

Unified Model Equations for Study of Microstructure Evolution

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Summary

Microstructural modeling is very important because it can provide a critical link between properties, mesoscopic length scale, and atomistic scale (multiscale modeling). There exist a couple of models and simulations to study microstructural evolution. It will be important and useful to discover unified model equations hidden in microstructure evolution. In this paper, I will derive the unified model equations for microstructure evolution. The governing equations in Lifshitz-Slyozov-Wagner theory and diffusion screening theory that modeled microstructural evolution are derived with some approximations from the unified model equations. The governing equations in multiparticle diffusion simulation and phase-field simulation in microstructure evolution are also derived from the unified model equations. The advantages and limitations for different theories and simulations in microstructure evolution are compared. This comparison can guide scientists to select computational tools for their needs in microstructure evolution. The unified model equations can be applied in many new technological fields, such as self-assembly in nanoscience.

Introduction

In a typical phase separation process, phase coarsening usually follows a temperature quench from an initially homogeneous phase that results in a two-phase structure. Specifically, a typical precipitation sequence occurring within a supersaturated solution, or matrix, initially involves nucleation of the second phase, then its growth, and, finally, onset of competitive coarsening among the precipitate particles. Phase coarsening is a common relaxation phenomenon occurring during late-stage microstructure evolution that is driven by a decrease in the total interfacial free energy of two-phase systems. Indeed, the physical and mechanical properties of two-phase materials, such as hardness and toughness, often depend on the material's average particle size and particle-size distribution function (PSD).

Many theories and simulations in microstructure evolution have been developed during the last 50 years. What are the similarities and the differences among the theories and simulations in microstructure evolution? What are the fundamental principles for these theories and simulations? What are the advantages and the limitations for these theories and simulations? Are there any unified model equations for these existing theories and simulations? In this paper, answers to these questions

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will be provided from a fundamental point of view. Understanding these questions will advance theories and simulations in microstructure evolution. Unified model equations will be derived for microstructure evolution, and some existing theories and simulations can be derived from the unified model equations.

Lifshitz-Slyozov-Wagner theory

The first quantitative description of phase coarsening was initiated by Lifshitz and Slyozov [1] and Wagner [2]. This theory is often referred to as the “LSW theory” and retains full validity only in the limit of a vanishing (zero) volume fraction. The prediction of LSW theory that the cube of the average length scale of particles increases linearly with time has, however, been shown to remain valid by numerous experiments, even in the case of non-zero volume fractions. Specifically, the authors found that systems entering the long-time limit of phase separation exhibit self-similar (affine) properties, such as a re-normalized PSD, wherein the microstructure changes continuously by just a single scale factor. In other words, certain metric features of the microstructure change by a simple magnification factor as annealing time increases. The growth rate of particle in LSW theory is

$$\left(\frac{dR}{dt}\right)_{LSW} = \frac{1}{R} \left(\frac{1}{R_c} - \frac{1}{R}\right), \quad (1)$$

where R_c and R are critical radius and radius, respectively. In the derivation of Eq.(1), all length scales are non-dimensionalized through the appropriate capillary length, $l_c = \frac{2\sigma V_m}{R_g T}$, where σ , V_m , R_g and T represent the surface energy, molar volume, universal gas constant, and absolute temperature, respectively. Physical coarsening time is non-dimensionalized through the characteristic diffusion time, $\tau_d = \frac{l_c^2}{DC_0}$, to yield the dimensionless time, t . Here D and C_0 are, respectively, the matrix interdiffusion coefficient and the equilibrium solute concentration in the matrix at a planar interface with the precipitate phase [3].

Diffusion screening theory

LSW theory ignores the effect of the volume fraction of the precipitate particles and their interactions by assuming that neighboring particles are far away from the particle of interest. However, in real systems such as alloys, a finite volume fraction of particles, $V_V \neq 0$, is distributed, often in close proximity, and both local and many-body interactions arise among the particles. Numerous attempts have been made over the past 50 years to improve upon LSW theory by extending its applicability to the more realistic situation of non-zero volume fractions (see recent book chapter [4] and paper [3] and references therein). In the case of non-zero volume fraction, the diffusion interactions among particles, which are many-body interactions, need to be considered. In order to approximately describe many-body interactions, we introduced diffusion screening length, R_D which sets the maximum

range over which the interactions occur, and beyond which such interactions cease. Quantitatively speaking, the diffusion potential at the surface of screening sphere is the average potential of the system or background potential. We found that diffusion screening length is related to the volume fraction and moments of PSD as follows [5].

$$R_D = \frac{1}{\sqrt{3}} \left(\frac{\langle R^3 \rangle}{\langle R \rangle} \right)^{1/2} V_V^{-1/2}. \quad (2)$$

Using the Poisson equation to describe the diffusion field, Gibbs-Thomson condition, and diffusion screening length, we developed a diffusion screening theory (DST) for the case of non-zero volume fraction. In DST, the interactions among particles increase the LSW growth rate by a factor of $(1 + R/R_D)$, described as follows

$$\left(\frac{dR}{dt} \right)_{DST} = \left(\frac{dR}{dt} \right)_{LSW} \left[1 + \frac{R}{R_D} \right]. \quad (3)$$

Following the LSW argument and self-similarity of late phase coarsening, PSD can be calculated, and it is in good agreement with experimental results [5]. Applying the stability conditions for largest particle in the system, the maximum size of particle and coarsening rate constant of particle can be predicted [5].

Pletcher [7], conducted experimental measurements to determine normalized maximum radius ρ_{max} in Al-Li alloy. He found that the normalized maximum radius $\rho_{max} = 1.76$ from experimental measurement when the precipitate volume fraction $V_V = 0.43$. The DST predicts that $\rho_{max} = 1.75$. Marqusee and Ross' prediction is $\rho_{max} = 1.82$ [6]. This shows that the prediction of the DST on the normalized maximum radius is in good agreement with the experimental measurement. The DST predicted that the coarsening rate constant is related to volume fraction by a complicated function and reduces to the value of the LSW theory when the volume fraction goes to zero.

Unified model equations

We choose a coarse-grained order-parameter field (e.g., concentration density) $\phi(\vec{x}, t)$ to describe the entire microstructure. This method can be used to study solid-solid, solid-liquid and liquid-liquid phase separating systems in three dimensions. A suitable Ginzburg-Landau free energy functional to describe an ordered phase in three dimensions is as follows in the dimensionless form

$$F[\phi] = \int d^3x \left[\frac{1}{2} (\nabla\phi)^2 + V(\phi) \right], \quad (4)$$

where the bulk free energy density $V(\phi)$ has a double-well structure. The minima of $V(\phi)$ occur at $\phi = \pm 1$, and we adopt the convention that $V(\pm 1) = 0$. The two minima of V correspond to the two equilibrium states in phase separation in binary

system, while the gradient-squared term in Eq.(4) is related to an energy cost with an interface between two phases.

From now on we limit our study to the case of a conserved order parameter. In the binary alloy system, it is clearly physically that A and B atoms can exchange only locally, and the free energy of the system will reach the minimum as system finishes phase separation, which leads to diffusive transport of the order parameter as follows

$$\frac{\partial \phi}{\partial t} = \nabla^2 \frac{\delta F}{\delta \phi} = -\nabla^2 [\nabla^2 \phi - V'(\phi)]. \quad (5)$$

Eq.(5) is called Cahn-Hilliard equation. Eqs.(4) and (5) are *unified model equations*.

Using the relationship developed in Allen and Cahn' paper [8],

$$\nabla^2 \phi = \frac{\partial \phi}{\partial g} (\nabla \cdot \hat{\mathbf{g}}) + \frac{\partial^2 \phi}{\partial g^2}, \quad (6)$$

then the chemical potential near the interface, Γ , can be rewritten as

$$\mu|_{\Gamma} = V'(\phi) - \frac{\partial \phi}{\partial g} \kappa - \frac{\partial^2 \phi}{\partial g^2}, \quad (7)$$

where $\kappa = \nabla \cdot \hat{\mathbf{g}}$ is the curvature, and $\hat{\mathbf{g}}$ is a unit vector normal to the interface. It is considered that μ and κ vary smoothly along the interface and that $\frac{\partial \phi}{\partial g}$ is sharply peaked at the interface in Eq.(7). Multiplying Eq.(7) by $\frac{\partial \phi}{\partial g}$ and then integrating over g through the interface yield the value of μ at the interface

$$\mu|_{\Gamma} \Delta \phi = \Delta V - \sigma \kappa, \quad (8)$$

where $\Delta \phi$ is the change in ϕ across the interface, and ΔV is the difference in minima of the potential for the two bulk phases. In the derivation of Eq.(8), both $\frac{\partial \phi}{\partial g} \rightarrow 0$ far from the interface and the identification of surface energy $\sigma = \int_{-\infty}^{\infty} (\frac{\partial \phi}{\partial g})^2 dg$ are applied [8].

The velocity v of the motion of the interface is related to the imbalance between the current following into and out of it as follows

$$v \Delta \phi = J_{out} - J_{in} = - \left[\frac{\partial \mu}{\partial g} \right] = - [\hat{\mathbf{g}} \cdot \nabla \mu], \quad (9)$$

where [...] represents the discontinuity across the interface.

Derivation of LSW theory

Now we study the case of a single spherical particle of minority phase Ω_+ (positive values of the order parameter) with a radius R , immersed in a sea of majority phase Ω_- (negative values of the order parameter), and separated by the interface Γ . We define $\phi_0(\vec{r}) = \phi_{eq}^+$ in Ω_+ , $\phi_0(\vec{r}) = \phi_{eq}^-$ in Ω_- , $\Delta\phi = \phi_{eq}^+ - \phi_{eq}^-$, a variable $\theta(\vec{r})$

$$\theta(x) = \frac{\phi(\vec{r}) - \phi_0(\vec{r})}{\phi_{eq}}, \tag{10}$$

and the dimensionless quantity L_0 ,

$$L_0 = \frac{\sigma}{2\phi_{eq}^2}, \tag{11}$$

where \vec{r} is the field point vector. Simplifying to the case where $V(\phi) = \phi^2(\phi^2 - 2)/4$ and the minima have equal depth and taking the minima to be $\phi = \pm 1$, we have $\Delta V = 0$, and Eq.(8) is reduced to usual Gibbs-Thomson condition as

$$\mu|_{\Gamma} = -\frac{\sigma\kappa}{\Delta\phi}. \tag{12}$$

First, the quasi-steady approximation, $\partial\phi/\partial t = 0$, is applied in Eq.(5). Second, to the first order, μ can be written as $\mu = \chi^{-1}(\phi(\vec{r}) - \phi_0(\vec{r}))$, where χ is the susceptibility defined as $\chi = (\partial\mu/\partial\phi)_{eq}^{-1}$. The coordinates and time are rescaled by the quantities L_0 and L_0^2 , respectively, but keep the same notation in Eq.(9) and Eq.(12). Finally, Eqs.(5), (9), and Eq.(12) can be reduced to

$$\nabla^2\theta(\vec{r}) = 0, \tag{13}$$

$$\theta(R) = \frac{1}{R}, \tag{14}$$

$$\frac{dR}{dt} = [\hat{g} \cdot \nabla\theta]_{\Gamma}. \tag{15}$$

The solution to Eq.(13) with the condition Eq.(14) is

$$\theta(r) = \frac{1 - \theta_0 R}{r} + \theta_0. \tag{16}$$

Now $\partial\theta/\partial r$ can be calculated from Eq.(16). After $\partial\theta/\partial r$ is substituted into Eq.(15), we can get the growth rate $\frac{dR}{dt}$, which is the same as the LSW growth rate, Eq.(1), with $R_c = 1/\theta_0$. θ_0 is the background-matrix dimensionless potential, and it is assumed to be uniform throughout the matrix phase. It shows that we can derive the LSW theory with some approximations from the unified model equations.

Derivation of governing equation in multiparticle diffusion simulation

Consider the case with many (say n) spherical particles of minority phase with different radii, R_i , immersed in a sea of majority phase. The contiguous spaces between the particles are filled by the matrix phase, throughout which the dispersoid population is embedded. Particles are located by specifying the positions of their centers with three coordinates representing the Cartesian vectors, \vec{r}_i , and by their radii, R_i . The diffusion transport to or from each phase domain occurs slowly enough to be considered quasi-steady so that the term $\partial\phi/\partial t = 0$ in Eq.(5). Following the same way as that used in the case of single particle, we can derive the following equations

$$\nabla^2\theta(\vec{r}) = 0, \quad (17)$$

$$\theta(R_i) = \frac{1}{R_i}, \quad (18)$$

$$\frac{dR_i}{dt} = [\hat{\mathbf{g}} \cdot \nabla\theta]_{\Gamma_i}, \quad (19)$$

The boundary conditions at the spherical interface of the i^{th} particle are specified through the Gibbs-Thomson condition, Eq.(18). Numerically solving Eqs.(17), (18), and (19) is multiparticle diffusion simulation (MDS).

Derivation of governing equations in diffusion screening theory

The interfaces in the conserved fields cannot move independently due to the requirement of conservation. At late times the dominant growth mechanism is that the order parameter transports from interfaces of high curvature to low curvature by diffusion through the intervening matrix phase. We first linearize Eq.(5) in one of the bulk phases, with $\phi \approx 1$. Substituting $\phi = 1 + \tilde{\phi}$ into Eq.(5) and expanding the term $V'(1 + \tilde{\phi})$ in Taylor series, and keeping linear term in $\tilde{\phi}$, we have

$$\frac{\partial\tilde{\phi}}{\partial t} = -\nabla^2[\nabla^2\tilde{\phi} - V''(1)\tilde{\phi}]. \quad (20)$$

Again it is assumed that the diffusion field relaxes quickly compared with the rate at which the interfaces move, and it is safe to have $\frac{\partial\tilde{\phi}}{\partial t} = 0$ in Eq.(20). With this assumption, Eq.(20) should be written as

$$\nabla^2\tilde{\phi} - V''(1)[\tilde{\phi} - \tilde{\phi}_\infty] = 0, \quad (21)$$

where ϕ_∞ is background diffusion potential in the matrix. Eq.(21) is nothing more than the starting equation of diffusion screening theory with $V''(1) = 1/R_D$ [5]. Using both Gibbs-Thomson condition and definition of diffusion screening length, we can derive the growth rate (Eq.(3)) in the DST from Eq.(21).

Conclusions

In summary, we have shown that, in the case of the conserved order parameter, the Ginzburg-Landau free energy functional (Eq.(4)) and governing equation (Eq.(5)) can account for the unified model equations for microstructural evolution. Phase field simulation (PFS) can be derived from the unified model equations without approximation. The LSW and DST theories and governing equations in MDS are derived from the unified model equations with some approximations. This convinces us that the LSW and DST theories, MDS, and PFS stem from same root, i.e., the unified model equations. The hidden relationships among the different theories and simulations are revealed in this paper. This new result will help investigators to understand and compare results in microstructure evolution more precisely and effectively. The error from which the quasi-steady approximation $\partial\phi/\partial t = 0$ can be determined through conducting both phase-field simulation and multiparticle diffusion simulation in the same system. The unified model equations show that under the condition of accepted error, scientists can select faster and economical computational tools to study microstructure evolution, rather than just use trial and error. The unified model equations have many new technological applications such as self-assembly in nanoscience [9].

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