Dynamics of Confined Polymer Melts: Topology and Entanglement

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ABSTRACT: Computer simulations of a special bond-fluctuation model are used to investigate the effects of chain topology on the dynamics of confined polymer melts. Short polymer chains with and without topological constraints exhibit nearly identical increases in relaxation times upon confinement. In longer chains, the effects of confinement are actually more pronounced for chains without topological constraints. These results suggest that entanglements are neither induced nor enhanced by confinement between impenetrable adsorbing surfaces. Implications of these results for rheological theories of confined polymer melts are discussed.

Introduction

The rheological properties of confined polymer liquids can determine the success or failure of devices that rely on effective lubrication. Polymeric lubricants are used with great success in hard disk drives, for example, where thin films of polymeric liquids form a protective, lubricating layer between the surface of the magnetic storage medium and the recording head.[1]

Experimental studies of polymer rheology in confined geometries have produced a wealth of fascinating results. Granick and co-workers[2−6] have directly measured the rheological response of thin films of low molecular weight polymeric liquids by subjecting them to oscillatory shear in the surface forces apparatus (SFA). The dynamical properties of the confined fluid remain bulklike until the film thickness, H, is reduced to several times the unperturbed radius of gyration, R_g. When H is decreased further, the relaxation dynamics are slowed considerably; the effective viscosity rises sharply[2] and the storage modulus, $G'(\omega)$, grows in comparison to the loss modulus, $G''(\omega)$.[3−6] The sluggish relaxation of the confined polymer melts in the surface forces apparatus suggests the presence of topological entanglement constraints, similar to those found in bulk polymer melts above a critical molecular weight for entanglements, M_c. In the bulk, entanglement constraints reflect the severe topological restrictions on chain motion which arise because polymer chains cannot cross through each other.[7−10] The polymers used in the SFA experiments were too short to be entangled in the bulk phase, however, so one is led to infer from the experiments that topological constraints become more severe upon confinement or that confinement lowers the value of M_c.[6]

Computer simulations have also been valuable tools in the study of thin-film rheology by providing information to complement the SFA experiments cited above. For example, several computer simulations[11−13] have reproduced the general qualitative features of the experiments while highlighting the importance of other, nontopological influences on chain dynamics. These additional factors include a wall-induced glass transition due to increased segment density near the surface[11,12] and a related slowing down of conformational transitions for adsorbed chains;[13] surface-induced entanglements are not required to explain the observed behavior. Thus despite the recent progress in experimental characterization and computer simulation of thin liquid polymer films, there are still questions regarding the molecular origin of the observed rheological behavior.

Uncertainty about the role of entanglements in confined polymer liquids must be resolved for further theoretical developments in this area. Most polymers used commercially as lubricants in disk drives, for example, are of fairly low molecular weight and are below the bulk entanglement threshold. As a result, their dynamics in the bulk can be described well by the Rouse model,[10,14] which neglects all entanglement effects and is successful for describing polymer melts of low molecular weight. The surface forces experiments[2−6] suggest, however, that entanglement effects must be incorporated into the theoretical description of these fluids under severe confinement. Rheological theories of these confined polymer melts could then be based on the reptation model[7−10] or other models[15−17] which account specifically for the dynamical effects of chain entanglements. The computer simulations,[11−13] on the other hand, suggest that segment−surface interactions may be the dominant factor in the sluggish dynamics of confined polymers of low molecular weight. This in turn implies that theoretical models might simply incorporate an external potential field into the basic Rouse model and account for the anisotropy introduced by the solid surfaces.[18−23] Further theoretical progress is hindered until fundamental issues regarding the effects of chain topology have been addressed.

In this paper, we seek to clarify the effects of topological constraints on the dynamics of confined polymer melts by conducting computer simulations with a new bond-fluctuation model.[24,25] The novel simulation technique allows us to control the topological character of the polymer chains through the "chain crossing condition"—the polymers may be allowed to cross through each other during the simulation or they may be strictly prohibited from crossing. (We use the term *topology* to denote only the presence or absence of chain crossing constraints, not to specify the chain architecture, e.g., linear, branched, ring, or star.) The chain crossing condition, or effective chain topology, does not significantly alter the structural characteristics of the polymers or even their local, segment-level dynamics. We can therefore conduct well-controlled computer experi-

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ments that isolate the dynamical effects of the polymer chain topology on confined polymer melts.

Model and Methods

The structure and dynamics of confined polymers are represented in the present work by a dynamic Monte Carlo model[24,25] that was inspired by the original bond-fluctuation models of Carmesin and Kremer and Deutsch and Binder.[26,27] Chains are composed of N monomers; each monomer occupies one site on a primary cubic lattice with lattice constant $a_{\mathrm{P}} = 1$. Bond lengths are allowed to take the values 1, $2^{1/2}$, and $3^{1/2}$. The Monte Carlo moves involve selecting a single monomer at random and attempting to move it to one of the six nearest-neighbor sites on the primary lattice. Excluded volume interactions for the monomers are enforced by rejecting any attempted moves which would result in double occupancy of a primary lattice site. Chain connectivity is maintained by rejecting moves which generate bond vectors in violation of the allowed bond lengths listed above. In addition, the effective chain topology can be controlled through special characteristics of the lattice model.

By virtue of the lattice geometry, the midpoints of all bonds must lie on a secondary cubic lattice with lattice constant $a_{\mathrm{s}} = {}^{1}/_{2}$. When excluded volume interactions are enforced for the monomers on the primary lattice and attempted moves of monomers are restricted to nearest-neighbor sites, any chain crossing in this model must occur through the overlap of bond midpoints. Chain crossings can therefore be rigorously forbidden by tracking the bond midpoints on the secondary lattice and forbidding their overlap. When this additional constraint on the bond midpoints is enforced, the polymer chains have the physically correct, noncrossing topology. Conversely, chain crossing can occur when this constraint is relaxed, and the polymers then have a hypothetical phantom topology. Since chain connectivity and excluded volume interactions among monomers are maintained in both cases, the chain topology in the present model has only a very small effect on the structure of the polymer chains. Even the local, monomer-level dynamics are changed only slightly when chain crossing is allowed.[24] As a result, the dynamical effects of chain topology can be assessed directly by conducting complementary sets of computer simulations in which the only difference is the chain crossing condition.

Impenetrable flat surfaces are introduced in this model by placing hard walls at lattice planes $z = 0$ and $z = H + 1$, where H is the width of the confining channel. Polymer segments in lattice planes $z = 1$ or $z = H$ are adsorbed. Segment−surface interactions are quantified by the adsorption energy per segment, E_z, and the activation barrier for surface diffusion of adsorbed segments, E_{xy}. Monte Carlo moves that correspond to segmental desorption are accepted with probability $p_z = \exp(-E_z/k_{\mathrm{B}}T)$, provided that the moves satisfy the constraints of excluded volume, connectivity, and chain topology. Attempted moves that correspond to surface diffusion and satisfy the other constraints are accepted with probability $p_{xy} = \exp(-E_{xy}/k_{\mathrm{B}}T)$. In the present study, we take $E_{xy} = E_z = 2k_{\mathrm{B}}T$ to represent moderately attractive segment−surface interactions. Since the excluded volume interactions are athermal, temperature enters the simulations only through the quantities $E_{xy}/k_{\mathrm{B}}T$ and $E_z/k_{\mathrm{B}}T$.

The simulations were conducted with monodisperse linear chains of lengths $N = 25$ and $N = 80$. The average segment density was 0.50. Previous simulations with the present model[24] and the original three-dimensioanl bond-fluctuation model[28] have shown that this density is representative of a polymer melt; chains in the bulk assume random coil configurations with dimensions that follow the scaling law for ideal random walks, $R_{\mathrm{g}} \sim N^{1/2}$. The simulation box is periodic in the directions parallel to the surface; the length of the box in these directions (20 lattice units) is large enough so that periodic images of the same chain do not interact. The generation and equilibration of chain configurations in the bulk have been described elsewhere;[24,25] the procedure was modified here to account for the impenetrable surfaces.

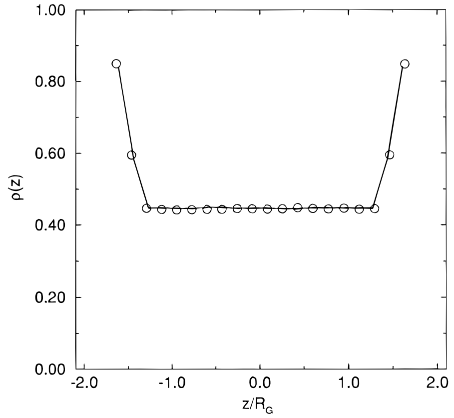

Figure 1. Segment density profiles, $\rho(z)$, for chains of length $N = 80$ confined between adsorbing surfaces separated by $H = 20$ lattice units; the abscissa is the distance from the center of the confined region normalized by the unperturbed radius of gyration. The open circles are data from simulations of chains with the phantom, crossing topology; the solid line shows data obtained from separate simulations of chains with the physically correct noncrossing topology.

The shorter chain length, $N = 25$, was chosen to correspond approximately with the molecular weight of poly(phenylmethylsiloxane) (PPMS) chains used in several SFA experiments.[3−6] For the PPMS chains with number-average molecular weight $M_{\mathrm{n}} = 10\,560$, $M_{\mathrm{n}}/M_{\mathrm{e}} \approx 0.88$, where M_{e} is the molecular weight between entanglements for bulk PPMS. For our model chains of length $N = 25$, $N/N_{\mathrm{e}} \approx 0.83$, where N_{e} is the estimated number of segments between entanglements in the present lattice model for chains in the bulk.[24,25] Thus like the PPMS chains used in the SFA experiments, our chains with $N = 25$ are too short to be entangled in the bulk. In contrast, the model chains of length $N = 80$ have $N/N_{\mathrm{e}} \approx 2.7$, so they are weakly entangled in the bulk phase.

Results and Discussion

Before the discussion of chain dynamics, we must demonstrate that the chain crossing condition has only small effects on static, structural properties. Figure 1 shows the segment density profile, $\rho(z)$, for chains of length $N = 80$ when the surfaces are separated by a distance $H = 20$. The favorable energy of adsorption ($E_z/k_{\mathrm{B}}T = 2$) causes the density near the surfaces to be enhanced relative to the density in the central region. This aspect of the present work matches the molecular dynamics simulations of Bitsanis and co-workers[12,13] and the lattice Monte Carlo simulations of Binder *et al.*[29] The most important feature to note, however, is that the density profiles for the crossing and noncrossing chains are nearly identical.

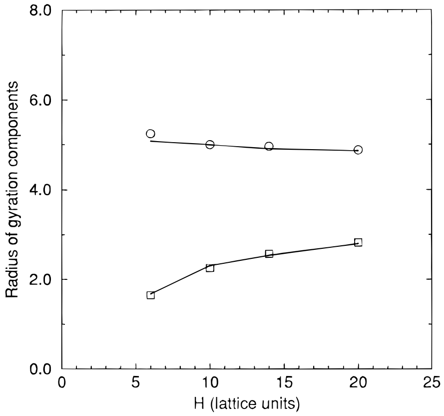

Figure 2. Components of the radius of gyration parallel and perpendicular to the adsorbing surfaces as a function of the distance separating the surfaces, H, for chains of length $N = 80$. As in Figure 1, the open symbols are data from simulations of crossing chains, while the solid lines show data from separate simulations of noncrossing chains. Circles show the xy component of $\langle R_g{}^2\rangle^{1/2}$; squares show the x component.

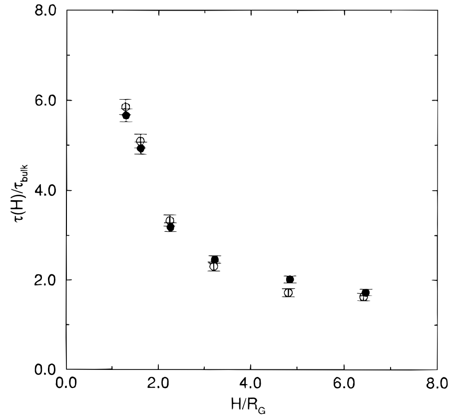

Figure 3. Relaxation times of the first Rouse coordinate of confined chains of length $N = 25$ as a function of the distance separating the confining surfaces, H. The relaxation times are normalized by the bulk relaxation time, and the separation distance is normalized by the unperturbed radius of gyration. The open circles are data from simulations of chains with the phantom, crossing topology; the filled circles are data obtained from separate simulations of chains with the physically correct noncrossing topology.

Figure 2 presents the components of the radius of gyration parallel and perpendicular to the surfaces, $\langle R^2_{g,xy}\rangle^{1/2}$ and $\langle R^2_{g,z}\rangle^{1/2}$, for the same simulations. As H decreases, the parallel component grows slightly while the perpendicular components shrinks, reflecting flatter chain conformations due to adsorption and confinement. As in Figure 1, the structural data from the crossing and noncrossing chains are nearly identical. Other structural quantities not shown, such as the pair correlation function, are also affected only slightly by the chain crossing condition. Differences between crossing the noncrossing simulations can therefore be traced directly to the dynamical effects of the polymer chain topology.

The simulations were conducted for confined polymer melts at equilibrium. The measured dynamical quantities should therefore be relevant to the linear viscoelastic behavior of confined polymer melts. To analyze the dynamical effects of confinement, we have decomposed the chain dynamics into individual modes. As in earlier simulations of polymer dynamics in the bulk[25,30,31] and near surfaces,[12] the decomposition can be performed using the normal coordinates for a Rouse chain,[14] even when the polymers do not exhibit Rouse-like dynamics. The Rouse modes, $\mathbf{X}_p(t)$, are defined as follows:

$$\mathbf{X}_p(t) = \frac{1}{N}\sum_{j=1}^{N} \mathbf{r}_j(t) \cos\left[\frac{\pi p(j - 1/2)}{N}\right] \qquad (1)$$

where p is the mode number; here we focus on the first Rouse mode, $\mathbf{X}_1$. To quantify the relaxation dynamics of the confined polymers, we have calculated the relaxation time, τ, associated with the autocorrelation function of the first Rouse coordinate:

$$\tau = \int_0^\infty \mathrm{d}t\, \langle \mathbf{X}_1(t)\cdot\mathbf{X}_1(0)\rangle / \langle X_1{}^2\rangle \qquad (2)$$

We can now proceed to discuss the chain dynamics.

Figure 3 presents the relaxation times defined by eq 2 as a function of H, the distance separating the two surfaces, for the crossing and noncrossing topology in chains of length $N = 25$. The relaxation times have been normalized by their values in the bulk phase at the same average density, τ_{bulk}. (In the bulk, noncrossing chains have longer relaxation times for the low-order, long-wavelength Rouse modes;[25] the normalization allows a fair comparison of the effects of confinement on the relaxation times.) In qualitative agreement with experiments[2-6] and previous simulations,[11-13] the relaxation times rise as the thickness of the polymeric liquid decreases below about $4R_g$. Quantitative comparisons are difficult to make because of differences in the strength of the segment–surface interactions for the systems studied in the surface forces apparatus; the MD simulations employed shorter chains and different surface interaction potentials.

In the context of the present study, the most important feature of the data in Figure 3 is that the normalized relaxation times for the two chain topologies are indistinguishable within the statistical uncertainty. Since the crossing chains have no topological constraints and cannot become entangled, this result suggests that entanglement constraints are not responsible for the sluggish dynamics of these confined polymer liquids. Given that the noncrossing chains of this length are just below the bulk entanglement threshold,[24,25] confinement must neither induce entanglements nor lower the critical entanglement molecular weight, M_c.

If topological constraints are not responsible for the increase in relaxation times, then confinement and adsorption must place other constraints on the confined fluids. Confinement alone (in the absence of favorable adsorption energetics) does of course restrict chain motion; local, segment-level motion that leads to diffusion and configurational relaxation is reduced by the impenetrable surfaces. Attractive segment–surface interactions provide additional kinetic constraints for adsorbed segments; both the increased density near the surface[12] and the activation barriers to desorption and surface diffusion, E_z and E_{xy}, act to reduce the mobility of adsorbed segments. These surface effects propagate into the central region (to segments that are not directly attached to the surface) through the constraint of chain connectivity.[32] Previous simulations of single adsorbed chains[33] have also observed a slowing of chain dynamics due to attractive segment-surface interactions; the degree of slowing increases with the strength of the interactions. One would expect similar trends in the polymer melt system studied here. A detailed exploration of the coupling between the kinetic constraints

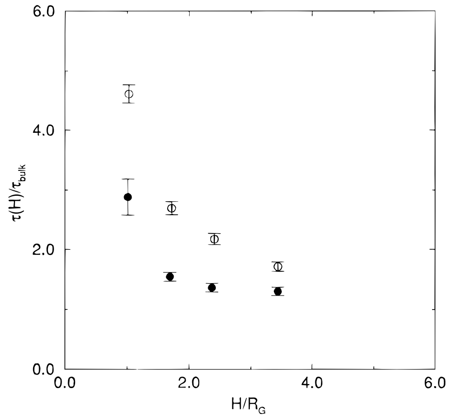

Figure 4. Relaxation times versus separation distance for chains of length $N = 80$. The data from crossing chains are shown in open circles, noncrossing chains in filled circles. The abscissa and ordinate are normalized as in Figure 3.

imposed by segment–surface interactions and the geometrical constraints imposed by chain topology remains for future study.

The simulation results for the longer chains provide additional insight into the effects of confinement on the dynamics of polymer melts. In Figure 4, the normalized relaxation times are shown as a function of the normalized separation distance for crossing and noncrossing chains of length $N = 80$. The relaxation times for the noncrossing chains remain close to their bulk value until $H \approx R_g$. Even for the thinnest film that was studied, the relaxation time is enlarged by less than a factor of 3 over its bulk value. The crossing chains, in contrast, exhibit a rise in relaxation times at larger values of H, and the normalized relaxation times of crossing chains are always larger (at a fixed value of H) than those of noncrossing chains.

The data in Figure 4 indicate that the crossing chains, which are free of topological constraints in the bulk phase, are slowed down by confinement (relative to the bulk) to a greater extent than the noncrossing chains, which do feel topological constraints in the bulk. This surprising result illustrates that entanglement constraints which are already present in the bulk have a larger influence on relaxation processes in the confined polymers than additional constraints which are introduced by the surfaces.[34] At small values of H where the relaxation times of the noncrossing chains do ultimately increase, the additional constraints imposed by the impenetrable adsorbing surfaces (which are responsible for the increased relaxation times of the crossing chains) must begin to affect the relaxation dynamics to a degree comparable to the bulk entanglement constraints.

Conclusions

We have presented computer simulations of confined polymer melts in order to examine the effects of chain topology on the relaxation dynamics. By simulating two distinct topological conditions—chains that may cross through each other and chains that are strictly prohibited from crossing—we have separated the effects of topological constraints from other features that may affect chain dynamics. Simulations with chains that are just below the bulk entanglement threshold indicate that confinement does not induce entanglements or enhance topological constraints. The relaxation dynamics of chains above the bulk entanglement threshold suggest that entanglement constraints which are already present in the bulk have a greater effect on the dynamics of confined polymer melts than the additional constraints due to confinement and adsorption.

The results presented here suggest that commercial lubricants in disk drives, which are below the bulk entanglement threshold, are not subject to topological entanglement constraints upon confinement. Rheological theories of these systems therefore do not need to account explicitly for the noncrossing chain topology. The linear viscoelastic properties of these confined polymer melts can be investigated through Rouse-like models which have been modified to account for the presence of solid surfaces;[18–21] nonlinear effects, such as shear thinning, can be treated through recently proposed scaling theories.[22,23]

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(34) Note that the data in Figure 4 represent relaxation times of the confined polymers normalized by the relaxation times in the bulk phase. In terms of unnormalized absolute magnitudes, the confined noncrossing chains still have larger relaxation times than the confined crossing chains.

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