International Journal of Thermophysics, Vol. 6, No. 6, 1985

Toward a Liquid-State Theory with Accurate Critical-Region Behavior[1]

J. S. Høye[2] and G. Stell[3]

A scaling-theory approach that yields the scaled thermodynamics in the critical region as the solution of an ordinary differential equation is given, along with a power-series "isocline" representation of the solution yielding a polynomial fit of a high accuracy. A means of extending the approach to the whole liquid-state region through a self-consistent integral equation for the radial distribution function is discussed. An alternative integral-equation approach and a simple application of scaling-theory results that has already been found to be globally useful are also noted.

KEY WORDS: critical region; isocline; radial distribution function; scaling; thermodynamics.

1. INTRODUCTION

For many engineering applications it is desirable to have expressions for thermodynamics functions and pair distribution functions that yield quantitatively accurate results over a domain that includes the critical point as well as the liquid-state region in the triple-point neighborhood. Here we discuss some results we have obtained toward that end. We begin in Section 2 by setting forth an approach of ours that yields a differential equation describing the thermodynamics of a fluid in its critical region, based on scaling assumptions. A preliminary study of the solution of the equation yields excellent agreement with experimental results. The solution,

---

[1] Invited paper presented at the Ninth Symposium on Thermophysical Properties, June 24–27, 1985, Boulder, Colorado, U.S.A.

[2] Institutt for Teoretisk Fysikk, Universitetet i Trondheim, N 7034 Trondheim—NTH, Norway.

[3] Departments of Mechanical Engineering and Chemistry, State University of New York, Stony Brook, New York 11794, U.S.A.

moreover, lends itself to a convenient analytic "isocline" representation as a means of treating critical-region thermodynamics. In Section 3 we discuss one means of incorporating a differential-equation approach into a theory of the pair distribution function $g(\vec{r})$ and also an alternative integral-equation approach based on an asymptotically exact form of the direct correlation function $c(\vec{r})$. In Section 4 we give a simple application of thermodynamic generalized-scaling (renormalization-group) results to obtain a useful expression for the latent heat of vaporization.

2. A DIFFERENTIAL-EQUATION APPROACH TO CRITICAL-REGION THERMODYNAMICS

Intense effort over the past two decades by many workers has made it overwhelmingly clear that in the critical region, the behavior of thermodynamic functions of interest, such as the Helmholtz and Gibbs free energy, is dominated by a scaling part that can be described by a homogeneous function of two variables. Let I be this singular scaling part of $-\beta F/N$, where F is the Helmholtz free energy, and $\beta^{-1}=k_B T$, with k_B Boltzmann's constant and T the absolute temperature. We introduce reduced variables t and $\Delta\rho$ in terms of T and number density ρ: $t=(\beta_c-\beta)/\beta_c$, $\Delta\rho=(\rho-\rho_c)/\rho_c$, where the c subscript denotes critical. [In this section we are concerned with limiting proportionalities and relations that we expect to become exact only as $t\to 0$, $\Delta\rho\to 0$. Thus $(T-T_c)/T_c$ would be an equally appropriate representation of t.] We denote the isothermal compressibility (susceptibility) as χ. Then (aside from trivial factors) $\partial I/\partial t$ is just the scaling part of the internal energy per particle, while $\partial^2 I/\partial(\Delta\rho)^2$ is just the inverse compressibility, χ^{-1}. We thus expect

$$\partial I/\partial t \sim \chi^{(\alpha-1)\gamma}$$

where α and γ are the critical exponents (in usual notation) describing the specific heat and compressibility dependence on t:

$$\partial^2 I/\partial t^2 \sim t^{-\alpha}, \qquad \chi \sim t^{-\gamma}, \qquad \Delta\rho=0, \qquad t\to 0 \tag{1}$$

From these proportionalities it follows that we expect, as a limiting relation that is approached as we approach the critical point in the one-phase region,

$$\partial I/\partial t \sim [\partial^2 I/\partial(\Delta\rho)^2]^{(1-\alpha)/\gamma} \tag{2}$$

Since χ does not completely specify the location of a point on the t, $\Delta\rho$ plane, we must also consider the role played by the direction in which we approach the critical point in that plane. This direction can be conveniently characterized as an angle θ in the t, $a|\Delta\rho|^{1/\beta}$ plane, in which the coexistence curve is given (sufficiently close to the critical point) by the straight line [1]

$$t = -a|\Delta\rho|^{1/\beta}, \qquad a = \text{const}$$

[We start having standard-notation conflicts here. This β is *not* $(k_B T)^{-1}$, but no confusion should arise, since we use t throughout as a temperature variable.] Since the scaling-theory picture, strongly butressed by renormalization-group computations, is consistent with the assumption that functions such as I and its derivatives are smooth in θ, we shall assume that the proportionality factor in Eq. (2) is a smooth function of θ, nonzero for $-(\pi/4) \leqslant \theta \leqslant (\pi/2)$. We have found, in fact, that a promising approach that is consistent with scaling-theory assumptions can be based on treating the factor as a constant, which yields the partial differential equation (pde)

$$\partial I/\partial t = \text{const}[\partial^2 I/\partial(\Delta\rho)^2]^{(1-\alpha)/\gamma} \tag{3}$$

One boundary condition (bc) for Eq. (3) immediately follows from the scaling relation for pressure along the critical isotherm,

$$\partial I/\partial(\Delta\rho) \sim |\Delta\rho|^{\delta}\, sgn\, \Delta\rho \qquad \text{at} \quad t = 0 \tag{4}$$

Another bc comes from Eq. (1). In terms of I itself, Eqs. (1) and (4) yield

$$\begin{aligned} I &= \text{const}\,|\Delta\rho|^{\delta+1} \qquad \text{for} \quad t = 0 \\ I &= \text{const}\, t^{2-\alpha} + \text{const}(\Delta\rho)^2 t^{\gamma} \qquad \text{as} \quad \Delta\rho \to 0, \qquad r > 0 \end{aligned} \tag{5}$$

Our next step is most conveniently taken in terms of the chemical potential μ. Letting $H(\rho, T) = \mu(\rho, T) - \mu(\rho_c, T)$ and $M = |\Delta\rho|$, we note that in the critical region

$$H \approx \text{const}\; \partial I/\partial M \tag{6}$$

Invoking the homogeneity of H in M and $|t|^{\beta}$ we can write [2]

$$H = |t|^{\beta\delta}\, y(x), \qquad x = M/|t|^{\beta} \tag{7}$$

Then

$$\partial H/\partial M = |t|^{\beta(\delta-1)}\, y'(x), \qquad \partial^2 H/\partial M^2 = |t|^{\beta(\delta-2)}\, y''(x) \tag{8}$$

while

$$\partial H/\partial t = (\beta|t|^{\beta\delta}/t)(\delta y - xy') \tag{9}$$

If we are thinking in magnetic language, H can be taken to be the magnetic field strength and M the magnitude of magnetization per spin. Then χ, the magnetic susceptibility, is $(\partial M/\partial H)_T$. [Here it is most convenient to let $t \equiv (T-T_c)/T$.] Upon differentiation with respect to M, Eq. (3) can then be reexpressed through the use of Eqs. (6)–(9) as the ordinary differential equation (ode)

$$y'' = \pm c[\delta y - xy'](y')^{(\gamma+\alpha-1)/\gamma} \tag{10}$$

where $c > 0$. The + refers to supercritical, $t > 0$, and the − refers to $t < 0$. Our bc can be reexpressed as

$$\begin{aligned} y(x \to \infty) &\to \text{const}\, x^{\delta} \qquad (t \lesseqgtr 0) \\ y(x \to 0) &\to \text{const}\, x \qquad (t > 0) \end{aligned} \tag{11}$$

We now have an ode to solve with boundary conditions that prove to yield a unique $y(x)$ and, hence, through Eq. (7), a unique $H(M, t)$. This function $y(x)$ and its ode are awkward to handle as they stand, however. A transformation to logarithmic variables U and V helps [2], where $x = 10^U = e^{\sigma U}$, $y = 10^V = e^{\sigma U}$. Letting $W = dV/dU = V_U$ one gets

$$W_U = \sigma\{W - W^2 \pm cx^2(\delta - W)[Wy/x]^{(\gamma+\alpha-1)/\gamma}\} \tag{12}$$

with

$$\begin{aligned} V(U \to \infty) &\to \delta U + \text{const}_1 \qquad (t \lesseqgtr 0) \\ V(U \to -\infty) &\to U + \text{const}_2 \qquad (t > 0) \end{aligned} \tag{13a}$$

The constant c in Eq. (12) and the constants in Eq. (13a) depend upon the form of the interaction potential and are hence not universal, but it turns out that changing them will result only in a translation in the U, V plane of the solution curve $V = V(U)$. In a trial computation with $\delta = 5$, $\beta = 1/3$, and $\gamma = 4/3$, the values $\text{const}_1 = 1/2$ and $\text{const}_2 = 1/2$ and $\text{const}_2 = 3/2$ gave us a good asymptotic match to simple-fluid data. Upon solving Eq. (12) to obtain $V(U)$, the value $c \approx 0.37$ was then found to yield an excellent overall fit. In summary our trial values were

$$\begin{aligned} &\delta = 5, \qquad \beta = \frac{1}{3}, \qquad \gamma = \frac{4}{3} \\ &\text{const}_1 = \frac{1}{2}, \qquad \text{const}_2 = \frac{3}{2}, \qquad c = 0.37 \end{aligned} \tag{13b}$$

The result is shown in Fig. 1, superimposed against many data exhibited in Fig. 3 of Ref. 2, to which we refer for further details of the data analysis.

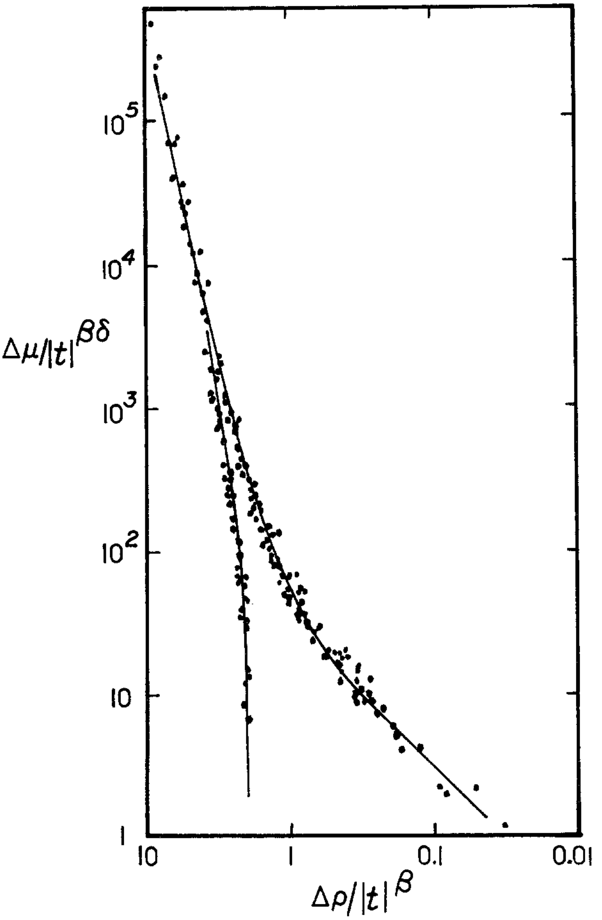

Fig. 1. The solid curve is our scaled equation of state in the critical region based on Eqs. (12)–(14). The points represent experimental data for various fluids from a figure in Ref. 2, where $\delta = 5$ and $\phi = 0.35$ were used in plotting the data.

As already noted many years ago by workers investigating scaled equations of state [3], the use of the U, V plane leaves something to be desired in displaying thermodynamic homogeneity, involving as it does separate branches for $t < 0$ and $t > 0$. A more convenient and powerful general representation for our purposes is the "isocline" representation, systematically discussed in great detail by Migdal [4]. He considers the function $\phi(m)$, where

$$H\chi^{(\beta+\gamma)/\gamma} = \phi(m), \qquad \chi = (\partial M/\partial T)_T \tag{14}$$

$$m = M\chi^{\beta/\gamma} \tag{15}$$

As he notes, (i) m and $\phi(m)$ stay finite $\leqslant 0(1)$ over the whole critical region, (ii) $\phi(m)$ has no singularities in the critical region and can be well represented by the series

$$\phi(m) = m + \phi_3 m^3 + \phi_5 m^5 + \cdots \tag{16}$$

and (iii) $\phi'(0) = 1$. If m_0 is the value of m on the critical isotherm $\phi(m_0) = [\beta/(\beta+\gamma)]m_0$ and $\phi'(m_0) = (\beta - 1)/(\beta + \gamma + 1)$.

Migdal focuses primarily on the two-term approximant to Eq. (16) (which is essentially Schofield's [5] "linear model") and the three-term approximant, which the conditions of iii will fully determine for a given m_0. For example, with $\beta = 1/3$ and $\gamma = 4/3$, one has

$$\phi(m) = \phi_3(m) = m(1 - z^2 + z^4/5) \tag{17}$$

with $z = m/m_0$. In the case of the four-term approximant we found that the satisfaction of iii leaves one remaining adjustable parameter. For example, with $\beta = 1/3$ and $\gamma = 4/3$,

$$\phi_4(m) = \phi_3(m) + Amz^2(1 - 2z^2 + z^4) \tag{18}$$

where A is the parameter to be adjusted.

The transformation necessary to go from the U, V to the $\phi(m)$ representation is obtained from the equations

$$\begin{aligned} &y'\chi = |t|^{-\beta(\delta-1)} \\ &m/x = (y')^{-\beta/\gamma}, \qquad \phi(m)/y = (y')^{-(\beta+\gamma)/\gamma} \\ &\phi(m) = m/W, \qquad y' = Wy/x \end{aligned} \tag{19}$$

From Eq. (12) one obtains V and W as functions of U. The isocline can then be computed directly from Eq. (19) by obtaining the corresponding $m = m(U)$ and $\phi(m) = \phi[m(U)]$. We note that our Eqs. (10) and (12) with their boundary conditions yield a $\phi(m)$ that satisfies condition iii. We show in Fig. 2 the solution to our equation in terms of $\phi(m)$ in the test case $\beta = 1/3$, $\gamma = 4/3$, and $c = 0.37$. The four-term approximant, with $A = -0.35$, is indistinguishable on this scale from the full $\phi(m)$. The three-term approximant is indicated by the dashed line in Fig. 2.

3. A DIFFERENTIAL-EQUATION APPROACH BASED ON THE PAIR CORRELATION FUNCTION

We now consider a differential-equation approach associated with the pair correlation function $g(\vec{r}) - 1 = h(\vec{r})$, using a self-consistent Ornstein-

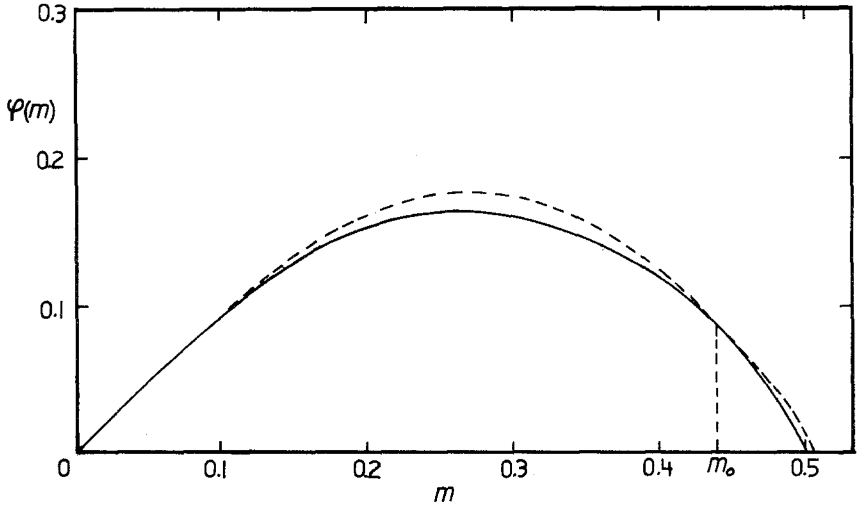

Fig. 2. The full curve is the isocline computed from Eqs. (12)–(14). The dashed line is its three-term approximant. The four-term approximant is indistinguishable from the full isocline on this scale.

Zernike approximation (SCOZA) we have been investigating [6]. It is based on the Ornstein-Zernike integral equation

$$h(\vec{r}_{12}) = c(\vec{r}_{12}) + \rho \int h(\vec{r}_{13})\, c(\vec{r}_{32})\, d\vec{r}_3 \tag{20a}$$

There is a core condition, with $r_{12} = |\vec{r}_{12}|$,

$$h(\vec{r}_{12}) = -1, \qquad r_{12} \leqslant \sigma \tag{20b}$$

In the simplest version of our SCOZA applied to the lattice gas, where $\sigma = 0$, we let

$$c(\vec{r}_{12}) = -A\phi(\vec{r}_{12})/k_B T, \qquad r_{12} > \sigma \tag{21}$$

with $\phi(\vec{r}_{12})$ the pair potential and A determined by requiring self-consistency between the internal energy and the compressibility (susceptibility) dependence on $h(\vec{r}_{12})$. In Ising-model language, let $\lambda =$ the partition function and $\mathscr{H} = \beta H$, with H the magnetic field and M the magnetization per spin. Here $\beta = a/kT$, with $a = \sum_i \phi(\vec{r}_{0i})/8$, a measure of interaction strength. Then letting

$$S(\beta, M) = \ln \lambda - M \tag{22}$$

we can make contact with our previous discussion by noting

$$\Delta S = S - S_c \sim I, \qquad t = \beta - \beta_c$$

Our self-consistent approximation yields a pde for S that will depend on details of the potential. Neglecting all features of a potential but its range (through its zeroth and second spatial moments) permits a simplified but representative ode of the form

$$S_\beta = M^2 + (1 + M^2)\gamma_R^3\{1 - [(M^2 - 1)S_{MM}]^{1/2}\} \tag{23a}$$

where γ_R is a measure of the inverse range of $\phi(\vec{r})$. The full boundary conditions are given both at $\beta = 0$ and at $M = \pm 1$ by

$$S = S_0(M) + \beta M^2, \qquad S_0 = \text{noninteracting spin result} \tag{23b}$$

As we approach critical we find that Eq. (23a) approaches (after a suitable renormalization of S, β, and M to absorb some trivial factors)

$$S_\beta = \frac{1}{2} M^2 - (-S_{MM})^{1/2} \tag{24}$$

We see that γ_R has disappeared in Eq. (24) in accordance with the hypothesis of universality by which such features will not affect critical behavior. Neglecting for the moment the bc given by Eq. (23b), to which we return below, we find that Eq. (24) has a scaling solution. To get the ode that it satisfies we can differentiate Eq. (24) with respect to M. We obtain from $S_{MM} = -\partial\mathscr{H}/\partial\mathscr{M}$

$$\mathscr{H}_\beta = -M + \mathscr{H}_{MM}/2(\mathscr{H}_M)^{1/12} \tag{25}$$

Introducing the variables $y = |\mathscr{H}|/|t|^{5/4}$ and $x = |M|(|t|^{-1/4})$, the equation for $y(x)$ that we obtain from Eq. (25) is

$$y'' = \pm\frac{1}{4}(5y - y'x)(y')^{1/2} + x(y')^{1/2} \tag{26}$$

This equation has the critical exponents

$$\delta = 5, \qquad \beta = \frac{1}{4}, \qquad \gamma = 1, \qquad \alpha = \frac{1}{2} \tag{27}$$

These are tricritical exponents. Tricriticality is associated with the confluence of two critical points and presumably arises here as a result of the self-consistency condition of our approximation forcing the merger of the critical point determined through the internal energy and the critical point determined through the susceptibility.

As we go further and further from the critical point, a separate analysis shows that the S of our SCOZA behaves more and more like the S obtained through the susceptibility relation in the mean spherical approximation (MSA). The MSA critical exponents obtained through this relation are

$$\delta = 5, \qquad \beta = \frac{1}{2}, \qquad \gamma = 2, \qquad \alpha = -1 \tag{28}$$

One might expect, therefore, as one takes our self-consistent approximation back to the critical point, that the effective exponents will reflect a crossover behavior from Eq. (28) to Eq. (27). Numerically this is exactly what we find, with effective exponents looking remarkably like

$$\delta \approx 5, \qquad \beta \approx \frac{1}{3}, \qquad \gamma \approx \frac{4}{3}, \qquad \alpha \gtrsim 0 \tag{29}$$

over a quite wide range of M and t. These effective exponents yield an approximation with very realistic critical behavior. What is *not* clear from our analysis is whether the true boundary conditions given by Eq. (23b) of the problem will permit the SCOZA actually to attain the scaling form given by Eq. (26) as a critical-point limit. Further progress in this direction is highly desirable; our goal is to put into analytic terms the results of our numerical analysis of the approximation in the crossover region.

The fact that self-consistency can perturb the MSA result [which one would get if $A = 1$ in Eq. (21)] in such a useful direction already seems intriguing and potentially very useful. This is especially true in light of the great improvement over the MSA results that the approximation was found to yield in an earlier study [7] of the nearest-neighbor lattice gas (or Ising model) away from the critical point. It gives the first two terms in the ρ expansion for $c(\vec{r})$ and, hence, the first three virial coefficients exactly. By the lattice-gas symmetry in $\rho(1-\rho)$ it is thus also highly accurate in the dense-fluid region of the lattice-gas T, ρ plane.

The results of Ref. 8 suggest an alternative way of going beyond the MSA based on using, instead of Eq. (21),

$$c(\vec{r}_{12}) = -\beta\phi(\vec{r}_{12}) + \mathscr{C}(r_{12}, \kappa), \qquad r_{12} > \sigma \tag{30}$$

where $\mathscr{C}(r, \kappa)$ is a homogeneous function in r^{-1} and κ of degree $(2-\eta)+d$, $\kappa =$ inverse correction length, and $d =$ the dimensionality. This form will incorporate many of the exact asymptotic features of $h(\vec{r})$ and $c(\vec{r})$ discussed in Refs. 8 and 9 if an appropriate homogeneous approximant to $\mathscr{C}$ is constructed and κ is then obtained self-consistently.

4. A SIMPLE APPLICATION OF GENERALIZED SCALING ARGUMENTS

In certain cases, one is interested in a function of a single thermodynamic variable, as in the case of the latent heat of vaporization L as a function of temperature. Here, for example, the singular part of L is expected to be of the form [10]

$$L_S = a_1 t^{\beta} + a_2 t^{\beta+\Delta} + a_3 t^{1-\alpha+\beta} + \cdots \tag{31}$$

where Δ is Wegner's first "gap" exponent [11] and $t = (T_c - T)/T_c$. When the exhibited terms in Eq. (31) were added to a regular term of the form

$$L_R = b_1 t + b_2 t^2 + b_3 t^3 \tag{32}$$

Torquato and Stell [10] found extremely good agreement with water data from the triple point to the critical point with appropriately fitted values of the (nonuniversal) constants a_i and b_i. Torquato and Smith [12] subsequently found good corresponding-state agreement for a wide variety of fluids using the same functional form to fit L/L_t vs $\tau = (T_c - T)/T_c - T_t$, where the subscript t refers to the triple point, while Sivaraman et al. [13] found a good generalized corresponding-state fit for L/RT_c using Eqs. (31) and (32) and an acentric factor.

ACKNOWLEDGMENTS

One of the authors (G.S.) gratefully acknowledges the support of the Office of Basic Energy Sciences, U.S. Department of Energy, and a fellowship from the John Simon Guggenheim Foundation.

REFERENCES

1. B. Widom, *J. Chem. Phys.* **43**:3898 (1965).
2. M. S. Green, M. Vicentini-Missoni, and J. M. H. Levelt Sengers, *Phys. Rev. Lett.* **18**:1113 (1967).
3. See, e.g., R. B. Griffiths, *Phys. Rev.* **158**:176 (1967); M. Vicentini-Missoni, J. M. H. Levelt Sengers, and M. S. Green, *Phys. Rev. Lett.* **22**:389 (1969).
4. A. A. Migdal, *Zh. Eksp. Theor. Fiz.* **62**:1559 (1972); *JETP* **35**:816 (1972).
5. P. Schofield, *Phys. Rev. Lett.* **22**:606 (1969).

6. J. S. Høye and G. Stell, *Mol. Phys.* **52**:1071 (1984).
7. Unpublished (1965) work done in preparing G. Stell, J. L. Lebowitz, S. Baer, and W. Theumann, *J. Math. Phys.* **7**:1532 (1966).
8. G. Stell, *Phys. Rev. B* **1**:2265 (1970).
9. R. Hocken and G. Stell, *Phys. Rev. A* **8**:887 (1973), Section II.
10. S. Torquato and G. Stell, *J. Chem. Phys.* **85**:3029 (1981); *I&EC Fund.* **21**:202 (1982).
11. F. J. Wegner, *Phys. Rev. B* **5**:4529 (1972).
12. S. Torquato and P. Smith, *J. Heat Transfer* **106**:253 (1984).
13. A. Sivaraman, J. Magee, and Riki Kobayashi, *Fluid Phase Eq.* **16**:1 (1984).