Molecular dynamics of supercooled polymer films

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Abstract. We present results of molecular dynamics simulations for a supercooled polymer melt confined between two smooth and purely repulsive walls. The thickness D of the film is about 7 times the bulk radius of gyration. For all temperatures studied, a significant increase of the monomer and chain mobilities with respect to the bulk is observed. Preliminary results suggest that structural relaxation times exhibit a power-law behavior in the vicinity of a critical temperature $T_{\mathrm{c}}(D) \approx 0.39$ (in Lennard-Jones units). This estimate of $T_{\mathrm{c}}(D)$ is about 14% smaller than the corresponding bulk value. Despite this significant decrease the time dependence of various mean-square displacements seems to be unaffected by confinement if data for the same reduced temperatures $T - T_{\mathrm{c}}$ of the bulk and the film are compared.

1. INTRODUCTION

Polymer films find important applications in the stabilization of colloids or as protective coatings in microelectronics. Due to the structural complexity of the polymer these films are generally not crystalline. Rather they exhibit an amorphous, glassy structure. An important information for materials design is therefore how the glass transition is affected by the thin film geometry. Experiments on model systems reveal a stratified phenomenology. If the interaction between the polymers and the substrate is attractive, the glass transition temperature T_{g} of the films becomes larger than the bulk value for small film thicknesses [1]. Intuitively, this effect can be attributed to chains which are close enough to the substrate to 'feel' the attractive interaction. The motion of these chains should be slowed down with respect to the bulk. In a thin film almost all chains touch the attractive substrate. So, T_{g} should increase.

On the other hand, experiments on freely standing polystyrene films (i.e., no solid substrate, but two polymer-air interfaces) [2] find a dramatic decrease of T_{g} by up to 20% if the film thickness becomes much smaller than the chain size. An interesting explanation of this observation in terms of an interplay between polymer-specific properties and free-volume concepts has been proposed [3]. This decrease becomes much weaker if one or even both of the free interfaces are replaced by a weakly interacting solid substrate. Whereas the strong depression of T_{g} in the freely standing film could possibly be attributed to the significant release of geometric constraints at the air-polymer interface, the acceleration of the rstructural relaxation of a polymer melt between two (almost) neutral solid substrate is much harder to understand intuitively. Therefore, we tried to develop a simple continuum model to study such a situation by molecular dynamics simulations. The present paper discusses some preliminary results.

2. MODEL OF THE SIMULATION

We have studied a polymer system confined between two walls. Each wall interacts with the monomers via the repulsive potential $U_{\mathrm{w}} = 1/z^9$ where z denotes the absolute value of the distance to the wall. In the tangential direction the wall is completely smooth.

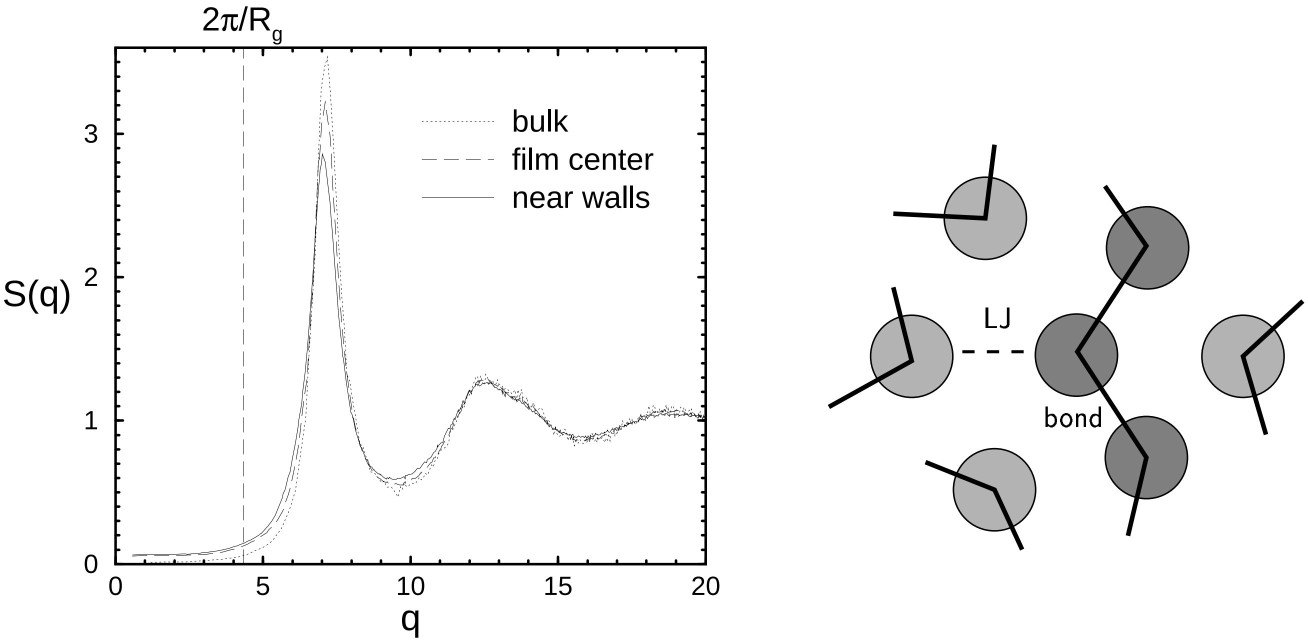

Figure 1. Left panel: Comparison of the static structure factor $S(q)$ of the melt in the bulk and in the film at $T = 0.46$ (critical temperature of mode-coupling theory in the bulk: $T_{\mathrm{c}} \simeq 0.45$ [4]). 'Near walls' and 'film center' mean averages over the regions close to the walls ($0 \leq z \leq 3.5$ and $6.5 \leq z \leq 10$) and the inner portion of the film ($3.5 \leq z \leq 6.5$). The vertical dashed line indicates the q-value corresponding to the bulk radius of gyration ($R_{\mathrm{g}}^2 \simeq 2.09$).
Right panel: Illustration of the potentials of the model. The bond-potential results from a superposition of the Lennard-Jones (LJ) and the FENE potentials. The minimum position of the bond-potential is smaller than that of the LJ-potential. This imcompatibility prevents crystallization, which is confirmed by the behavior of $S(q)$.

A truncated and shifted Lennard-Jones (LJ) potential was used for the interaction between all monomers of the system, i.e., $U_{\mathrm{LJ}}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^{6}]$ if $r < r_{\mathrm{c}}$ and $U_{\mathrm{LJ}}(r) = 0$ otherwise. Here, $r_{\mathrm{c}} = 2 \times 2^{1/6}\sigma$ where $\epsilon = 1$, $\sigma = 1$ (Lennard–Jones units). Connectivity between adjacent monomers of a chain was ensured by $U_{\mathrm{FENE}}(r) = -kR_0^2 \ln[1 - (r/R_0)^2]$ with $k = 15$ and $R_0 = 1.5$. The chain length is $N = 10$ ($<$ entanglement chain length). More details about the model can be found in [4, 5]. All film data correspond to a thickness $D = 10 \approx 7R_{\mathrm{g}}$ (R_{g} is the bulk radius of gyration). The linear dimension in direction parallel to the walls was $L = 10.9$. Our simulations are done at constant pressure [6]. The external pressure normal to the walls was set to $P_{\mathrm{n}} = 1$.

Non-bonded monomers prefer an average distance of $2^{1/6}$ due to LJ-interaction, whereas connected monomers tend to keep a distance of $0.9 - 1.0$ depending on the confinement. Our model contains therefore two incompatible length scales whose competition prevents crystallization at lower temperatures (see Fig. 1). This makes the model suitable for the study of the glass transition [7].

2. FILM VERSUS BULK DYNAMICS

For a polymeric system various kinds of displacements can be defined, such as the displacement of all monomers g_0, of inner monomers g_1, of the chains' center of mass g_3 or of the end monomers g_4. For instance, g_0 and g_3 are given by

$$g_0(t) = \frac{1}{NM} \sum_{i=1}^{NM} \left\langle [\boldsymbol{r}_i(t) - \boldsymbol{r}_i(0)]^2 \right\rangle \ , \quad g_3(t) = \frac{1}{M} \sum_{j=1}^{M} \left\langle [\boldsymbol{r}_{\mathrm{cm}}^j(t) - \boldsymbol{r}_{\mathrm{cm}}^j(0)]^2 \right\rangle \ , \tag{1}$$

where M denotes the number of chains and N the chain length. For the film these displacements are calculated parallel to the walls ($g_{0,||}$, $g_{1,||}$, etc.) so that $\boldsymbol{r} = (x, y, z)$ has to be replaced by $\boldsymbol{r}_{||} = (x, y)$.

Figure 2 compares $1.5\, g_{3,||}$ for the inner portion and the wall region of the film at $T = 0.45$ with g_3 of the bulk at $T = 0.46$. Note that the critical temperature of mode-coupling theory (MCT) is

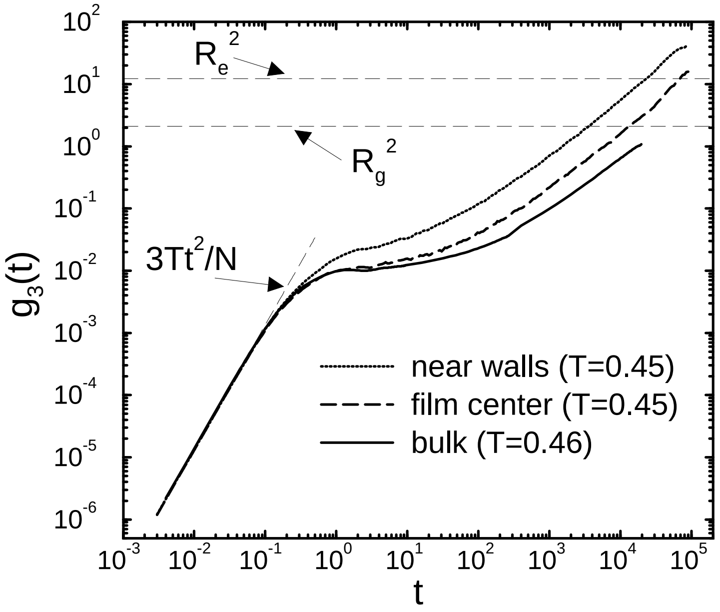

Figure 2. Mean-square displacement of the chains' center of mass, $g_3(t)$, for the bulk (at $T = 0.46$; note $T_c \simeq 0.45$) and in the film (at $T = 0.45$). For the film the displacements parallel to the wall are shown, which were multiplied by 3/2 to adjust them to the scale of the bulk. 'Near walls' and 'film center' mean averages over the regions close to the walls ($0 \leq z \leq 3.5$ and $6.5 \leq z \leq 10$) and the inner portion of the film ($3.5 \leq z \leq 6.5$). Only those chains which always remain in these regions were used for averaging. Two vertical dashed lines indicate the bulk end-to-end distance ($R_e^2 \simeq 12.3$) and radius of gyration ($R_g^2 \simeq 2.09$). The initial increase of $g_3(t)$ is ballistic, i.e., $g_3(t) \sim t^2$, the slope being determined by the thermal velocity. This behavior is indicated for $T = 0.46$.

$T_c \simeq 0.45$ for the bulk [4]. At very short times, the displacements increase ballistically ($g_3 \sim t^2$). The center of mass then behaves like a 'free particle'. It neither feels the presence of other chains nor of the walls. Therefore, film and bulk data coincide. However, as time increases, the interaction with the surrounding polymers slows the dynamics down and a plateau develops: A chain is then blocked in a 'cage' formed by its neighbors, from which it can only escape gradually. This blocking is more effective in the bulk than in the film. Chains close to the walls are faster than those in the film center and these are in turn faster than those of the bulk.

When averaging displacements over the whole film, the resulting curves resemble corresponding bulk data at higher temperature. To quantify this effect we calculated relaxation times from g_0, g_1, g_3 and g_4 by

$$g_{i,||}(\tau_{g,i}) := R^2_{g,||} \qquad (R^2_{g,||} = 2R_g^2/3, i = 0, 1, 3, 4)\ . \tag{2}$$

Since MCT was rather successful in describing the bulk dynamics [4, 5, 7], we tried to fit $\tau_{g,i}$ by

$$\tau_{g,i}(T) \propto |T - T_c(D)|^{-\gamma}\ . \tag{3}$$

The fits gave values for γ close to the bulk result $\gamma = 2.09$. Therefore, we fixed $\gamma = 2.09$ and determined $T_c(D)$. This yields $T_c(D) \simeq 0.39$ (see Fig. 3), a value which is significantly smaller (about 14%) than $T_c(\infty)$ ($\simeq 0.45$) of the bulk. Contrary to T_c, γ seems not to be affected by the confinement. Since γ is directly related to other MCT-exponents which determine the time dependence of the displacements in the plateau region, it should be possible to superimpose the simulation data of the bulk and the film when using the same distance to the respective critical temperatures. Figure 3 supports this expectation. The dominant influence of completely smooth walls on the dynamics seems to be a reduction of T_c, i.e., a mere shift of the temperature axis. This observation has to be tested by further investigations.

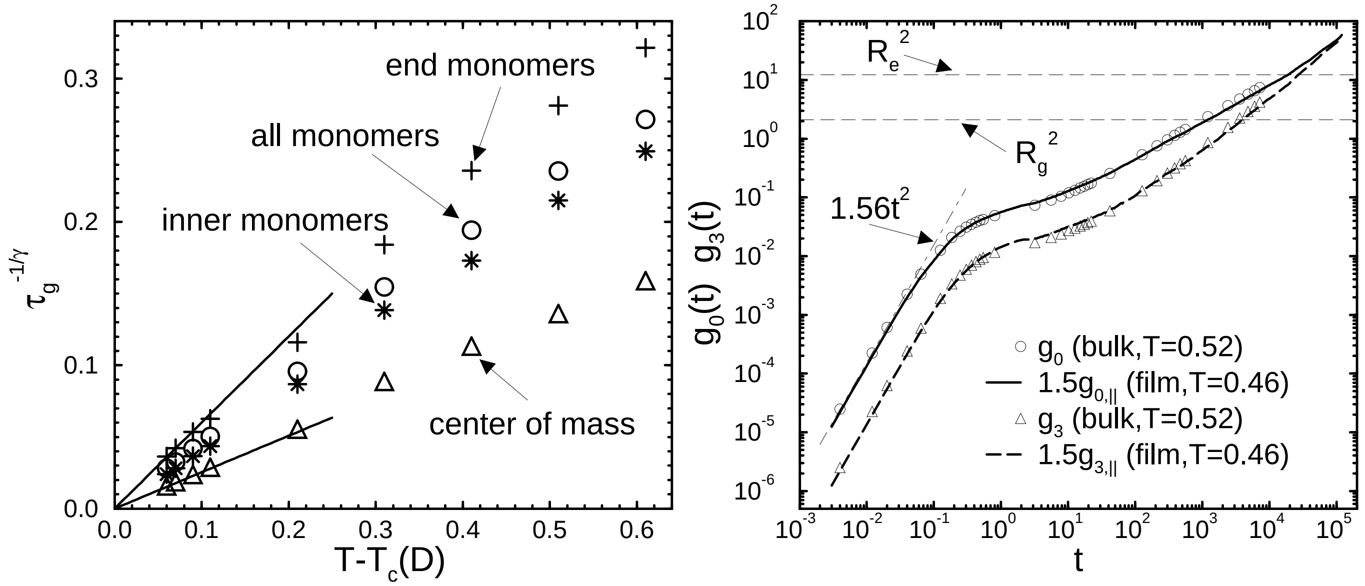

Figure 3. Left panel: Plot of $\tau_{\rm g}^{-1/\gamma}$ versus $T - T_{\rm c}(D)$. The time $\tau_{\rm g}$ was determined by Eq. (2) for the mean-square displacements of inner, end and all monomers and of the chains' center of mass. The mode-coupling exponent γ was taken from the bulk analysis ($\gamma = 2.09$ [4]). Holding $\gamma = 2.09$ fixed and fitting Eq. (3) to the last four data points (indicated by the solid lines) an average result of $T_{\rm c}(D) \simeq 0.39$ was obtained. This was used to rescale the temperature axis. Right panel: Mean-square displacements for all monomers, $g_0(t)$, and for the chains' center of mass $g_3(t)$ at the same $T - T_{\rm c} = 0.07$ for the bulk ($T = 0.52$, $T_{\rm c} = 0.45$) and for the film ($T = 0.46$, $T_{\rm c} = 0.39$). The displacements of the film were calculated parallel to the wall and averaged over the whole system. They were multiplied by $3/2$ to match the scale of the bulk. The bulk end-to-end distance ($R_{\rm e}^2 \simeq 12.3$) and radius of gyration ($R_{\rm g}^2 \simeq 2.09$) are indicated by vertical dashed lines. The other dashed line shows the initial ballistic motion of the monomers, i.e., $g_0(t) \sim t^2$, whose slope is $3T$. The corresponding numerical values for $T = 0.46$ ($= 1.38$) and $T = 0.52$ ($= 1.56$) cannot be distinguished on the scale of the figure.

3. Conclusions

We have reported molecular dynamics results on a polymer film of thickness $D \approx 7R_{\rm g}$ confined between two repulsive, completely smooth walls. Evidence was found for a significant reduction of $T_{\rm c}$ compared to the bulk. A qualitative explanation of this effect could be as follows: The walls do not hinder any motion parallel to them. Monomers close to them are thus subject to a significant friction only from the bulk side, but not from the walls. However, monomers in the film center are hindered by their neighbours from both sides. The larger displacements inside the film compared to the bulk can then be understood as a consequence of this faster mobility which is transferred towards the inner part. If this interpretation is correct, the effect should become weaker if one replaces the smooth walls by particles of monomer size.

Acknowledgments

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