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# Nucleation near the spinodal: Limitations of mean field density functional theory

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We investigate the diverging size of the critical nucleus near the spinodal using the gradient theory (GT) of van der Waals and Cahn and Hilliard and mean field density functional theory (MFDFT). As is well known, GT predicts that at the spinodal the free energy barrier to nucleation vanishes while the radius of the critical fluctuation diverges. We show numerically that the scaling behavior found by Cahn and Hilliard for these quantities holds quantitatively for both GT and MFDFT. We also show that the excess number of molecules  $\Delta g$  satisfies Cahn-Hilliard scaling near the spinodal and is consistent with the nucleation theorem. From the latter result, it is clear that the divergence of  $\Delta g$  is due to the divergence of the mean field isothermal compressibility of the fluid at the spinodal. Finally, we develop a Ginzburg criterion for the validity of the mean field scaling relations. For real fluids with short-range attractive interactions, the near-spinodal scaling behavior occurs in a fluctuation dominated regime for which the mean field theory is invalid. Based on the nucleation theorem and on Wang's treatment of fluctuations near the spinodal in polymer blends, we infer a finite size for the critical nucleus at the pseudospinodal identified by Wang. © 2004 American Institute of Physics. [DOI: 10.1063/1.1801273]

## I. INTRODUCTION

Because of its simplicity and ease of use, classical nucleation theory<sup>1-3</sup> is frequently used to explain and interpret a wide range of nucleation phenomena. Despite its shortcomings, the classical approach has been quite successful in predicting critical supersaturations for many vapors. It is far less successful in predicting absolute nucleation rates and their variation with temperature. In recent years, efforts to improve this situation have led to new theoretical approaches that attempt in different ways to treat nonclassical effects due to the small size and inhomogeneous nature of the nucleus.<sup>4-29</sup> Among these approaches, mean field density functional theory (MFDFT) (Refs. 4 and 5) is a powerful technique that has been extensively used to explore various systems. Although less accurate, an even more approximate form of density functional theory, known as gradient theory (GT),<sup>30-36</sup> is easier to apply because of its semiempirical character and is also of interest.

Several recent papers have been concerned, at least partly, with nucleation near the mean field spinodal in vapor-liquid systems.<sup>22-29</sup> In our earlier work on this topic,<sup>26</sup> we found close numerical agreement between GT and MFDFT near the spinodal. Here, we extend that study by examining several issues concerning nucleation near the spinodal that have not received much attention in the vapor-liquid nucleation community. It is well-known that the classical theory predicts a finite nucleation barrier and a small critical size at the spinodal, while the nonclassical MFDFT and GT predict that the barrier vanishes, as Gibbs<sup>37</sup> had anticipated. The GT also predicts that the spatial size of the critical fluctuation diverges at the spinodal.<sup>32,38</sup> Similar behavior is expected for DFT since, as shown, e.g., by Evans,<sup>39</sup> it reduces to GT

whenever spatial density gradients are small, as near the spinodal. Here, we investigate this problem explicitly using MFDFT for both droplet and bubble nucleation in a hard sphere Yukawa fluid.<sup>4,26</sup> We characterize the size of the critical fluctuation by the excess number of molecules it contains, and examine its behavior using a scaling approach first suggested by Cahn and Hilliard.<sup>32</sup> We show that a size divergence formally identical to that of GT is found. We also show that this behavior is consistent with the nucleation theorem.<sup>40-42</sup> Finally, we develop a Ginzburg criterion<sup>43,44</sup> to establish the limits of validity of this mean field approach near the spinodal. For real fluids with short range interactions, this Ginzburg criterion is violated near the spinodal. Thus, MFDFT is not self-consistent for simple fluids near the spinodal. Since its predictions there are unreliable, earlier studies that rely heavily on MFDFT or GT near the spinodal may require reassessment.

Following summaries of the DFT and GT approaches in Sec. II, we present the scaling analysis, numerical results, connection to the nucleation theorem, and the Ginzburg criterion in Sec. III. We conclude the paper by drawing some connections to earlier work and discussing some practical implications of this work.

## II. SUMMARY OF BASIC FORMALISM

### A. Density functional theory

Consider a system with a spherical nucleus centered at the origin. Far from the interfacial region the bulk fluid density is  $\rho_B$  and the pressure is  $p_B$ . The distribution of matter within the nucleus and through the interfacial zone is described by the density profile  $\rho(r)$ , where  $r$  is the radial distance from the origin. Following the perturbative ap-

proach of Oxtoby and Evans,<sup>4</sup> the grand potential for the nonuniform system is written as the functional

$$\Omega[\rho(\mathbf{r})] = \int \{f[\rho(\mathbf{r})] - \mu_B \rho(\mathbf{r})\} d\mathbf{r}. \quad (1)$$

Here,  $f$  is the Helmholtz free energy density of the inhomogeneous fluid,

$$f[\rho(\mathbf{r})] = f_h[\rho(\mathbf{r})] + \frac{1}{2} \rho(\mathbf{r}) \int \rho(\mathbf{r}') w_2(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}', \quad (2)$$

$f_h(\rho)$  is the Helmholtz free energy density of a uniform hard sphere fluid of density  $\rho$ , and  $\mu_B$  is the chemical potential of the uniform bulk phase. Equation (2) has the classic form of the van der Waals model,<sup>45,46</sup> reflecting the use of a local density approximation for the effects of the short-range repulsive forces and a mean field treatment of the weak, long-range attractive forces.<sup>4,5,47</sup> For the attractive pair potential  $w_2$  we use the Yukawa function

$$w_2(r) = -\alpha \lambda^2 \exp(-\lambda r) / (4\pi r), \quad (3)$$

where the parameter  $\alpha$  governs the strength of the interaction and  $\lambda$  is the inverse range parameter. Starting with Sullivan's seminal treatment of adsorption,<sup>47</sup> the model defined by Eqs. (2) [or (4)] and (3) has been used for over two decades to describe successfully many interfacial phenomena including wetting,<sup>48-50</sup> capillary condensation,<sup>51</sup> liquid-liquid<sup>52</sup> and liquid-vapor<sup>52,53</sup> interfacial structure, and nucleation<sup>4,8,9,14,26</sup> of droplets and bubbles.

After functional differentiation of Eq. (1), the density profile that makes  $\Omega$  an extremum is the solution to the integral Euler-Lagrange equation,

$$\mu_h[\rho(\mathbf{r})] = \mu_B - \int \rho(\mathbf{r}') w_2(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}', \quad (4)$$

where  $\mu_h(\rho)$  is the chemical potential of the hard sphere fluid at density  $\rho$ . Alternatively, since the Yukawa function is essentially the Green's function of the Helmholtz equation, we can act with  $\nabla^2$  on Eq. (4) to obtain the second-order differential equation<sup>8,14,26,47</sup>

$$\nabla^2 \mu_h = \lambda^2 (\mu_h - \mu_B - \alpha \rho), \quad (5)$$

whose solution also yields  $\rho(r)$ , but is much easier to solve numerically than Eq. (4).

The reversible work of droplet formation  $W$  is defined as the difference of the grand potentials for the nonuniform system and the initial uniform system  $\Omega(\rho_B)$  with density  $\rho_B$  and pressure  $p_B$ ,

$$W = \Delta\Omega = \Omega[\rho(\mathbf{r})] - \Omega(\rho_B), \quad (6)$$

where<sup>4</sup> for a system of uniform density and volume  $V$

$$-\Omega(\rho)/V = p(\rho) = p_h(\rho) - \alpha \rho^2/2, \quad (7)$$

and  $p_h(\rho)$  is the pressure of a hard sphere system. Using Eqs. (1) and (7), Eq. (6) becomes

$$W = \int \{f[\rho(\mathbf{r})] - f_0(\rho_B) - (\rho(\mathbf{r}) - \rho_B) \mu_B\} d\mathbf{r}, \quad (8)$$

where the Helmholtz free energy density of the uniform fluid,  $f_0$ , is expressed either as

$$f_0(\rho) = \rho \mu_0 - p \quad (9)$$

or

$$f_0(\rho) = f_h(\rho) - \alpha \rho^2/2, \quad (10)$$

and  $\mu_0(\rho) \equiv \partial f_0 / \partial \rho$  is the chemical potential of the homogeneous fluid at density  $\rho$ ,

$$\mu_0(\rho) \equiv \mu_h(\rho) - \alpha \rho. \quad (11)$$

Note that  $\mu_B = \mu_0(\rho_B)$ . Explicit expressions for  $f_h$ ,  $p_h$ , and  $\mu_h$  as functions of  $\rho$  are available elsewhere.<sup>5,8,26,54</sup>

## B. Gradient theory

In gradient theory, instead of Eq. (2), the Helmholtz free energy density of the inhomogeneous fluid is now given as the weakly nonlocal form<sup>30-35</sup>

$$f = f_0(\rho) + \frac{c}{2} (\nabla \rho)^2. \quad (12)$$

The influence parameter  $c$  is a weak function of density that is assumed to be a constant at a given temperature.<sup>33</sup> Under this assumption,  $f$  becomes purely local and  $c$  can be calculated from the known surface tension of the planar interface of the two-phase equilibrium system.<sup>55</sup> The formal expression, Eq. (8), for  $W$  is, of course, still applicable. The equilibrium density profile  $\rho$  corresponding to an extremum of the reversible work functional is determined by the Euler-Lagrange equation,<sup>32,33</sup>

$$\mu_B = \mu_0(\rho) - c \nabla^2 \rho. \quad (13)$$

The mean field equation of state for the hard sphere-Yukawa fluid is given by Eq. (7), and the corresponding Helmholtz free energy density  $f_0(\rho)$  and chemical potential  $\mu_0(\rho)$  are given by Eqs. (10) and (11), respectively.

## C. Numerical analysis

As described in greater detail elsewhere,<sup>26</sup> we solved Eqs. (5) and (13) using an iterative central finite difference scheme. For calculations at bulk densities very close to the spinodal value, we took care to enlarge the spatial domain over which the equations are solved and to increase the number of grid points in the differencing scheme. Close to the spinodal, the density profile decays very slowly, and if the outer boundary conditions are not imposed at sufficiently large  $r$ , the calculated density profile decays too quickly. Ultimately these finite domain effects limit how closely the bulk density can approach the spinodal value before the numerical results deviate from the expected scaling behavior discussed below. Due to the nonlinearity of the differential equations, an iterative solution procedure beginning with a guessed trial solution was used. Convergence was usually rapid (<10 iterations), and continued iteration for hundreds of cycles showed that the solutions were stable, unlike those found by solving the integral equation.<sup>4</sup>

### III. CAHN-HILLIARD SCALING ANALYSIS

#### A. Gradient theory

Cahn and Hilliard<sup>32</sup> developed their theory for nucleation in an incompressible binary fluid, but the theory for a one-component compressible fluid is formally identical to it. In their analysis of the properties of a spherical critical nucleus, Cahn and Hilliard<sup>32</sup> found it useful to rewrite Eq. (8) for  $W$  as

$$W = \int \left\{ \Delta f' - \frac{1}{2}(\rho - \rho_B) \frac{\partial \Delta f'}{\partial \rho} \right\} d\mathbf{r}, \quad (14)$$

by assuming that  $c$  was independent of  $\rho$  and defining  $\Delta f'$  as

$$\Delta f' = f_0(\rho) - f_0(\rho_B) - (\rho - \rho_B)\mu_B. \quad (15)$$

Near the spinodal density  $\rho_S$ ,  $\Delta f'$  may be accurately approximated by a third-order Taylor series expansion,<sup>32</sup>

$$\Delta f' = \zeta [3(\rho_S - \rho_B)(\rho - \rho_B)^2 - (\rho - \rho_B)^3], \quad (16)$$

where  $6\zeta = -(\partial^3 \Delta f' / \partial \rho^3)_{\rho = \rho_S}$ . Using the dimensionless variables  $Y = (\rho - \rho_B) / (\rho_S - \rho_B)$  and  $R = r [2\zeta(\rho_S - \rho_B) / c]^{1/2}$ , and Eqs. (14) and (16), Cahn and Hilliard<sup>32</sup> showed that  $W$  scales as the 3/2 power of the density difference,

$$W = \pi I_3 (2\zeta)^{-1/2} c^{3/2} (\rho_S - \rho_B)^{3/2}. \quad (17)$$

Here,  $I_3$  is the value of the dimensionless integral  $I_p$  for  $p = 3$ ,

$$I_p = \int_0^\infty Y^p R^2 dR. \quad (18)$$

The function  $Y$  is the solution to a scaled form<sup>32</sup> for the Euler-Lagrange equation, Eq. (13), for a spherically symmetric drop, asymptotically valid near the spinodal, which we write compactly as

$$d^2(RY)/dR^2 = 3R(2Y - Y^2)/2. \quad (19)$$

As Cahn and Hilliard noted, for  $\rho_B$  sufficiently close to  $\rho_S$ , the dimensionless density profile  $Y$  will be independent of  $\rho_B$ . They also characterized the size of the critical nucleus in terms of  $r_{1/2}$ , defined by the requirement that  $\rho(r_{1/2}) = (\rho_0 + \rho_B)/2$ , where  $\rho_0 \equiv \rho(0)$  is the density at the center of the nucleus. It follows from the definition of  $R$  that

$$r_{1/2} = R_{1/2} (c/2\zeta)^{1/2} (\rho_S - \rho_B)^{-1/2}, \quad (20)$$

where  $R_{1/2}$  is a constant. As the bulk density approaches the spinodal value,  $r_{1/2}$  diverges.<sup>32</sup>

The size of the critical nucleus can also be viewed in terms of the excess number of molecules in the nucleus,  $\Delta g$ , defined for spherical nuclei as

$$\Delta g = 4\pi \int_0^\infty [\rho(r) - \rho_B] r^2 dr. \quad (21)$$

Using the dimensionless variables  $Y$  and  $R$ , it follows from Eq. (21) that  $\Delta g$  diverges with the density difference in the same manner as  $r_{1/2}$ ,

$$\Delta g = 4\pi I_1 (c/2\zeta)^{3/2} (\rho_S - \rho_B)^{-1/2}, \quad (22)$$

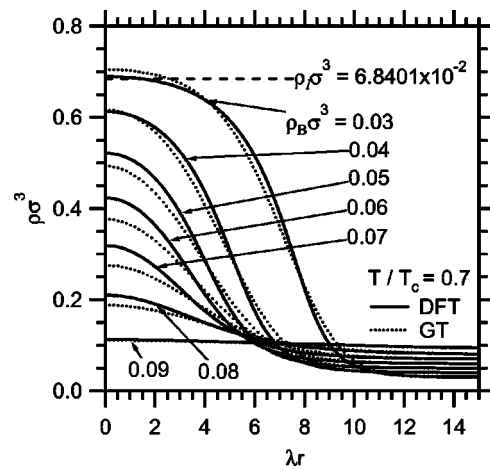


FIG. 1. Density profiles of hard sphere Yukawa droplets calculated using gradient theory (GT) and density functional theory (DFT) for various  $\rho_B$  plotted using regular variables. Also marked is the value of the bulk equilibrium density  $\rho_l$ .

where  $I_1$  is another dimensionless integral defined by Eq. (18).

#### B. Density functional theory

As shown, e.g., by Evans in Sec. VI of his comprehensive review,<sup>39</sup> DFT rigorously reduces to GT when the density gradients are small everywhere. Thus, it follows that as the spinodal is approached DFT will display the same Cahn-Hilliard scaling behavior as GT. Moreover, the two theories can be made to agree quantitatively by evaluating the influence parameter  $c$  using Eq. (73) of Evans<sup>39</sup> or Eq. (11.1.24) of Davis.<sup>55</sup> It follows that  $c = \alpha/\lambda^2$ . An explicit demonstration of these points, based on the asymptotic behavior of Eq. (5), is given in the Appendix.

#### C. Numerical results

To confirm the accuracy of our numerical solutions and to explore the range of validity of these scaling laws, we calculated density profiles by numerically solving Eqs. (5) and (13) at several values of  $\rho_B$ , both near and far from the

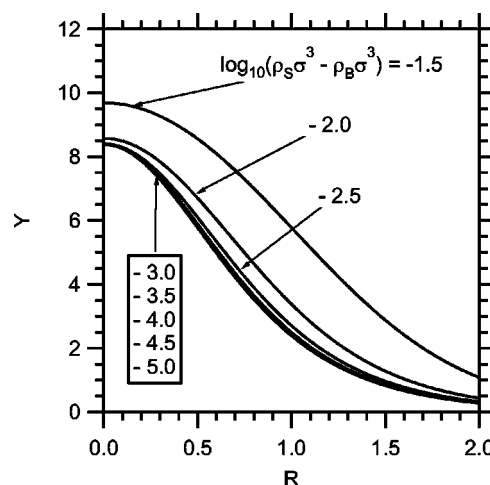


FIG. 2. Density profiles of hard sphere Yukawa droplets calculated using gradient theory for various  $\rho_B$  plotted using scaled variables.

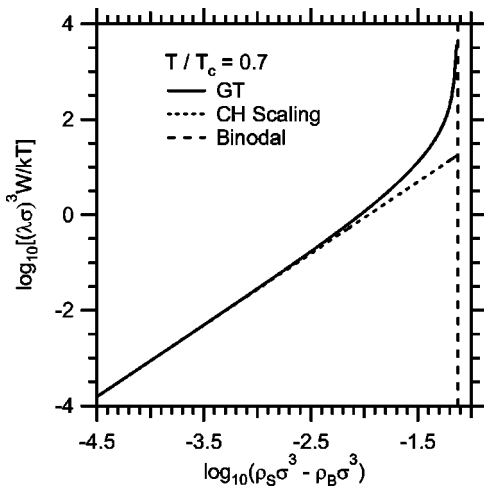


FIG. 3. Cahn-Hilliard scaling behavior of the reversible work found using gradient theory.

spinodal density,  $\tilde{\rho}_S = \sigma^3 \rho_S = 0.09248$  at  $T/T_C = 0.7$ . (The hard sphere diameter is  $\sigma$ ;  $T_C$  is the critical temperature.) These are shown in Fig. 1 using regular variables. The gradient theory profiles are shown again in Fig. 2 using the scaled variables  $Y$  and  $R$ . In Fig. 1, at  $\rho = \sigma^3 \rho_S = 0.09$ , which is very close to  $\tilde{\rho}_S$ , the flatness of the profile is apparent. In Fig. 2, the lower five profiles are indistinguishable from the numerical solution to Eq. (19). With our improved numerical technique, we can cite more accurate values for several quantities reported by Cahn and Hilliard.<sup>32</sup> Rounded to three figures, these are  $Y(0) = 8.38$ ,  $R_{1/2} = 0.704$ , and  $I_3 = 32.1$ . The respective values of Cahn and Hilliard, 8.1, 0.73, and 31.4, obtained on an analog computer, are in fair agreement with our results. As an independent check of the accuracy of our solution, we numerically integrated Eq. (19) using a fourth-order Runge-Kutta method starting at  $R = 0$ . The behavior of  $Y$  at large  $R$  is actually quite sensitive to the value of  $Y(0)$ , and in this way we verified the cited value.

The gradient theory results for  $W$  and  $\Delta g$ , calculated with the numerical density profiles, are shown in Figs. 3

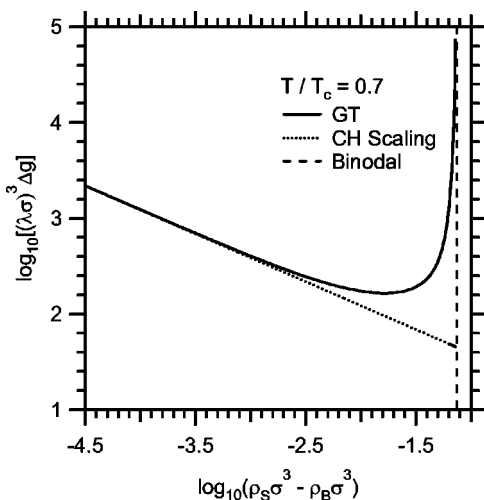


FIG. 4. Cahn-Hilliard scaling behavior of the excess number  $\Delta g$  found using gradient theory.

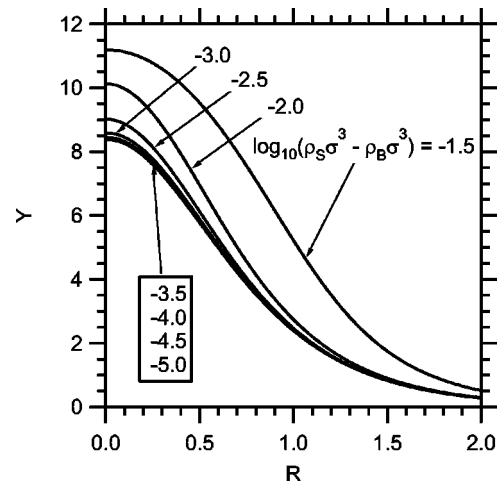


FIG. 5. Density profiles of hard sphere Yukawa fluid droplets calculated using density functional theory for various  $\rho_B$  plotted using scaled variables.

and 4. The bulk density difference  $\Delta\tilde{\rho} (\equiv \tilde{\rho}_S - \tilde{\rho}_B)$ , at which scaling behavior begins to hold varies slightly with the property, starting for  $W$  at  $\log_{10} \Delta\tilde{\rho} \approx -2.5$  and for  $\Delta g$  at  $\log_{10} \Delta\tilde{\rho} \approx -3$ .

Quantitative verification of this scaling behavior for density functional theory is demonstrated in Figs. 5–9. Several droplet density profiles, shown using regular variables in Fig. 1, are replotted using scaled variables  $Y$  and  $R$  in Fig. 5. The density profiles clearly obey the Cahn-Hilliard scaling behavior as the spinodal is approached. The scaling behavior of  $W$  and  $\Delta g$  is illustrated in Figs. 6 and 7, respectively, for droplets. The scaling region begins at larger values of  $\Delta\tilde{\rho}$  than for GT, starting for  $W$  at  $\log_{10} \Delta\tilde{\rho} \approx -2$  and for  $\Delta g$  at  $\log_{10} \Delta\tilde{\rho} \approx -2.2$ . Similar results for bubbles are shown in Figs. 8 and 9. Note that the scaling region for bubbles begins at larger values of  $|\Delta\tilde{\rho}|$  than for droplets, starting for  $W$  at  $\log_{10} |\Delta\tilde{\rho}| \approx -1.3$  and for  $\Delta g$  at  $\log_{10} |\Delta\tilde{\rho}| \approx -2$ , although the numerical results slightly undershoot the scaling behavior beginning at  $\log_{10} |\Delta\tilde{\rho}| \approx -1.4$ . Other asymmetries between droplet and bubble behavior have been noted in earlier

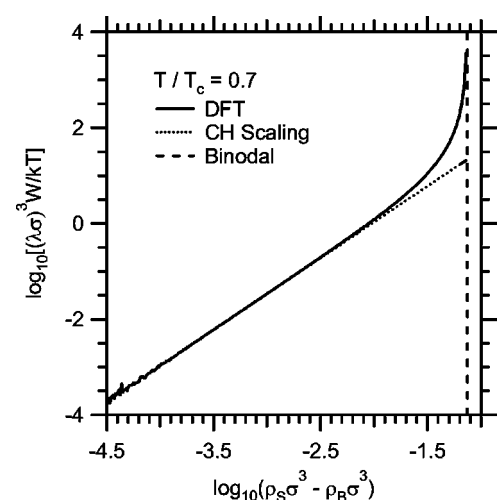


FIG. 6. Cahn-Hilliard scaling behavior of the reversible work for hard sphere Yukawa droplets found using density functional theory.

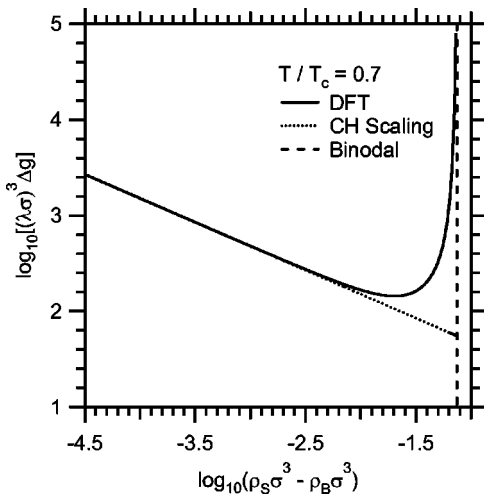


FIG. 7. Cahn-Hilliard scaling behavior of the excess number  $\Delta g$  for hard sphere Yukawa droplets found using density functional theory.

work.<sup>4,16,25,36</sup> Excellent agreement is again found in the scaling regions. For all results shown, any deviations from scaling at very small values of  $|\Delta\tilde{\rho}|$  are due to the finite domain effects discussed earlier.

#### D. Scaling and the nucleation theorem

The nucleation theorem<sup>40-42</sup> allows one to determine  $\Delta g$  rigorously from the equation

$$\Delta g = - \left( \frac{\partial W}{\partial \mu_B} \right)_T \quad (23)$$

From Figs. 3 and 6 we see that the Cahn and Hilliard scaling law accurately gives  $W$  as a function of  $\rho_B$ . From the chain rule and a familiar thermodynamic identity, we may write Eq. (23) as

$$\Delta g = - \left( \frac{\partial W}{\partial \rho_B} \right)_T \left( \frac{\partial \rho_B}{\partial \mu_B} \right)_T = - \left( \frac{\partial W}{\partial \rho_B} \right)_T \rho_B^2 \kappa, \quad (24)$$

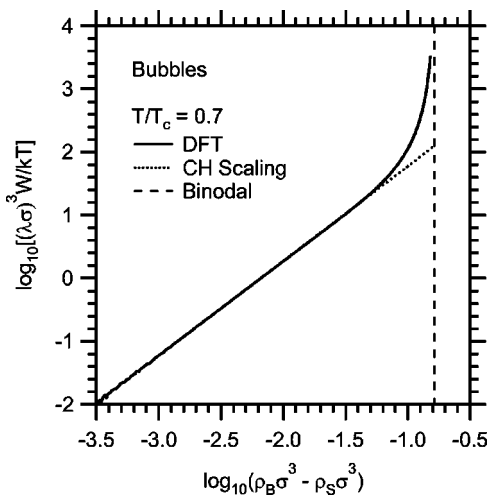


FIG. 8. Cahn-Hilliard scaling behavior of the reversible work for hard sphere Yukawa bubbles found using density functional theory.

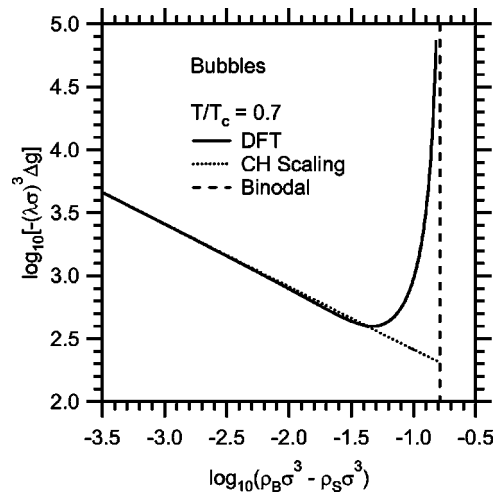


FIG. 9. Cahn-Hilliard scaling behavior of the excess number  $\Delta g$  for hard sphere Yukawa bubbles found using density functional theory.

where  $\kappa$  is the isothermal compressibility. Near the spinodal, the well-known result<sup>1</sup>

$$\left( \frac{\partial \rho_B}{\partial \mu_B} \right)_T = \rho_B^2 \kappa = [6\zeta(\rho_S - \rho_B)]^{-1}, \quad (25)$$

follows from Eq. (16) [or from Eqs. (11) and (A2)]. Then, from Eqs. (17), (24), and (25), we obtain

$$\Delta g = \frac{\pi}{2} \left( \frac{c}{2\zeta} \right)^{3/2} I_3 (\rho_S - \rho_B)^{-1/2}. \quad (26)$$

This result reproduces the divergent behavior found in Eq. (22), whose physical origin is now seen to lie in the divergence of  $\kappa (\sim |\rho_S - \rho_B|^{-1})$  for mean field theories of fluid phase equilibrium.<sup>1</sup> The connection with  $\kappa$  is quite understandable in view of that property's role in regulating density fluctuations in a fluid<sup>1,42</sup> and the recognition that the critical nucleus is itself a density fluctuation in a metastable fluid. The magnitude of  $\Delta g$  given by Eq. (26) also agrees with Eq. (22) since it can be shown analytically or numerically that  $I_3 = 8I_1$ .

#### E. Ginzburg criterion

Levanyuk<sup>43</sup> and Ginzburg<sup>44</sup> developed a test for the self-consistency of mean field theory near a critical point. The first application to nucleation was made by Binder,<sup>56</sup> who developed a Ginzburg criterion based on the temperature difference from the spinodal. Very recently these ideas were used by Wood and Wang<sup>57</sup> and generalized by Wang<sup>58</sup> to include compositional fluctuations in polymer blends. Here we develop a different kind of Ginzburg criterion to assess the singular behavior of density fluctuations near the spinodal. The idea is simply that for the mean field predictions to be valid, fluctuations in the order parameter should be small on the scale of the correlation length  $\xi$ . More precisely, following Goldenfeld<sup>59</sup> we may formulate the Ginzburg criterion in a  $d$ -dimensional space as

$$\frac{|\int_V d^d r G(\mathbf{r})|}{\int_V d^d r (\eta(\mathbf{r}))^2} \ll 1, \quad (27)$$

where  $G$  is the two-point correlation function for fluctuations in the order parameter  $\eta$ , and the integrals are taken over the correlation volume  $V = \xi^d$ . The relevant order parameter is the difference in density between the nucleus and the bulk vapor phase,  $\eta(\mathbf{r}) = \rho(\mathbf{r}) - \rho_B$ , and near the spinodal this is well approximated by  $\Delta\rho$ , where  $\Delta\rho \equiv \rho_S - \rho_B$ . The correlation length  $\xi$  is proportional to  $r_{1/2}$ . To show this, we proceed roughly in the manner of Goldenfeld<sup>59</sup> to find an equation for  $G(\mathbf{r})$  in the vicinity of the spinodal. Since the two Euler-Lagrange equations (5) and (13) are asymptotically equivalent near the spinodal, we work with the latter, simpler equation. First, we expand  $\mu_0$  to second-order or, equivalently, differentiate Eq. (16) to find

$$\mu_0(\rho) - \mu_B = 6\zeta\Delta\rho\eta(\mathbf{r}) - 3\zeta[\eta(\mathbf{r})]^2, \quad (28)$$

and substitute this into Eq. (13). Then we multiply the resulting differential equation by  $\eta(\mathbf{r}')$ , average  $\langle(\dots)\rangle$  over all fluctuations, and approximate  $\langle\eta^2(\mathbf{r})\eta(\mathbf{r}')\rangle$  as  $\langle\eta(\mathbf{r})\eta(\mathbf{r}')\rangle\Delta\rho$ , which is acceptable near the spinodal where  $\rho(\mathbf{r})$  varies slowly. We obtain

$$\nabla^2 G - 3\zeta(\Delta\rho/c)G = 0, \quad (29)$$

where  $G(\mathbf{r}-\mathbf{r}') = \langle\eta(\mathbf{r})\eta(\mathbf{r}')\rangle$ . It follows from Eq. (29) that the correlation length is

$$\xi = (3\zeta\Delta\rho/c)^{-1/2}, \quad (30)$$

which is essentially the same as Eq. (20). The same expression holds for DFT upon replacing  $c$  by  $\alpha/\lambda^2$ .

We now evaluate Eq. (27). From the static susceptibility sum rule,<sup>59</sup> the numerator equals  $kT\rho_B^2\kappa$ , while the denominator is simply  $\xi^d(\Delta\rho)^2$ , since the density varies slowly within the nucleus. Thus, for the mean field predictions to be valid near the spinodal, the inequality  $kT\rho_B^2\kappa \ll \xi^d(\Delta\rho)^2$  must be satisfied. With the use of Eqs. (25) and (30), this inequality takes the explicit form,

$$\frac{kT}{6\zeta} \left( \frac{3\zeta}{c} \right)^{3/2} (\Delta\rho)^{-(3-d/2)} \ll 1. \quad (31)$$

It is clear that this inequality cannot be satisfied as  $\Delta\rho \rightarrow 0$  unless  $d > 6$ . This result, in agreement with earlier studies,<sup>58,60–62</sup> defines the upper critical dimension beyond which mean field theory is valid. Thus, in three dimensions the specific scaling predictions of GT and MFDFT cannot be correct near the spinodal. For critical phenomena in fluid systems, the upper critical dimension is 4. The increase to 6 indicates that fluctuations are even more important near the spinodal than near the critical point, and accurate results in this region can only be obtained from a theory that properly treats fluctuations.<sup>58</sup> A related question is the size of the fluctuation dominated region, or how closely can the spinodal be approached before mean field theory breaks down? An estimate can be found by evaluating more precisely the denominator of Eq. (27) in the asymptotic Cahn and Hilliard scaling regime. Restricting ourselves to  $d=3$  and introducing the scaled variables  $Y$  and  $R$ , [cf. Eq. (A4)] we rewrite Eq. (27) as

$$\frac{\lambda^3}{4\pi I_2} \frac{kT}{6\zeta} \left( \frac{2\zeta}{\alpha} \right)^{3/2} (\Delta\rho)^{-3/2} \ll 1, \quad (32)$$

where  $I_2$  is defined by Eq. (18). The only essential difference between Eqs. (31) and (32) is the improved numerical precision of the latter. After introducing dimensionless densities  $\tilde{\rho} = \rho\sigma^3$  and numerically evaluating the relevant quantities<sup>63</sup> at  $T/T_c = 0.7$ , we find the explicit inequalities,

$$3.12 \times 10^{-4} (\lambda\sigma)^3 (\Delta\tilde{\rho})_{\text{vap}}^{-3/2} \ll 1 \quad (33)$$

for droplet nucleation near the vapor spinodal ( $\tilde{\rho}_S = 0.0925$ ), and

$$1.77 \times 10^{-4} (\lambda\sigma)^3 (|\Delta\tilde{\rho}|_{\text{liq}})^{-3/2} \ll 1 \quad (34)$$

for bubble nucleation near the liquid spinodal ( $\tilde{\rho}_S = 0.521$ ). The minimum values of  $\Delta\tilde{\rho}$  that satisfy these inequalities clearly depend on the specific value used for  $\lambda\sigma$ , i.e., on the range of the potential. Let us consider the inequality to be satisfied when the left side of either Eq. (33) or (34) equals 0.1. For  $\lambda\sigma = 1$ , we then see that MFDFT is valid for  $\log_{10}(\Delta\tilde{\rho})_{\text{vap}} > -1.67$  and  $\log_{10}|\Delta\tilde{\rho}|_{\text{liq}} > -1.84$ . For droplet nucleation in Figs. 6 and 7, the entire scaling region lies at smaller values of  $\Delta\tilde{\rho}$  for which the MFDFT is invalid. For bubble nucleation in Figs. 8 and 9, the scaling region lies partially within the acceptable density range, but if  $\lambda\sigma = 2$  is used, the range of acceptable densities changes to  $\log_{10}|\Delta\tilde{\rho}|_{\text{liq}} > -1.23$ , which now excludes the entire scaling region. Only if we make the Yukawa potential very long ranged, by insisting that  $\lambda\sigma \ll 1$ , will the Ginzburg criterion be satisfied for values of  $\Delta\rho$  that lie well within the scaling region. Even in this case, the mean field scaling predictions will eventually become invalid as  $\Delta\rho \rightarrow 0$ , unless we first go to the limit of infinitely long-range forces,  $\lambda = 0$ . This behavior merely confirms what has long been known, namely, that mean field theory improves as either the system dimension or the range of the force increases, and it becomes exact for forces of infinite range. To properly model simple fluid systems using realistic values for  $\sigma$ , Oxtoby and Evans<sup>4</sup> found that  $\lambda\sigma > 1.5$  was typical. In our own recent work, we found semiquantitative, qualitatively reasonable results for the thermodynamic properties of bulk mixtures of water and pentanol using the values  $\lambda\sigma = 2.967$  for water and 4.544 for pentanol. Thus, for values of  $\lambda\sigma$  needed to simulate the properties of real fluids, GT and MFDFT will be valid generally only for densities lying outside of the scaling region.

#### IV. DISCUSSION

Limitations and characteristics of MFDFT and GT near the spinodal have been noted in previous studies. In recent work on polymer phase separation, Wang<sup>58</sup> developed a Ginzburg criterion based on both composition and temperature considerations to establish limits for the validity of mean field theory near the spinodal. Wang<sup>58</sup> also showed that a mean field spinodal, defined by the divergence of the static susceptibility, does not exist for  $d < 4$ . It is replaced by a pseudospinodal, lying outside of the mean field spinodal, at which the susceptibility  $\kappa$  reaches a finite maximum. The pseudospinodal is associated with a small nucleation barrier,  $W \sim kT$ . Thus, it defines a region in which phase separation may exhibit characteristics of both nucleation and spinodal decomposition, establishing a link to the original ideas of Binder.<sup>56</sup> See Ref. 1, pp. 209–216 for an illuminating sum-

mary. Related behavior was found in important pioneering work by Klein and Unger,<sup>61,62</sup> who investigated magnetic systems using  $\psi^4$  field theory with a Landau-Ginzburg model free energy functional. They showed that for systems with weak long-range attractive forces (WLRF), the critical fluctuation is a ramified droplet of diverging size. They also found sharp spinodals when  $d < 6$  only for WLRF. Sharp spinodals are, thus, artifacts of mean field equations of state for physical systems with short-range forces. The scaling behavior of  $W$  and the critical radius was identical to that found here. Since the Yukawa potential gives rise to WLRF as  $\lambda\sigma \rightarrow 0$ , it is not surprising that the behavior of the critical nucleus predicted by MFDFT and GT for fluid and magnetic systems are the same, since these systems belong to the same universality class. In short, mean field theories are qualitatively acceptable descriptions of metastability for WLRF systems near the spinodal only in the long-range limit.<sup>64</sup>

Some other interesting theoretical consequences arise if we examine the dependence of  $W$  and  $\Delta g$  on  $\lambda$  and  $\Delta\rho$  in the scaling region near the spinodal for systems of different dimensionality. We can generalize Eqs. (14) and (21) to  $d$  dimensions for spherically symmetric nuclei simply by replacing  $d\mathbf{r}$  with  $\omega_d r^{d-1} dr$ , where  $\omega_d$  is a  $d$ -dependent geometric factor. After introducing the scaled density  $Y$  and length  $R$ , Eq. (A4), into these expressions, we easily find the asymptotic dependence to be  $W \sim \lambda^{-d} (\Delta\rho)^{3-d/2}$  and  $\Delta g \sim \lambda^{-d} (\Delta\rho)^{1-d/2}$ . The critical radius, which is directly proportional to  $r_{1/2}$ , Eq. (20), has the same asymptotic dependence in all dimensions:  $r_{1/2} \sim \lambda^{-1} (\Delta\rho)^{-1/2}$ . It is curious that  $r_{1/2}$ , which measures the spatial extent of the critical fluctuation, diverges in all dimensions, whereas  $\Delta g$ , which measures the amount of material in the nucleus, only diverges for  $d > 2$ . Note that the dependence of  $W$  and  $\Delta g$  on  $\lambda$  and  $\Delta\rho$  is consistent with the nucleation theorem discussed in Sec. III D. For  $d < 6$  and  $\lambda \neq 0$ , we find that  $W \rightarrow 0$  as  $\Delta\rho \rightarrow 0$ , in agreement with Klein and Unger and in accord with Gibbs's expectations<sup>37</sup> for the limit of metastability. In contrast, for  $d > 6$  we find, as did Klein and Unger, that  $W$  and  $\Delta g$  diverge as  $\Delta\rho \rightarrow 0$ . In systems of high dimensionality, the spinodal, thus, acts as a quasibinodal with nucleation becoming increasingly more difficult as the spinodal is approached. In this case, Klein and Unger actually showed that the lifetime of the metastable state became infinite at the spinodal. This behavior, of course, only pertains to an instantaneous quench to the spinodal density; in a gradual quench starting farther from the spinodal, the system would first undergo nucleation where  $W$  was smaller, and this would destroy the metastable state. Now note what happens as  $\lambda \rightarrow 0$ , i.e., as the range of the potential becomes infinite, but  $\Delta\rho \neq 0$ . In this case,  $W$  diverges everywhere: Nucleation does not occur anywhere in a system with infinitely long-range weak attractive forces. Note that this behavior is independent of the dimensionality of the system and is valid throughout the entire metastable region, since dimensional analysis of Eq. (8) also yields the result  $W \sim \lambda^{-d}$ . The divergence of  $W$  implies that the fluid remains in a single homogeneous phase as its density varies continuously throughout the metastable region. It is the type of behavior inferred from the mean field equation of state.

We conclude with a few comments of a more practical nature. The main challenge to applicability of the mean field scaling results to nucleation in simple fluids is that real gas-liquid systems are characterized by short-range interactions. As noted earlier, the Ginzburg criterion is not satisfied in the asymptotic scaling region for systems with short-range forces. Thus, the asymptotic scaling results are not likely to be applicable to these systems. For guidance as to what to expect instead, we can turn first to Wang's recent fluctuation theory.<sup>58</sup> The combination of the nucleation theorem, Eq. (24), and Wang's result for the susceptibility  $\kappa$  implies that the excess number and, hence, the critical size will not be divergent at the pseudospinodal. This agrees with the recent experimental results of Lefebvre *et al.*<sup>65</sup> on nucleation in polymer blends. We would expect similar behavior in vapor-liquid nucleation for which, at present, there is no experimental indication for an increasing  $\Delta g$  with increasing supersaturation  $S$ . At the highest nucleation rates ( $\approx 10^{17} \text{ cm}^{-3} \text{ s}^{-1}$ ) measured in vapor systems, i.e., those made with supersonic nozzles,<sup>66-69</sup> only small critical cluster sizes (5–10 molecules) that decrease with increasing  $S$  have been found.<sup>69</sup> Although these results are not definitive because the measurement conditions still lie far from the estimated mean field spinodal,<sup>69</sup> the prospects for a closer approach to the vapor spinodal appear dim. In nozzle expansions, the very high nucleation rates already cause the collapse of the metastable state well before reaching the spinodal. Alternative methods with significantly higher cooling rates, such as free jet expansions, are available, but these rapidly produce nearly collisionless vapors in which cluster growth kinetics is effectively terminated. Experiments on bubble nucleation may be more successful in approaching spinodal conditions.<sup>70</sup>

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## APPENDIX

We consider the behavior of Eq. (5) near the spinodal to show that MFDFT asymptotically obeys Cahn-Hilliard scaling. First, it follows from Eqs. (10) and (15) that  $\partial\Delta f'/\partial\rho = \mu_h - \mu_B - \alpha\rho$ , which simplifies the right side of Eq. (5). Next, we use the chain rule to rewrite  $\nabla^2\mu_h$  in terms of density derivatives and use this result to express Eq. (5) as

$$\frac{\partial\mu_h}{\partial\rho} \frac{\partial^2\rho}{\partial r^2} + \frac{\partial^2\mu_h}{\partial\rho^2} \left(\frac{\partial\rho}{\partial r}\right)^2 + \frac{2}{r} \frac{\partial\mu_h}{\partial\rho} \frac{\partial\rho}{\partial r} = \lambda^2 \frac{\partial\Delta f'}{\partial\rho}. \quad (\text{A1})$$

Now, close to the spinodal the density profile is very flat, and  $\partial\mu_h/\partial\rho$  is well approximated by a Taylor series expansion about the spinodal density. This gives

$$\frac{\partial\mu_h}{\partial\rho} = \alpha - 6\zeta(\rho - \rho_S), \quad (\text{A2})$$



where  $\alpha = (\partial\mu_h/\partial\rho)_{\rho=\rho_S}$  and  $6\zeta = -(\partial^2\mu_h/\partial\rho^2)_{\rho=\rho_S}$ .

With Eqs. (A2) and (16) and the use of the scaled density variable  $Y$ , Eq. (A1) can then be written as

$$\begin{aligned} & [1 + (6\zeta/\alpha)(\rho_S - \rho_B)(1 - Y)][\partial^2(rY)/\partial r^2] \\ & - (6\zeta/\alpha)(\rho_S - \rho_B)r(\partial Y/\partial r)^2 \\ & = \frac{3}{2}(2\lambda^2\zeta/\alpha)(\rho_S - \rho_B)r(2Y - Y^2). \end{aligned} \quad (\text{A3})$$

The form of this equation suggests that the appropriate scaled length variable  $R$  should be

$$R = r[2\lambda^2\zeta(\rho_S - \rho_B)/\alpha]^{1/2}, \quad (\text{A4})$$

which is identical to  $R$  of Cahn and Hilliard aside from the replacement of  $c$  by  $\alpha/\lambda^2$ . After introducing  $R$  into Eq. (A3) and taking the limit  $\rho_B \rightarrow \rho_S$ , we recover Eq. (19), the scaled Euler-Lagrange equation of Cahn and Hilliard. This asymptotic convergence of the GT and DFT Euler-Lagrange equations implies that the C-H scaling behavior should be obeyed. It follows from the analysis of Evans<sup>39</sup> that Eq. (8) can be written in the form of Eq. (14) near the spinodal. Thus, the scaling results for  $W$ ,  $r_{1/2}$ , and  $\Delta g$  are obtained from Eqs. (17), (20), and (22) simply by replacing  $c$  with  $\alpha/\lambda^2$ .

- <sup>1</sup>P. Debenedetti, *Metastable Liquids* (Princeton University Press, Princeton, NJ, 1996).  
<sup>2</sup>J. Schmelzer, G. Röpke, and R. Mahnke, *Aggregation Phenomena in Complex Systems* (Wiley-VCH, New York, 1999).  
<sup>3</sup>D. Kashchiev, *Nucleation: Basic Theory with Applications* (Butterworth-Heinemann, Oxford, 2000).  
<sup>4</sup>D. W. Oxtoby and R. Evans, *J. Chem. Phys.* **89**, 7521 (1988).  
<sup>5</sup>X. C. Zeng and D. W. Oxtoby, *J. Chem. Phys.* **94**, 4472 (1991).  
<sup>6</sup>B. N. Hale, *Metall. Trans. A* **23**, 1863 (1992).  
<sup>7</sup>L. Gránásy, *Europhys. Lett.* **24**, 121 (1993).  
<sup>8</sup>I. Hadjiagapiou, *J. Phys.: Condens. Matter* **6**, 5303 (1994).  
<sup>9</sup>R. M. Nyquist, V. Talanquer, and D. W. Oxtoby, *J. Chem. Phys.* **103**, 1175 (1995).  
<sup>10</sup>B. N. Hale, *Aust. J. Phys.* **49**, 425 (1996).  
<sup>11</sup>R. McGraw and A. Laaksonen, *Phys. Rev. Lett.* **76**, 2754 (1996).  
<sup>12</sup>A. Laaksonen and R. McGraw, *Europhys. Lett.* **35**, 367 (1996).  
<sup>13</sup>L. Gránásy, *J. Chem. Phys.* **104**, 5188 (1996).  
<sup>14</sup>M. Iwamatsu and K. Horii, *J. Non-Cryst. Solids* **205–207**, 919 (1996).  
<sup>15</sup>J. C. Barrett, *J. Phys.: Condens. Matter* **9**, L19 (1997).  
<sup>16</sup>K. Koga and X. C. Zeng, *J. Chem. Phys.* **110**, 3466 (1999).  
<sup>17</sup>J. C. Barrett, *J. Chem. Phys.* **111**, 5938 (1999).  
<sup>18</sup>L. Gránásy and D. W. Oxtoby, *J. Chem. Phys.* **112**, 2399 (2000).  
<sup>19</sup>J. W. P. Schmelzer, J. Schmelzer, Jr., and I. S. Gutzow, *J. Chem. Phys.* **112**, 3820 (2000).  
<sup>20</sup>P. Schaaf, B. Senger, J.-C. Voegel, R. K. Bowles, and H. Reiss, *J. Chem. Phys.* **114**, 8091 (2001).  
<sup>21</sup>G. K. Schenter, S. M. Kathmann, and B. C. Garrett, *J. Chem. Phys.* **116**, 4275 (2002); **110**, 7951 (1999); *Phys. Rev. Lett.* **82**, 3484 (1999).  
<sup>22</sup>V. Talanquer, *J. Chem. Phys.* **106**, 9957 (1997).  
<sup>23</sup>V. K. Shen and P. G. Debenedetti, *J. Chem. Phys.* **114**, 4149 (2001).  
<sup>24</sup>D. Kashchiev, *J. Chem. Phys.* **118**, 1837 (2003).  
<sup>25</sup>I. Kusaka, *J. Chem. Phys.* **118**, 5510 (2003).  
<sup>26</sup>J.-S. Li and G. Wilemski, *J. Chem. Phys.* **118**, 2845 (2003).  
<sup>27</sup>S. Punnathanam and D. S. Corti, *J. Chem. Phys.* **119**, 10224 (2003).  
<sup>28</sup>J. W. P. Schmelzer and V. G. Baidakov, *J. Chem. Phys.* **119**, 10759 (2003).  
<sup>29</sup>D. Kashchiev, *J. Chem. Phys.* **120**, 3749 (2004).

- <sup>30</sup>J. D. van der Waals, *Verh. Kon. Akad. Wetensch. (Ie Sect.)* **1**, 1 (1893).  
<sup>31</sup>J. W. Cahn and J. E. Hilliard, *J. Chem. Phys.* **28**, 258 (1958).  
<sup>32</sup>J. W. Cahn and J. E. Hilliard, *J. Chem. Phys.* **31**, 688 (1959).  
<sup>33</sup>A. H. Falls, L. E. Scriven, and H. T. Davis, *J. Chem. Phys.* **75**, 3986 (1981).  
<sup>34</sup>H. T. Davis and L. E. Scriven, *Adv. Chem. Phys.* **49**, 357 (1982).  
<sup>35</sup>H. Tomino, I. Kusaka, K. Nishioka, and T. Takai, *J. Cryst. Growth* **113**, 633 (1991).  
<sup>36</sup>M. Iwamatsu, *J. Phys.: Condens. Matter* **5**, 7537 (1993).  
<sup>37</sup>J. W. Gibbs, *Trans. Conn. Acad. Arts Sci.* **3**, 343 (1878), reprinted in *The Scientific Papers of J. W. Gibbs* (Dover, New York, 1961), Vol. 1.  
<sup>38</sup>GT also predicts that the thermodynamic radius of the surface of tension  $r_{ST}$  goes to zero at the spinodal in accordance with Gibbs's expectations (Ref. 37). This is not mentioned by Cahn and Hilliard, but it is implied, e.g., by the results and definitions of Falls, Scriven, and Davis (Ref. 33) and shown explicitly by Tomino *et al.* (Ref. 35) and Iwamatsu (Ref. 36). This behavior is not at odds with a diverging critical size because it is the equimolar radius or  $r_{1/2}$  [Eq. (20)] that determines the spatial extent of the nucleus and not  $r_{ST}$ .  
<sup>39</sup>R. Evans, *Adv. Phys.* **28**, 143 (1979).  
<sup>40</sup>Y. Viisanen, R. Strey, and H. Reiss, *J. Chem. Phys.* **99**, 4680 (1993).  
<sup>41</sup>D. W. Oxtoby and D. Kashchiev, *J. Chem. Phys.* **100**, 7665 (1994).  
<sup>42</sup>R. K. Bowles, D. Reguera, Y. Djikaev, and H. Reiss, *J. Chem. Phys.* **115**, 1853 (2001).  
<sup>43</sup>A. P. Levanyuk, *Sov. Phys. JETP* **36**, 571 (1959).  
<sup>44</sup>V. L. Ginzburg, *Sov. Phys. Solid State* **2**, 1824 (1960).  
<sup>45</sup>N. G. van Kampen, *Phys. Rev.* **135**, A362 (1964).  
<sup>46</sup>J. K. Percus, *Trans. N. Y. Acad. Sci.* **26**, 1062 (1964).  
<sup>47</sup>D. E. Sullivan, *Phys. Rev. B* **20**, 3991 (1979).  
<sup>48</sup>D. E. Sullivan, *J. Chem. Phys.* **74**, 2604 (1981).  
<sup>49</sup>P. Tarazona and R. Evans, *Mol. Phys.* **47**, 1033 (1982).  
<sup>50</sup>P. Tarazona and R. Evans, *Mol. Phys.* **48**, 799 (1983).  
<sup>51</sup>R. Evans, U. M. B. Marconi, and P. Tarazona, *J. Chem. Soc., Faraday Trans. 2* **82**, 1763 (1986).  
<sup>52</sup>P. Tarazona, M. M. Telo da Gama, and R. Evans, *Mol. Phys.* **49**, 283 (1983).  
<sup>53</sup>B. Q. Lu, R. Evans, and M. M. Telo da Gama, *Mol. Phys.* **55**, 1319 (1985).  
<sup>54</sup>N. F. Carnahan and K. E. Starling, *J. Chem. Phys.* **51**, 635 (1969).  
<sup>55</sup>H. T. Davis, *Statistical Mechanics of Phases, Interfaces, and Thin Films* (VCH, New York, 1996).  
<sup>56</sup>K. Binder, *Phys. Rev. A* **29**, 341 (1984).  
<sup>57</sup>S. M. Wood and Z.-G. Wang, *J. Chem. Phys.* **116**, 2289 (2002).  
<sup>58</sup>Z.-G. Wang, *J. Chem. Phys.* **117**, 481 (2002).  
<sup>59</sup>N. Goldenfeld, *Lectures on Phase Transitions and the Renormalization Group* (Perseus, Reading, MA, 1992).  
<sup>60</sup>Y. Saito, *Prog. Theor. Phys.* **59**, 375 (1978).  
<sup>61</sup>W. Klein and C. Unger, *Phys. Rev. B* **28**, 445 (1983).  
<sup>62</sup>C. Unger and W. Klein, *Phys. Rev. B* **29**, 2698 (1984).  
<sup>63</sup>It is easy to show using Eq. (19) that  $I_2 = 2I_1$ ; also we have the relation (Ref. 47),  $\alpha = 11.102kT_c\sigma^3$ , where  $T_c$  is the critical temperature.  
<sup>64</sup>P. A. Rikvold and B. M. Gorman, in *Annual Reviews of Computational Physics I*, edited by D. Stauffer (World Scientific, Singapore, 1994), p. 149.  
<sup>65</sup>A. A. Lefebvre, J. H. Lee, N. P. Balsara, and B. Hammouda, *J. Chem. Phys.* **116**, 4777 (2002).  
<sup>66</sup>K. A. Streletsky, Y. Zvinevich, B. E. Wyslouzil, and R. Strey, *J. Chem. Phys.* **116**, 4058 (2002).  
<sup>67</sup>A. Khan, C. H. Heath, U. M. Dieregswiler, B. E. Wyslouzil, and R. Strey, *J. Chem. Phys.* **119**, 3138 (2003).  
<sup>68</sup>C. H. Heath, K. A. Streletsky, B. E. Wyslouzil, J. Wölk, and R. Strey, *J. Chem. Phys.* **118**, 5465 (2003).  
<sup>69</sup>Y. J. Kim, B. E. Wyslouzil, G. Wilemski, J. Wölk, and R. Strey, *J. Phys. Chem. A* **108**, 4365 (2004).  
<sup>70</sup>V. G. Baidakov, A. M. Kaverin, and G. Sh. Boltachev, *J. Chem. Phys.* **106**, 5648 (1997).