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A coarse-grained molecular dynamics study of segmental structure and mobility in capped crosslinked copolymer films

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We present results from molecular-dynamics simulations of a generic bead-spring model of polymer chains confined between solid walls and report on the glass-transition temperature and segmental dynamics as a function of film thickness and mesh size (the end-to-end distance of the sub-chains in the crosslinked polymer networks). Apparently, the glass-transition temperature displayed a steep increase for mesh-size values much smaller than the radius of gyration of the bulk chains, otherwise it remained invariant to mesh-size variations. The rise in the glass-transition temperature with decreasing mesh size and film thickness was accompanied by a monotonic slowing-down of segmental dynamics on all studied length scales. This observation is attributed to the correspondingly decreased width of the bulk density layer that was obtained in films whose thickness was larger than the end-to-end distance of the bulk polymer chains. To test this hypothesis, additional simulations were performed in which the crystalline walls were replaced with amorphous or rough walls. In the amorphous case, the high polymer density close to the walls vanished, but the dynamic response of the film was not affected. The rough walls, on the other hand, only slightly decreased the density close to the walls and led to a minor slowing-down in the dynamics at large length-scales.

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I. INTRODUCTION

It is well established that polymer properties change when the material is supported on a substrate or confined between walls whose distance approaches nanoscopic length scales. Thin polymer films are important for the microelectronics industry, and confined polymers in general have been frequently used as a simplified model of composite materials in which confinement effects play an important role in affecting macromechanics, friction, and wear resistance.

Polymer nanocomposites, especially, comprise a family of materials with an abundant of industrial applications, e.g., in the manufacturing of car tires. The mechanical properties of elastomer-based nanocomposites, consisting of inorganic nanoparticles dispersed in the polymer matrix, depend drastically on the interactions between the polymer matrix and the nanofillers. Different dynamic moduli can be obtained by tuning these interactions, which leads to the desired increase of mechanical reinforcement at low strain magnitudes. However, a significant loss of the composite’s rigidity appears at higher strain magnitudes. This loss of rigidity is colloquially called the “Payne effect.” It is believed that the Payne effect arises from the interrelation of the material’s viscoelastic properties with its microstructure, the polymer’s segmental mobility (especially in the interfacial layers), and the chemistry-specific polymer-filler interactions. Rigorous control of molecular-scale phenomena may therefore lead to the design of improved nanocomposites with tailor-made mechanical properties. Contemporary computer simulations, complimentary to experimental investigations, constitute an exemplary approach for providing additional insight into the essential physical mechanisms that are responsible for the modified mechanics of filled elastomers in relation to the mechanical properties of bulk polymers. In such composite materials additional interfaces are created once the filler volume fraction is increased, which may result in a situation where the polymer chains will be effectively confined among the filler particles.

To study these confinement effects, we performed molecular-dynamics (MD) simulations of bead-spring polymer films confined between two solid (crystalline and amorphous) walls. Simulations of the corresponding bulk polymer were also performed to provide with necessary comparisons. In a previous publication, we discussed the influence of confinement and cross-link density on the structural properties of the polymer melt, whereas presently we focused our attention on segmental dynamics. The influence of the walls’ structure on the density distribution and mobility of the confined polymer is also discussed. Note that we did not intend to provide a thorough review of the research efforts devoted to confinement effects, which is a formidable task in itself, but instead mentioned below only a few, and from our point of view, important studies.

The dynamics in thin polymer films have been studied extensively with a variety of experimental methods. The consensus is that the dynamic response of a polymer film is highly dependent on the degree of confinement, the presence of free interfaces, and the polymer-wall interactions. The results, though, seem rather influenced by the employed experimental technique and the preparation procedure of the samples, as contradictory results have often been reported. For instance, a number of ellipsometry and fluorescence results indicate a large suppression in the $T_g$, whereas incoherent neutron scattering experiments suggest both enhancement and suppression.
in the $T_g$, as inferred by mobility measurements.\textsuperscript{26–30} The effect of the polymer-wall interactions becomes important when the thickness of the film becomes smaller than a specified length scale.\textsuperscript{31,32} Dynamic fragility, a measure of the glass transition abruptness of glass-forming materials, has been employed to explain why certain polymers display different confinement effects than others. For example, recent results of Evans et al.\textsuperscript{32} obtained by differential scanning calorimetry experiments with single-layered polymer films supported on silicon substrates (systems with no substantial polymer-substrate interactions), showed a one-to-one correlation between higher fragility and the amplitude of the $T_g$ shift upon changing the film thickness.

Simulations of polymer chains confined between structureless, attractive walls, have shown an acceleration in the dynamics compared to the bulk polymer.\textsuperscript{33} A similar behavior has been observed in films with structure walls and high polymer density,\textsuperscript{34} whereas the opposite has been reported in films of lower density.\textsuperscript{35} Binder et al.\textsuperscript{33} performed molecular-dynamics and Monte Carlo simulations of short polymer chains confined between structureless walls and reported an acceleration of the overall segmental dynamics upon increasing the degree of confinement. A higher segmental mobility in the interfacial layers than in the middle layers of the films was observed as well. The authors argued in favor of the lubricating effect of the walls: presumably, the smooth surface did not exert any friction on nearby monomers and therefore caused an overall acceleration of the segmental relaxation process. Simulations of freely standing atactic-polypolypropylene films, performed by Mansfield and Theodorou,\textsuperscript{36} suggested that the role played by a free interface is to increase the mobility of the nearest polymer segments and therefore to reduce the overall glass-transition temperature of the films. Essentially, it has been confirmed that the glass-transition temperature in films is significantly different from that of the bulk, depending on the strength of the wall-polymer interactions.\textsuperscript{37,38} In addition, molecular-dynamics simulations of a filler particle surrounded by polymer chains showed that for attractive polymer-filler interactions, the glass-transition temperature was higher than in the pure polymer melt, whereas the opposite was observed when unfavorable adhesion interactions were employed.\textsuperscript{38}

Despite the high attention that has been given to the effect of confinement and adhesion interactions on the glass-transition temperature and segmental dynamics in thin polymer films, the combined effect of cross-linking and confinement is much less investigated, especially with molecular-dynamics simulations.\textsuperscript{39} Lin and Khare\textsuperscript{40} used a single-step polymerization algorithm to generate a crosslinked epoxy-based composite and concluded that the incorporation of filler particles (which essentially confined the polymer matrix in between) decreased the volumetric thermal-expansion coefficient but did not change the glass-transition temperature. Liu et al.\textsuperscript{41,42} performed molecular-dynamics simulations of model elastomers to study the effect of temperature, pressure, and cross-link density variations on structure and dynamics. They reported an increased glass-transition temperature $T_g$ with increased pressure or degree of cross-linking and showed that the time-pressure superposition principle was valid at the chain length scale but failed at smaller scales, seemingly due to the increased heterogeneity in the relaxation of the incoherent scattering function, whereas the opposite was observed for the time-temperature superposition. Fan and Yuen\textsuperscript{43} simulated the glass-transition temperature, the linear thermal-expansion coefficients, and Young’s modulus of cured epoxies and showed that the simulated thermomechanical properties were in close agreement with experimental results. Bandyopadhyay et al.\textsuperscript{44,45} studied the distribution of cross-links in epoxy polymers and found that the coefficient of thermal expansion (CTE) decreased with increasing the degree of cross-linking and attributed their observations to the (cross-link induced) inhibition of the polymer-network volume expansion upon heating. Yang and Qi\textsuperscript{46} employed MD simulations to calculate a collection of thermomechanical properties in crosslinked epoxy networks: upon cross-linking, the $T_g$ increased whereas the CTE in the rubbery state decreased. They also showed that the CTE in the glassy state did not depend on the curing degree, in good agreement with existing simulations.

The purpose of the present study is to provide with rather general insights into the effects that the surface structure (crystalline vs amorphous), cross-link density $\rho_{cl}$ and film thickness $L_{\text{film}}$ may exert on the glass-transition temperature and segmental relaxation of the bead-spring copolymer model. Further, we aim to produce a basis for future studies which will attempt to connect the macroscopic mechanical properties of the microscopic dynamics that are observed in similarly confined polymer models. Therefore, no effort was made to provide a one-to-one correspondence with experimental results since we are interested in the generalized “universal” behavior of confined polymers and not in properties that may depend on chemical details. Implications concerning the development of heterogeneous dynamics in polymer films are also discussed. A word of caution is in order though.

The employed model is described in Section II. In Section III, we present our findings on the influence of variations in cross-link density and confinement on the glass-transition temperature in films with crystalline walls. Subsequently, we consider the segmental relaxation by means of the incoherent intermediate scattering function, which can be probed by neutron scattering experiments and allows the examination of the dynamic response of the films on different length scales. This section culminates to a discussion concerning the influence that was exerted by the geometrical properties of the walls on the structure and dynamics of the confined polymer, which was modeled by means of the spatial distribution of monomers upon replacing the crystalline walls with amorphous ones. The paper is finalized in Section IV with conclusions.

## II. SIMULATED MODELS AND METHODS

We performed molecular-dynamics constant temperature–constant pressure (NPT) simulations of coarse-grained, amorphous polymer systems consisting of non-entangled polymer chains, confined between two crystalline or amorphous walls. The simulations were performed using the LAMMPS MD software package.\textsuperscript{47} Periodic boundary conditions were implemented in all three dimensions of the simulation box. The polymer melt consisted of 100 linear random copolymer
chains of 50 monomers per chain. 40 of the monomer units in each chain (type A) were of different type than the rest (type B). Each crystalline wall was composed of three lateral layers of equally sized non-bonded beads arranged in a hexagonal closed packed regular lattice. They were periodically infinite along the lateral dimensions and confined the polymer melt along the perpendicular direction (Fig. 1). We used three layers, which along with their periodic images amounted to six layers for each of the two walls, to avoid interactions among the polymer chains and their periodic images. The thickness of the six crystalline wall layers was calculated equal to 4.64σ regardless of temperature or pressure.

The Lennard-Jones (LJ) units of measurement are used throughout the text, i.e., m is the unit of mass, ε is the unit of energy, σ is the unit of length, and τ = σ√m/ε is the unit of time. Newton’s equations of motion were integrated using the velocity-Verlet algorithm with a time step of δτ = 0.001τ.

Non-bonded interactions were modelled with a modified LJ 12-6 potential,

\[ U_{bn(r)} = 4\varepsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} + S_f(r) \left( r < r_{cut}^{out} \right) . \]  

In Eq. (1), \( S_f(r) \) denotes a switching function that ramped the energy (and force) smoothly to zero between \( r_{cut}^{in} = 3.25\sigma \) and \( r_{cut}^{out} = 3.50\sigma \). The LJ parameters for the monomer units were \( \sigma_{AA} = \sigma, \ v_{AA} = \varepsilon, m_A = m, \sigma_{BB} = 1.2\sigma, \ m_B = (\sigma_B)^3m, \ v_{BB} = \varepsilon, \) and for the beads of the crystalline walls \( \sigma_{SS} = 0.85\sigma \) and \( \varepsilon_{SS} = 100\varepsilon \). The LJ parameters between beads of different types were calculated according to Lorentz-Berthelot rule, \( \sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2 \), but the LJ energy parameters were predefined, i.e., \( \varepsilon_{AB} = \varepsilon_{AW} = \varepsilon_{BW} = \varepsilon \). The interaction strength between wall beads, \( \varepsilon_{WW} \), was chosen large enough to ensure that the crystallinity of the walls was never broken. This high value of \( \varepsilon_{WW} \) was the reason of the relatively small time step magnitude that was chosen. The size of the wall beads, \( \sigma_{WW} \), was smaller than the smallest monomer type to avoid the adsorption of the monomer units on the internal wall layers. The chosen parameters were based on previous studies of similar model systems. The amorphous walls were created by increasing the diameter of a random number of wall-beads from its original value of 0.85σ to 1.10σ to make the whole system relaxed to a new state of equilibrium.

Covalently bonded beads interacted through a combination of an attractive Finite-Extensible-Nonlinear-Elastic (FENE) potential and a repulsive and truncated LJ 12-6 potential,

\[ U_{bn(r)} = -0.5k_{FENE}R_{max}^2\ln\left(1 - \left( \frac{r}{R_{max}} \right)^2 \right) + 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] + \varepsilon. \]  

The parameters \( k_{FENE} \) and \( R_{max} \) denote the stiffness and the maximum elongation of the spring, respectively, \( \varepsilon \) is the LJ energy parameter, and \( \sigma \) is the collision diameter of the interacting pair of beads. The stiffness and maximum elongation of the bonded potential were set equal to \( k_{FENE} = 30\varepsilon/\sigma^2 \) and \( R_{max} = 1.5\sigma \), respectively. The LJ parameters \( \varepsilon \) and \( \sigma \) had the same values with their non-bonded counterparts. This particular choice of bonded and non-bonded interactions prevents chain crossings and full crystallization and allows the system to undergo a transition to a supercooled state, allowing thus the study of the glass-transition temperature in a generalized context (i.e., disregarding material-specific properties). Further, bead-spring polymer chains do not become stiffer with decreasing temperature. The effect of these characteristics of the employed model on the conformational behavior of the chains, especially at low temperatures, was not included in the present investigation. Finally, we note that the smaller length scale accessible to these kinds of models cannot be smaller than the typical Kuhn-length values of rubbers (close to 1 nm).

Three polymer films with different thickness were simulated. At fixed temperature \( T = 0.8\varepsilon/k_B \) and isotropic pressure \( P = 0\varepsilon/\sigma^3 \), the thicknesses of the films with crystalline walls were 18.8σ (thick film), 10.1σ (thin film), and 4.3σ (ultrathin film), which approximately corresponded to 5.2, 2.8, and 1.2 times, respectively, larger than the average radius of gyration of the chains in the non-crosslinked bulk. Films with different thicknesses had different lateral dimensions so that they would have the same film-averaged mass density at fixed temperature and pressure. Due to the crystallinity of the walls, the lateral dimensions of each film were only approximately equal, but in all cases, the difference was smaller than 0.5σ. The thickness of the films decreased with decreasing temperature, Figure 2, with a larger absolute decrease observed in thicker films.

![FIG. 1. An illustration of typical snapshots of the computed molecular trajectory. The simulated films consisted of random copolymer chains confined between two crystalline walls. Three different colors denote different bead types.](image-url)

![FIG. 2. Simulated film thickness as a function of temperature in the films with crystalline walls. The thickness of the film was decreasing with decreasing temperature, while the average lateral dimensions of the periodic box remained constant owing to the crystallinity of the walls. In each case, an average isotropic pressure \( P = 0\varepsilon/\sigma^3 \) was imposed on the whole system. The error bars were smaller than the size of the data points.](image-url)
During the equilibration and production runs, we used the values recommended in the LAMMPS manual for the thermostat and barostat parameters, i.e., temperature and pressure were allowed to relax to the specified value over a time-span of 0.1τ and 1.0τ, respectively.\(^\text{17}\) We regarded the simulated systems as equilibrated after the autocorrelation function \(\varphi_{ee}(t)\) of the end-to-end vector \(\mathbf{R}_{ee}\) of the chains,\

\[
\varphi_{ee}(t) = \frac{\langle \mathbf{R}_{ee}(t_0) \cdot \mathbf{R}_{ee}(t_0 + t) \rangle - \langle \mathbf{R}_{ee} \rangle^2}{\langle \mathbf{R}_{ee}^2 \rangle - \langle \mathbf{R}_{ee} \rangle^2},
\]

had decayed to zero. In reality, we allowed the systems to equilibrate for longer times (\(\Delta t \approx 90,000\tau\)) than the relaxation time of \(\varphi_{ee}\) to ensure that a thorough equilibration was established. The equilibration procedure was described in more detail in a previous publication.\(^\text{13}\)

We simulated both crosslinked and non-crosslinked polymer systems, using a static method of cross-linking to produce the polymer networks. Namely, the last snapshot of the equilibration trajectory of each system was used to create cross-link bonds between randomly chosen pairs of monomer units (regardless of their type) until the desired value of the cross-link (number) density

\[
\rho_{cl} = \frac{\text{total number of crosslinks}}{\text{number of chains}}
\]

was achieved. The following cross-linking protocol was employed: First, all the monomer pairs belonging to different polymer chains lying at a distance shorter than 1.4σ (smaller than the maximum elongation length of the FENE springs) were identified. Subsequently, the order of the chosen pairs was “shuffled” using a pseudo-random number generator. Finally, a number of those pairs were linked by the same FENE springs, starting from the first one in the shuffled sequence, until the target cross-link density was reached. Using this method, cross-linked clusters were created with only a small fraction of free (non-cross-linked) chains. We used the following cross-link density values of \(\rho_{cl} = \{1, 2, 3, 4, 8\}\) cross-links per chain, which corresponded to a variable mesh size (the end-to-end distance of the subchains) \(L_{\text{mesh}} = \{4.7, 3.0, 2.3, 2.2, 1.7\}\) σ. The \(L_{\text{mesh}}\) values were calculated directly from the simulation trajectories. The standard deviation of the average mesh-size values was approximately 0.8−1.7σ (higher average value of the mesh size corresponded to a higher standard deviation). Thus, the polydispersity of the end-to-end distance of the subchains of the crosslinked mesh was rather high, since the standard deviation was comparable to the average mesh size value. We also note that a number of free chains were always present in the crosslinked systems.

The end-to-end distance of the polymer chains was calculated equal to \(R_{ee} = 8.9 \pm 0.1\)σ, by averaging over all studied systems at \(T = 0.8\varepsilon/\kappa_B\) including all different cross-link densities and degrees of confinement, and the radius of gyration was \(R_{g} = 3.6 \pm 0.1\)σ. The latter was found not much different from the radius of gyration of the bulk polymer chains at the same temperature, \(R_{g} = 3.7 \pm 0.1\)σ. The spatial distribution of cross-links along the direction perpendicular to the walls displayed some deviations from uniformity, as a higher concentration of cross-links was produced closer to the walls. This was probably due to a higher polymer density in the polymer-wall interfacial layers than in the middle of the films.\(^\text{13}\)

The effect of film thickness and mesh-size on segmental mobility was studied at temperatures above \(T_g\)\((L_{\text{film}}, L_{\text{mesh}})\), i.e., above the glass-transition temperature of a specific film thickness \(L_{\text{film}}\) and mesh size \(L_{\text{mesh}}\). All simulated systems can be safely regarded as well-equilibrated in this high-temperature range. To further study the relaxation of single “particle” motions, we calculated the incoherent intermediate scattering function

\[
S_{\text{inc}}(q, t) = \frac{1}{N} \sum_{j=1}^{N} \exp \left\{ -i\mathbf{q} \cdot \left[ \mathbf{r}_j(t) - \mathbf{r}_j(0) \right] \right\},
\]

which is measured in neutron-scattering experiments to probe the various relaxation modes in macromolecular systems.\(^\text{19}\) In Eq. (5), \(N\) denotes the total number of monomers in the system (in our simulations, these were individual bead segments), \(r_j(t)\) is the position of the \(j\)th monomer at time \(t\), and \(\mathbf{q}\) is the scattering vector that defines the length scale \(l_q = 2\pi/q\) with the dominant contributions to the relaxation process. Thus, relaxation times on different length scales can be calculated by varying the magnitude \(q\) of the scattering vector.\(^\text{20}\) In Section III, we present our simulation results of the incoherent relaxation in the region between \(q = 7.0\)σ\(^{−1}\), which corresponded approximately to the first peak in the overall static structure factor\(^\text{13}\) and \(q = 1.0\)σ\(^{−1}\), which corresponded to a length scale between the end-to-end distance and the gyration radius of the chains. The \(S_{\text{inc}}(q, t)\) for a given \(q\) was computed by calculating the average value of three wave vectors \(\mathbf{q}\) with the same magnitude but different directions along the primary Cartesian axes, unless otherwise stated.

III. RESULTS AND DISCUSSION

A. Glass-transition temperature

Simulations of coarse-grained polymers can only access dynamical processes on scales larger than the effective bead size; local (intra-monomer) scale dynamics are inaccessible. Nevertheless, these large scale dynamics are those which are mainly responsible for controlling the rheological properties of a glass-forming material.\(^\text{19}\) These properties depend considerably on how larger or smaller is the working temperature from the \(T_g\), and therefore, we devoted a part of our research for the computation of the glass-transition temperature of the studied films.

We followed a volumetric method to calculate the \(T_g\) (see Figure 2), which is similar to the experimental determination of the \(T_g\) using ellipsometry. Namely, after the simulated systems were equilibrated at \(T = 1.5\varepsilon/\kappa_B\) and \(P = 0\varepsilon/\sigma^3\), we performed \(NPT\) simulations during which we kept lowering the temperature by 0.02ε/κ_B per 10^3τ in a stepwise fashion from 1.5ε/κ_B to 0.1ε/κ_B. The \(T_g\) was determined from the change in slope of the film-averaged density-temperature curves above and below the glass-transition region.\(^\text{13,14}\)

The simulations showed that the \(T_g\) values were affected by variations in both cross-link density (or equivalently, the mesh size \(L_{\text{mesh}}\)) and film thickness, but to a different extent.
The dependence of the glass-transition temperature (a) and the ratio of the glass-transition temperature compared to the corresponding crosslinked chains. Confinement led to a strong increase of the ratio, respectively, at \( T_{\text{g}} \) was 3\%, 2\%, and 4\% for the thick, thin, and ultrathin films, \( L_{\text{g}} \) in the film thickness. The change in thickness among the non-crosslinked and the highest crosslinked films (\( L_{\text{mesh}} \approx 18.8\sigma \)) and thin (\( L_{\text{film}} \approx 10.1\sigma \)) films, at \( T = 0.8\varepsilon/k_B \), the film averaged relaxation displayed a pronounced plateau only at \( q = 1.0\sigma^{-1} \), and, presumably, at larger length-scales. In the ultrathin film, however, we observed plateaus already for \( q < 3.0\sigma^{-1} \), i.e., for scattering lengths \( l_q > 2.1\sigma \). The film thickness in this case, \( L_{\text{film}} \approx 4.3\sigma \), was smaller than the largest probed length-scale, \( l_1 = 6.3\sigma \). In contrast, the relaxation of \( S_{\text{inc}}(q, t) \), when only dimensions parallel to the walls were taken into account, always decayed to zero, Figure 4(a). In general, at \( T = 0.8\varepsilon/k_B \), plateaus in the relaxation of the film averaged \( S_{\text{inc}}(q, t) \) were observed on length-scales that were at least half the film thickness.

The calculated \( T_{\text{g}} \) in the films was higher than the \( T_{\text{g}} \) in the bulk under the same constant mesh size value, Figure 3. A smaller film thickness resulted in a higher \( T_{\text{g}} \). The size of the crosslinked mesh was found to affect the \( T_{\text{g}} \) only when \( L_{\text{mesh}} \ll R_g \), where \( R_g \) is the radius of gyration of the non-crosslinked chains. Confinement led to a strong increase of the glass-transition temperature compared to the corresponding bulk values. The \( T_{\text{film}}^{\text{ff}}/T_{\text{bulk}}^{\text{ff}} \) ratio, however, was not affected by the mesh size and was equal to 1.1, 1.15, and 1.5, for the thick, thin, and ultrathin film, respectively, Figure 3(b). A gradual alignment of the intra-chain bonds parallel to the crystalline walls was observed near the polymer-wall interface as the temperature was approaching the glass-transition value (not shown).

**B. Segmental dynamics**

Overall, a smaller film thickness or a shorter mesh size resulted in a slower relaxation of single-bead motions. It should be noted, though, that these two parameters were not decoupled: a change in the mesh size induced also a small change in the film thickness. The change in thickness among the non-crosslinked and the highest crosslinked films (\( L_{\text{mesh}} = 1.7\sigma \)) was 3\%, 2\%, and 4\% for the thick, thin, and ultrathin films, respectively, at \( T = 0.8\varepsilon/k_B \). At the same temperature, the large-scale long-time decay of the film-averaged \( S_{\text{inc}}(q, t) \) culminated in non-zero plateaus whose magnitude depended on \( q \), when large-scale motion was probed.21

Since no plateaus were detected in the relaxation of the film averaged \( S_{\text{inc}}(q, t) \) in the non-crosslinked polymer bulk, their appearance in the non-crosslinked films can be reasonably attributed to the confinement effect of the walls, i.e., to the induced maximum attainable displacement of the polymer segments along the direction perpendicular to the walls. In those systems, plateaus were observed on large length-scales, i.e., length-scales comparable to the size of the polymer chains, Figure 4(a). As the film thickness decreased, and larger length-scales were probed, the magnitude of the plateaus increased. In the thick (\( L_{\text{film}} \approx 18.8\sigma \)) and thin (\( L_{\text{film}} \approx 10.1\sigma \)) films, at \( T = 0.8\varepsilon/k_B \), the film averaged relaxation displayed a pronounced plateau only at \( q = 1.0\sigma^{-1} \), and, presumably, at larger length-scales. In the ultrathin film, however, we observed plateaus already for \( q < 3.0\sigma^{-1} \), i.e., for scattering lengths \( l_q > 2.1\sigma \). The film thickness in this case, \( L_{\text{film}} \approx 4.3\sigma \), was smaller than the largest probed length-scale, \( l_1 = 6.3\sigma \). In contrast, the relaxation of \( S_{\text{inc}}(q, t) \), when only dimensions parallel to the walls were taken into account, always decayed to zero, Figure 4(b). In general, at \( T = 0.8\varepsilon/k_B \), plateaus in the relaxation of the film averaged \( S_{\text{inc}}(q, t) \) were observed on length-scales that were at least half the film thickness.

**FIG. 3.** The dependence of the glass-transition temperature (a) and the ratio of the glass-transition temperature between the films and the bulk polymer (b) on the mesh size for films of different thickness.

**FIG. 4.** Relaxation of \( S_{\text{inc}}(q, t) \) in the non-crosslinked thick and ultrathin films at \( T = 0.8\varepsilon/k_B \) and \( P = 0.05\varepsilon/\sigma^2 \). Only large scale relaxations are shown, i.e., \( q = (1, 2, 3)\sigma^{-1} \) or \( l_q = (6.3, 3.1, 2.1)\sigma \). The values of \( q \) were calculated by averaging over \( q \) vectors with the same magnitude \( q \) along the three principal Cartesian axes (a) and the two Cartesian axes parallel to the walls (b).
The appearance of non-zero plateaus in the relaxation of $S_{inc}(q,t)$ was more noticeable in the crosslinked systems, which indicates the extra hindrance to large-scale flow upon cross-linking, Figure 5. The influence of the mesh size on the magnitude of the plateaus was stronger than the influence of the film thickness. The decay of $S_{inc}(q,t)$ at $q = 1.0 \sigma^{-1}$ was significantly slower in the strongly crosslinked systems, due to the considerable constraints that were imposed by the cross-links on large scale motions. On the other hand, on shorter scales, where the mesh size was comparable or even larger than the probed length scale of relaxation $l_q$, the mesh size had a much weaker effect on the decay of $S_{inc}(q,t)$. For instance, the mesh size in the highest crosslinked systems, $L_{mesh} = 1.7 \sigma$, was noticeably larger than the shortest length scale of relaxation, $l_t = 0.9 \sigma$, and therefore could not have affected the mobility of such small segments.

To account for the non-zero plateau values in the decay of $S_{inc}(q,t)$, we extracted the relaxation times of $S_{inc}(q,t)$ by fitting it with a modified form of the KWW (Kohlrausch-Williams-Watts) stretched exponential function,

$$S_{inc}(q,t) = (1 - a) \exp \left( -\frac{t}{\tau_0} \right)^\beta + a. \quad (6)$$

In Eq. (6), $a$ is the magnitude of the plateau, and $\tau_0$ is the characteristic time of relaxation on a length scale defined by the magnitude $q$. The exponent $\beta$ is used to quantify the deviation from the exponential decay. Values of $\beta$ that are smaller than unity can be attributed either to the development of heterogeneous dynamics or to a single homogeneous (but non-exponential) relaxation mechanism.43

The obtained characteristic relaxation times displayed a dependence on film thickness and mesh size that was similar to the dependence of the glass-transition temperature (compare Figures 3 and 6). The $\tau_{q}^{film}/\tau_{q}^{bulk}$ ratio displayed a similar behavior, whereas (as we have already mentioned) the $\tau_{q}^{film}/\tau_{Tg}^{bulk}$ ratio was not affected by the size of the crosslinked mesh. The Kuhn-length of the polymer chains was calculated equal to $L_K = 1.55 \sigma$, based on the end-to-end distance of the chains averaged over all the studied systems. The onset of the increase in the relaxation times can be distinguished at a length-scale in-between the radius of gyration and the Kuhn-length of the polymer chains, which may indicate the characteristic alpha-relaxation scale.

For Rouse segmental dynamics,50 the dependence of the relaxation time $\tau_q$ on the probed length scale is expected to follow the power law $\tau_q \sim q^{-4}$, though in polymer melts approaching the glass-transition, a crossover to a time scaling of $\tau_q \sim q^{-2}$ can be observed, signifying a departure from dynamic homogeneity.51 In any case, in thin polymer films a departure from homogeneity should be anticipated even when temperature is larger than $T_g$.

To examine the power law scaling $\tau_q \sim q^{-m}$, we fitted the calculated relaxation times at $T = 0.8e/k_B$ in the interval $q \in [1.0, 7.0] \sigma^{-1}$, Figure 7(a).13 The value of the scaling exponent $m$ displayed a non-monotonic dependence on confinement. Concerning its dependence on the mesh-size, $m$ values were fluctuating around 3.2 in the non- and weakly crosslinked systems, depending on film thickness, Figure 7(b). Once the mesh size became smaller than the radius of gyration of the bulk polymer chains, the value of $m$ decreased rapidly by a fraction of 16%. This decrease might have been induced by increased heterogeneity caused by the presence of the crystalline walls.

Higher dynamic heterogeneity in thinner films with higher cross-link density was also implied by the KWW $\beta$ exponent, which displayed a similar qualitative behavior upon changing the film thickness or mesh size, as smaller values of $\beta$ imply a broader distribution of relaxation times, which is in turn related to a higher dynamic fragility of glass-forming polymer melts.43 $\beta$ decreased linearly with a decreasing mesh size for $L_{mesh} > R_g$, after which a rather steep decrease was observed for mesh-size values smaller than $R_g$, Figure 8.

This behavior was detected for all simulated length scales ($0.9 \sigma$–6.3 $\sigma$). On the other hand, the effect of confinement on $\beta$ was more pronounced when small size segments were probed, i.e., $l_q < 2.1 \sigma$, whereas it was gradually damped on larger length-scales. On these scales, thinner films displayed lower $\beta$ values. This is illustrated in Figure 9, where a higher deviation from the Arrhenius temperature dependence of the characteristic relaxation time can be seen in more crosslinked and thinner films. The monotonic decrease of the $\beta$ coefficient with decreasing mesh size is in agreement with previously published simulation results,43 while similar results have also been obtained experimentally in bulk polymer networks.52–54
Evolution of characteristic relaxation times

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C. Effect of wall structure

Thinner films, as well as any film in relation to the bulk polymer, displayed a larger deviation from the Rouse dynamics, lower values of the film averaged KWW β exponent, and a larger deviation from the Arrhenius temperature dependence of the characteristic relaxation times. These results may be attributed to the increased number of oscillations in the density distribution of the monomer beads along the direction perpendicular to the walls. At a distance $z < 4\sigma$ from the walls, the monomer units were distributed in oscillating density layers of gradually decreasing amplitude, Figure 10, which has already been reported by previous simulation results in films, as well as in nanocomposites. The average density farther away from the walls in the thick and thin films was constant and equal to the bulk value, whereas in the ultrathin film ($L_{\text{film}} < R_g$), no bulk density layer was observed. Overall, the bulk density layer was smaller in thinner films. The density distribution along the direction perpendicular to the walls was therefore more inhomogeneous in thinner films, which might have induced the development of distinct dynamic environments, thus leading to a wider spectrum of relaxation processes.

The structure of the films perpendicular to the walls was not affected noticeably by the mesh size, Figure 10(b), whereas a higher temperature resulted in a decreased amplitude of peaks in the density profile, Figure 10(a). This effect was dumped for the density layers farther away. This observation is attributed to entropic effects resulting in a less ordered packing of the monomer units at higher temperatures, which led to a decreased film-averaged polymer density. Note also that although the film-averaged density was smaller at lower temperatures, the density layers appeared at the exact same distance from the wall. The fact that the positions of the oscillating density layers superimposed in the three films implies a constant thickness of the wall-polymer interface independent of the thickness of the film.

Note that the calculated density distributions were identical regardless of whether we performed the simulations under the NPT or NVT ensemble (not shown), during the latter of which we only allowed the pressure component perpendicular to the walls to fluctuate around $P_{zz} = 0\varepsilon/\sigma^3$ while kept the lateral pressure components constant.

To affirm whether the observed ordering of the monomer beads close to the walls was induced by the latter’s crystalline structure, we performed additional simulations, first, of the thick film at $T = 1.5\varepsilon/k_B$, in which the crystalline walls were replaced with amorphous walls, and second, of all the films (thick, thin, and ultrathin) at $T = 0.85\varepsilon/k_B$, in which we replaced the crystalline with rough walls, Figure 11.

The amorphous walls were created by increasing the diameter of half of the wall beads from their original value from $0.85\sigma$ to $1.10\sigma$, whereupon we let the whole system equilibrate at the same temperature under NPT conditions. We subsequently subjected the thick film to NPT simulations, at temperature $T = 1.5\varepsilon/k_B$ and isotropic pressure $P = 0.0\varepsilon/\sigma^3$, for $\Delta t = 20000\tau$. During the simulations the volume of the simulation box increased from $V_{\text{box}} = 7357\sigma^3$, which was obtained during the NPT simulation of the thick film with crystalline walls at the same operating conditions, to $V_{\text{box}} = 7741\sigma^3$. The calculated density profiles, Figure 12, indicate that the pronounced density layer, which was observed close to

FIG. 6. Evolution of characteristic relaxation times $\tau_q$ with mesh size for different values of the film thickness. Results are shown at two different length-scales: the chain scale, defined by $g = 1.0\sigma^{-1}$ (left panel), and the segmental scale, defined by $g = 7.0\sigma^{-1}$ (right panel).

FIG. 11. The average density farther away from the walls in the thick and thin films was constant and equal to the bulk value, whereas in the ultrathin film ($L_{\text{film}} < R_g$), no bulk density layer was observed. Overall, the bulk density layer was smaller in thinner films. The density distribution along the direction perpendicular to the walls was therefore more inhomogeneous in thinner films, which might have induced the development of distinct dynamic environments, thus leading to a wider spectrum of relaxation processes.

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the crystalline walls, disappeared when amorphous walls were used. At the same time, the density profile throughout the rest of the film was not affected by the structure of the walls.

To create the rough walls, we deleted half of the beads in the two internal surfaces (that were in contact with the polymer). Since the distance between two vertical layers in a HCP crystalline solid is $l_z = \sigma_{ss} \sqrt{6}/3$, the removal of the beads resulted in a roughness width of $0.7\sigma$ (the diameter of the spheres comprising the walls was $\sigma_{ss} = 0.85\sigma$). This can be clearly seen in Figure 13(b). We subsequently performed NPT simulations at constant isotropic pressure $P = 0.0\epsilon/\sigma^3$ and $T = 0.8\epsilon/k_B$. According to the simulation results, the thickness of all three films (thick, thin, and ultrathin) attained immediately a smaller value than the thickness of the corresponding films with crystalline walls, though presumably the free volume available to the polymer chains remained constant in all cases. The decrease in film thickness was close to 1.5% for the thick film and smaller for the rest of the films. Additionally, when rough walls were used, the density profiles overlapped for all studied values of the film thickness. Thus, only the width of the bulk-density layer was affected by the value of the film thickness. The same observation was also made in films with crystalline walls. The density profiles for films with rough walls are illustrated in Figure 13(a).

Figure 13(a) illustrates clearly that the bulk-density layer, which was present in the middle of the thin film with crystalline walls, disappeared when rough walls were used; thus, it was present only in the thick film. The average thickness of the thin
FIG. 10. Spatial distribution of the polymer mass density as a function of the distance from the walls along the perpendicular direction (in the thick film). Only half of the film is shown. (a): Density distribution in the thick film at different temperatures. (b): Density distribution in the thick film with different mesh size values at $T = 0.8\varepsilon/k_B$. The width and position of the density layers were not affected by either mesh size or temperature.

The film was $L_z = 10.1\sigma$ for crystalline walls, and $L_z = 9.6\sigma$ for rough walls, with $L_z$ denoting the minimum distance between the internal surfaces of the two walls. The average end-to-end distance of the chains in the bulk polymer was $R_{ee} = 8.95 \pm 0.08\sigma$, which indicates that the bulk-density layer may already disappear even when the thickness of the film is larger than the end-to-end distance of the bulk polymer chains.

In Figure 13(b), a comparison is offered between the thick films with either crystalline or rough walls at $T = 0.8\varepsilon/k_B$. After the replacement of crystalline with rough walls, the percentage of the bulk-density increased from 35.6% to 41.2% of the film thickness. An increased number of peaks were also observed.

Turning our attention to the effect of wall structure on dynamics, we report the following observations. The replacement of the crystalline with amorphous walls in the thick film had two main effects. First, it resulted in a 5% increase in the volume of the simulation box, and second, the density distribution became more homogeneous and on average was closer to the bulk value, Figure 12. Intuitively, we would expect their combined effect to induce faster dynamics when amorphous instead of crystalline walls were used. However, that was not...
IV. CONCLUSIONS

In this paper, we presented molecular-dynamics results concerning the glass-transition temperature and segmental dynamics as a function of film thickness and mesh size (the end-to-end distance of the subchains in the crosslinked polymer networks) of a generic bead-spring model of copolymer chains confined between solid walls.

The glass-transition temperature displayed a steep increase once the mesh size became smaller than the radius of gyration of the bulk chains, otherwise it remained invariant to mesh-size variations. The rise in the glass-transition temperature with decreasing mesh size and film thickness was accompanied by a monotonic slowing-down of segmental dynamics on all studied length-scales, as quantified by the decay of the incoherent scattering function. These observations are attributed to the constrains imposed by the presence of the walls on the maximum attainable displacement of the monomer units and to the decreased width of the bulk density layer that was obtained in thinner films. Only films whose thickness was larger than the end-to-end distance of the bulk polymer chains displayed a middle layer of bulk density.

Confinement and cross-link effects prevented certain length-scale dependent relaxation processes from relaxing fully. Higher dynamic fragility (as measured by means of the $\beta$ coefficient, and the deviation from the Arrhenius dependence of the relaxation times on temperature) was observed when smaller values of film thickness and mesh size were used. More fragile glass-forming films displayed larger $T_g$ values. The ratios of relaxation times in the films against those in the bulk displayed a steep dependence on the size of the crosslinked mesh at length-scales smaller than the bulk radius of gyration, reminiscent of the $T_g$ dependence. The threshold from which on this behavior was observed was independent of film thickness. Longer chains should be used in order to elucidate on this observation.

The high polymer density that was observed close to the crystalline walls vanished when we replaced the crystalline with amorphous walls, whereas the density throughout the rest of the film remained invariant. The introduction of rough walls resulted in a higher number of oscillations in the density profile of the films and a smaller magnitude of the oscillations in the wall-polymer interface due to a fraction of monomers becoming adsorbed inside the walls. By comparing the dynamic response amongst films with different wall structures, we reported that the wall structure affected the large-scale dynamics, only to a small degree. A higher degree of roughness could lead to slower dynamic response, though additional simulations are required to affirm this.

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