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Phase separation dynamics in binary systems containing mobile particles with variable Brownian motion

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Abstract. This study investigates the spinodal decomposition dynamics in binary mixtures containing mobile particles by combining the Cahn–Hilliard equation with Langevin dynamics for particles with Brownian motion changes proportional to their mobility. We solve the Cahn–Hilliard equation numerically using a semi-implicit Fourier spectral method, and show that the domain growth rate first increases with the increase in particle mobility, and then decreases. The effect of filler particle concentration on the domain growth depends on its mobility: when the particle mobility is low, the domain growth rate decreases with the increase in particle concentration; whereas when the particle mobility is high, the domain growth rate decreases and then increases and finally decreases again with the increase in particle concentration. The proposed model suggests the possibility of controlling macroscopic behaviour of binary alloys by altering filler particle properties.

Keywords. Spinodal decomposition; Cahn–Hilliard; simulation; particles; Brownian motion.

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1. Introduction

Spinodal decomposition (SD) describes the kinetics of phase separation in multicomponent alloys or fluids as a result of quenching from a thermodynamically unstable single-phase homogeneous state to a coexisting state of the phase diagram [1,2]. In contrast to nucleation and growth, the SD has a negative diffusion constant, i.e. uphill diffusion, and requires no thermal activation energy to occur in the unstable rather than the metastable region of a phase diagram.

The SD has been the subject of many experimental and theoretical studies. Douglass *et al* [3] investigated the SD in Al/Zn alloys and thin polymer blend films [4] and showed that the SD significantly enhanced mechanical properties. Yaldram *et al* [5] investigated the phase separation and clustering in the ABV (A atom, B atom, vacancy) model using Monte Carlo simulation. Puri *et al* [6–8] studied the surface-directed SD and wetting layer growth kinetics in a semi-infinite geometry.

Significant effort has also been made on the growth law of domain size $R \propto t^n$, where t is the time after the quench and n is an exponent that depends on many system aspects, including the initial composition [9] and order parameter mobility [10]. Filler particles

introduced into the system may also significantly affect the dynamics, changing the phase separation morphology [11–14]. Tanaka *et al* [15–17] studied the interaction between the wetting and phase separation in binary fluid mixtures containing glass spheres and showed that the pattern evolution was strongly affected by dynamic coupling between the phase separation and wetting.

The effect of filler particles on domain morphology depends strongly on the coupling interaction strength. Ginzburg *et al* [11–13] showed that the phase wetting filler particles formed a continuous phase and others formed isolated domains with the decrease in the growth rate with the increase in the filler particle concentration or mobility under no or low coupling interaction conditions. In contrast, under the strong coupling interaction [13], the phase wetting filler particles self-assembled into distinct islands, while the other phases percolated to form a continuous phase with the reduced growth rate [18] for increasing the filler particle concentration or decreasing the mobility. Later, Laradji *et al* [19] showed that the quenched particles slowed the kinetics but annealed the filler particles by only affecting the exponent of the power law.

However, previous studies have not considered the effects of particles with higher mobility. Therefore,

the current study investigates how the high mobility particles, which can promote SD, can affect the domain growth rate as more are introduced into the system, and how this interacts with the filler particles.

2. Model

We conducted a set of simulations considering a phase separating symmetric binary (AB) mixture characterised by a conservative order parameter $u(\vec{r}, t)$ that represents the difference between local A and B concentrations at position $\vec{r}$:

$$u(\vec{r}, t) = u_A(\vec{r}, t) - u_B(\vec{r}, t).$$

We consider the case where the diameter of the filler particle is equal to 1, i.e. equals the mesh size, and the filler particle interaction is of short range and repulsive. All particles undergo Brownian motion, with the dynamics of phase separation and filler particle motion governed by the Cahn–Hilliard equation [20–22]:

$$\frac{\partial u(\vec{r}, t)}{\partial t} = \Delta \left[\frac{\delta F_1(u, R_i)}{\delta u} \right] + \eta(\vec{r}, t), \quad (u, t) \in \Omega \times R^+ \quad (1)$$

and the Langevin [11] equation

$$\frac{d\vec{R}_i}{dt} = -M_p \left[\frac{\partial}{\partial R_i} F_2(u, R_i) + \zeta_i \right], \quad (2)$$

respectively, where R_i is the position of the centre of the ith particle and $\eta(\vec{r}, t)$ is the Gaussian thermal noise. ζ_i is a noise term offering Brownian motion to filler particles, and

$$F_1(u, R_i) = \int \left[f(u) + \varepsilon(\nabla u)^2/2 \right] d^2r$$
$$+ \sum_i \int V(\vec{r} - \vec{R}_i)(u(\vec{r}) - u_s)^2 d^2r \quad (3)$$

is the total free energy functional of the system, where $f(u) = u^4/4 - u^2/2$ is the bulk free energy density, assuming the binary mixture is symmetrical; ε is the interfacial energy parameter; u_s is the order parameter on the particle surface, which is equal to that of the wettable phase; and for short-range coupling interactions

$$V(\vec{r}) = C \exp(r_0 - |\vec{r}|),$$

where C is a constant indicating the coupling strength and r_0 is the particle radius.

Similarly, the force acting on the ith particle due to both coupling with the matrix materials and the repulsive force from all other particles is

$$F_2(u, R_i) = \sum_i \int V(\vec{r} - \vec{R}_i)(u(\vec{r}) - u_s)^2 d^2\vec{r}$$
$$+ \sum_{j \neq i} V_1(\vec{R}_j - \vec{R}_i). \quad (4)$$

Substituting eqs (3) and (4) into eqs (1) and (2),

$$\frac{\partial u(\vec{r}, t)}{\partial t} = \Delta \left[u^3 - u + u_{\text{cpl}} - \varepsilon \Delta u \right] + \eta(\vec{r}, t),$$
$$(u, t) \in \Omega \times R^+, \quad (5)$$

$$\frac{d\vec{R}_i}{dt} = -M_p \left[\int (u(\vec{r}) - u_s)^2 V'(\vec{r} - \vec{R}_i) \frac{\vec{R}_i - \vec{r}}{|\vec{R}_i - \vec{r}|} d^2\vec{r} \right.$$
$$\left. + \sum_{j \neq i} V_1'(\vec{R}_j - \vec{R}_i) \frac{\vec{R}_i - \vec{R}_j}{|\vec{R}_i - \vec{R}_j|} + \zeta_i \right], \quad (6)$$

where

$$u_{\text{cpl}} = 2(u - u_s) \sum_i V(\vec{r} - \vec{R}_i)$$

and

$$V_1(\vec{r}) = C \exp(2r_0 - |\vec{r}|).$$

Many methods have been developed to solve this type of nonlinear evolution [23], and we adopt the semi-implicit Fourier spectral method [24] to solve these numerically. The continuous system is projected onto a two-dimensional 256×256 mesh grid, with the spatial mesh size Δx, and the periodic boundary conditions for both x and y directions. We Fourier transform eq. (5), and then apply semi-implicit schemes to the time variable:

$$\frac{u(\vec{k}, t)^{n+1} - u(\vec{k}, t)^n}{\Delta t}$$
$$= -k^2 \left(u^3 - u + u_{\text{cpl}} \right)_k^n - \varepsilon k^4 u_k^{n+1} + \eta(\vec{k}, t)^n,$$
$$(u, t) \in \Omega \times R^+, \quad (7)$$

where $\vec{k}$ is the Fourier vector in the Fourier space, and the subscript refers to the Fourier transform from real to the Fourier space.

This study focussed on the strong coupling case where the Brownian motion was small compared to that caused by coupling interactions. Therefore, specific values of some parameters in our model were $\varepsilon = 10^{-4}$ [25], $r_0 = 1$, $C = 0.1$, $u_s = -1$ and $\Delta t = 1.0$. We consider the total number of filler particles = 0, 100, 200, 300, 400 and 500; and the particle mobility $M_p = 3, 6$ and 9. All simulations were performed 10 times with the initial composition randomly distributed between -0.05 and 0.05.
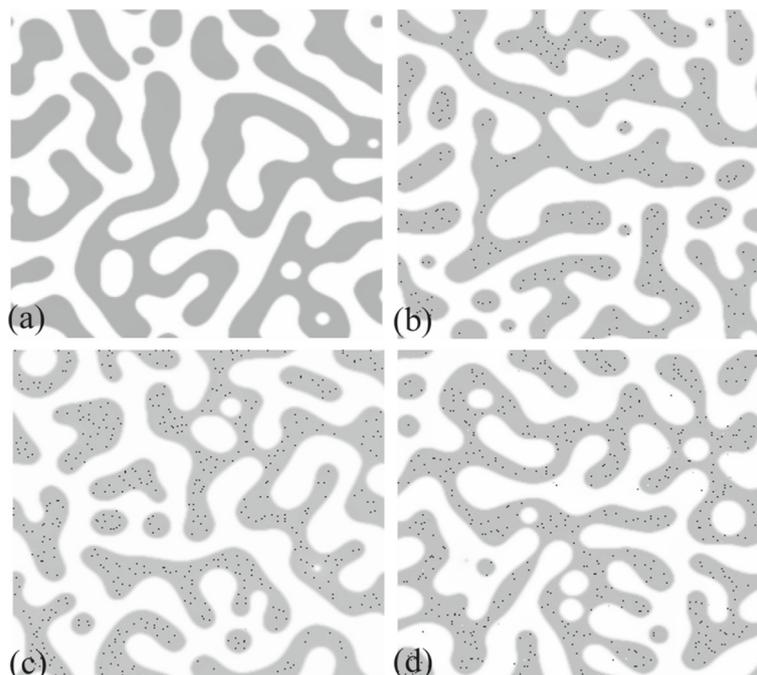
Figure 1. Snapshots during the SD evolution at $t = 10{,}000$ for (**a**) pure binary system; (**b**) $N = 300, M_\mathrm{p} = 6$; (**c**) $N = 500, M_\mathrm{p} = 6$ and (**d**) $N = 500, M_\mathrm{p} = 9$ (N and M_p are the particle number and the particle mobility, respectively).

3. Results

3.1 *Morphology*

Figure 1 shows the effect of filler particles on the domain structure morphology. Figure 1a shows the structure of a typical pure binary system for comparison and figures 1b–1d show configurations at $t = 10{,}000$ for $N = 300, M_\mathrm{p} = 6$; $N = 500, M_\mathrm{p} = 6$; $N = 500, M_\mathrm{p} = 9$, respectively. The bicontinuous morphology of the pure symmetric binary mixture is broken by filler particles, and the phase wetting filler particles self-assemble into distinct islands while the other phase is continuous. This broken and self-assembling effect is enhanced as particle concentration increases from 300 to 500 (figures 1b and 1c, respectively), but the broken effect weakens and the bicontinuous morphology appears again as particle mobility increases from 6 to 9 (figures 1c and 1d, respectively). In contrast to figure 1c, some particles are out of the wettable phases in figure 1d.

Figure 2 shows the typical dynamical evolution of the radial correlation function for pure binary systems. The domain structure is obviously in the oscillations of the function about zero. As phase separation proceeds, spatial correlations extend along the radial axis.

3.2 *Growth rate*

Figure 3 shows the effect of particle mobility on the domain growth rate. While there are some regions with a positive correlation between the growth rate and particle mobility, these are not constant over the whole range, in contrast to Laradji [18], with the growth rate first increasing, and then decreasing with the increase in particle mobility.

Figure 4 shows the effect of particle concentration on the domain growth rate. When the particle mobility is low (figure 4a), the domain growth rate decreases with the increase in particle concentration, which is consistent with Laradji [18]. However, when the particle mobility is high (figure 4b), the domain growth rate first decreases, then increases, and finally decreases again with the increase in particle concentration, in contrast to Ginzburg *et al* [11] and Laradji [18].

4. Discussion

4.1 *Effect of particle mobility*

Ginzburg *et al* [11] ignored the coupling interactions, and so filler particles experienced purely the Brownian motion even though the order parameter field evolution was influenced by the order parameter on the particle surface. Consequently, the order parameter field was disrupted by random particle 'jumps' and the growth rate decreased with the increase in concentration or mobility. Balazs [13] and Laradji [18] included coupling interactions, allowing the order parameter field and particles to affect each other, evolving to the morphology where all particles were distributed in wettable phases. These
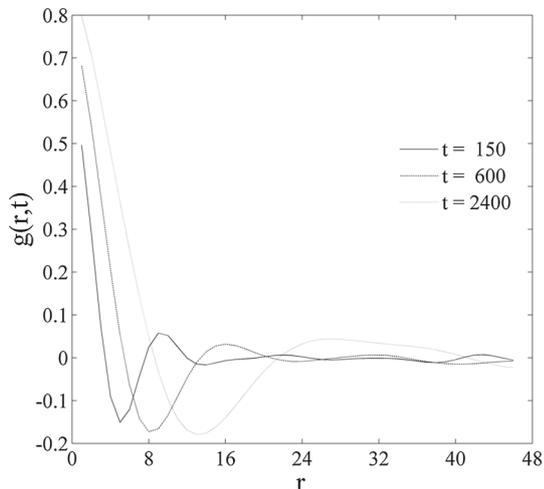
Figure 2. Time dependence of the radial pair correlation function. The lines correspond to $t = 150$ (solid line), $t = 600$ (dashed line) and $t = 2400$ (dotted line).
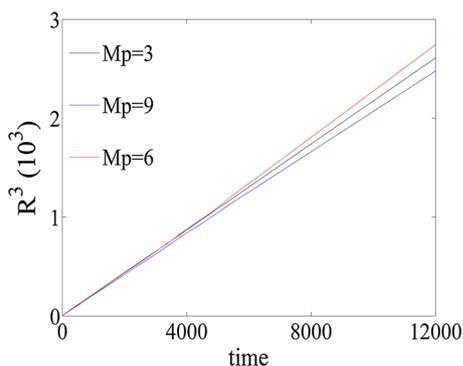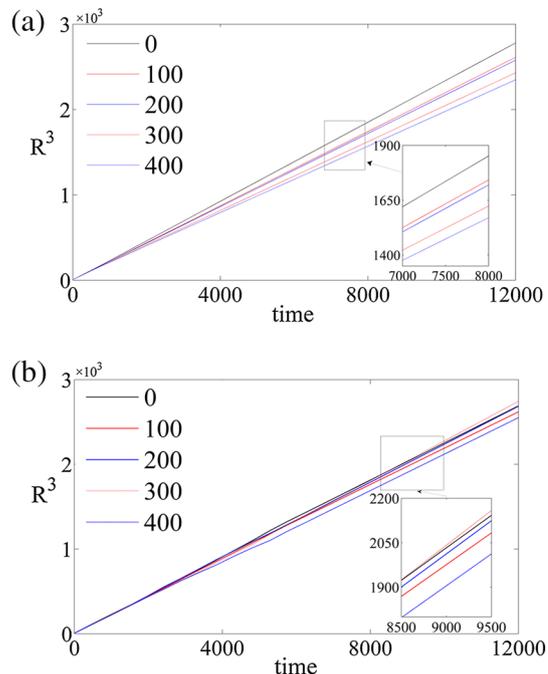

Figure 3. Characteristic length as a function of time for different particle mobilities when particle number is 300. M_p is the particle mobility. All data are averaged over 10 runs.

Figure 4. Characteristic length as a function of time for various particle numbers: (**a**) $M_p = 3$ and (**b**) $M_p = 6$. M_p is the particle mobility. All data are averaged over 10 runs.

particles were 'seeds', and so the phase separation was promoted with the increase in particle mobility.

However, the particle Brownian motion was not controlled by the particle mobility in the previous studies and hence remained constant when the particle mobility changed. This should be reconsidered since the magnitude of the particle Brownian motion increases as their mobility increases, e.g. when their mass decreases.

The current study assumed that the particle Brownian motion changed proportionately as the particle mobility changed. Hence the magnitude of particle Brownian motion increased when the particle mobility increased. Consequently, the particles were sufficiently active to jump randomly even in pure phases, swelling the boundaries of pure phases, as shown in figure 1c. However, when the particle mobility was sufficiently high, most particle jumps were to the next nearest-neighbour sites or even farther. Thus, figure 1d shows some black dots in

white areas, which are defects caused by the increased particle mobility.

4.2 *Effect of particle concentration*

When the particle mobility is low, we found that particles are able to move towards the wettable phases at early and intermediate times, but most of these particles in the wettable bulk phase are not sufficiently active at later times, even near the phase boundaries, as the coupling interaction is vanishingly small. In this case, particles on the phase boundaries can pin the boundaries which prevent them from moving. A few particles are left outside the wettable phases under low mobility in the intermediate stage although the morphology in the late stage is similar to the previous studies [13,18]. The pin effect is enhanced as the particle concentration increases.

In contrast, even when the particle mobility was high, most particles were not moving in the Laradji model, as the particle Brownian motion was unchanged. Thus, more particles implied slower domain growth rate. However, in the current model, particles with high mobility are sufficiently active to keep pace with wettable phase boundary movements, and most can move randomly in the wettable bulk phases. Hence, the particles on the wettable phase boundaries swell the phase. Although this is similar to the case of diblock polymer systems [26], this

study ignored the repulsive force among the particles. Therefore, the mutual repulsion force among the particles meant that the wettable phases were unable to cover all the particles as particle concentration increased, causing some particles to be expelled. These expelled particles created many extra interfaces or defects and offset the swelling effect. The swell effect is not significant when the particle concentration is low as the wettable phases are not crowded. Thus, the growth rate decreased initially with the increase in the particle concentration.

5. Conclusion

This study conducted a series of simulations to investigate the SD dynamics in binary mixtures containing mobile particles. The results show that the growth rate first increases and then decreases with the increase in filler particle mobility for the strong coupling interaction case.

However, the effect of filler particle concentration on the domain growth depends on the particle mobility. When the particle mobility is low, particles can slow down the phase separation and the growth rate decreased with the increase in particle concentration. In contrast, when the particle mobility is high, the growth rate first decreased, then increased, and finally decreased again with the increase in the filler particle concentration, showing two concentration inflection points that may depend on both the particle mobility and mutual repulsive force.

The current model suggests the possible control of the synthesis rate, microstructure and hence macroscopic behaviour of binary alloys by altering some filler particle properties, such as concentration, size or density, which should be verified experimentally in future studies.

Acknowledgement

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