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# Shear-Induced Ordering in Thin Films of Diblock Copolymer Melts

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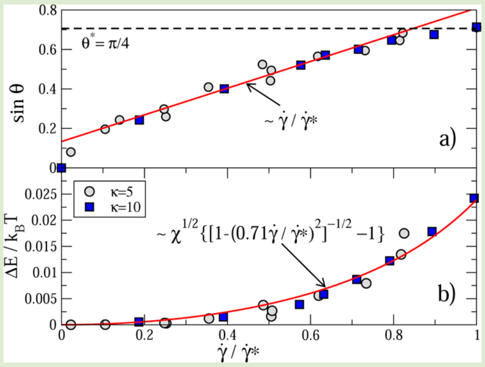
**ABSTRACT:** By means of molecular dynamics simulations we investigate the response of thin, symmetric diblock copolymer melts under shear in the limit of strong segregation with nonselective substrates, where vertically oriented lamellae form. Under small shear perpendicular to the lamellar orientation, we observe an inclination of the lamellar layers. At a critical shear rate, the lamellar layers become distorted and, for very large shear, recombine with a new orientation along the direction of shear. Our simulations are accompanied by a novel, easily understandable theoretical approach to predict the critical shear rate, at which the interfaces become distorted and shear-induced reorientation sets in. This allows one to calculate quantities such as the inclination angle or the pair interaction energy as a function of applied shear rate. Our results are relevant for many technical applications, where defect-free, long-range ordered structures are needed.



Understanding and controlling the microdomain orientation of self-assembled structures in block copolymer melts is essential for a variety of applications, such as photonics and flexible electronics like organic photovoltaics or nanolithography.[1−4] While the domain size of such self-assembled structures typically ranges from 10 to 100 nm,[5] technical applications need defect-free, long-range ordered structures.[6] This can be achieved by external fields such as shear-induced flow fields.[7−9] Thus, it is important to understand thoroughly the processes involved during shear-driven ordering on a microscopic level.

In this Letter, we focus on sheared thin films of symmetric diblock copolymer melts, which are confined by two nonselective, atomically smooth walls. When the incompatibility between the two blocks of a copolymer is large enough, the melt undergoes a phase separation, and lamellar structures emerge.[6] Two basic modes of shear may be considered: along the lamellar interfaces and perpendicular to them. Obviously, the latter case is the one of interest, as shear perpendicular to the interfaces leads to a reorientation of lamellae along the direction of shear[10] and eventually to the desired long-range ordering.[6] By means of molecular dynamics (MD) simulations of a standard polymer (Kremer−Grest) model,[11] we study how this transition takes place. We propose a theoretical approach to calculate the critical shear rate, where lamellar layers become distorted before they can start to reorient. Our predictions for the inclination angle and the change of surface interaction energy are in good agreement with the numerical data.

For shear perpendicular to the lamellar interfaces, we find stationary inclined interfaces below a critical shear rate. Above the critical rate, the lamellar interfaces dissolve and, at very large shear rates, reorient along the shear direction, such that the shear now is directed along the interfaces. In this regime, both modes of shear (along and perpendicular to the interfaces) reveal the same response. The focus of the present study is on the effect of perpendicular shear below the critical shear rate.

Our numerical approach is well established and has been used in many studies to model polymers in equilibrium and in out-of-equilibrium situations.[12] In this coarse-grained model, monomers are represented by spheres, where the excluded volume interaction is simulated using a cut and shifted Lennard-Jones (LJ) potential. Upon variation of cutoff range and interaction strength, it is possible to control the character of attraction/repulsion between monomers belonging to the same/different part of the diblocks. The connectivity along a polymer chain is assured via finitely extensible, nonlinear, elastic (FENE) springs.[11] Using MD simulations, we integrate the equations of motion with the Velocity−Verlet algorithm.[13] The time step of our simulations is $\tau = 5 \times 10^{-3}$. Temperature is kept constant at $k_BT = 1$ ($k_B$ the Boltzmann constant) by a dissipative-particle-dynamics (DPD) thermostat.[13] The latter allows for tuning the monomeric friction constant. Throughout this Letter, we use $\kappa = 5$ (LJ units) as the damping constant of the DPD thermostat, unless mentioned otherwise.

The two confining walls each consist of Lennard-Jones spheres arranged on a square lattice, where the lattice constant is chosen such that monomers cannot pass through them. Parallel to the walls, in $x$- and $y$-directions, we impose periodic boundary conditions. Further details about the numerical model can be found in ref 14.

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Stationary shear is performed by moving the upper wall with constant velocity $v_a$ and the lower one with velocity $-v_a$ in the $x$-direction. Since we keep the distance between the walls fixed at $D = 25\sigma$ (with $\sigma$ being the monomer diameter), we apply a constant shear rate $\dot{\gamma}_a = 2v_a/D$.

The extensions of the walls in $x$- (shear-) and $y$-directions are $L_x = L_y = 50\sigma$. Each diblock contains $N = 24$ repeating units.

Figure 1 displays snapshots from our MD simulations at different shear rates. The critical shear rate, at which the lamellar interfaces become distorted, turns out to be $\dot{\gamma}_a^* \approx 0.006$. Below this value, the lamellar interfaces can relax fast enough and remain intact. When the shear rate exceeds the critical value, the interfaces become distorted and, for very large shear rates, align along the direction of shear. The critical shear rate should be determined by the relaxation rate of the lamellar interface fluctuations; i.e., it should be the inverse of a time scale that is characteristic for the interface fluctuations.

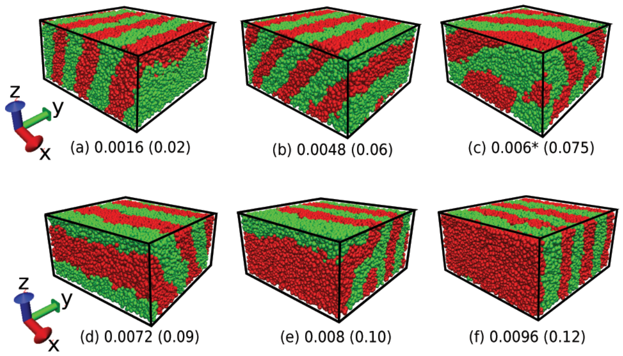

**Figure 1.** Steady-state configurations at different shear rates for shear perpendicular to the lamellar interfaces (along $x$-axis). Values indicated within the brackets are the corresponding applied wall velocities. (a) and (b) represent structures below the critical shear rate; (c) is at the critical shear rate; and (d)−(f) are above the critical value. Wall atoms are transparent, and the two blocks of the copolymers are red and green spheres, respectively.

The interaction between wall atoms and monomers is independent of monomer type (nonselective substrates) and only slightly attractive. Thus, we observe a strong slip motion, where the monomer layers closest to the walls adopt velocities below the applied one. For shear along the lamellar interfaces, the velocity of the outermost monomer layer, $v$, increases proportional to the applied shear velocity (see Figure 2a). When shear is applied perpendicular to the interfaces, the melt appears to reveal only a very little response below the critical velocity (or shear rate) (see region (i) in Figure 2a). Above the critical shear rate, there is a region (ii), where the lamellar interfaces are distorted. Here, the monomers move considerably. At larger shear velocities, the lamellae are oriented along the shear direction. Therefore, the data for both shear modes superimpose in region (iii). In the following, we consider $v$ as the true (effective) velocity and $\dot{\gamma} \equiv 2v/D$ as the shear rate.

To study the onset of shear-induced long-range ordering, we focus on regime (i) with shear rates below the critical value. Here, we can use a simple geometrical argument to calculate the dependence of lamellar inclination on shear rate. The inclination follows from a balance between the interfacial tension force along the shear direction acting on the outermost polymer layer (the layer closest to the sheared surface) and the force needed to maintain constant velocity of the substrates, i.e., the friction force.

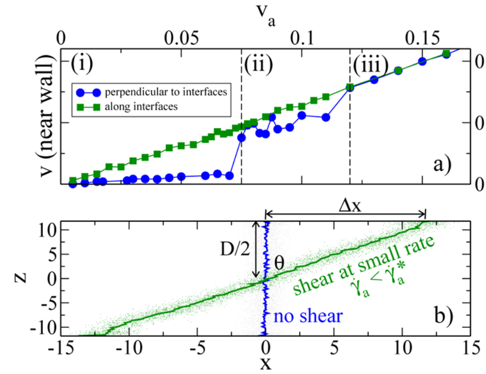

**Figure 2.** (a) Averaged velocity of the outermost layers as a function of applied wall velocity. (b) Shape of the lamellar interface line without shear and at small, constant shear rate. Dots are the interface positions at different times, and the solid line is the time average. Upon shearing, the interface line is inclined by an angle $\theta$, and the interface position near the wall is displaced by an amount $\Delta x$.

The displacement of the interface position (Figure 2b), $\Delta x$, can be expressed by the strain

$$\gamma = \frac{2\Delta x}{D} = \tan\theta \tag{1}$$

where $\theta$ denotes the inclination angle. Note that $\Delta x$ also can be interpreted as the displacement of a monomer within the outermost layer,[15] such that the time derivative of $\gamma$ becomes the shear rate.[16]

Assuming a straight interface line, the relative change of surface area can be expressed as

$$\frac{\Delta S}{S_0} = \frac{S_{\dot{\gamma}} - S_0}{S_0} = \frac{1}{\cos\theta} - 1 \tag{2}$$

Here, $S_{\dot{\gamma}}$ and $S_0$, respectively, are the surface area with and without shear (see Figure 2b). To first order in $\Delta S$, this yields for the change in surface free energy

$$\Delta F_S \sim \left(\frac{1}{\cos\theta} - 1\right)\chi^{1/2} k_B T \tag{3}$$

On the right hand side of eq 3 we introduced the Flory−Huggins parameter, $\chi$, to describe the coupling between surface area and surface tension. We anticipate that there is an additional contribution to the free energy, resulting from the deformation of chains during lamellae deformation. However, for sufficiently large shear rates, this contribution may be neglected when compared to the change in surface tension.[14]

The force in shear direction, $f_S$, resulting from lamellar inclination is related to the change of surface free energy via $f_S = dF_S/dx = (dF_S/d\theta)(d\theta/dx)$. Thus, with eqs 1 and 3 we obtain

$$f_S \sim \frac{2\chi^{1/2} k_B T}{D} \sin\theta \tag{4}$$

This force has to be balanced by the friction force. The latter reads $f_R = \Gamma\dot{\gamma}D/2$, with $\Gamma$ being a model-dependent friction constant. Finally, we arrive at

$$\sin\theta = c\frac{\dot{\gamma}}{\dot{\gamma}^*} \tag{5}$$

with $c$ being a numerical constant and the critical shear rate

$$\dot{\gamma}^* = \frac{4k_B T\chi^{1/2}}{\Gamma D^2} \tag{6}$$

Equation 5 appears to be in very good agreement with our simulation data, as can be seen from Figure 3a. We show data for two monomeric friction constants, $\kappa = 5$ (as used in Figures 1 and 2) and $\kappa = 10$, introduced via the DPD thermostat.[13] To determine the critical shear rate, we used $\Gamma$ as a fitting parameter. The fact that we obtain $\Gamma(\kappa = 10)/\Gamma(\kappa = 5) = 1.21$ (instead of 2) indicates that the effective friction constant is not a linear function of $\kappa$. Furthermore, we notice an offset of the data, which can be explained by the deformation of chains, when an addition term proportional to $(\Delta S)^2$ is included in eq 3.[14]

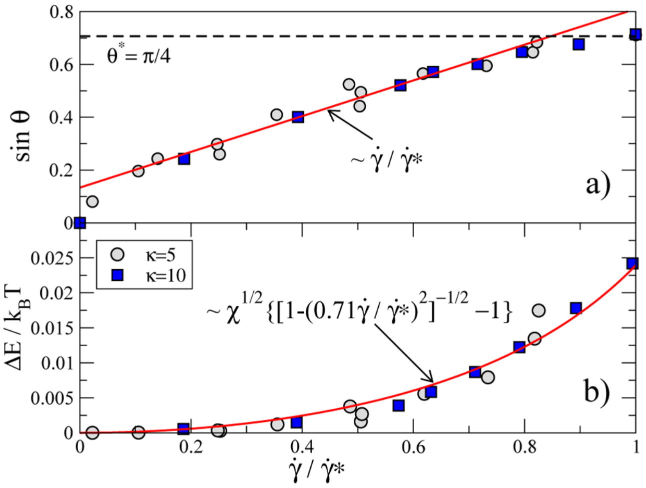

**Figure 3.** (a) sin $\theta$ as a function of rescaled shear rate for two values of the monomeric friction constant, $\kappa$. Horizontal dashed line indicates the value corresponding to $\theta^* = \pi/4$. The value of sin $\theta$ increases linearly with shear rate (see eq 5). (b) Change of pair interaction energy within the lamellar interface as a function of reduced shear rate. We find good agreement with our theoretical approach [see eq 8].

The critical inclination angle, at which the lamellar structure dissolves, is given by $\theta^* = \pi/4$. This value has been reported in an earlier study.[17] Here, we provide a simple argument to reason it: By definition, the critical shear rate and the concomitant time scale, identified before as the typical time scale of interface fluctuations, $\tau$, are related via $\dot{\gamma}^*\tau = 1$. On the other hand, for the given geometry (Figure 2b), one may connect the critical shear rate to the critical strain, $\gamma^*$, via $\dot{\gamma}^* = \gamma^*/\tau$, such that the critical strain is unity. With eq 1, this yields a critical inclination angle of $\theta^* = \pi/4$. Above this value, the forces along the interface line overcome the perpendicular forces, and the interface dissolves.

With the critical inclination angle known, it is possible to determine the numerical constant in eq 5 as $c = \sin\theta^*$, such that

$$\sin\theta \approx 0.71\frac{\dot{\gamma}}{\dot{\gamma}^*} \tag{7}$$

The straight line in Figure 3a corresponds to a slope of 0.68, which underestimates the theoretical prediction but bears a statistical error.

Using eqs 3 and 7, we obtain the change of pair interaction energy, $\Delta E$, due to inclination

$$\frac{\Delta E}{k_B T} \sim \chi^{1/2}\left(\frac{1}{\sqrt{1 - (0.71\dot{\gamma}/\dot{\gamma}^*)^2}} - 1\right) \tag{8}$$

As Figure 3b shows, we find a nice qualitative agreement with our simulation data. There is no offset in the data because the pair interaction energy is independent of chain deformation.

It should be emphasized that we derived our expression for the critical shear rate [eq 6] without the usage of any polymer-specific properties, e.g., the degree of polymerization. Material properties like surface tension, melt viscosity, and monomeric friction coefficient enter only via the Flory−Huggins parameter and the effective friction constant.[18] Therefore, eq 6 should hold for nonpolymeric systems as well, provided that the critical shear rate solely depends on the characteristic time scale for interface fluctuations. Thus, the presented model may be applied to somewhat different problems, for instance, oil/water interfaces.

In conclusion, we present a theoretical model to determine the critical shear rate, at which lamellar layers of diblock copolymer melts in thin films under perpendicular shear become distorted and start to orient along the shear direction. Following eq 6, we find that this critical shear rate should increase linearly with temperature and the square root of the Flory−Huggins parameter. Simultaneously, $\dot{\gamma}^*$ is predicted to be inversely proportional to the squared distance between the surfaces.[19] Further studies are needed to test these predictions. So far, our data from molecular dynamics simulations reveal good agreement for the inclination angle of the lamellar interfaces and the pair interaction energy. Since our approach does not contain any polymer-specific properties, it should be applicable to similar, nonpolymeric systems as well.

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### Notes

The authors declare no competing financial interest.

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(15) Correspondingly, $\theta(t)$ can be defined via the monomer displacement at time $t$.

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(18) The specific interaction between wall atoms and monomers determines the hydrodynamic boundary conditions (slip length) but does not enter into the problem otherwise. The resulting slip is accounted for by introducing an effective shear rate.

(19) Note that the effective friction constant can depend on surface separation and may alter the $D^{-2}$ dependence.