Noise of microstructural environments in late-stage phase coarsening

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Multiparticle diffusion equations were modeled to simulate the dynamics of late-stage phase coarsening in the region of lower volume fractions. Local environmental information and particle interactions within each coarsening ''locale'' are included in our simulations. These studies reveal that locale fluctuations occur in the growth rates of particles due to their differing environments. Multiplicative noise provides a sound basis to describe locale fluctuation in late-stage coarsening. A Fokker-Planck equation for the particle size distribution and its asymptotic solution are obtained.

Phase coarsening is a common relaxation process during late-stage microstructural evolution that leads to a decrease in the excess total interfacial energy of two-phase systems. During phase coarsening, larger particles tend to grow by absorbing solute atoms at the expense of small particles that tend to dissolve by losing them. Over time, this "competitive diffusion" results in an increase in the *average* size of the particle population, and in a concomitant decrease in the number density of particles. Indeed, the physical properties of two-phase materials depend on the material's average particle size and particle size distribution function (PSD). The theory of phase coarsening was initiated by Lifshitz and Slyozov [1] and Wagner [2]. This theory is often referred to as Lifshitz-Slyozov-Wagner (LSW) theory, and retains full validity only in the limit of a vanishing volume fraction. The prediction of LSW theory that the cube of the average length scale of particles increases linearly with time is shown to be valid even in the case of finite volume fractions by numerous experiments. The literature describing the evolution of two-phase microstructures with nonzero volume fractions consists of several kinds of mean-field theories [3]. Recently, Glicksman *et al.* [4] reviewed the interaction effects expected among dispersed particles, and discussed how such multiparticle interactions influence the kinetics of phase coarsening and broaden PSD. The PSD's predicted from mean-field theories are narrower than those observed in experiments [5].

LSW theory and mean-field theories, in general, predict that particles with identical size have the same growth rates, regardless of their location and environment in a microstructure. Experiments [6], however, clearly show the presence of fluctuations indicating that particles of same size exhibit different growth rates. Rogers *et al.* [7] found that some particles larger than their nearest neighbors shrank in their experiment, and suggested that growth rates of individual particles depend not only on their size, but also on the details of the local environment. Fluctuations during phase coarsening were first demonstrated by Voorhees and Glicksman simulations [8]. Wang *et al.* [9] then developed a stochastic analytic model of coarsening that employed a Fokker-Planck equation (FPE) to estimate the PSD. Marsh and Glicksman [10] have briefly discussed the issue of microstructure fluctuations. Recently, Pande and Rajagopal [11] analyzed grain growth and phase coarsening using a stochastic approach.

Different fluctuation terms were assumed to operate in Refs. [9] and [11] and, consequently, these studies yielded different types of FPEs. Nonetheless, scant attention has as yet been paid to studying the character and strength of the fluctuations arising from the influence of "locales" or individual microstructural environments of the surrounding particles. Moreover, a broadly accepted stochastic theory of phase coarsening is not currently available. In this paper, we use multiparticle diffusion to simulate the coarsening process, study the character of the fluctuations, and suggest a stochastic theory for the coarsening analysis.

The two-phase coarsening system consists of n polydisperse spherical precipitates suspended throughout a three-dimensional matrix. Some additional simplifying assumptions are needed: (1) the kinetics of coarsening is determined solely by volume diffusion through the matrix; and (2) the diffusion transport to or from each phase domain occurs slowly enough to be considered quasistatic. These assumptions justify approximating the diffusion equation with Laplace's equation to describe the concentration fields, in the matrix, $\nabla^2 \mathcal{C}(\mathbf{r}) = 0$, where $\mathcal{C}(\mathbf{r}) \equiv [c(\mathbf{r}) - c_0]/c_0$ defines a dimensionless diffusion potential; $c(\mathbf{r})$ is the concentration at any field point defined by the position vector $\mathbf{r}$, and c_0 denotes the equilibrium solubility at a flat interface between the matrix and particle phases. The boundary conditions at the spherical interface of the ith particle are specified through the Gibbs-Thomson local equilibrium solubility relation, namely, $\mathcal{C}(R_i) = 1/R_i$, where R_i is the radius of the ith particle scaled by the capillary length [17].

The solution to Laplace's equation for n particles may be represented as the superposition of n dimensionless concentration fields summed over the system of particles, namely,

$$\mathcal{C}(\mathbf{r}) = \sum_{i=1}^{n} \frac{B_i}{|\mathbf{r} - \mathbf{r_i}|} + \mathcal{C}_\infty, \qquad (1)$$

where $\mathbf{r_i}$ is a vector that locates the center of the ith particle in the microstructure. The ith particle's total volume flux $4\pi B_i$ and the far-field potential $\mathcal{C}_\infty$ comprise $n+1$ unknowns. The microstructure's global mass conservation law for a discrete system consisting of n spherical particles may be expressed through the volume fluxes as $\Sigma_{i=1}^{n} B_i = 0$. Using Eq. (1) along with the mass conservation law, one obtains after a few steps of algebra

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$$C_\infty = \frac{1}{\langle R \rangle} - \frac{1}{n \langle R \rangle} \sum_{k=1}^{n} B_k \sum_{j \neq k}^{n} \frac{R_j}{r_{jk}}, \qquad (2)$$

where r_{jk} is the distance between the centers of any pair of particles j and k, and $\langle R \rangle$ is the average radius. The relationship for the far-field potential, Eq. (2), expresses microstructure responses that include interactions among particles. For finite system, Eq. (2) clearly demonstrates that the far-field potential C_∞ depends explicitly on *locale* information concerning particle positions and the distances between particle pairs. Moreover, Eq. (2) includes enough detailed environmental information to describe the locale of every particle, and, most importantly, its subtle influence on the particle's diffusion-limited growth or shrinkage.

Weins and Cahn [12] were the first to use a few particles to simulate discrete coarsening events. Then Voorhees and Glicksman [8] used several hundred particles to simulate phase coarsening. Later, Beenakker [13] further improved multiparticle simulation procedures and incorporated several thousand particles in his simulation. More recently, others [14–18] have continued to improve upon large-scale accurate simulations of phase coarsening processes. Phase coarsening kinetics is simulated by placing n particles of the dispersoid phase within a cubic simulation box. The contiguous spaces between the particles represent the matrix phase in which the dispersoid population is embedded. Particles are located by specifying the positions of their centers and by their radii. The dimensionless form of the growth rate of the ith particle can be written as

$$\frac{dR_i}{dt} = -\frac{B_i}{R_i^2} \quad (i = 1, 2, \ldots, n), \qquad (3)$$

where R_i is known at the evolution time t. The time is non-dimensionalized by a characteristic diffusion time [17]. The Runge-Kutta method was used to integrate the growth rate numerically. Substituting Eq. (1) into Gibbs-Thomson condition for n particles, one obtains a system of linear equations, which may be cast into matrix form as

$$\mathbf{A'} \cdot \mathbf{B'} = \mathbf{U'}, \qquad (4)$$

where $\mathbf{A'}$, $\mathbf{B'}$, and $\mathbf{U'}$ are, respectively, $n \times n$, $n \times 1$, and $n \times 1$ matrices. These matrices can be found in our paper [17]. The Gauss-Seidel method was employed to solve this system of linear equations, Eq. (4), yielding at each time step values for the B_i's. Substitution of the updated B_i's back into Eq. (3) dynamically advances the coarsening by updating the radii of all the particles and their coordinates at any time step.

We simulated microstructures with dispersoid volume fractions $V_V = 10^{-4}$, $V_V = 10^{-3}$, $V_V = 10^{-2}$, and $V_V = 10^{-1}$. Typical microstructure cross sections of these simulated two-phase coarsening system are shown in Figs. 1(a) and 1(b). Specifically, Figs. 1(a) and 1(b) are planar cross sections taken through a simulated evolving microstructure, the volume fraction for which is 0.1. Comparison of these cross sections clearly shows the process of phase coarsening progressing, as the small particles shrink and large particles grow, and their overall number density decreases. What seem
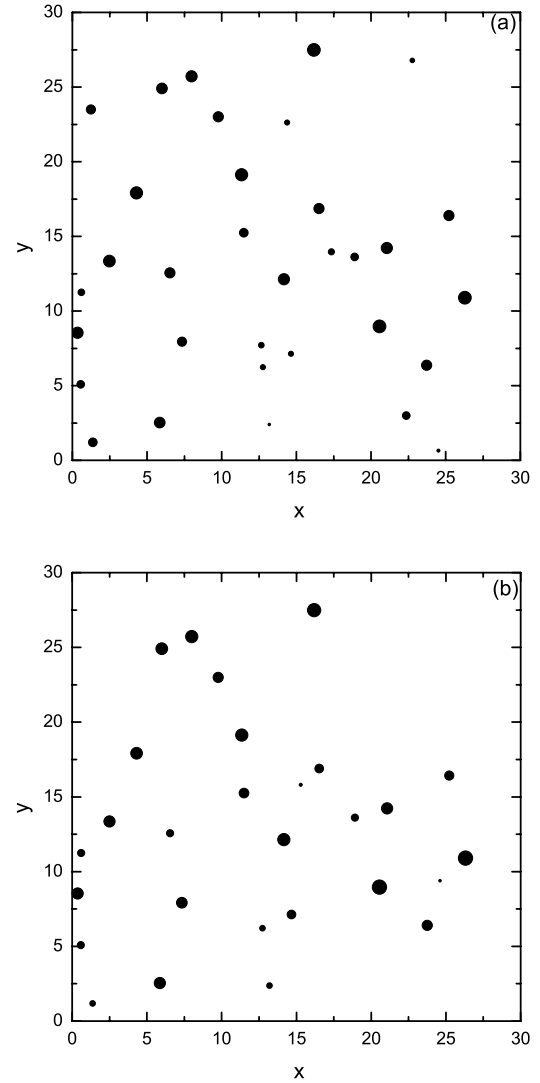

FIG. 1. The microstructures of the simulating system (a) initial state, computer time $t = 0$, and (b) $t = 0.375$. The particles are black and the matrix is white.

to be small "new" particles appearing in Fig. 1(b) is just the three-dimensional effect of some particles which were beyond the plane of view in Fig. 1(a) growing and intersecting with the cross section shown in Fig. 1(b).

LSW theory and mean-field models predict that particles with identical sizes have the *same* volume fluxes, regardless of their locations within the microstructure. By contrast, our simulations reveal that the volume fluxes of the particles are different, even for particles with the same radii, since they are located in different microstructural environments. Figure 2 shows the volume fluxes $B(\rho)$ simulated for $V_V = 10^{-1}$, where ρ is the normalized radius $R/\langle R \rangle$. For comparison, the average trend of the volume fluxes [4] has been shown analytically to be $B(\rho) = (1-\rho)(1+\rho/\rho_0)$. Here ρ_0 is the normalized Debye diffusion length $\rho_0 \equiv R_0/\langle R \rangle = \sqrt{\langle \rho^3 \rangle/(3\langle \rho \rangle V_V)}$ [4]. The volume fluxes in LSW theory, $B(\rho) = 1 - \rho$, is also plotted in Fig. 2. The plot demonstrates that the average volume flux functions with particle-particle interactions steadily deviate from the linear-mean-field LSW prediction that lacks interactions. The nonlinear character of
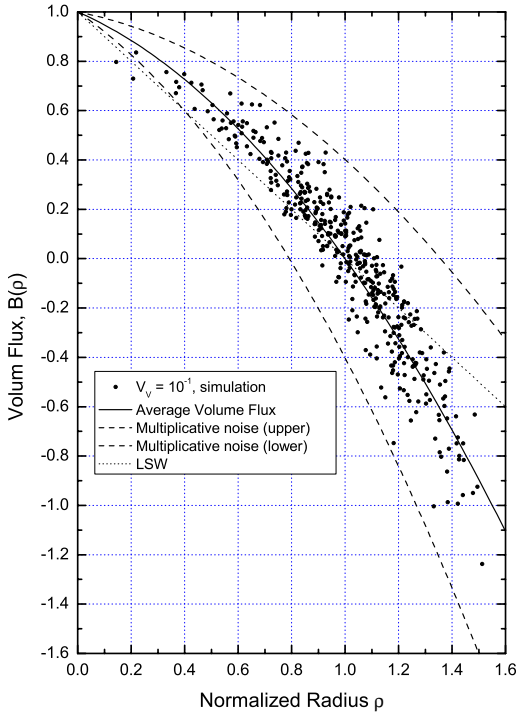
FIG. 2. Volume flux $B(\rho)$ versus scaled particle radius ρ. Data are from simulations at $V_V = 0.1$.

the particle volume flux versus particle size increases steadily with increasing volume fraction. Moreover, particles of identical size exhibit a range of B_i values. It means that growth rates of particles with identical size are different and deviate from that of our mean-field prediction. In fact, due to local variations of concentration of particles with identical size, the growth rates are not exactly equal to the mean value. Experimental results [6,7] also confirmed these effect. We use "locale noise" or "locale fluctuation" to describe the effect of local variations of concentration of particles with identical size. However, here the "locale noise" is different from thermal noise. The locale noise is from the local variations of concentration of particles with identical size, i.e., from different environments of particles of identical size. It is not related to thermal noise at all.

Of particular interest is to note that particles, particularly those close to the average size, actually behave unpredictably, by sometimes growing or dissolving rapidly. To reiterate, were these critically sized particles to act in a deterministic, mean-field manner, they would neither grow nor shrink. Our simulations also show that the strength of locale noise for the volume fluxes increases with increasing volume fraction. In addition, we found that larger particles experience stronger locale noise in their growth rates than do the smaller particles. The dispersion of locale noise with particle size is caused by the spatial localization of the diffusion field surrounding small particles. This observation suggests that these fluctuations are correlated with the size of a particle and with the volume fraction of the microstructure. In order to clarify the nature of locale noise found in these simulations, we recently developed estimates of the expected noise bands using statistical sampling theory. The expected variance from the mean value in a smaller volume of sample is proportional

to $1/\sqrt{N_s}$, where N_s is the number of volume points sampled. The number of volume points is proportional to the volume of a spherical shell representative of the local environment surrounding the particle of interest. We derived the following expression for the locale noise of the particle volume flux,

$$\zeta\left(\frac{\rho}{\rho_0}\right) = \frac{\rho}{2\rho_0}\left(1 + \frac{\rho}{\rho_0}\right)\boldsymbol{\eta}. \qquad (5)$$

Here $\boldsymbol{\eta}$ is a Gaussian random variable with mean value zero and unit width, and $\zeta(\rho/\rho_0)$ is the Gaussian multiplicative noise. In Fig. 2, all the simulation data are scattered between bands of the multiplicative noise, showing that Gaussian multiplicative noise provides a reasonable match with the simulations.

Considering that there exists a spectrum of fluctuations in the volume fluxes, one must consider adding a multiplicative noise term to the growth rate [4]. The resulting expression for a particle's growth rate is

$$\frac{dR}{dt} = \frac{1}{R}\left(\frac{1}{R^*} - \frac{1}{R}\right)\left(1 + \frac{R}{R_0}\right) + \frac{1}{2R_0}\left(\frac{1}{R} + \frac{1}{R_0}\right)\boldsymbol{\eta}. \qquad (6)$$

Equation (6), a stochastic differential equation, provides the kinetic law for particles in a "noisy" microstructure. The governing equation for the PSD associated with Eq. (6) is an FPE, rather than the continuity equation used in mean-field theories. First, we introduce new scaled variables as follows: $u = R/R_0, d\tau = dt/R^{*3}$, and the constant $K = dV^*/dt$ is the rate constant describing the growth rate of the critical volume V^*. Using Stratonovich's calculus for stochastic differential equations, one can show that the FPE associated with Eq. (6) is

$$\frac{\partial F(u,\tau)}{\partial \tau} = -\frac{\partial}{\partial u}D_1(u)F(u,\tau) + \frac{\partial^2}{\partial u^2}D_2(u)F(u,\tau), \quad (7)$$

where $D_1(u) = [2(u - 1/\rho_0)/\rho_0^2 u^2](1 + u) - (1/4\rho_0^6 u^3)(1 + u) - Ku$ and $D_2(u) = (1/4\rho_0^6 u^2)(1 + u)^2$. $F(u,\tau)du$ is the number of particles per unit volume, the scaled sizes of which are between u and $u + du$ at time τ. In the case of LSW theory, the volume fraction vanishes, so $\rho_0 \to \infty$, and Eq. (7) reduces to the standard continuity equation. Because the particles attain a nonzero size at large times, there exists the natural boundary condition $F(0,\tau) = 0$ for Eq. (7). In addition, the volume fraction constraint over the dispersed phase in three dimensions may be expressed as $\int_0^\infty u^3 F(u,\tau)du = 3V_V/4\pi R_0^3$.

According to the hypothesis of statistical self-similarity in microstructural evolution [19], $F(u,\tau)$ can be recast in a product function form, namely, $F(u,\tau) = F_0(u)H(\tau)$. Here $F_0(u)$ is the time-independent, scaled PSD. The function $H(\tau)$ is the explicit time-dependent portion of the PSD that specifies the temporal behavior. After some involved calculation [20], Eq. (7) can be rewritten as

$$\frac{d^2F_0(u)}{du^2} + p(u)\frac{dF_0(u)}{du} + q(u)F_0(u) = 0, \qquad (8)$$

where

$$p(u) = \frac{4\rho_0^6 K u^3}{(1+u)^2} - \frac{3+8\rho_0^4 u(u-1/\rho_0)}{u(1+u)}$$

and

$$q(u) = \frac{3+(2-16\rho_0^3)u+8\rho_0^4(1-1/\rho_0)u^2+8Ku^4}{u^2(1+u)^2}$$
$$+ \frac{4\rho_0^6 K u^2}{(1+u)^2}.$$

Considering $u \ll 1$, keeping the first order of u in $p(u)$ and $q(u)$, and using the method of series expansion, we can obtain the solution of Eq. (8) as

$$F_0(u) = u^3 \sum_{n=0}^{\infty} a_n u^n, \tag{9}$$

where the coefficients are

$$a_n = \frac{7+24\rho_0^3-(8\rho_0^3+3)(n+3)}{(n+3)(n-1)+3} a_{n-1}.$$

The coefficient a_0 is a normalized constant of $F_0(u)$ given as $\int_0^\infty F_0(u)du = 1$. One can see how the interaction and fluctuation effects influence the scaled PSD through ρ_0. To our knowledge, this is the first time that explicit effects of interactions and fluctuations are introduced to the scaled PSD. Most experimental observations and computer simulations of coarsening kinetics present the PSD in terms of normalized particle radii, as $g(\rho)$. It can be obtained via the transformation $g(\rho) = F_0(u)/\rho_0$. We calculated $g(\rho)$, for the case of $V_V = 0.12$, in accordane with Eq. (9). Figure 3 shows the PSDs obtained from the FPE with noise and from mean-field theory without noise [4]. Clearly, the addition of microstructural locale noise broadens the PSD.

In summary, we simulated microstructure evolution in a two-phase system by solving the discrete multiparticle diffu-
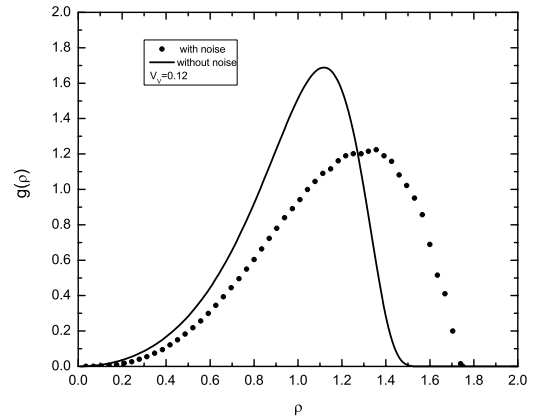

FIG. 3. PSDs are obtained with and without stochastic effect, respectively, at $V_V = 0.12$.

sion equation for many interacting particles near steady state. Our simulations show that there exist locale fluctuations in the growth rate of particles during microstructure evolution, for both sparse finite microstructures ($V_V = 10^{-4}$) and moderately dense ones ($V_V = 0.1$). Simulations and Eq. (5) indicate that larger particles experience stronger locale fluctuations than do smaller ones, and systems with higher volume fractions experience stronger locale fluctuations than do systems with lower ones. We found that locale fluctuations can be described approximately by multiplicative Gaussian noise, a finding which is also supported by these simulations. We then derived stochastic kinetic equation describing the growth rate of interacting particles, in distinction with deterministic kinetics found in conventional coarsening theory. The FPE associated with the stochastic aspects of microstructural coarsening is presented, and an asymptotic solution to this FPE was found. Clear evidence is shown for the fact that the locale noise broadens the PSD.

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