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Phase separation kinetics of nematic polymers: Coupling between compositional order and orientational order

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We numerically investigate phase separation kinetics of liquid crystalline polymers in a nematic state using time-dependent Ginzburg-Landau equations for the compositional and the orientational order parameters ϕ and S_{ij}. The kinetics is significantly influenced by (i) the presence of the off-diagonal kinetic coefficient $\Lambda_{\phi S}$, (ii) the coupling between $\nabla\phi$ and S_{ij} in the free energy, and (iii) the dependence of the kinetic coefficients on the orientational order. [S1063-651X(98)51312-8]

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Liquid crystalline polymers (LCP's) have attracted much interest because of their technological applications, such as fibers of high tensile strength and optical devices. Phase behavior of LCP's has also been an important and fascinating problem of statistical mechanics, because of the rich variety of behaviors caused by the coupling between compositional order and orientational order, and it has been shown that the phase diagram of LCP's and their mixtures sensitively depends on temperature or their interaction [1]. The coupling between compositional order and orientational order also plays a significant role in phase separation kinetics of LCP's. For example, mixtures of LCP's and low molecular weight liquid crystals in a nematic state exhibit a phase separation to form a striated pattern parallel to the nematic orientation [2]. Although there has been some theoretical effort [3–7], the understanding of how orientational order affects phase separation kinetics of LCP's is still unsatisfactory. In a previous work [7], we derived the equations of motion for the compositional and the orientational order parameters by using the biased reptation model [8], and performed numerical simulations of phase separation, starting from an isotropic initial condition. In this Rapid Communication we study kinetics of phase separation from a nematic state to check how phase separation kinetics is influenced by orientational order.

We consider a solution of main-chain liquid crystalline homopolymers and define the following two order parameters: the volume fraction of polymers $\phi(\boldsymbol{r}) = \Sigma_\alpha \int_0^L d\tau\, \hat{\phi}^\alpha(\tau,\boldsymbol{r})$ and the orientational order $S_{ij}(\boldsymbol{r}) = \Sigma_\alpha \int_0^L d\tau\, \hat{S}_{ij}^\alpha(\tau,\boldsymbol{r})$, with

$$\hat{\phi}^\alpha(\tau,\boldsymbol{r}) = \frac{v_0}{b}\,\delta(\boldsymbol{r}-\boldsymbol{R}^\alpha(\tau)), \tag{1}$$

$$\hat{S}_{ij}^\alpha(\tau,\boldsymbol{r}) = \frac{v_0}{b}\left[u_i^\alpha(\tau)u_j^\alpha(\tau) - \frac{\delta_{ij}}{d}\right]\delta(\boldsymbol{r}-\boldsymbol{R}^\alpha(\tau)). \tag{2}$$

Here N, v_0, and b are the degree of polymerization, the monomer volume, and the average distance between adjacent monomers, respectively. The configuration of the αth chain is represented by $\boldsymbol{R}^\alpha(\tau)$, where τ parameterizes the position along the chain running from 0 to $L = Nb$, and $u_i^\alpha(\tau) \equiv \partial R_i^\alpha(\tau)/\partial\tau$. The d is the spatial dimension of the system. From the definition S_{ij} is symmetric, and $S_{ij}=0$ in the equilibrium isotropic state.

In a previous work [7], using the biased reptation model [8], we have derived the equations of motion for these order parameters, which read

$$\frac{\partial}{\partial t}\phi(\boldsymbol{r}) = \int d\boldsymbol{r}' \left\{ \Lambda_{\phi\phi}(\boldsymbol{r},\boldsymbol{r}')\frac{\delta(\beta F)}{\delta\phi(\boldsymbol{r}')} + \Lambda_{\phi S_{\mu\nu}}(\boldsymbol{r},\boldsymbol{r}')\frac{\delta(\beta F)}{\delta S_{\mu\nu}(\boldsymbol{r}')} \right\}, \tag{3}$$

$$\frac{\partial}{\partial t}S_{ij}(\boldsymbol{r}) = \int d\boldsymbol{r}' \left\{ \Lambda_{\phi S_{ij}}(\boldsymbol{r}',\boldsymbol{r})\frac{\delta(\beta F)}{\delta\phi(\boldsymbol{r}')} + \Lambda_{S_{ij}S_{\mu\nu}}(\boldsymbol{r},\boldsymbol{r}')\frac{\delta(\beta F)}{\delta S_{\mu\nu}(\boldsymbol{r}')} \right\}. \tag{4}$$

Hereafter, summations over repeated Greek indices are implied and F is the free energy of the system, which will be given below. The kinetic coefficients are [7,8]

$$\Lambda_{\psi_1\psi_2}(\boldsymbol{r},\boldsymbol{r}') = -D_c n \int_0^L d\tau \int_0^L d\tau' \frac{\partial^2}{\partial\tau\partial\tau'} \times \langle \hat{\psi}_1^\alpha(\tau,\boldsymbol{r})\hat{\psi}_2^\alpha(\tau',\boldsymbol{r}')\rangle, \tag{5}$$

where $\psi_1, \psi_2 = \phi$ or S_{ij}. D_c is the diffusion constant for the motion along a chain and n is the number of polymer chains in the system. The averages $\langle\,\rangle$ are taken in the local equilibrium state specified by $\phi(\boldsymbol{r})$ and $S(\boldsymbol{r})$.

The single chain Hamiltonian that we use for the calculations of the kinetic coefficients is that of a wormlike chain [9–11], $\beta\mathcal{H} = \beta(\mathcal{H}_0 + \mathcal{H}_1)$, with

$$\beta\mathcal{H}_0\{\boldsymbol{R}(\tau)\} = \int_0^L d\tau \left\{ \frac{d}{2lb}\boldsymbol{u}(\tau)^2 + \frac{\epsilon b}{2}\left(\frac{\partial\boldsymbol{u}(\tau)}{\partial\tau}\right)^2 \right\}, \tag{6}$$

$$\beta\mathcal{H}_1\{\boldsymbol{R}(\tau),h_{\phi(\boldsymbol{r})},h_{S_{ij}(\boldsymbol{r})}\}=\int d\boldsymbol{r}\int_0^L d\tau\{h_\phi(\boldsymbol{r})\hat{\phi}(\tau,\boldsymbol{r})+h_{S_{ij}}(\boldsymbol{r})\hat{S}_{ij}(\tau,\boldsymbol{r})\}. \tag{7}$$

Here β is the inverse temperature and we have introduced the fields $h_\phi(\boldsymbol{r})$ and $h_{S_{ij}}(\boldsymbol{r})$ conjugate to the order parameters. The ϵ in $\mathcal{H}_0$ is a dimensionless bending elastic constant and we set $l=4\epsilon/d$ [10,11] to ensure that $\langle|\boldsymbol{u}(\tau)|^2\rangle_0$ (statistical average over $e^{-\beta\mathcal{H}_0}$) is equal to unity. The following calculations are done for the rigid rod limit $\epsilon\to\infty$. We note that this model does not impose the constraint $|\boldsymbol{u}(\tau)|=1$ at each τ and allows the fluctuation of the segment length. That is, we do not assume that S_{ij} is traceless.

In calculating $\Lambda_{\phi S_{ij}}$ and $\Lambda_{S_{ij}S_{\mu\nu}}$, we use the approximation as in Ref. [7] that the average in Eq. (5) is taken over the unperturbed Hamiltonian $\mathcal{H}_0$. To incorporate the anisotropy of the diffusion due to the orientational order, we calculate $\Lambda_{\phi\phi}$ by taking the average over the full Hamiltonian $\mathcal{H}$ and making a perturbation expansion up to first order in h_ϕ and $h_{S_{ij}}$. The fields are calculated by using a density functional theory [11] and are given by, in a mean field approximation,

$$h_\phi(\boldsymbol{r})=-\frac{\ln\,\phi(\boldsymbol{r})}{v_0N}, \tag{8}$$

$$\frac{1}{2}(h_{S_{ij}}(\boldsymbol{r})+h_{S_{ji}}(\boldsymbol{r}))=-\frac{d^2Q_{ij}(\boldsymbol{r})}{2v_0N}, \tag{9}$$

where $Q_{ij}\equiv S_{ij}/\phi$ is the orientational order per monomer, and only the lowest order terms in Q_{ij} are retained. Similar treatment has been employed by Kawakatsu [12] for the phase separation kinetics of block copolymer melts. Then, Eqs. (3) and (4) can be rewritten as

$$\frac{\partial}{\partial t}\phi(\boldsymbol{r})=\frac{\beta D_c v_0 N\overline{\phi}}{d}\left\{\partial_\mu[\partial_\mu+(\partial_\mu\overline{h}_\phi)-\overline{h}_{S_{\mu\nu}}\partial_\nu]\frac{\delta F}{\delta\phi(\boldsymbol{r})}+\frac{2}{d}\partial_\mu\partial_\nu\frac{\delta F}{\delta S_{\mu\nu}(\boldsymbol{r})}\right\}, \tag{10}$$

$$\frac{\partial}{\partial t}S_{ij}(\boldsymbol{r})=\frac{\beta D_c v_0 N\overline{\phi}}{d}\left\{\frac{2}{d}\partial_i\partial_j\frac{\delta F}{\delta\phi(\boldsymbol{r})}+\frac{2}{d^2}\left(\nabla^2\frac{\delta F}{\delta S_{ij}(\boldsymbol{r})}+2\left(\partial_i\partial_\mu\frac{\delta F}{\delta S_{j\mu}(\boldsymbol{r})}+\partial_j\partial_\mu\frac{\delta F}{\delta S_{i\mu}(\boldsymbol{r})}\right)\right)\right\}, \tag{11}$$

where $\overline{\phi}$ is the average volume fraction of the polymers, $\overline{h}_\phi=v_0Nh_\phi$, and $\overline{h}_{S_{ij}}=(v_0N/d)(h_{S_{ij}}+h_{S_{ji}})$. In Eqs. (10) and (11) we have made a gradient expansion and retained only the lowest order terms in the gradients. Note that the diffusion of ϕ due to $\Lambda_{\phi\phi}$ is isotropic without $\overline{h}_\phi$ and $\overline{h}_{S_{ij}}$, and that by introducing $\overline{h}_{S_{ij}}$, we can incorporate the effect that polymers have a stronger tendency to diffuse parallel to the nematic direction.

We numerically integrate Eqs. (10) and (11) on a two-dimensional 128×128 square lattice with the periodic boundary conditions, using the Euler scheme. The free energy is taken to be [7,11]

$$\begin{aligned}v_0\beta F=\int d\boldsymbol{r}\Bigg\{&\frac{\phi}{N}\ln\,\phi+\frac{1-\phi}{N'}\ln(1-\phi)+\chi\phi(1-\phi)\\&-\frac{\phi}{2N}\mathrm{Tr}[\log(1+dQ)-dQ]\\&-\frac{1}{2}w\phi^2\mathrm{Tr}[Q-(1/d)\mathrm{Tr}\;Q]^2+\frac{1}{2}W\phi(\mathrm{Tr}\;Q)^2\\&+\frac{1}{2\phi}C_0(\partial_i\phi)^2+L_0\left(\partial_i\phi\partial_jQ_{ij}+\frac{1}{2\phi}Q_{ij}\partial_i\phi\partial_j\phi\right)\\&+\frac{1}{2}L_1\phi(\partial_kQ_{ij})^2+\frac{1}{2}L_2\phi\partial_iQ_{ij}\partial_kQ_{kj}\Bigg\}.\end{aligned} \tag{12}$$

The first line is the Flory-Huggins energy with an isotropic interaction parameter χ. The following two lines are the energy due to the orientation, and the term proportional to w is the Maier-Saupe anisotropic interaction, which favors the nematic order. The term proportional to W is added as a penalty for the fluctuation of the segment length. The last two lines are the gradient energy, due to inhomogeneity, with $C_0=Nb^2/12d, L_0=Nb^2/12, L_1=dNb^2/24$, and $L_2=dNb^2/6$ [11].

For simplicity we set $N=N'$ and choose the parameters $\chi N=2.7$ and $wN=WN=5$. The average volume fraction of polymers $\overline{\phi}$ is set to 0.5. The grid size and the time step are taken to be $\Delta x=0.25Nb$ and $\Delta t=\Delta\tau\phi_{min}[d(Nb)^2/D_c\overline{\phi}]$, respectively, where ϕ_{min} is the minimum value of ϕ. We set $\Delta\tau=0.0001$ in cases 1, 2, and 3 (see below), and $\Delta\tau=0.000\,05$ in case 4. We prepare the nematic initial conditions oriented parallel to the x axis by assigning to ϕ and Q_{ij} at each lattice point random numbers uniformly distributed in $[\overline{\phi}-0.01,\overline{\phi}+0.01]$ and $[\overline{Q_{ij}}-0.05,\overline{Q_{ij}}+0.05]$, respectively, with $\overline{Q}_{xx}=-\overline{Q}_{yy}=0.3$ and $\overline{Q}_{xy}=0$. Note that phase separation between a nematic phase, rich in polymers, and an isotropic phase, poor in polymers, occurs when we choose the parameters above.

We investigate how phase separation kinetics is influenced by the coupling between the compositional order ϕ and the orientational order S_{ij} (or Q_{ij}), which appears, in our model, in (i) the presence of the off-diagonal kinetic coefficient $\Lambda_{\phi S}$, (ii) the coupling of ϕ and S_{ij} in the free energy F, and (iii) the dependence of the kinetic coefficients on the orientational order. We first check the effect of the off-diagonal component of the kinetic coefficient $\Lambda_{\phi S}$. Although earlier studies [4,5] based on a phenomenological argument neglected it, recent studies [6,7] showed that the off-diagonal kinetic coefficient should appear in the kinetic equations of LCP's. Here we show the results without $\overline{h}_\phi$ and $\overline{h}_{S_{ij}}$, and with $L_0=L_2=0$ in the free energy F. Notice that by setting $L_0=L_2=0$, rotation of the frame and rotation of polymers (or the orthogonal transformation of Q_{ij}) become uncorrelated, thus the free energy possesses no anisot-

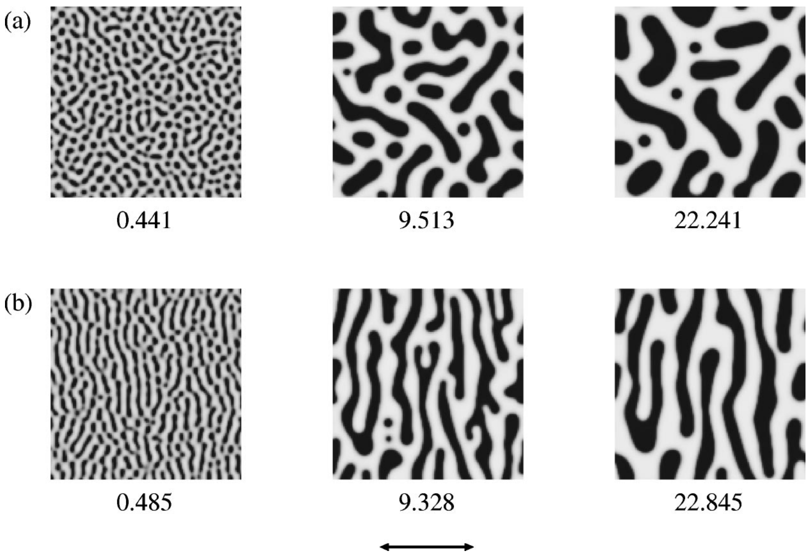

FIG. 1. Time evolution of the composition (ϕ) profile for (a) case 1 (without $\Lambda_{\phi S}$) and (b) case 2 (with $\Lambda_{\phi S}$). Darkness represents ϕ. The numbers are times after quench in units of $d(Nb)^2/D_c\overline{\phi}$. The arrow indicates the direction of the nematic orientation.

ropy even in a nematic state. We show the time evolution of the composition profile in Fig. 1(a) without $\Lambda_{\phi S}$'s in the kinetic equations (10) and (11) (refer to case 1 below), and in Fig. 1(b) with $\Lambda_{\phi S}$'s (case 2). Apparently no anisotropy is found in case 1, while we can observe a stripe pattern perpendicular to the nematic orientation in case 2. We stress here that the anisotropy found in case 2 arises for a purely kinetic reason because there is no anisotropy in the free energy as stated above, and it can be understood by a simple linear analysis of the growing mode, although we do not show the detail of the calculation. Our results show that the off-diagonal components of the kinetic coefficients may play an important role in phase separation kinetics.

Next we investigate the effect of the coupling between ϕ and S_{ij} in the free energy, and how kinetics is altered due to the modification of the kinetic coefficient $\Lambda_{\phi\phi}$ by the conjugate fields h_ϕ and $h_{S_{ij}}$. Thus, we recover the terms proportional to L_0 and L_2 in the free energy. In the calculation below, we also retain $\Lambda_{\phi S}$, and to avoid numerical difficulties, $\overline{h}_{S_{ij}}$ and L_0 are multiplied by 0.7. We show the time evolution of the composition profile in Fig. 2(a) without the fields $\overline{h}_\phi$ and $\overline{h}_{S_{ij}}$ (case 3), and in Fig. 2(b) with these fields (case 4). Contrary to case 2, a striated pattern parallel to the nematic orientation is obtained in case 3, which closely resembles that in an experiment of nematic-nematic phase separation [2], while in case 4, we can observe a stripe pattern perpendicular to the nematic orientation similar to that in case 2. We note that the free energy of an interface, parallel to the nematic orientation, is lower than that of a perpendicular one due to the terms proportional to L_0 in the free energy, which leads to the pattern parallel to the nematic orientation in case 3. We also note that the tendency of polymers to diffuse, parallel to the nematic orientation, leads to the density modulation, perpendicular to the nematic orientation as in case 4, which is schematically illustrated in Fig. 3.

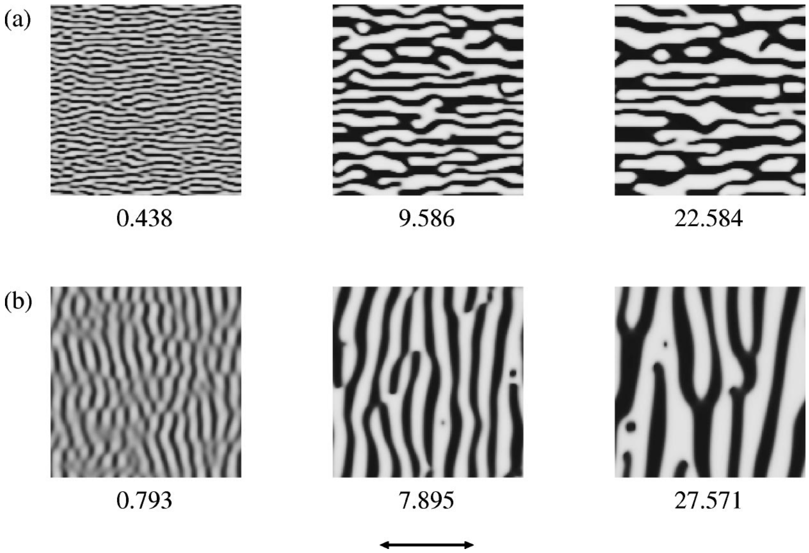

FIG. 2. Time evolution of the composition profile for (a) case 3 (without $\overline{h}_\phi$ and $\overline{h}_{S_{ij}}$) and (b) case 4 (with $\overline{h}_\phi$ and $\overline{h}_{S_{ij}}$).

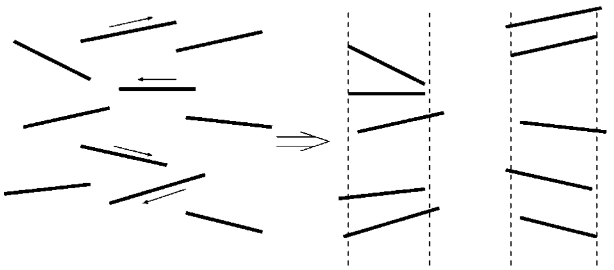

FIG. 3. Schematic illustration of the kinetic effect leading to the density modulation, perpendicular to the nematic orientation (indicated by dashed lines).

In Fig. 4 we show the time evolution of the characteristic lengths in the x and y directions, $l_i(t)=2\pi/\overline{k_i}(t)$ $(i=x,y)$. The characteristic wave number $\overline{k_i}(t)$ is defined as $\overline{k_i}(t)=\int dk\, d\theta |k_i| S(k,\theta,t)/\int dk\, d\theta S(k,\theta,t)$ [13], where $S(k,\theta,t)=S(k_x=k\cos\theta,k_y=k\sin\theta,t)=\langle|\phi(\mathbf{k},t)|^2\rangle$ is the structure factor and $\phi(\mathbf{k},t)$ is the Fourier transform of $\phi(\mathbf{r},t)$. The characteristic lengths evolve with time for all cases (the saturation of l_y in case 4 is attributed to the finite size effect), and l_x in case 3 and l_y in cases 2 and 4 are larger than those in case 1, as can be seen in Figs. 1 and 2. We note that l_y in case 3 evolves as $l_y \sim t^{\alpha}$, with $\alpha \simeq 1/3$, which is a typical growth law for conserved systems [14], and has been obtained by experiments [2].

In summary, we have numerically integrated the equations of motion of LCP's for the compositional and the orientational order parameters from a nematic initial condition. We have shown that the phase separation kinetics sensitively depends on the form of the kinetic equations and of the free energy. Finally, we comment on the reason phase separation of nematic polymers in an experiment [2] leads to the pattern similar to that in case 3, not in case 4. Since polymers are allowed to move only along themselves in the biased reptation model, our model cannot incorporate the rotational diffusion and the diffusion perpendicular to the polymers, which reduces the anisotropy in the kinetic coefficients, and may play an important role in actual experiments. When we prepare a mixture of LCP's and flexible polymers with LCP's in a nematic state, phase separation may result in a pattern, such as in case 4, because the rotational diffusion and the diffusion perpendicular to the polymers are suppressed, due to the topological constraints imposed by flexible polymers.

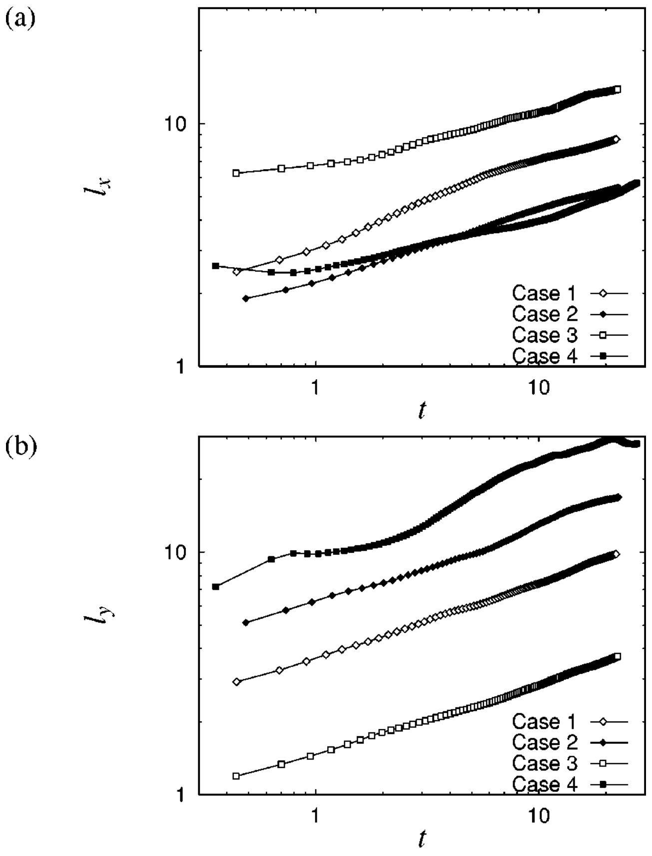

FIG. 4. Time evolution of the characteristic lengths (a) l_x and (b)l_y. Time is measured in units of $d(Nb)^2/D_c\overline{\phi}$.

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