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Mechanical properties and local mobility of atactic-polystyrene films under constant-shear deformation

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We have performed molecular-dynamics simulations of atactic polystyrene thin films to study the effect of shear rate, pressure, and temperature on the stress-strain behaviour, the relevant energetic contributions and non-affine displacements of polymer chains during constant-shear deformation. Under this deformation sliding motion is observed at high shear rates between the top substrate and top polymer layer, which disappears when the shear rate decreases. At low shear rates stick-slip motion of the whole film with respect to the bottom substrate takes place. We found that at low shear rates the yield stress logarithmically depends on the shear rate; this behaviour can be explained in terms of the Eyring model. It was also observed that an increase in the normal pressure leads to an increase in the yield stress in agreement with experiments. The contributions to the total shear stress and energy are mainly given by the excluded-volume interactions. It corresponds to a local translational dynamics under constant shear in which particles are forced to leave their original cages much earlier as compared to the case of the isotropic, non-sheared film. Moreover, it was observed that under constant-shear deformation the polymer glass is deformed non-affinely. As a result, the middle part of the film is much more deformed than the layers close to the supporting substrates, meaning that the well-known effect of shear-banding occurs. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4754736>]

I. INTRODUCTION

Thin glassy polymer films are commonly used as lubricants in different technological applications to decrease the friction between solid surfaces.^{1,2} The frictional and rheological properties on the nanoscale can be probed in experiments by using a surface forces apparatus or atomic force microscope,^{3–7} and also by means of the molecular-dynamics (MD) simulations.^{8–12}

The polymer glass is not in the thermodynamically stable crystalline state, is amorphous in its nature, and can plastically deform under some conditions (for example, under uniaxial compression, or under uniaxial extension if brittle fracture can be prevented). As a solid material it behaves rigid and resists plastic deformation up to a certain limit. If the deformation goes beyond this limit the polymer glass starts to flow and deforms plastically. It is important to note that there is a transition from the plastic deformations to the sliding motion. It was shown that in polymers, the sliding motion occurs only when the frequency of the applied shear is above a critical value and the sample is deformed faster than the intrinsic relaxation time.¹³

The effect of the hydrostatic pressure, temperature, strain rate, and physical ageing on the mechanical properties of glassy polymers is well known. It was found that the shear and Young's moduli noticeably increase with increase of the pressure for various polymers.^{14–18} However, for polystyrene,

a rather slight increase of Young's modulus with pressure has been found.¹⁹ The temperature and strain-rate dependencies of the stress-strain characteristics have been investigated by Li *et al.*²⁰ They performed atomistic Monte Carlo simulations of uniaxial tension of an amorphous linear polyethylene-like glassy polymer. They found that with increasing strain in the elastic region mechanical work is stored as non-bonded internal energy, and that in the yield regime the intra-chain contributions start to play a role.

Many studies have been performed to understand the underlying mechanisms of plastic deformation at the yield peak. The well known and still widely used Eyring theory is usually applied to describe the temperature and pressure dependencies of the yield stress on strain rate.²¹ According to this theory, stress, having a similar effect as temperature, causes an increase of mobility in the direction of the applied load. The main cause of a simple deformation is a shift of the potential energy barrier upon applied stress. This theory describes the plastic deformations as jumps between energy minima, and the rate of such jumps $\dot{\gamma}$ can be written as

$$\dot{\gamma} = \dot{\gamma}_0 \exp\left(-\frac{\Delta H}{RT}\right) \sinh\left(\frac{v\sigma}{RT}\right), \quad (1)$$

where ΔH is the activation energy or energy barrier which has to be overpassed in order to initialize plastic deformations, v is the activation volume, which is required for the rearrangements, $R = 8.314 \text{ J/(mol K)}$ is the universal gas constant, σ is the applied stress, and $\dot{\gamma}_0$ is some pre-exponential factor in the Eyring model.^{21,22} At high yield stresses $\sinh(x) \approx \exp(x)/2$,

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and the above equation can be rewritten as

$$\sigma_Y = \frac{\Delta H}{v} + \frac{RT}{v} \ln \frac{2\dot{\gamma}}{\dot{\gamma}_0}. \quad (2)$$

Although the Eyring model describes the decrease of the yield stress rather well for higher temperatures and for lower strain rates,²³ it does not take into account the effect of the physical ageing,²⁴ which has also significant influence on the yield stress.^{25–27}

The aim of the present study is to perform MD simulations of atactic-polystyrene (aPS) thin capped films, i.e., with two—top and bottom—supporting substrates, to study the effect of shear rate, pressure, and temperature on the stress-strain behaviour during constant-shear-rate deformation. The main goal is to extract the shear modulus and the yield stress at different temperatures, external pressures, and at different shear rates. The relevant contributions to the total shear stress and total internal energy are also monitored. To gain insights into the local dynamics of the polymer film upon constant-shear-rate deformation the non-affine displacements of polymer segments and the local segmental translational dynamics are studied.

The paper is organized as follows. In Sec. II, we give the description of the model of the capped aPS film together with the deformation protocol. In Sec. III, we discuss the mechanical properties of capped films upon constant-strain-rate shear deformation. Our conclusions are given in Sec. IV of the paper.

II. SIMULATION DETAILS

A. Simulation model

The atactic-polystyrene chains used in this study are modeled with the help of a united-atom representation.²⁸ In this representation all hydrogen atoms are not presented explicitly, but, instead, they are collapsed onto the carbon atoms and the combined atoms are treated as effective particles, i.e., united atoms. The motivation of using this model is that computations are much faster for the united-atom model than for the all-atom model.²⁹

Each simulated atactic-polystyrene chain consists of 80 (641 united atoms) monomers, with molecular weight $M_w = 8.6 \times 10^3$, which is below the entanglement molecular weight $M_e = 1.3 \times 10^4$. The average gyration radius of these chains is found to be about 2 nm. The stereochemical configurations of the aromatic groups were generated in each chain at random, so that the ratio of the number of *meso* to the number of *racemic* dyads was near unity. Additionally, each aPS chain has been prepared with different tacticity.

To study the mechanical behaviour of aPS films under shear deformation we have prepared films capped by two identical substrates. Each simulated capped film consists of 16 chains, with 10256 united atoms, and is placed inside a simulation box with fixed to 7×7 nm lateral dimensions. Periodic boundary conditions are implemented only in the *X* and *Y* directions. In *Z* direction the periodic boundary conditions are not applied.

In simulated aPS films all interactions between united atoms are described by the following potential:

$$U_{\text{aPS}} = \epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + k_l (r_{ij} - l_0)^2 + k_\theta (\theta_{ijk} - \theta_0)^2 + k_\phi \cos(n\phi_{ijkl}). \quad (3)$$

The potential U_{aPS} includes the contributions from excluded-volume interactions ($\sim \epsilon_{ij}$) between united atoms that are on different chains or are separated by more than three covalent bonds; a stretching potential ($\sim k_l$) between two neighboring atoms *i* and *j* that have shared valence electrons; a bending potential ($\sim k_\theta$) for all bond angles, including those in the phenyl rings; finally, proper-torsion and improper-torsion potentials ($\sim k_\phi$). In this aPS model the Coulomb interactions are not taken into account. For more details of the used force-field we refer to Ref. 30.

The leapfrog variant of the velocity Verlet algorithm has been used to integrate Newton's equations of motion with an integration time step $\Delta t = 4$ fs. The simulations have been performed in *NVT* ensemble. The temperature and pressure in simulated systems are controlled with the help of the collisional thermostat³¹ and Berendsen barostat,³² correspondingly.

B. Polymer-substrate interactions

In order to simulate capped aPS films, completely smooth, structureless substrates are introduced in the *XY*-plane of the simulation box. In simulating the structureless substrates the interactions between substrate and polymer chains are described by the van der Waals interactions between implicit atoms of the substrate and polymer segments, and have the form of a truncated and shifted 9-3 Lennard-Jones (LJ) potential:

$$U_1(z) = \frac{1}{2} \epsilon \left[\left(\frac{z_{\min}}{z} \right)^9 - 3 \left(\frac{z_{\min}}{z} \right)^3 \right] - U_1(z_{\text{cut}}). \quad (4)$$

Here *z* denotes the distance from the monomer to the substrate and ϵ is the strength of the attraction to the substrate. $z_{\min} = 0.3$ nm is the distance at the minimum of the potential and $z_{\text{cut}} = 0.9$ nm is the cut-off distance. This potential is similar to that used by Müller and MacDowell in simulations for a bead-spring model film,³³ except that in their case the potential was not truncated or shifted. For a bead-spring model the wetting transition occurs at $\epsilon = 0.4$ kcal/mol at 300 K,³³ while in the present MD simulations the potential strength ϵ is set to 5.0 kcal/mol, i.e., complete wetting of polymer segments has been simulated. This potential mimics the van der Waals interactions between the atoms of the substrate and polymer segments, and can be obtained by integrating the 12-6 LJ potential over a half space.³⁴

On top of this potential, Eq. (4), an additional second potential $U_2(x, y, z)$ that reconstructs the structure of substrate and mimics a crystalline lattice of substrate atoms has been implemented. The form of the second potential was originally

introduced in Ref. 35,

$$U_2(x, y, z) = Ae^{-\alpha z} \left[B \cos^2 \left(\frac{\pi}{a} x \right) + C \cos^2 \left(\frac{\pi}{a} y \right) + D \cos^2 \left(\frac{\pi}{a} (x + y) \right) \right]. \quad (5)$$

In this equation $\alpha = 5 \text{ nm}^{-1}$, $A = 0.3 \text{ kcal/mol}$, $B = C = 50$, and $D = 1$; z denotes the distance from the monomer to the substrate and x, y correspond to the lateral directions, where periodicity is built in. This potential was truncated at $z_{\text{cut}} = 0.4 \text{ nm}$. The parameter $a = 0.5 \text{ nm}$ corresponds to the lattice parameter and is comparable to the size of the single phenyl ring. This choice of the lattice parameter allows us to have good physical junctions between polymer monomers and the substrate, and to prevent a sliding of monomers under applied shear deformation. If the lattice parameter is smaller than 0.5 nm the polymer monomers move freely, and for example, can slide with respect to the substrate when shear is applied along the X -axis. We did not study the effects of the variation of the parameters of this potential on the stick-slip motion which will be discussed later in Sec. III. Perhaps the sliding motion would start later (at larger shear rates) if the wetting would be stronger. Nevertheless, we believe that the general picture which is observed (see Sec. III), i.e., the stick-slip motion which is followed by the sliding motion, will not be changed.

C. Preparation of capped films

In Ref. 28, we explained the simulation procedure (equilibration and preparation) for the supported films (with one free interface and one supporting interface), and of different thicknesses. In this paper we provide details about preparation of capped films (confined by two identical substrates), which will be used for studying the mechanical response of the films under shear.

As the initial point of the simulation of the capped film we use results earlier produced for a supported 16-chains aPS film at low temperature, 300 K .²⁸ Note that the bulk glass-transition temperature T_g is about 380 K . This film has been initially placed inside the simulation box with lateral dimensions $7 \times 7 \text{ nm}$ in the X and Y directions. In the Z direction two identical confining substrates have been placed at $z = 0 \text{ nm}$ (bottom substrate) and $z = 7 \text{ nm}$ (top substrate). Both substrates are modeled with the help of the potentials, Eqs. (4) and (5), as discussed above.

After a short (about 500 ps) pre-equilibration the top substrate was moved down from $z = 7 \text{ nm}$ to $z = 5 \text{ nm}$ with compressing velocity $1 \times 10^{-4} \text{ nm/ps}$. During compression of the aPS film we monitored the normal pressure. At the end of this compression, two films at normal pressures 32 MPa and 52 MPa and temperature 300 K have been chosen, with the film thickness of 5.4 nm and 5 nm , correspondingly. Additionally, the capped film at 52 MPa has been heated up to 370 K with heating velocity 0.01 K/ps . Due to the confinement the pressure inside the film increased drastically. In order to decrease the internal pressure back to 52 MPa at 370 K the film thickness was increased by about 1% . Finally, we ob-

tained three capped films: two films at two normal pressures (32 MPa and 52 MPa) and one temperature (300 K); and another film at pressure 52 MPa and temperature 370 K .

D. Deformation protocols

During simulations the stress was calculated with the help of the symmetric stress tensor $\tau^{\alpha\beta}$ using the virial expression:

$$\tau^{\alpha\beta} = \left\langle -\frac{1}{V} \sum_{i=1}^N \left(\frac{p_i^\alpha p_i^\beta}{m_i} + r_i^\alpha F_i^\beta \right) \right\rangle, \quad (6)$$

where $\alpha, \beta = x, y, z$; angular brackets $\langle \dots \rangle$ correspond to the ensemble averaging over all N united atoms, with momentum $p_i^{\alpha,\beta}$, mass m_i , position r_i^α and total force F_i^β acting on the particle i . From this expression the external normal pressure was calculated as $P_z = -\tau^{zz}$. Constant shear deformation was applied horizontally in the X -direction only to the upper substrate of the capped film, in a plane perpendicular to the Z -direction, and the shear stress was calculated as $\tau^{xz} = \sigma^{xz} = \sigma$ (henceforth we will drop the superscript xz). The shear deformation has been done at different shear velocities, $v = (0.5\text{--}10) \times 10^{-3} \text{ nm/ps}$ and for different shear strains. The shear strain γ and shear rate $\dot{\gamma}$ are defined as $\gamma = \Delta x/H$ and $\dot{\gamma} = v/H$; here Δx is the displacement of the top substrate, $H \simeq 5 \text{ nm}$ is the film thickness, and v is the shear velocity. For films of this thickness the simulated shear rate is changed by more than two orders of magnitude from $\dot{\gamma} = 1 \times 10^8 \text{ s}^{-1}$ to $\dot{\gamma} = 200 \times 10^8 \text{ s}^{-1}$. Initially, each capped film (at two temperatures, 300 K and 370 K) has been simulated for 100 ns in the absence of the shear deformation. Then constant-strain-rate deformation has been implemented.

During constant-strain-rate shear deformation each film has been sheared only in one direction up to the maximal value of the shear strain of $\gamma = 50\%$, at eight different shear strain rates, $\dot{\gamma} = (1, 2, 4, 10, 20, 40, 100, 200) \times 10^8 \text{ s}^{-1}$, in order to probe different characteristic regimes in the stress-strain dependencies, i.e., the elastic regime, yield regime, softening, etc. During deformation the shear stress is averaged over a certain period of time, which is different for different shear rates, and is also averaged over 5 independent runs.

III. SIMULATION RESULTS

A. Stress-strain dependencies: Shear modulus and yield peak

In Figure 1 a typical stress-strain behaviour of a glassy polymer during constant-strain-rate deformation is shown. During this experiment the stress-strain response of a glassy polymer normally exhibits four distinct deformation regimes. The first regime is referred to as the linear viscoelastic regime, during which the polymer film is subjected to a low strain, usually up to 2% – 3% . In this regime the material strongly resists deformation and the stress needed to deform the sample increases (almost) linearly with the strain. After the linear elastic regime the nonlinear deformation of a sample takes place. In this case the stress does not change linearly with the strain, and the polymer sample starts to deform plastically.

FIG. 1. Schematic illustration of a typical stress-strain response of a glassy polymer upon shear deformation. Here the shear modulus G is defined as a slope in a linear elastic regime.

Subsequently yielding takes place at yield stress, σ_Y . Sometimes it is difficult to define the exact stress at which plastic deformation begins, and therefore, the yield stress is often taken as a stress needed to induce a specified amount of permanent strain, typically 2%. The construction used to find the yield stress is shown in Figure 1, in which a line of slope G is drawn from the strain axis at 2%. Then, the point of intersection of this line with the stress-strain curve is the yield stress.

As the deformation strain increases by a few percent beyond the yield peak, the stress subsequently drops. Such drop of the stress is referred to as strain softening. If the deformation is continued polymer flow is observed, which smoothly transits to the last regime, which is ascribed to the strain hardening. During this regime the polymer sample is deformed by more than 20% of strain, where the polymer chains become oriented which leads to the increase of the stress. In this paper, we study the shear deformation where the strain hardening regime is absent for all simulated shear rates. Therefore, in this work we mainly focus on the linear viscoelastic and yield regimes.

The measured shear stress σ as a function of the applied constant-shear strain γ is presented in Figure 2(a) for the

highest shear rate, $\dot{\gamma} = 200 \times 10^8 \text{ s}^{-1}$, for two normal pressures and at fixed temperature 300 K. Figure 2(b) presents the shear stress measured at two temperatures 300 K and 370 K and at one external normal pressure 52 MPa, at the same value of the shear rate. Initially, all dependencies show an elastic region (up to $\gamma = 2\%$) followed by the yield peak (at $\gamma \sim 5\%$). In both cases, Figures 2(a) and 2(b), the stress regularly rises and drops by $\Delta\sigma \sim 20\text{--}25 \text{ MPa}$ every $\Delta\gamma = 10\%$ which corresponds to the period ($a = 0.5 \text{ nm}$) of the simulated crystalline structure of the substrate, Eq. (5). It means that initially polymer segments are completely moved by the top substrate. As soon as the top substrate is moved by approximately $\Delta x = 0.5 \text{ nm}$ the polymer segments jump back to their initial positions, which results in decreased shear stress, and sliding takes place. The main cause of this sliding motion is that the rate of deformation is much faster than the internal relaxation rate of the polymer segments at the top layer. In Ref. 13 it was shown that sliding motion occurs only when the applied shear rate is above a critical value, i.e., $\dot{\gamma} \gg \dot{\gamma}_{\text{cr}}$. This can be understood in the sense that the sample is deformed much faster than the intrinsic relaxation time, i.e., $1/\dot{\gamma} \ll \tau_{\text{relax}}$, of polymer chain. In Ref. 36, by measuring the local segmental mobility we show that the relaxation time of the atactic-polystyrene chain segments (at temperature 300 K and pressure 52 MPa) is more than 100 ns, and additionally, due to the ageing effect,³⁷ this time is shifted to larger values with increase of the simulation time. At the lowest shear rate where the sliding motion is still observed ($\dot{\gamma}_{\text{sl}} = 40 \times 10^8 \text{ s}^{-1}$), the characteristic deformation time is equal to $1/\dot{\gamma}_{\text{sl}} = 250 \text{ ps}$, which is still much smaller than the relaxation time. It means that the deformation is still so fast that the polymers do not have enough time to react on the perturbation. In order to increase further the deformation time (i.e., to decrease the shear rate) requires more central processing unit time. The lowest shear rate, $1/\dot{\gamma} = 10 \text{ ns}$ that we are able to cover in this study ($\dot{\gamma} = 1 \times 10^8 \text{ s}^{-1}$) is still too fast; however, this is much closer to the time when the α -relaxation process (the translational motion of polymer segments out of their cages) starts.³⁶

At high shear rate the influence of pressure on the shear stress, Figure 2(a), is reflected by a small shift of the overall

FIG. 2. The stress-strain curves for the 16-chains aPS capped film at normal pressure 32 MPa (circles) and 52 MPa (squares) at temperature 300 K (a) and at pressure 52 MPa and at two temperatures 300 K (filled squares) and 370 K (open squares) (b). In both figures the measured shear stress is taken at the highest simulated shear rate $\dot{\gamma} = 200 \times 10^8 \text{ s}^{-1}$.

FIG. 3. The stress-strain curves for the 16 aPS capped film at normal pressure 32 MPa (circles) and 52 MPa (squares) at temperature 300 K (a) and pressure 52 MPa at two temperatures 300 K (filled squares) and 370 K (open squares) (b). In both figures the shear stress is taken at the lowest simulated shear rate $\dot{\gamma} = 1 \times 10^8 \text{ s}^{-1}$.

stress-strain curve (after the yield peak) to larger shear strains, while the influence of temperature is rather weak, Figure 2(b). Larger pressure also produces a larger value of the yield stress.

At low shear rate the stress-strain curves exhibit pronounced linear elastic regimes, Figure 3, which span larger regions of γ (up to $\gamma \sim 5\%$ – 7%) than at high shear rate. However, for consistency with the high-shear-rate results we will in further analysis consider only part of this regime, up to $\gamma \leq 2\%$. At low shear rate the yield tooth is also clearly visible. At high shear rates, Figure 2, softening might be read off from the regular drops in the shear stress, while for the lowest shear rates, Figure 3, the softening is clearly observable only for the high normal pressure of 52 MPa, and is almost absent for the low normal pressure of 32 MPa. In our shear deformation the strain-hardening is absent for all simulated shear rates. Instead of this, the last regime, which starts roughly at $\gamma \sim 12\%$ – 15% , is always a combination of stick and slip motions, as can be seen by rises and drops of the shear stress.

Despite large fluctuations the difference between the stress-strain curves at two different normal pressures, Figure 2(a), and different temperatures, Figure 2(b), is clearly visible, but is rather small. As soon as the shear rate decreases the difference between the curves increases: the yield tooth is always larger for the higher pressure, Figure 3(a), and for the lower temperature, Figure 3(b). Physically, it means that at high normal pressure polymer segments have to overcome a high energy barrier in order to flow. Later we will estimate the value for the energy barrier and the size of the volume at which the plastic flow occurs. It is known that the energy barrier linearly increases with pressure.²² Therefore, we can say that the simulated stress-strain curves have qualitatively the correct trend. As the temperature increases towards the glass transition, the distance between the particles also increases, causing an increase of volume and hence of monomer mobility. This results in a lower value of the yield peak, meaning that at higher temperature a lower yield stress is observed, Figure 3(b).

From the stress-strain curves we estimate the shear modulus G by measuring a slope of the linear elastic region (up to $\gamma = 2\%$), Figure 1. The simulation results give the value

of the shear modulus $G \sim 0.5 \text{ GPa}$, which is more than twice smaller than the experimental value (1.2 GPa) for bulk aPS at 300 K.^{38,39} First of all, we note that the value of G depends on the strain interval which is taken for the present calculations and varies from $G = 0.45 \text{ GPa}$ to $G = 0.52 \text{ GPa}$ at $\dot{\gamma} = 1 \times 10^8 \text{ s}^{-1}$. Additionally, we simulated a thicker capped film that contains 32 chains of aPS (80 monomers per chain) of 9 nm thickness, and performed shear deformations with constant shear by 50%. The stress-strain curves are not presented here. The simulations of thicker aPS films showed that the shear modulus is, $G \simeq 0.7 \text{ GPa}$ at $\dot{\gamma} = 1 \times 10^8 \text{ s}^{-1}$. These results are in a qualitative agreement with experimental findings of Christopher *et al.*⁴⁰ who found a strong dependence of the elastic modulus on film thickness. They found that below 40 nm the apparent modulus of PS films decreases drastically, with an order of magnitude compared to the bulk value. Qualitatively the same effect was observed by Böhme and de Pablo⁴¹ using molecular-dynamics simulations of a model polymer, and in more recent work of Li and Strachan⁴² who also used the same technique to simulate free-standing nanofilms composed of a thermoset polymer, diglycidyl ether of Bisphenol A with 3,30-diaminodiphenyl sulfone.

Figures 4(a) and 4(b) show that in the stick-slip regime (low shear rate) the simulated shear modulus slightly increases with increasing shear rate, which is in agreement with the viscoelasticity theory, in which the shear modulus weakly increases at higher frequencies. Despite rather weak dependencies, Figure 4, it is clearly seen that the pressure and temperature dependencies of the shear modulus have the qualitatively correct trend: the shear modulus is always higher for the higher pressure and for the lower temperature at all shear rates. As it is known the shear modulus is a function of temperature^{14,43} and pressure.^{15,16} Following Sauer,¹⁶ the linear change with pressure can be written as

$$G = G_0 + nP, \quad (7)$$

where the prefactor $n = 3(3 - 4\nu)/(2(1 + \nu))$ is a function of the Poisson ratio ν . Noticeably, by fitting the pressure dependence of the shear modulus, at the fixed shear rate $\dot{\gamma} = 1 \times 10^8 \text{ s}^{-1}$, we found that the value of ν is 0.33, which is very close to the experimental value 0.34 in Ref. 44.

FIG. 4. Shear modulus as a function of the shear rate at two normal pressures and fixed temperature 300 K (a) and two temperatures at fixed normal pressure 52 MPa (b). The dashed lines in both figures denote roughly the transition from the sliding regime to the stick-slip regime.

From the stress-strain curves, the yield peak can be defined as well. There are few approaches that can be usually used to identify it.²² However, the measured stress-strain curves have different overall shapes; sometimes a true peak in the stress is absent, so we should choose one approach which is applicable for all simulated results. One way to define the yield point is to calculate the initial linear slope in the elastic regime and then to make an offset by 2%, as suggested in Ref. 22 and schematically illustrated in Figure 1. This method has been used in this study to define the yield stress for all simulated shear rates, temperatures, and pressures. We found that the measured yield stress logarithmically depends on the shear rate, Figure 5, but only at low shear rates.

This behaviour can be explained in terms of the Eyring model,²² which suggests that the yield stress is an activated rate process. Equation (1) can be adapted and used to write the yield stress in terms of the shear rate, as

$$\sigma_Y = \sigma_{0,Y}^* + s \ln \dot{\gamma}, \quad (8)$$

where $\sigma_{0,Y}^* = \Delta H / \nu - s \ln(\dot{\gamma}_0/2)$ and $s = RT/\nu$. Here ΔH is the energy barrier which has to be overpassed in order to start plastic deformation, and ν is the shear activation volume

that is required for the shear rearrangements. The shear activation volume can be calculated by fitting data in Figure 5 and by measuring the slope s at fixed temperature T in the stick-slip regime. The value for the activation energy ΔH can be extracted by fitting the temperature dependence of the yield stress, inset in Figure 5(a), to Eq. (8) and calculating the extrapolated yield stress at zero temperature. The estimations of the activation energy are very rough, and longer simulations using more temperatures, are necessary to give more precise results.

The fitting value of the activation volume is $\nu \sim 1.4 \text{ nm}^3$ and the activation energy is $\Delta H \sim 75 \text{ kJ/mol}$. The characteristic size of the element with such volume which starts to flow is about $\sim 1.1 \text{ nm}$, which is roughly comparable with the size of a single aPS monomer. This value of ν is larger than the 0.36 nm^3 obtained from the simulations of uniaxial-deformed aPS in a bulk.⁴⁵ The experiments on miscible polystyrene-poly(2,6-dimethyl-1,4-phenylene oxide) blends performed by Govaert and co-workers⁴⁶ showed that the shear activation volume for bulk polystyrene is about $\sim 1.5 \text{ nm}^3$, which is slightly higher than the simulated value for the films in our study.

FIG. 5. Yield stress as a function of the shear rate at two temperatures (a) and two normal pressures (b). Insets: the yield stress as a function of temperature (a) and normal pressure (b). The vertical arrows in the insets denote the increase of the shear rate from $\dot{\gamma} = 1 \times 10^8 \text{ s}^{-1}$ to $\dot{\gamma} = 20 \times 10^8 \text{ s}^{-1}$. The dashed lines in both figures denote roughly the transition from the sliding regime to the stick-slip regime.

FIG. 6. Applied work W and internal energy U at high $\dot{\gamma} = 200 \times 10^8 \text{ s}^{-1}$ (a) and low $\dot{\gamma} = 1 \times 10^8 \text{ s}^{-1}$ (b) shear rates, temperature 300 K, and pressure 52 MPa.

The pressure dependence of the yield stress in the stick-slip regime, Eq. (2), can be also explained in terms of the Eyring model. However, in order to do so, the component with the stress P should be added to the Eyring equation, Eq. (2), as $\Delta H + P\Omega$,²²

$$\sigma_Y = \frac{\Delta H + P\Omega}{v} + \frac{RT}{v} \ln \left(\frac{2\dot{\gamma}}{\dot{\gamma}_0} \right), \quad (9)$$

where Ω is the pressure-activated volume. This equation can be rewritten in terms of the pressure as

$$\sigma_Y = \sigma_c + \beta P, \quad (10)$$

where $\sigma_c = \Delta H/v + RT \ln(2\dot{\gamma}/\dot{\gamma}_0)/v$ is the yield stress at zero applied normal pressure and $\beta = \Omega/v$, which shows how fast the yield stress changes with pressure. By fitting the pressure dependencies of the yield stress, see inset in Figure 5(b), using Eq. (10) we found that the yield stress at zero applied normal pressure changes from $\sigma_c = 2.1 \text{ MPa}$ at $\dot{\gamma} = 2 \times 10^8 \text{ s}^{-1}$ to $\sigma_c = 15.7 \text{ MPa}$ at $\dot{\gamma} = 20 \times 10^8 \text{ s}^{-1}$ and the average value for β is $\beta = 0.73 \pm 0.06$. We should note that the fitting parameters σ_c and β depend on the considered system under shear. It was found, for example, that for polymer-metal interfaces $\sigma_c = 31.5 \text{ MPa}$ and $\beta = 0.07$, while for polymer-polymer interfaces these parameters are smaller: $\sigma_c = 1.4 \text{ MPa}$ and $\beta = 9 \times 10^{-4}$.⁴⁷ It could mean that the value of β might depend on the method which is used to measure the yield stress.⁴⁸ Again, these estimations are very rough, and longer simulations using more pressures, are necessary to give more precise results.

The above calculations work only when the film is plastically deformed. In the sliding regime (at high $\dot{\gamma}$, $\dot{\gamma} \geq 3 \times 10^9 \text{ s}^{-1}$, see Figure 5) there is no real plastic deformation of the simulated films. Therefore, the qualitative trends of the shear moduli, Figure 4, and the yield peaks, Figure 5 in this regime are different from those in the stick-slip regime and the films internally actually never enter a flow state.

The Eyring behaviour breaks down at $\dot{\gamma}_{max} \geq 3 \times 10^9 \text{ s}^{-1}$. The adhesion strength can be defined as the maximal force divided by the width of the specimen. The yield stress at $\dot{\gamma}_{max}$ is equal to $\sim 50 \text{ MPa}$ at 300 K. This roughly estimates the adhesion strength of the film.

B. Energy and stress partitioning

The work W is calculated as product of the total force F_{xz} applied to the top substrate and the displacement of this substrate dL_x in the X-direction

$$dW = F_{xz}dL_x = V\sigma_{xz}d\gamma_x, \quad (11)$$

where $V = L_x L_y H$ is the volume of the film, $\sigma_{xz} = F_{xz}/(L_x L_y)$ is the shear stress, and $\gamma_x = dx/H$ is the shear strain.

Figures 6(a) and 6(b) present the applied work W on the aPS thin film, and the change in the internal energy ΔU during constant-strain rate deformation at high $\dot{\gamma} = 200 \times 10^8 \text{ s}^{-1}$, and low $\dot{\gamma} = 1 \times 10^8 \text{ s}^{-1}$ shear rates, correspondingly. The simulation results show that the calculated work in Figure 6 is of the same order of magnitude as in experiments on deformation of polystyrene in a bulk.⁴⁹

At high shear rate, Figure 6(a), the internal energy of the film does not change significantly upon shear deformation and the work done on the sample is totally dissipated, causing the heating of the system. The oscillations in the applied work are connected with the oscillations in the shear stress, Figure 2(a), which are related with the sliding motions of the polymer segments, as was explained in Sec. III A.

At low shear rate, Figure 6(b), the work done on the film is partly converted into internal energy and the rest is dissipated in a form of heat. Up to about $\gamma = 20\%$ shear strain a fast increase of the internal energy takes place, which is connected with the local rearrangements of monomers, and for larger strains saturation of the internal energy is observed. The individual contributions to the internal energy are considered in more detail later.

Both at high and low shear rates part of the applied work is converted into heat meaning that deformed systems are heated up, which is in agreement with the experiments.⁴⁹ However, it should be noticed that in the current simulations we use a thermostat, which nullifies the increase of temperature. Still, the heat can be calculated as a difference between ΔW and U at fixed shear strain.

At $\dot{\gamma} = 1 \times 10^8 \text{ s}^{-1}$ the contributions to the internal energy and to the total stress from the excluded-volume interactions, stretching of covalent bonds, bending and dihedral-angle torsions are shown in Figure 7. As can be seen in

FIG. 7. Various contributions to the energy (a) and to the shear stress (b) during the constant shear deformation at low shear rate, $\dot{\gamma} = 1 \times 10^8 \text{ s}^{-1}$, temperature 300 K, and pressure 32 MPa.

Figure 7(a), up to about 20% shear strain the increase in the internal energy is mainly governed by the fast increase in the non-bonded, excluded-volume interactions. At the intermediate shear strains, $\gamma = 20\%$ – 30% , this contribution reaches a plateau, and after $\gamma = 30\%$ shear strain it even slightly decreases. The further increase in the total internal energy at the intermediate and higher shear strains is mainly given by bending contributions. The energy contributions from the dihedral torsion and stretching of covalent bonds weakly contribute to the total internal energy.

In Figure 7(b) the different contributions to the total shear stress at low shear rate, $\dot{\gamma} = 1 \times 10^8 \text{ s}^{-1}$, are shown. As can be seen from this figure, the main contribution to the total shear stress is also given by a large positive contribution from the excluded-volume interactions only at low shear strains (up to the yield peak). Below the yield peak there is no large stretching of covalent bonds, as is indicated by the plateau in Figure 7(b) for the stretching contribution (blue curve). Above the yield peak, at high (more than 10%) shear strain, a large negative contribution is coming from the stretching of the covalent bonds. Starting from about 15% the excluded-volume contribution and stretching contribution almost compensate each other. Starting from about 20%, the contribution from the bending of valence angles reaches a plateau which is slightly lower than the plateau from the total shear stress.

C. Local translational mobility during shear deformation

In order to see how the polymer chains are deformed locally upon constant-shear deformation we monitored the time dependence of the average coordinate $\langle X \rangle$ over all monomers in different layers. The simulated film was divided into ten equal layers, with $h \simeq 0.5 \text{ nm}$ thickness for each layer. In Figure 8(a), the change of the average coordinate $\langle X \rangle$ with shear strain γ is presented only for the top layer at 8 different shear rates. Initially, when the shear strain is $\gamma = 0$ the average coordinate in each layer is equal to $\langle X \rangle \sim 3.3\text{--}3.4 \text{ nm}$, which is just very close to half of the lateral size of the simulated box, $L_x = 7 \text{ nm}$.

At high shear rate $\dot{\gamma} = 200 \times 10^8 \text{ s}^{-1}$, the average coordinate fluctuates upon shearing with a very small drift (the lowest curve in Figure 8(a)), which can be explained by the small rearrangements of monomers close to the moving substrate. For the shear rates $\dot{\gamma} = 100 \times 10^8 \text{ s}^{-1}$ and $\dot{\gamma} = 40 \times 10^8 \text{ s}^{-1}$, the top polymer layer is initially moving with the substrate, however at shear strain $\gamma > 0.1$ it goes back. In this case the polymer film is just slightly deformed, but at these three values of shear rates slippage is observed. At lower shear rates, $\dot{\gamma} = 20 \times 10^8 \text{ s}^{-1}$ and $\dot{\gamma} = 4 \times 10^8 \text{ s}^{-1}$, the polymer chains start to deform plastically. Two jumps in the average coordinate (at $\gamma \sim 20\%$ and $\gamma \sim 40\%$) correspond

FIG. 8. (a) Change of the average X coordinate for the top layer upon shear deformation with different shear rates. (b) Change of the average X coordinate for different layers in a capped film upon shear deformation at low, $\dot{\gamma} = 4 \times 10^8 \text{ s}^{-1}$, shear rate. In both figures the calculations were made at 300 K and 52 MPa.

FIG. 9. (a) Ratio of the averaged velocity of the polymer segments in different layers of simulated film to the actual velocity of the top substrate at normal pressure 52 MPa, temperature 300 K, and for high and low shear rates. The dashed line denotes the velocity profile in the case of the ideal affine shear deformation. (b) X-component of the mean squared displacements of all particles in the top layer during shear deformation at high and low shear rates and also for non-sheared film (diamonds). The slopes 2 and 0.5 denote the ballistic and sub-diffusive motion of polymer segments.

to the moment of time when the polymer chains are not able any more to follow the substrate and simply go back. For the lowest shear rates the shear deformation is so slow that polymer segments just follow the top substrate and at some moment of time chains cannot deform anymore and the film as a whole is moving forward by 0.5 nm, as is clearly seen from the displacement of the layer close to the bottom substrate, Figure 8(b).

By calculating the slopes of the curves in Figure 8(b), we measure the layer-averaged (averaged over all layer particles) velocity upon deformation. Such calculations are made for different shear rates; the velocity profiles at temperature 300 K, pressure 52 MPa for high and low shear rates are shown in Figure 9(a). From this figure it is clearly visible that at low shear rate, $\dot{\gamma} = 1 \times 10^8 \text{ s}^{-1}$, the velocities in three top layers are very close to the speed of deformation, meaning that these layers move together with the top substrate. Bottom layers are rather weakly affected during deformation at the same shear rates. Such strong difference between shear velocities of top and bottom parts causes high deformations in the middle layers. This effect is usually ascribed to the shear banding and is observable over different length and time scales.⁵⁰ We should mention that due to the shear banding, the middle part of the film is highly deformed as compared to the top and bottom parts, meaning that most plastic deformations occur in the middle part. The shear-banding effect also appears at the highest shear rates, as can be seen from Figure 9(a). In this case, the shear banding occurs between the shear-affected 3rd top layer and the non-sheared 4th layer, as indicated by arrows in Figure 9(a).

The effect of the shear deformation on the local translational mobility has been studied by measuring the X-component of the mean squared displacement (MSD) $\langle \tilde{X}^2(t) \rangle$ of all united-atoms in the top layer of the non-deformed capped film (diamonds), and for the highly (squares) and slowly (circles) deformed capped films, Figure 9(b).

Two main processes can be observed in the MSD: the in-cage β -relaxation process, which is connected to the motion of the united atoms within a cage made by the surrounding

particles, and the α -process, which is ascribed to the out-of-cage escape, i.e., to the diffusive motion of particles.

At high shear rate the MSD has a non-trivial shape: initially, the curve has a slope close to 2 that corresponds to the ballistic motion. Then, a fast increase in the MSD up to the yield point (time at which the yield peak occurs is denoted by a vertical arrow) is observed. After that several maxima and minima in the MSD are visible, which correspond to the stick-slip motion.

At low shear rates the polymer film is plastically deformed, and convective translational motion of each layer together with stochastic Brownian motion contribute to the total translational mobility. We have used the following procedure to separate these two contributions. First, the average coordinate $\langle X \rangle$ is calculated every time step for each united-atom in the simulated film, as shown in Figure 8(b). Then, by calculating the slopes of curves in Figure 8(b) we measure the average velocity v_l of the corresponding layer upon deformation. After that, all coordinates of all united atoms in layers are modified every time step as $\tilde{X}_{i,l}(t) = X_{i,l}(t) - v_l t$. Finally, the modified coordinates $\tilde{X}_{i,l}(t)$ that correspond to the stochastic Brownian motion are used to calculate the MSD $\langle \tilde{X}_l^2(t) \rangle = \langle [\tilde{X}_{i,l}(t + t_0) - \tilde{X}_{i,l}(t)]^2 \rangle$.

The calculated MSD during the deformation at low shear rate (circles, $\dot{\gamma} = 1 \times 10^8 \text{ s}^{-1}$) exhibits a plateau (β -process) and the out-of-cage escape (α -process), which occurs at $t \simeq 200 \text{ ps}$ (indicated by the vertical arrow as the end of the elastic regime); this is significantly earlier as compared to the isotropic non-sheared film (diamonds), meaning that particles are forced to leave their original cages earlier.

IV. CONCLUSIONS

Molecular-dynamics simulations have been used to study the deformation mechanisms that appear during constant-shear deformation of atactic-polystyrene capped films. The constant-shear deformation has been performed at different shear rates, temperatures, and pressures to investigate the influence of these external parameters on mechanical properties of the films. We found that mechanical properties of aPS

films can be simulated by MD in qualitative and, to some extent, in quantitative agreement with other simulations and experiments.

At low shear rates the simulated stress-strain behaviour shows qualitatively the same trend as that obtained in simulations of model glasses, and in experiments on amorphous polymers, i.e., the elastic regime followed by the yield peak and softening. After the softening regime, at low shear rates, the polymer film starts to flow, while at high shear rates the sliding motion is observed. At high shear rates pressure and temperature rather weakly influence the stress-strain behaviour, while at low shear rates they have a strong effect on the stress-strain behaviour. The simulated shear modulus for aPS is almost twice smaller as compared to the experimental value in bulk and increases with shear rate. The calculated yield tooth increases with increasing shear rate, increasing pressure, and decreasing temperature.

Depending on the shear rate the work applied to deform the films is redistributed differently between heat dissipation and an internal energy. At high shear rates, i.e., during the sliding motion, the entire work done on the sample is totally dissipated, causing heating of the system. At low shear rates, this work is also partly converted into an increase of the total internal energy, which is mainly governed by an increase of excluded-volume interactions.

A large contribution to the total shear stress is given by the excluded-volume interactions, meaning that polymer segments are forced to leave their original positions. The latter is reflected in an increase of the local segmental dynamics, and an earlier transition to the cage-escape regime is observed.

The calculation of the average displacement of polymer segments in different film layers showed that upon constant-shear deformation at high shear rates, the top layers are weakly deformed while the middle and bottom layers are at rest, causing the well-known shear-banding effect. The shear-banding effect is also observed at low shear rates. Due to the fast motion of the top layers and almost immobile bottom layers, the middle part is then highly deformed plastically; this may rejuvenate the polymer in these layers.

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