerations argue against it, while experimental results support it. The strongest argument against the pseudospinodal is that it is inconsistent with the usual analyticity requirements imposed on scaling equations of state.[3] Specifically, as Chu *et al.*[2] show, the assumption of a pseudospinodal leads to an equation of state that is not analytic in density on the critical isochore for temperatures greater than the critical temperature. Their argument can also be used to show that the equation of state will not be analytic in temperature on the critical isotherm. Although the equation will be smooth enough to fit data, its lack of analyticity is inconsistent with what has been proved for some and what is expected from other theoretical models. Even though there is no proof that the equation of state for liquid-gas systems must be analytic in the one-phase region,[4] there is no reason to expect nonanalyticity there. Because of this Chu *et al.* conclude that the assumption of a pseudospinodal is unacceptable. On the other hand, they find that their light-scattering data *support* the concept of a pseudospinodal. This is also true of thermal-diffusivity and diffusion-coefficient data taken by Benedek,[1] and of viscosity data taken by Izumi and Miyake.[5]

In this paper we present more phenomenological results supporting the usefulness of the pseudospinodal. We show that an equation of state can be derived from it which is successful for liquid-gas [and universality class (3, 1)] systems. The derived equation of state fits PVT data as well as other phenomenological equations and is easy to use. In addition, it has no unphysical adjustable parameters and is applicable in the metastable region, which should make it useful in surface tension and nucleation studies. We also show that the equation can be integrated to give a simple expression for the Helmholtz free energy. From this expression we calculate the critical amplitude ratio for specific heat, and find that it agrees with that predicted by model systems for the universality class (3, 1) and with the experimental data. We find the same to be true of the critical amplitude ratios for the isothermal compressibility and correlation length, as well as for two other universal amplitude ratios R_χ and R_c. It is this success in predicting universal amplitude ratios that we find most impressive.

Although the equation of state derived from the pseudospinodal is quite useful and has several advantages over other phenomenological equations, it has two difficulties that would normally be considered quite serious. First, it is not analytic in the one-phase region on the critical isochore and critical isotherm. Second, it is only successful when applied to universality class (3, 1) systems. Neither of these problems is surprising; both are a consequence of the starting assumption. As mentioned above, the nonanalyticity in the one-

phase region is exactly that predicted by Chu *et al.* for *any* equation of state derived from the pseudospinodal assumption. Since the pseudospinodal assumption used here is based on data from universality (3, 1) systems, we do not expect the derived equation of state to apply to other universality classes. Indeed, we find that in the spherical model the pseudospinodal assumption has an extra term compared with the one assumed here, and thus leads to a different equation of state. This suggests that the form of the pseudospinodal can depend on the particular universality class, and that a pseudospinodal valid for one class need not produce an equation of state valid for other classes.

However, given the controversy surrounding the pseudospinodal, it is still useful to consider an equation of state derived from it, in spite of the two difficulties discussed above. From the practical side, the derived equation is easy to use, fits PVT data as successfully as the MLSG and parametric equations, and has several advantages over them. From a more aesthetic point of view, the fact that the pseudospinodal leads to a successful and useful equation of state gives new evidence supporting the concept, which goes beyond the direct numerical fits to data presented so far. For these reasons we present the equation here, and hope that besides proving useful it will stimulate more inquiry into the question of the pseudospinodal.

The outline of this paper is as follows: in Sec. II we present the pseudospinodal assumption explicitly, and show how an equation of state can be derived from it. We then use this equation to fit PVT data, and compare the fit with that of other phenomenological equations. In Sec. III, we show how the equation of state can be used to predict universal amplitude ratios accurately. Finally, in Sec. IV, we summarize our results and discuss possibilities for future work.

II. EQUATION OF STATE AND ITS FIT TO PVT DATA

A. Derivation of equation

In the critical region, the equation of state can be written as[3,6]

$$\Delta\mu = \Delta\rho \mid \Delta\rho \mid^{\delta-1} h(x) . \tag{1}$$

In this equation $\Delta\mu$ is the relative chemical potential

$$\Delta\mu = [\mu(\rho, T) - \mu(\rho_c, T)]\rho_c/P_c ,$$

where ρ_c and P_c are the density and pressure at the critical point, T is the temperature, and

$$\Delta\rho = (\rho - \rho_c)/\rho_c .$$

The scaling variable x is given by

$$x = t \mid \Delta\rho \mid^{-1/\beta} , \tag{2}$$

where t is the reduced temperature $(T - T_c)/T_c$, and T_c is the critical temperature. The exponents β and δ are the usual ones describing the coexistence curve and the critical isotherm. From thermodynamics, the isothermal compressibility K_T is given by

$$(K_T\rho^2)^{-1} = (\partial\mu/\partial\rho)_T , \tag{3}$$

and, using Eq. (1), we find the standard relation

$$K_T^{-1} = \mid \Delta\rho \mid^{\delta-1} (\rho/\rho_c)^2 P_c[\delta h(x) - (x/\beta)h'(x)] , \tag{4}$$

with the prime denoting differentiation with respect to x.

The concept of the pseudospinodal gives an independent expresion for K_T^{-1}. The pseudospinodal represents the limit of metastability of the one-phase state in the two-phase region. On any given isochore the compressibility diverges as the temperature approaches the pseudospinodal temperature. In keeping with the form of the pseudospinodal supported by experimental data,[1,2,5] we assume that the isothermal compressibility diverges at the pseudospinodal as

$$K_T = (\rho_c/\rho)^2 P_c^{-1}\Gamma\{[T - T_s(\rho)]/T_c\}^{-\gamma} , \tag{5}$$

with $\gamma = \beta\delta - \beta$. We call this the *pseudospinodal assumption*. Note that on the critical isochore Eq. (5) reduces to the usual expression

$$K_T = P_c^{-1}\Gamma t^{-\gamma} ,$$

since $T_s(\rho_c) = T_c$.

If Eq. (5) is compared with Eq. (4) we obtain a first-order linear differential equation for $h(x)$:

$$h'(x) - \left(\frac{\beta\delta}{x}\right)h(x) = \left(\frac{C}{x}\right)\left(1 + \frac{x}{x_1}\right)^{\gamma} , \tag{6}$$

with $C = -\beta x_1^{\gamma}/\Gamma$ and

$$x_1 = \mid \Delta\rho \mid^{-1/\beta} [T_c - T_s(\rho)]/T_c , \tag{7}$$

the value of x on the pseudospinodal. Equation (6) has the homogeneous solution $kx^{\beta\delta}$, with k a constant to be determined by the boundary conditions. The general solution to Eq. (6) is

$$h(x) = kx^{\beta\delta} + (x_1^{\gamma}/\delta\Gamma)\,{}_2F_1(-\gamma, -\beta\delta; 1 - \beta\delta; z) , \tag{8}$$

where

$$z = -x/x_1 \tag{9}$$

and ${}_2F_1$ is the hypergeometric function. That Eq. (8) is a solution to Eq. (6) can be verified by substitution. [Eq. (22) on p. 102 and Eq. (4) on p. 101 of Erdélyi[7] will prove helpful here.]

The conditions imposed on $h(x)$ are that (i) it is real, (ii) it is continuous across $z = -1 (x = x_1)$, and

(iii) that $h(x) \to x^\gamma$ as $x \to \infty$ ($z \to -\infty$).[3] The second condition can be met by using an analytic continuation formula for the hypergeometric series (Eq. 2, p. 108 of Erdélyi), and the continuation plus condition (iii) determines the constant k. The resulting equation of state is

$$h(x) = D[z \mid z \mid^{\beta\delta-1}\Gamma(1-\beta\delta)\Gamma(\beta)/\Gamma(-\gamma) + {}_2F_1(-\gamma, -\beta\delta; 1-\beta\delta; z)], \quad \mid z \mid \leq 1, \tag{10a}$$

$$= D\delta(-z)^\gamma {}_2F_1(-\gamma, \beta; 1+\beta; z^{-1}), \quad \mid z \mid \geq 1, \tag{10b}$$

where Eq. (10b) is the analytic continuation of the solution (10a) into the region $\mid z \mid > 1$. In these equations

$$D = x_1^\gamma/\delta\Gamma, \tag{11}$$

z is given by Eq. (9), and $\Gamma(y)$ is the gamma function [not to be confused with the amplitude included in Eq. (5)].

To see if Eqs. (10) are at least reasonable, we first check that they reduce to the van der Waals equation of state in the mean-field-theory limit. The van der Waals exponents are $\beta = \frac{1}{2}$, $\gamma = 1$, $\delta = 3$. Setting $\gamma = 1$ terminates the hypergeometric series in (10a) at the first power in z and makes the coefficient of the homogeneous term zero. Equations (10a) and (10b) both give

$$h(x) = x_1\Gamma^{-1}[\delta^{-1} - (x/x_1)\gamma\beta(1-\beta\delta)^{-1}] = \Gamma^{-1}(x_0 + x),$$

where we have used the result (valid for the van der Waals model[8]) $x_1 = x_0\beta\delta/(\beta\delta - 1)$. Thus the derived equation of state reduces to the proper mean-field limit.

B. Fitting equation of state to PVT data

In order to see how well Eqs. (10a) and (10b) represent real PVT data, we replace the hypogeometric functions by their explicit series representations to give

$$h(x) = D\left(z \mid z \mid^{\beta\delta-1}\frac{\Gamma(1-\beta\delta)\Gamma(\beta)}{\Gamma(-\gamma)} - \beta\delta\sum_{n=0}^{\infty}\frac{(-\gamma)_n}{n-\beta\delta}\frac{z^n}{n!}\right), \quad \mid z \mid \leq 1, \tag{11a}$$

$$= D\beta\delta(-z)^\gamma\sum_{n=0}^{\infty}\frac{(-\gamma)_n}{n+\beta}\frac{z^n}{n!}, \quad \mid z \mid \geq 1, \tag{11b}$$

with D given by Eq. (11), z by Eq. (9), and

$$(-\gamma)_n = \Gamma(n-\gamma)/\Gamma(-\gamma) = \prod_{j=1}^{n}(-\gamma+j-1).$$

When fitting PVT data we find that for about 90% of the points we need only three terms in the appropriate series to get $h(x)$ to an accuracy of one part in 10^4. Thus in practice $h(x)$ is a simple polynomial and is easy to use.

In principle the comparison of Eq. (11) with PVT data is quite simple. The values of β, δ, Γ, and x_0 (and ρ_c and T_c, which appear in the independent variable x) are determined experimentally. The coefficient x_1 is found from the requirement $h(-x_0) = 0$, i.e.,

$$-\left|\frac{x_0}{x_1}\right|^{\beta\delta}\frac{\Gamma(1-\beta\delta)\Gamma(\beta)}{\Gamma(-\gamma)} + {}_2F_1\left(-\gamma, -\beta\delta; 1-\beta\delta; \frac{x_0}{x_1}\right) = 0, \tag{12}$$

which can be solved numerically to give the ratio x_0/x_1. In this way the function $h(x)$ is completely determined by four physical parameters ($\beta, \delta, x_0, \Gamma$), the minimum necessary under the hypothesis of two-scale-factor universality,[9] and can be compared with its experimental value $\mid \Delta\mu \mid / \mid \Delta\rho \mid^\delta$.

In practice the four physical parameters (as well as ρ_c and T_c) are only fixed within ranges defined by experimental uncertainties. We have used a grid search constrained by these ranges to find the values of the physical parameters that produce the best fit.

Since our goal was to compare the fit of our equation to PVT data with that of other phenomenological equations, we followed the analysis of Levelt Sengers *et al.*[10] as closely as possible, and fitted the data they present. Since this data is some distance from the critical point, we do not expect the exponents which give the best fit to be very close to the most recent theoretical values[11,12] of $\beta = 0.324 \pm 0.006$ and $\delta = 4.82 \pm 0.06$. Rather, we expect x_0 and β to fall within the range determined by coexistence-curve data, and T_c to be close to the experimental value of the critical temperature.

The quality of the fit was determined by the method described by Levelt Sengers *et al.*, which consists of minimizing the reduced variance

$$\chi^2 = (n-k)^{-1}\sum_{i=1}^{n}\frac{[g_t(x_i) - g_{\text{expt}}(x_i)]^2}{\sigma^2}. \tag{13}$$

Here, following Levelt Sengers *et al.*, we define

$$g_t(x) = [x_0/(x+x_0)]h(x), \tag{14}$$

$$g_{\text{expt}}(x) = [x_0/(x+x_0)] \mid \Delta\mu \mid / \mid \Delta\rho \mid^\delta, \tag{15}$$

and find that

$$\sigma^2 = g_{\text{expt}}^2\left[\left(\frac{\sigma_t}{t}\right)^2\left(\frac{x}{x+x_0}\right)^2 + \left(\frac{\sigma_{\Delta\rho}}{\Delta\rho}\right)^2\left(\delta - \frac{x}{x+x_0}\frac{1}{\beta}\right)^2 + \left(\frac{\sigma_{\Delta\mu}}{\Delta\mu}\right)^2\right]. \tag{16}$$

The absolute-weight assignments σ_t, $\sigma_{\Delta\mu}$, and $\sigma_{\Delta\rho}$ were taken from their paper, and, following them, we only attempted to fit data within a critical re-

gion defined by $|t|<0.03$ and $|\Delta\rho|<0.25$. No data points within this region were discarded.

In the case of helium-4, Levelt Sengers *et al.* give experimental values and ranges for x_0, β, T_c, and ρ_c. Fixing ρ_c at their value, we find a minimum χ^2 of 2.4 for

$$\beta=0.36,\quad x_0=0.38,\quad T_c=5.191\ \text{K},$$
$$\Gamma=0.16,\ \delta=4.18\quad(\chi^2=2.4). \tag{17}$$

This compares well with the minimum χ^2 calculated by Levelt Sengers *et al.* of 2.52 for the MLSG equation and 2.44 for the linear model. The values of β, x_0, and Γ are essentially the same as those which give the best fit of the other equations, with β and x_0 both falling within the experimental range determined from coexistence-curve data. The values of δ and T_c are, respectively, slightly lower and higher than those giving the best fit for the other equations. If we fix T_c at the average experimental value[10] of 5.1885 K, we find a minimum χ^2 of 2.9 for

$$\beta=0.36,\quad x_0=0.37,\quad \Gamma=0.15,$$
$$\delta=4.24\quad(T_c=5.1885\ \text{K},\ \chi^2=2.9), \tag{18}$$

which is also acceptable, given the uncertainties in the data.

A graph of the theoretical versus experimental values of $h(x)$ is presented in Fig. 1. The solid line represents the theoretical curve for helium-4 calculated from Eq. (11) with the best-fit parameters given in Eq. (17). The circles represent the experimental values of $|\Delta\mu|/|\Delta\rho|^{\delta}$ given by Levelt Sengers *et al.* The fit is seen to be quite good, and certainly comparable to a similar fit of the MLSG equation.[13] A scatter plot is presented in Fig. 2 which also compares well with similar

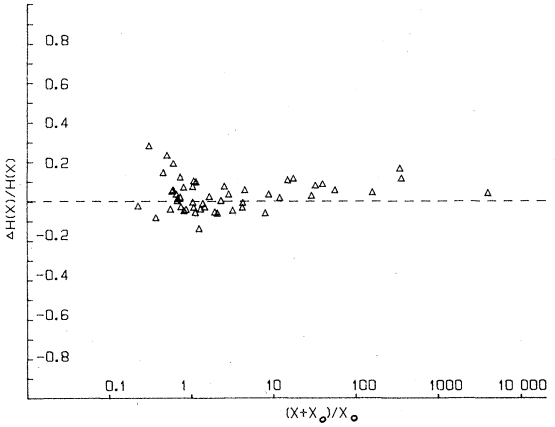

FIG. 2. Deviation plot for the points in Fig. 1, with $\Delta h(x)/h(x)=(h_{\text{theor}}-h_{\text{exp}})/h_{\text{exp}}$.

plots from the MLSG equation[10,13] and the linear model.[10]

For xenon, we find a minimum χ^2 of 1.8 for

$$\beta=0.37,\quad x_0=0.19,\quad T_c=289.75\ \text{K},$$
$$\Gamma=0.06,\quad \delta=4.35\ (\chi^2=1.8). \tag{19}$$

Again β and x_0 fall within the experimental ranges, and are essentially the same as the values which produce the best fits for the MLSG equation and the linear model.[10] The best fit for the MLSG equation has $\chi^2=1.99$, and for the linear model $\chi^2=1.46$. Again the δ in Eq. (18) is a little lower than those that give the best fit for the other two equations, while T_c is a little higher. If we fix T_c at 289.74 K, which gives the best fit for the other equations, we find $\chi^2=1.9$ with the same values of the physical parameters given in Eq. (19). Graphs for xenon using the parameters of Eq. (19) are shown in Figs. 3 and 4.

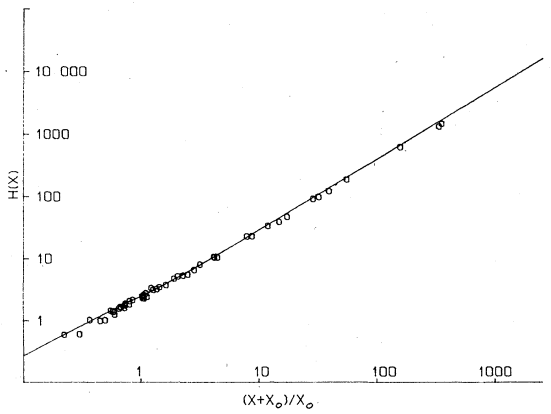

FIG. 1. Graph of the experimental values of $h(x)$ for helium-4 [dots], as calculated from Levelt Sengers *et al.* (Ref. 10), vs the theoretical value of $h(x)$ calculated from Eq. (11) [line].

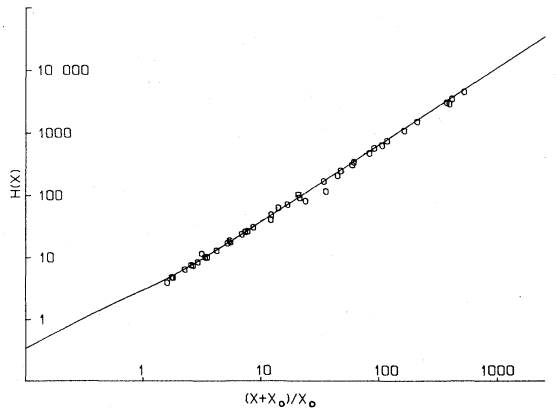

FIG. 3. Graph of the experimental values of $h(x)$ for xenon [dots], as calculated from Levelt Sengers *et al.* (Ref. 10), vs the theoretical value of $h(x)$ calculated from Eq. (11) [line].

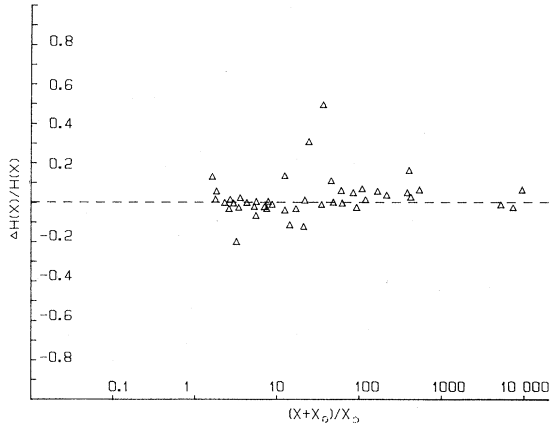

FIG. 4. Deviation plot for the points in Fig. 3, with $\Delta h(x)/h(x) = (h_{\text{theor}} - h_{\text{exp}})/h_{\text{exp}}$.

In conclusion, we see that for helium-4 and xenon, the equation of state derived from the pseudospinodal can fit PVT data as successfully as other phenomenological equations *without* using any unphysical, adjustable parameters, and is easy to use. Work on fitting PVT data from other gases is in progress, and will be reported in a later work.

C. Analyticity of equation of state

As predicted by Chu *et al.*,[2] the equation of state given in Eqs. (10) and (11) is analytic in $\Delta\rho$ and t every where except on the critical isochore ($\Delta\rho = 0$) and critical isotherm ($t = 0$). The nonanalyticity in temperature on the critical isotherm is due to the $x \mid x \mid^{\beta\delta-1}$ term, which makes the equation of state have only one continous derivative in temperature at $x = 0$ for $\beta \sim \frac{1}{3}$ and $\delta \sim 4.8$. The nonanalyticity in density on the critical isochore can be seen by examining the power series for $\Delta\mu$ as $x \to \infty$ ($\Delta\rho \to 0$). In this case, $h(x)$ is represented by Eq. (11b), and is a power series of terms $x^{\gamma-n}$, with $n = 0, 1, 2, \ldots$. Using x as given by Eq. (2) in this series, we find

$$\Delta\mu = \Delta\rho \sum_{n=0}^{\infty} f_n(t) \Delta\rho^{n/\beta}, \quad x \to \infty . \tag{20}$$

For $\beta \sim \frac{1}{3}$, $\Delta\mu$ has four continuous derivatives in density on the critical isochore, but is not analytic there. On the other hand, $\Delta\mu$ is smooth on both the critical isochore and isotherm (satisfying Griffith's original intent[4]), and the uncertainties in the data make the experimental determination of derivatives of $\Delta\mu$ very difficult. In any case, as discussed above, the nonanalyticity is to be expected from the approach and comes from assuming that the pseudospinodal has the same exponent β as the coexistence curve—an assumption required by the scaling hypothesis[2] and supported by data.[1,2,5] A modification that might eliminate this nonanalyticity is discussed in the Conclusion.

III. UNIVERSAL AMPLITUDE RATIOS

In Sec. III we calculate the critical amplitude ratios for the isothermal compressibility, correlation length, and specific heat. In addition, we also calculate the universal amplitude ratios R_χ and R_c.[14] We find that all of the predicted values compare well with those from other theoretical methods and with the experimental data. This means that the equation of state (10) is the only phenomenological equation able to simultaneously fit both PVT data and the critical amplitude ratio for specific heat.[15] We show that all of the amplitude predictions are quite straightforward, and follow directly from the pseudospinodal assumption and the equation of state.

The easiest ratios to calculate are Γ/Γ' and ξ_0'/ξ_0, the critical amplitude ratios for the isothermal compressibility and correlation length. We calculate Γ/Γ' as follows: if the critical point is approached from below along the coexistence curve, then

$$K_T = \Gamma' \mid t \mid^{-\gamma} (\rho_c/\rho)^2 P_c^{-1} . \tag{21}$$

The pseudospinodal assumption [Eq. (5)] gives an independent expression for K_T also valid on the coexistence curve. If we equate the two we find

$$\Gamma/\Gamma' = (x_1/x_0 - 1)^{\gamma} . \tag{22}$$

The ratio x_1/x_0 is uniquely determined by β and δ from Eq. (12), thus making it a constant for the universality class. For the most recent theoretical values[11,12] of $\beta = 0.324 \pm 0.006$, $\delta = 4.82 \pm 0.06$, we find $x_0/x_1 = 0.218 \pm 0.003$ and

$$\Gamma/\Gamma' = 4.86 \pm 0.4 . \tag{23}$$

This value compares well with the experimental values of 4.5 (Ref. 10) and 4.9,[16] and with the values predicted by the series Ising model (5.07) and the ϵ expansion (4.80).[14]

Relations analogous to Eq. (22) can be obtained for other parameters diverging on the compressibility pseudospinodal. For example, the correlation-length ratio satisfies the equation

$$\xi_0'/\xi_0 = (x_1/x_0 - 1)^{-\nu} . \tag{24}$$

Using the above values of β, δ, and $\nu = 0.63 \pm 0.002$ (Refs. 11 and 12), we find

$$\xi_0'/\xi_0 = 0.448 \pm 0.016 . \tag{25}$$

This compares quite well with the experimental values quoted by Sengers and Levelt Sengers[17] of 0.49 ± 0.05 and 0.45 ± 0.1, and with the prediction from the series Ising model of 0.51.[17]

Before discussing the specific-heat critical amplitude ratio, we can calculate[14]

$$R_\chi = D\Gamma B^{\delta-1} = \tilde{\Gamma}\,. \tag{26}$$

Using $B = x_0^{-\beta}$ and $D = x_1^{\gamma}/\delta\Gamma$, we find

$$R_\chi = (x_1/x_0)\gamma\,\delta^{-1}, \tag{27}$$

which gives the numerical result $R_\chi = 1.4 \pm 0.1$ for (as above) $\gamma = 1.241 \pm 0.004$ and $\delta = 4.82 \pm 0.06$. This is comparable to the experimental values of 1.4 (Ref. 10) and 1.69.[16] The series Ising model prediction is 1.75, and that of the ϵ expansion[14] is 1.6.

Before calculating the critical amplitude ratio A/A' for specific heat we note that the three ratios discussed above are all completely determined by β and δ, and by the zero of the equation of state (which is itself determined by β and δ). We will find this is also true of the ratio A/A'. Thus the universality of the amplitudes is ensured in this approach. Whether the dependence of all critical amplitude ratios on the zero of the equation of state is a general feature, or is just an artifact of the pseudospinodal approach is as yet unknown. However, this dependence is new, and its significance remains to be explored.

The calculation of the ratio A/A' is also straightforward, though more tedious. Following the standard procedure,[3,13] we write

$$A(\Delta\rho, t) = |\,\Delta\rho\,|^{\delta+1} a(x) \tag{28}$$

for the critical part of the Helmholtz free energy per unit volume in dimensionless units. Using equations (1), (28) and $\Delta\mu = [\partial A/\partial(\Delta\rho)]_T$, one finds that the scaled part of the free energy is related to $h(x)$ by

$$\beta h(x) = -xa'(x) + \beta(\delta+1)a(x)\,,$$

with solution

$$a(x) = cx^{2-\alpha} + \beta x^{2-\alpha}\int_x^\infty y^{\alpha-3}h(y)dy\,. \tag{29}$$

In this equation $\alpha = 2 - \beta(\delta+1)$ is the specific-heat exponent (which for fluids is about $\frac{1}{8}$) and c is a constant to be determined by the boundary conditions. Since $h(x)$ is given by a power series, Eq. (29) is easy to integrate. Following the standard procedure,[13] we can use Eq. (29) to obtain A and A'. The only new feature is that in order to make the integral in (29) convergent at $x = 0$, not only do we need to subtract off the first two terms in the power-series expansion of $h(x)$ (as is usually done), but the homogeneous term as well. We find

$$A = \alpha\beta(1-\alpha)(2-\alpha) \times \int_0^\infty dy\, y^{\alpha-3}\left[h(y) - h_0 - h_1 y + k\left(\frac{y}{x_1}\right)^{\beta\delta}\right] \tag{30}$$

and

$$A' = \alpha\beta(2-\alpha)(1-\alpha)x_0^{\alpha-2}\left[x_0^{2-\alpha}\int_{-x_0}^{0} |\,y\,|^{\alpha-3}\left(h(y) + k\,\frac{y}{x_1}\,|\,\frac{y}{x_1}\,|^{\beta\delta-1} - h_0 - h_1 y\right)dy - \frac{k}{\beta}\left(\frac{x_0}{x_1}\right)^{\beta\delta} - \frac{h_0}{2-\alpha} + \frac{h_1 x_0}{1-\alpha}\right]. \tag{31}$$

These expressions are completely analogous to those of Barmatz *et al.*[15] for $0 < \alpha < 1$, the only difference being our treatment of the homogeneous term. The constants are easily seen to be

$$k = D\Gamma(1-\beta\delta)\Gamma(\beta)/\Gamma(-\gamma)\,, \tag{32}$$

$$h_0 = D\,,$$

$$h_1 = -D\beta\delta\gamma/(1-\beta\delta)x_1\,, \tag{33}$$

with D given by Eq. (11). If the series (11) for $h(x)$ is substituted into Eqs. (30) and (31), then it is straightforward to calculate A/A'. Again we find that the ratio is determined by β, δ, and the ratio x_0/x_1 (which is the zero of the equation of state). We also find that A/A' varies quite rapidly as β and δ vary within their currently accepted ranges. For $\beta = 0.324$, $\delta = 4.82$ we find

$$A/A' = 0.58.$$

This lies within the range of experimentally measured values, whose minimum is 0.44 (for He^3) and maximum is 0.63 (for xenon).[15] The series Ising model predicts a value of 0.51, and the ϵ expansion[14] a value of 0.55.

If we let β vary by ± 0.006 around 0.324, and δ by 0.06 around 4.82, the variation of A/A' is extraordinarily large. For example, if we fix β at 0.324 and allow δ to vary, A/A' has a minimum value of 0.45 for the minimum δ (4.76), and has a maximum value of 0.78 for the maximum δ (4.88). This large variation is probably due to the nonanalyticity of the equation of state at $x = 0$.

Finally, having calculated A and R_χ, we can calculate the universal amplitude ratio R_c[14]. If we use

$$\tilde{A} = D^{-1}x_0^{2-\alpha}A\,,$$

then $R_c = \tilde{A}R_\chi$, and we find

$$R_c = 0.04 \pm 0.01\,.$$

This is comparable to the results from the series Ising method (0.059) and the ϵ expansion[14] (0.066).

IV. CONCLUSION

The approach presented here is based on the concept of a pseudospinodal described by Eq. (5).

Although the pseudospinodal leads to an equation of state with (expected) nonanalyticities in the one-phase region, we see that the equation is quite successful in fitting PVT data and critical amplitude ratios for universality class (3, 1) systems. As mentioned in the Introduction, we find that the pseudospinodal equation in the spherical model [universality class (3, $n \to \infty$)] is the same as Eq. (5), but with an extra (density-dependent) term on the right-hand side. It is possible that this term should also be present in Eq. (5), but that its magnitude for universality class (3, 1) systems is so small that it has not yet been discovered experimentally. A term like this could change the values of δ and T_c which give the best fits of the equation of state to PVT data, and might possibly affect the analytic properties of $h(x)$. We are currently investigating this possibility.

In conclusion, we have demonstrated that the concept of the pseudospinodal leads to a successful equation of state for universality class (3, 1) systems which is as good at fitting PVT data as other phenomenological equations, and has several advantages over them. This provides additional evidence that the concept of the pseudospinodal is a useful one, and should not be discarded solely for reasons connected with analyticity. We hope this work stimulates more experimental and theoretical interest in the pseudospinodal.

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