Orientations of the lamellar phase of block copolymer melts under oscillatory shear flow

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We develop a theory to describe the reorientation phenomena in the lamellar phase of block copolymer melts under reciprocating shear flow. We show that, similar to the steady shear, the oscillating flow anisotropically suppresses fluctuations and gives rise to the $\parallel \rightarrow \perp$ transition. The experimentally observed high-frequency reverse transition is explained in terms of interaction between the melt and the shear-cell walls.

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The behavior of the lamellar phase (a striped pattern) of block copolymer melts under oscillatory shear flow has attracted attention of numerous experimental studies [1–6]. Shear flow is known to influence the order-disorder transition (ODT) temperature and the orientation of the lamellae with respect to the shear geometry. Thus, in the vicinity of ODT at low frequencies the lamellae orient with their normal parallel to the shear gradient (the parallel orientation), while at higher frequencies their normal is perpendicular to the velocity and the gradient directions (the perpendicular orientation). Further increase of frequency results in reappearance of the parallel orientation [5]. Here, we propose an explanation of this orientation behavior that is usually referred to as a double-flip phenomena.

Earlier theories, which deal with steady shear, emphasize the role of compositional fluctuations [7–9]. The stable orientation is seen as a result of interaction between the shear flow and the fluctuation spectra. In equilibrium, fluctuations destroy the long-range correlations and, therefore, lower the ODT temperature with respect to its mean-field value. Imposition of shear breaks the rotational symmetry and anisotropically suppresses fluctuations. The direction of the strongest suppression will have the highest ODT temperature and the corresponding orientation of lamellae will be selected. We will show that the selected orientation depends on the amplitude and frequency of the flow. We base our analysis on the Fokker-Planck equation for the probability density $P[\phi]$,

$$\frac{\partial P}{\partial t}[\phi,t]=\int_k \frac{\delta}{\delta\phi_{\mathbf{k}}}\left[\mu\left(\frac{\delta}{\delta\phi_{-\mathbf{k}}}+\frac{\delta H[\phi]}{\delta\phi_{-\mathbf{k}}}\right)-A\omega\cos\omega t k_x\frac{\partial}{\partial k_y}\phi_{\mathbf{k}}\right]P[\phi,t]. \quad (1)$$

Here $\phi_{\mathbf{k}}$ is a fluctuating scalar field described by the Brazovskii Hamiltonian [10]

$$H[\phi]=\frac{1}{2}\int_k[\tau+(k-k_0)^2]\phi_{\mathbf{k}}\phi_{-\mathbf{k}}+\frac{1}{4!}\int_{k_1}\int_{k_2}\int_{k_3}\int_{k_4}\lambda(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4)\phi_{\mathbf{k}_1}\phi_{\mathbf{k}_2}\phi_{\mathbf{k}_3}\phi_{\mathbf{k}_4}, \quad (2)$$

τ is a temperature-controlling parameter, k_0^{-1} is an intrinsic length scale of the block-copolymer melt arising from the interplay of interactions and the chain connectivity, μ is an Onsager coefficient that is approximated by $\mu=\mu(k_0)$ and assumed to be frequency independent [11–13]. The last term in Eq. (1) describes a coupling between the shear flow $\mathbf{v}=A\omega\cos\omega t y\mathbf{e}_x$ and the gradient of the order parameter. Here we assume that this form of flow is valid for all ω and A.

The Fokker-Planck equation (1) generates the equations for the amplitude of the average order-parameter profile $\langle\phi_{\mathbf{k}}\rangle=a(\delta_{\mathbf{k},k_0\mathbf{n}}+\delta_{\mathbf{k},-k_0\mathbf{n}})$ oriented along the unit vector $\mathbf{n}$,

$$\frac{1}{\mu}\frac{\partial a}{\partial t}=-r(\mathbf{n})a+\frac{\lambda}{2}(1-\beta)a^3, \quad (3)$$

and for the structure factor $S(\mathbf{k})=\langle\phi_{\mathbf{k}}\phi_{-\mathbf{k}}\rangle-\langle\phi_{\mathbf{k}}\rangle\langle\phi_{-\mathbf{k}}\rangle$,

$$\frac{1}{2\mu}\frac{\partial S(\mathbf{k})}{\partial t}-\frac{A\omega}{2\mu}\cos\omega t k_x\frac{\partial S(\mathbf{k})}{\partial k_y}+S(\mathbf{k})S(\mathbf{k})_0^{-1}=1, \quad (4)$$

where

$$S_0^{-1}(\mathbf{k})=r(\hat{\mathbf{k}})+(k-k_0)^2, \quad (5)$$

$$r(\hat{\mathbf{k}})\equiv r-\hat{\mathbf{k}}\cdot\vec{\mathbf{e}}\cdot\hat{\mathbf{k}}=\tau+\lambda a^2(1-\beta(\mathbf{n}\cdot\hat{\mathbf{k}})^2)+\sigma(\hat{\mathbf{k}}),$$

$$\sigma(\hat{\mathbf{k}})=\frac{\lambda}{2}\int\frac{d\mathbf{q}}{(2\pi)^3}S(\mathbf{q})[1-\beta(\hat{\mathbf{k}}\cdot\hat{\mathbf{q}})^2].$$

The interaction [14] between fluctuations $\lambda(\mathbf{k},-\mathbf{k},\mathbf{q},-\mathbf{q})=\lambda[1-\beta(\hat{\mathbf{k}}\cdot\hat{\mathbf{q}})^2]$, with $\hat{\mathbf{k}}=\mathbf{k}/k$, renormalizes the temperature $r(\hat{\mathbf{k}})$ and makes it anisotropic in the presence of shear.

The stability criterion for an orientation is derived from Eq. (3). It has a potential form $\partial a/\partial t=-(\mu/2)\partial\Phi(a)/\partial a$, with

$$\Phi(a,\mathbf{n})=-\frac{1}{4}\lambda a^4(1-\beta)+2\int_0^a da' r(\mathbf{n})a'. \quad (6)$$

Generally, the potential Φ is time dependent. In steady state, however, it oscillates around some average value. In order to simplify our analysis we coarse grain the time scale with the period of oscillations and consider the time-independent version of Eqs. (5), (6) with $\sigma(\hat{\mathbf{k}},t)$ replaced by $\overline{\sigma}(\hat{\mathbf{k}})$

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$=(\omega/2\pi)\int_0^{2\pi/\omega} dt\,\sigma(\hat{\mathbf{k}},t)$. In this model, the minimum of $\Phi(a,\mathbf{n})$ determines the stable orientation [15]. The potential Φ can be viewed as a dynamical extension of the equilibrium free energy. Together with the solution of Eq. (4),

$$S(\mathbf{k},t)=2\mu\int_0^t d\tau\exp\left[-2\mu\int_\tau^t ds S_0^{-1}(\mathbf{k}(s))\right], \qquad (7)$$

$$\mathbf{k}(s)=[k_x,k_y+Ak_x(\sin\omega t-\sin\omega s),k_z],$$

it allows us to construct the orientational phase diagram.

First we consider the low-amplitude shear ($A\ll 1$). In this case we expand the exponent in Eq. (7) up to $O(A^2)$ and obtain

$$\bar{\sigma}(\mathbf{n})=\sigma_1-\frac{3\pi\beta}{56}\left(\frac{A\varpi}{2\mu}\right)^2\frac{\alpha^2\lambda}{r^{7/2}}\left(n_y^2+\frac{n_z^2}{3}\right), \quad \varpi\ll 1,$$

$$\bar{\sigma}(\mathbf{n})=\sigma_2-\frac{2\pi\beta}{35}A^2\frac{\alpha^2\lambda}{r^{3/2}}\left(n_y^2+\frac{n_z^2}{3}\right), \quad \varpi\gg 1, \qquad (8)$$

where $\alpha=k_0^2/(4\pi)$, $\varpi=\omega/(2\mu)$, and σ_1,σ_2 absorb the orientation-independent terms. In the low-amplitude regime, the fluctuation spectra is only slightly influenced by shear flow. Equations (8) show that this regime is a perturbation of the equilibrium state with $\bar{\sigma}=\sigma_0$. When the frequency is low, the typical time of the critical fluctuation development is much shorter than $\dot{\gamma}^{-1}\equiv(A\omega)^{-1}$ and the flow simply translates fluctuations in space. At high frequencies, the lifetime of the critical fluctuations exceeds the characteristic time of the flow. However, since the amplitude of deformation is small, fluctuations live in an averaged environment, similar to the equilibrium one. Then the properties of the melt cannot depend on the frequency, which is shown by Eq. (8). To determine the stable orientation we follow Fredrickson and note that the fluctuation integral $\bar{\sigma}$ is smaller for the parallel orientation ($n_y=1$). The fluctuations are weaker in this direction and, therefore, we predict the parallel orientation to be stable in the low-amplitude regime.

For the finite-amplitude shear, the fluctuation integral $\bar{\sigma}$ can be evaluated with the help of Eq. (7) near $k_x\approx 0$,

$$\bar{\sigma}(\mathbf{n})=c_1(\alpha\lambda)^{2/3}\left(\frac{D_*}{A\omega}\right)^{1/3}\left[1-\frac{\beta}{7}(2n_y^2+3n_z^2)\right], \quad \omega\ll 1,$$

$$\bar{\sigma}(\mathbf{n})=c_2\frac{A_*}{A}\left\{\ln^2\epsilon-\pi^2-\beta\left[4n_y^2\ln\frac{\epsilon}{e^4}+n_z^2\left(16-\pi^2+\ln^2\frac{\epsilon}{e^4}\right)\right]\right\}, \quad \omega\gg 1,$$

$$D_*=\mu\lambda\sqrt{\alpha}, \quad A_*=\lambda\sqrt{\alpha}, \quad \epsilon=\frac{32\sqrt{3}A^2k_0^2}{r(\mathbf{n})},$$

$$c_1=\frac{\Gamma\left(\frac{1}{6}\right)3^{1/6}}{\pi^{2/3}}, \quad c_2=\frac{\sqrt{2}}{16\pi^{3/2}3^{1/4}}.$$

This regime no longer resembles the equilibrium state. Indeed, in equilibrium [10] as well as under low-amplitude shear the spinodal temperature, given by $r(\mathbf{n})|_{a=0}=0$, is suppressed by fluctuations to $\tau_s=-\infty$. Unlikely, from Eq. (9) $\tau_s(\mathbf{n})=-\bar{\sigma}(\mathbf{n})$ asymptotically approaches zero as $A\to\infty$. We conclude that the flow strongly suppresses fluctuations and restores the mean-field behavior. We also see that $\tau_s(n_z)>\tau_s(n_y)$ and, therefore, we expect the perpendicular orientation to appear below the spinodal. Analysis of the potential Φ shows that this orientation will persist for lower temperatures.

The transition from the parallel to perpendicular orientations can be located with the help of the method from Ref. [16]. We interpolate $\bar{\sigma}$ in between the $A\to 0$ and $A\to\infty$ regimes and solve the equation $\tau_s(n_y)=\tau_s(n_z)$ to obtain the transition line in the $A-\omega$ plane

$$A\omega\approx 10^3\mu k_0^2\sim N^{-3}, \quad \varpi\ll 1, \qquad (9)$$

where N is a number of monomers in a polymer chain. For high frequencies, $\bar{\sigma}$ is independent of ω and we predict the transition line to be given by $A=\text{const}$. Recent experimental work [5] argues that at low frequencies the transition between the orientations occurs at $A\sim\omega^{-1}$, while at higher frequencies the transition line starts to level off. This is in a full agreement with our predictions.

Finally, we want to discuss the reappearance of the parallel orientation at high frequencies. This behavior cannot arise from the flow–fluctuation interaction discussed above. Some authors argue that the assumption of slow flow in Eq. (1) is responsible for the failure of the theory to predict the parallel orientation at high frequencies [6,17]. We, however, support a different opinion. Balsara *et al.* noticed [18] that in equilibrium the walls of shear cell induce the parallel alignment through the whole 0.5-mm sample, while Laurer *et al.* observed [19] that under shear there is always a near-surface layer of the parallel lamellae independent of the bulk orientation. Therefore, we propose that the high-frequency parallel orientation of the lamellae is caused by interactions of the shear-cell walls with the melt. Fredrickson has shown [20] that in equilibrium this interaction will lead to the parallel alignment. Recently we discussed this effect for a steady shear [16] and showed that in the presence of this interaction the stable orientation is given by the minimum of $\Phi'=\Phi-2\eta a\delta_{n_y,1}$, where η is proportional to the Flory-Huggins strength of interaction between the walls and melt. Minimization of the modified potential Φ' gives for the $\perp\to\parallel$ transition temperature

$$\tau_1=-\bar{\sigma}(n_y)-\frac{[\bar{\sigma}(n_y)-\bar{\sigma}(n_z)]^4}{8\eta^2\lambda(1-\beta)}, \qquad (10)$$

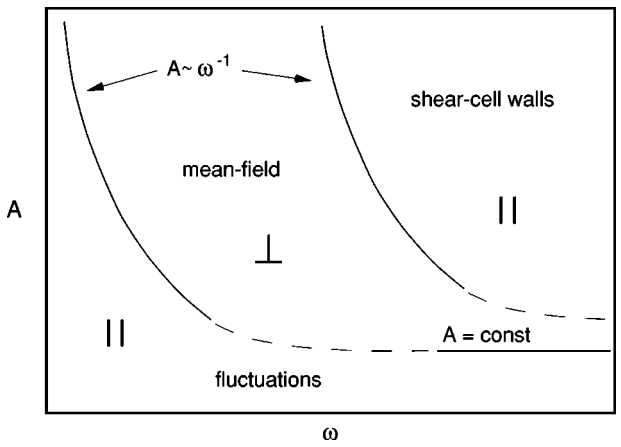

FIG. 1. Orientational diagram. In each region the dominating effect is stated.

with $\bar{\sigma}(\mathbf{n})$ from Eq. (9). If we fix temperature, the line of the second transition will be again given by $A\sim\omega^{-1}$, $\varpi\ll 1$ and $A=\text{const}$, $\varpi\gg 1$ with coefficients depending on η. This is in a qualitative agreement with experiments [5]. A detailed comparison is impossible because of the lack of experimental data. Our assumption can be verified by performing measurement in various material shear cells.

We summarize our results in an orientational diagram (Fig. 1). The low-frequency regime resembles the steady shear behavior. The corresponding expressions for $\bar{\sigma}$ [Eqs. (8), (9)] are similar to those for the steady shear [8,9] with an effective shear rate $\dot{\gamma}=A\omega$. The high-frequency part of the diagram fundamentally differs from the steady shear. When the frequency exceeds some critical value, which is of order of the relaxation time for the critical fluctuations, the further increase of frequency does not change the behavior of the system. Therefore, in the high-frequency limit $\bar{\sigma}(\mathbf{n})$ together with the spinodal temperature $\tau_s(\mathbf{n})$ appears to be independent of ω.

The first transition from the parallel to perpendicular orientation corresponds to a change in character of the flow–fluctuation interaction. This change is associated with a strong suppression of fluctuation and a crossover from the fluctuation to mean-field type of behavior. Our estimate for the critical effective shear rate [Eq. (9)] shows that [11–13,16] $\dot{\gamma}_c\sim N^{-3}$. When $N\to\infty$, the fluctuation region disappears [10] and $\dot{\gamma}_c\to 0$.

To explain the second transition we make use of recent experiments [18,19] and argue that the high-frequency parallel orientation is stabilized by the preferable interaction of the shear-cell walls with one of the components of the melt. Validity of this hypothesis requires further experimental studies.

At the end we want to emphasize that the presented picture is applicable for any system (polymers, surfactants, microemulsions) described by the Brazovskii Hamiltonian [Eq. (2)].

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