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Scattering function of the disordered phase of block copolymers under shear flow

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Abstract

The scattering function of the disordered phase of a block copolymer (BCP) melt under a steady shear flow is investigated by the cell dynamical system (CDS) approach. Agreement with previous theoretical calculations indicates the applicability of the CDS approach to the disordered phase as well as the ordered phase.

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Block copolymers (BCP) are linear chains typically composed of two homopolymer subchains grafted covalently at one end. Their properties have attracted great scientific and technological interest. It is well-known that the BCP system exhibits various fascinating periodic structures as well as a homogeneous disordered phase depending on the temperature or the molecular composition. The mesoscopic description of these equilibrium phases has been rather well established according to the theory by Leibler for the weak segregation regime [1], or that by Ohta and Kawasaki for the strong segregation regime [2].

In this Letter, using the cell dynamical system (CDS) approach [3,4], we investigate the effect of a steady shear flow on the scattering function of the disordered phase in a BCP system. The present computer simulation is motivated by the previous mean field calculation of Fredrickson, who showed that the shear flow affects the scattering function highly anisotropically, whereas the peak intensity is considerably attenuated [5]. In our computer simulation, we especially pay attention to the scaling analysis of the attenuation rate in the peak intensity. So far the CDS approaches have been used only to simulate the ordered phase (low temperature phase) in the spinodal decomposition or in the micro-phase separation of the BCP system. Our result shows that the CDS method is also applicable to investigating the high temperature disordered phase at least in the latter case.

According to a previous theory [1], the order parameter of the BCP system can be introduced in the following way. Let $\phi_a(\boldsymbol{r})$ and $\phi_b(\boldsymbol{r})$ denote the

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local volume fraction of segments a and b; N_a and N_b represent the degrees of polymerization of blocks a and b, respectively. Under the condition that the molten phase is incompressible ($\phi_a(\boldsymbol{r}) + \phi_b(\boldsymbol{r}) = 1$), the system can be described by a single order parameter $\psi(\boldsymbol{r}) = \phi_a(\boldsymbol{r}) - \phi_b(\boldsymbol{r})$. The spatial average of $\psi(\boldsymbol{r})$ is determined solely by the relation $\bar{\psi} = 2f - 1$, with $f = N_a/(N_a + N_b)$, where f is the block ratio. For the dynamics of the BCP system, Oono and Shiwa first proposed an equation of motion for the time dependent order parameter $\psi(\boldsymbol{r}, t)$ [4]. Recently Ohta et al. generalized this equation to the case in which a macroscopic flow $\boldsymbol{v}$ is present [6],

$$\frac{\partial\psi}{\partial t} + \nabla\cdot(\boldsymbol{v}\psi) = \nabla^2\left(-D\nabla^2\psi - \tau\psi + u\psi^3\right) - B\left(\psi - \bar{\psi}\right). \tag{1}$$

In the above, B, D, τ and u are positive phenomenological parameters and the last term is due to the long range interaction. (The transport coefficient has been eliminated in Eq. (1) after an appropriate scaling.) As for the macroscopic flow in Eq. (1), we consider the following shear flow,

$$v_x(\boldsymbol{r}) = \dot{\gamma}y, \quad v_y = v_z = 0, \tag{2}$$

where the shear rate $\dot{\gamma}$ is the time derivative of the shear strain γ. In this case, the convective term in Eq. (1) becomes $\dot{\gamma}y(\partial\psi/\partial x)$ and we are allowed to perform our simulation in two-dimensional space [6].

The CDS model for spinodal decomposition proved to be an efficient algorithm for numerical simulations [3]. As a slight modification of this model, Oono and Shiwa proposed the corresponding CDS model of Eq. (1) [4], and a subsequent detailed investigation has been performed by Bahiana and Oono [7]. In the present simulation, we employ the same CDS model as in Ref. [6] where the rheological properties of the hexagonal phase under an applied shear flow are reported. The difference equation for the order parameter $\psi(\boldsymbol{n}, t)$ is given by

$$\begin{aligned}\psi(\boldsymbol{n}, t+1) &= \psi(\boldsymbol{n}, t) - B\left[\psi(\boldsymbol{n}, t) - \bar{\psi}\right] \\ &\quad - \tfrac{1}{2}\dot{\gamma}\left[\psi(n_x+1, n_y, t) - \psi(n_x-1, n_y, t)\right] \\ &\quad + \langle\langle I(\boldsymbol{n}, t)\rangle\rangle - I(\boldsymbol{n}, t) + C\eta(\boldsymbol{n}, t),\end{aligned} \tag{3}$$

with

$$I(\boldsymbol{n}, t) = -A\tanh\psi(\boldsymbol{n}, t) + \psi(\boldsymbol{n}, t) - D\left[\langle\langle\psi(\boldsymbol{n}, t)\rangle\rangle - \psi(\boldsymbol{n}, t)\right], \tag{4}$$

where $\boldsymbol{n} = (n_x, n_y)$ assigns the two-dimensional lattice point. The operator $\langle\langle X\rangle\rangle$ defines the isotropic spatial average of the quantity X, and is defined on the square lattice by $\langle\langle X\rangle\rangle = \frac{1}{6}\Sigma X$(nearest-neighbor cells) + $\frac{1}{12}\Sigma X$(next-nearest-neighbor cells) [3]. The last term on the r.h.s. of Eq. (3) represents the noise term, C being the noise amplitude and $\eta(\boldsymbol{n}, t) = \eta_x(n_x + 1, n_y, t) - \eta_x(n_x, n_y, t) + \eta_y(n_x, n_y + 1, t) - \eta_y(n_x, n_y, t)$, where η_x and η_y are random numbers uniformly distributed in the interval $[-1, 1]$ [7]. In the present simulation, we have fixed the parameters to the values $B = 0.02$, $C = 0.01$, $D = 0.5$, $\bar{\psi} = 0$, whereas the shear rate has been changed for the values $\dot{\gamma} = 0$, 1×10^{-4}, 3×10^{-4}, 5×10^{-4} and 1×10^{-3}.

The linear stability analysis based on Eq. (1) without any flow ($\boldsymbol{v} = 0$) shows that the spinodal line is determined by $(\tau - 3u\bar{\psi}^2)^2 - 4BD = 0$ [8]. Since the line of microphase-separation temperature (MST) and the spinodal line coincides for $\bar{\psi} = 0$ (symmetric BCP), the transition temperature between the lamellar phase and the disordered phase is given by $\tau_c = 2\sqrt{BD} = 0.2$ for above values of parameters. Hence the corresponding critical value of A in Eq. (4) should be $A_c = 1 + \tau_c = 1.2$. We have chosen several values of A to lie between 1.190 and 1.199 representing just above the transition temperature. (In general the flow changes the locus of the spinodal and MST, but we do not consider this problem here.)

In our simulation we have studied a system on a square lattice of size $L\times L = 64\times64$ and the initial distribution of $\psi(\boldsymbol{n})$ is specified by a random uniform distribution in the range $[-0.025, 0, 025]$. In the presence of the shear flow given by Eq. (2), the required boundary condition should satisfy $\psi(n_x, n_y, t) = \psi(n_x + iL + \gamma jL, n_y + jL, t)$ for arbitrary integers i and j [6]. The Fourier components $\psi(\boldsymbol{k}, t)$ under this sheared boundary condition can be calculated by performing the affine transforma-

tion of $\psi(\boldsymbol{n}, t)$ as

$$\psi(k_x, k_y, t) = \int_0^L \mathrm{d}x' \int_0^L \mathrm{d}y \times \psi(x, y, t) \exp\left[\mathrm{i}(k_x x + k_y y)\right], \tag{5}$$

where $x' = x - \gamma y$ and $\boldsymbol{k} = (k_x, k_y) = (2\pi/L)(m, n - \gamma m)$ with m and n integers [6]. The scattering functions $S(\boldsymbol{k}) = \langle |\psi(\boldsymbol{k})|^2 \rangle$ have been computed after 5000 time steps, which is long enough to observe the steady state behavior of the system. We have also checked that $S(\boldsymbol{k})$ does not change appreciably for longer runs up to 10000 time steps. In order to improve the statistics, the average has been taken over 200 sample patterns for each parameter set. It is important to add the noise in this simulation since we are close to the transition point.

For a fixed value of $A = 1.198$, two-dimensional scattering patterns $S(\boldsymbol{k})$ are presented for (a) $\dot{\gamma} = 0$, (b) 3×10^{-4}, (c) 5×10^{-4} and (d) 1×10^{-3} in Fig. 1. The dark area denotes the region of higher scattering intensity. When there is no applied shear flow ($\dot{\gamma} = 0$), the scattering pattern is isotropic and the radius of the circular ring corresponds to the absolute value of the most unstable wave vector with which the lamellar pattern will be developed below the transition temperature. As the shear rate is increased, the pattern becomes more and more anisotropic. Depending on the direction in the scattering patterns, the peak positions in $S(\boldsymbol{k})$ are shifted towards larger or smaller value of $k = |\boldsymbol{k}|$ as compared to the case

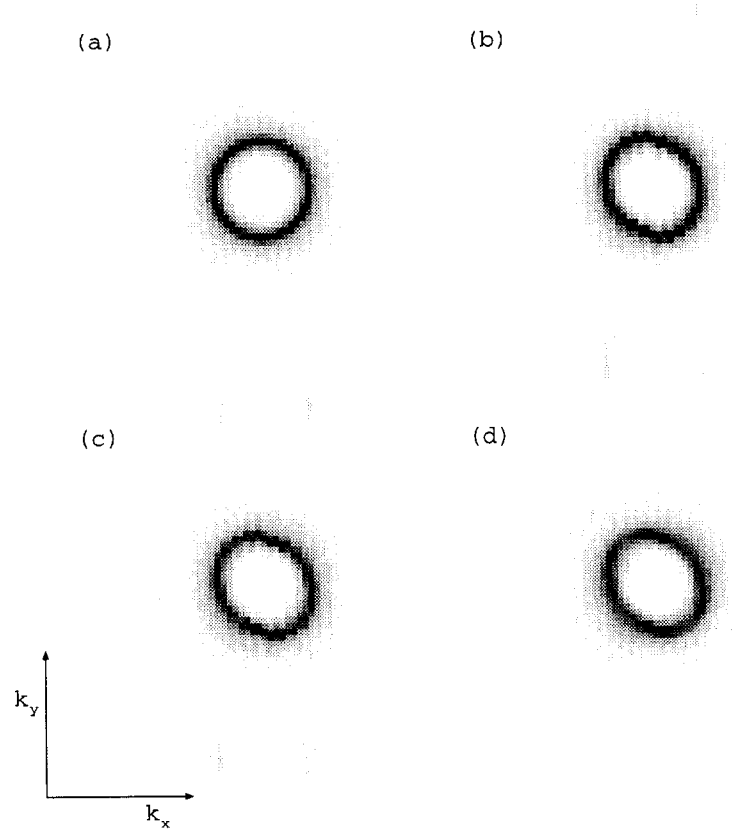

Fig. 1. Two-dimensional scattering patterns for $A = 1.198$ and (a) $\dot{\gamma} = 0$, (b) 3×10^{-4}, (c) 5×10^{-4} and (d) 1×10^{-3}. The dark area denotes the region of higher scattering intensity.

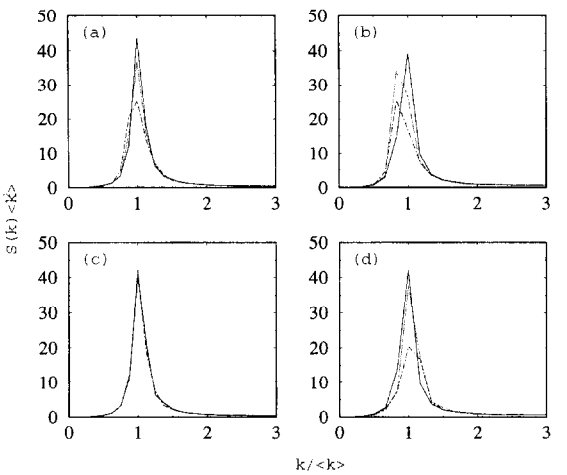

Fig. 2. $S(k)\langle k\rangle^2$ as a function of the scaled wavevectors $k/\langle k\rangle$ for $A = 1.198$ and (a) $\phi = 0$, (b) $\frac{1}{4}\pi$, (c) $\frac{1}{2}\pi$ and (d) $\frac{3}{4}\pi$. $\langle k\rangle$ is the location of the peak in the absence of shear flow for $A = 1.198$. The solid, dotted and dot-dashed lines represent $\dot{\gamma} = 0$, 3×10^{-4} and 1×10^{-3}, respectively.

of $\dot{\gamma} = 0$. To specify the orientation of $\boldsymbol{k}$ in the k_x–k_y plane, we let ϕ denote the polar angle measured relative to the k_x-axis. For the same fixed value of $A = 1.198$, the shape of the scattering functions for $\dot{\gamma} = 0$ (solid), 3×10^{-4} (dotted) and 1×10^{-3} (dot-dashed) are presented in each graph of Fig. 2 corresponding to the direction of (a) $\phi = 0$, (b) $\frac{1}{4}\pi$, (c) $\frac{1}{2}\pi$ and (d) $\frac{3}{4}\pi$. In these four graphs, the dimensionless quantities $S(k)\langle k\rangle^2$ are plotted as a function of the normalized wavevector $k/\langle k\rangle$, where $\langle k\rangle$ is the averaged peak position for $A = 1.198$ and $\dot{\gamma} = 0$. Considering the symmetry of Eq. (2), the scattering function should not be changed by the shear flow for $\phi = \frac{1}{2}\pi$ ($k_x = 0$) and this requirement is well reproduced in Fig. 2c, where we see no appreciable difference in the scattering function for different values of $\dot{\gamma}$. As was predicted by Fredrickson [5], the scattering peak should be shifted to smaller values of k for $\phi = 0$ and $\frac{1}{4}\pi$ whereas the peak is shifted to larger k for $\phi = \frac{3}{4}\pi$. Moreover the peak height is significantly attenuated in all directions except for $\phi = \frac{1}{2}\pi$. One can also observe that the larger the shear rate $\dot{\gamma}$, the larger both the peak shift and the attenuation are.

For different values of A, the effect of the shear flow turns out to give rise to the same effect as described above for $A = 1.198$. However as the temperature approaches the transition temperature, the peak intensity is more attenuated, even if the shear rate is kept unchanged. In order to summarize these behaviors, we look at the attenuation rate defined by

$$\Gamma(A, \dot{\gamma}, \phi) = \frac{I(A, \dot{\gamma}, \phi)}{I(A, \dot{\gamma}=0, \phi)} \leqslant 1, \tag{6}$$

where $I(A, \dot{\gamma}, \phi)$ is the maximum value of $S(k)$ depending on A, $\dot{\gamma}$ and ϕ. Recalling the lowest order calculation of the maximum peak intensity by Fredrickson [5], we anticipate the following scaling form,

$$\Gamma(A, \dot{\gamma}, \phi) = f(x, \phi),$$
$$\text{with } x = \dot{\gamma}^2/(1.2 - A)^3. \tag{7}$$

In the limit of $x \to 0$, $f(x)$ should behave as $f(x) \to 1$. Fig. 3 is the log-linear plot of $f(x,\phi = \frac{1}{4}\pi)$ as a function of x. Although the data collapse is not satisfactory due to the large error bars, the above described qualitative behavior is well reproduced.

Below the transition temperature ($A > 1.2$) and in the absence of the shear flow, the above CDS model does not provide a well-defined lamellar structure but rather a complicated bicontinous pattern in contrast to the real system. Bahiana and Oono tried to avoid this difficulty by performing such as three-dimensional simulation, adding sufficiently large thermal noise, imposing a bending penalty or taking into account the hydrodynamic interactions, but none of these attempts could change the pattern significantly

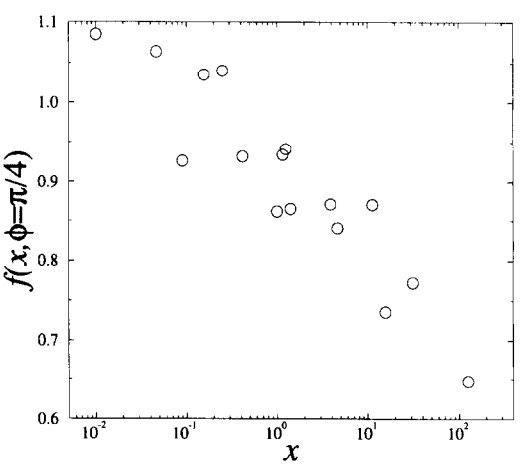

Fig. 3. Log-linear plot of $f(x, \phi = \frac{1}{4}\pi)$ as a function of x.

[7]. In spite of these difficulties, we found that a well-ordered lamellar structure can be obtained by imposing a macroscopic shear flow given by Eq. (2). The scattering pattern of such a lamellar structure exhibits two sharp spots on $k_x = 0$ with much larger intensity than that of disordered phase.

In summary, we investigated the scattering function of the disordered phase of a BCP melt under a steady shear flow through the CDS approach. The results indicate that the CDS approach is also applicable to the disordered phase.

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