Molecular Simulation of Ultrathin Polymeric Films near the Glass Transition

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Properties such as the glass transition temperature (T_g) and the diffusion coefficient of ultrathin polymeric films are shown to depend on the dimensions of the system. In this work, a hard-sphere molecular dynamics methodology has been applied to simulate such systems. We investigate the influence that substrates have on the behavior of thin polymer films; we report evidence suggesting that, depending on the strength of substrate-polymer interactions, the glass transition temperature for a thin film can be significantly lower or higher than that of the bulk.

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Polymer thin films are ubiquitous in technological applications, ranging from the manufacture of electronic devices to the production of paper. For applications in the electronics sector, the ever-present drive towards smaller circuits has led many to consider the use of ultrathin polymer films for various aspects of nanofabrication. In recent years, experimental evidence has been reported suggesting that transport properties in ultrathin films are appreciably different from those in the bulk. The origin of the deviations from bulk behavior, however, remains elusive.

Forrest *et al.* established that freestanding poly(styrene) (PS) films exhibit a reduction in their T_g in films thinner than 60 nm [1]. Keddie *et al.* showed that the T_g of poly(methyl methacrylate) (PMMA) on gold-coated silicon and PS on hydrogen terminated silicon surfaces decreased for thicknesses below 60 nm [2,3]. In contrast, they also found that T_g increases with decreasing thickness for PMMA on a silicon oxide substrate. Subsequently, Wallace *et al.* [4] reported that the T_g of PS *increased* above the bulk value on hydrogen terminated silicon surfaces.

In a thin-film geometry, the surfaces constitute a significant fraction of the overall system; substrate-polymer interactions and free interfaces therefore play a crucial role on the T_g of ultrathin films. What that role is, however, remains a subject of considerable debate. Changes in T_g should result in increased or decreased molecular mobility in thin films. Based on diffusion experiments, however, it is unclear how and to what extent mobility is altered in supported films [5–7].

Some of the apparent discrepancies in the literature could be attributed to the use of different experimental techniques with varying sensitivity to surface effects [2–4,8], and to the difficulty in controlling surface chemistry. Molecular simulations of well-defined ultrathin films could help elucidate the behavior of the glass transition temperature in such systems, and help establish whether it increases or decreases in the presence of various substrates.

Unfortunately, simulation studies of ultrathin polymer glasses as a function of thickness have been scarce. Recently, however, Baschnagel *et al.* have examined the dynamics of short lattice chains in films of various thicknesses [9]; they find that, upon confinement by neutral walls, the relaxation times for the scattering functions decay with film thickness, particularly in ultrathin systems. Varnik *et al.* report that short chains near a neutral wall diffuse faster than chains in the bulk [10].

In this work we use a coarse-grained, continuum representation of unentangled polymers to conduct molecular simulations of ultrathin films in the near vicinity of the glass transition. We consider three systems: a freestanding film and two types of supported films. In order to extend the dynamic range of our simulations beyond that accessible to conventional molecular dynamics, we use a hard-sphere based simulation technique. Our numerical results suggest that, depending on the nature of substrate-polymer interactions, the glass transition temperature of ultrathin polymer films can be significantly higher or lower than that of the bulk. Our calculations also show that diffusion coefficients in ultrathin films are strongly influenced by the presence of free or solid interfaces.

I. Apparent glass transition.—To represent the polymer, we have taken Rapaport's model [11,12] and included a square-well interaction potential between all interaction sites in the system; each polymer molecule consists of 16 square-well spherical interaction sites interconnected by fully flexible strings. The reduced parameters used for the square-well potential energy function are $\epsilon = 1$ (well depth) and $\lambda = 1.5\sigma$ (well width), with σ being the diameter of each monomer. The length of the links connecting successive monomers of a polymer molecule is $\delta = 0.025\sigma$. In all cases, the simulation cell is a quadrangular prism with a height 6 times longer than the length of the base edges. For freestanding films, periodic boundary conditions are used in all directions. For supported films, an attractive wall is placed at the bottom of the simulation box where the polymer can be deposited. Periodic boundary conditions are imposed in the x and y directions parallel to the plane of the film. The number of chains used for simulations ranges from 98 (for 6σ films) to 700 (for 56σ films).

Two methods are used to estimate apparent glass transition temperatures. In the first of these, the thickness of a

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thin film is simulated as a function of temperature. In the second technique, we examine the temperature dependence of mobility; an extrapolation to low temperatures yields an estimate of the glass transition. The rate at which a bulk material is quenched during a simulation is above the cooling rates that can be achieved in conventional experiments. The simulated apparent glass transition temperatures reported here should therefore be viewed as an upper limit to the values determined at slower, experimentally relevant cooling rates. As a side note, however, we do point out that given the dimensions of the films considered in this work, a simple analysis using Fourier's law indicates that it would in principle be possible to achieve relatively large cooling rates in the laboratory. In our simulations, a series of average density profiles are collected for each film at different temperatures. The total thickness of the film is determined by means of a Gibbs dividing surface construction. We find that the density of our films is relatively uniform, except in the immediate vicinity of a solid substrate, where packing effects dominate the local structure. The thickness of the film is then examined as a function of temperature, and an apparent glass transition temperature is assumed to occur at the point where the thermal expansion coefficient of the film undergoes an abrupt change.

Polymer thin films—supported and freestanding—were formed by gradual cooling of the system after holding its temperature close to the critical point ($T^* = 2.2$) [13] for a period of time. One of the dimensions of the simulation box is significantly longer than the other two; the freestanding film that forms normal to the longer box edge is the result of a spontaneous minimization of the surface area, which reduces the free energy of the system. Supported films are formed by allowing polymer molecules to condense on an attractive substrate; after an initial equilibration period, the system is cooled down slowly and molecules gradually form a film on the substrate.

The temperature sequence employed in this work consisted of a series of step temperature changes. The initial configuration for any given temperature was taken to be the final configuration for the previous, higher temperature. Every simulation was prefaced by an extensive equilibration period. Only the second half of the data produced at each temperature were considered in the results reported here. With this protocol, the cooling rate is estimated to be in excess of 10^9 K s^{-1} for a typical polymeric material. It is conceivable that, upon cooling a simulated thin film, residual stresses could arise as a result of the contraction of the film. Unfortunately, the statistical uncertainty of our stress calculations is too high to determine whether the resulting values are significant or not.

Our results indicate that freestanding films exhibit a decrease in the apparent glass transition temperature when ultrathin dimensions are reached—in this case below 30σ. The other two supported films investigated here differ in the strength of the polymer-substrate attraction. In one case we used an attractive substrate having the same range and interaction strength parameters as the polymer. In the other case we used a "strongly" attractive surface, with a polymer-surface interaction energy twice as strong as that between polymer segments. The weakly attractive supported system exhibits a decrease of apparent T_g with decreasing thickness (Fig. 1). For the strongly attractive system, the apparent T_g increases for thinner films. Interestingly, the onset of the changes in the apparent T_g occurs at around 30σ for all three systems.

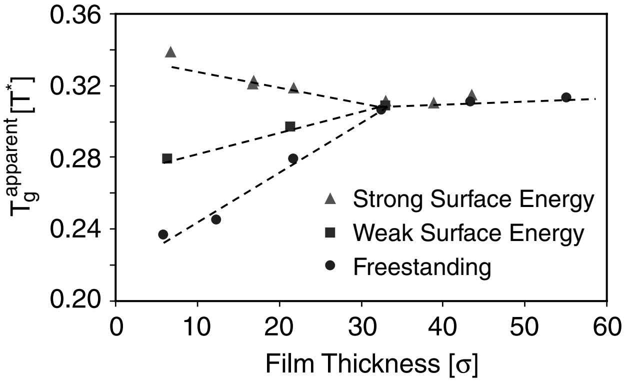

FIG. 1. Apparent glass transition temperature vs film thickness. The estimated uncertainty in simulated T_g's is approximately four times the size of the symbols.

II. Mobility.—A film of thickness 20σ was chosen to examine the segmental mobility for both supported and freestanding geometries. The 20σ film was chosen because, according to Fig. 1, at that thickness an increase in T_g is observed for a strongly attractive substrate, and a decrease is found for the freestanding film. We define mobility as the "local" mean-square displacement for each bead of the film. At the beginning of a production run ($t = 0$), the position of each bead in the system is recorded (in the direction normal to the substrate); the total distance traveled by each bead in three dimensions is then calculated at the end of the simulation (10^8 steps). The original position of the beads at $t = 0$ is used to define the ordinate axis in Fig. 2, which shows "mobility" profiles for freestanding and supported 20σ-thick films. The coordinates of individual segments are sampled every 10^4 steps.

Figure 2(a) shows that freestanding films exhibit a smooth decay of segmental mobility from the free surface to the center of the film. In contrast, Fig. 2(b) suggests that in supported films mobility is low in the immediate vicinity of the substrate, and that it gradually increases as the free interface is approached. The average radius of gyration (R_g) of the chains in these films is approximately 1.9σ; the films in Fig. 2 are therefore approximately $10R_g$ thick. The chains near the substrate are oriented parallel to it, and are slightly flattened with respect to those in the interior of the film. Near the substrate, the system exhibits small, nearly position-independent particle displacements (within the time scale of our simulations). We also note that those monomers which happen to be near the substrate at $t = 0$ undergo a small-amplitude, rattling motion around their original position, but do not leave the immediate vicinity of the substrate during the time

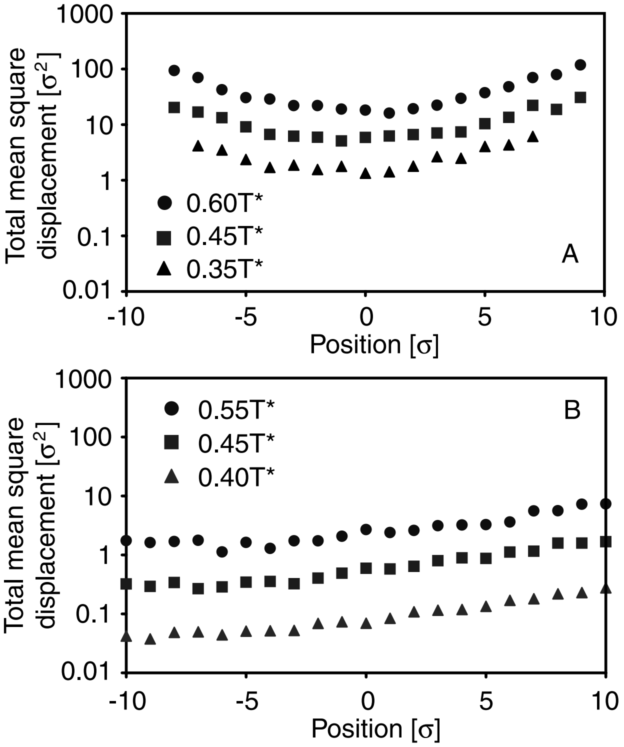

FIG. 2. High and Low mobility zones. (a) Freestanding film. The total simulation times are $t^* = 1905$, 2220, and 2315 at $T^* = 0.6$, 0.45, and 0.35, respectively. (b) Supported film. The total simulation times are $t^* = 2370$, 2425, and 2460 at $T^* = 0.55$, 0.45, and 0.40, respectively.

scale of our simulations. After some distance from the substrate, however, our results suggest that sites exhibit an almost linear increase of mobility with the proximity of the free surface. Note that experimental evidence in favor of a mobility gradient in polymer films has been presented in the literature [7,14].

III. Diffusion.—In order to calculate diffusion coefficients for 20σ films, only the lateral components of the displacement are taken into account in the evaluation of mean-square displacements. For reference, a bulk system was also simulated and, in that case, the three lateral components of the displacement were considered. Note that the density of the thin films increases as the temperature is lowered. Our simulations of bulk systems, however, are carried out at constant volume. To take such a contraction effect into consideration, our bulk simulations are conducted at the density encountered in the films at one of the lowest temperatures; for the bulk we use $\eta = 0.47$, which is the packing fraction corresponding to a 20σ-thick supported film at $T^* = 0.40$.

Figure 3 shows that at high temperatures the diffusion coefficient in both films (freestanding and supported) is slightly smaller than in the bulk. The inset corresponds to the logarithmic plot of the mean-square displacement as a function of time for the "slowest" system (lowest T^* and strong attraction); it serves to show that the expected linear relation is reached in all of our simulations. As the temperature is lowered, the freestanding film exhibits a higher diffusivity than the bulk. In contrast, the film supported on the strongly attractive substrate exhibits a markedly lower diffusivity than the bulk. These results are consistent with the apparent T_gs deduced from simulations of film contraction.

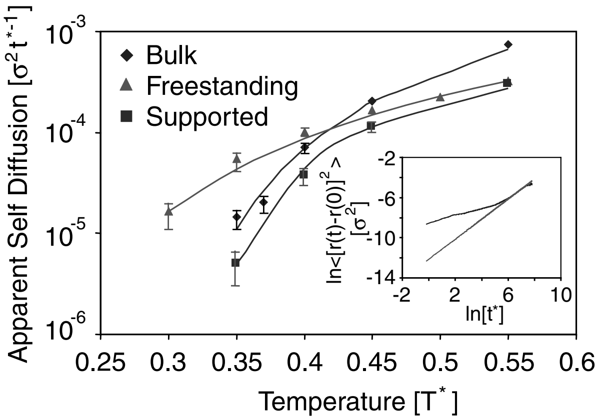

FIG. 3. Apparent self-diffusion coefficients in 20σ-thick films. The inset shows the log-log plot of the mean-square displacement (in σ^2) vs time (in t^*) for the supported film at $0.35T^*$; the straight line in that figure has unit slope. The packing fraction for all bulk simulations is $\eta = 0.47$. For supported films, $\eta = 0.42$, 0.44, 0.47, and 0.51 (at $T^* = 0.55$, 0.45, 0.4, and 0.35, respectively). For freestanding films $\eta = 0.42$, 0.43, 0.439, 0.455, 0.46, and 0.47 (at $T^* = 0.55$, 0.5, 0.45, 0.4, 0.35, and 0.3, respectively).

A modified Williams-Landel-Ferry equation (WLF) has often been used to fit experimental data and results of simulations for many polymers [15,16]. In that equation, the temperature dependence of diffusion is given by

$$\log\frac{D(T)}{D(T_g)} = \frac{C_1(T - T_g)}{C_2 + (T - T_g)}, \tag{1}$$

where $D(T)$ is the diffusivity of the sample, $D(T_g)$ is the diffusivity at the glass transition, and C_1 and C_2 are two pseudouniversal constants.

The polymer diffusion coefficient at the glass transition $D(T_g)$ was set at $10^{-17}\ \sigma^2 t^{*-1}$ [17]. Table I compares the WLF fitting results and the apparent glass transition temperatures estimated by the quenching method. Although the apparent glass transitions calculated by both methods agree qualitatively, those estimated from the diffusion simulation must be, and are, in fact, lower than those obtained from quenching simulations. Interestingly, the parameters C_1 and C_2 are not the same for the three systems, in spite of the fact that the polymeric material is the same in all three cases. This could be interpreted in terms of different relaxation times (which affect C_1), and distinct polymer

TABLE I. Apparent glass transition temperatures for three combinations of substrate-polymer interactions.

System	C_1	C_2	T_g^{WLF}	T_g^{apparent}
Freestanding	14.71	0.044	0.07	0.28
Bulk	15.03	0.026	0.24	0.31
Supported	14.08	0.013	0.29	0.32

fragility in the supported and freestanding films, which is related to C_2 and T_g [17,18]. On the basis of viscosity and relaxation-time data for polymers, it has been argued that if C_1 is in the 16 to 17 range, then fragility $= 1 - C_2/T_g$ [17]. The C_1 constants estimated for our model fluid are slightly below that range, but we can still view the ratio of C_2 and T_g as a rough measure of fragility; in that case, the calculated fragilities of the three systems (bulk, supported film, and freestanding film) are 0.89, 0.96, and 0.38, respectively. This simple analysis shows how the presence or absence of a substrate can induce changes in the relaxation times of ultrathin films, which in turn translate into changes of the transport and thermophysical properties of the material.

IV. Discussion and Conclusions.—The results presented here support the observation that the strength of the interactions between the substrate and a polymer can alter significantly the glass transition temperature of ultrathin films. Our results indicate that "strong" interactions between the substrate and the polymer increase the apparent T_g above the bulk value. These findings agree with our own local-thermal-probe and ellipsometry measurements of T_g [8]. In contrast, for freestanding films, our numerical data suggest that the apparent T_g is significantly lower than the bulk value. This latter result is consistent with the experimental data of Forrest *et al.* [1]. Our results also suggest that, for a given polymer, deviations of T_g from bulk behavior occur at approximately the same film thickness, regardless of the type of surface. This observation remains to be verified by measurements of T_g for a given polymer on different surfaces. Such measurements are currently under way in our laboratory.

For supported films, in the immediate vicinity of the substrate (the first few monomer layers), our results hint that mobility remains nearly unaltered by the distance to the surface. Away from the substrate, mobility increases with the proximity of the polymer-vacuum interface. The diffusion coefficients for supported and freestanding films are consistent with this picture; at the lower temperatures studied in this work, diffusion is several orders of magnitude faster in the freestanding film than on the supported film.

The picture of glass-forming systems that has emerged over the last decade depicts them as consisting of dynamic, collectively rearranging regions, characterized by a characteristic length scale [19]. In contrast, the results presented here suggest that in thin films a strongly attractive substrate provides a template for "slow" regions to form, and that such regions are always slow. Furthermore, as the thickness of a film decreases, the fraction of molecules influenced by the substrate increases, thereby reducing the dynamics of the entire film. The resulting large, slow-mobility regions are responsible for a higher glass transition temperature than in the bulk. In contrast, a free surface facilitates molecular mobility, with a corresponding decrease of T_g.

These results should be relatively general in that they were inferred from a minimalistic model of the system. It is interesting, however, to relate our predictions to experimental data. If we view our polymer model as consisting of freely jointed segments of length equal to the Kuhn length, then for polystyrene $\sigma \approx 2$ nm, and the observed deviations of the apparent T_g from the bulk start to occur at a thickness of approximately 60 nm. Our experiments for poly(styrene) on silicon oxide indicate that a decrease of T_g from the bulk value starts to occur also at about 60 nm, consistent with our theoretical observations. Note, however, that this is only one of several possible interpretations of our model; new simulations of less coarse-grained systems could shed new light on the behavior of various relaxation processes on the glass transition of thin polymer films.

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