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GLASS TRANSITION IN THIN POLYMER FILMS: A MOLECULAR DYNAMICS STUDY

FATHOLLAH VARNIK*, KURT BINDER
Johannes Gutenberg-Universität, Staudinger Weg 7
D–55099 Mainz, Germany
E-mail: varnik@uni-mainz.de, binder@uni-mainz.de

JÖRG BASCHNAGEL
Institut Charles Sadron, 6 rue Boussingault
67083 Strasbourg, France
E-mail: baschnag@ics.u-strasbg.fr

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A melt of non-entangled polymer chains confined between two smooth and purely repulsive walls is studied for various film thicknesses D and temperatures. The dynamics of the supercooled films is qualitatively identical to that of the bulk, but the walls lead to faster relaxation. To quantify this observation we analyze the data by the mode-coupling theory (MCT) of the glass transition. We find that the critical temperature of MCT, $T_{\rm c}(D)$, decreases with D and that $T - T_{\rm c}(D)$ is a relevant temperature scale. The static structure factor and dynamic correlation functions at intermediate times coincide with bulk behavior when compared for the same $T - T_{\rm c}(D)$.

Keywords: glass transition; structural glasses; polymer dynamics; thin polymer films

1. Introduction

Due to their thermal and elastic properties, polymers are often used as protective coatings in microelectronics, optical wave guides and other thermally fragile materials.[1] Furthermore, the high dielectric constant of many polymeric materials motivates their application in quite new fields, such as porters for electric (micro-) circuits.[2] In all of these applications, the polymers form an interface with another material. It is thus important to understand to what extent the properties of the polymers are influenced by the interface. In particular, one would like to know whether and how the glass transition temperature is influenced by the polymer-substrate interactions. The study of the glass transition in thin polymer films can help to find an answer to this interesting question.

In fact, experiments on thin polymer films [3,4,5,6] and also computer simulations [7] show a dependence of $T_{\rm g}$ on the film thickness D. However, the observed trends

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[*] present address: CECAM, ENS Lyon, 46 Alée d'Italie, 69007 Lyon, France

strongly depend on the system under consideration.[3,4,7] If the interaction between the polymers and the substrate is attractive, T_g of the films becomes larger than the bulk value for small D.[3] On the other hand, the opposite effect, $T_\mathrm{g}(\mathrm{film}) < \mathrm{T}_\mathrm{g}(\mathrm{bulk})$, is observed for weak polymer-substrate attraction or polymer-vacuum interface.[5,6]

In this context, molecular dynamics (MD) simulations can help elucidating the problem. An advantage of MD simulations is the detailed information about all particle positions and momenta at any time. This allows one to analyze simultaneously many different quantities. The systems studied can be chemically realistic or fairly simplified models. In the latter case one attempts to focus on general properties of the physical phenomenon. The following sections discuss such a simple model for a glass forming polymer melt confined between two walls.

2. A bead spring polymer model

We simulate a bead-spring model of a polymer melt. Consecutive monomers along a chain are bound by an anharmonic spring U_F, [8] while all monomers interact by a truncated and shifted Lennard-Jones potential U_LJ, [9]

$$U_\mathrm{F}(l) = -0.5kR_0^2 \ln\left[1-(l/R_0)^2\right] \quad \text{and} \quad U_\mathrm{LJ}(r) = \begin{cases} V(r)-V(r_\mathrm{c}) & \text{for } r < r_\mathrm{c}\,, \\ 0 & \text{else}\,. \end{cases} \tag{1}$$

Here, l is the bond length, $r_\mathrm{c} = 2\times 2^{1/6}\sigma$ and $V(r) = 4\epsilon\left[(\sigma/r)^{12} - (\sigma/r)^{6}\right]$. The lateral system size was about $L_x = L_y \approx 10\sigma \approx 7R_\mathrm{g}$, where R_g is the chain's radius of gyration. For this system finite size effects are practically absent.[10]

If the parameters are chosen as $\varepsilon = 1$, $\sigma = 1$ (fixing units of temperature and length), $k=30$, and $R_0=1.5$, the model exhibits two independent length scales, the minimum positions of the bond and of the Lennard-Jones potentials. The existence of these competing lengths favors an amorphous structure when cooling the liquid towards low T.[11,12] Previous studies in the bulk have shown [13] that the static structure factor $S(q)$ ($q =$ wave number) resembles real experiments very closely, that the density exhibits a kink at a (cooling rate dependent) $T_\mathrm{g} \approx 0.41$, that an analysis in terms of mode coupling theory [14] yields a critical temperature $T_\mathrm{c} \approx 0.45$, and that the Vogel-Fulcher-Tammann (VFT-) temperature is $T_0 \approx 0.34$.

3. Effects of the confinment

The polymer chains of our model are confined between two identical, perfectly smooth and purely repulsive walls.[15] The wall potential is $U_\mathrm{wall} = z^{-9}$, z denoting the transverse distance of a particle from a wall. The left panel of Fig. 1 shows the static structure factor, $S(q)$, at $T=0.46$ (note that $T_\mathrm{c}^\mathrm{bulk}=0.45$) for the bulk and for films of thicknesses $D=5$ and $D=10$. The main differences between the bulk and the film are found for small q and for the maximum position q_max. The compressibility of the film is higher, the value of q_max is shifted to slightly lower q and the magnitude of $S(q_\mathrm{max})$ is smaller than in the bulk. In the bulk one can observe a similar shift of q_max and decrease of $S(q_\mathrm{max})$ as the temperature increases.

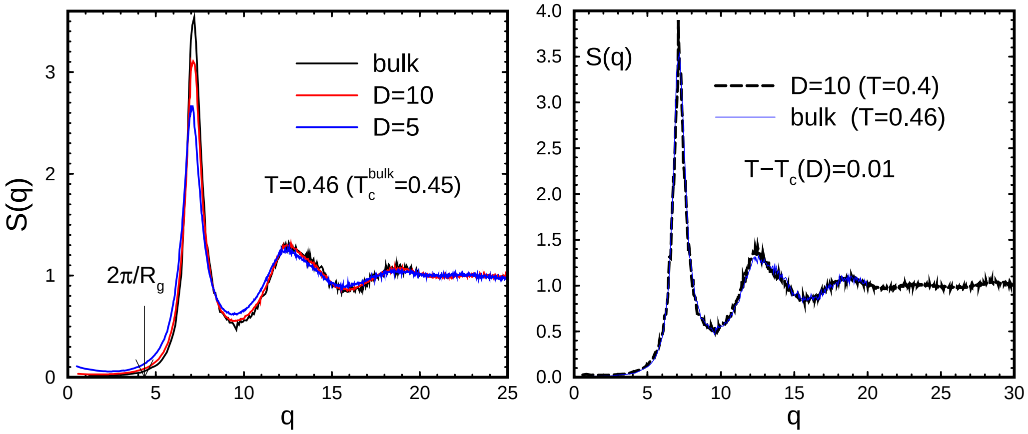

Figure 1: Left panel: Structure factor, $S(q)$, of the film compared to that of the bulk. The compressibility of the film is higher, the value of $q_{\max}$ is shifted to slightly lower q and the magnitude of $S(q_{\max})$ is smaller than in the bulk. Right panel: Comparison of the $S(q)$ of a film of thickness $D=10$ at $T=0.4$ with that of the bulk at $T=0.46$. Note that $T_{\mathrm{c}}(D=10)=0.39$ and $T_{\mathrm{c}}^{\mathrm{bulk}}=0.45$. Thus, $S(q)$ of the bulk and of the film coincide when compared for the same $T-T_{\mathrm{c}}$.

Therefore, the local packing of the monomers in the film seems to resemble that of the bulk at a higher temperature. Since the local structure of the melt has an important influence on its dynamic behavior in the supercooled state.[14] the left panel of Fig. 1 suggests that the film relaxes more easily than the bulk at the same temperature.

This expectation is borne out by a comparison of the mean-square displacements (MSD) of the films with the bulk. The left panel of Fig. 2 shows the MSD of all monomers, $g_0(t) = \left\langle[\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2\right\rangle$, and of the chains' center of mass, $g_3(t) = \left\langle[\mathbf{r}_{\mathrm{cm}}(t) - \mathbf{r}_{\mathrm{cm}}(0)]^2\right\rangle$, for $D = 10$ at $T=0.46$. At early and intermediate times the MSD's superimpose with the bulk data obtained at $T=0.52$. The right panel of the figure illustrates that this finding is not a mere coincidence, but also valid for other film thicknesses if the data are compared at the same $T - T_{\mathrm{c}}(D)$. Since the static structure factor exhibits the same superposition property [see right panel of Fig. 1], this suggests that the relaxation of a monomer in its local environment ("cage"), which is visible in the intermediate time window, where g_1 is close to $6r_{\mathrm{sc}}^2$ ($r_{\mathrm{sc}} \simeq 0.1\sigma$ = Lindemann parameter[16,17]), is determined by $S(q)$, as expected by MCT. However, as the monomers leave their cage, other (polymer-specific) factors begin to dominate the dynamics.

The critical temperatures used in Figs. 1 and 2 were computed from the α-relaxation time τ, which obeys a power law,

$$\tau(T) \propto (T - T_{\mathrm{c}})^{-\gamma}\,, \tag{2}$$

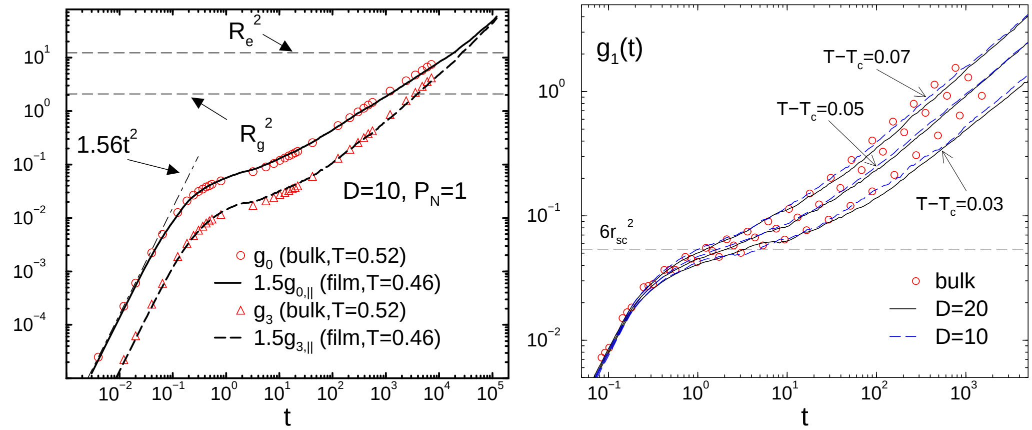

Figure 2: Left panel: Log-log plot of the mean-square displacements g_0 and g_3 versus time for a film of thickness $D=10$ at $T=0.46$ and the bulk at $T=0.52$. Both data sets are obtained at the external pressure $P_\mathrm{N}=1$. The dashed horizontal lines indicate the bulk mean-square end-to-end distance ($R_\mathrm{e}^2 \approx 12.3$) and the gyration radius ($R_\mathrm{g}^2 \approx 2.09$). The displacements in the film are computed in direction parallel to the wall, thus containing two independent coordinates only. In the bulk, however, all three coordinates are taken into account. The film data are therefore multiplied by a factor of 3/2. Right panel: Same comparison between bulk and films, but now for the mean-square displacement of the innermost monomer, g_1, and two film thicknesses at various distances from $T_\mathrm{c}(D)$ ($r_\mathrm{sc} \simeq 0.1\sigma$ = Lindemann parameter of the model[16,17]).

for temperatures close to T_c according to idealized MCT.[14] Although mode-coupling theory was originally developped for simple liquids, it could be successfully applied to the present polymer model in bulk.[9,16,17,18] Hence, one can test to what extent MCT can also describe the dynamics in confined geometry. We thus defined relaxation times, $\tau_{g,i}$, from the mean-square displacements, $g_i(t=\tau_{g,i})=1$, and tried to fit $\tau(T)$ by Eq. (2). Here, the index i denotes different choices of MSD's (i.e., $i=0=$ all monomers, $i=1=$ innermost monomers, etc.). The left panel of Fig. 3 shows $\tau_{g,i}^{-1/\gamma}$ for an extremely thin film of thickness $D=5$ (note that D stands for the wall-to-wall separation, the width of the region with non-vanishing density is therefore $D-2\approx 3$). In fact, the increase of $\tau_{g,i}$ upon cooling is well described by Eq. (2). The right panel of the figure depicts the critical temperatures, $T_\mathrm{c}(D)$, obtained from these fits.

Another possibility to fit the relaxation times at low temperatures is the (empirical) Vogel-Fulcher-Tammann (VFT-) equation

$$\tau(T) \propto \exp\left[\frac{c(D)}{T-T_0(D)}\right] . \qquad (3)$$

Here, $T_0 < T_\mathrm{g}$ is the so-called VFT-temperature and c is a positive constant. We

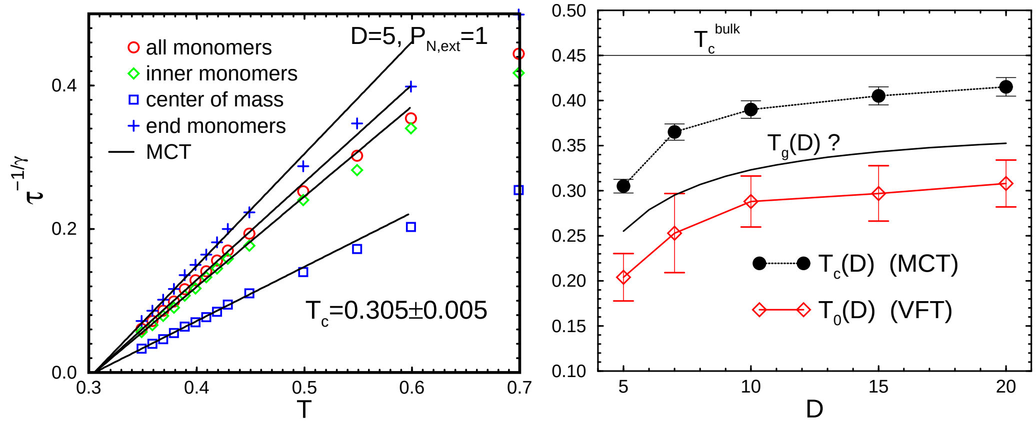

Figure 3: Left panel: $\tau_{g,i}^{-1/\gamma}$ ($\gamma = 2.5$) for a film of thickness $D = 5$. At low temperatures, the data are linarized for all different kinds of relaxation times (i denotes the different MSD's, i.e., all monomers, inner monomers, etc.). Thus, the increase of $\tau_{g,i}$ upon cooling is well described by the power law (2). Right panel: $T_{\mathrm{c}}(D)$ as obtained from fits like that shown in the left panel of this figure. The VFT-temperature, $T_0(D)$, obtained from fits to Eq. (3), is also shown. Note that the glass transition temperature T_{g} lies *between* these two temperatures: $T_{\mathrm{c}} < T_{\mathrm{g}} < T_0$. Thus, $T_{\mathrm{g}}(D)$ lies somewhere between $T_0(D)$ and $T_{\mathrm{c}}(D)$. The solid line gives a suggestion for the possible form of $T_{\mathrm{g}}(D)$ determined from the empirical relation $T_{\mathrm{c}} \approx 1.2T_{\mathrm{g}}$.

used the VFT-formula as an independent approach and determined T_0 for various film thicknesses. A plot of $T_{\mathrm{c}}(D)$ and $T_0(D)$ is shown in the right panel of Fig. 3. As $T_0 < T_{\mathrm{g}} < T_{\mathrm{c}}$, the figure suggests that also the glass transition temperature should be reduced for stronger confinements. The fact that $T_0 < T_{\mathrm{c}}$ also implies that, compared to a MCT-fit [see Eq. (2)], a fit to Eq. (3) involves an extrapolation towards a farther temperature thus leading to a larger uncertainity in T_0. This explains the large error bars in the case of $T_0(D)$.

4. Conclusion

We presented MD simulation results of thin (non-entangled) polymer films. The film geometry was realized by introducing two perfectly smooth and purely repulsive walls. Our main finding is that the dynamics of the supercooled films is accelerated compared to the bulk so that characteristic temperatures, such as $T_{\mathrm{c}}(D)$ or $T_0(D)$, decrease with decreasing film thickness. Partly, this can be rationalized in the framework of mode-coupling theory by the temperature dependence of the static structure factor, for which the relevant temperature scale seems to be $T - T_{\mathrm{c}}$. A more detailed analysis to what extent MCT can be applied to our model is under way.[19]

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