Influence of Confinement on the Fragility of Antiplasticized and Pure Polymer Films

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(Received 13 February 2006; revised manuscript received 1 May 2006; published 27 July 2006)

We investigate by molecular dynamics simulation how thin film confinement modifies the fragility of a model glass-forming liquid characterized previously in the bulk. Film confinement is found to reduce the relative fragility of the polymer fluid, leading to effects similar to simulations of the addition of an antiplasticizer additive. A reduction of fragility is not observed for the antiplasticized polymer film. These effects are interpreted in terms of variation in the string (cooperatively moving segments) concentration with film confinement and the addition of antiplasticizing additives.

DOI: 10.1103/PhysRevLett.97.045502 PACS numbers: 61.43.Fs, 64.70.Pf

Diverse nanotechnology applications require an understanding of the property changes of glass-forming materials under conditions of nanoscale confinement (thin polymer films, features formed by nanoscale lithography, nanoimprinting, etc.). This fundamental technological problem has lead to experimental [1–4], and computational [5–7] studies seeking to characterize the role of confinement on glass formation in polymer films. In spite of these efforts, a consensus has yet to emerge about the effect of confinement on film properties. Most past studies have focused on the apparent glass transition temperature, T_g; it remains unclear how changes in that temperature correspond to changes of molecular mobility in ultrathin films. In this Letter, we gain significant new insights into these confinement effects by comparing the influence of confinement to the effect of antiplasticizer additives that, likewise, influence molecular packing. Fundamental studies of antiplasticizers have been extremely limited. One of their main characteristics is that, in contrast to the more widely studied plasticizers, antiplasticizer additives reduce T_g but *increase* the stiffness (shear and bulk modulus) of a polymeric material [8–11].

We surmise that a proper understanding of the influence of confinement on the dynamics of glass-forming films requires a characterization of the relative rate at which structural relaxation changes with temperature in comparison to a homogeneous fluid. This relative rate can be quantified through the so-called fragility (the strength of the temperature dependence of the structural relaxation) [12] of the polymer, and its response to antiplasticizers and confinement.

Recent theoretical arguments ascribe the change in fragility in polymer liquids [13] to variations in packing efficiency that arise from monomer structural shape. Based on these arguments, we hypothesize that the fragility of thin polymer films should differ from the bulk because the packing frustration must build to its bulk value with increasing thickness; under high confinement conditions this packing frustration should be weaker. This viewpoint leads to the general expectation, confirmed by simulations [5], that confinement should normally cause a reduction of liquid fragility, although the effect should be much smaller in strong glass-forming fluids that suffer from a lesser degree of packing frustration to begin with. More importantly, we also hypothesize that the addition of an antiplasticizer will lead to a stronger glass former, thereby reducing or even eliminating the confinement effects that are generally observed in thin polymer films.

To address the merit of this viewpoint, we perform molecular dynamics simulations of a confined (free standing) pure polymer film (referred to as the “PP” system) exhibiting “fragile” glass formation in the bulk, similar to synthetic polymers such as poly(styrene). The fragility of the pure polymer is compared to that of an antiplasticized polymer film (referred to as the “AP” system). Our simulations show that confinement of the PP system induces a large shift in the fragility and the relaxation times. In contrast, the AP melt shows little change in its fragility and a smaller shift of relaxation times upon confinement. It is also observed that cooperative molecular relaxation processes (stringlike motions) are highly inhomogeneous in the PP films, where free-surface effects propagate throughout the films. The AP films are much more homogeneous, and cooperative motion is only perturbed in the immediate vicinity of the free surface. Our results imply that finite-size effects on glass-forming liquids should be more important in fragile glass-forming liquids and should be highly dependent on fluid fragility, thereby providing a rationale for the sensitivity of polymer film confinement effects [14] to chain molecular structure.

The explicit model considered in this work has been fully characterized in the literature [5]; for conciseness, only its main elements are recounted here. The polymer consists of chains of 32 spherical Lennard-Jones (LJ) sites connected via a stiff harmonic spring. The LJ parameters for the polymer monomers are set to unity. The antiplasticizer additive consists of spherical LJ sites with a σ value that is half that of the polymer monomers ($\sigma = 0.5$); the ϵ parameter remains unity, which promotes entropic mixing. The mass of the antiplasticizer particles is 1/8 that of the polymer monomers, consistent with the relative volumes of each particle. The concentration of antiplasticizer particles in the AP systems is 5% by mass, or 30% by mole. For bulk configurations, we first simulate in an NPT ensemble at zero pressure at each T of interest to obtain an average density (ρ). Production runs are then conducted in the NVT ensemble at the average ρ. This lead to mass densities ranging from $\rho = 0.98$ at $1.1T_c$ to $\rho = 0.93$ at T_A (defined below) for the PP system, and $\rho = 1.01$ at $1.1T_c$ to $\rho = 0.96$ at T_A for the AP system. To prepare thin films, we began with a bulk configuration and doubled the length of the simulation box in the z direction, creating a free-standing film with surfaces perpendicular to the z direction. This was followed by an equilibration period of 10^7 time steps (one time step was $\Delta t = 0.001\tau_{\mathrm{LJ}}$, where $\tau_{\mathrm{LJ}} = \sqrt{\sigma^2 m/\epsilon}$ is the LJ time) using molecular dynamics at $T = 0.6$. This procedure for thin film generation yielded films that were 8.81σ and 9.03σ for the PP and AP systems, respectively, at $T \approx 1.23T_c$. After equilibration, temperature was lowered by $\Delta T = 0.01$ every 50 000 time steps to the range of interest, followed by an additional 2×10^6 time steps for equilibration. Production runs proceeded until at least 20 times the relaxation time at each T. In this work we restrict ourselves to the range $T \geq 1.1T_c$; for such temperatures, the relaxation times are reasonably small and are amenable to study by molecular dynamics simulations. All values reported in this Letter are in units reduced by the LJ parameters of the polymer monomer.

Several characteristic T's are used to characterize glass-forming materials [13]. These are inferred from the T dependence of specific relaxation times. The relaxation times considered in this work are extracted from the bond autocorrelation function, $C_b(t)$, of the bonds along the polymer backbone [15]. The relaxation times, τ, are defined as the time where $C_b(t)$ decays to $1/e \approx 0.368$, and are shown in Fig. 1. The reproducibility of our results was examined by generating three independent configurations at each T and examining the difference in τ. The run-to-run variation in τ was less than 4%, except at the lowest $T(1.1T_c)$, where the variation was approximately 10%. These uncertainties were propagated to the characteristic T's via a sensitivity analysis. The characteristic temperature where the relaxation times begin to deviate from Arrhenius behavior is denoted by T_A [16]; in a sense, T_A marks the onset of the glass-forming regime [13]. The values of T_A are shown in Table I, and the uncertainties are estimated to be less than 0.01 on all T_A values. We use T_c to designate the temperature where the system enters a second dynamic regime of glass formation and the temperature dependence of τ changes due to changing features of the energy landscape [13]. It is obtained by fitting τ to

$$\tau = A(T - T_c)^{-\gamma}, \tag{1}$$

where A and γ are adjustable parameters. The results of fitting to Eq. (1) are shown in the main part of Fig. 1. The

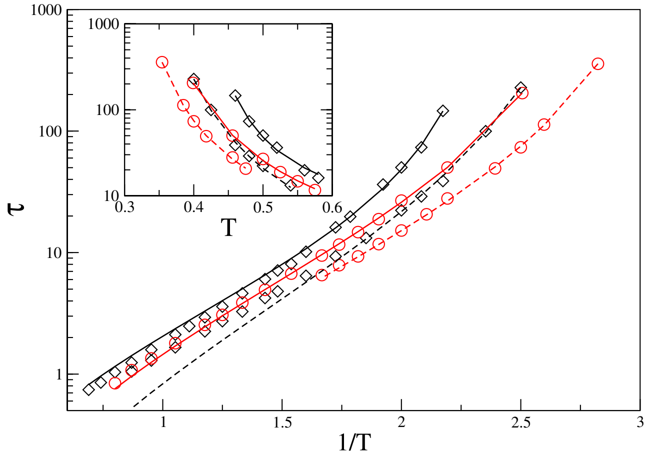

FIG. 1 (color online). Relaxation times plotted against T. The lines are fits to Eq. (1). The red circles (○) are for the AP system, the black diamonds (◇) are for the PP system, solid lines are used for the bulk configurations, and dashed lines for the thin films. The inset shows fits to Eq. (2) for the PP and AP film systems. All figures available online in color.

fits are excellent at lower temperatures, and they degrade as T increases. This is expected, since Eq. (1) is valid only close to T_c. The fitted parameters of fitting to Eq. (1) are shown in Table I, and the uncertainties in all values of T_c are less than 2%. The change in T_c is much smaller upon confinement for the AP systems compared to the PP systems.

Two additional characteristic temperatures, denoted by T_0 and T_g, are obtained through fits to the Vogel-Fulcher-Tammann-Hesse (VFTH) equation

$$\tau = \tau_0 e^{DT_0/T-T_0}, \tag{2}$$

where T_0 represents the "end" of the broad glass-formation regime. The value of D obtained from Eq. (2) provides an estimate of the fragility of the system; higher values of D correspond to "stronger" (or less fragile) glass formers [12]. The parameters in Eq. (2) are given in Table I.

In this work, the glass transition temperature T_g is taken to be the temperature where $\tau \approx 100$ s. If we assume that our value of τ_0, obtained in Eq. (2), is $\tau_0 \sim O(10^{-13})$ s,

TABLE I. Values of the characteristic T's and parameters of Eqs. (1) and (2) for the PP bulk (bPP), PP films (fPP), AP bulk (bAP), and AP films (fAP).

Parameter	bPP	fPP	bAP	fAP
T_A	0.59	0.56	0.51	0.51
T_c	0.42	0.35	0.34	0.31
T_g	0.37	0.27	0.26	0.25
T_0	0.36	0.24	0.23	0.24
γ	1.59	2.26	2.01	2.09
D	1.01	4.20	4.03	2.85

then T_g corresponds to the temperature where Eq. (2) predicts $\tau/\tau_0 = 10^{15}$. It should be noted that Eq. (2) is strictly valid in the low-temperature regime of glass formation, between T_c and T_g. Since none of our data lie in this regime, we fit Eq. (2) to τ values at the six lowest T's investigated here, and acknowledge that the large extrapolation required to obtain T_0 and T_g likely introduces a significant uncertainty in their estimation. This uncertainty is calculated to be less than 8% in all cases. We also note that the values of T_0 and T_g are only provided to enable comparisons to previous works on thin polymer films [which also fit to Eq. (2) above T_c]; the trends observed in this work are consistent with literature reports [6,7].

Having established the behavior of several characteristic T's, we now proceed to examine the cooperative mechanisms responsible for structural relaxation in the systems considered in this work. Entropy-based models on the dynamics of glass formation describe cooperatively rearranging regions of particles which grow upon cooling towards T_g [17]. Identifying these regions with the stringlike structures previously identified in glass-forming systems in the literature [18] implies that, at a common reduced temperature, T/T_c, the strings in the liquid should become smaller if the glass formation becomes stronger. The definition of the strings has been described previously [18,19]. For the PP systems, our procedure is identical to previous works [18,19]. Mobile particles were defined as those which had moved farther than the Brownian motion prediction over a time window determined from the maximum in the non-Gaussian parameter; 6% of the PP monomers were mobile, and this was not a function of T. In the AP system, the time window and Brownian predictions were determined from the motion of the polymer monomers; however, the mobile particles were defined as *all* particles which had moved farther than the Brownian prediction. This turned out to be approximately 23% of the antiplasticized system, and was also independent of temperature. While there is a drastic difference in the number of particles defined as mobile for the AP and PP systems, the results discussed below justify our approach. The mobile particles were analyzed for stringlike behavior. Two particles are defined as being part of the same string if the following relation is true:

$$\min[|\mathbf{r}_i(0) - \mathbf{r}_j(t^*)|, |\mathbf{r}_i(t^*) - \mathbf{r}_j(0)|] \leq \delta = 0.6\sigma_{ij}, \quad (3)$$

where σ_{ij} is the effective σ between the two particles for the LJ potential. This inclusion of σ_{ij} in the definition of δ in Eq. (3) makes our definition of the strings slightly different than in Ref. [18] and is necessary to properly account for the different sizes of the polymer monomers and the antiplasticizer particles.

Figure 2 shows the average string length (L_s) as a function of T for the PP and AP thin films. Results for the bulk are also shown for comparison. For the pure polymer, we find that the strings become shorter for the films, indicating that the material is less likely to relax cooperatively, and consistent with the picture that strong glass formers require smaller CRRs to relax compared to fragile ones. In contrast, the overall change in the length of the strings, L_s, is quite small when the AP system is confined to a thin film. We observe a small increase in L_s as T_c is approached from above. This is due to a depletion of antiplasticizer particles near the free surface, and an increase in the cooperativity near the free surface (not shown); the center of the film retains a bulklike antiplasticized polymer behavior. The fact that smaller strings are found in the antiplasticized polymer, even though we are looking at a larger number of particles for stringlike cooperativity, is a reassuring confirmation of the method employed to define the mobile particles. The composition of the strings as is shown in the inset to Fig. 2 as a function of temperature; the cooperative strings contain a large fraction of antiplasticizer particles, and that fraction increases as the temperature is lowered. In the thin films, the concentration of antiplasticizer in the strings is somewhat smaller than in the bulk, but it is still larger than the overall mole fraction of 30%.

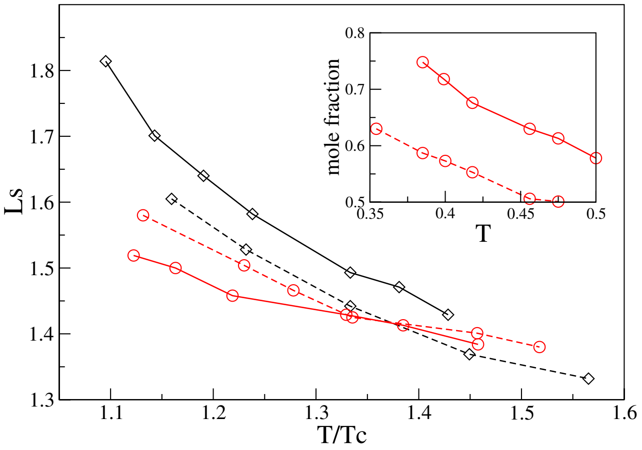

FIG. 2 (color online). Average string length as a function of T/T_c for the AP (○) and PP (◇) in the bulk (solid lines) and thin films (dashed lines). The inset shows the mole fraction of antiplasticizer particles in the cooperative strings ($L_s \geq 2$) in the AP bulk (solid) and thin film (dashed) systems at various T's.

We can gain insight into how confinement alters the nature of particle movement in thin polymer films by examining the distribution of mobile particles as a function of position away from the free surface, and by comparing relaxations near the free surface to those at the center of the film. Figure 3 shows the probability of finding a mobile particle at a given z position in the film at two different temperatures for the pure polymer and the mixture. The mobile particles are much more likely to reside near the free surfaces in the pure system, where the density is slightly reduced. For the AP mixture, this effect is not nearly as dramatic; the distribution of mobile particles in the AP film is much more homogeneous than in the pure

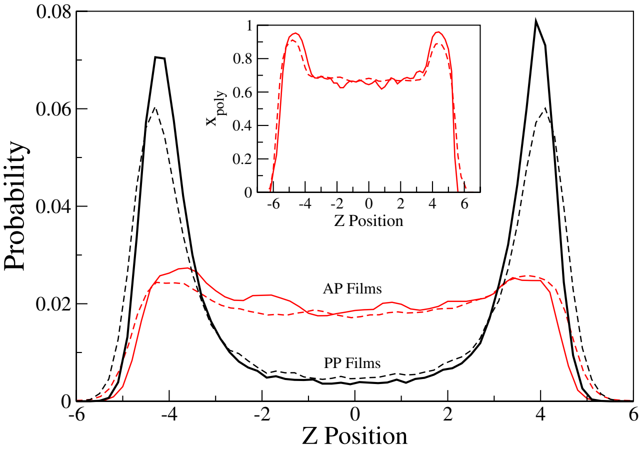

FIG. 3 (color online). String density within PP and AP polymer films at $T = 1.23T_c$ (solid lines) and $T = 1.51T_c$ (dashed lines). The inset shows the local composition (mole fraction polymer) of the AP films at the same two T's.

films. The inset to Fig. 3 shows the composition profile of the antiplasticized films; antiplasticizer particles do not segregate to the free surface (where more free volume is available). In fact, the free surface consists of mostly polymer monomers. We also see from Fig. 3 that raising T slightly expands the films, thereby leading to a slight suppression of the peaks near the free surfaces.

Overall, our results suggest that confining a fragile polymeric fluid to a thin film not only changes the glass transition temperature, but also changes the very nature of glass formation in these fluids. The packing frustration effects that are predicted to be responsible for fragile glass formation [13] can apparently be relieved either through confinement or the addition of an antiplasticizer additive, as both processes render fragile glass formers stronger. We find that the confinement of a strong (antiplasticized) glass former reduces the length scale over which the free surfaces affect the dynamics compared to the confined fragile glass former, and leads to smaller changes in fragility or the characteristic T's with confinement. These observations are consistent with and help explain recent experimental observations by Ellison *et al.* [2], who found that two different dopants (which made the polymer a stronger glass former in the bulk) could eliminate confinement effects on the T_g of supported PS films. These authors also found that simply adding the polymer monomer *did not* eliminate the confinement effects. In their discussion they suggest that the reduction of confinement effects is likely due the smaller CRRs associated with stronger glass-forming fluids, and our results substantiate this suggestion.

This work is supported by the SRC (No. 2005-OC-985) and the UW-NSEC.

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