Structural Relaxation and Dynamic Heterogeneity in a Polymer Melt at Attractive Surfaces

Grant D. Smith, Dmitry Bedrov, and Oleg Borodin

*Department of Materials Science and Engineering, University of Utah, 122 South Central Campus Drive,
Room 304, Salt Lake City, Utah 84112, USA*

Molecular dynamics simulations of polymer melts at flat and structured surfaces reveal that, for the former, slow dynamics and increased dynamic heterogeneity for an adsorbed polymer is due to densification of the polymer in a surface layer, while, for the latter, the energy topography of the surface plays the dominant role in determining dynamics of interfacial polymer. The dramatic increase in structural relaxation time for polymer melts at the attractive structured surface is largely the result of dynamic heterogeneity induced by the surface and does not resemble dynamics of a bulk melt approaching T_g.

The dynamics of melt polymers near solid surfaces are of tremendous interest for a wide range of materials including polymer-nanoparticle composites [1] and highly confined polymers [2]. Simulation [3,4] and experimental studies [5–7] have shown that the structural relaxation time of melt polymers in the vicinity of solid surfaces with which they have strong, attractive interactions can be dramatically greater than that of the corresponding bulk polymer at the same thermodynamic conditions. This increase in relaxation time has been associated with an increase in glass transition temperature T_g for interfacial polymer seen in both simulations [3] and experimental studies [1,8].

Simulation [3,9,10] and experimental studies [9,11] reveal that attractive interfaces engender density oscillations (layers) in a polymer melt whose amplitude decays rapidly with distance from the surface (e.g., see inset in Fig. 1). Simulations also indicate that the influence of the surface on polymer dynamics is localized to the first few layers of polymer near the surface and is most dramatic for polymer segments adsorbed on the polymer surface (the first polymer layer) [3,4]. Hence, understanding the relaxation behavior of polymers in the layer adjacent to an attractive surface is key to understanding the dynamics of interfacial and confined polymers. The fundamental origins of these increased relaxation times for polymers at strongly attractive surfaces remain unclear. Detailed analysis of simulations of roughly spherical nanoparticles in a coarse-grained bead-spring polymer matrix [4] indicated that reduced segmental motion along the surface of the particle can be associated with the energy topography of the nanoparticle surface. In contrast, a recent density functional theory analysis of polymer chains confined between flat, structureless surfaces associated the slowing of polymer dynamics with increased density of the polymer in layers near the surface [12].

Recent simulation studies [13] have also revealed the important role of dynamic heterogeneity in governing relaxation behavior in polymer melts. Dynamic heterogeneity, reflected, for example, in an increasingly non-

Gaussian character of atomic displacements as temperature decreases toward T_g, can be quantified by the first non-Gaussian correction to the incoherent dynamic structure factor $I(q, t)$ given by [14]

$$I(q, t) = I^{\text{Gauss}}(q, t)X\{1 + \tfrac{1}{2}[q^2\langle R(t)^2\rangle/6]^2\alpha_2(t) + \cdots\},$$

where

$$I^{\text{Gauss}}(q, t) = \exp[-q^2\langle R(t)^2\rangle/6],$$

$$\alpha_2(t) = \frac{3\langle R(t)^4\rangle}{5\langle R(t)^2\rangle^2} - 1.$$

$\langle R(t)^2\rangle$ is the mean-square displacement of scattering centers (e.g., monomers) at time t, and q is the magnitude of the scattering vector. Non-Gaussian displacements can result in much slower relaxation, quantified by the rate of
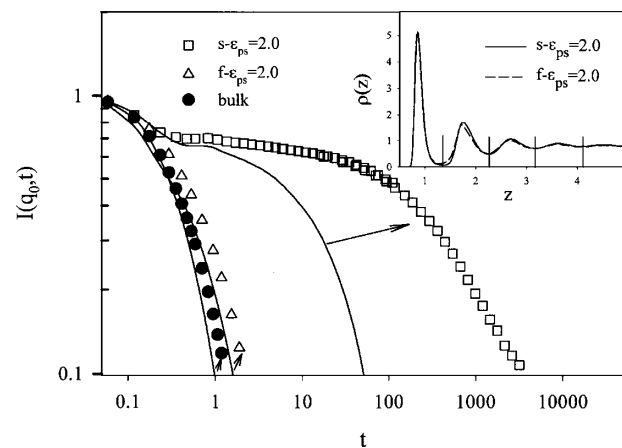

FIG. 1. Incoherent dynamic structure factor of the first polymer layer at the structured surface (open squares) and flat surface (open triangles) for $\varepsilon_{ps} = 2$. Also shown is the dynamic structure factor for the bulk melt. The solid lines are the corresponding dynamic structure factors obtained assuming Gaussian distributed bead displacements. The inset shows the density of polymer beads as a function of distance from the surfaces; vertical lines denote layer boundaries.

decay of $I(q, t)$, compared to a more dynamically homogeneous material with the same intrinsic dynamics quantified by $\langle R(t)^2 \rangle$.

For polymers near attractive surfaces, increased structural relaxation time relative to the bulk melt may be due to a decrease in the rate of intrinsic polymer dynamics for adsorbed polymer segments, an increase in non-Gaussianity (heterogeneity) of monomer displacements for adsorbed polymer, or both. In turn, this (these) effect(s) may be a consequence of the energy topography of the surface, densification of the polymer at the surface, or a combination of these effects. In order to help clarify the roles of heterogeneity, surface structure, and polymer densification in the observed slowing of structural relaxation of polymers near attractive surfaces, we have conducted simulations of a coarse-grained bead-spring polymer melt confined between attractive structured and structureless (flat) surfaces. The polymer model and simulation methodology are described in detail in our previous work [4,10]. Briefly, the systems consisted of 100 polymer chains of 20 beads. All polymer beads interact by a Lennard-Jones potential with a well depth of $\varepsilon_{pp} = 1$ with a zero energy at $r = 1 = \sigma$. The bead-bead bond length was constrained at 0.935. The polymer was confined between parallel surfaces nominally at $z = 0$ and 10 with periodic boundary conditions in the x and y directions. The actual spacing between surfaces was adjusted to give a density (beads/σ^3) of $\rho = 0.87$ in the center of each film. The atomistic surfaces consisted of two layers of polymer beads in a square array with lattice parameter equal to the diameter of the beads. Polymer-surface (bead-bead) interaction energies $\varepsilon_{ps} = \varepsilon_{pp} = 1$ and $\varepsilon_{ps} = 2\varepsilon_{pp} = 2$ were investigated. For the flat surfaces the polymer bead-surface potential is given as

$$U(z) = A\varepsilon_{ps}[z^{-9} - z^{-3}].$$

where parameter A was adjusted such that the polymer density profiles obtained for structured and flat surfaces were nearly indistinguishable, as shown in Fig. 1. Simulations were performed using the simulation package Lucretius [15] at reduced temperature $T = 1.0$ defined in terms of the well depth for the polymer bead-bead interaction ($\varepsilon_{pp} = 1$). Simulations of a bulk melt (3D periodic boundary conditions) were also performed at $T = 1.0$, $\rho = 0.87$. All potentials were shifted and truncated at 2.5σ. Our integration time step was 5.9×10^{-3} in units of $(m\sigma/\varepsilon_{pp})^{1/2}$ where m is the bead mass, with a total simulation time of approximately 6×10^4 for each system.

We have investigated the behavior of incoherent dynamic structure factor for each layer j (e.g., see Fig. 1, inset) of the polymer films given as

$$I_j(q_0, t) = \frac{1}{2\pi N_j} \left\langle \int_0^{2\pi} \cos[q_0 R^{xy}(t) \cos\theta] d\theta \right\rangle$$

and

$$I_j^{\text{Gauss}}(q_0, t) = \exp[-q_0^2 \langle R_j^{xy}(t)^2 \rangle / 4],$$

where $q_0 = 7$ corresponds to the first peak in the static structure factor for the bulk melt and $\langle R_j^{xy}(t)^2 \rangle$ is the mean-squared bead displacement of the N_j beads in the jth layer parallel to the surfaces. Here we investigated only motion parallel to the surface as a division of the material into layers of thickness comparable to $2\pi/q_0$ resulting in artifacts in the 3D dynamic structure factor from contribution of motion perpendicular to the layers. The integral was evaluated numerically utilizing 180 equally spaced q vectors in the xy plane. The relationship for $I_j(q_0, t)$ assumes isotropic motion, while that for $I_j^{\text{Gauss}}(q_0, t)$ assumes both isotropic motion and Gaussian-distributed displacements of the scattering centers.

$I_j(q_0, t)$ for the first polymer layer at structured and flat surfaces for $\varepsilon_{ps} = 2$ as well as $I(q_0, t)$ for the bulk melt are shown in Fig. 1. Structural relaxation times, defined as the time at which the structure factor decays to 0.1, normalized by the relaxation time of the bulk polymer, are given in Table I for all systems studied. As anticipated, the structural relaxation time for the polymer near the attractive surfaces (first layer) is much greater than that of the bulk polymer, particularly for the structured surface. Polymer dynamics for layer 2 showed much less influence on the surface and those for layers beyond layer 2 were essentially indistinguishable from the bulk melt. The dynamic structure factor of the film could be represented quite accurately as a weighted sum of contributions from the first two layers with the remainder of the material treated as bulk polymer.

Comparison of $I(q_0, t)$ and $I^{\text{Gauss}}(q_0, t)$ (Fig. 1) or, correspondingly, τ/τ^{Gauss}, given in Table I, reveals that heterogeneity, manifested in the non-Gaussianity of bead displacements, makes an insignificant contribution to the structural relaxation time for the bulk melt, consistent with the fact that the bulk is well above its glass transition temperature of approximately $T_g = 0.35$ [16]. In contrast, for the adsorbed polymer layer non-Gaussian effects are important, particularly for the structured surface, and increase dramatically with the strength of the polymer-surface interaction. For the structured surface dynamic heterogeneity induced by the surface plays

TABLE I. Normalized structural relaxation times for adsorbed and bulk polymer.

Relax. time	Structured		Flat	
	$\varepsilon_{ps} = 1$	$\varepsilon_{ps} = 2$	$\varepsilon_{ps} = 1$	$\varepsilon_{ps} = 2$
		Layer 1		
τ	8.3	2444	1.1	2.2
τ^{Gauss}	1.4	53	0.8	1.5
τ/τ^{Gauss}	5.9	46	1.4	1.5
		Bulk melt		
τ/τ^{Gauss}		1.3		

a role comparable to that of slower intrinsic dynamics in the dramatically increased structural relaxation time for interfacial polymer. For example, for the structured surface with $\varepsilon_{ps} = 2$, the structural relaxation time is approximately 3 orders of magnitude greater for the first layer than for the bulk ($\log \tau = 3.4$), with half of this being due to intrinsically slower dynamics ($\log \tau^{Gauss} = 1.7$) and half associated with dynamic heterogeneity ($\log \tau / \tau^{Gauss} = 1.7$).

Dynamic heterogeneity in the adsorbed polymer layer was further investigated by comparing the magnitude of $\alpha_2(t)$, the mean-square bead displacement $\langle R^{xy}(t)^2 \rangle$, and the distribution of bead displacements $P(R^{xy})$ for polymer segments in the first layer at $t = t_{max}$, the time corresponding to the maximum in $\alpha_2(t)$, for each system studied. Values of t_{max}, $\langle R^{xy}(t_{max})^2 \rangle$, and $\alpha_2(t_{max})$ are tabulated in Table II. For bulk polymer melts t_{max} corresponds to the caging time, i.e., the time scale upon which segments begin to move beyond the cage of their neighbors. The caging time increases with decreasing temperature and is expected to diverge as T_g approached [13,17]. As our bulk melt is well above T_g, t_{max} is small and the corresponding $\alpha_2(t_{max})$ is modest. Table II shows that t_{max} and $\alpha_2(t_{max})$ are greater for the adsorbed polymer and increase with increasing strength of the polymer-surface interaction, particularly for the structured surface.

We can gain insight into the fundamental roles of surface energy topography and polymer densification on the dynamics of adsorbed polymer by comparing values of $\langle R^{xy}(t_{max})^2 \rangle$ given in Table II for each system. For the flat surface $\langle R^{xy}(t_{max})^2 \rangle$ values correspond to that for the bulk melt, revealing that caging effects in the first polymer layer of the flat interface are occurring on the same length scale as those in the bulk melt. This indicates that densification of the first layer in the flat surface is promoting neighbor caging similar to that observed in the bulk melt with decreasing temperature and, hence, leads to reduced dynamics and increased heterogeneity similar to that observed in bulk polymers approaching the glass transition temperature [13]. In contrast, a structured surface with the same polymer density profile as a flat surface exhibits much stronger caging effects as mani-

fested in dramatically longer caging (and hence structural relaxation times) and greater non-Gaussianity [large $\alpha_2(t_{max})$] than observed for the flat surface. For the structured surface the length scale of the caging decreases with increasing strength of the polymer-surface interaction. To further illustrate this effect, we performed additional simulations for a structured surface at $\varepsilon_{ps} = 3$ (see Table II). Here the caging length scale reflects the amplitude of vibration of adsorbed polymer beads within energy wells on the structured surface, which become deeper (leading to reduced vibrational amplitudes) with the increase of strength of the polymer-surface interaction.

The above analysis indicates that the reduced dynamics and increased heterogeneity for polymer segments adsorbed on the structured surface are due to polymer beads becoming trapped within energy wells on the surface that become increasingly deep with increasing ε_{ps}. These effects are much stronger than density-induced neighbor caging observed for the flat surface. We concluded that the densification of the surface layer *per se,* responsible for slowing dynamics and increased heterogeneity for adsorbed polymers at the flat surface, is unimportant for the structured surface. This is further illustrated in Fig. 2, which shows clearly the much longer relaxation time for the structured surface at the same surface density as a flat surface and the significantly different scaling of relaxation time with density for the structured and flat surfaces.

We can gain insight into the relaxation mechanism polymer segments adsorbed on the structured surface by investigating the distribution of bead displacements $P(R^{xy})$ at t_{max}, shown in Fig. 3 for each system studied. Also shown is $P(R^{xy})$ for the corresponding Gaussian distributions [yielding the same $\langle (R^{xy})^2 \rangle$ as the actual distributions] for each system. The distributions for adsorbed polymer at the flat surface show deviation from Gaussian behavior but do not show any indication of the emergence of a second peak. Similar behavior is

TABLE II. Comparison of non-Gaussian properties of bead displacements for adsorbed polymers.

System[a]	t_{max}	$\alpha_2(t_{max})$	$\langle R^2(t_{max}) \rangle$	γ[b]
Bulk	0.47	0.35	0.096	$\cdots$
$s - \varepsilon_{ps} = 1$	1.89	0.68	0.225	0.80
$s - \varepsilon_{ps} = 2$	13.3	3.03	0.086	0.95
$s - \varepsilon_{ps} = 3$	496	10.2	0.027	1.00
$f - \varepsilon_{ps} = 1$	0.59	0.35	0.122	0.80
$f - \varepsilon_{ps} = 2$	1.18	0.37	0.137	0.95

[a]s = structured surface, f = flat surface.
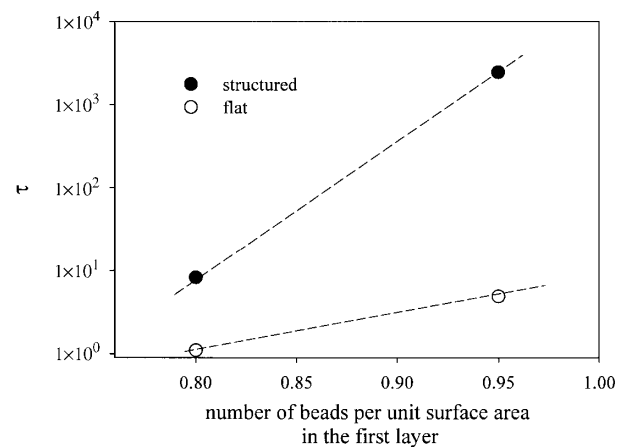[b]Surface density of beads (number of beads in the first layer per unit surface area).

FIG. 2. Structural relaxation time for the first polymer layer for structured and flat surfaces as a function of bead surface density in the first layer.
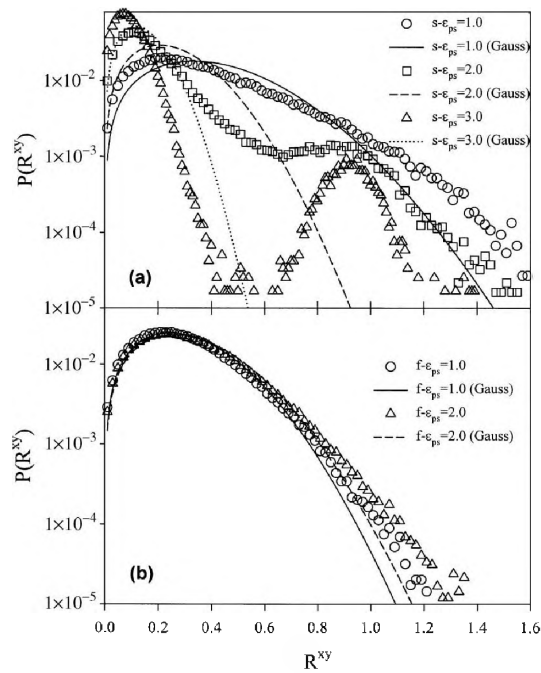
FIG. 3. Distribution of bead displacements at times corresponding to the maximum in $\alpha_2(t)$ for (a) the structured surface and (b) the flat surface. Lines show the corresponding Gaussian distributions (R^{xy}) yielding equivalent $\langle R^{xy}(t_{max})^2 \rangle$.

observed for segment distributions in bulk polymer melts approaching T_g [13]. Much more dramatic deviations from Gaussian behavior are manifested for the structured surface. Particularly for the larger polymer-surface interaction energies, there is a clear two-peak structure to the distributions. The first peak reflects segments that remain trapped in their cages (surface energy wells) on the caging time scale, while the second peak, which is manifested on a length scale corresponding to the surface structure, reflects segments which have left their original well for neighboring wells. Similar behavior was observed in our recent simulations of micelle forming telechelic polymer solutions, where on the caging time scale the majority of attractive polymer ends remained trapped within their original micelle but where also a clear contribution from those who had migrated to neighboring micelles could also be observed [17].

In summary, our molecular dynamics simulation study of the dynamics of polymers at attractive interfaces reveals that slowed structural relaxation compared to the bulk melt polymer is due to both slower intrinsic dynamics for the adsorbed polymer and increased dynamic heterogeneity within the adsorbed polymer layer. For the structureless surface, the influence of the interface on the dynamics of adsorbed polymer can be associated with increased neighbor caging due to densification of polymer within the adsorbed layer. The slower intrinsic dynamics and increasing dynamic heterogeneity with increasing strength of the surface-polymer attraction for the flat surface resembles behavior observed for bulk polymer melts with decreasing temperature. In contrast, for the structured surface, simulations indicate that densification of the polymer in the adsorbed layer is *not* fundamentally responsible for the dramatically slowed dynamics and increased dynamic heterogeneity of the adsorbed polymer compared to both the bulk polymer and polymer adsorbed to the flat surface. Rather, the *specific topography* of the surface plays a dominant role, with polymer segments becoming caged within surface energy wells and relaxation that occurs by migration of segments to neighboring energy wells.

[1] G. Tsagaropoulos and A. Eiseberg, Macromolecules **28**, 396 (1995); **28**, 6067 (1995).

[2] *Polymer Surfaces, Interfaces, and Thin Films*, edited by A. Karim and S. Kumar (World Scientific, Singapore, 2000).

[3] F. W. Starr, T. B. Schrøder, and S. C. Glotzer, Phys. Rev. E **64**, 021802 (2001); Macromolecules **35**, 4481 (2002).

[4] G. D. Smith, D. Bedrov, L. Li, and O. Byutner, J. Chem. Phys. **117**, 9478 (2002).

[5] S. Gagliardi, V. Arrighi, R. Ferguson, and M. T. F. Telling, Physica (Amsterdam) **301B**, 110 (2001).

[6] Gy. Török, V. T. Lebedev, L. Cser, D. N. Orlova, Gy. Káli, A. I. Sibilev, V. L. Alexeev, V. A. Bershtein, V. P. Budtov, V. N. Zgonnik, L. V. Vinogradova, and E. Yu. Melenevskaya, Physica (Amsterdam) **297B**, 45 (2001).

[7] E. K. Lin, R. Kolb, S. K. Satija, and W. L. Wu, Macromolecules **32**, 3753 (1999).

[8] W. E. Wallace, J. H. van Zanten, and W. L. Wu, Phys. Rev. E **52**, 3329 (1995); J. H. van Zanten, W. E. Wallace, and W. L. Wu, Phys. Rev. E **53**, 2053 (1996).

[9] D. Y. Yoon, M. Vacatello, and G. D. Smith, in *Monte Carlo and Molecular Dynamics Simulations in Polymer Science*, edited by K. Binder (Oxford, New York, 1995).

[10] J. S. Smith, D. Bedrov, and G. D. Smith, Compos. Sci. Technol. (to be published).

[11] Y. Yang, K. Hill, and J. G. Harris, Langmuir **9**, 1983 (1993).

[12] J. D. McCoy and J. G. Curro, J. Chem. Phys. **116**, 9154 (2002).

[13] G. D. Smith, W. Paul, M. Monkenbusch, and D. Richter, J. Chem. Phys. **114**, 4285 (2001); G. D. Smith, O. Borodin, and W. Paul, J. Chem. Phys. **117**, 10350 (2002); G. D. Smith, W. Paul, and D. Bedrov (to be published).

[14] W. van Megan, T. C. Mortensen, S. R. Williams, and J. Müller, Phys. Rev. E **58**, 6073 (1998).

[15] http://lucretius.mse.utah.edu

[16] C. Bennemann, W. Paul, K. Binder, and B. Dünweg, Phys. Rev. E **57**, 843 (1998).

[17] D. Bedrov, G. D. Smith, and J. F. Douglas, Europhys. Lett. **59**, 384 (2002).