Free Energy of a Nonuniform System. III. Nucleation in a Two-Component Incompressible Fluid

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By finding the saddle point in the expression derived in Paper I (see reference 8) for the free energy of a nonuniform system, we have derived the properties of a critical nucleus in a two-component metastable fluid.

At very low supersaturations, we find that the properties of the nucleus approach those predicted by the classical theory that assumes the nucleus to be homogeneous with an interfacial energy that does not vary with curvature. However, with increasing supersaturation, the following changes occur in the properties of the critical nucleus. (a) The work required for its formation becomes progressively less than that given by the classical theory, and approaches continuously to zero at the spinodal. (b) The interface with the exterior phase becomes more diffuse until eventually no part of the nucleus is even approximately homogeneous. (c) The composition at the center of the nucleus approaches that of the exterior phase. (d) The radius and excess concentration in the nucleus at first decrease, then pass through a minimum and become infinite again at the spinodal.

These properties are deduced without resort to any specific solution model. In addition, they are evaluated for a regular solution to permit a quantitative comparison with the predictions of previous treatments.

1. INTRODUCTION

IN this paper we will be considering the stability of an incompressible homogeneous fluid that is unstable in the presence of a bulk quantity of a second, more stable phase. We will first have to determine whether the original phase is metastable; that is whether it is stable with respect to all possible infinitesimal changes in the absence of the second phase. If this is so, then there will be a nucleation barrier to the transformation to the more stable phase. It is our purpose to estimate the height of this barrier by calculating the minimum work required to place the original phase in a state from which it can thereafter transform spontaneously.

In his classic treatment of stability of phases, Gibbs[1] separated into two categories the infinitesimal changes to which a metastable phase must be resistant. One is a change that is infinitesimal in degree but large in extent, as exemplified by a small composition fluctuation spread over a large volume. If a phase is unstable with respect to such a fluctuation, then there is no barrier θother than a diffusional one$_q$ to a continuous transformation to the more stable phase. Gibbs formulated the general conditions necessary for this type of instability. Specifically, it can be shown that a two-component solution will transform spontaneously, if $(\partial^2 G/\partial c^2)_{T,P} < 0$, where G is the Gibbs free energy per mole of solution and c the composition. On a phase diagram, the boundary of the unstable region is defined by the locus of $(\partial^2 G/\partial c^2)_{T,P} = 0$ and is usually called the spinodal.

The second category of changes considered by Gibbs are those that are large in degree but small in extent, an example being that of an infinitesimal droplet of material with properties approaching those of the more stable phase. A metastable phase is always stable with respect to the formation of such a droplet provided it has a positive surface tension. Between the extremes of an infinitesimal droplet and a bulk quantity of the more stable phase, there is a critical-size droplet which is in unstable equilibrium with the exterior phase. With any further infinitesimal increase in size, such a droplet (or critical nucleus) can continue to grow without any further external intervention.

Gibbs recognized that a critical nucleus might be so small that no part of it could be homogeneous. Nevertheless, because of his definition of surface tension, he was able to develop a self-consistent formulation for the properties of a critical nucleus as if it were homogeneous up to a sharp boundary with the exterior phase. The reason why he resorted to this artificial model was to allow application of thermodynamic principles that had been developed for homogeneous phases. In particular, the requirement that the chemical potential of each component be constant throughout a system in stable or unstable equilibrium uniquely determines the composition and pressure of a homogeneous critical nucleus. The difference in pressure, ΔP, between the nucleus and the exterior phase is also equal to the decrease in Helmholtz free energy accompanying the formation of a unit volume of bulk nucleus material, at the pressure and composition at which it will be in equilibrium with the exterior phase. (It should be noted that the change in the Gibbs free energy is zero under these conditions.)

In order to preserve hydrostatic equilibrium, the radius r of the critical nucleus must be such that

$$\Delta P = 2\sigma/r, \qquad (1.1)$$

where σ is a suitably defined surface tension. If the

[1] J. W. Gibbs, *Collected Works* (Yale University Press, New Haven, Connecticut, 1948), Vol. 1, pp. 105–115, 252–258.

radius of the droplet is greater than r, the pressure exerted by the surface is insufficient to prevent the growth of the droplet. On the other hand, a droplet having a radius less than r will collapse because the pressure exerted by the surface is then greater than ΔP.

Having fixed the size, composition, and pressure of the critical nucleus, Gibbs[2] obtained the following expressions for the minimum work required for its formation:

$$W = 4\pi r^2 \sigma - (4\pi/3) r^3 \Delta P, \qquad (1.2)$$

$$W = (16\pi/3) [\sigma^3/(\Delta P)^2], \qquad (1.3)$$

$$= (2\pi/3) r^3 \Delta P, \qquad (1.4)$$

$$= (4\pi/3) r^2 \sigma. \qquad (1.5)$$

The last three forms are obtained from Eq. (1.2) by the successive elimination of r, σ, and ΔP by means of Eq. (1.1).

In what we shall hereafter refer to as the "classical" treatment of nucleation, these equations have been used with σ set equal to the tension of a flat interface between the two coexisting stable phases and a ΔP corresponding to the increase in pressure required to maintain bulk nucleus material in equilibrium with the exterior phase. Such a procedure, however, is strictly correct only for the limiting case when ΔP approaches zero. For finite values of ΔP, the Eqs. (1.1)–(1.5) provide, in effect, nothing more than a definition of r and σ in terms of ΔP and W. Gibbs was well aware of this limitation, but he was not particularly concerned by it, since he believed that as long as W was positive, a phase could remain indefinitely in a metastable state. He was interested, therefore, only in establishing the sign of W, and for this purpose his treatment was sufficient.

However, it was subsequently recognized that a critical nucleus can be formed by thermal fluctuations if W is less than, say, 60 kT. Thus to predict the actual limit of metastability, an absolute evaluation of W is required. The previous work on this problem has been reviewed by others.[3,4] For the present we need to note only that most previous treatments have been based on the classical theory referred to earlier, or on a modification in which a correction is made for the variation of surface tension with either composition[5] or curvature.[6] In most instances (see Discussion) these treatments predict the persistence of a barrier to transformation within the spinodal, a result which is contrary to that reached by Gibbs. However, others (e.g., Borelius[7]) have taken the view that the actual limit of stability is coincident with the spinodal.

Our own approach is based on an expression previously derived[8] for the free energy of a nonuniform system. This expression permits the properties of a critical nucleus to be calculated without any assumption about its homogeneity. In addition, it is unnecessary to divide the energy of a nucleus into a surface and volume term.

In order to simplify the thermodynamics, we have chosen to limit the present treatment to a system in which the partial molar volumes are independent of composition and pressure. However, this restriction is not necessary and we intend to give the more general treatment in a subsequent paper. In anticipation of this later work, it may be stated that present results will remain satisfactory approximations for many practical systems.

We shall be concerned only with the thermodynamics of nucleation and not with its application to kinetic theory. In the next two sections we shall develop the general properties of the critical nucleus, postponing to Sec. 4 the introduction of a specific solution model.

2. DETERMINATION OF SADDLE POINT

In an earlier paper,[8] to which we shall hereafter refer as paper I, it was demonstrated that the free energy of a small element of a solution having a spatial variation in composition can be represented by the sum of two terms; one being the free energy that the element would have if surrounded by material of the same composition as itself, and the other, a term which to a first approximation is proportional to the square of the composition gradient. Hart[9] has subsequently developed an alternative treatment of inhomogeneous systems. In a comparison of the two treatments, Cahn[10] demonstrated that they lead to identical results. Apart from a slight change in notation,* we shall, therefore, retain the formulation of paper I.

For the Helmholtz free energy of a two-component system which is both incompressible and isotropic we have

$$F = \int_V [f'(c) + \kappa(\nabla c)^2] dV, \qquad (2.1)$$

where $f'(c)$ is the Helmholtz free energy per unit volume of a homogeneous system of composition c, and $\kappa(\nabla c)^2$ is a gradient energy which is defined† as

[2] Reference 1, p. 254.
[3] J. H. Hollomon and D. Turnbull, Prog. in Metal Phys. **4**, 333 (1953).
[4] R. S. Bradley, Quart. Revs. (London) **5**, 315 (1951).
[5] R. Becker, Ann. phys. **32**, 128 (1938).
[6] F. P. Buff and J. G. Kirkwood, J. Chem. Phys. **18**, 991 (1950).
[7] G. Borelius, Arkiv. Mat. Astron. Fys. **A32**, 1 (1945).

[8] J. W. Cahn and J. E. Hilliard, J. Chem. Phys. **28**, 258 (1958).
[9] E. W. Hart, Phys. Rev. **113**, 412 (1959).
[10] J. W. Cahn, J. Chem. Phys. **30**, 1121 (1959).
* In paper I, Δf and other quantities were defined in terms of a change *per atom*. However, starting with paper II, it has been found to be more convenient to use quantities based on a unit volume. In addition, a prime instead of a subscript zero is now being employed to denote the value of a quantity in the absence of a gradient.

† This particular definition was introduced in Paper II to facilitate comparison with the treatment of Hart.[9] It automatically includes all the gradient-energy terms in the expansion given in paper I.
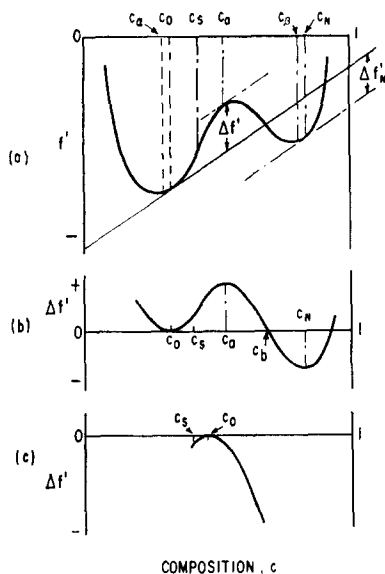
FIG. 1. (a) Helmholtz free energy, f', of a homogeneous two-component fluid. $\Delta f'$ is the difference between the curve f' and the line tangent to it at c_0. (b) $\Delta f'$ for $c_0 < c_s$. (c) $\Delta f'$ for $c_0 > c_s$. (c_0, initial composition of fluid; c_s, spinodal; c_m, composition of classical nucleus; c_α and c_β, compositions of coexisting stable phases.)

COMPOSITION, c

the difference between f' and the actual free-energy density. For small gradients, κ is approximately independent of the gradient and is given‡ by

$$\kappa = -[\partial^2 f/\partial c \partial \nabla^2 c]' + (\tfrac{1}{2})[\partial^2 f/(\partial \mid \nabla c \mid)^2]', \quad (2.2)$$

in which the prime denotes that the derivatives are to be evaluated for the limit of small ∇c and $\nabla^2 c$.

Equation (2.1) holds true for any composition fluctuation. It has many of the properties to be expected in a nucleation treatment. For small composition fluctuations $[c < c_a$ in Fig. 1(a)$]$ which keep the average composition of a metastable system constant, F increases irrespective of the spatial extent of the fluctuation. But with increasing difference in composition between the exterior phase and the fluctuation, the integrated value of f' eventually decreases faster than the gradient-energy contribution increases. When this happens, there is no further impediment to a continuous growth of the fluctuation.

There are infinitely many paths by which an initially unstable fluctuation can grow into a stable one, but we are interested only in those paths going over the lowest free-energy barrier. The top of such a barrier is a saddle point and it is here that a fluctuation becomes a critical nucleus. At the saddle point the system is in equilibrium (although an unstable one). Consequently, for a closed system at constant temperature and volume, the Helmholtz free energy must be stationary with respect to a change in composition at any point in the system. The form of the critical nucleus is thus defined by the functional dependence of composition on position that yields an extremal of Eq. (2.1) subject to the condition that the average composition remain constant, or

$$\int_V (c - c_0) dV = 0, \quad (2.3)$$

where c_0 is both the initial and average composition. Application of the Euler equation to Eq. (2.1) and neglecting the higher order gradient terms, yields as the requirement for an extremal in F,

$$2\kappa\nabla^2 c + (\partial\kappa/\partial c)(\nabla c)^2 = \partial f'/\partial c + \lambda,$$

where λ is a Lagrangian multiplier introduced by the subsidiary condition Eq. (2.3). If we assume, as did Gibbs,[1] that the system is sufficiently large for there to be a negligible change§ in the composition of the exterior phase during nucleation, then λ is readily identified with $-(\partial f'/\partial c)_{c=c_0}$, so that the Euler equation becomes

$$2\kappa\nabla^2 c + (\partial\kappa/\partial c)(\nabla c)^2 = (\partial f'/\partial c) - (\partial f'/\partial c)_{c=c_0}. \quad (2.4)$$

The solution to this equation, subject to the necessary boundary conditions, describes the spatial compositional variation in a critical nucleus.

We will now consider the work, W, required to form a critical nucleus. For a closed system at constant temperature and volume, W is given by the change in F accompanying the formation of a critical nucleus in an initially homogeneous solution. Thus

$$W = \int_V [f'(c) - f'(c_0) + \kappa(\nabla c)^2] dV, \quad (2.5)$$

where c must satisfy the Euler equation, (2.4). It is convenient to express the first two terms of the integrand in terms of a quantity $\Delta f'$, defined, as shown in Fig. 1(a), by

$$\Delta f' = f'(c) - f'(c_0) - (c - c_0)(\partial f'/\partial c)_{c=c_0}. \quad (2.6)$$

By substituting Eq. (2.6) in (2.4) and (2.5), and applying Eq. (2.3), we obtain

$$W = \int_V [\Delta f' + \kappa(\nabla c)^2] dV, \quad (2.7)$$

and

$$2\kappa\nabla^2 c + (\partial\kappa/\partial c)(\nabla c)^2 = \partial\Delta f'/\partial c. \quad (2.8)$$

The essential difference between these equations and those of the classical theory is that no assumption is made here about the homogeneity of the nucleus.

For an isotropic system, or one having cubic symmetry (and these are the only cases that we shall be considering), the critical nucleus will be spherically symmetric. Thus Eqs. (2.7) and (2.8) can be re-

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‡ The factor of $(\tfrac{1}{2})$ in the second term of Eq. (2.2) was inadvertently omitted in the definition given in paper I.

§ It will be shown in Paper IV that the error in W introduced by this assumption is of the order of the reciprocal of the total volume of the system.

written in terms of the radius, r

$$W = 4\pi \int_0^\infty [\Delta f' + \kappa (dc/dr)^2] r^2 dr, \qquad (2.9)$$

and

$$2\kappa (d^2c/dr^2) + (4\kappa/r)(dc/dr) + (\partial \kappa/\partial c)(dc/dr)^2$$
$$= (\partial \Delta f'/\partial c). \qquad (2.10)$$

To be physically acceptable, solutions of Eq. (2.10) have to satisfy the following boundary conditions:

$$dc/dr = 0 \quad \text{at} \quad r = 0 \quad \text{and} \quad r = \infty, \qquad (2.11)$$

and

$$c = c_0 \quad \text{at} \quad r = \infty. \qquad (2.12)$$

For a one-dimensional composition variation across a flat interface, $r = \infty$ and the $(2/r)(dc/dr)$ term in Eq. (2.10) vanishes. It is then possible, as shown in Paper I, to integrate this equation, thereby obtaining an expression for the interfacial free energy that contains only $\Delta f'$ and κ. However, for a nucleus, it is necessary first to solve Eq. (2.10) for the composition variation $c(r)$ which then can be substituted in Eq. (2.9) to evaluate W. When κ is independent of composition, the computation is facilitated by expressing Eq. (2.9) in the form

$$W = 4\pi \int_0^\infty \{ \Delta f' - [(c - c_0)/2](\partial \Delta f'/\partial c) \} r^2 dr. \qquad (2.13)$$

This transformation is accomplished by use of the divergence theorem in conjunction with Eqs. (2.7), (2.8), and (2.11).

3. GENERAL PROPERTIES OF THE CRITICAL NUCLEUS

In this section we shall demonstrate that certain properties of the critical nucleus can be deduced without introducing any specific solution model for the evaluation of $\Delta f'$. We shall first consider those properties which are determined by the form of the Euler equation, and then examine the functional dependence of W for three limiting cases, in two of which $\Delta f'$ can be expanded in a power series.

A. Properties Determined by the Form of the Euler Equation

Property I. $\Delta f'$ of the Material at the Center of the Nucleus is Negative

This is more restrictive than the obvious condition that $(\partial \Delta f'/\partial c)_{r=0}$ be negative.[7] The material at the center of the nucleus not only has to have reached the composition c_a (Fig. 1) at which its free energy decreases with increasing c, but it must already be stable (i.e., $c > c_b$) with respect to the matrix material.

Proof.—Integrating Eq. (2.10) with respect to c

from the center of the nucleus to infinity we obtain

$$\int_0^\infty [\kappa (d^2c/dr^2)(dc/dr) + (2\kappa/r)(dc/dr)^2$$
$$+ \tfrac{1}{2}(d\kappa/dc)(dc/dr)^3] dr$$
$$= \tfrac{1}{2}[\Delta f'(r = \infty) - \Delta f'(r = 0)]. \qquad (3.1)$$

But, by virtue of boundary conditions Eqs. (2.11) and (2.12),

$$\int_0^\infty [\kappa (d^2c/dr^2)(dc/dr) + \tfrac{1}{2}(d\kappa/dc)(dc/dr)^3] dr$$
$$= [(\kappa/2)(dc/dr)^2]_0^\infty = 0,$$

and

$$\Delta f'(r = \infty) = 0.$$

Hence Eq. (3.1) reduces to

$$\int_0^\infty (2\kappa/r)(dc/dr)^2 dr = -\tfrac{1}{2}\Delta f'(r = 0); \qquad (3.2)$$

thus, since the integrand is always positive,

$$\Delta f'(r = 0) < 0.$$

Property II. At low supersaturation, i.e., as $c_0 \pm c_\alpha$ the critical nucleus resembles that of the classical theory in the following respects.

(a) *The composition, c_n, at the center of the nucleus approaches the equilibrium composition c_β.*

Proof.—From property I, we know that

$$c_n > c_b \quad \text{but, as} \quad c_0 \to c_\alpha, \quad c_b \to c_\beta.$$

Hence

$$c_n \to c_\beta.$$

(b) *The specific free energy associated with the interface approaches that of a flat interface.*

Proof.—Changing the variable of integration in Eq. (3.2) from r to c, we obtain

$$\int_{c_n}^{c_0} (2\kappa/r)(dc/dr) dc = -\tfrac{1}{2}\Delta f'(c_n) \to 0, \quad \text{as} \quad c_0 \to c_\alpha. \qquad (3.3)$$

Since $(2/r)(dc/dr)$ is everywhere negative, it must also approach zero and therefore can be neglected in comparison with the other term which remains finite in Eq. (2.10). Thus as $c_0 \to c_\alpha$, this equation reduces to

$$2\kappa (d^2c/dx^2) + (\partial \kappa/\partial c)(dc/dx)^2 = \partial \Delta f'/\partial c,$$

which can be integrated to give

$$\kappa (dc/dx)^2 = \Delta f', \qquad (3.4)$$

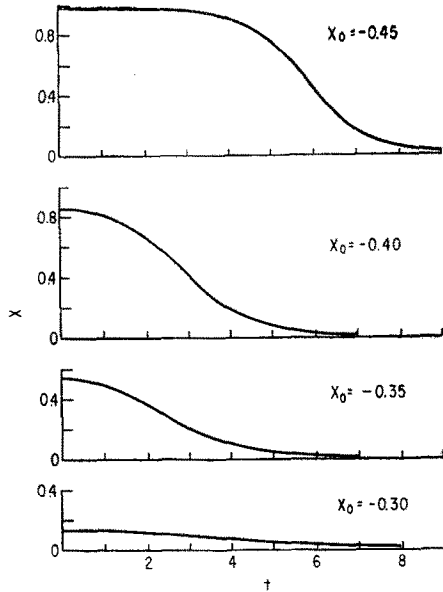where x is a linear distance. In Paper I, it was shown that Eq. (3.4) describes the composition variation

FIG. 2. Normalized composition profiles of the critical nucleus in the region $T \sim T_c$.

across a flat interface having a specific free energy σ, given by

$$\sigma = 2 \int_{-\infty}^{+\infty} \kappa (dc/dx)^2 dx,$$

$$= 2 \int_{-\infty}^{+\infty} \Delta f' dx. \quad (3.5)$$

(c) *The radius of the nucleus approaches infinity.*

Proof.—Applying the mean value theorem to Eq. (3.2) and comparing the result with Eq. (3.5) we find

$$\bar{r} = -2\sigma/\Delta f'(r=0),$$

where $\bar{r}$ is a mean radius of the nucleus surface. But, according to Eq. (3.3), $\Delta f'(r=0) = 0$ as $c_0 \to c_\alpha$, therefore $\bar{r} \to \infty$ as $c_0 \to c_\alpha$.

The preceding equation for $\bar{r}$ can be considered analogous to the Kelvin relationship Eq. (1.1) since, if the nucleus is homogeneous in the vicinity of $r=0$, then $-\Delta f'(r=0)$ is the pressure difference between the exterior phase and the center of the nucleus.

B. Properties near the Critical Temperature

In Eq. (2.20) of Paper I, it was shown that near the critical temperature T_c, the free energy f' of a homogeneous solution could be expanded about the critical composition c_c to give

$$f'(X) - f'(X_\alpha) - (X - X_\alpha)(\partial f'/\partial X)_{X=X_\alpha}$$

$$= \gamma(c_\alpha - c_c)^4 (1 - 4X^2)^2, \quad (3.6)$$

where

$$\gamma = (\partial^4 f'/\partial c^4)_{\text{crit.}}/4!, \quad (3.7)$$

$$X = (c - c_c)/2(c_\alpha - c_c), \quad (3.8)$$

and c_α is the equilibrium composition. It also was shown that c_α is related to T by

$$4\gamma[(c_\alpha - c_c)^2]_{T \sim T_c} = (T_c - T)(\partial^3 f'/\partial T \partial c^2)_{\text{crit.}}. \quad (3.9)$$

Substitution of Eq. (3.6) in Eq. (2.6) gives

$$\Delta f' = \gamma(c_\alpha - c_c)^4 [(1 - 4X^2)^2 - (1 - 4X_0^2)^2$$
$$+ 16(4X_0^3 - X_0)(X_0 - X)], \quad (3.10)$$

and hence, by differentiation,

$$\partial \Delta f'/\partial c = \tfrac{1}{2}(c_\alpha - c_c)^{-1}(\partial \Delta f'/\partial X)$$

$$= 8\gamma(c_\alpha - c_c)^3 [(4X^3 - X) - (4X_0^3 - X_0)]. \quad (3.11)$$

Providing that $\partial \kappa/\partial c$ remains finite at the critical point, or its square is less than order $[1/(c_c - c_\alpha)]^2$ then, sufficiently close to the critical point, the term in $\partial \kappa/\partial c$ in the Euler equation [Eq. (2.10)] can be neglected. Furthermore, ν can be assumed to have a constant value $\kappa_c{}^5$.

To reduce the Euler equation to a dimensionless form, it is convenient to introduce the following parameter in place of the radial distance, r,

$$t = [2\gamma(c_\alpha - c_c)^2/\kappa_c]^{\frac{1}{2}} r. \quad (3.12)$$

Changing the variables in Eq. (2.10) by means of Eqs. (3.8), (3.11), and (3.12), we obtain for the Euler equation

$$(d^2X/dt^2) + (2/t)(dX/dt)$$

$$- [(4X^3 - X) - (4X_0^3 - X_0)] = 0. \quad (3.13)$$

After substituting Eqs. (3.10), (3.11), and (3.12) in Eq. (2.13), we obtain for the work, W_c, of nucleation in the vicinity of the critical point

$$W_c = [32\pi\kappa_c{}^{\frac{3}{2}}/(2\gamma)^{\frac{1}{2}}](c_\alpha - c_c)I_c; \quad (3.14)$$

where I_c is the value of the integral

$$I_c = \int_0^\infty (X_0 + X)(X_0 - X)^3 t^2 dt, \quad (3.15)$$

where X must satisfy Eq. (3.13) and is subjected to the boundary conditions Eqs. (2.11) and (2.12). An analog computer was used in order to obtain solutions of Eq. (3.13) for several values of X_0 between the equilibrium composition $X_\alpha = -\tfrac{1}{2}$ and the spinodal $X_s = -\tfrac{1}{12}^{\frac{1}{2}}$. (The latter value is obtained by equating the derivative of Eq. (3.11) to zero and solving for X.) It will be seen from the solutions shown in Fig. 2, that as the composition of the initial phase approaches the spinodal, the interface of the nucleus becomes progressively more diffuse and, at the same time, the excess composition at the center of the nucleus approaches zero. The corresponding variation in I_c [as computed from Eq.

(3.15)] is depicted in Fig. 3. The integral (and therefore W) is infinite at the equilibrium composition, and zero at the spinodal. It is apparent from a comparison of Eqs. (3.9) and (3.14) that for a constant value of X_0, W_c is proportional to $(T_c - T)^{\frac{1}{4}}$. We shall now explore in more detail the properties of the nucleus at these two limits.

C. Properties Near the Spinodal Composition

When $c_0 \sim c_s$, we can expand $\Delta f'$ in a Taylor's series about c_0 and thus obtain an expression that is valid at all temperatures. The first and second terms in such an expansion vanish because both $\Delta f'(c_0)$ and $(\partial \Delta f'/\partial c)_{c=c_0}$ are 0. In addition, we can use the property $(\partial^2 \Delta f'/\partial c^2)_{c=c_s} = 0$ to eliminate the term in $(\partial^2 \Delta f'/\partial c^2)_{c=c_0}$. Neglecting the derivatives higher than the third, the remaining terms give

$$\Delta f'_{(c_0 \sim c_s)} = \xi [3(c_s - c_0)(c - c_0)^2 - (c - c_0)^3], \quad (3.16)$$

in which

$$\xi = -\frac{1}{6}(\partial^3 \Delta f'/\partial c^3)_{c=c_s}. \quad (3.17)$$

Provided that κ can be expanded about c_0, it is easily shown that for c_0 sufficiently close to c_s the term in $\partial \kappa/\partial c$ in Eq. (2.10) can be neglected, and κ can be assumed to have a constant value κ_s.

Introducing the parameters

$$Y = (c - c_0)/(c_s - c_0), \quad (3.18)$$

and

$$R = [\xi(c_s - c_0)/\kappa_s]^{\frac{1}{2}} r, \quad (3.19)$$

we obtain from Eqs. (2.13) and (3.16) for the work, W_s, near the spinodal

$$W_s = 4\pi \xi^{-\frac{1}{2}} \kappa_s^{\frac{3}{2}}(c_s - c_0)^{\frac{3}{2}} I_s, \quad (3.20)$$

in which I_s is the value of the dimensionless integral

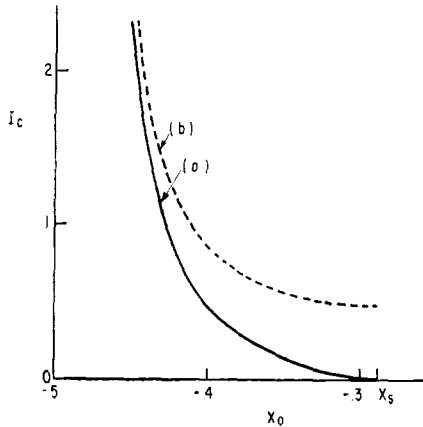$$I_s = \frac{1}{2} \int_0^\infty Y^3 R^2 dR, \quad (3.21)$$

FIG. 3. (a) Variation with X_0 of the value of the integral I_c defined by Eq. (3.15). (b) I for a classical nucleus.
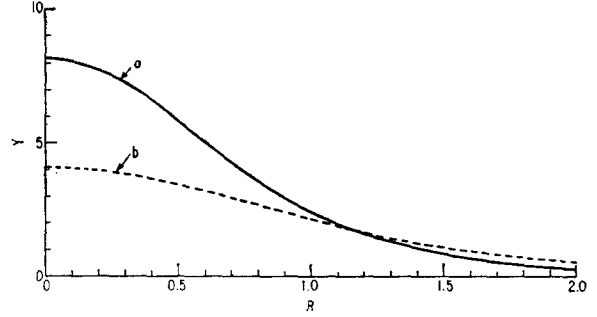

FIG. 4. (a) Normalized composition profile of critical nucleus near the spinodal. (b) Profile drawn to the same scale as (a) in order to indicate change when $(c_0 - c_s)$ is reduced by a factor of $\frac{1}{2}$.

for the solution of the Euler equation

$$(d^2Y/dR^2) + (2/R)(dY/dR) - \frac{3}{2}(2Y - Y^2) = 0. \quad (3.22)$$

The analog computer was again used to solve this equation. The normalized profile (Fig. 4) of the nucleus is independent of the initial composition c_0, providing of course, that c_0 is sufficiently close to c_s to justify our assumptions.

The value¶ of I_s was estimated by a variational method to be 15.7; whereas, a numerical integration of Eq. (3.21) using the Y versus R curve shown in Fig. 4 yielded 16.5. Since the variational method should give a value higher than the true one, we conclude that the analog solution is slightly in error. Therefore, we shall use the variational estimate of $I_s = 15.7$ which, when substituted in Eq. (3.20), gives

$$W_s = 197 \xi^{-\frac{1}{2}} \kappa_s^{\frac{3}{2}}(c_s - c_0)^{\frac{3}{2}}. \quad (3.23)$$

For the composition at the center of the nucleus, we have from Fig. 4 that the value of Y at the center is 8.1 and hence, by Eq. (3.18)

$$(c_n - c_0) = 8.1(c_s - c_0), \quad (3.24)$$

where c_n is the composition at the center of the nucleus. Also, if we denote by $r_{\frac{1}{2}}$ the radius at which the composition is $\frac{1}{2}(c_n - c_0)$, then by Eq. (3.19)

$$r_{\frac{1}{2}} = [\kappa/\xi(c_s - c_0)]^{\frac{1}{2}} R_{\frac{1}{2}},$$
$$= 0.73[\kappa/\xi]^{\frac{1}{2}}(c_s - c_0)^{-\frac{1}{2}}. \quad (3.25)$$

Thus, somewhat suprisingly, even though the nucleus increases in extent and in the excess material it contains, the work of formation nevertheless goes to zero.

D. Properties Near the Equilibrium Composition

We shall utilize the general result (proved in Sec. 3A) that as c_0 approaches the equilibrium composition c_α, the properties of the critical nucleus approach

¶ This was obtained using the trial function $Y = \alpha \, \text{sech} \, (R/\beta)$ in which α and β are constants whose values are chosen to minimize Eq. (2.9). Two other trial functions, $Y = \alpha \exp[-(R/\beta)^2]$ and $Y = \alpha (R/\beta)/[(1 + R^2/\beta^2) \sinh(R/\beta)]$ gave values for I_s of 16.1 and 16.7, respectively.

those predicted by the classical theory. In particular, the radius of the nucleus is large compared with the thickness of its interface, and its composition is close to the equilibrium one. Setting ΔP in Eq. (1.3) equal to the change in Helmholtz free energy $\Delta f_N'$ as defined in Fig. 1, we obtain

$$W_{cl} = (16\pi/3)(\Delta f_N')^{-2}\sigma^3, \qquad (3.26)$$

in which we can now identify σ with the tension between the two phases in equilibrium across a flat interface. It is evident from Fig. 1(a) that

$$\Delta f_N' \sim -(c_\beta - c_\alpha)(\partial \Delta f'/\partial c)_{c=c_0},$$
$$\sim \psi(c_\beta - c_\alpha)(c_0 - c_\alpha), \qquad (3.27)$$

in which

$$\psi = (\partial^2 \Delta f'/\partial c^2)_{c=c_\alpha}. \qquad (3.28)$$

Therefore, we can rewrite Eq. (3.26)

$$W_{cl} = (16\pi/3)[\psi(c_\beta - c_\alpha)]^{-2}\sigma^3(c_0 - c_\alpha)^{-2}. \qquad (3.29)$$

Similarly, for the radius we have from Eq. (1.1)

$$r = [2\sigma/\psi(c_\beta - c_\alpha)](c_0 - c_\alpha)^{-1}. \qquad (3.30)$$

Thus, as c_0 approaches c_α, W goes to infinity as $(c_0 - c_\alpha)^{-2}$, and the radius goes to infinity as $(c_0 - c_\alpha)^{-1}$.

E. Summary of General Treatment

Our purpose in this section has been to establish the general properties of a critical nucleus. We have found that certain of the properties can be deduced merely from the form of the Euler equation. But, for a more detailed description, it has been necessary to obtain normalized solutions to this equation for the three limiting cases, in two of which $\Delta f'$ can be expressed as an expansion. We have found that the classical nucleation theory represents one of these limiting cases in which c_0 approaches the equilibrium composition. However, with increasing supersaturation, the properties of the nucleus become progressively less classical and eventually, as the spinodal composition is reached, all resemblance to a classical nucleus is lost.

4. NUCLEATION IN A REGULAR SOLUTION

A. Evaluation of the Parameters

In order to establish the absolute value of W and its composition dependence in the regions not covered by the foregoing limiting cases, it is necessary to introduce a specific function for $\Delta f'$. In principle, any solution model yielding a $\Delta f'$ function of the required form in the metastable and unstable regions could be used. Alternatively, the function could be derived from an extrapolation of experimentally determined free energies into the two-phase region.

For the purpose of illustrating the results of the present treatment, we shall use the regular solution model, which has been a choice of other authors because of its simplicity. We shall denote by the subscript R

those properties which refer specifically to a regular solution. It was shown in Paper I [Eq. (3.12)] that the gradient-energy coefficient κ_R for a regular solution is independent of temperature and composition and is given by

$$\kappa_R = N_V k T_c \lambda^2, \qquad (4.1)$$

in which the number of molecules per unit volume, N_V, has been introduced because of the change adopted in the present paper of defining quantities in terms of a unit volume. The parameter λ is a rms interaction distance. Because of its sensitivity to the long-range interatomic forces, it is best estimated for a particular system from experimental measurements of e.g., the interfacial free energy. However in the calculations to be presented, we shall use the following theoretical value computed in Paper I for a Lennard-Jones 6–12 potential:

$$\lambda = (11/7)^{\frac{1}{2}} r_0 = (11/7)^{\frac{1}{2}} (6/\pi N_V)^{\frac{1}{3}}, \qquad (4.2)$$

in which r_0 is the intermolecular distance.

We shall also utilize the following well known properties of a regular solution:

$$f_R'/N_V = \omega c(1-c) + kT[c \ln c + (1-c) \ln(1-c)], \qquad (4.3)$$

where ω is an interaction energy which, for a system with a miscibility gap, is positive and is related to the critical temperature by

$$\omega = 2kT_c. \qquad (4.4)$$

In addition,

$$c_c = \tfrac{1}{2}, \qquad (4.5)$$

$$c_s(1-c_s) = \tfrac{1}{4} T/T_c, \qquad (4.6)$$

$$\ln[c_\alpha/(1-c_\alpha)] = 2(2c_\alpha - 1) T_c/T, \qquad (4.7)$$

and

$$c_\alpha = (1-c_\beta). \qquad (4.8)$$

The substitution of Eqs. (4.3) and (4.4) in Eq. (2.6) gives

$$\Delta f_R'/N_V = -kT_c\{2(c-c_0)^2 - (T/T_c)[c \ln(c/c_0)$$
$$+ (1-c) \ln(1-c)/(1-c_0)]\}. \qquad (4.9)$$

We can also evaluate the parameters defined by Eqs. (3.7), (3.17), and (3.28)

$$\gamma_R = 4N_V k T_c/3, \qquad (4.10)$$

$$\xi_R = N_V(1-2c_s)kT/\{6[c_s(1-c_s)]^2\}, \qquad (4.11)$$

$$= N_V(8kT_c/3)(T_c/T)[1-(T/T_c)]^{\frac{1}{2}}, \qquad (4.12)$$

and

$$\psi_R = -4N_V k T_c\left\{1 - \frac{T/T_c}{4c_\alpha(1-c_\alpha)}\right\}. \qquad (4.13)$$

Also, from Eqs. (3.9), (4.3), and (4.10), we obtain

$$(c_c - c_\alpha)^2_{T \sim T_c} = 3(T_c - T)/4T_c. \qquad (4.14)$$

Consider next the coefficients of W for the three limiting cases $c_0 \sim c_\alpha$, $c_0 \sim c_s$, and $T \sim T_c$. With the appropriate substitutions in Eq. (3.14) we obtain

$$W_c = 12\pi N_V \lambda^3 [2(T_c - T)/T_c]^{\frac{3}{2}} I_c k T_c,$$

$$\sim 200 [(T_c - T)/T_c]^{\frac{3}{2}} I_c k T_c. \qquad (4.15)$$

Similarly, for Eq. (3.23) we have,

$$W_s \sim 460 (T/T_c)^{\frac{3}{4}} [(T_c - T)/T_c]^{-1/4} k T_c (c_s - c_0)^{\frac{3}{2}}. \qquad (4.16)$$

For the limiting case $c_0 \sim c_\alpha$, it is not worthwhile to express the coefficients appearing in Eq. (3.29) as a function of temperature, because of the complicated dependence of σ_R, the interfacial free energy of a flat interface in a regular solution. Instead, a value of σ_R for a particular temperature can be evaluated from Fig. 3 and Eq. (3.19) of Paper I; it can then be used in conjunction with Eqs. (3.26) and (3.27) to determine W_{s1}.

B. Properties of the Critical Nucleus at $T/T_c = 0.8656$

The Euler equation, Eq. (2.10), was solved for a regular solution in which the equilibrium compositions of the two phases are 0.2 and 0.8. These correspond to a reduced temperature of $T/T_c = 0.8656 \cdots$ and a spinodal composition of $c_s = 0.3167 \cdots$. The profiles of nuclei obtained on the analog computer at c_0 values of 0.225, 0.250, 0.275, and 0.300 were similar in form to the sequence depicted in Fig. 2.

We shall now consider the various properties of the critical nucleus as a function of c_0, and compare them where appropriate with the predictions of previous
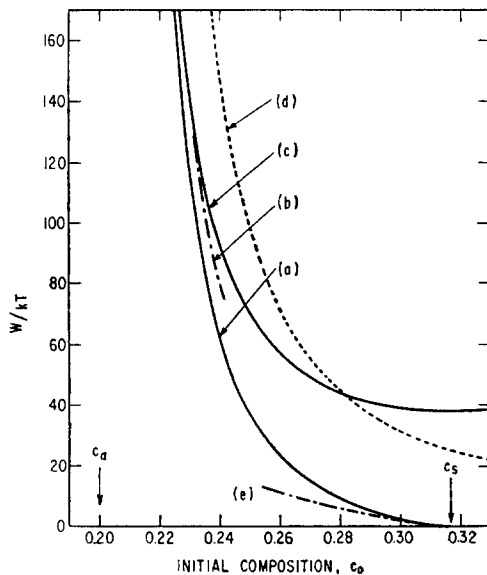
FIG. 5. Variation of W/kt with c_0 in a regular solution at $T/T_c = 0.8656 \cdots$ and $(\lambda/r_0) = (11/7)^{\frac{1}{2}}$ according to (a) present treatment; (b) limiting case of $c_0 \sim c_\alpha$; (c) classical theory; (d) theory of Becker; and (e) limiting case of $c_0 \sim c_s$.
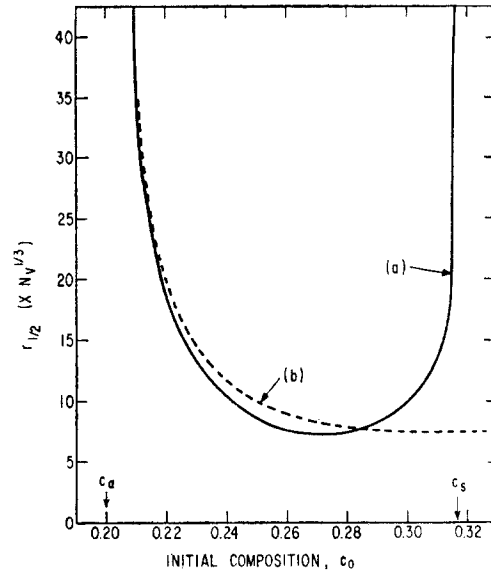
FIG. 6. Variation with c_0 in a regular solution at $T/T_c = 0.8656 \cdots$ and $(\lambda/r_0) = (11/7)^{\frac{1}{2}}$ of the radius of the critical nucleus according to (a) present treatment, and (b) classical theory.

theories. In Fig. 5, the following curves are drawn for the variation of W with c_0:

(a) Computed by means of Eq. (2.13) from the analog solutions of Eq. (2.10).

(b) Computed from Eq. (3.29) for the limiting case $c_0 \sim c_\alpha$ with $\sigma_R = 0.145 N_V^{2/3} k T_c$, this being the interfacial energy calculated in paper I for a flat interface between the equilibrium phases of a regular solution at $T/T_c = 0.8656 \cdots$ for a value of λ given by Eq. (4.2).

(c) Computed from Eq. (3.26) for a classical nucleus with a value of $\Delta f_N'$ at the composition for which the nucleus would be in equilibrium with the exterior phase. The value used for σ_R was that given in (b).

(d) Computed from Becker's modification[5] of the classical theory in which it is assumed that the nucleus is composed of homogeneous material with the composition c_β of the final equilibrium phase. The value used for σ is $0.529 N_V^{2/3} (c_\beta - c_0)^2 k T_c$, which is calculated on the basis of nearest-neighbor interactions only.

(e) Computed from Eq. (4.16) for the limiting case $c_0 \sim c_s$.

It will be noted that the W given by the present treatment [curve (a)] is always less than that for a classical nucleus, and in addition it continuously approaches a zero value at the spinodal. Curve (d) for Becker's treatment is not strictly comparable with the other curves, since it was computed on the basis of nearest-neighbor interactions only. If the same assumption were to be made in our treatment, the calculated value of W would have been reduced by approximately a factor of ten.

The radius of the critical nucleus at which the composition is $(c_n - c_0)/2$ is plotted in Fig. 6. Near the
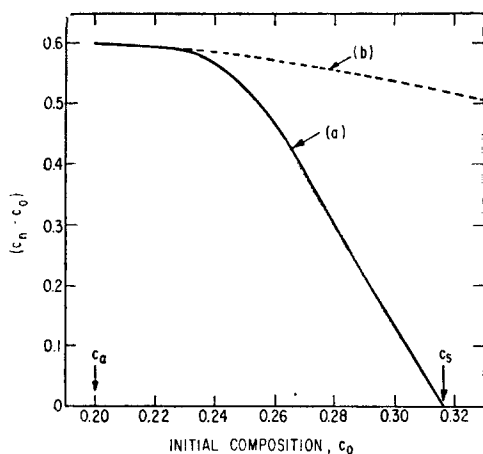
FIG. 7. Variation with c_0 in a regular solution at $T/T_c = 0.8656\cdots$ and $(\lambda/r_0) = (11/7)^{\frac{1}{2}}$ of the composition difference between the center of the nucleus and the external phase according to (a) present treatment, and (b) classical theory.

equilibrium composition, the radius is slightly less than that shown by curve (b) for a classical nucleus. But with increasing c_0, the radius eventually passes through a minimum and approaches infinity at the spinodal. A hypothetical homogeneous nucleus having the composition of a classical nucleus and the excess concentration of the actual nucleus would, in the vicinity of c_α, have a radius larger than $r_{\frac{1}{2}}$, but less than that of the classical nucleus.

The composition difference, $(c_n - c_0)$, between the center of the nucleus and the exterior phase (Fig. 7) decreases more rapidly than for a classical nucleus and approaches linearly to zero at the spinodal in accordance with Eq. (3.24).

C. Variation of Properties with Temperature

For a given ratio of $(c_0 - c_\alpha)/(c_\beta - c_\alpha)$, the radius of the critical nucleus increases and W decreases with increasing temperature. The nucleus also becomes more classical in shape.

For the purpose of indicating the supersaturation required for an observable nucleation rate, the locus of $W = 60kT$ is drawn on the phase diagram in Fig. 8. It will be noted that the undercooling required to initiate the transformation goes to zero at the critical composition. This result is in agreement with the experimental data of Oriani[11] for the CCl_4—C_7F_{14} system. Also included in Fig. 8, is the $W = 60kT$ locus calculated from Becker's theory.[5] According to this curve, a finite degree of undercooling is always required for nucleation, even at the critical composition. In comparing curves (a) and (b) it should be again borne in mind that with nearest-neighbor interactions only curve (a) would have been displaced to such an extent that it would have been nearly coincident with the phase boundary.

[11] R. A. Oriani, J. Chem. Phys. 25, 186 (1956).

In conclusion, it must be emphasized that all the evaluations made in this section have been based on calculated value for κ (or λ/r_0) given by Eqs. (4.1) and (4.2). Therefore, the evaluations must be regarded only as approximations, even if the system is a perfect regular solution.

5. DISCUSSION AND SUMMARY

In the present treatment, we have determined the free energy of formation and other properties of a critical nucleus by treating it as a fluctuation which is in unstable equilibrium with the exterior phase. We have demonstrated that the general properties of such a nucleus in a two-component incompressible fluid can be deduced without resort to any specific solution model. By way of a summary, we shall compare these properties with those of the classical nucleus as the exterior phase changes from the equilibrium to the spinodal composition or as the supersaturation increases.

At low supersaturations, the ratio of the W's, radii, and other properties of the two nuclei approach unity. Thus, so long as we consider only the relative error, the equations of Gibbs cited in the introduction provide an increasingly accurate description of the nucleus as the exterior phase approaches the equilibrium composition.

As the supersaturation increases, the nucleus begins to differ from the classical nucleus in the following respects: (a) W becomes proportionally less; (b) the pressure and composition at the center of the nucleus are less than those of a classical nucleus; (c) at first, the
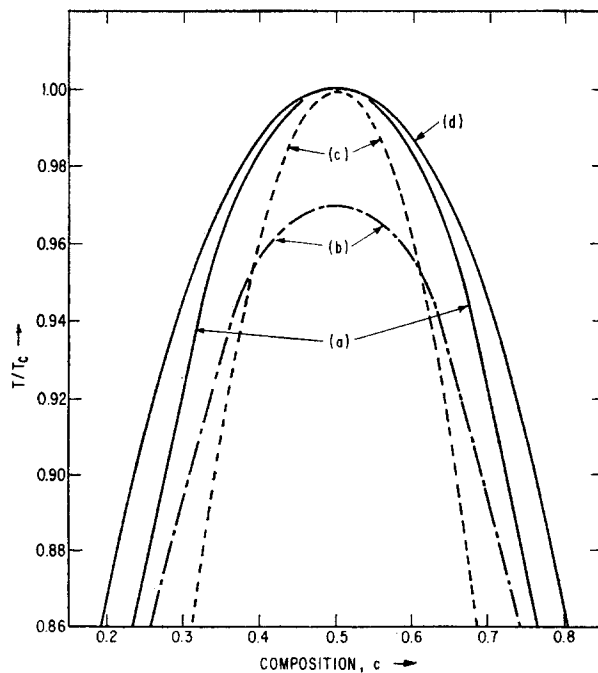

FIG. 8. Locus of $W = 60\ kT$ for a regular solution according to (a) present treatment with $(\lambda/r_0) = (11/7)^{\frac{1}{2}}$, and (b) treatment of Becker (for nearest-neighbor mode 1). Curve (c) is the spinodal, and (d) the phase boundary.

radius remains less than that of a classical nucleus, but eventually it passes through a minimum and thereafter increases; and (d) the thickness of the interface is greater than that of a flat interface between the equilibrium phases.

With still higher supersaturations near the spinodal, all resemblance to a classical nucleus is lost. In particular: (a) the free energy approaches zero; (b) the composition at the center approaches c_0; (c) the radius becomes infinite; and (d) no part of the nucleus is even approximately homogeneous. The critical nucleus therefore can be regarded as a composition fluctuation which is small in degree but large in extent.

We shall now consider some of these properties in greater detail. In the first place, it is apparent that the classical theory provides the simplest means of calculating W. It is, therefore, very desirable to establish the conditions under which it can be satisfactorily applied to experimental data. From kinetic theory, we know that homogeneous nucleation will occur at a perceptible rate when W is about 60 kT or less. For a classical nucleus to have an energy less than 60 kT its radius must, according to Eq. (1.5), satisfy

$$r < (45kT/\pi\sigma)^{\frac{1}{2}}. \tag{5.1}$$

Now we can assume the classical theory to apply if the interface of the nucleus has a thickness, l, which is much smaller than the radius, or

$$l \ll r < (45kT/\pi\sigma)^{\frac{1}{2}},$$

which yields

$$(\pi\sigma l^2/45kT) \ll 1. \tag{5.2}$$

We suggest that this condition be used as a criterion as to whether or not nucleation will occur in a classical mode. By use of Eqs. (2.15) and (2.25) of Paper I, the product σl^2 in inequality (5.2) can be written

$$\sigma l^2 \sim \tfrac{4}{3}(c_\beta - c_\alpha)^3 \kappa^{\frac{3}{2}}(\Delta f')_{\max}^{-\frac{1}{2}}, \tag{5.3}$$

in which $(\Delta f')_{\max}$ is the maximum value of $\Delta f'$ when $c_0 = c_\alpha$. The inequality (5.2) will always be satisfied sufficiently close to the critical point since, in this region, l varies as $(T_c - T)^{-\frac{1}{2}}$ and σ as $(T_c - T)^{\frac{3}{2}}$; thus σl^2 approaches zero as $(T_c - T)^{\frac{1}{2}}$. Nucleation will occur, therefore, in a classical mode along a curve which lies just inside the top of the miscibility gap and is tangent to it with the same curvature at the critical point. For a regular solution, σl^2 can be evaluated in terms of λ/r_0, where λ is the interaction distance defined by Eq. (4.1) and r_0 is the intermolecular distance. In order to indicate the temperature range over which classical nucleation will be observed in a regular solution, the left-hand side of inequality (5.2) has been plotted in Fig. 9 for values of λ/r_0 corresponding to: (a) nearest-neighbor
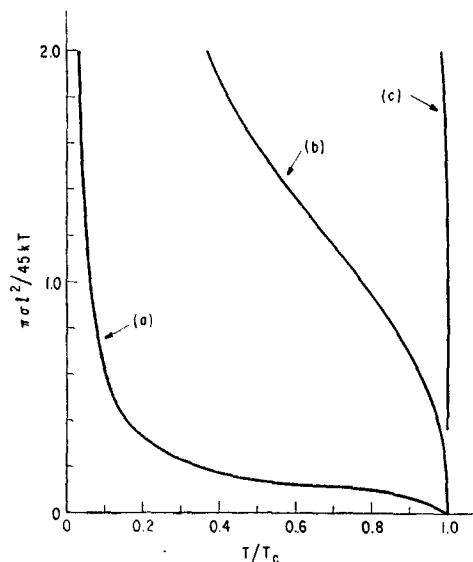

FIG. 9. Variation with reduced temperature of $(\pi\sigma l^2/45\ kT)$, where σ is the specific free energy and l the thickness of a flat interface, in a regular solution with: (a) $\lambda/r_0 = (1/3)^{\frac{1}{2}}$ (nearest-neighbor interactions only); (b) $\lambda/r_0 = (11/7)^{\frac{1}{2}}$ (Lennard-Jones 6–12 potential); and (c) $\lambda/r_0 = 3.4$ (experimental value[7] for cyclohexane-aniline solutions). According to inequality (5.2), the condition for observable nucleation in a classical mode is: $(\pi\sigma l^2/45kT) \ll 1$.

interactions only; (b) a Lennard-Jones 6–12 potential (which was used for the calculations in Sec. 4); and (c) a value estimated in Paper I from experimental measurements of the interfacial free energy between coexisting phases of the cyclohexane-aniline system. It is evident from the figure that for (b) and (c) observable nucleation in the classical mode is restricted to the immediate vicinity of the critical point.

Turning now to the region near the spinodal—in fluid systems for which a spinodal exists, it marks the limit of metastability of the homogeneous phase. Since we have found that W decreases monotonically to zero at the spinodal, nucleation will always set in before the spinodal is reached. However, if κ is sufficiently large relative to the maximum in $\Delta f'$, the point at which observable nucleation occurs will be very nearly coincident with the spinodal. But as will be seen from Fig. 8, this is not true for a regular solution with a 6–12 potential.

It is instructive to examine why W is zero at and beyond the spinodal. In Paper I, we found that the interfacial energy could be represented as the sum of two integrals, one representing the contribution of the "gradient energy" and the other the free energy required to form material of intermediate composition. The former contribution decreases, and the latter increases, with increasing thickness of the interface. The equilibrium thickness is such that the sum of the two integrals is a minimum. For a nucleus, the situation is somewhat different, since over part of the composition range $\Delta f'$ is negative [see Fig. 1(b)] and so

TABLE I. Comparison of various nucleation theories with regard to the behavior predicted for W in the vicinity of the spinodal.[a]

Nucleation theory	W at unstable limit of metastable region. $(c_0 \rightarrow c_s)$	Nature of change in W in passing into unstable region.	W in unstable region. $(c_0 > c_s)$	Limiting value of W in the metastable region as $c_0 \rightarrow c_s$ and $T \rightarrow T_c$.
		Three-dimensional models		
Gibbs[b]	$(16\pi\sigma^3/3\Delta f^2)$	Discontinuous unless σ has become zero	0	Depends upon interface model
Becker[c]	$(16\pi\sigma^3/3\Delta f^2)$ $=[256\pi(N_A m\omega)^3/3\xi^2]$	Continuous	$(16\pi\sigma^3/3\Delta f^2)$	∞
Hobstetter[d]	$[16\pi(N_A m\omega)^3/3\xi^2]$	Discontinuous	0	∞
Present Work	$[197\kappa^{3/2}(c_s - c_0)^{3/2}/\xi^{1/2}]$	Continuous	0	0
		One-dimensional models		
Becker	2σ	Continuous	2σ	0
Hobstetter	$18m\omega(c_s - c_0)^2$	Continuous	0	0
Hillert[e]	$[18(3m\omega)^{1/2}\xi^{1/2}/5](c_s - c_0)^{5/2}$	Continuous	0	0

[a] The quantities ω and ξ are defined in Eqs. (4.4) and (3.17); m is the fractional number of nearest neighbors for a given atom which are in an adjacent plane, and N_A the number of atoms per unit area at the interface. The relationships were derived on the assumption that the product mN_A is independent of orientation.
[b] See reference 1.
[c] See reference 5.
[d] See reference 13.
[e] See reference 12.

reduces the free energy which has to be expended in forming the material of intermediate composition. As the spinodal is approached, the range over which $\Delta f'$ is positive decreases, and at the same time the maximum positive value attained by $\Delta f'$ also decreases. These two factors favor an increasingly diffuse interface. Finally, at the spinodal and beyond, $\Delta f'$, decreases monotonically with increasing composition difference so that there is no barrier to the formation of an infinitely diffuse interface. Thus, in effect σ can be considered to vanish at the spinodal.

As we have previously indicated, most of the existing nucleation theories approach one another and the present treatment in the properties predicted for the limit of zero supersaturation. However, as shown by Table I, they are markedly at variance in their predictions of W in the vicinity of the spinodal. The only other theory which agrees qualitatively with the present treatment is that due to Hillert.[12] Unfortunately, his calculations were confined to a one-dimensional model which is of doubtful physical significance in the metastable region. A one-dimensional classical nucleus, for instance, would just consist of two point-boundaries regardless of the supersaturation.

It is interesting to note that Hobstetter's treatment[13] gives a discontinuous change in W at the spinodal; in the metastable region it approaches a limit at c_s of

($\frac{1}{16}$) of W for a Becker nucleus, and then drops to zero in the unstable region. This treatment retains the assumption that the nucleus is homogeneous but differs from Becker's in that a composition is selected which minimizes W. This procedure can be considered as a variational method which, because it has one parameter more than Becker's theory, gives a better approximation to W. However, it results in a nucleus composition for which the chemical potentials of the compontents are not equal to those of the exterior phase. Were it not for the manner in which the nucleus is constrained to a uniform composition, there would be a spontaneous change in the concentration at the center. The absolute difference in chemical potentials between the nucleus and the exterior phase increases with increasing supersaturation, and one therefore, would, expect Hobstetter's treatment to give a progressively poorer approximation for W as c_0 approaches the spinodal.

In the second part of Table I, we have added the one-dimensional analogs of the treatments of Becker and Hobstetter in order to demonstrate that there can be a marked change in the predicted properties when a one-dimensional model is extended to three dimensions.

In conclusion, we should like to review the assumptions upon which this treatment is founded. The first is that the free energy of the homogeneous system in the metastable and unstable regions can be represented by a continuous function of the form indicated in Fig. 1(a). Secondly, in the general formulation presented in

[12] M. Hillert, "A theory of nucleation for solid metallic solutions," Doc. Sci. thesis, Massachusetts Institute of Technology, Cambridge (1956).
[13] J. N. Hobstetter, Trans. Am. Inst. Mining Met. Petrol. Engrs. **180**, 121 (1949).

Paper I, it was assumed that composition derivatives higher than the second could be neglected in the expansion of the free-energy of a nonuniform system. This implies that the ratio of the maximum in $\Delta f'$ to the gradient-energy coefficient κ should be small relative to the intermolecular distance. Since the maximum in $\Delta f'$ decreases with increasing supersaturation, it is evident that the latter condition will always be satisfied sufficiently near the spinodal.

Finally, it must be emphasized that the results we have presented are strictly applicable only to incompressible fluids. Nucleation in solids may follow an entirely different pattern because of the strain energy contribution.