APPLICATION OF MONTE CARLO METHOD TO PHASE SEPARATION DYNAMICS OF COMPLEX SYSTEMS

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We report the application of the Monte Carlo simulation to phase separation dynamics. First, we deal with the phase separation under shear flow. The thermal effect on the phase separation is discussed, and the anisotropic growth exponents in the late stage are estimated. Next, we study the effect of surfactants on the three-component solvents. We obtain the mixture of macrophase separation and microphase separation, and investigate the dynamics of both phase separations.

1. Introduction

The phase separation dynamics has attracted a lot of attention in recent decades. Complex fluids, such as polymers, emulsions, and colloidal suspension, are of current interest. For simple systems it is considered that the domain-size growth in the late stage is governed by an algebraic law, $R(t) \sim t^n$. The classical Lifshitz-Slyozov theory gives the growth exponent $n=1/3$ in the case of the spinodal decomposition of the conserved order parameter. In contrast, the late-stage ordering process of the nonconserved order parameter is described by the classical Lifshitz-Allen-Cahn law, $n = 1/2$.

However, the dynamics of more complex systems, such as the phase separation problem under shear flow, is not simple, and more attention has been given to these systems. Computer simulation is a powerful method, and as a mesoscopic approach, the time-dependent Ginzburg-Landau (TDGL) model is frequently used for the simulation of phase separation.

In the present paper, we use the Monte Carlo simulation based on the lattice model instead. We apply the Monte Carlo method to two problems; the phase separation under shear flow and the phase separation of three-component solvents with surfactants. In the former problem, we mainly focus on the late-stage dynamics. In
the latter problem, we pay attention to the mixture of the macrophase separation and microphase separation. It is to be noted that we often encounter the problem of slow dynamics in simulational studies of ordering process of phase separation. We briefly make a remark on the method to overcome the slow dynamics.

2. Phase Separation under Shear Flow

The anisotropic domain growth has been observed for the phase separation under shear flow both experimentally and theoretically. It is interesting to study the anisotropic domain growth law in the late stage. Here, we develop a new simulation method to study the domain growth under shear flow based on the lattice model. We can systematically study the effect of thermal fluctuations on phase separation for a wide range of temperatures including the critical temperature without any particular assumption.

![Fig. 1. The schematic illustration of the shear process in the lattice model.](image)

We treat the two-dimensional model, and consider the case that the velocity field is given by

\[ v_x = \gamma y, \quad v_y = 0 \]  

(2.1) where \( \gamma \) is the shear rate. In the lattice model, it corresponds to the relative slide of adjacent layers with one lattice spacing at the rate of \( \gamma \) in unit time, which is schematically shown in Fig. 1. Using this fact, we introduce shear flow in the Monte Carlo simulation of the phase separation dynamics. A similar idea was suggested by Chan. We employ the Kawasaki nearest-neighbor pair exchange for the Ising model because the system with the conserved order-parameter is assumed for the phase separation problem. The Hamiltonian of our system is given by

\[ H = -J \sum_{(i,j)} \sigma_i \sigma_j \]  

(2.2)
with the Ising coupling $J$. After the usual Metropolis spin-update process of one Monte Carlo step per spin, we perform the shear-flow process; we pick up a pair of adjacent layers to make a slide with the probability of $\gamma N_{\text{layer}}$, where $N_{\text{layer}}$ is the number of the layers. It is to be noted that the Lees-Edwards boundary condition is naturally demanded with the introduction of such a shear-flow process.

We have made simulations for the square lattice, and the typical system size is $256 \times 256$ and $128 \times 128$. The volume fraction of each of the two components is chosen to be 0.5. We start from a random configuration, and quench a system to certain lower temperature. We change the shear rate $\gamma$ and the quenching temperature to study the thermal effect on the phase separation.

Performing the fast Fourier transform, we calculate the structure factor $S(k)$.

![Fig. 2. The real-space snapshots (top) and corresponding structure factors (bottom). The system size is 128 x 128. The shear rate $\gamma$ is 0.001, and the time is (a) 5000 MCS and (b) 20000 MCS. The quenching temperatures are $T=0.6, 1.2, 1.8, \text{ and } 2.4$ from left to right.](image)

We note that the Lees-Edwards boundary condition should be taken into account when performing the Fourier transform. This is the same situation as the study of the equilibrium properties of the Ising model with the tilted boundary condition. Examples of the real-space snapshots and corresponding structure factors are given in Fig. 2, where the system size is $128 \times 128$. The shear rate $\gamma$ is 0.001, and the time is 5000 MCS and 20000 MCS for Fig. 2(a) and (b), respectively. The quenching temperatures are $T=0.6, 1.2, 1.8, \text{ and } 2.4$ from left to right. We measure the temperature in unit of $J$. We note that the transition temperature of the present
system without shear flow is the Ising critical temperature, $T_c = 2.269 \ldots$. From the figures, we see that below $T_c$, the shape of domain is elongated in the $x$ direction due to the effect of shear as time grows, which results in the break of the symmetry between $k_x$ and $k_y$. If there is no shear flow, the domain growth becomes very slow at low temperatures. It is because the thermal diffusion is not so frequent there. In contrast, the effect of shear becomes prominent at very low temperatures. There is a rapid elongation of the domain in the direction of shear flow. At higher temperatures, even if the domain elongates, the string-like domain breaks again because of thermal fluctuations. Thus, thermal fluctuations play a role of hindering the effect of shear.

Let us consider the anisotropic growth in the late stage. If we assume that the structure factor $S(k)$ has the elliptic symmetry as suggested from Fig. 2, we can calculate the slope of the principal axis, and the moments of $k$ along principal and subsidiary axes. We plot the time evolution of the second moments $k_+$ and $k_-$, which are the moments along the principal and subsidiary axes, respectively, in Fig. 3. We use the logarithmic scales, and the data for various shear rates, that is, $\gamma = 0.00025, 0.001$ and 0.004, are plotted in the same figure. We have chosen $\gamma t$ as the horizontal axis. The quenching temperature is 0.6, and the average has been taken over 16 samples for each $\gamma$. From the figure, we see how the domain deforms as time grows; $\langle k_+^2 \rangle$ and $\langle k_-^2 \rangle$ start to separate.

![Fig. 3. The logarithmic plot of $\langle k_\pm^2 \rangle$ as a function of $\gamma t$. The slopes of the straight lines are -1.4 and -0.2.](image)

The anisotropic growth exponents in the late stage are recently discussed by Corberi, Gonnella, and Lamura using the TDGL model. They have used the one-loop approximation for the TDGL model. In our notation, the domain growth in
the late stage is denoted by

\[ \langle k^2_+ \rangle \sim t^{-2\alpha_x}, \quad t \to \infty \]  \hspace{1cm} (2.3)
\[ \langle k^2_- \rangle \sim t^{-2\alpha_y}, \quad t \to \infty \]  \hspace{1cm} (2.4)

with the anisotropic growth exponents \( \alpha_x \) and \( \alpha_y \). In the late stage, the subsidiary axis \( k_\perp \) for \( S(\hat{k}) \) corresponds to the direction of elongation \( x \) in real space. The growth exponent is given by 1/3 for the system without shear flow.\(^7\) We may estimate from the slope of the straight lines in Fig. 3 that \( \alpha_x = 0.7 \) and \( \alpha_y = 0.1 \). These values are smaller than the prediction of Ref. 9, that is, \( \alpha_x = 5/4 \) and \( \alpha_y = 1/4 \). This is because the one-loop approximation employed in Ref. 9 neglects nonlinear mode-coupling effect, which is important in the late stage dynamics. Quite recently, Corberi, Gonnela and Lamura have reported a new calculation using a renormalization group approach. Their new values of \( \alpha \)'s are \( \alpha_x = 4/3 \) and \( \alpha_y = 1/3 \), which are still different from our numerical estimates. The details of the present calculation will be published elsewhere.\(^8\)

3. Three-Component Solvents with Surfactants

The effects of surfactants in binary mixtures is an interesting problem. It produces various phases. The growth of domain size is hampered, and the microphase separation occurs as in the case of block copolymers. The lattice model has been used to investigate the effects of surfactants. 15,16 The dynamics of the surfactant systems has been also studied using the lattice model by the Monte Carlo simulation. 17,18

![Fig. 4. Illustration of the lattice model of solvents with surfactants.](image)

Here, we study the phase separation of three-component solvents with surfactants. We can obtain a variety of interesting phases by increasing the number of components from two to three. We consider the mixture of macrophase separation...
and microphase separation for three-component systems. We use the Monte Carlo simulation to study the lattice model. Three-component solvents are represented by the three-state (A, B, C) Potts spins. We represent the surfactants by diblock copolymer chains which are composed of two states, that is, A-B, B-C, or C-A. We illustrate our model in Fig. 4. In this case, the segment number of two states in the diblock copolymer are 3 and 3. We assume that the interaction between the solvent particles and that between the solvent particle and the monomer in the surfactant are the same. We use the Kawasaki pair exchange for solvents, and slithering-snake motions for the move of surfactants. These update processes are shown in Fig. 5.

![Fig. 5. Monte Carlo update processes; (a) Kawasaki pair exchange and (b) slithering-snake motion.](image)

Our system suffers from the problem of slow dynamics, especially because of the existence of surfactants. To accelerate the phase separation, we use the trick of the replica-exchange Monte Carlo method. Although the dynamics including the replica-exchange process is not a simple one, it has been shown that the replica-exchange Monte Carlo method works well even for the estimate of the growth exponent in the case of ordering process with an algebraic growth law.

We have made simulations for several cases changing the volume fractions of solvents and surfactants. Here, we show the result of one case. We put only one type of surfactants, say A-B, in the three-component solvents. The number of solvent particles for A, B and C are chosen as the same. Starting from the random configuration, we quench the system at low temperature. A typical snapshot in the late stage is given in Fig. 6. A and B particles are represented by black and gray squares, and C particles by white ones. We observe the microphase separation of A and B particles. We also see the macrophase separation of C particles and the mixture of other particles. Thus, we find the mixture of macrophase separation and microphase separation. We should note that similar phenomena of complex phase separation have been studied in copolymer-homopolymer mixtures.

To study the dynamics of each phase separation process, we calculate the structure factors, $S_{CC}(k) = \langle |\rho_C(k)|^2 \rangle$ and $S_{AB}(k) = \langle |\rho_A(k) - \rho_B(k)|^2 \rangle$, for macrophase separation and microphase separation, respectively. Here, $\rho(k)$ is the Fourier transform of density, and $\langle \cdots \rangle$ denotes the thermal average. The temporal evolution of the first moments of each structure factor are shown in Fig. 7. We obtain the sepa-
rate growth behavior for both phase separation processes. The growth exponent of macrophase separation is very close to the Lifshitz-Slyozov value of $1/3$, whereas the microphase separation is much slower. We will report the details of the present study elsewhere.

4. Summary

We have reported the Monte Carlo studies of two problems concerning the phase separation dynamics. The first one is the phase separation dynamics under shear flow. Developing a new Monte Carlo method to study the phase separation dynamics under shear flow, we have studied the thermal effect on the phase separation. We have also discussed the anisotropic growth exponents in the late stage. The second problem is the effect of surfactants on the three-component solvents. We have obtained a mixture of macrophase separation and microphase separation, and have discussed the dynamics of these phase separations.

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Fig. 7. Temporal growth of the first moment of the structure factors $S(\vec{k})$ which represent macrophase (CC) and microphase (AB) separations. The slope of the straight line is -1/3.

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