

Coarsening of random interfaces in the spinodal decomposition of a binary fluid

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The growth of random interfaces during the late stage spinodal decomposition for a near symmetric quench of a binary fluid is analyzed. Inertial effects are neglected, and the motion of the interface is determined by a balance between the surface tension, which tends to reduce the curvature, and the viscous stresses in the fluid. The interface is described by an "area distribution function" $A(K,t)$, defined so that $A(K,t)dKd\mathbf{x}$ is the area of the interface with curvature in the interval dK about K in the volume $d\mathbf{x}$ at time t . Here, $K=(K_1^2+K_2^2)^{1/2}$ is the magnitude of the curvature, and K_1 and K_2 are the principal curvatures. There is a change in the area distribution function due to a change in the curvature, and due to the tangential compression of the interface. Phenomenological relations for the change in curvature and surface area are obtained using the assumption that the only length scale affecting the dynamics of the interface at a point is the radius of curvature at that point. These relations are inserted in the conservation equation for the interface, and a similarity solution is obtained for the area distribution function. This solution indicates that the area of the interface decreases proportional to t^{-1} in the late stages of coarsening, and the mean curvature also decreases proportional to t^{-1} . The effect of the motion of the interface on the interfacial concentration profile and interfacial energy is analyzed using a perturbation analysis. The diffusion equation for the concentration in the interfacial region contains an additional source term due to the convective transport of material caused by the motion of the interface, and this causes a correction to the equilibrium concentration profile of the interface. The excess interfacial energy due to the nonequilibrium motion of the interface is calculated using the Cahn–Hilliard square gradient free energy for a near-critical quench. It is found that the variation in the concentration causes an increase in the interfacial energy which is proportional to the curvature K of the interface. © 1998 American Institute of Physics. [S0021-9606(98)51906-X]

I. INTRODUCTION

The rate of coarsening in the late stage spinodal decomposition of binary fluids depends on the relative concentration of the two species. For a near symmetric quench, the system consists of a random interface, and the coarsening occurs due to a reduction in curvature caused by the surface tension of the interface. A suspension of droplets in a continuous matrix is observed for an off-symmetric quench, and the coarsening in this case occurs due to the convective and diffusive transport of the minority phase from the matrix into the droplet. The classical Lifshitz–Slyozov¹ theory predicts that the average radius of the droplets grows proportional to $t^{1/3}$ in the late stages of spinodal decomposition, and this scaling law has been observed in the late stage decomposition in solid alloys. In fluids, the convective transport of material from the fluid to the droplets due to the Brownian motion of the droplets could influence the rate of growth. It is found² that the convective effects have only a minor effect on the scaling exponent, and the growth law is given by $R_m \propto t^{(4/13)}$ or $R_m \propto t^{(6/19)}$ depending on the boundary condition for the fluid velocity field at the surface of the droplet. However, the rate of growth (which is the prefactor in the scaling law) could be considerably higher in fluids. This is in agreement with experimental results^{3,4} which observe a scaling close to the $t^{1/3}$ predicted by the Lifshitz–Slyozov theory.

The rate of coarsening of random interfaces for nearly symmetric quenches is less well understood. The Ohta, Jasnow, Kawasaki⁵ theory for the rate of growth of a random interface in the order–disorder transition in solids was based on a constitutive equation for the normal velocity at a point as a function of the radius of curvature at that point. This theory predicted that the characteristic length for the quench of random interfaces has a scaling law $l \propto t^{(1/2)}$, and the results of this theory was found to be in agreement with the Monte Carlo simulations of Humayun and Bray.⁶ For a system with conserved order parameter, the equivalent scaling relation $l \propto t^{(1/3)}$ was obtained by Bray.⁶

The theories for the coarsening of interfaces in fluids are more approximate. Siggia⁷ used a simple qualitative argument, regarding the time required for the breakup of an interface due to a capillary instability, to obtain a scaling law $l \propto t$ for the characteristic length of the interface. Furukawa⁸ obtained a similar scaling relation based on the balance between surface tension and viscous dissipation. This scaling law has also been observed in experiments of near symmetric quenches.^{3,4}

The rate of coarsening of an interface in a near symmetric quench is the subject of the present analysis. This analysis augments the previous work on the subject in two ways. The first is to provide a more quantitative description of the

coarsening of the interface. An area distribution function $A(K, t)$ is defined such that $A(K, t)d\mathbf{x}dK$ is the area of the interface with the magnitude of the curvature in the interval dK about K in the volume $d\mathbf{x}$ at time t , and the area distribution function is independent of the position \mathbf{x} because the system is considered homogeneous. There is a change in the area distribution function due to a change in the curvature K , as well as due to the contraction of the area due to the tangential motion of the interface. Constitutive equations for the change in curvature and change in area are obtained based on dimensional analysis and the assumption that the only length scale affecting the dynamics of the interface at a point is the radius of curvature of the interface K^{-1} at that point. These constitutive relations are obtained in the limit where the regime where hydrodynamic effects are dominant, and the effect of diffusion on the interface motion is neglected. In addition, it is possible to obtain simple forms of the constitutive relation only for the case of a conserved order parameter fluid system, and the reasons for this are discussed in the next section. These are incorporated into a conservation equation for the change in the area distribution function. A similarity solution is obtained for this conservation equation for the case where the area distribution function is independent of curvature at the start of the coarsening process, and expressions for the evolution of the mean curvature and area density (interface area per unit volume) are derived. The mean curvature decreases proportional to t^{-1} , in agreement with previous results, and the area density also decreases proportional to t^{-1} in the late stages. A similar analysis is carried out for solid the order-disorder transition in solids, and it is found that the curvature decreases proportional to $t^{-1/2}$, in agreement with the predictions of Ohta, Jasnow, and Kawasaki⁵ and simulation results.⁶

The previous studies have assumed that the interface is of infinitesimal thickness and has a constant surface tension. This approximation is applicable in the late stages of coarsening, when the interface concentration profile is close to the equilibrium concentration profile. The motion of the interface causes a change in the curvature of the interface, and a contraction due to the tangential motion along the interface. This contraction could alter the concentration profile at the interface, which in turn changes the interfacial energy. The first correction to the interfacial energy due to the interface motion, which is the second objective of the present analysis, is calculated in Sec. III. The method of analysis is very similar to that used by Langer and Sekerka⁹ for the mobility of an interface in the spinodal decomposition in a solid. However, convective transport is also included in the present analysis, since the motion of an interface in a fluid is considered. In addition, the primary interest in the present analysis is the variation of the interfacial energy due to dynamical effects, while the focus of the analysis of Langer and Sekerka⁹ was the change in the mobility of the interface due to nonequilibrium effects. The Cahn-Hilliard square gradient approximation is used for the dependence of the free energy on the concentration, and a diffusion equation is written for the variation of the concentration. This diffusion equation contains an additional source term, which is the change in the interface concentration due to interface motion. In the “quasi

steady” approximation, there is a balance between the divergence of the diffusive flux and the rate of change of concentration due to interface motion. This balance equation is solved to obtain the correction to the interfacial concentration profile due to interface motion, and the correction to the interfacial energy (excess free energy per unit area of the interface) is determined. It is found that the correction to the interfacial energy is positive and proportional to the curvature K , indicating that sections of the interface with higher curvature have a higher interfacial energy and coarsen faster than sections with a lower curvature.

II. COARSENING OF A RANDOM INTERFACE

A nearly symmetric quench of a binary liquid in the late stages of spinodal decomposition is considered, where the two phases form a bicontinuous pattern separated by sharp interfaces of random orientation. Due to the bicontinuous nature of the system, the pressure in the two phases are equal. In addition, the dilute limit is considered where the interface is “noninteracting,” so that the motion of one section of the interface does not affect another section. The rate of coarsening is determined by a balance between the surface tension, which tends to reduce the curvature of the surface, and the viscous stresses, which offer frictional resistance to the motion of the interface. The shape of the interface is determined by the “principal curvatures” K_1 and K_2 , which are the extrema of the curvatures at any point on the surface, or by the magnitude $K = (K_1^2 + K_2^2)^{1/2}$ and the angle $\tan(\theta) = (K_2/K_1)$. For the present purposes, an “area distribution function” for the interface curvature, $A(K, \theta, t)$, is defined such that $A(K, \theta, t)dKd\theta d\mathbf{x}$ is the area with curvature in the interval dK about K and $d\theta$ about θ in the differential volume $d\mathbf{x}$ about the position \mathbf{x} at time t . There are two reasons for a change in the area distribution function—a change in the area due to the tangential motion of the material points along the surface, and a change in the curvature of the surface. The difference equation relating the area distribution function at times t and $t + \Delta t$ is

$$A(K, \theta, t + \Delta t) = A[K - (\Delta t)d_t K, \theta - (\Delta t)d_t \theta, t] + \Delta_c A[K - (\Delta t)d_t K, \theta - (\Delta t)d_t \theta, t], \quad (1)$$

where $d_t K$ and $d_t \theta$ are the rates of change of the position (K, θ) in “curvature space,” and $\Delta_c A$ is the variation in the area due to tangential compression along the interface. The above conservation equation is a “Lagrangian” equation which incorporates the fact that the area occupying the position (K, θ) at time $t + \Delta t$ was at the position $[K - (\Delta t)d_t K, \theta - (\Delta t)d_t \theta]$ at the time t . The differential form of the conservation equation in the limit $\Delta t \rightarrow 0$ is

$$\frac{dA}{dt} = -\frac{dK}{dt} \frac{\partial A}{\partial K} - \frac{d\theta}{dt} \frac{\partial A}{\partial \theta} + \frac{\partial_c A}{\partial t}, \quad (2)$$

where $(\partial_c A/\partial t)$ is the rate of change of surface area due to the tangential motion along the interface. The above conservation equation is further simplified by averaging over the θ

coordinate, since we are only interested in the rate of change of the curvature K , to give the following equation for the area distribution $A(K, t)$:

$$\frac{dA(K, t)}{dt} = -\frac{dK}{dt} \frac{\partial A(K, t)}{\partial K} + \frac{\partial_c A(K, t)}{\partial t}. \quad (3)$$

To solve the above equation, it is necessary to obtain the rate of change of curvature (dK/dt) and the rate of change of area ($\partial_c A(K, t)/\partial t$). Though the exact evaluation of these quantities requires a microscopic model for the interface dynamics, the K dependence of these can be obtained from dimensional arguments. The motion of the interface is usually dominated by viscous effects for typical binary fluid systems. The Reynolds number, (UL/ν) , which is the ratio of inertial and viscous effects, is usually small. For example, in water, the kinematic viscosity $\nu \sim 10^{-6} \text{m}^2 \text{s}^{-1}$, and the velocity U can be estimated as the thermal fluctuation velocity $(T/(4\pi/3\rho L^3))$, which is $O(10^{-12}/L^{3/2}) \text{m s}^{-1}$, at room temperature, and L is a typical length measured in meters. Here, the density ρ has been estimated as 10^3kg m^{-3} , and T is the product of the Boltzmann constant and the temperature. With this estimate, the ratio of inertial and viscous forces is $O(10^{-6}/L^{1/2})$, which is small for lengths greater than a nanometer. Consequently, the motion of the interface is dominated by viscous effects, and the only fluid properties that affect the rate of change of curvature are the surface tension γ and the fluid viscosity μ . For example, the fluid velocity at any point \mathbf{x} due to the forces acting at other points in the fluid is

$$u_i(\mathbf{x}) = \int d\mathbf{x}' J_{ij}(\mathbf{x} - \mathbf{x}') F_j(\mathbf{x}'), \quad (4)$$

where $J_{ij}(\mathbf{x} - \mathbf{x}')$ is the Oseen tensor

$$J_{ij}(\mathbf{x} - \mathbf{x}') = \frac{1}{8\pi\mu} \left(\frac{r_i r_j}{r^3} + \frac{\delta_{ij}}{r} \right), \quad (5)$$

where $\mathbf{r} = \mathbf{x} - \mathbf{x}'$. In the above expression, the fluid velocity at any point depends only on the viscosity μ and the force \mathbf{F} . If the force at any point depends only on the local curvature γ , then the only material parameters affecting the rate of change of curvature are the surface tension γ and the viscosity μ . This is different from the dynamics of the interface in the conserved order parameter case in a solid system, since the coarsening can occur due to the flow and deformation of the fluid in the two phases, which is influenced by the viscosity of the fluid. It should also be noted that the Stokes equations for a low Reynolds number flow, which are used to obtain the Oseen tensor, conserve fluid density in the two phases separately. Since we are assuming that the interface motion is due to the fluid flow and deformation rather than the diffusion across the interface, these equations are consistent with the conservation requirements for the concentration field if concentration equation is also conservative. The concentration equation does not appear directly in this section, because of the assumption that the resistance to interface motion is due to viscous flow alone. However, the correction

to the interface dynamics due to diffusion is considered in the next section, and the concentration equation used there is conservative.

In a solid the dynamics of the interface is different, and the resistance to interface motion in a conserved order parameter system has a very different form which is discussed a little later. In a solid alloy, the motion of the interface occurs due to the diffusion of the components across the interface, since the underlying crystal structure is frozen. In a conserved order-disorder transition in a solid, the motion of different sections of the interface are not independent due to the requirement of conservation of total magnetization, and so the conservation equation has a different form given in Bray.⁶ This is very different from the motion in the case of a fluid, where the resistance is due to viscous stresses exerted by fluid flow. Consequently, the equations for the rate of change of curvature have different forms in these cases.

If we stipulate that the only length scale affecting the dynamics of the interface at a point is K^{-1} at that point, there is only one possible form for the rate of change of the curvature

$$\frac{dK}{dt} = -\frac{a_1 \gamma K^2}{\mu}, \quad (6)$$

where a_1 is a positive constant because the curvature of the interface decreases with time. The rate of change of area is related to the tangential motion of the interface as follows:

$$\frac{\partial_c A(K, t)}{\partial t} = A(K, t) \nabla_t \cdot \mathbf{v}_t, \quad (7)$$

where ∇_t is the two dimensional gradient operator along the interface, and \mathbf{v}_t is the velocity along the interface. If the only length scale that determines the interface dynamics at a given position is K^{-1} , then the above equation shows that there is only one possible form for the rate of change of area,

$$\frac{1}{A} \frac{\partial_c A}{\partial t} = -\frac{a_2 \gamma K}{\mu}, \quad (8)$$

where a_2 is a positive constant because the area decreases with time.

Inserting the ‘‘constitutive’’ Eqs. (6) and (8) into the conservation Eq. (3), the following equation for the area distribution is obtained:

$$\frac{dA}{dt} = \frac{a_1 \gamma K^2}{\mu} \frac{dA}{dK} - \frac{a_2 \gamma K}{\mu} A. \quad (9)$$

The above equation has to be solved subject to an appropriate initial condition at $t=0$. If the initial condition is homogeneous, i.e., A is independent of K at $t=0$, it is possible to obtain a similarity solution for the conservation Eq. (9). The similarity variable η is defined as $\eta = (a_1 \gamma K t / \mu)$, and the conservation equation expressed in terms of this variable is

$$\frac{dA(\eta)}{d\eta} = \eta \frac{dA(\eta)}{d\eta} - aA(\eta), \quad (10)$$

where $a = (a_2/a_1)$. The solution of the above equation is

$$A = A_0(1 - \eta)^a \text{ for } \eta \leq 1$$

$$= A'_0(\eta - 1)^a \text{ for } \eta \geq 1, \tag{11}$$

where the constants A_0 and A'_0 are determined from the boundary conditions. Note that the constants A_0 and A'_0 could be different, because the solution contains a branch point in the complex plane at $\eta = 1$. The requirement that $A \rightarrow 0$ for $\eta \rightarrow \infty$ implies that $A'_0 = 0$, while the constant A_0 is the value of the distribution function at $t = 0$ ($\eta = 0$). This gives the solution for the area distribution function

$$A = A_0(1 - \eta)^a \text{ for } \eta \leq 1$$

$$= 0 \text{ for } \eta \geq 1. \tag{12}$$

It is useful to note the following two special cases. In the limit $a \rightarrow 0$, which corresponds to the case where there is no change in area due to tangential motion at the interface, the area distribution function is a constant at all times. In the limit $a \gg 1$, which corresponds to the case where the coarsening occurs due to a reduction in area without any change in curvature, the distribution function is of the form

$$A = A_0 \exp(-a\eta). \tag{13}$$

The moments of the curvature distribution can now be determined quite easily from the area distribution function (12). The total interfacial area per unit volume at any time t is given by

$$\text{Area}(t) = \int dK A(K, t)$$

$$= \frac{\mu}{\gamma a_1 t} \int_0^1 d\eta A(\eta) \tag{14}$$

$$= \frac{A_0 \mu}{t \gamma a_1 (a + 1)}.$$

The average curvature at a time t is

$$\langle K \rangle = \frac{1}{\text{Area}(t)} \int dK K A(K, t) \tag{15}$$

$$= \frac{\mu}{t \gamma a_1 (a + 2)}.$$

The above equations indicate that the total area and the average curvature of the interface decrease proportional to t^{-1} in the limit $t \gg 1$. The prediction regarding the time dependence of the curvature of the surface is identical to that of Siggia⁷ using capillary instability arguments. The present analysis is more quantitative than that of Siggia, because it also predicts the probability distribution of the curvature of the interface. However, there is a phenomenological constant a in the theory which has to be determined from the detailed microscopic dynamics of the interface. This is difficult to obtain analytically, and has to be obtained using simulations or by matching the predictions with experimental results.

It is useful to make a brief digression to obtain qualitatively similar results for the growth of a random interface in the order-disorder transition in solids. In this case, the motion of the interface occurs due to diffusive transport of the

constituents. For a system where the order parameter (concentration field) is not conserved, Ohta, Jasnow, and Kawasaki⁵ assumed that the velocity of the interface is proportional to the curvature $v \propto K$, and obtained an equation of the form

$$\frac{\partial u(\mathbf{x}, t)}{\partial t} = D \nabla^2 u(\mathbf{x}, t), \tag{16}$$

where $z = u(\mathbf{x}, t)$ represents the equation of the interface. In this case, the material properties influencing the motion of the interface is the diffusion coefficient D (with units of length²/time). If the motion of a section of the interface with curvature K is a function of the curvature K only, then the rates of change of curvature and area (analogous to 6 and 8) are

$$\frac{dK}{dt} = -a_1 D K^3, \tag{17}$$

$$\frac{1}{A} \frac{\partial_c A}{\partial t} = -a_2 D K^2. \tag{18}$$

Inserting these into the conservation Eq. (3), and defining the similarity variable $\eta = a_1 D K^2 t$, the following equation is obtained for the probability distribution function $A(\eta)$:

$$\frac{dA(\eta)}{d\eta} = -2\eta \frac{dA(\eta)}{d\eta} - aA(\eta), \tag{19}$$

where $a = (a_2/a_1)$ as before. This equation can be easily solved for a homogeneous initial condition $A = A_0$ at $t = 0$ to obtain

$$A(\eta) = A_0(1 - 2\eta)^{a/2} \text{ for } \eta \leq (1/2)$$

$$= 0 \text{ for } \eta \geq (1/2). \tag{20}$$

The area per unit volume and the mean curvature are easily obtained from the above expression. The total area per unit volume is

$$\text{Area}(t) = \int dK A(K, t)$$

$$= \frac{1}{2(Da_1 t)^{1/2}} \int_0^{1/2} d\eta \eta^{-1/2} A(\eta)$$

$$= \frac{1}{2(Da_1 t)^{1/2}} \sqrt{\frac{\pi}{2}} \frac{\Gamma(1 + (a/2))}{\Gamma[(3/2) + (a/2)]}, \tag{21}$$

where $\Gamma(x)$ is the gamma function. The average curvature at a time t is

$$\langle K \rangle = \frac{1}{\text{Area}(t)} \int dK K A(K, t)$$

$$= \frac{1}{(Da_1 t)^{1/2}} \frac{1}{a + 2} \left\{ \sqrt{\frac{\pi}{2}} \frac{\Gamma(1 + (a/2))}{\Gamma[(3/2) + (a/2)]} \right\}^{-1}. \tag{22}$$

The present analysis predicts that the area and the mean curvature decrease proportional to $t^{-1/2}$ in the order-disorder transition in solids. The scaling law for the mean curvature is in agreement with the previous result of Ohta, Jasnow, and

Kawasaki⁵ for a random interface in the order–disorder transition in solids, and the scaling is independent of the spatial dimension.

For a system with conserved order parameter,⁶ the motion of different sections of the interface are not independent, and the velocity is proportional to the gradient of the curvature $v = L \nabla K$. In this case, the dynamics of the interface depends only on the constant L which has units of length³/time, and it can easily be verified using methods similar to those used above that the curvature decreases proportional to $t^{-1/3}$. This is in agreement with the Lifshitz–Slyozov scaling law for the coarsening of droplets in a solid alloy.

III. EFFECT OF FINITE INTERFACE THICKNESS

The effect of the interaction between the motion of the interface and the concentration variation within the interface is analyzed in the present section. In the previous section, it was assumed that the interface is of infinitesimal thickness, and the interfacial energy per unit area of the interface is a constant. However, the motion of the interface causes a change in the area due to tangential motion along the interface, and this tangential motion could result in a change in the interfacial energy due to a variation in the interfacial concentration profile. This variation is studied using a perturbation analysis when the interfacial concentration profile is close to the concentration profile at equilibrium.

The equilibrium concentration profile of the interface between two fluids is obtained by minimizing the free energy per unit area along the interface,¹⁰ which is the surface tension of the interface, is

$$F[c] = \int dz \left[\Delta f(c) + \frac{1}{2} \kappa |d_z c|^2 \right], \quad (23)$$

where c is the concentration field, z is the coordinate perpendicular to the interface, and $d_z \equiv (d/dz)$. $\Delta f(c)$ is the difference between the free energy at a concentration c and the free energy of the two coexisting phases, and the second term on the right is the square gradient term. The concentration profile at equilibrium is easily obtained by minimizing the free energy with respect to variations in c and $d_z c$

$$d_z c = \left[\frac{\Delta f(c)}{\kappa} \right]^{1/2}. \quad (24)$$

The above equation for the interfacial concentration profile has to be solved numerically in general, but an analytical solution exists for the near critical regime where the free energy has the symmetric form

$$\Delta f(c) = \chi (c_0^2 - c^2)^2, \quad (25)$$

where $\pm c_0$ are the concentrations of the coexisting phases. In the present analysis, attention is restricted to the near critical quench, since an analytical solution for the concentration profile is available for this regime. However, the present analysis can easily be modified to include other situations where a numerical solution has to be obtained for the equi-

librium concentration profile. The equilibrium concentration profile is easily evaluated using a scaled concentration field $\psi = (c/c_0)$,

$$\psi_e = \tanh(z/h), \quad (26)$$

where $h = [c_0(\chi/\kappa)^{1/2}]^{-1}$ is the thickness of the interface, and ψ_e is the concentration field at equilibrium. The equilibrium surface tension, which is the free energy per unit area of the equilibrium interface, is

$$\gamma_e = \chi c_0^4 h. \quad (27)$$

In an interface which is not at equilibrium, the evolution of the concentration field is given by the diffusion equation

$$\frac{\partial c}{\partial t} = D \partial_z^2 \frac{\delta F}{\delta c} - v_z \partial_z c, \quad (28)$$

where D is the diffusion coefficient and $-v_z \partial_z c$ is the change in the concentration due to convective transport in the z direction which is discussed a little later. Equation (28), expressed in terms of the scaled concentration $\psi = (c/c_0)$ and scaled normal coordinate $z^* (z/h)$, reduces to

$$\frac{\partial \psi}{\partial t} = D^* \partial_{z^*}^2 \left[-\frac{1}{4} \partial_{z^*}^2 \psi - \psi(1 - \psi^2) \right] - (v_z/h) \partial_{z^*} \psi, \quad (29)$$

where $D^* = (4\chi D c_0^2/h^2)$. It is convenient to define a concentration field which represents the deviation of the local concentration from its equilibrium value, $\phi(z, t) = \psi(z, t) - \psi_e(z)$. The diffusion equation for the field $\phi(z, t)$ is

$$\frac{\partial \phi}{\partial t} = D^* \partial_{z^*}^2 \left(-\frac{1}{4} \partial_{z^*}^2 \phi - \phi + 3\psi_e^2 \phi + 3\psi_e \phi^2 + \phi^3 \right) - (v_z/h) \partial_{z^*} (\psi_e + \phi). \quad (30)$$

The velocity v_z is determined from the mass conservation condition at the interface

$$d_z v_z + \nabla_t \cdot \mathbf{v}_t = 0, \quad (31)$$

where \mathbf{v}_t is the tangential velocity at the interface, and ∇_t is the tangential gradient operator. The surface compression $\nabla_t \cdot \mathbf{v}_t$ is given by Eq. (8) with the assumption that the only length scale affecting the dynamics of the system is K^{-1} . The length scale for the variation of the tangential velocity due to the interface motion is K^{-1} , and the variation of the tangential velocity over lengths comparable to the interface thickness is $hK\mathbf{v}_t$. For a thin interface, ($hK \ll 1$), and the tangential velocity can be considered to be independent of the perpendicular distance from the interface over distances comparable to the interface thickness h . With this approximation, the normal velocity at the interface is

$$v_z = -z \nabla_t \cdot \mathbf{v}_t = \frac{a_2 \gamma K z}{\mu}. \quad (32)$$

The above expression indicates that the normal velocity diverges for $|z| \gg 1$, due to the invalidity of the assumption of constant tangential velocity for $|z| \sim K^{-1}$. However, this di-

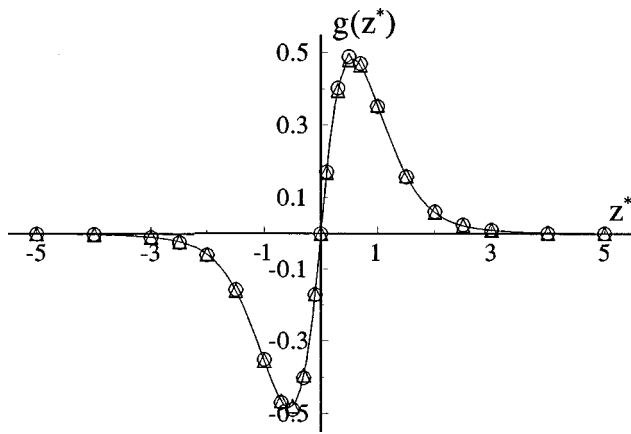


FIG. 1. Variation of the dimensionless concentration $g(z^*)$ [Eq. (36)] as a function of the dimensionless distance perpendicular to the interface z^* . \circ , solution obtained by including ten terms in the Laguerre polynomial expansion; Δ , solution obtained by including seven terms in the Laguerre polynomial expansion.

vergence does not cause difficulties in the analysis because the gradient of the concentration $\partial_z c$ decays faster than z^{-1} in this limit, and the product $v_z \partial_z c$ is finite.

The conservation Eq. (30) is solved using the ‘‘quasi steady’’ approximation, where it is assumed that the concentration field in the interface responds instantaneously to the constraints imposed by the interface motion. The time scale for the variation of the concentration field in the interface is $(1/D^*)$ and the time scale for the motion of the interface is $(\mu/\gamma K)$, and the quasi steady approximation is valid in the limit $(hK)(\gamma/\mu D^* h) \ll 1$. In addition, we make the linear approximation $\phi \ll \psi_e$, which is valid in the late stages of interfacial growth. With these two assumptions, the equation for the concentration field is

$$D^* \partial_z^2 \left(-\frac{1}{4} \partial_{z^*}^2 \phi - \phi + 3\psi_e^2 \phi \right) = \frac{a_2 \gamma K z^*}{\mu} \partial_{z^*} \psi_e. \quad (33)$$

This equation can be solved to obtain the concentration field ϕ . An analytical solution cannot be obtained, but it is possible to obtain a solution using an expansion in an appropriate orthogonal function space. In the limit $z \gg 1$, the solution has the form

$$\phi = \frac{a_2 \gamma K z^* \exp(-2z^*)}{2\mu D^*}. \quad (34)$$

The above behavior is best incorporated using a series of Laguerre polynomials as the basis functions

$$\phi(z^*) = \frac{a_2 \gamma K h z^*}{\mu D^*} \sum_{n=2}^{n_f} l_n [L(n, 2z^*) - 1] \exp(-2z^*), \quad (35)$$

where $L(n, 2z^*)$ are Laguerre polynomials. The above expansion is appropriate because it reproduces the correct behavior in the limits $z^* = 0$ and $z^* \rightarrow \infty$. The Laguerre polynomials are defined so that $L(n, x) = 1$ at $x = 0$. Consequently, the basis functions used in expansion (35) are all zero at $z^* = 0$, in agreement with the requirements of symmetry for the present case. In the limit $z^* \rightarrow \infty$, expan-

sion (35) correctly reproduces the behavior $\phi(z^*) \propto z^* \exp(-2z^*)$. The coefficients l_n by inserting the above expansion into conservation eq. (30), and evaluating the coefficients l_n . The function $g(z^*)$, defined as

$$g(z^*) = \frac{\mu D^* \phi(z^*)}{a_2 \gamma K h^2} \quad (36)$$

is shown as a function of z^* in Fig. 1. From this figure, it is seen that there is very little variation in $\phi(z^*)$ when the number of function n_f is changed from 7 to 10, and consequently n_f is set equal to 10 in the subsequent calculations.

The change in the interfacial energy per unit area due to a variation in the interfacial concentration can now be evaluated using a linear approximation,

$$\begin{aligned} \Delta F &= c_0^2 \int dz \{ 4\chi c_0^2 [\psi_e(z^*)^3 - \psi_e(z^*)] \phi(z^*) \\ &\quad + (\kappa/h^2)(d_{z^*} \psi_e)(d_{z^*} \phi) \} \\ &= \frac{a_2 p c_0^4 \chi \gamma K h}{\mu D^*}. \end{aligned} \quad (37)$$

The constant p was evaluated numerically using the solution for $\phi(z^*)$ (Fig. 1), and the value of the constant was found to be 0.0462. The low numerical value of the coefficient is due to the opposing contributions to the interfacial energy due to the terms proportional to Δf and the square gradient term. The effect of the correction to the concentration due to the square gradient term tends to increase the energy of the interface, while its effect on the term proportional to Δf tends to decrease the energy of the interface, and consequently the sum of these two contributions has a low numerical value. The ratio of the change in the interfacial energy due to nonequilibrium effects and the equilibrium surface tension is

$$\frac{\Delta F}{\gamma_e} = \frac{0.0462 a_2 \gamma K}{\mu D^*}. \quad (38)$$

IV. CONCLUSIONS

The area distribution function for a random interface was determined in Sec. II using certain simplifications, and it is useful at the outset to recall these simplifications and discuss the scope for future improvements. A two dimensional surface in three dimensional space is completely characterized if the principal curvatures K_1 and K_2 , which are the extrema of the curvatures along orthogonal directions, are specified at every point, or by the magnitude $K = (K_1^2 + K_2^2)^{1/2}$ and $\tan(\theta) = (K_2/K_1)$. In this case, it is appropriate to define the area distribution function $A(K, \theta, t)$ such that $A(K, \theta, t) dK d\theta dx$ is the area with magnitude of curvature in the interval dK about K , polar angle in the interval $d\theta$ about θ in the volume x . In Sec. II, the area distribution was integrated over the θ coordinate, and a conservation equation was written for this distribution function which is only a function of the magnitude of the curvature K . Consequently, only the magnitude of the curvature can be calculated using the present analysis, and the analysis does not distinguish

between interfaces with the same K but different ratios of principal curvatures. For example, there is no distinction between interfaces in the form of two dimensional waves and in the form of three dimensional waves if the magnitude of the curvature are the same. A more complete description of the interface would require the inclusion of both the principal curvatures in the analysis. This limitation does not exist for a one dimensional interface in two dimensional space, and the results of the present analysis should be directly applicable in this case.

Expressions for the rate of change of curvature and the rate of change of surface area due to tangential compression were derived using the assumption that the only material properties affecting the interface motion are the surface tension γ and the viscosity of the fluid μ , and the only length scale affecting the dynamics of the interface is the inverse of the magnitude of the curvature at that point. It should be noted that the rate of change of curvature and area of the interface are averages of the corresponding microscopic values over the polar coordinate $\theta = \arctan(K_2/K_1)$. In a more complete description, where the dependence on the angle θ is included, the normal velocity could be a function of both the curvature K^{-1} and the angle θ , and it would be necessary to carry out a microscopic analysis to obtain the exact values of the velocity. This would require the solution of the Stokes equations for the fluid subject to a jump in the normal stress condition across the interface; this type of analysis is likely to be complicated by the long range nature of the hydrodynamic interactions in the viscous limit.

The expressions for the rate of change of curvature and the rate of change of surface area due to compression were used to obtain an equation for the time rate of change of the area distribution function. A similarity solution was obtained for the conservation equation for the case where the area distribution function is independent of curvature at the start of the coarsening process. It would be necessary to obtain a numerical solution for the general case where the area distribution function is dependent on the curvature at the start of the coarsening process. The area distribution functions contains a parameter a , which is the ratio of the rate of change of the interfacial area due to tangential compression of the interface and the rate of change of the curvature due to normal motion of the interface. This phenomenological constant has to be determined from a microscopic analysis of the motion of the interface using simulation techniques or by comparison of the theoretical predictions with experiments.

The analysis predicts that the total interfacial area decreases proportional to t^{-1} in the late stages of spinodal decomposition, and the average curvature also decreases proportional to t^{-1} . These two results are the result of the same physics, since there is only one length scale in the problem. The latter result is in agreement with the theoretical results of Siggia⁷ and Furukawa⁸ which were derived using qualitative arguments, and with previous experimental results,^{3,4} but the former does not appear to have been derived before. In addition, the present analysis also provides expressions for the area density (12) and the mean curvature (13) as a function of the constant a appearing in the equation for the area den-

sity (9). The analysis was also extended to a the order-disorder transition in solids where the dynamics of the interface is dependent on the diffusion coefficient in the solid and the surface tension in the interface, and the analysis predicted that the area of the interface decreases proportional to $t^{-1/2}$, and the average curvature also decreases proportional to $t^{-1/2}$. The latter result is in agreement with the theory of Ohta, Jasnow, and Kawasaki,⁵ and with previous simulation results.⁶

In Sec. III, the effect of interface motion on the concentration profile at the interface was analyzed. The Cahn-Hilliard square gradient theory was used to describe the concentration dependence of the free energy. The concentration variation in the interface was described using a diffusion equation which contained a convective term which incorporated the convective transport due to the tangential compression of the interface. This equation was solved for the function $\phi(z)$, which is the difference between the actual concentration profile and the concentration profile at equilibrium. Terms linear in the concentration deviation ϕ were retained, and the diffusion equation was solved using the "quasi steady" approximation where there is a balance between the diffusive transport and the concentration source due to the compression of the interface. The rate of convective transport due to the compression of the interface is proportional to the curvature K , and consequently the deviation of the concentration profile from the equilibrium concentration profile is also proportional to K . The correction to the interfacial energy due to the deviation in the concentration ϕ was calculated. It was found that the correction to the interfacial energy is positive and proportional to K , indicating that regions with higher curvature have a larger normal velocity and coarsen faster than regions with lower curvature.

The analysis of Sec. III provides a first step towards incorporating the interaction between the large scale interface motion and the small scale concentration variation in the interface. An analytical solution for the correction to the interfacial energy due to concentration variation was possible because the linearization approximation was made, where only terms linear $\phi(z)$, the difference between the concentration and the equilibrium concentration, were retained. However, numerical solutions can easily be obtained for the full nonlinear equation, and this would help in extending the analysis to earlier times in the spinodal decomposition process where the effect of the interaction would be significant.

¹J. D. Gunton and G. Droz, *Introduction to the Theory of Metastable and Unstable States*, Lecture Notes in Physics No. 183 (Springer, Berlin, 1983).

²V. Kumaran, J. Chem. Phys. (submitted).

³H. Tanaka, J. Chem. Phys. **105**, 10099 (1996).

⁴N. C. Wong and C. M. Knobler, Phys. Rev. A **24**, 3205 (1981).

⁵T. Ohta, D. Jasnow, and K. Kawasaki, Phys. Rev. Lett. **49**, 1223 (1982).

⁶A. J. Bray, *Domain Growth and Coarsening*, in *Phase Transition and Relaxation in Systems with Competing Energy Scales*, edited by T. Riste and D. Sherrington (Kluwer Academic, the Netherlands, 1993).

⁷E. D. Siggia, Phys. Rev. A **20**, 595 (1979).

⁸H. Furukawa, Adv. Phys. **34**, 703 (1985).

⁹J. S. Langer and R. F. Sekerka, Acta Metall. **23**, 1225 (1975).

¹⁰J. W. Cahn and J. E. Hilliard, J. Chem. Phys. **28**, 258 (1958).