On the orientation of lamellar block copolymer phases under shear

Blair Fraser, Colin Denniston, and Martin H. Müser
Dept. of Applied Mathematics, University of Western Ontario, London, Canada, N6A 5B7

Abstract

Self-assembled lamellar structures composed of block copolymers are simulated by molecular dynamics. The response of a bulk system to external shear is investigated, in particular the average energy, the entropy production, and the stability of the lamellae's orientation. We distinguish two orientations, a parallel orientation in which the normal to the lamellae sheets lies in the direction of the shear gradient, and a perpendicular orientation in which the normal lies perpendicular to the shear gradient and shear direction. The perpendicular phase is stable throughout all shear rates. The parallel phase has higher internal energy and larger entropy production than the perpendicular phase and moreover becomes unstable at relatively small shear rates. The perpendicular orientation should therefore be more stable at any finite shear rate. Surface effects are probably responsible for the stability of the parallel phase observed experimentally at small shear rates.

1   Introduction

In recent years, understanding block copolymer systems has become a topic of great interest to materials scientists. Traditional applications of diblock copolymers take advantage of the exotic mechanical properties these materials are known to display. More recent applications of block copolymers typically come in the field of nano-fabrication where they are used to self-assemble detail on a nanoscale. These applications rely on the long-range order of diblock-copolymer melts [1, 2, 3, 4]. However, typical samples, equilibrated under zero-shear, often exhibit numerous grains of differing phase or orientation.

Under shear, grains are forced to align in directions compatible with the shear flow, thereby increasing the long-range order. Shear can also be used to preserve the microstructure of the sample at higher temperatures [5], where a sample may be easier to manipulate. It is for these reasons that in the manufacturing process, block-copolymers may be subjected to shear flow. It is therefore important to understand the effect that this may have on the internal microstructure of the copolymer melt.

Today the equilibrium properties of block copolymers have been well studied. However, the complex behavior these materials display in out of equilibrium conditions [6, 7, 8, 9, 10] is poorly understood. For example, in diblock copolymers in the lamellar phase, experiments have shown it is possible to use shear rate to select between the two possible lamellar orientations aligned with the shear flow [8, 6]. Thus, shear can be used as a switch to flip a lamellar system from one orientation to another and back. It is the origin of this effect that we invesgate here.

2 Methods

Our methodology is described in detail in Ref. [11] and we just summarize it here. We study 524 linear block copolymers consisting of one block comprised of 10 A monomers and one of 10 B monomers, for a total of 10480 monomers. A Lennard Jones potential with a short-range cutoff radius of $r_c = 2^{1/6}\sigma$ is used for the interaction between any pair of monomers, where σ is the Lennard Jones radius, which is set to unity. Adjacent monomers in a chain are connected via the so-called finitely extensible nonlinear elastic potential, which ensures connectivity and prevents unphysical chain crossings [12, 13]. Like monomers experience an additional attractive potential, characterized by a parameter γ, chosen sufficiently strong so as to induce a phase separation into lamellar phases [14, 15]. At a temperature of $T = 1.0$, a value of $\gamma = 1.3$ is on the lammelar ordered side of the spinodal, but still weak enough to allow molecular rearrangements in a reasonable amount of computation time [11].

Most of the simulations were run with a fixed simulation cell geometry, which was chosen such that the pressure is isotropic at zero shear rate, high enough for the lamellar phase to be stable, and low enough for the polymers to diffuse within the lamellae during the time scale of the simulation. Periodic boundary conditions are applied in two directions of a cubic box of linear size $L = 18.2\sigma$. In the remaining direction, shear is enforced with the help of Lees-Edwards boundary conditions [16]. The box size was chosen such that the simulation cell was able to accomodate (twice) the natural period ($\sim 9.1\sigma$) of the lamellar spacing along the parallel and the perpendicula direction. As shear is to be applied to the simulation, the choice of thermostat is an important one. The dissipative particle dynamics (DPD) thermostat [17, 15, 18, 19], which thermostats on the centre of mass of interacting particles, allows the temperature to be maintained without breaking Galilean invariance.

Both constant pressure and constant volume simulations were performed, both yielding similar conclusions. The shear invokes anistropic stresses in a constrained box geometry. In order to simulate constant stress conditions, two out of the three (diagonal) components of the stress tensor can be fixed using a barostat. The simulation cell was allowed to fluctuate along the parallel and perpendicular direction, i.e., the two (potentially) 'solid' directions of the system, as described in our previous study [11]. While similar conclusions can be drawn from both constant volume and constant pressure simulations, whenever the lamellae reoriented under shear, in a constant pressure simulations the simulation cell typically shrinks considerably along one dimension to the extent that we were left with one lamella. The reason for this shrinking is that the system loses one of its solid directions during reorientation, which lead to a collapse of the simulation cell as discussed previously [11].

3 Results

This study is mainly concerned with the question whether there is a preferred orientation of a *bulk* lamellar phase of simple block copolymers under shear. The shear geometry is shown in Fig. 1(a). Two linearly independent orientations of the lamellae are compatible with the shear, the parallel configuration depicted in Fig. 1(b), and the perpendicular orientation shown in Fig. 1(p). Configurations in which the lamellae's director has a component parallel to shear

direction disintegrate at any finite shear rate. When the shear rate goes to zero, the parallel and perpendicular phase become degenerate because they can be mapped onto one another by a 90° rotation. This symmetry operation is broken under finite shear.

Unfortunaltely, there is no straightforward way to determine thermodynamic stability under external driving. The first reason is that it is difficult to evaluate free energies, even in the absence of shear, i.e., concepts such as thermodynamic integration have to be employed. The second reason is that there is no general quantitative critereon such as free-energy minimization for out-of-equilibrium situations. However, it is easy to evaluate metastability of various phases, simply by starting off in one phase and by investigating whether the initial phase remains stable for the course of the experiment or the simulation.

In our previous study [11], we assessed metastability. We started our simulations in either the parallel phase or the perpendicular phase and gradually increased the shear rate starting from a quiescent state. The perpendicular phase persisted for all shear rates $\dot{\epsilon}$ investigated, i.e., up to $\dot{\epsilon} = 0.04$. In contrast, the parallel phase becomes unstable at a shear rate slightly larger than 0.01. In the small range, $0.0125 \leq \dot{\epsilon} \leq 0.0175$, we found that shear is not able to fully reorient the lamellae. The system becomes stuck in a tilted phase as a consequence of the constraints induced by the periodic boundary conditions - and the slow, collective dynamics of the polymers. The time evolution of a partial reorientation process is shown as a figure series in Fig. 1. Simulations of shear rates $\dot{\epsilon} > 0.02$ result in similar figure series, except that the final orientation ends up in the fully perpendicular orientation.

The metastability of the two phases can be understood within a simple model involving the torque experienced by polymer chains. We calculate the tensor of gyration for each polymer in the simulation box by locating its center of mass (x_c, y_c, z_c) and finding $\mathbf{G}_{\alpha\beta} = \langle (r_{i\alpha} - r_{i\alpha c})(r_{i\beta} - r_{i\beta c}) \rangle$, where $r_{i\alpha)} \in \{x_i, y_i, z_i\}$ are the coordinates of each monomer in the polymer chain and the index c denotes the polymer's instantaneous center of mass. The eigenvectors of $\mathbf{G}$ give the major and minor axes of the ellipsoid that, on average, describe the polymers. In equilibrium, $\mathbf{G}$ is uniaxial 1 and can be described by a unit vecotr along its principal axes $\mathbf{n}$. As one might expect, $\mathbf{n}$ is perpendicular to the lammelae in equilbrium. In a system started in the parallel state, there is a viscous torque due the the shear than causes the angle θ between the normal to the lammelae and $\mathbf{n}$ gradually to increase (the polymers "lean" into the shear). The resulting tilt follows the equation [11]

$$\dot{\theta} = \frac{\dot{\epsilon}}{2}(-1 + \lambda \cos 2\theta) - s \sin 2\theta, \tag{1}$$

where λ is a dimensionless ratio of viscosities related to the relative magnitude of the rotational and aligning flow effects, and s is a dimensionless ratio of elastic and viscous and effects. In order for the parallel state to remain metastable, it must satisfy this equation with $\dot{\theta} = 0$. As one might expect, such solutions have $\theta = 0$ at $\dot{\epsilon} = 0$ and θ increases as the shear rate is increased. In addition, it must be linearly stable to small perturbations (i.e. if θ_0 satisfies the equation with $\dot{\theta} = 0$, then a small perurbation must shrink rather than grow in time). For $\theta > 45°$, no linearly stable solution exists and the system must flip into the perpendicular state. Thus at high shear rates only the perpendicular state is stable.

This is in agreement with experiments which demonstrate that as the shear rate is increased the system undergoes a transition from the parallel to perpendicular state [6]. However, these

experiments have suggested that this transition is reversible in the sense that as the shear rate is decreased, the system undergoes a transition back from the perpendicular to the parallel phase. This cannot be explained in terms of metastability. Both our analysis and simulations suggest that both states are metastable at low shear rates. In the simulations, no transition from the parallel phase to any other state is ever observed. Indeed our model would suggest that the viscous torque on a molcule, measured relative to it's principal axis, in the parallel state is zero. As the torque can usually be considered to be a derivative of the free energy with respect to angular variations, this would strongly suggest that the parallel state has the lower free energy and should hence be favored.

In order to assess whether there is some other reason to favor the perpendicular state at low shear rates we have investigated several other measures. In particular, we analyzed internal (configurational) energy $\langle V_{\text{pot}} \rangle$, entropy production $\dot{S}$ in our system, systems annealed from a random configuration under shear, and the influence of variations in the molecular potentials.

In equilibrium, parallel and perpendicular states are degenerate, and have equivalent internal energy and entropy. We will examine the internal energy and entropy separately. Phases with small internal energy are more stable than those with larger internal energy. Fig. 2 shows that the perpendicular phase always has lower $\langle V_{\text{pot}} \rangle$ than the parallel or the partially oriented phase at any given shear rate. The curvature of the $\langle V_{\text{pot}} \rangle$ curve at small $\dot{\epsilon}$ is approximately four times as large in the parallel phase than in the perpendicular phase. This again indicates a strong preference for the perpendicular phase.

While the entropy itself is difficult to measure in a simulation, entropy production is not. The latter term is related to the external work done on the system per unit time, i.e., stress times strain rate times volume, or alternatively, the energy absorbed into the thermostat per time unit. Moreover, systems generally prefer to reduce entropy production in out-of-equilibrium situations [20]. Fig. 3 shows that the entropy production is smaller in the perpendicular than in the parallel phase at any given shear rate. The curvature at small values of $\dot{\epsilon}$ differ approximately by a factor of two. Thus, also from an entropy production standpoint, the perpendicular phase appears to be the more thermodynamically stable phase compared to the parallel phase.

To see if it is possible for a low shear rate to select a state (rather than reorient an existing one), we also ran a set of eight simulations in which the initial configuration was disordered or in which the normal of the lamellar planes were parallel to the shear flow direction. Shearing at a rate of $\dot{\epsilon} = 0.005$ resulted in a distribution of approximately 50% for either phase. It would have required too many simulations to evaluate quantitatively how much the perpendicular phase is preferred under the given initial conditions using this method. However, it clearly does not show a preference for the parallel phase.

We also explored possibilities to alter the interactions within our systems to investigate how 'universal' our findings were. For example, we introduced terms which made the polymers stiffer, and hence more liquid crystal like. In equilibrium, the layered structure is analgous to a smectic A liquid crystal which tends to prefer a 'parallel-type' orientation under similar shear conditions, although the reasons for this are still unclear, as theory would suggest that the perpendicular phase would give the easiest shear direction [21]. It is thought there, that defects give some rigidity to the perpendicular phase and if very small oscillating shear is applied, the perpendicular phase regains its expected fluidity. These alteration made the diffences in $\langle V_{\text{pot}} \rangle$

and $\dot{S}$ even clearer and strongly favoring the perpendicular phase. We also altered the boundary conditions to be partially constant stress and quantitatively similar results were found. We thus believe that our simulations very strongly indicate that bulk effects favour the perpendicular orientation over the parallel orientation at any non-zero shear rate.

4   Conclusions

In this study, we used molecular dynamics simulation of a generic model for diblock copolymers to study how shear affects the stability of lamellar phases. In our simulations of bulk systems, where shear was imposed via boundary conditions rather than through driving walls, we found that for any finite shear rate, entropy production and average energy are smallest if the lamellae's normal is perpendicular to the shear and the shear gradient direction. This finding strongly suggests that this orientation corresponds to the global minimum for the bulk.

This conclusion leaves open the question why the parallel orientation is often preferred experimentally. Unless there is a fortuitous symmetry in surface energy with the confining walls of an experimental apparatus, one of the two monomer species will be more likely to adhere to the walls than the other one. This interaction will then break the degeneracy between the two orientations, which would otherwise be present in the absence of shear. Thus the parallel orientation at small shear rates may be the consequence of surface effects as it has been speculated by some experimental studies [9, 22].

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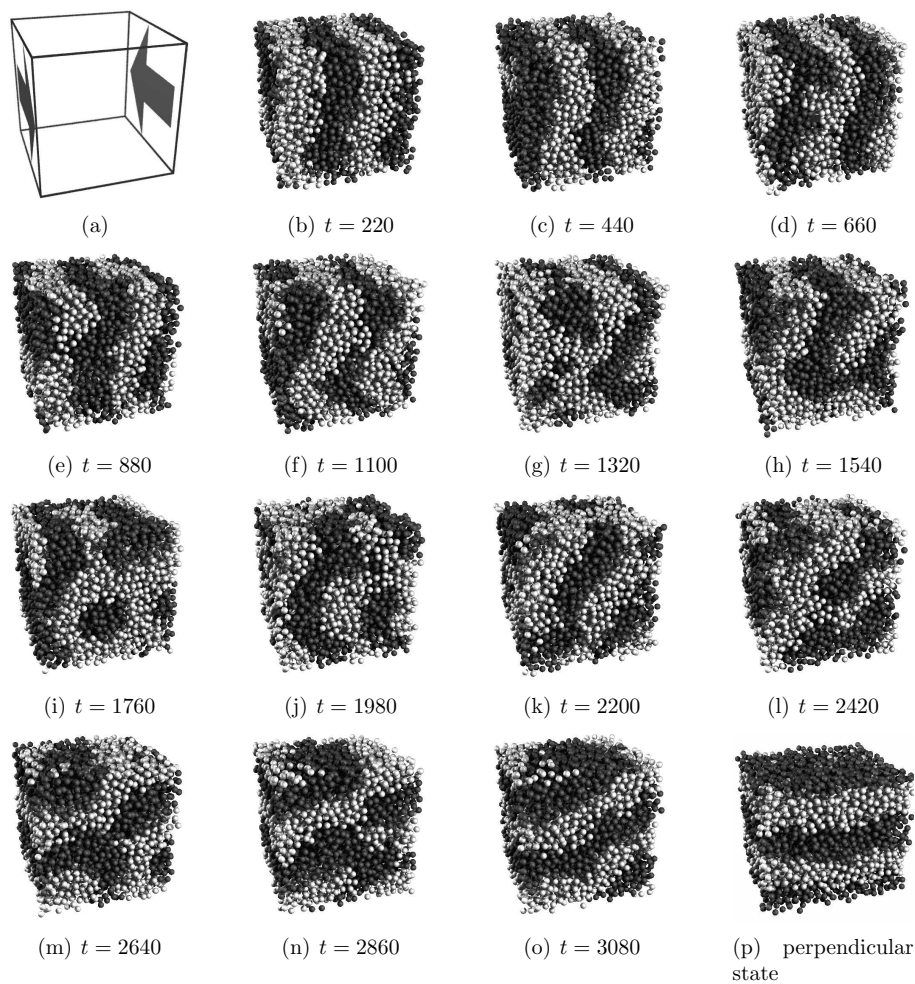
Figure 1: An initially parallel orientation sheared at a rate of 0.015. The system was equilibrated at times $t \leq 0$ and shear was switched on at $t = 0$. Part (a) shows the imposed shear and (b)-(o) show snapshots of the simulations at different instances of time. The reorientation of the lamellae from parallel to perpendicular is only partial. If the system is sheared at a higher rate (e.g. 0.02 in Lennard Jones units) the system will fully reorient to the perpendicular state shown in (p).
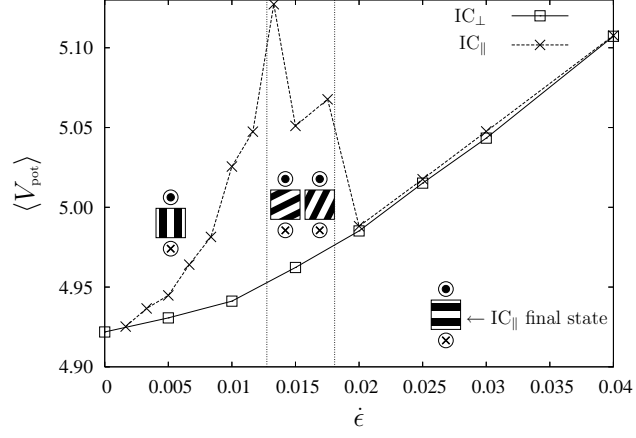
Figure 2: Potential Energy for various shear rates. Points marked by a box (□) denote initial conditions in the perpendicular phase, and those marked by a cross (×) denote initial conditions in the parallel phase. Small inset figures indicate the most common final orientation for an initial condition in the parallel orientation. In these inset figures, the shear direction is normal to the plane of the page, and the shear gradient is vertical on the page.
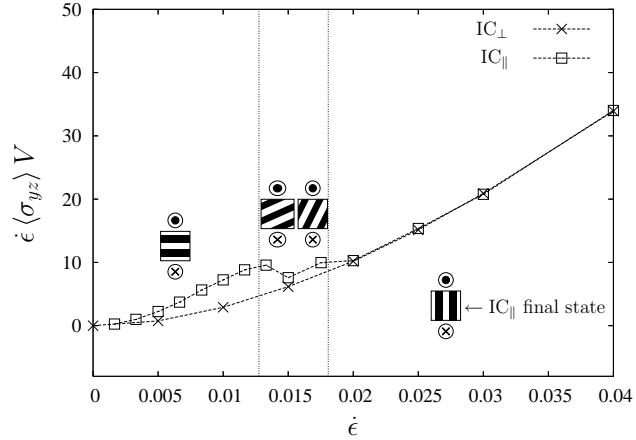

Figure 3: Dissipated Energy for various shear rates. Points marked by a box (□) denote initial conditions in the perpendicular phase, and those marked by a cross (×) denote initial conditions in the parallel phase.