STRESS RELAXATION IN DIBLOCK COPOLYMERS

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Abstract
We study stress relaxation in a strongly segregated lamellar mesophase of diblock copolymers. We consider the extreme limit in which chains are highly stretched and with their junction points confined to narrow interfaces. A lamella can be divided into “stress blobs” at some distance $z$ from the interface, with well defined local modulus $G(z, \omega)$ at frequency $\omega$. For sliding (compressional) stress the total modulus is transmitted in series (parallel) across the layer. We evaluate the local $G(z,t)$ which shows, for a given height, a very broad spectrum of relaxation times.

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Block copolymers made with incompatible blocks form a rich variety of domain structures. At equilibrium, a dense collection of monodisperse A-B diblock copolymer chains assemble themselves in minimum free energy configurations. Symmetric diblock copolymers with highly repulsive interactions between A-B segments microphase separate into a lamellar order with A-B junction points highly confined into interfaces to decrease the number of contacts between the two different blocks. The width of these lamellae is determined by a balance between the reduction of unfavorable contacts between A and B blocks and the decrease of chain entropy due to the stretching of the block polymer.

The rheological behavior of diblock copolymers in a lamellar mesophase is of great importance due to the numerous practical applications of these systems. The understanding of how polymer domains flow and of how rheological properties differ from those of the much more familiar homogeneous melt presents an important and challenging theoretical problem. Exploratory rheological studies of lamellar domains have revealed strong departures from the behavior of simple melts. Theories have begun to grapple with these observations. The motion of end-confined chains appears to differ strongly from that of simpler polymers. Thus, the dynamic response to deformation in block copolymer domains shows distinctive retardation and broadening; correspondingly, the disentanglement dynamics of end-confined chains are expected to be much different from that of unconfined polymer melts and solutions.

Two cases for the linear response to a small step strain should be considered: a compression of the layers and a shear tending to slide the layers past one another. The block chains have their translational motion highly restricted as one chain end is strongly confined to the interface, so usual reptation, which is believed to be the dominant relaxation mechanism of homogeneous system consisting of long flexible polymers chains such as melts (and also, for example, the disordered phase of diblock copolymers) is highly suppressed. The disentanglement motion of the block chains with one end anchored at the interface resembles that of star polymers, for which relaxation proceeds by arm retraction along the tube (contour length fluctuations). In addition, the block chains are highly stretched along the direction perpendicular to the lamella, while still retaining their unperturbed (Gaussian) size in the directions parallel to the interface. In fact, relaxation proceeds at different rate in different places (depending how far the regions of interest are from the interface) and, for example, one can define a local stress modulus $G(z, t)$ with $z$ the distance from the interface, with regions at different $z$ involving quite different time scales. In this contribution we investigate these distinctive and novel features of heterogeneous materials.

II. THE EQUILIBRIUM LAMELLA

Here we restate several relevant properties of copolymer chains as given, for example, in Refs. and. For simplicity, we consider that all interfaces are flat, parallel to each other and separated by a distance $2h$. We suppose that each surface contains $\sigma$ chains per unit of area. In the incompressible melt state each chain fills a volume $V$ proportional to the chain molecular weight (and to its chemical length). Hence, the thickness of the layer $h$ is just given by $h = V/\sigma$. Polymers in the melt satisfy Gaussian statistics. Thus, the end-to-end distance, which is the characteristic dimension of an unperturbed polymer coil, is simply given by $R^2 = V/b$, with $b$ a microscopic length which only depends on the local structure of the chain and liquid, usually of about a few Angstroms. We only study here the long chain limit of $V >> b^3$.

The block chains ending at the interfaces fill uniformly the regions between planes so each chain must extend over distances of the order of $h$. Stretching the chain a distance $h$ reduces the entropy of the random walk thus requiring work of the order of $(h/R)^2 k_b T$. We are interested in high energy interfaces with $(h/R) >> 1$. If a step strain is applied to the liquid, at very short times it behaves like a rubber with modulus $G_0$. From the elastic energy stored by the liquid one can obtain the typical volume per entanglement $R^2_e$ via $G_0 = k_b T/R^2_e$. This $R_e$ is independent of the molecular weight of the chain; hence long chains ($R >> R_e$) are highly entangled.

Since the copolymers are strongly stretched in the lamellar mesophase, configurational integrals are dominated by the classical extremum of the action (Hamiltonian), which corresponds to the most probable (“classical”) configuration of the block extending from the interface into a microdomain. In this approximation, the free energy functional for the copolymer blocks in a mesophase domain consist of non-interacting Gaussian chains in a self-consistent external potential (pressure field) $p(z)$, where $z$ is the distance perpendicular to the interface. This $p(z)$ is the free energy cost of bringing a segment to the height $z$ from some initial reference position, and it forces the chains to assume a stretched state. We call $v$ the volume displaced by the piece of the chain extending from the free end at $z_0$ to the height $z$. The “classical” configuration of a chain is given by the trajectory $z(v)$ of a fictitious
Newtonian particle of unit mass in an external potential $p(z)$ which starting at some point $z_0$ at "time" $v = 0$ falls to the $z = 0$ surface (interface) in a "time" $V$. The "equal time" property for monodisperse systems gives a parabolic potential $p(z) = p_0(1 - (h^2/z^2))$ with $p_0/k_B T = \pi^2 h^2 b/(8V^2)$ and the chain "equation of motion"

$$z = z_0 \cos \left( \frac{\pi v}{2V} \right).$$  

(1)

It remains to specify the distribution of end positions $z_0$. This distribution is found by imposing the constitutive properties of the melt or solution under consideration. For example, for a marginal solvent the local volume fraction is proportional to the pressure $p$. Instead, for a melt the local volume fraction is unity everywhere and we obtain

$$\epsilon(z_0) = \frac{\sigma z_0}{h^2 [1 - (z_0^2/h^2)]^{1/2}},$$

(2)

where $\epsilon(z_0)$ is the distribution of free ends per unit area per unit height. Chains from opposite interfaces can penetrate each other as long as work done against the potential $p(z)$ is of the order of $k_B T$. Although the energy $p_0 V$ of these chains is typically much greater than $k_B T$ there is a small region near the midplane where $p << p_0$. In a region of size $\xi = R(R/h)^{-1/3}$ near this midplane chain segments of size $\xi$ have energy of order $k_B T$ or less. In this "interpenetration zone" the effects of stretching are unimportant and the chains from the two opposite interfaces interpenetrate freely. In the large $V$ limit of interest, we have $h >> R >> \xi >> R_e$, so segments that live in the interpenetration zone are still highly entangled. Figure 1 illustrates the relevant lengths of the equilibrium lamellar phase of strongly segregated diblock copolymers.

FIG. 1. Relevant lengths in a lamella.
After a step-strain is applied to the liquid, the initial shear distorts the entangled copolymer chains. Since the number of entanglements per unit of volume is a local property of the melt, the initial value of the associated modulus $G_0$ is the same as that of a homopolymer melt. Over time the chains disentangle and the associated distortion disappears. For the relaxation of sliding stress, the relevant entanglements are those of the interpenetration region. The stress is initially held by the entanglements in the interpenetration zone as chains from one interface exert force on chains on the other. Since there is only weak interpenetration, one would expect that the two opposite sides disengage relatively fast. On the other hand, over scales larger than $R_e$ the stress redistributes more or less uniformly propagating down to the interfaces, so not only the interpenetration region is of relevance in the relaxation mechanism of the sliding stress. Compressional stress directly involves the whole chain and not only interpenetration segments. These entanglements are typically between adjacent chains of the same layer, so disentanglement of opposing layers is not sufficient to relax the stress. Thus, compressional relaxation is expected to proceed slower than sliding stress relaxation.

At the most local level, stress is transmitted along the chains, but in a larger scale, within a radius several times $R_e$, chains “collide” with many other chains redistributing the stress more or less uniformly among adjacent chains. At this distance the stress can be treated as a smoothly varying quantity. We then divide the liquid into imaginary cubes (“stress blobs”) each with a well defined dynamic modulus $G(z, \omega)$ at a height $z$ and frequency $\omega$. To evaluate the local modulus $G(z, \omega)$ we imagine subjecting the single stress blob to a step-strain experiment illustrated in Figure 2. The stress relaxes as the initial entanglements disappear. Notice that while the stress is defined locally, the disentanglement motion is not. To release an entanglement between two chains, it is required that the end of either chain pass through the entanglement point. Of course, the ends are typically many stress blobs away. Knowing the chains trailing volumes $v$ from the height $z$ to their free ends provides one of the necessary ingredients to predict how quickly a given stress blob relaxes.

FIG. 2. A blob of size of a few times $R_e$ is subject to a stress-strain experiment. Although the stress is defined locally, the free ends of the entangled chains could be far away.

As ends of the block polymers are attached to the interface, reptation of the chains is highly restricted, and relaxation of stress points is expected to proceed by retraction of the tube in analogy with star polymers. The time distribution
for the retraction of segments of volume \( v \) provides a second important ingredient to evaluate the local modulus \( G(z, t) \). Given the relaxation behavior of these stress blobs, one can readily find how the overall stress relaxes. Layers must be treated as a composite material of many sublayers, each with a dynamic modulus \( G(z, \omega) \). For the sliding shear, the stress is transmitted in series across the layer. During the sliding stress relaxation, the stresses are constant for all \( z \) while the strain is the average of the strains over all \( z \). The weakest element dominates (blobs closer to the height \( h \)). In the compressional stress, the system is qualitatively like a stack of rubber sheets which are clamped together and stretched: the stress is transmitted in parallel along each sheet. The strongest moduli dominates and the relaxation time is controlled by the blobs closest to the interface. Clearly the relaxation is strongly anisotropic.

The local modulus \( G(z, t) \) is then given by

\[
G(z, t) = \frac{kT}{R^2} \int_0^V \int_0^{V \phi_z(v_1)\rho_z(v_2)P_{v_1}(t)P_{v_2}(t) \, dz \, dv_2 \, dv_1.}
\]

(3)

The quantity \( \rho_z(v) \) is the (normalized) density of probability that a monomer in the stress blob at a height \( z \) belongs to a chain that, from that height to the free chain end, displaces a volume \( v \). \( P_z(t) \) gives the probability that a trailing segment of volume \( v \) has not yet retraced its length in a time \( t \). Then, the integral in Eq. (3) gives the survival probability at time \( t \) of a stress point at \( z \), assuming that entanglements are two body processes in accord with the double reptation model \( [13] \). In our simplest picture we also assume intra- and inter-blob statistical independence. That is, the release of a stress point in a blob at height \( z \) is independent of similar event at \( z' \), and that releasing a constraint within a stress blob will not trigger the release of many others. We also assume that entanglement points are uniformly distributed (as monomers in the melt are).

**A. Height Dependent Trailing Volume Distribution**

The distribution \( \phi_z(v) \) is obtained within the above sketched “classical approximation” of the self-consistent field method appropriate for weak excluded volume and moderately high surface coverage for strongly stretched chains. The local melt volume fraction \( \phi_z(z_0) \) at a height \( z \) contributed by chains with free ends in the interval \( \Delta z_0 = [z_0, z_0 + dz_0] \) (with \( z \leq z_0 \leq h \)) is obtained as

\[
\phi_z(z_0) dz_0 = \epsilon(z_0) \left| \frac{dz}{dv} \right| dz_0,
\]

(4)

where \( \epsilon(z_0) dz_0 \) given by (2) is the number of fictitious particles per unit area falling to the interface at \( z = 0 \) from the height interval \( \Delta z_0 \) and \( |dz/dv| \) is the particles velocity at \( z \).

For a given height \( z \), when the free end is at \( z_0 \), the volume \( v \) of the chain trailing segment is uniquely determined by the equation of motion, Eq (1), which relates \( z \), \( z_0 \) and \( v \). Then, the density of trailing volume \( v \) at \( z \) is simply obtained from (4) changing variables from \( z_0 \) to \( v \) and keeping \( z \) fixed. That is, we should replace \( z_0 \) by \( z_0(z, v) \) and multiply (4) by the Jacobian \( dz_0 = |dz_0/dv| \, dv \). Then, the density distribution of trailing volume \( v \) at a height \( z \) is given by

\[
\rho_z(v) dv = \frac{\epsilon(z_0(z, v))}{|dz_0/dv|} \left| \frac{dz_0}{dv} \right| dz_0 \, dv.
\]

(5)

After performing the algebra and using equations (1), (2) and (5) we obtain

\[
\rho_z(v) = \frac{(z/h)}{V \cos(\pi v/2V) \left[ \cos^2(\pi v/2V) - (z/h)^2 \right]^{1/2}}, 0 < v < v_{max}(z),
\]

(6)

with \( \rho_z(v) \) vanishing for \( v_{max}(z) < v \leq V \). The function \( \rho_z(v) \) posseses a integrable singularity at \( v_{max}/V = (2/\pi) \arccos(z/h) \) indicating that most chains in the stress blob at height \( z \) have a trailing segments of volume \( v_{max}(z) \).

Clearly, near the middle of the lamella, when \( z \approx h \), the trailing segments are very short. Conversely, near the interface with \( z \approx 0 \), the trailing segments are of the size of the full chain. Nevertheless, and in contrast with the Alexander [13]-de Gennes [14] picture, there is a distribution of trailing volumes which, in turn, gives rise to a distribution of relaxation times (or frequencies) over an extended time region. These results which arise from the “classical mechanical” description of the stretched polymer chain are slightly altered when “quantum” fluctuations are taken into consideration. (The major modification are the disappearance of the singularity in \( \rho_z(v) \) and the existence of the penetration zone of width \( \xi \).)
B. Trailing Volume Survival Probability

The calculation of the probability $P_v(t)$ proceeds similarly to that of Pearson and Helfand [16] in their study of relaxation of star polymers. In the tube model, the primitive chain consists of $\overline{L}/a$ segments with $\overline{L} = V/bR_e$ the length of the primitive tube and $a = R_e$ its step length ($R_e$ is the typical distance between entanglements).

In the long chain limit under consideration there are a large number $\alpha$ of entanglements per chain, that is $\alpha = R^2/R_e^2 \gg 1$. We define a variable $x = \overline{L} - L$ which measures how much the primitive chain has contracted. $P_v(t)$ is the probability that in time $t$ the primitive tube of initial length $\overline{L} + \Delta \overline{L}$, with $\Delta \overline{L}$ the root-mean-square fluctuation of the tube length, has not yet contracted an amount $y = (v/V)\Delta \overline{L}$ by an spontaneous thermal fluctuation. $\Delta \overline{L} = (\overline{L}/(3\alpha)^{1/2}) \approx (t_R D)^{1/2}$ where $D = k_B T/\zeta$, $\zeta$ and $t_R$ are, respectively, the diffusion constant, the chain friction constant, and the Rouse time.

We call $p(x, t; x_0; y)$ the density of probability that the end of the chain is at position $x$ at time $t$, given that initially $(t = 0)$ was at $|x_0| \leq \Delta \overline{L}$ and provided that the length of the primitive tube was never smaller than $\overline{L} - y$. It can be obtained by solving a first-passage problem [16]. This probability density is the same as that of a diffusing particle (the free chain end) in the harmonic potential $U = (3nk_B T/2\overline{L}^2)x^2$ with an absorbing barrier at $y$. Then, the survival probability at time $t$ of a tail of volume $v$ is given by $P_v(t) = \int_0^t dx \: p(x, t; x_0; y)$, since, as long as $x \leq y$, the primitive chain has never contracted by an amount larger than $y$. In the limiting case of $t \gg t_R$ and of $x \gg \Delta \overline{L}$ the probability $P_v(t)$ is obtained as [16]

$$P_v(t) = \exp(-t/t_v),$$

where the time $t_v$ is the typical time at which a segment of trailing volume $v$ (measured from the free chain end) has retracted the tube, and it is given by

$$t_v = t_V \frac{\exp[-(3\alpha/2)(1 - (v/V)^2)]}{v/V}. $$

(8)

The time $t_V$ at which the whole chain has retracted the tube is

$$t_V = \frac{\zeta \overline{L}^2}{3\alpha k_B T}(2\pi/3\alpha)^{1/2} \exp(3\alpha/2),$$

(9)

hence, it is exponentially large in the chain molecular weight $M$ ($\alpha = R^2/R_e^2 = M/M_e$, with $M_e$ the entanglement molecular weight). Clearly, for long chains $t_V$ is much larger than both, the Rouse time $t_R \propto M^2$, and the entanglement time $t_e \propto M^{3.4}$ of linear melts and concentrated solutions. Similar conclusions apply to $t_v$ if $\alpha \gg 1$ and $v > V/\alpha^{1/2}$.

Eq. (8) indicates that $t_{v+\Delta v}$ is several times larger that $t_v$ if $\Delta v \approx 1/\alpha$. This very strong dependence of $t_v$ on the volume $v$ of the trailing segment suggest that the stress relaxation of the lamellar system is very sensitive to the trailing volume distribution. Moreover, from the above discussion one can conclude that, for large values of $\alpha$, the function $P_v(t)$ is very well approximated by the theta function

$$P_v(t) = \Theta(v - v(t)),$$

(10)

with $v(t)$ obtained by inverting $t_v$ of (8). This is because, from Eq.(8), a given time $t'$ has associated to it a volume $v'$ such that $t_{v'} = t'$. Then, if $v > v'$ ($v < v'$), we have $t_v >> t_{v'}$ ($t_v << t_{v'}$).

Now we are ready to evaluate the local modulus $G(z, t)$ defined in (3). Using Eqs. (6) and (10) we obtain

$$G(z, t) = \frac{k_B T}{R_e^3} \left[ \int_0^V dv p_z(v) P_v(t) \right] = \frac{k_B T}{R_e^3} \left[ \int_{v(t)}^{v_{\text{max}}(z)} dv p_z(v) \right]^2,$$

(11)

which is valid for $t_R << t < t_V$. This integral can be solved in closed form as

$$G(z, t) = \frac{k_B T}{R_e^3} \left[ 1 - \frac{2}{\pi} \arctan \left( \frac{(z/h) \sin(\pi v(t)/2V)}{(\cos^2(\pi v(t)/2V) - (z/h)^2)^{1/2}} \right) \right]^2.$$

(12)

The logarithm of the local modulus $\log G(z, t)$ as a function of $\log(t/t_V)$ is depicted in Figure 3 for various values of $(z/h)$. Clearly, the trailing volume distribution leads to a very broad (unbounded in the large $\alpha$ limit) spectrum of relaxation times at a given height $z$ above the interface.
FIG. 3. log\((G(z,t)/G_0)\) vs. log\((t/t_V)\) for various values of \((z/h)\). We have taken \((2\alpha/3) = 100\).

IV. DISCUSSION AND CONCLUSIONS

Stress relaxation in heterogeneous systems such as the lamellar phase of diblock copolymers proceeds at different rates in different spatial regions as shown in Figure 3. Thus we find that at intermediate times the diblock layer has three co-existing zones of strongly different rheology: the region near the midplane is a quickly relaxing liquid; the regions near each A-B interface are unrelaxed rubber. Remarkably, this heterogeneity arises from different parts within a given chain. We would have obtained similar heterogeneity even if we had neglected the dispersion of the chains through the layer, as in Alexander [14]-de Gennes [15] model. When we include this dispersion, as in Figure 3, we find in addition a very broad relaxation spectrum, even at a given height \(z\). This broad spectrum results because of a) a distribution of tail lengths \(v\) at a given height \(z\), and b) the exponential increase of the relaxation time with the tail length \(v\).

Contrary to our expectations, Eq.(12) predicts that \(G(z,t) = 0\) at the midplane \((z = h)\). This is because within the “classical approximation” we have neglected the penetration zone of width \(\xi\). In this region, chains are Gaussian and hence the distribution of trailing segments is exponential in the trailing volume \(v\); that is \(\rho_{z=0}(v) = \exp(-v/v_\xi)\), with \(v_\xi = b\xi^2\) the mean volume of trailing segments living in the penetration region. In this region, segments are still highly entangled \((\xi \gg R_e)\) and stress relaxation proceeds as discussed in Sec. 3 replacing the trailing volume distribution (6) by the exponential one. Then, we obtain the local modulus for a stress blob at the midplane \(G(z = 0, t) = (k_B T/R_0^2) \exp(-v(t)/v_\xi)\) valid for \(t_R << t < t_{v_\xi}\).

The \(G(z,t)\) of (12) is the mean value at time \(t\) of the stress modulus for a blob at height \(z\). In fact, stress moduli at \((z,t)\) are distributed according to the binomial distribution. This is because in a given blob at a given time, there are many stress points, each having a probability \(p\) to be alive. The probability \(p(z,t)\) is given by the factor in Eq.(11) that multiplies the plateau modulus \(G_0\). In principle, the local modulus \(G(z,t)\) could be measured using local probes. On the other hand, the local modulus is the main ingredient to evaluate the total modulus for either sliding or compressional stress. It is straightforward to find these moduli using Eq. (12). It is also straightforward to extend this equation to account for the interpenetration zone. Our work in this direction is in progress.
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