

## Wetting-driven structure formation of a binary mixture in the presence of a mobile particle pinning potential

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We investigate the pattern formation on the solid substrate of phase-separating films containing mobile wetting particles with a preferential attraction for one component of the mixtures. The presence of mobile particles under the surface-particle interaction modulation breaks the isotropy of the bulk phase-separating process, leading to the formation of orientational structure due to the interplay between phase separation and wetting particle ordering under a modulated pinning potential at the late stage. Simulations suggest that the phase-separation morphology can be changed through the adjustment of the wettable-phase-particle interaction and the surface-particle interaction. It provides some important insights into this “wetting-directed spinodal decomposition.”

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There has been much interest in the study of phase-ordering dynamics in a wide variety of physical systems [1–26]. When a binary mixture composed of two species of molecules  $A$  and  $B$  is quenched below the critical coexistence temperature  $T_c$ , the system subsequently segregates into domains which are rich in either  $A$  or  $B$ . The morphology of such systems may be an interconnected domain structure or isolated clusters, and changes continuously in space and time. For an ordinary mixture such as binary fluids and polymer blends, these domains grow as time goes on, and finally phase separation becomes macroscopic. Recently, much interest has been focused on the interplay between phase separation and wetting in the spinodal region, and it has been shown that the morphology and growth dynamics of phase separation can be dramatically altered by wetting phenomena in a solid wall, porous medium, and gel-type network structure [27–29]. The phases formed at late stage are rearranged to lower the total energy of liquid-liquid and solid-liquid interfacial energies. In many technological applications, it is very useful to understand how to control the final morphology and domain growth of phase-separating materials by the dynamic interplay between phase separation and wetting. The presence of a surface can significantly alter the phase-separating process. Interestingly, Wiltzius *et al.* [28] studied a polymer mixture in the unstable two-phase region in contact with a quartz wall, and found two different growth modes: a slow mode corresponding to the bulk growth and a fast-growth pattern which occurs parallel to the interface of the polymer mixture with a quartz window. Lately, the pattern evolution in a binary mixture with the inclusion of a mobile solid wall of particles was another interesting and complex problem [29]. Tanaka *et al.* [29] examined experimentally the properties of a polymer mixture containing small glass spheres which are wet by one of the components. Their results revealed that mobile particles may form a percolating network because of geometrical confinement of particles into the wettable phase, and thus arrest phase separation. Although these studies have shown that polymeric materials undergo dramatic changes in the morphology and dynamics of the phase-separating growth by the interplay between phase separation and wetting dynamics, phase separation

still led to an isotropic, disordered morphology of the coexisting phases at some intermediate time. The presence of a surface with selective energy variations can significantly create a rich diversity of new structures and useful nanocomposites. Boltau *et al.* [30] have shown experimentally that the domains of a phase-separating mixture of polymers in a thin film can be guided into arbitrary structures by a surface with a prepatterned variation of surface energies. Their result indicated that a transfer of the difference in surface energies can lead to a composition variation of a binary polymer film, although the details of the surface-induced demixing process are not yet known. On the other hand, polymer mixtures can undergo dramatic changes in orientational order in response to externally applied perturbations. Some previous studies have considered the application of external fields (electric, shear flow, temperature, and gravity) to perturb phase separation of a binary liquid mixture and another self-organization process [26,31–33]. In this paper, we investigate a phase-separating film on a substrate surface, and add a small concentration of particles with a modulated pinning potential distribution under the surface-particle interaction. The interaction between the mixture and the substrate surfaces is assumed to be neglected, i.e., the substrates are neutral (nonselective) to the polymer blend. Note that hydrodynamic effects, which prevail in the very latest stages of phase separation in polymer blends, are neglected in the present model. One of the realistic systems which corresponds to our model is a thin fluid layer on a surface or between two plates [17], where hydrodynamic interactions are minimized. We use a two-order-parameter model proposed by Komura *et al.* [34,35] to simulate the in-plane segregation of a two-dimensional binary mixture induced by mobile particles which are wet by phase  $B$ , and show that the phase-separating orientational structure is formed as a result of the fact that the wetting phase  $B$  tends to surround mobile particles and particles must be confined to move under the constraint by a modulation of the surface-particle interaction, leading to the competition between wetting and mobile particle energy transfer in the phase-separation process. This wetting dynamics will drive an isotropic decomposition into a modulated striped domain structure of separated fluid  $A$

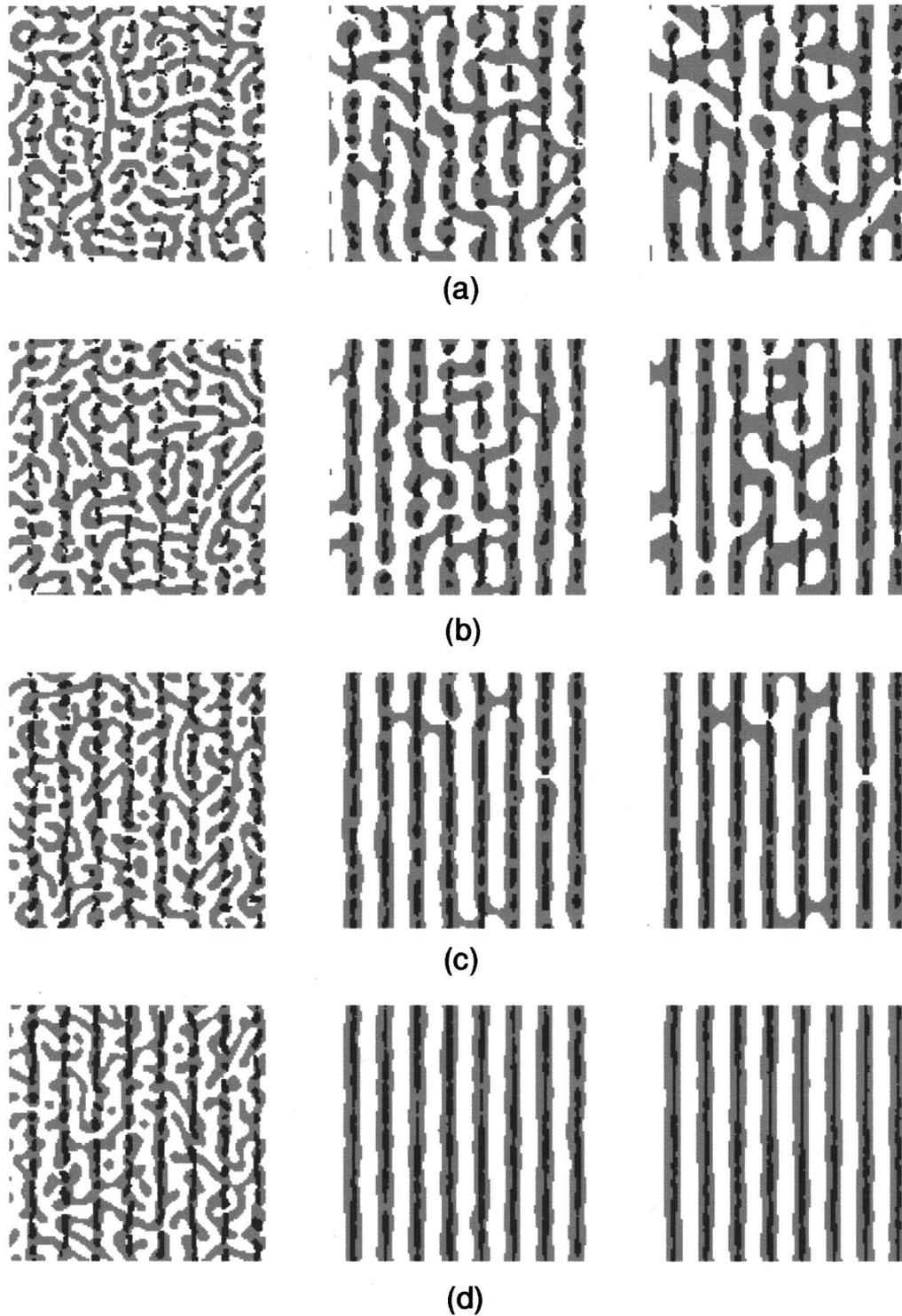


FIG. 1. Pattern evolution of a  $128 \times 128$  two-dimensional lattice with particle concentration 5% with (a)  $g_2=0.02$ , (b)  $g_2=0.03$ , (c)  $g_2=0.04$ , and (d)  $g_2=0.06$ . Phase *A* is represented by the white region, phase *B* by the gray region, and the wetting particles by black.

and *B* phases even if the wetting particle concentration is very small. The present system is of practical interest as polymer materials are often filled with additives [36] that improve their mechanical, chemical, and other properties. It may be a simple and ideal system to form some small-scaled or orientational structures by adjusting the wetting phase-particle interaction and the surface-particle interaction, and provide a new tool for the physical design of soft-matter

materials. On the other hand, It will also be useful to understand the dynamics aspect of the interplay among three kinetics processes: phase separation, wetting, and phase ordering.

We study a binary mixture of two fluids *A* and *B* with the inclusion of mobile wetting particles. The coordinates of the planar surface are defined in the *x* and *y* axes. The local volume fractions of the components *A*, *B*, and the particles

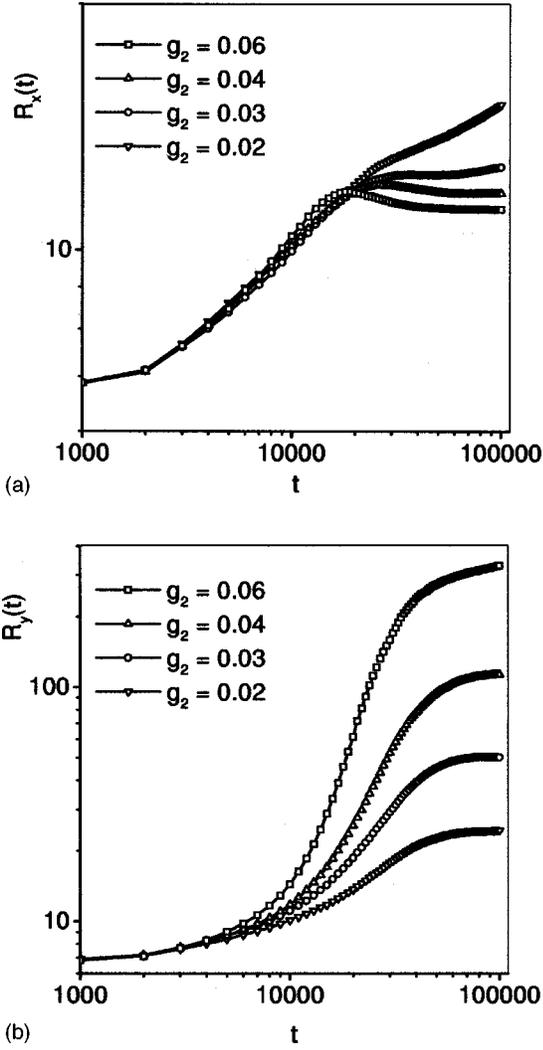


FIG. 2. The time evolution of the characteristic length for various values of particle periodic pinning strength  $g_2$  with (a)  $R_x(t)$  and (b)  $R_y(t)$ .

are denoted by  $\phi_A(x,y)$ ,  $\phi_B(x,y)$ , and  $\rho(x,y)$ , respectively. We assume that the total density  $\phi_A(x,y) + \phi_B(x,y) + \rho(x,y)$  is constant. Under the incompressibility condition, two of the local volume fractions will be independent. We take  $\Phi(x,y) = \phi_A(x,y) - \phi_B(x,y)$  and  $\rho(x,y)$  as the independent variables. The order parameter  $\Phi(x,y)$  gives the local concentration difference between A ( $\Phi > 0$ ) and B ( $\Phi < 0$ ) phases, whereas the order parameter  $\rho(x,y)$  describes the local particle concentration. The dynamics of the mixture is described by the coupled time-dependent Ginzburg-Landau equations [11–20,34,35] for the two order parameters  $\Phi(x,y)$  and  $\rho(x,y)$ . The free-energy function of the system is given by

$$F = \int \int dx dy \left( -\frac{a}{2} \Phi^2 + \frac{b}{4} \Phi^4 + \frac{d}{2} (\nabla \Phi)^2 + e \rho^2 (\rho - \rho_s)^2 + g_1 \rho \Phi + g_2 \rho \sin(2\pi x/L_p) \right), \quad (1)$$

where parameters  $a$ ,  $b$ ,  $d$ ,  $e$ ,  $g_1$ , and  $g_2$  are positive constants. The  $e$  term allows the coexistence of the two bulk

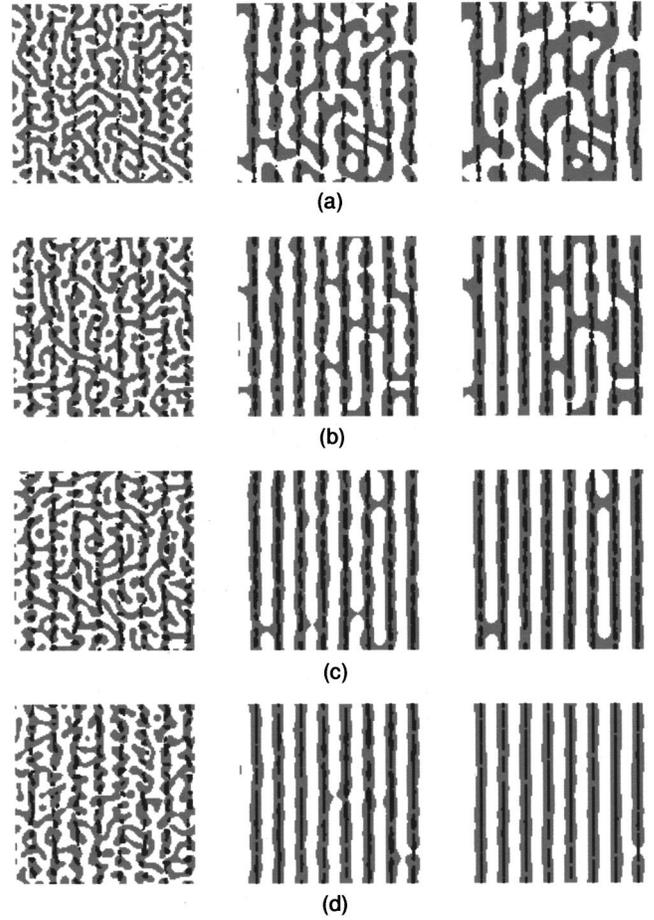


FIG. 3. Pattern evolution of a  $128 \times 128$  two-dimensional lattice with particle concentration 5% with (a)  $g_1 = 0.02$ , (b)  $g_1 = 0.04$ , (c)  $g_1 = 0.06$ , and (d)  $g_1 = 0.08$ . Phase A is represented by the white region, phase B by the gray region, and the wetting particles by black.

states [34,35], i.e.,  $\rho = 0$  and  $\rho = \rho_s$ . The state  $\rho = 0$  corresponds to the case in which the system is locally occupied either by A or B, whereas  $\rho = \rho_s$  corresponds to the case in which the local volume is occupied only by the wetting particles. Here we take into account a cross term  $g_1$  between the order parameters  $\Phi$  and  $\rho$  due to the coupling between the mixture and particles.  $g_1 > 0$  means that the particle is energetically favorable in the B phase ( $\Phi < 0$ ), and  $g_1$  is the strength of the wetting. The last coupling term  $g_2$  in Eq. (1) means that the wetting particle tends to be modulated in the  $x$  direction with a period  $L_p$  under the influence of the surface-particle interaction, and  $g_2$  is the strength of the chemical potential pinning a particle at the substrate surface.

The dynamics of the phase-separating process can be obtained from the coupled set of equations [34],

$$\begin{aligned} \frac{\partial \Phi}{\partial t} &= M_\Phi \nabla^2 \frac{\delta F}{\delta \Phi}, \\ \frac{\partial \rho}{\partial t} &= M_\rho \nabla^2 \frac{\delta F}{\delta \rho}. \end{aligned} \quad (2)$$

Here  $M_\Phi$  and  $M_\rho$  are transport coefficients.

We carry out numerical simulations of the model system in an  $L \times L$  two-dimensional square lattice with  $L=128$  and periodic boundary conditions, using the cell dynamical system (CDS) approach proposed by Oono and Puri [37]. The CDS is a computationally efficient space-time discretized variation of the Cahn-Hilliard-Cook model. The CDS equations corresponding to Eq. (2) are written as follows:

$$\begin{aligned}\Phi(x,y,t+1) &= \Phi(x,y,t) + M_\Phi(\langle\langle I_\Phi \rangle\rangle - I_\Phi), \\ \rho(x,y,t+1) &= \rho(x,y,t) + M_\rho(\langle\langle I_\rho \rangle\rangle - I_\rho),\end{aligned}\quad (3)$$

where

$$\begin{aligned}I_\Phi &= -D(\langle\langle \Phi \rangle\rangle - \Phi) - A \tanh \Phi + \Phi + g_1 \rho, \\ I_\rho &= E\rho(\rho - \rho_s)(2\rho - \rho_s) + g_1 \Phi + g_2 \sin(2\pi x/L_p).\end{aligned}\quad (4)$$

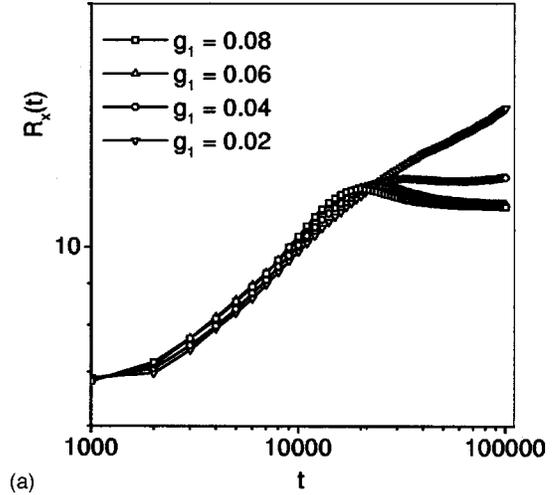
For the original cell dynamics system, the lattice size ( $\Delta x$  or  $\Delta y$ ) and the time step  $\Delta t$  were both set to be unity. The CDS parameters  $A$ ,  $D$ , and  $E$  in Eq. (4) are related to the free-energy parameters in Eq. (1) by  $A=1+a$ ,  $D=d$ , and  $E=2e$  [35].  $\langle\langle X \rangle\rangle$  represents the average over all the neighbors of lattice  $x, y$  on the two-dimensional square lattice, with

$$\langle\langle X \rangle\rangle = \frac{1}{6} \sum_{NN} X + \frac{1}{12} \sum_{NNN} X, \quad (5)$$

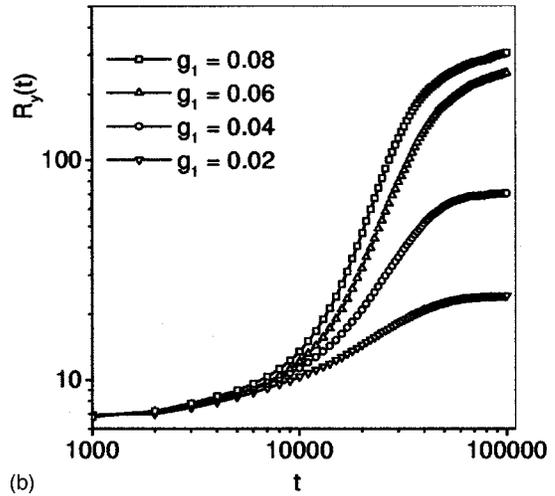
where NN and NNN represent nearest-neighbor and next-nearest-neighbor cells, respectively.  $\langle\langle X \rangle\rangle - X$  is essentially the isotropized discrete Laplacian  $\nabla^2 X$ , but the choice of Eq. (5) will give the better isotropy of the patterns [37].

The structure factor is defined by  $S(\mathbf{k}, t) = \langle |\Phi(\mathbf{k}, t)|^2 \rangle$ , where  $\Phi(\mathbf{k}, t)$  is the Fourier component of  $\Phi(x, y, t)$ , and the sum runs over all lattice sites with  $\mathbf{k} = (2\pi/L)(m\mathbf{i} + n\mathbf{j})$  in which  $m, n = 1, 2, 3, \dots, L$  and the  $\langle \dots \rangle$  denotes the thermal average over a number of repeating runs from independent initial conditions. The domain size  $R(t)$  in the  $x$  and  $y$  directions is derived from the inverse of the first moment of the structure factor  $S(\mathbf{k}, t)$  as  $R_i(t) = 2\pi / \langle k_i(t) \rangle$  ( $i=x$  or  $y$ ), where  $\langle k_i(t) \rangle = \int d\mathbf{k} k_i S(\mathbf{k}, t) / \int d\mathbf{k} S(\mathbf{k}, t)$ .

Our simulations are performed with equal concentration of  $A$  and  $B$  phase 47.5% and wetting particle phase 5%. We start from initial random conditions. The ranges of  $\Phi$  and  $\rho$  at  $t=0$  are  $\bar{\Phi} - s < \Phi < \bar{\Phi} + s$  and  $\bar{\rho} - s < \rho < \bar{\rho} + s$  with the random fluctuation  $s=0.01$ , where the spatial averages of  $\Phi$  and  $\rho$  are  $\bar{\Phi}=0$  and  $\bar{\rho}=0.05$ , respectively. In our simulations, we fix the parameters as  $A=1.3$ ,  $E=0.25$ ,  $\rho_s=1$ ,  $L_p=16$ ,  $D=0.5$ , and  $M_\Phi=M_\rho=0.05$ . The results are averaged over 20 independent runs. We first study the effect of varying the strength of the particle pinning potential  $g_2$  on the domain morphology and growth dynamics when the wetting strength  $g_1$  is 0.05. Figures 1(a), 1(b), 1(c), and 1(d) show the time evolution phase separation for  $g_2=0.02$ ,  $g_2=0.03$ ,  $g_2=0.04$ , and  $g_2=0.06$  at times in the simulation corresponding to  $t=10\,000$ ,  $40\,000$ , and  $100\,000$ , respectively. The  $A$ -rich domain for  $\Phi > 0$  is shown as white whereas the  $B$ -rich domain for  $\Phi < 0$  is indicated by gray. The area shown by black indicates the wetting particles where  $\rho$  is about  $\rho_s=1$ . The domain morphology depends on the strength of the wetting particle pinning potential  $g_2$ . As



(a)



(b)

FIG. 4. The time evolution of the characteristic length for various values of the wetting strength  $g_1$  with (a)  $R_x(t)$  and (b)  $R_y(t)$ .

the strength of the particle pinning potential  $g_2$  is increased, we see from Fig. 1 that the competition between the wetting dynamics and mobile particle ordering will drive an isotropic decomposition into a periodic striped domain structure of separated fluid  $A$  and  $B$  phases. The wetting particles prefer to be in the bulk of the wettable phase  $B$  because this is energetically favorable.

In order to study domain growth of  $A$  and  $B$  phases, we show in Fig. 2 the time evolution of the domain size  $R(t)$  in the  $x$  and  $y$  directions as a function of time in a double logarithmic plot. The growth speed of  $R_y$  aligned with the striped direction is much larger than that of  $R_x$ , as can be seen in Fig. 2. From Fig. 2(a), we see that the domain growth in the  $x$  direction is not appreciably affected by the variation of  $g_2$  at early and intermediate times, but the domain size  $R_x$  clearly becomes smaller as  $g_2$  increases at the late stage. On the other hand, we see from Fig. 2(b) that as  $g_2$  increases, a dramatic increase in the growth rate of the characteristic domain size  $R_y$  in the  $y$  direction is observed.

Next we investigate the wetting effect between the wetting particle and the  $B$  phase, and how the pattern is altered due to the variation of the wetting strength  $g_1$  when  $g_2$  is fixed as  $g_2=0.04$ . In Fig. 3, we show the time evolution of the system morphology when  $g_1$  is changed as  $g_1=0.02$ ,

$g_1=0.04$ ,  $g_1=0.06$ , and  $g_1=0.08$ , at times in the simulation corresponding to  $t=10\,000$ ,  $40\,000$ , and  $100\,000$ , respectively. A similar pattern of growth is observed with an increase of  $g_1$ . Figure 4 shows the time evolution of the corresponding domain size  $R(t)$  in the  $x$  and  $y$  directions on a log-log plot. As the strength of the wetting  $g_1$  is increased, we find that the wetting strength has a similar effect to the strength of the wetting particle pinning potential. In the present model, the wetting dynamics plays an important role in determining the morphology and growth dynamics of the system at the late stage.

In conclusion, we have studied the pattern evolutions of a binary liquid mixture in the presence of wetting particles with the periodic pinning potential due to the surface-particle interaction modulation, and considered the effects of the wet-

table phase-particle and the surface-particle interactions on the morphology change and domain growth of the system undergoing phase separation. The morphology and dynamics of the phase-separation process can be dramatically altered as a function of the strengths of the wetting  $g_1$  and particle pinning potential  $g_2$ . Our numerical simulations reveal that a striped domain morphology can be observed with an increase of  $g_1$  and  $g_2$ , respectively. Our study shows possibilities for the physical design of a diversity of morphologies of soft-matter materials through the adjustment of the type of the particle pinning potential and wetting strength.

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