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Curvature dependence of the interfacial tension in binary nucleation

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The curvature dependence of the interfacial tension in binary nucleation was formulated by employing Tolman's [J. Chem. Phys. **16**, 758 (1948)] idea for the variation of state and the thermodynamics of inhomogeneous systems due to Cahn and Hilliard [J. Chem. Phys. **28**, 258 (1958); **30**, 1121 (1959); **31**, 688 (1959)] and Hart [Phys. Rev. **113**, 412 (1959)]. To investigate the numerical significance of the curvature dependence, the inhomogeneous regular solution model due to Cahn and Hilliard was employed. The interfacial tension was found to decrease with curvature and to be about 20% smaller than the value of the flat interface at a radius of 3 or 6 intermolecular distance for $T=0.5T_c$ or $0.8656T_c$, respectively. The reversible work to form a critical nucleus predicted by the present theory is significantly lower than that obtained by neglecting the curvature dependence of the interfacial tension. Thus, neglect of the curvature dependence may severely underestimate the nucleation rate.

I. INTRODUCTION

In homogeneous nucleation in a binary system where supersaturation is attained under constant temperature and pressure, not only the size of the critical nucleus but also the composition profile at the interfacial region will change in accordance with supersaturation because the compositions both in the parent phase and within the nucleus depend upon supersaturation. Hence the value of the interfacial tension is expected to depend on the supersaturation due to those effects. This phenomenon can be described as a curvature dependence of the interfacial tension because the composition profile is uniquely determined for a given size of the critical nucleus, but the effect may be more pronounced than that in a single-component case as investigated by Tolman,[1-3] because the composition profile as well as the curvature will change in a binary system. Thus the curvature dependence of the interfacial tension must be clarified to achieve a reliable theory of homogeneous nucleation in binary systems, and the present article intends to do this.

II. THE GOVERNING EQUATION

Consider a binary fluid system where a critical nucleus, which is assumed to be spherical, of the second phase β exists within the parent phase α. When an infinitesimal change occurs in the state of the system, the value of the interfacial tension γ will be modified according to the general relation[4]

$$d\gamma=-s^s dT-\Gamma_1 d\mu_1-\Gamma_2 d\mu_2 \ , \tag{1}$$

where s^s, Γ_1, and Γ_2 denote the superficial densities of the entropy and the component substances; T the temperature; and μ_1 and μ_2 the chemical potentials. It is important to note that the surface of tension is chosen as the dividing surface in deriving Eq. (1).

Three intensive variables of the parent phase α can be varied independently in the present system, and the pressure p^α, the mole fraction x_2^α of the second component, and the temperature T may be chosen as independent variables. Note that the Gibbs-phase rule governs a system with a flat interface, hence it is not relevant to the present situation. Consider the case where x_2^α is varied under T and p^α kept invariant. The curvature q of the surface of tension for the critical nucleus changes as x_2^α is varied. Although the curvature q itself is not an externally controllable variable, let us exchange the roles of x_2^α and q, and consider q as an independent variable. It then follows from Eq. (1) that

$$\left(\frac{\partial\gamma}{\partial q}\right)_{T,p^\alpha}=-\Gamma_1\left(\frac{\partial\mu_1}{\partial q}\right)_{T,p^\alpha}-\Gamma_2\left(\frac{\partial\mu_2}{\partial q}\right)_{T,p^\alpha} . \tag{2}$$

Following Koenig,[5] let us rewrite the partial derivatives in the right-hand side (RHS) of Eq. (2) in terms of the more accessible quantities. We employ the following equation for the bulk α phase:

$$d\mu_i^\alpha=-s_i^\alpha dT+v_i^\alpha dp^\alpha+\left(\frac{\partial\mu_i^\alpha}{\partial x_2^\alpha}\right)_{T,p^\alpha} dx_2^\alpha, \quad i=1,2 \tag{3}$$

where μ_i^α, s_i^α, and v_i^α denote the chemical potential, the partial molecular entropy, and the partial molecular volume of the ith component for the bulk α phase. It follows from Eq. (3) that

$$\begin{aligned}\left(\frac{\partial\mu_i^\alpha}{\partial q}\right)_{T,p^\alpha}&=\left(\frac{\partial\mu_i^\alpha}{\partial x_2^\alpha}\right)_{T,p^\alpha}\left(\frac{\partial x_2^\alpha}{\partial q}\right)_{T,p^\alpha}\\&=\left(\frac{\partial\mu_i^\alpha}{\partial x_2^\alpha}\right)_{T,p^\alpha}\left(\frac{\partial x_2^\alpha}{\partial p^\beta}\right)_{T,p^\alpha}\left(\frac{\partial p^\beta}{\partial q}\right)_{T,p^\alpha} ,\end{aligned}$$
$$i=1,2 \tag{4}$$

where p^{β} denotes the pressure of the bulk β phase which possesses the same temperature and the chemical potentials as those of the system under consideration. Choice of the surface of tension as the dividing surface results in the Laplace equation[4]

$$p^{\beta}-p^{\alpha}=2\gamma q \ , \tag{5}$$

and it follows from Eq. (5) that

$$\left[\frac{\partial p^{\beta}}{\partial q}\right]_{T,p^{\alpha}}=2\left[\gamma+q\left[\frac{\partial \gamma}{\partial q}\right]_{T,p^{\alpha}}\right] . \tag{6}$$

Substituting Eq. (6) into Eq. (4) we get

$$\left[\frac{\partial \mu_i^{\alpha}}{\partial q}\right]_{T,p^{\alpha}}=2\left[\gamma+q\left[\frac{\partial \gamma}{\partial q}\right]_{T,p^{\alpha}}\right]w_i \ , \quad i=1,2 \tag{7}$$

where we put as follows for brevity:

$$w_i=\left[\frac{\partial \mu_i^{\alpha}}{\partial x_2^{\alpha}}\right]_{T,p^{\alpha}}\left[\frac{\partial x_2^{\alpha}}{\partial p^{\beta}}\right]_{T,p^{\alpha}} , \quad i=1,2 \ . \tag{8}$$

Noting that $\mu_i^{\alpha}=\mu_i$ and substituting Eq. (7) into Eq. (2), we get

$$\left[\frac{\partial \ln\gamma}{\partial q}\right]_{T,p^{\alpha}}=-\frac{2(\Gamma_1 w_1+\Gamma_2 w_2)}{1+2q(\Gamma_1 w_1+\Gamma_2 w_2)} . \tag{9}$$

This equation was derived by Koenig[5] and governs the dependence of the interfacial tension γ on the curvature q of the surface of tension under temperature T and pressure p^{α} of the parent phase kept invariant. The change in the curvature q is induced in practice by varying the composition x_2^{α}.

Let us follow Koenig[5] again to rewrite Eq. (9) into an alternative form. We introduce the auxiliary dividing surface, whose radius is denoted as R^*, through the following conditions:

$$\Gamma_1^* w_1+\Gamma_2^* w_2=0 \ , \tag{10}$$

$$N_1=\frac{4\pi}{3}(R^*)^3 c_1^{\beta}+\left[V-\frac{4\pi}{3}(R^*)^3\right]c_1^{\alpha}+4\pi(R^*)^2\Gamma_1^* \ , \tag{11}$$

$$N_2=\frac{4\pi}{3}(R^*)^3 c_2^{\beta}+\left[V-\frac{4\pi}{3}(R^*)^3\right]c_2^{\alpha}+4\pi(R^*)^2\Gamma_2^* \ , \tag{12}$$

where Γ_1^* and Γ_2^* denote the superficial densities with respect to the auxiliary dividing surface, N_1 and N_2 are the total numbers of molecules of the respective components in the system, V is the volume of the system, and c_i^{α} and c_i^{β} are the number densities of the molecules of the ith component in the bulk α and β phases which possess the same temperature and chemical potentials as those of the system. Defining δ as

$$\delta=R^*-R \ , \tag{13}$$

where R denotes the radius of the surface of tension, Eq (9) may be rewritten as

$$\left[\frac{\partial \ln\gamma}{\partial q}\right]_{T,p^{\alpha}}=-\frac{2\delta(1+\delta q+\delta^2q^2/3)Q}{1+2\delta q(1+\delta q+\delta^2q^2/3)Q} \ , \tag{14}$$

where Q represents the following:

$$Q=w_1(c_1^{\beta}-c_1^{\alpha})+w_2(c_2^{\beta}-c_2^{\alpha}) \ . \tag{15}$$

Making use of the relations

$$c_i^{\alpha}=\frac{x_i^{\alpha}}{v^{\alpha}} \ , \quad c_i^{\beta}=\frac{x_i^{\beta}}{v^{\beta}} \ , \quad i=1,2 \tag{16}$$

where v^{α} and v^{β} denote the mean molecular volumes of the bulk α and β phases, Eq. (15) may be rewritten as

$$Q=\frac{w_1x_1^{\beta}+w_2x_2^{\beta}}{v^{\beta}}-\frac{w_1x_1^{\alpha}+w_2x_2^{\alpha}}{v^{\alpha}} . \tag{17}$$

Employing the Gibbs-Duhem relation for the bulk phases,

$$s^{\alpha}dT-v^{\alpha}dp^{\alpha}+x_1^{\alpha}d\mu_1^{\alpha}+x_2^{\alpha}d\mu_2^{\alpha}=0 \ , \tag{18}$$

$$s^{\beta}dT-v^{\beta}dp^{\beta}+x_1^{\beta}d\mu_1^{\beta}+x_2^{\beta}d\mu_2^{\beta}=0 \ , \tag{19}$$

where s^{α} and s^{β} denote the mean molecular entropies of the bulk phases, we get

$$x_1^{\alpha}\left[\frac{\partial \mu_1^{\alpha}}{\partial p^{\beta}}\right]_{T,p^{\alpha}}+x_2^{\alpha}\left[\frac{\partial \mu_2^{\alpha}}{\partial p^{\beta}}\right]_{T,p^{\alpha}}=0 \ , \tag{20}$$

$$-v^{\beta}+x_1^{\beta}\left[\frac{\partial \mu_1^{\alpha}}{\partial p^{\beta}}\right]_{T,p^{\alpha}}+x_2^{\beta}\left[\frac{\partial \mu_2^{\alpha}}{\partial p^{\beta}}\right]_{T,p^{\alpha}}=0 \ , \tag{21}$$

in which $\mu_i^{\beta}=\mu_i^{\alpha}$ are utilized. Noting that w_i may be written as

$$w_i=\left[\frac{\partial \mu_i^{\alpha}}{\partial p^{\beta}}\right]_{T,p^{\alpha}} , \quad i=1,2 \tag{22}$$

and substituting those into Eqs. (20) and (21), we get

$$w_1x_1^{\alpha}+w_2x_2^{\alpha}=0 \ , \tag{23}$$

$$w_1x_1^{\beta}+w_2x_2^{\beta}=v^{\beta} \ . \tag{24}$$

Substitution of Eqs. (23) and (24) into Eq. (17) results in

$$Q=1 \ , \tag{25}$$

and we finally obtain the desired alternative form:

$$\left[\frac{\partial \ln\gamma}{\partial q}\right]_{T,p^{\alpha}}=-\frac{2\delta(1+\delta q+\delta^2q^2/3)}{1+2\delta q(1+\delta q+\delta^2q^2/3)} . \tag{26}$$

Equation (26) is known as the Gibbs-Tolman-Koenig equation.

III. LOCATION OF THE SURFACE OF TENSION AND THE DETAILED EXPRESSION FOR THE INTERFACIAL TENSION

A. Spherical interface

To proceed further with Eq (9) or Eq. (26), the surface of tension must be located. We extend Tolman's work,[1] which is for single-component cases, to binary systems. Tolman[1] devised the quasithermodynamic method to cope with the inhomogeneous region at the interface, while we employ here the thermodynamics of inhomogeneous systems due to Cahn and Hilliard,[6-8], and Hart.[9]

Consider, as a system, the domain *ABCD* containing the interface and having a conic shape intersected by two spheres as shown in Fig. 1. The boundaries *AB* and *CD* are supposed to pass through the homogeneous regions of the α and the β phases, respectively. When the size of the critical nucleus becomes extremely small, there may be no homogeneous region even at the center, hence the boundary *AB* cannot be chosen in this case. Although Eq. (9) or Eq. (26) remains valid even for this case, Tolman's method is no longer applicable and we exclude a situation such as this from the following consideration. The boundary *ABCDA* enclosing the system is supposed to be a mathematical one and does not possess any physical effect besides the role of defining the domain for consideration.[4,10,11]

Under the choice of the surface of tension as the dividing surface, the following equation holds for an arbitrary variation from the equilibrium state:[4]

$$\delta F=-S\delta T+\mu_1\delta N_1+\mu_2\delta N_2-p^\alpha\delta V^\alpha -p^\beta\delta V^\beta+\gamma\delta A\ , \tag{27}$$

where F and S denote the Helmholtz free energy and the entropy of the system; V^α and V^β, the volumes enclosed by the boundaries *ABYXA* and *CDXYC*, respectively; and A, the area of the surface of tension. Note that the term due to a variation in the curvature q of the dividing surface is eliminated in Eq. (27) through employment of the surface of tension as the dividing surface. Let us consider a specific variation for the system in which arbitrary variations δA and δq are taken under the conditions that

$$\delta T=\delta V^\alpha=\delta V^\beta=0\ , \tag{28}$$

and that the properties of the homogeneous regions on both sides of the interface are unaltered and the properties in the inhomogeneous region at the interface are also unaltered except to the extent of the secondary effect due to variation in the curvature.[1,4] We select this particular variation to simplify the further treatment,[1] and whether such a variation is consistent with the maintenance of equilibrium is of no consequence to the validity of Eq. (27) because only the initial state is supposed to be in equilibrium.[4,12]

To simplify the mathematical treatment, we set the origin of the radial coordinate at the surface of tension and denote the distance from the origin as ξ. Denoting as θ the solid angle subtended by the interface around the center of curvature, the area A of the surface of tension is given by

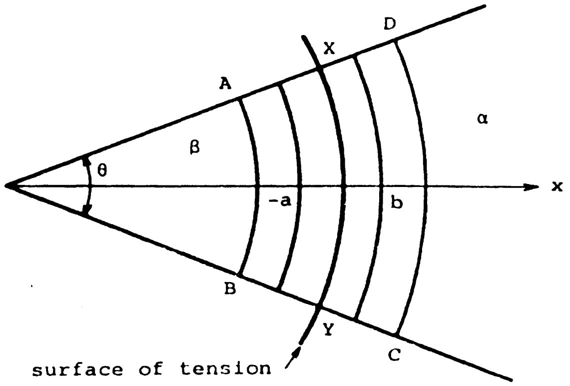

FIG. 1. System defined by the mathematical boundary and containing a spherical interface.

$$A=\theta R^2\ , \tag{29}$$

and the area $A(\xi)$ of any concentric surface located at ξ may be expressed as

$$A(\xi)=\theta(R+\xi)^2=A(1+q\xi)^2\ . \tag{30}$$

Then, taking $\xi=-a$ and b close to but sufficiently far from the origin so that the homogeneous α and β phases exist at $\xi\geq b$ and $\xi\leq -a$, the volumes V^α and V^β are given by

$$V^\alpha=V_b^\alpha+A\int_0^b(1+q\xi)^2d\xi\ , \tag{31}$$

$$V^\beta=V_a^\beta+A\int_{-a}^0(1+q\xi)^2d\xi\ , \tag{32}$$

where V_b^α and V_a^β denote the volumes at $\xi\geq b$ and $\xi\leq -a$, respectively. It follows for the presently specified variation that

$$\delta V^\alpha=\delta V_b^\alpha+\delta A\int_0^b(1+q\xi)^2d\xi+2A\,\delta q\int_0^b\xi(1+q\xi)d\xi =0\ , \tag{33}$$

$$\delta V^\beta=\delta V_a^\beta+\delta A\int_{-a}^0(1+q\xi)^2d\xi +2A\,\delta q\int_{-a}^0\xi(1+q\xi)d\xi=0\ . \tag{34}$$

The variations δN_i in the number of molecules are

$$\delta N_i=c_i^\alpha\delta V_b^\alpha+\delta A\int_0^b c_i(1+q\xi)^2d\xi+2A\,\delta q\int_0^b c_i\xi(1+q\xi)d\xi+c_i^\beta\delta V_a^\beta+\delta A\int_{-a}^0 c_i(1+q\xi)^2d\xi +2A\,\delta q\int_{-a}^0 c_i\xi(1+q\xi)d\xi\ ,\quad i=1,2 \tag{35}$$

where c_i denotes the number densities of molecules in the interfacial region. Since the properties of matter are supposed to be unaltered in taking the variation, the number densities c_i, c_i^α, and c_i^β represent the values at the equilibrium state before the variation. Multiplying Eq. (33) by c_i^α and Eq. (34) by c_i^β and subtracting the results from Eq. (35), we get

$$\delta N_i=\delta A\int_0^b(c_i-c_i^\alpha)(1+q\xi)^2d\xi+2A\,\delta q\int_0^b(c_i-c_i^\alpha)\xi(1+q\xi)d\xi+\delta A\int_{-a}^0(c_i-c_i^\beta)(1+q\xi)^2d\xi$$
$$+2A\,\delta q\int_{-a}^0(c_i-c_i^\beta)\xi(1+q\xi)d\xi\ ,\quad i=1,2\ . \tag{36}$$

To consider the variation δF of the Helmholtz free energy accompanied with the specified variation, we employ the thermodynamics of inhomogeneous systems,[6-9] which provides, for incompressible and isotropic systems, the Helmholtz free-energy density f in the following form:

$$f=f^0(x_2)+\kappa(\nabla x_2)^2\ , \tag{37}$$

where $f^0(x_2)$ denotes the value for the hypothetical homogeneous system defined by the values of T and x_2 at ξ, and κ, the coefficient of the gradient energy term, is in general a function of ∇x_2 as well as T and x_2 at ξ. Note that another variable, for example, the number density, c_1+c_2, is no longer independent under the assumption of incompressibility. Following the procedure similar to that used to derive Eq. (36), we get

$$\delta F=\delta A\int_0^b[f^0+\kappa(\nabla x_2)^2-f^\alpha](1+q\xi)^2d\xi+2A\,\delta q\int_0^b[f^0+\kappa(\nabla x_2)^2-f^\alpha]\xi(1+q\xi)d\xi$$
$$+\delta A\int_{-a}^0[f^0+\kappa(\nabla x_2)^2-f^\beta](1+q\xi)^2d\xi+2A\,\delta q\int_{-a}^0[f^0+\kappa(\nabla x_2)^2-f^\beta]\xi(1+q\xi)d\xi\ , \tag{38}$$

where f^α and f^β denote the values for the homogeneous α and β regions in the system, respectively. It follows from Eqs. (36) and (38) that

$$\delta F=\mu_1\delta N_1+\mu_2\delta N_2+\delta A\int_0^b[f^0+\kappa(\nabla x_2)^2-f^\alpha-g+g^\alpha](1+q\xi)^2d\xi$$
$$+2A\,\delta q\int_0^b[f^0+\kappa(\nabla x_2)^2-f^\alpha-g+g^\alpha]\xi(1+q\xi)d\xi+\delta A\int_{-a}^0[f^0+\kappa(\nabla x_2)^2-f^\beta-g+g^\beta](1+q\xi)^2d\xi$$
$$+2A\,\delta q\int_{-a}^0[f^0+\kappa(\nabla x_2)^2-f^\beta-g+g^\beta]\xi(1+q\xi)d\xi\ , \tag{39}$$

where g, g^α, and g^β represent the following:

$$g=\mu_1c_1+\mu_2c_2\ ,\quad g^\alpha=\mu_1c_1^\alpha+\mu_2c_2^\alpha\ ,\quad g^\beta=\mu_1c_1^\beta+\mu_2c_2^\beta\ . \tag{40}$$

The chemical potentials μ_1 and μ_2 in Eq (40) may of course be identified with μ_1^α and μ_2^α for the bulk α phase at (T,p^α,x_2^α). Comparing Eq. (39) with Eq. (27) and noting Eq. (28), we obtain the detailed expressions for γ and the equation of locating the surface of tension as follows:

$$\gamma=\int_{-a}^0[f^0+\kappa(\nabla x_2)^2-f^\beta-g+g^\beta](1+q\xi)^2d\xi+\int_0^b[f^0+\kappa(\nabla x_2)^2-f^\alpha-g+g^\alpha](1+q\xi)^2d\xi\ , \tag{41}$$

$$\int_{-a}^0[f^0+\kappa(\nabla x_2)^2-f^\beta-g+g^\beta]\xi(1+q\xi)d\xi+\int_0^b[f^0+\kappa(\nabla x_2)^2-f^\alpha-g+g^\alpha]\xi(1+q\xi)d\xi=0\ . \tag{42}$$

B. Equilibrium composition profile

To proceed further with those equations, the equilibrium composition profile must be known for a given state which is defined by (T,p^α,x_2^α). Taking as the system a spherical domain defined by the boundary of the radius r_0 and whose center coincides with that of the spherical nucleus of the β phase, the equilibrium profile may be determined by an extremum condition of the thermodynamic potential Φ defined as follows against an arbitrary infinitesimal variation of the profile under the condition of the constant values for T,μ_1^α, μ_2^α, and r_0:

$$\Phi=E-TS-\mu_1^\alpha N_1-\mu_2^\alpha N_2\ . \tag{43}$$

The radius r_0 is supposed to be so large that the boundary passes through the homogeneous region of the α phase. Employing Eq. (37), Φ may be rewritten as

$$\Phi=\int_0^{r_0}\left\{f^0(x_2)+\kappa\left[\frac{dx_2}{dr}\right]^2-(c_1+c_2)[\mu_1^\alpha(1-x_2)+\mu_2^\alpha x_2]\right\}4\pi r^2dr\ . \tag{44}$$

We neglect the variation of the number density c_1+c_2 in accordance with the assumption of incompressibility. Further, anticipating the application of the present formalism to the regular solution model, we assume that the density c_1+c_2 is independent of the composition and that κ is a constant. Then, an application of the calculus of variation results in the following Euler equation:

$$2\kappa\frac{d^2x_2}{dr^2}+4\kappa\frac{1}{r}\frac{dx_2}{dr}-\left[\frac{\partial f^0}{\partial x_2}\right]_T-(c_1+c_2)(\mu_1^\alpha-\mu_2^\alpha)=0\ . \tag{45}$$

Noting that the Helmholtz free-energy density for the bulk α phase is given by

$$f^0=(c_1+c_2)[\mu_1^\alpha(1-x_2^\alpha)+\mu_2^\alpha x_2^\alpha]-p^\alpha \tag{46}$$

and taking T, x_2^α, and p^α as the independent variables to determine the value of f^0, it follows that

$$\left[\frac{\partial f^0}{\partial x_2^\alpha}\right]_{T,p^\alpha}=-(c_1+c_2)(\mu_1^\alpha-\mu_2^\alpha)+(c_1+c_2)\left[(1-x_2^\alpha)\left[\frac{\partial \mu_1^\alpha}{\partial x_2^\alpha}\right]_{T,p^\alpha}+x_2^\alpha\left[\frac{\partial \mu_1^\alpha}{\partial x_2^\alpha}\right]_{T,p^\alpha}\right] . \tag{47}$$

Since the second term in Eq. (47) vanishes identically[13] and the dependence of f^0 on p^α may be neglected under the assumption of incompressibility, employment of Eq. (47) in Eq. (45) results in

$$2\kappa\frac{d^2x_2}{dr^2}+4\kappa\frac{1}{r}\frac{dx_2}{dr}-\left[\frac{\partial f^0}{\partial x_2}\right]_T+\left[\frac{\partial f^0}{\partial x_2^\alpha}\right]_T=0 . \tag{48}$$

The equilibrium composition profile is determined by Eq. (48) under the boundary condition that

$$x_2=x_2^\alpha \text{ as } r\rightarrow\infty$$

and

$$\frac{dx_2}{dr}=0 \text{ at } r=0 . \tag{49}$$

Recalling that the radius of the surface of tension is represented by R, Eq. (42), to locate the surface of tension, may be rewritten as

$$R^3(p^\alpha-p^\beta)+3R\left\{(p^\beta r_a^2-p^\alpha r_b^2)-2\int_{r_a}^{r_b}\left[f^0+\kappa\left[\frac{dx_2}{dr}\right]^2-g\right]r\,dr\right\}+2(p^\alpha r_b^3-p^\beta r_a^3)+6\int_{r_a}^{r_b}\left[f^0+\kappa\left[\frac{dx_2}{dr}\right]^2-g\right]r^2dr=0 , \tag{50}$$

where r_a and r_b may be arbitrarily chosen within the homogeneous regions in the β-phase nucleus and in the α parent phase, respectively, and the relations

$$g^\alpha-f^\alpha=p^\alpha , \quad g^\beta-f^\beta=p^\beta \tag{51}$$

have been utilized. Noting that the composition profile obeys Eq. (48), the integrals in Eq. (50) may be transformed into the following more easily integrable forms:

$$\int_{r_a}^{r_b}\left[f^0+\kappa\left[\frac{dx_2}{dr}\right]^2-g\right]r\,dr=\frac{1}{2}(f^\alpha r_b^2-f^\beta r_a^2)-\frac{1}{2}\left[\frac{\partial f^0}{\partial x_2^\alpha}\right]_T(x_2^\alpha r_b^2-x_2^\beta r_a^2)+\left[\frac{\partial f^0}{\partial x_2^\alpha}\right]_T\int_{r_a}^{r_b}x_2 r\,dr-\int_{r_a}^{r_b}gr\,dr , \tag{52}$$

$$\int_{r_a}^{r_b}\left[f^0+\kappa\left[\frac{dx_2}{dr}\right]^2-g\right]r^2dr=(f^\alpha r_b^3-f^\beta r_a^3)-\left[\frac{\partial f^0}{\partial x_2^\alpha}\right]_T(x_2^\alpha r_b^3-x_2^\beta r_a^3)-2\int_{r_a}^{r_b}f^0r^2dr+3\left[\frac{\partial f^0}{\partial x_2^\alpha}\right]_T\int_{r_a}^{r_b}x_2r^2dr-\int_{r_a}^{r_b}gr^2dr , \tag{53}$$

in which the critical nucleus is assumed to be so large that the homogeneous properties of the bulk β phase are attained at r_a. The composition x_2^α in the parent phase may usually be approximated by its initial value. Equation (41) for γ may also be rewritten as follows by making use of Eqs. (42) and (48):

$$\gamma=ap^\beta(1-\tfrac{1}{2}qa)+bp^\alpha(1+\tfrac{1}{2}qb)-\int_{-a}^{b}g(1+q\xi)d\xi+\left[\frac{\partial f^0}{\partial x_2^\alpha}\right]_T\int_{-a}^{b}x_2(1+q\xi)d\xi+\tfrac{1}{2}[f^\alpha(R+b)(1+qb)-f^\beta(R-a)(1-qa)]-\frac{1}{2}\left[\frac{\partial f^0}{\partial x_2^\alpha}\right]_T[x_2^\alpha(R+b)(1+qb)-x_2^\beta(R-a)(1-qa)] . \tag{54}$$

C. Flat interface

Although the formalism derived above is in principle applicable to the cases where the radii of the surface of tension are extremely large, it is desirable for numerical evaluation to derive the separate formalism for flat interfaces. Since the value of the interfacial tension is, in the case of a flat interface, independent of the location for the dividing surface,[4] we may choose the location such that

$$\mu_1\Gamma_1+\mu_2\Gamma_2=0 \tag{55}$$

is satisfied. When the dividing surface is so chosen, the interfacial tension γ_∞, where the subscript indicates the flat interface, is given by the superficial density of the Helmholtz free energy.[4]

Under the approximation that the density c_1+c_2 is independent of the composition, it is possible to locate the dividing surface such that $\Gamma_1=\Gamma_2=0$, as shown below, and this location is the one to be determined by Eq. (55) in this case. Take the z-axis to be perpendicular to the interface and direct if from the β phase toward the α phase with the origin at an arbitrarily chosen point within the homogeneous β phase. Suppose that the dividing surface is at $z=L$, then the superficial densities Γ_1 and Γ_2 are given by

$$\begin{aligned}\Gamma_1 &= \int_0^{z_0}(c_1+c_2)(1-x_2)dz-(c_1^\beta+c_2^\beta)(1-x_2^\beta)L\\ &\quad -(c_1^\alpha+c_2^\alpha)(1-x_2^\alpha)(z_0-L)\ ,\\ \Gamma_2 &= \int_0^{z_0}(c_1+c_2)x_2dz-(c_1^\beta+c_2^\beta)x_2^\beta L\\ &\quad -(c_1^\alpha+c_2^\alpha)x_2^\alpha(z_0-L)\ ,\end{aligned} \tag{56}$$

where $z=z_0$ is located at an arbitrarily chosen point within the homogeneous α phase. Employing the approximation that

$$c_1+c_2=c_1^\alpha+c_2^\alpha=c_1^\beta+c_2^\beta\ , \tag{57}$$

both of the conditions $\Gamma_1=0$ and $\Gamma_2=0$ result in

$$L=\frac{\int_0^{z_0}x_2dz-x_2^\alpha z_0}{(x_2^\beta-x_2^\alpha)}\ . \tag{58}$$

Thus the interfacial tension γ_∞ is given by

$$\begin{aligned}\gamma_\infty &= \int_0^{z_0}\left[f^0(x_2)+\kappa\left[\frac{dx_2}{dz}\right]^2\right]dz\\ &\quad -[f^\alpha(z_0-L)+f^\beta L]\ .\end{aligned} \tag{59}$$

The equilibrium composition profile for a flat interface is determined by an extremum condition of the following thermodynamic potential under the given values for T, μ_1^α, μ_2^α, and z_0:

$$\begin{aligned}\hat{\Phi} = \int_0^{z_0}\Bigg[& f^0(x_2)+\kappa\left[\frac{dx_2}{dz}\right]^2\\ & -(c_1+c_2)[\mu_1^\alpha(1-x_2)+\mu_2^\alpha x_2]\Bigg]dz\ .\end{aligned} \tag{60}$$

The corresponding Euler equation becomes

$$2\kappa\left[\frac{d^2x_2}{dz^2}\right]-\left[\frac{\partial f^0}{\partial x_2}\right]_T-(c_1+c_2)(\mu_1^\alpha-\mu_2^\alpha)=0\ . \tag{61}$$

Consideration similar to that leading to Eq. (48) from Eq. (45) results in

$$-(c_1+c_2)(\mu_1^\alpha-\mu_2^\alpha)=\left[\frac{\partial f^0}{\partial x_2^\alpha}\right]_T=\left[\frac{\partial f^0}{\partial x_2^\beta}\right]_T\ , \tag{62}$$

where the condition that $\mu_1^\beta=\mu_1^\alpha$ and $\mu_2^\beta=\mu_2^\alpha$ is utilized. The boundary condition for Eq. (61) is given by

$$x_2=x_2^\alpha \text{ as } z\to\infty\ ,\quad x_2=x_2^\beta \text{ as } z\to-\infty\ . \tag{63}$$

IV. NUMERICAL EXAMPLE FOR THE REGULAR SOLUTION MODEL

A. Formulation

To study the numerical significance of the curvature dependence of the interfacial tension in binary systems, let us apply the present formalism to the regular-solution model. Cahn and Hilliard[6,8] developed the regular-solution model for the inhomogeneous system and obtained the coefficient κ of the gradient energy term in Eq. (37) as

$$\kappa=\omega\lambda^2/2v\ , \tag{64}$$

where

$$\omega=\frac{4\pi}{v}\int_0^\infty r^2\rho(r)\nu(r)dr\ , \tag{65}$$

$$\lambda^2=\frac{\int_0^\infty r^4\rho(r)\nu(r)dr}{3\int_0^\infty r^2\rho(r)\nu(r)dr}\ , \tag{66}$$

and

$$\nu(r)=u_{12}(r)-[u_{11}(r)+u_{22}(r)]/2. \tag{67}$$

ω is related to the critical temperature T_c by[8]

$$\omega=2kT_c\ , \tag{68}$$

where k denotes Boltzmann's constant. In Eqs. (65) and (66), $\rho(r)$ represents the reduced radial distribution function which is assumed to be independent of the composition, $u_{12}(r)$ in Eq. (67) represents the interaction potential between the first- and the second-component molecules at the distance r, and $u_{11}(r)$ and $u_{22}(r)$ represent similar quantities. The parameter λ represents the rms effective "interaction distance" for the energy.[6]

Helmholtz free-energy density $f^0(x_2)$ for the homogeneous system is given by

$$f^0(x_2)=(1-x_2)f_1^0+x_2f_2^0+(1/v)\{\omega x_2(1-x_2)+kT[x_2\ln x_2+(1-x_2)\ln(1-x_2)]\}\ , \tag{69}$$

where f_1^0 and f_2^0 denote the Helmholtz free-energy densities for the respective single-component systems at T. Chemical potentials μ_1^α and μ_2^α for the state defined by (T,p^α,x_2^α) are

$$\mu_1^\alpha=vf_1^0+\omega(x_2^\alpha)^2+kT\ln(1-x_2^\alpha)+p^\alpha v\ , \tag{70}$$

$$\mu_2^\alpha = vf_2^0 + \omega(1-x_2^\alpha)^2 + kT\ln x_2^\alpha + p^\alpha v \ . \tag{71}$$

Hence, $g(x_2)$ in Eq. (40) is given by

$$g(x_2) = (1-x_2)f_1^0 + x_2 f_2^0 + (1/v)\{\omega(1-x_2)(x_2^\alpha)^2 + \omega x_2(1-x_2^\alpha)^2 + kT[(1-x_2)\ln(1-x_2^\alpha) + x_2\ln x_2^\alpha]\} + p^\alpha \ . \tag{72}$$

The pressure p^β and the composition x_2^β for the bulk β phase can be obtained by equating the chemical potentials for the α and the β phases as

$$\omega(x_2^\alpha)^2 + kT\ln(1-x_2^\alpha) + p^\alpha v = \omega(x_2^\beta)^2 + kT\ln(1-x_2^\beta) + p^\beta v \ ,$$
$$\omega(1-x_2^\alpha)^2 + kT\ln x_2^\alpha + p^\alpha v = \omega(1-x_2^\beta)^2 + kT\ln x_2^\beta + p^\beta v \ . \tag{73}$$

Employing Eq. (68), Eq. (73) may be rewritten as

$$4(x_2^\alpha - x_2^\beta) + (T/T_c)\ln\frac{x_2^\beta(1-x_2^\alpha)}{x_2^\alpha(1-x_2^\beta)} = 0 \ , \tag{74}$$

$$p^\beta = p^\alpha + \frac{kT_c}{v}\left[2[(x_2^\alpha)^2 - (x_2^\beta)^2] + (T/T_c)\ln\frac{1-x_2^\alpha}{1-x_2^\beta}\right] . \tag{75}$$

From Eqs. (69) and (72) together with Eq. (68), $f^0 - g$ in Eqs. (41), (42), (44), and (60) is given by

$$f^0 - g = \frac{kT_c}{v}\left[2[x_2(1-x_2) - (1-x_2)(x_2^\alpha)^2 - x_2(1-x_2^\alpha)^2] + (T/T_c)\left[(1-x_2)\ln\frac{1-x_2}{1-x_2^\alpha} + x_2\ln\frac{x_2}{x_2^\alpha}\right]\right] - p^\alpha \ . \tag{76}$$

Since the last term $-p^\alpha$ in Eq. (76) does not affect the extremum property of either Φ or $\hat{\Phi}$ in Eq. (44) or Eq. (60), the equilibrium composition profile is not influenced by p^α. Substituting Eq. (76) into Eqs. (41) and (42), and considering Eqs. (51) and (75), we see that neither the location of the surface of tension nor the value of the surface tension depends on p^α. For a flat interface, p^β becomes identical to p^α due to Eq. (5) and Eq. (73) determines the equilibrium compositions for the α and the β phases, thus

$$x_2^\beta = 1 - x_2^\alpha \tag{77}$$

and x_2^α is to be determined by solving

$$2(2x_2^\alpha - 1) + (T/T_c)\ln\frac{1-x_2^\alpha}{x_2^\alpha} = 0 \ . \tag{78}$$

Due to Eq. (77), the location L of the dividing surface in Eq. (58) becomes

$$L = \frac{1}{1-2x_2^\alpha}\int_0^{z_0}(x_2 - x_2^\alpha)dz \ . \tag{79}$$

Substituting Eq. (79) into Eq. (59) and manipulating the results, we obtain

$$\gamma_\infty = \int_0^{z_0}\frac{kT_c}{v}\left[2x_2(1-x_2) + (T/T_c)[x_2\ln x_2 + (1-x_2)\ln(1-x_2)] + \lambda^2\left(\frac{dx_2}{dz}\right)^2 - 2x_2^\alpha(1-x_2^\alpha) - (T/T_c)[x_2^\alpha\ln x_2^\alpha + (1-x_2^\alpha)\ln(1-x_2^\alpha)]\right]dz \ . \tag{80}$$

We see from Eq. (80) that the value of γ_∞ is invariant against a shift of the interface along its normal direction. Note also that $\hat{\Phi}$ in Eq. (60) is invariant against a shift of the composition profile along the z axis because $f^0 - g$ is equal to $-p^\alpha$ in both the homogeneous α and the homogeneous β phases for a flat interface.

B. Numerical results

Since f_1^0 and f_2^0 in Eq. (69) do not influence the properties of our present interest, the system is characterized by the values of λ, r_i, and T_c, in which r_i denotes the average intermolecular distance. Following Cahn and Hilliard,[6] we assign the value $\sqrt{11/7}r_i$ to λ, which was obtained for the Lennard-Jones potential. To give the results wider generality, we normalize the distance and the temperature by r_i and T_c, respectively, and use the dimensionless quantities for the numerical work. Since p^α does not affect the results under the present model as already discussed, we assign zero to p^α for convenience. The phase diagram for the regular solution is shown in Fig. 2, which was calculated from Eqs. (77) and (78).

To obtain the equilibrium profiles, we employ the Rayleigh-Ritz method by assuming the following functional form for the solution:

$$x_2(r) = (x_2^\beta - x_2^\alpha)\frac{(e^{-\sigma\tau}+1)(e^{(r_0-\sigma)\tau}+1)}{e^{(r_0-\sigma)\tau} - e^{-\sigma\tau}} \times \left[\frac{1}{e^{(r-\sigma)\tau}+1} - \frac{1}{e^{(r_0-\sigma)\tau}+1}\right] + x_2^\alpha \ . \tag{81}$$

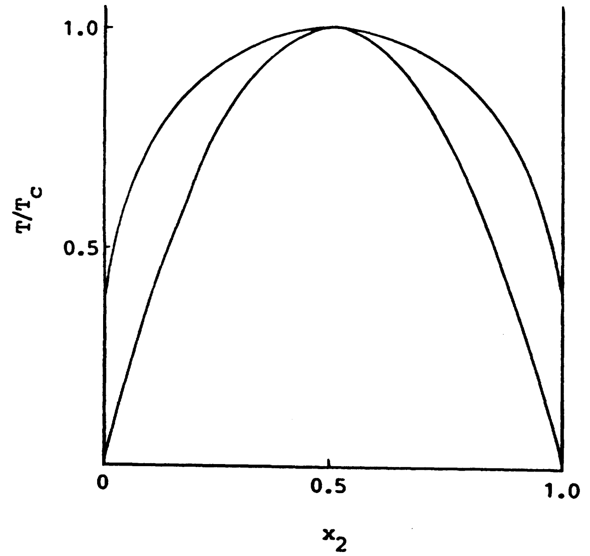

FIG. 2. Phase diagram for the regular solution.

It is assumed in Eq. (81) that the composition at $r=0$ is equal to the equilibrium value for the bulk β phase, x_2^β, obtained from Eq. (74) and the composition at $r=r_0$ is x_2^α for the bulk α phase. The value for r_0 is taken to be sufficiently large. Equation (81) cannot be applied for an extremely small nucleus in which the bulk composition x_2^β is not attained even at the center. The parameters σ and τ adjust, respectively, the size of the nucleus and the composition profile at the interfacial region. The value of those parameters are determined such that Φ in Eq. (44) takes an extremum value. An example of the numerical results is given in Fig. 3, where $\Delta\Phi$ represents the difference $\Phi(x_2)-\Phi(x_2^\alpha)$. Equation (81) is applied also to the flat interface, but $\hat{\Phi}$ in Eq. (60) is invariant for the variation of σ in this case and the value of τ is determined so as to make $\hat{\Phi}$ the minimum. The equilibrium composition profiles are shown in Figs. 4 and 5 for the two temperatures, $T/T_c=0.5$ and 0.8656.

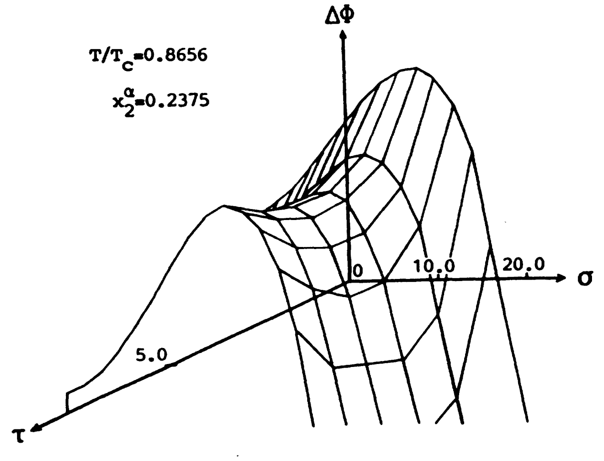

FIG. 3. Thermodynamic potential $\Delta\Phi$ to determine the equilibrium composition profile.

Once the composition profiles are determined, the radii of the surface of tension for the critical nuclei can be obtained by solving Eq. (50), and the results are shown also in Figs. 4 and 5. To obtain δ in the Gibbs-Tolman-Koenig equation, (26), the radius R^* of the auxiliary dividing surface must be calculated for the present regular solution model. Due to the assumption that the molecular volume is independent of the composition, we have

$$\Gamma_1^*+\Gamma_2^*=0 . \tag{82}$$

It follows for the regular solution that

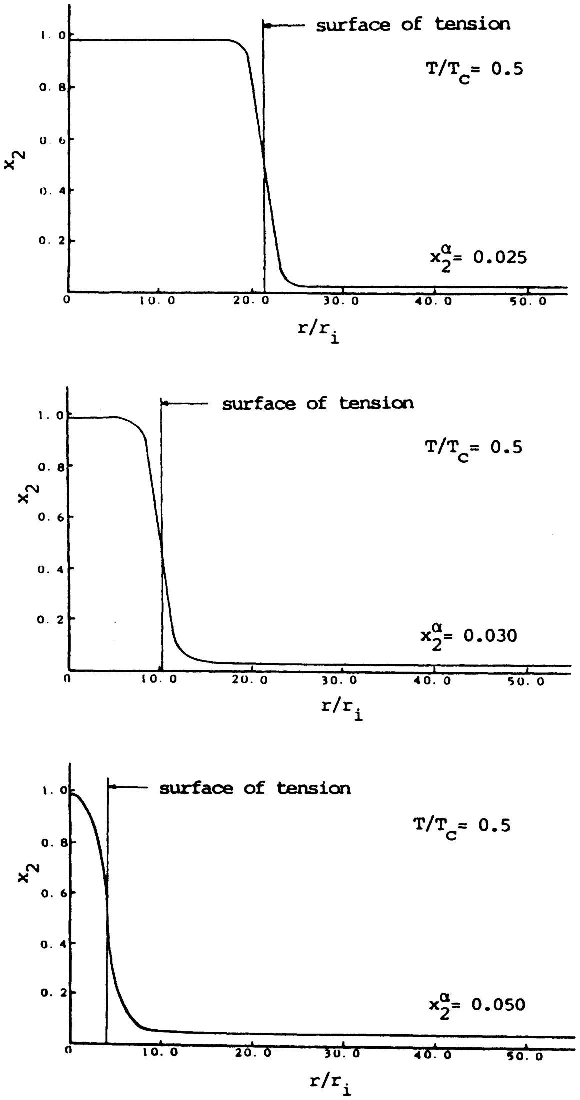

FIG. 4. Equilibrium composition profiles and the locations of the surface of tension at $T/T_c=0.5$.

$$w_1-w_2=4kT_c\left[\frac{\partial x_2^\alpha}{\partial p^\beta}\right]_{T,p^\alpha}\left[1+\frac{T/T_c}{4x_2^\alpha(x_2^\alpha-1)}\right] . \tag{83}$$

Since the RHS of Eq. (83) is nonzero in the range $x_2^e < x_2 < x_2^s$, where x_2^e and x_2^s denote the equilibrium and the spinodal compositions, Eqs. (10) and (82) result in

$$\Gamma_1^*=\Gamma_2^*=0 . \tag{84}$$

Thus it follows from Eq. (12) that

$$R^*=\left[\left[3\int_0^{r_1}(x_2-x_2^\alpha)r^2dr\right]/(x_2^\beta-x_2^\alpha)\right]^{1/3} , \tag{85}$$

where r_1 may be taken arbitrarily within the homogeneous α phase. Since R and R^* are known, δ can be calculated and the results are shown in Fig. 6.

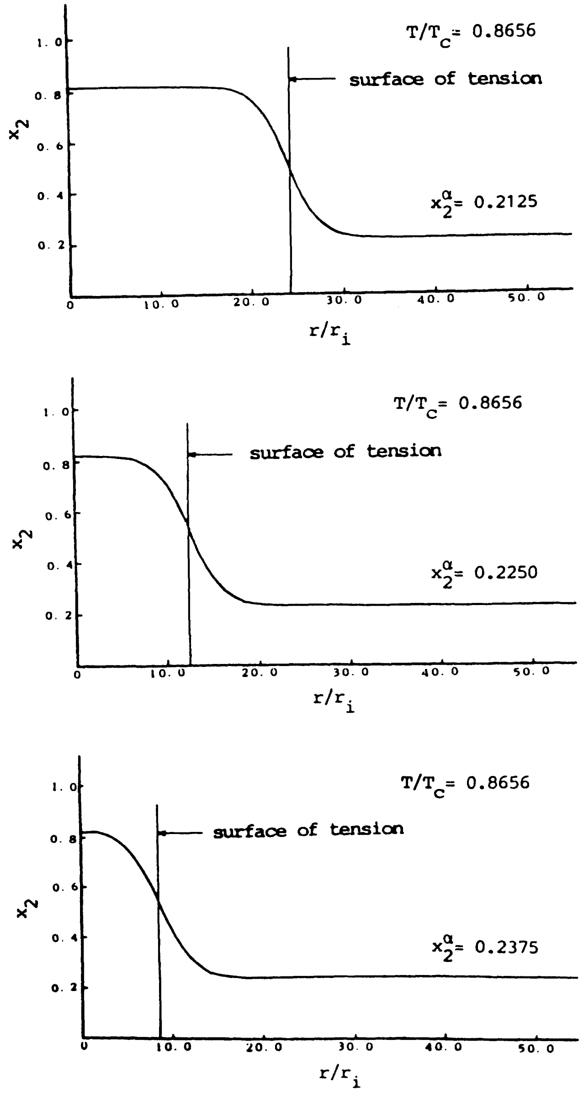

FIG. 5. Equilibrium composition profiles and the locations of the surface of tension at $T/T_c=0.8656$.

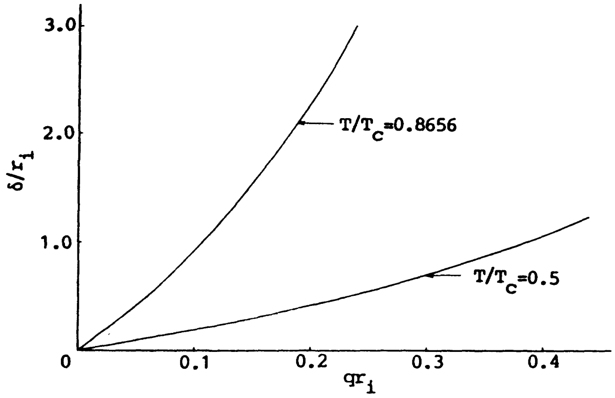

FIG. 6. Curvature dependence of δ at $T/T_c=0.5$ and 0.8656.

Although the present formulas are applicable also to the flat interface as a limit, separate consideration for the flat interface is desirable to improve the numerical accuracy. In the limit of the flat interface, Eq. (42) becomes

$$\int_{-a}^{b}\left[f^0+p^\alpha-g+\kappa\left[\frac{dx_2}{d\xi}\right]^2\right]\xi\,d\xi=0 , \tag{86}$$

and the location of the surface of tension is determined as the origin of the ξ-axis which satisfies this equation. Suppose that the surface of tension is located at the position where $x_2=0.5$. We assume the composition profile to be in the form of Eq. (81), but we change the coordinate from r to $\xi=r-R$ and assign R to σ. Assigning, further, large values to R and r_0-R to conform to the flat interface, we finally obtain

$$x_2(\xi)=x_2^\alpha+\frac{1-2x_2^\alpha}{e^{\tau\xi}+1} , \tag{87}$$

in which Eq. (77) is utilized. $x_2(\xi)$ in Eq. (87) possesses the property

$$x_2(-\xi)=1-x_2(\xi) , \tag{88}$$

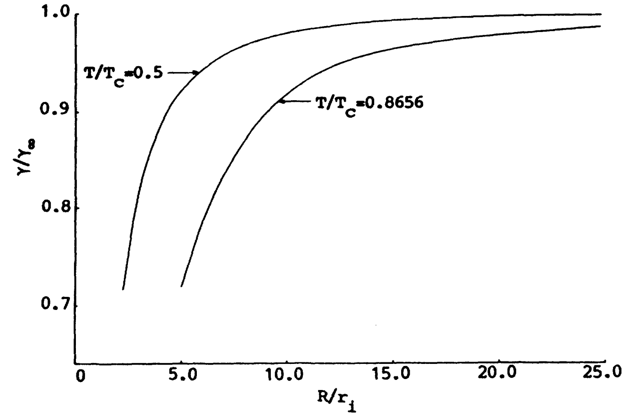

FIG. 7. Curvature dependence of the interfacial tension at $T/T_c=0.5$ and 0.8656.

and $(dx_2/d\xi)$ is shown to be an even function. Noting Eq. (78), we can show that

$$f^0(x_2)+p^\alpha-g(x_2)=f^0(1-x_2)+p^\alpha-g(1-x_2)\ . \quad (89)$$

Equations (88) and (89) indicate that $f^0+p^\alpha-g$ is an even function, hence Eq. (86) is satisfied by the present choice for the origin. That is, for the flat interface, the surface of tension is located at the position where $x_2=0.5$. If follows from Eqs. (77), (88), and the relation similar to Eq. (82) that

$$\Gamma_1=\Gamma_2=0\ . \quad (90)$$

Equations (84) and (90) result in

$$\delta=0 \quad (91)$$

for the flat interface under the present model. This result is utilized in Fig. 6.

The Gibbs-Tolman-Koenig equation (26) was integrated numerically by making use of δ in Fig. 6, and the results are given in Fig. 7. The interfacial tension of the flat interface, γ_∞, was calculated from Eq. (80) and the results were used to determine the integration constant of Eq. (26). The values of γ_∞ are $0.703kT_cr_i/v$ at $T/T_c=0.5$ and $0.118kT_cr_i/v$ at $T/T_c=0.8656$, respectively. The interfacial tension γ can also be calculated from Eq. (41), and the values thus obtained are consistent with those in Fig. 7. Since the RHS of Eq. (54) may be rewritten as $R(p^\beta-p^\alpha)/2$ by a mathematical manipulation, γ can be calculated also from the Laplace equation,

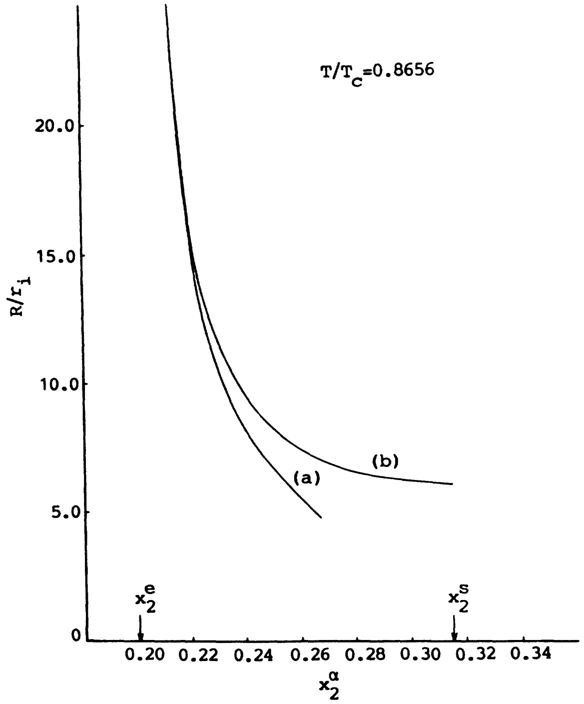

FIG. 9. Radius of the critical nucleus vs supersaturation at $T/T_c=0.8656$. x_2^e and x_2^s denote the equilibrium composition and the spinodal composition, respectively. Curve (*a*), present theory. Curve (*b*), obtained from $R_\infty=2\gamma_\infty/(p^\beta-p^\alpha)$.

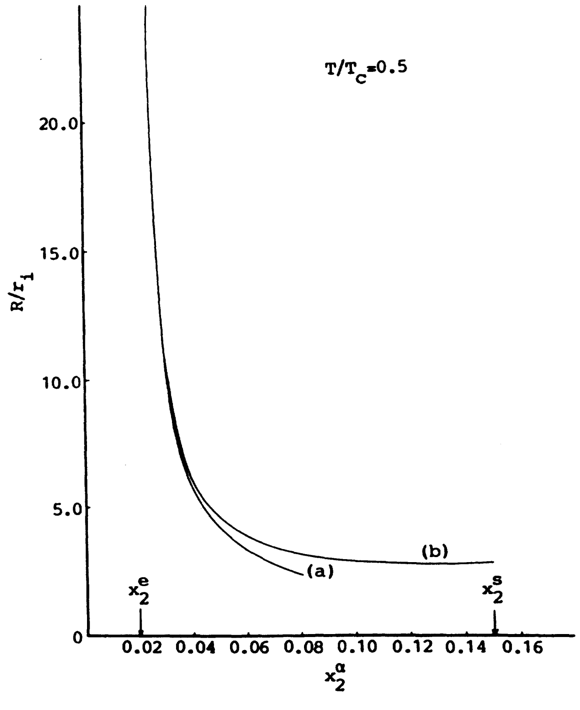

FIG. 8. Radius of the critical nucleus vs supersaturation at $T/T_c=0.5$. x_2^e and x_2^s denote the equilibrium composition and the spinodal composition, respectively. Curve (*a*), present theory. Curve (*b*), obtained from $R_\infty=2\gamma_\infty/(p^\beta-p^\alpha)$.

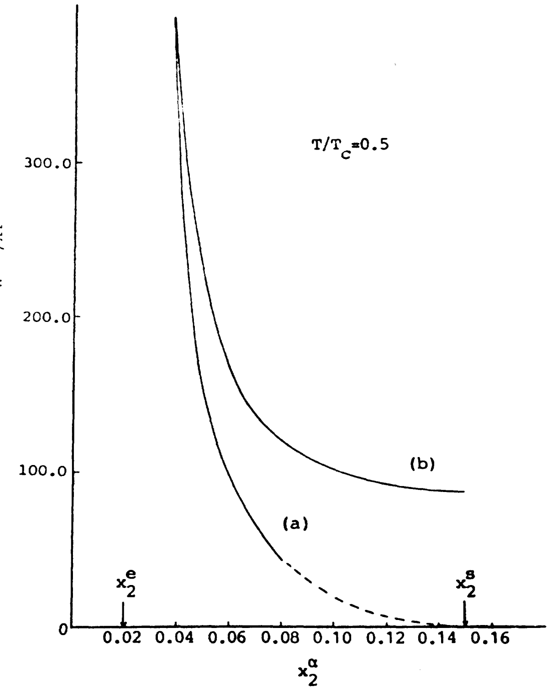

FIG. 10. Reversible work to form a critical nucleus vs supersaturation at $T/T_c=0.5$. Curve (*a*), present theory. Curve (*b*), obtained from $W^{\rm rev}=4\pi R_\infty^2\gamma_\infty/3$.

as it should be.

To predict the reversible work of forming a critical nucleus under a given state $(T,p^{\alpha},x_2^{\alpha})$ of the parent phase, we first evaluate p^{β} from the conditions $\mu_i^{\beta}=\mu_i^{\alpha}$, $i=1,2$, then calculate R from the Laplace equation (5) by employing the knowledge we have on γ. When the curvature dependence of γ is properly taken into consideration, we of course get the values indicated in Figs. 4 and 5. If the curvature dependence of γ is neglected and γ_{∞} is used throughout the size range, the radius of a critical nucleus thus predicted, which is denoted as R_{∞}, will be incorrect. As seen in Figs. 8 and 9, the discrepancy becomes significant as the degree of supersaturation is increased. The reversible work W^{rev} to form a critical nucleus is given by[4]

$$W^{\text{rev}}=4\pi R^2\gamma/3\ , \tag{92}$$

and, in Figs. 10 and 11, the values predicted by the present theory, which are denoted as (*a*), are compared with those obtained by neglecting the curvature dependence of γ, which are denoted as (*b*). Dashed parts of the curves are extrapolations to the size range of the nuclei in which no homogeneous state exists, even at the center. The present formalism must be extended to deal with this size range.

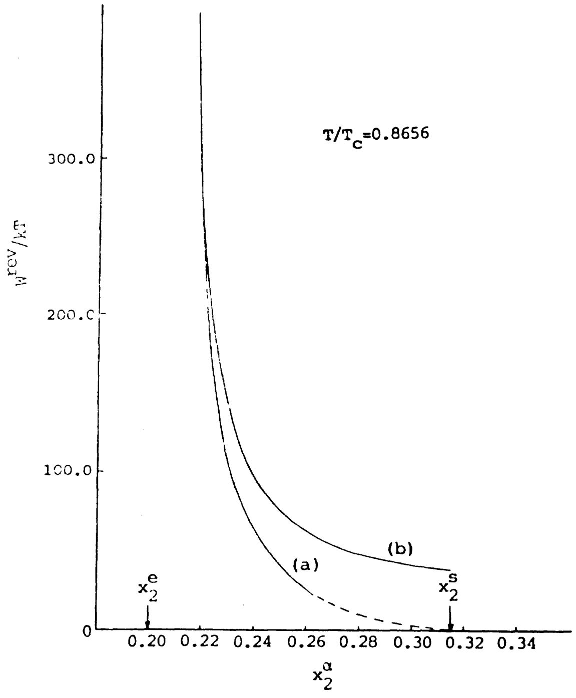

FIG. 11. Reversible work to form a critical nucleus vs supersaturation at $T/T_c=0.8656$. Curve (*a*), present theory. Curve (*b*), obtained from $W^{\text{rev}}=4\pi R_{\infty}^2\gamma_{\infty}/3$.

V. DISCUSSION

The Rayleigh-Ritz method was employed in the present work to obtain the equilibrium composition profiles due to the difficulty in solving the nonlinear differential equations (48) and (61). Although the assumed functional form (81) seems to be reasonable, it is difficult to estimate the error involved.

The most striking feature of the numerical results is the large discrepancy in the reversible work to form a critical nucleus between the values predicted by the present theory and those obtained by using γ_{∞} throughout. Solid curves in Figs. 10 and 11 signify the results for the sufficiently large nuclei in which the homogeneous state is regarded to be retained at least in the central region. As for the largest discrepancy in this size range of the nucleus, the value of $\exp(-W^{\text{rev}}/kT)$ predicted by the present theory is about 10^{32} times larger than that of the curve (*b*) for $T/T_c=0.5$ and about 10^{16} times larger for $T/T_c=0.8656$. Thus neglect of the curvature dependence of the interfacial tension may severely underestimate the nucleation rate because it is proportional to $\exp(-W^{\text{rev}}/kT)$. Moreover, the present theory seems to predict, when extrapolated as indicated by the dashed curves, the vanishingly small reversible work as the spinodal composition is approached. This feature is consistent with that found by Cahn and Hilliard.[8]

The present theory is concerned with the situation where supersaturation is attained by changing the composition of the parent phase under a given temperature and a pressure. Whereas, supersaturation is achieved more often by lowering the temperature under a given composition and a pressure, and the critical degree of undercooling is the quantity of interest. To cope with this situation, the Gibbs-Tolman-Koening equation (26) must be reformulated. However, the formulas in Secs. III and IV are all valid for a general state of the parent phase, thus the critical degree of undercooling can be investigated by using those formulas. This project, including the reformulation of the Gibbs-Tolman-Koenig equation, is left for a future work.

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