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Viscous flow and coarsening of microdomains in diblock copolymer thin films

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For thin block copolymer (BCP) films on a homogeneous substrate, a fast domain growth exponent has recently been observed in experiments. This growth exponent is larger than what one would expect from theoretical considerations of two-dimensional coarsening of small molecular liquid mixtures in the viscous regime. Thus it is not clear whether the growth kinetics is truly different for block copolymer films, or if the observed anomalous exponent is a result of a possible dimensional crossover from two to three dimensions. To address part of this question, we have carried out numerical simulations of ordering and domain growth in a two-dimensional system of BCP melts. The model calculations reported here explicitly include viscous, hydrodynamic flow and provide a scaling description of the growth of domains in a quenched BCP system. Our results indicate that the growth kinetics of BCP melts in two dimensions belong to the same dynamical universality class of small molecular liquid mixtures in the viscosity dominated regime.

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Experimental techniques have recently been developed [1–3] to create surfaces patterned with imprinted structures that can be used to guide the structure formation in thin films of polymer mixtures and block copolymers. A major interest in these studies is to control the morphology of thin films by carefully choosing external parameters such as type of substrates, film thickness, applied electric fields [4], etc. Control of morphology in these thin films may lead to important applications in diverse areas such as templating in lithographic processes, optical devices, and surfaces with molecular recognition capabilities [5]. Two different types of patterned surfaces have been used in recent experimental studies. In one such study, the surface pattern size is comparable [3] to the bulk characteristic size of the ordered block copolymer (BCP) lamellae. These types of nanoperiodic, patterned surfaces are created by selectively depositing metal atoms on the grooves of a miscut silicon substrate. In another set of experiments, the patterned surface used [1,6,7] contains self-assembled monolayers of two different end-terminating thiols preferring either of the two subchains of the BCP chains. The lateral size of these surface patterns is much larger (of the order of microns) than the characteristic size of the BCP lamellae. In such a situation, viscous hydrodynamics is a major factor influencing domain coarsening in symmetric films. It is not totally clear though how viscous flow controls the transport of copolymers and the formation of defects in such a situation. Numerical simulations of growth kinetics incorporating viscous flow in a model system of BCP will be quite useful in this context.

In small molecular liquid mixtures, domain growth is controlled by a variety of transport mechanisms due to the coupling of the order parameter to hydrodynamics [8–10]. After an initial transient, the characteristic size of the domains, $R(t)$, grows with a power law $R(t)\sim t^n$, where n is the domain growth exponent. The value of n depends on the mechanism controlling the growth of domains. Domain growth at *early times* is governed by a diffusive mechanism theoretically identified by Lifshitz and Slyozov [11]. This mechanism leads to a growth law given by $R(t)\sim t^{1/3}$. At late times, hydrodynamic effects become important and the growth exponent changes from the Lifshitz-Slyozov value of $n=1/3$. Depending on whether viscous forces or inertial effects of the fluid mixture dominate, the growth law in three dimensions can take one of the following forms [12,13] for a liquid mixture of *critical* composition:

$$R(t)\sim t \quad (\text{viscosity controlled}), \tag{1}$$

$$R(t)\sim t^{2/3} \quad (\text{fluid inertia controlled}). \tag{2}$$

For a two-dimensional critical liquid mixture, however, the growth laws in the presence of hydrodynamics are different [9,13–16] from the three-dimensional ones listed in Eqs. (1) and (2), and are given by

$$R(t)\sim t^{1/2} \quad (\text{viscosity controlled}), \tag{3}$$

$$R(t)\sim t^{2/3} \quad (\text{fluid inertia controlled}). \tag{4}$$

For symmetric BCP melts, one would resort to *dynamical universality* and expect that the domain growth exponents would be the same as in the viscosity dominated regime discussed above. However, for thin BCP films on a *homogeneous* substrate, a faster domain growth exponent has recently been observed [6,7] for surface relief structures (islands and holes). Although two-dimensional viscous flow dominates the kinetics in such a system, the growth exponent measured is larger than what one would expect from theoretical considerations in the two-dimensional coarsening of small molecular liquid mixtures in the viscous regime. Thus many questions arise. One possibility is that the growth kinetics is truly different for block copolymer films even in theoretical models for purely two-dimensional systems. It is also possible that these films are actually in the crossover region between two- and three-dimensional systems and this yields an effective exponent that is larger than the two-dimensional value (but smaller than the three-dimensional result). Other possibilities include effects of an edge free energy on the coarsening of islands. In this paper, we have addressed the first question, i.e., what is the theoretical growth exponent in a two-dimensional system of block copolymers in the presence of viscous, hydrodynamic flow. Unless this important question is answered, any comparison between theory and experiment will not be meaningful for such a complex system. It should be noted, however, that for the island domains, there is no upper limit to the lateral domain growth while in the present simulation the kinetics of copolymer domain growth ceases as the domain size approaches the equilibrium value.

The theoretical model widely used for studying phase separation is the Cahn-Hilliard-Cook (CHC) model [8,9]. In CHC theory, the time variation of a conserved field variable $\phi(\vec{r},t)$ representing the local concentration of one of the components of the mixture, is related to the functional derivative of a coarse-grained free-energy functional $F[\phi]$ plus a thermal noise term:

$$\frac{\partial\phi}{\partial t}=M\nabla^2\frac{\delta F}{\delta\phi}+\nu(\vec{r},t), \tag{5}$$

where M is the mobility (assumed to be a constant here) and $\nu(\vec{r},t)$ is the Gaussian (thermal) noise term obeying the fluctuation dissipation relation:

$$\langle\nu(\vec{r},t)\nu(\vec{r}\,',t')\rangle=-2k_BTM\nabla^2\delta(\vec{r}-\vec{r}\,')\delta(t-t'). \tag{6}$$

The free-energy functional for block copolymers used in our numerical study is originally due to Ohta and Kawasaki [17]. This is given by (in units of k_BT)

$$F[\phi(\vec{r},t)]=\int d\vec{r}\left[-\frac{\xi^{-2}}{2}\phi^2+\frac{1}{4}\phi^4+\frac{1}{2}|\nabla\phi|^2 + b\int d\vec{r}\,'G(\vec{r},\vec{r}\,')\phi(\vec{r},t)\phi(\vec{r}\,',t)\right]. \tag{7}$$

Here $\phi(\vec{r},t)$ is the concentration field, and G is the Green's function for the Laplace equation, i.e., $\nabla^2G=-\delta(\vec{r}-\vec{r}\,')$. It is possible to make a direct connection to the underlying molecular parameters, such as χ and N, by following the calculations of Ohta and Kawasaki. For example, the parameter b can be written as

$$b=\frac{6}{N^2f(1-f)}, \tag{8}$$

where f is the block ratio for the BCP molecules ($f=1/2$ for a symmetric BCP chain). Thus b depends on the chain length of the copolymers in the following way [18]. $b\sim N^{-2}$. The parameter ξ is the correlation length of the system $\xi^2=B(f)/\overline{\chi}$, where $B(f)=N/[4f(1-f)]$, $\overline{\chi}=2N\chi-s(f)/[2f^2(1-f)^2]$, and $s(f)$ is a slowly varying function of f with $s(f=1/2)=0.9$. Although the free-energy expansion used in the Ohta-Kawasaki theory has been obtained by using a local approximation for the higher order couplings and may not be quantitatively correct [19] in the strong-segregation regime, one of the main advantages of the model is that it can be suitably revised to incorporate viscous flow in the BCP melt system.

The viscous hydrodynamic flow can be taken into account in the simulation following the so-called model-*H* formulation by Hohenberg and Halperin [10]. In this formulation the order parameter ϕ and the velocity field $\mathbf{u}$ satisfy the following set of equations:

$$\frac{\partial\phi}{\partial t}+\mathbf{u}\cdot\nabla\phi=M\cdot\nabla^2\frac{\delta F}{\delta\phi}+\zeta, \tag{9}$$

$$\rho\left(\frac{\partial u}{\partial t}+\mathbf{u}\cdot\nabla\mathbf{u}\right)=\eta\nabla^2\mathbf{u}-\phi\nabla\frac{\delta F}{\delta\phi}-\nabla P+\varepsilon, \tag{10}$$

along with the incompressibility condition, $\nabla\cdot\mathbf{u}=0$. Here, Eq. (9) is a modified Cahn-Hilliard equation and Eq. (10) is a modified Navier-Stokes equation. ζ and ε are the thermal noise terms.

After a suitable rescaling, the resulting equations can be written in the following form:

$$\frac{\partial\Phi}{\partial t}+\mathbf{v}\cdot\nabla\Phi=\nabla^2\mu, \tag{11}$$

$$\nabla^2\mathbf{v}=C\Phi\nabla\mu+\nabla P, \tag{12}$$

$$\nabla\cdot\mathbf{v}=0, \tag{13}$$

where $C\propto\eta^{-1}$, and the chemical potential μ is defined as follows:

$$\mu\equiv\frac{\delta F}{\delta\Phi}=-\Phi+\Phi^3-\nabla^2\Phi+b\int d^2\mathbf{r}'G(\mathbf{r}-\mathbf{r}')\Phi(\mathbf{r}'). \tag{14}$$

Since the fluid is highly viscous, the inertial terms in the Navier-Stokes equation are neglected here (overdamped limit approximation). In addition, for the deep quench cases considered here the thermal noise terms are also not included in the numerical calculations. The model simulation, however, does not neglect diffusion; Eq. (11) includes contributions from both diffusion due to imbalance in chemical potential and advective flow.

We employ a fast Fourier transform method [9] to solve the equations for the order parameter and the rescaled velocity field on a square lattice with periodic boundary conditions. Our system size is $L=128$ in most cases, although some runs are made with a system size of $L=256$ to make sure that finite-size effects are not important for the measurements. In Fig. 1 we show a series of snapshots for a typical run with $b=0.005$. We compute the microdomain size as a function of time and chain length in the following way. First, we calculate the pair correlation function $g(r,t,b)$ and define the location of the first zero of this pair correlation function, $R(t,b)$, as a measure of the microdomain size. When the system reaches equilibrium, $R(t,b)$ becomes independent of time t, and we take that value $R_{\mathrm{eq}}(b)$ as a measure of the characteristic size of the microdomains in equilibrium. In Fig. 2, we show a log-log plot of R_{eq} versus b. The data falls on a straight line indicating that

$$R_{\mathrm{eq}}\sim b^{-\theta}. \tag{15}$$

We find that the best fit to the data yields an exponent of $\theta=0.30\pm0.02$. Note that $b\sim N^{-2}$ and thus $R_{\mathrm{eq}}\sim N^{0.60\pm0.04}$,

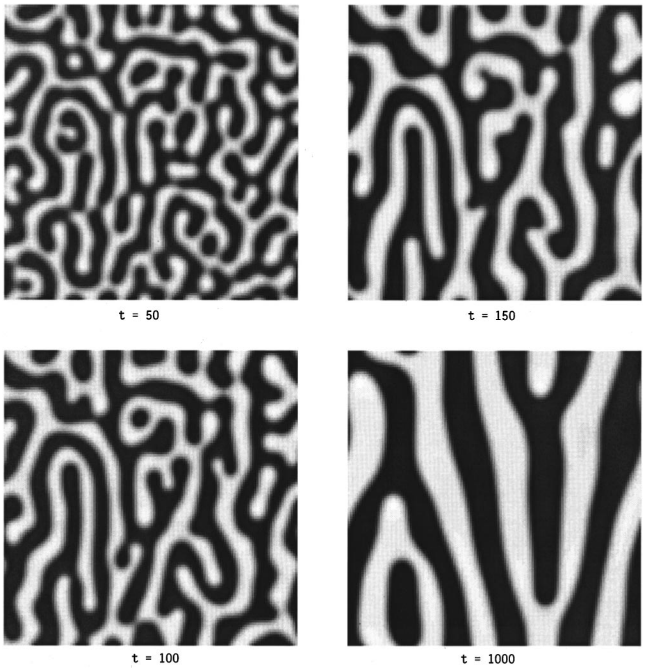

FIG. 1. Coarsening of domains in quenched BCP melt under viscous flow at various times. Here $b=0.005$.

which compares reasonably well with the established exponent of 2/3 in the strong-segregation limit [20].

A scaling hypothesis for the characteristic length $R(t,b)$ has been proposed by Liu and Goldenfeld [21]. They propose a scaling form

$$R(t,b)=b^{-\theta}F(tb^{\gamma}), \tag{16}$$

where $F(x)$ is a scaling function independent of t and b, and γ is a crossover exponent. This scaling hypothesis has been tested [21,22] in numerical simulations in the absence of hydrodynamic flow. Here, we investigate the scaling behavior when viscous, hydrodynamic flow controls domain growth. We note that as $x\to\infty$, $R(t,b)\sim b^{-\theta}$, while as $x\to 0$, $R(t,b)\sim b^{n}$. This leads to an expression for γ as

$$\gamma=\frac{\theta}{n}. \tag{17}$$

For domain growth controlled by viscous hydrodynamics in two dimensions, $n=1/2$. This leads to $\gamma=2\theta$. Finally, since $R_{\mathrm{eq}}\sim b^{-\theta}$, one can recast the scaling expression [Eq. (16)] in the following form:

$$R(t,b)=R_{\mathrm{eq}}\mathcal{F}(tb^{2\theta}). \tag{18}$$

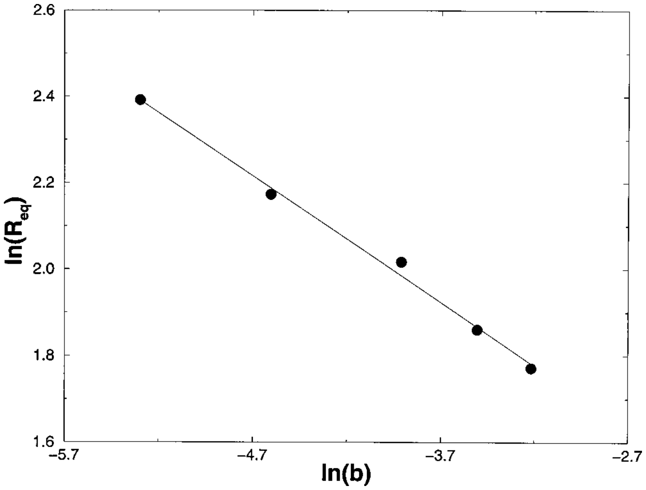

FIG. 2. Log-log plot of R_{eq} versus b. The data falls on a straight line indicating that $R_{\mathrm{eq}}\sim b^{-\theta}$. The straight line fit to the data yields an exponent of $\theta=0.30\pm0.02$.

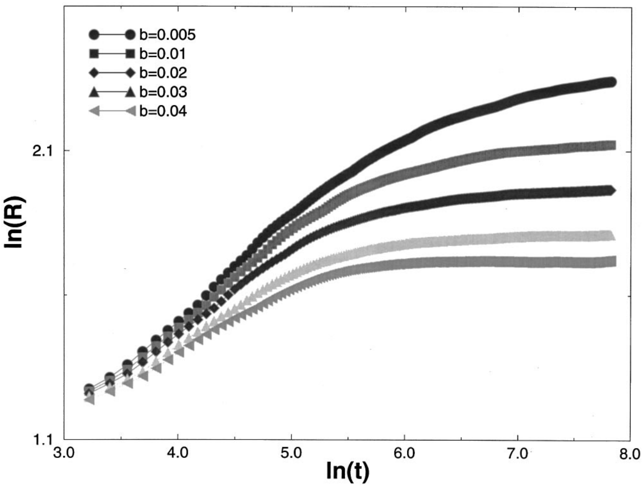

FIG. 3. Log-log plot of $R(t,b)$ versus t for various values of b.

We show our raw data for $\ln R(t,b)$ versus $\ln t$ for various values of b in Fig. 3 and test the above scaling form [Eq. (18)] in Fig. 4 by taking $\theta=0.60$, which was obtained earlier. As can be seen from the above figure, the scaling works fairly well. This strongly suggests that the domain growth exponent is $n=1/2$ for two-dimensional models of block copolymers in the viscous regime.

In summary, we have carried out numerical simulations of ordering and domain growth in a two-dimensional system of BCP melt. The model calculations reported here explicitly

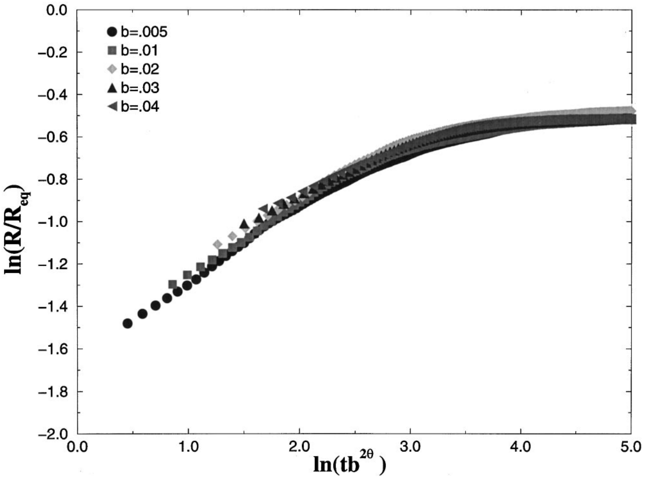

FIG. 4. Test of the scaling form [21] with $\theta=0.60$, which was obtained earlier. Scaling works fairly well and this strongly suggests that the domain growth exponent is $n=1/2$ for two-dimensional models of block copolymers in the viscous regime (see text).

include viscous, hydrodynamic flow and provide a scaling description for the growth of domains in a quenched BCP system. Our results indicate that the growth kinetics of BCP melts in two dimensions belong to the same dynamical universality class of small molecular liquid mixtures in the viscosity dominated regime. This suggests that the faster domain growth exponent recently observed in thin block copolymer films on a homogeneous substrate may have originated from a dimensional crossover from two to three dimensions. It would be extremely interesting to numerically study coarsening exponents in BCP systems as a function of the film thickness so that a dimensional crossover from two dimensions to three dimensions can be accessed.

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