

On the tribology and rheology of polymer brushes in good solvent conditions: a molecular dynamics study

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Abstract

Tribological and rheological properties of two polymer brushes in relative sliding motion and good solvent conditions are investigated by means of molecular dynamics (MD) simulations. The lateral forces between the brushes are found to decrease logarithmically with increasing relative sliding velocity v_0 over a range of more than one decade in v_0 . We also observe an almost logarithmic relaxation of the end-to-end distance vector that occurs after sliding is stopped. The coincidence of these logarithmic dependencies support the picture that friction between polymer brushes is small due to the retraction of the polymers from the interpenetration zone. The shear stress relaxes almost instantly in our simulations after sliding is stopped, unless poor solvent conditions are considered.

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1. Introduction

The present study is motivated by the desire to better understand friction between two solid surfaces bearing polymer brushes in good solvent conditions. Polymer brushes form when a sufficiently large number of polymers are chemically bonded to surfaces with one of their two endgroups. Good solvent conditions imply that the effective forces between non-bonded monomers are purely repulsive and thus correspond to excluded volume interactions. Revealing the atomistic origins of friction and lubrication between such surfaces is an active field of research both experimentally and in terms of computer simulations (for reviews, see [1,2]). The main advantage of using polymer brushes in good solvent conditions as a lubricant is the strong reduction of friction and wear in tribological contacts [3], which makes such systems promising candidates for technological applications.

The kinetic friction force F_k between brush bearing surfaces in solvents is composed of two contributions, namely, that stemming from interactions of the brushes with the solvent and the direct lateral forces between the brushes. While it is not possible to separate these two contributions experi-

mentally in a straightforward manner, theoretical models in general and computer simulations in particular make such an analysis possible. Moreover, computer simulations allow one to study the conformations of the polymer chains in detail and thus link rheological and tribological properties. Most analytical studies of our system of interest known to us have focused on the interaction between the solvent flow and an isolated brush [4–7]. One central issue discussed in these works is the effect of solvent flow on the brush height. Only Rabin and Alexander [4] predict an unperturbed brush height, while the other theoretical treatments predict brush swelling as a consequence of the solvent flow. From simple kinetic considerations, one would expect larger drag friction between solvent and brush in the latter case than if the brush height remained unperturbed or even shrank. Molecular dynamics (MD) simulations of contacts at constant velocity [2,8,9] are in disagreement with solvent flow induced brush swelling and thus support Rabin and Alexander. Note, however, that generally the solvent is not incorporated explicitly. The perhaps most realistic modeling of solvent flow into a single brush was done by Doyle et al. [10] in terms of so-called Brownian dynamics. Their study also disfavored brush swelling.

Only few studies are concerned with the coupling between the brushes and the interplay of kinetic friction force F_k , brush rheology, and brush relaxation. One such investigation was recently reported by Tadmor et al. [11] who argued that

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friction was reduced due to a sliding induced disentanglement of polymers belonging to opposing brushes. The relaxation of the shear stress was investigated as well as the effect of aging on shear stress maxima that occurred after sliding was re-initiated in opposite direction to the original motion. Nonetheless, such experiments only allow one to extract information on the brush rheology *indirectly* through the tribological response. In this paper, we want to investigate their relationship directly by extending a previous molecular dynamics study [12], in which we found that the kinetic friction coefficient μ_k between the brushes decreased with increasing sliding velocity v_0 . This decrease of μ_k coincided with a reduced brush interpenetration and with shear alignment, which was found to be significantly more pronounced for grafted than for adsorbed polymers. At fixed load, the *net* shear stress σ_s increased nevertheless with v_0 due to the solvent flow into the brushes, although the *direct* (thermodynamic) shear stress σ_{br} between the brushes decreased with increasing v_0 . σ_{br} is defined as the sum of all effective forces parallel to the sliding direction between monomers belonging to the upper brush and those monomers belonging to the lower brush, normalized by the area of contact A .

Experimentally, much smaller absolute sliding velocities are employed than in simulations, which reduces the effect of the solvent flow with respect to MD studies. At the same time, the experimental degree of polymerization and thus the mutual brush interdigitation is much larger than in a numerical analysis. This implies that in experiments, the tilting is more likely to be induced by the direct brush–brush interactions as compared to our previous simulation where tilting was strongly enhanced through the solvent flow, which was modeled by a standard Langevin thermostat [12]. In order to mimic the experimental situation better, it would thus be necessary to strongly reduce the effect of the thermostat, i.e. by switching it off parallel to the sliding direction. This will then enable one to explore the velocity dependence of F_k in detail when the tilting is due to mutual brush–brush interactions.

The purpose of this paper is to establish the connection between tribological and rheological behavior of sliding polymer brushes in good solvent conditions in terms of an MD study much more directly than this would be possible experimentally. In the following, a brief description of the employed model will be given. The steady-state sliding friction forces will then be analyzed as a function of velocity for different realizations before we study the structural relaxation of the polymers after the system is brought to a halt. Finally, we will summarize and discuss our main results.

2. Model

In this study, we perform standard molecular dynamics simulations of a coarse-grained model, which is well established for the investigation of friction between polymer bearing surfaces [2]. Polymers are modeled as bead–spring chains, where appropriate potentials ensure excluded volume

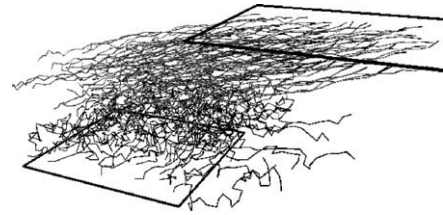


Fig. 1. Snapshot of sliding walls bearing engrafted polymers in good solvent at large sliding velocities. Periodic boundary conditions are employed parallel to the surfaces. Black polymers are attached to the bottom wall and gray polymers to the top wall.

interactions between the beads as well as the connectivity along the backbone of the chain. One end of each polymer is tethered to a random position on one of the two atomically smooth surfaces. A snapshot of the simulation is shown in Fig. 1 in order to visualize the set-up of the simulations.

Both surfaces bear the same amount of grafted polymers. The solvent is not treated explicitly, but in terms of a Langevin thermostat, which, however, is switched off parallel to the sliding direction. In the other directions, a damping force proportional to velocity with a prefactor γ is applied in order to prevent the system from heating. Due to the absence of the solvent, heat transfer would otherwise be artificially small. Including solvent atoms would slow down the simulations distinctly and prevent us from accessing the relevant length and time scales. As done previously, good solvent conditions are mimicked by the effective interactions between monomers. We employ the same model as in our earlier paper, where we provide a more quantitative description of the parameters describing the interactions [12]. All data presented in the following figures are expressed within the Lennard–Jones (LJ) units of [12]. Note that in order to compare our results to experiments, it will be necessary to scale length and time scales in a meaningful way, because the polymers used in experiments have a much larger degree of polymerization N than those in our simulations. This issue is also discussed in more detail in [12].

An important quantity is the employed grafting density α_g , which is stated in units of the critical drafting density $\alpha_g^* = (1/\pi)R_{gyr}^2$, where R_{gyr} is the radius of gyration of free chains in solution. At α_g^* , chains are starting to overlap leading to stretching of the polymers perpendicular to the walls. Above α_g^* the brush height increases approximately linearly with the degree of polymerization even if the absolute volume fraction is well below unity. We chose normal separations D between our flat walls such that the normal forces F_N can be approximated by a power law $D^{-4.2}$, which mimics the behavior displayed, for instance, in Fig. 9 of [1].

3. Results for steady-state sliding

It has been an ongoing debate whether brushes swell or shrink when exposed to an external solvent flow. Assuming

a tangential force acting on the end of a brush, Rabin and Alexander [4] predicted an unperturbed brush height. Later, Barrat [6] suggested that the excluded volume interactions within a brush increases due to the solvent flow. This argument leads to shear induced brush swelling. Both points of view should remain qualitatively similar when a brush rubs against another brush, because the opposing brush plays to some (qualitative) degree the role of the moving solvent. Although the quantitative details will differ between the two scenarios, the arguments with respect to brush swelling will remain similar. There are various ways, how brush swelling can be detected. First, by observing normal motion of the upper plate (provided the normal force is constant) or by measuring/calculating the normal force between the plates (provided the separation is kept constant). This method is an indirect observation of the brush height and it was discussed in a previous work [12], favoring absence of brush swelling or shrinking. Second, brush swelling can be detected by analyzing the end-to-end vectors of the grafted polymers. This is done in the main part of Fig. 2, where predictions by the two models are compared to results from our MD simulations. We find that there is a somewhat more satisfactory agreement with the predictions by Rabin and Alexander than by those favoring brush swelling. This finding is in qualitative agreement with previous simulations of related model systems (see [10], and references therein).

It is interesting to note that the swelling barely depends on whether the thermostat is switched on or switched off parallel to the sliding direction. The main effect of the thermostat is that the additional drag force enhances the inclination, but it barely effects the swelling. The precise choice of the thermostat's damping constant γ has also little effect on

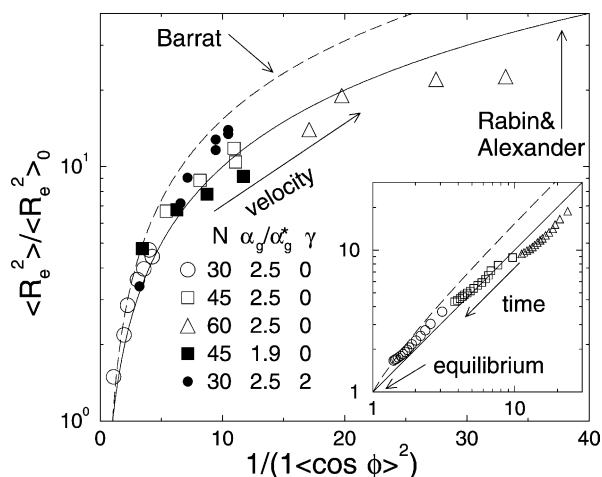


Fig. 2. Average squared end-to-end distance $\langle R_e^2 \rangle$ normalized by its zero-velocity value as a function of tilting as determined by the inclination ϕ during steady-state sliding. Chain lengths N , sliding velocity, and grafting densities α_g are varied, wall separation is fixed at $D = 17.5$. For $\gamma = 2$, the thermostat was also applied parallel to sliding. Theoretical predictions of [4,6] are included. Inset: relaxation of polymer stretching and tilting as a function of time after sliding is stopped. Note the double-logarithmic scale.

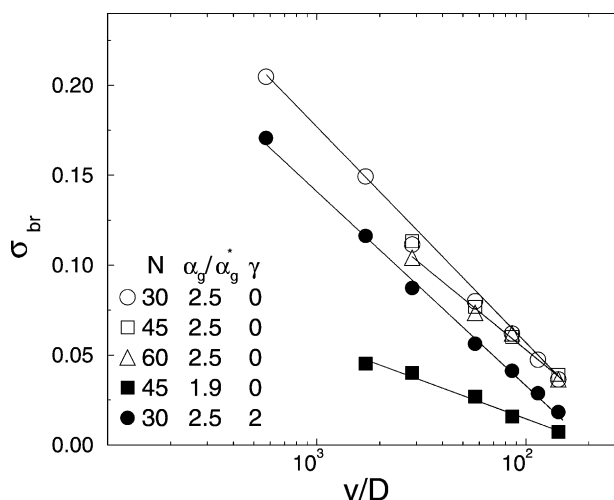


Fig. 3. Shear stress σ_{br} as a function of velocity at wall separation $D = 17.5$. Lines are drawn to guide the eye.

the dependence of σ_{br} on the mutual brush interdigitation, which was a central observable in our previous work. Nevertheless, interdigitation and σ_{br} are both strongly reduced individually when the thermostat acts parallel to the sliding direction.

An important steady-state quantity that has not yet been investigated in detail is the velocity dependence of the shear stress. The data obtained in this study exhibits a logarithmic decrease with increasing v_0 as shown in Fig. 3 within the limited velocity window accessible to the simulations. A re-analysis of the data from our previous study, in which the thermostat also acted parallel to sliding, also yields this logarithmic decrease of $\sigma_{br}(v_0)$. Here, we want to give a brief discussion of the origin of this $\ln v_0$ dependence and the range of its applicability. For large v_0 , friction is bound to below by the simple requirement that σ_s cannot become negative. In the opposite limit of arbitrary small v_0 , the system is close to thermal equilibrium, thus linear response theory applies and $\sigma_{br} \propto v_0$ for $v_0 \rightarrow 0$. Hence, Fig. 3 implies that our system is far away from equilibrium even at the smallest velocity, which was $v_0 = 0.01$ in LJ units. At this velocity, one has to make almost 100,000 MD steps in order to move the upper wall by the radius of gyration of a free chain, which is just a small fraction of the steps necessary to reach steady state. Thus, these calculations signify a rather large numerical effort.

The $\ln v_0$ dependence between these two regimes may be explained by the following phenomenological but generic argument: The (apparent) free energy barriers $\Delta\mathcal{F}$ that prevent a system from relaxing towards equilibrium depend on some internal parameter ξ , which in the present case, could possibly be the degree of interpenetration or the average end-to-end radius. If the initial condition is such that ξ is sufficiently far away from its equilibrium value to decrease $\Delta\mathcal{F}$ by significantly more than the thermal energy, then the relaxation will slow down considerably as the system

approaches equilibrium. Such considerations have first been discussed by Prandtl in a pioneering and yet largely ignored publication [13]. They can be shown to lead to logarithmic behavior in either the time or alternatively in the velocity domain. In our study, however, the free energy barriers are likely to be dominated by the entropic contribution. This makes our system different from many others in which potential energy plays the main role.

4. Results for relaxation after stop

When the upper wall is brought to an immediate halt, the brush shear stress σ_{br} and the brush structure start to relax towards their zero-velocity equilibrium values. In the following, we will analyze the normalized relaxation function $C_A(t)$ of the type

$$C_A(t) = \frac{\mathcal{A}(t) - \mathcal{A}(\infty)}{\mathcal{A}(0) - \mathcal{A}(\infty)}, \quad (1)$$

where t refers to time and \mathcal{A} to the observable of interest.

In the good solvent conditions considered up to here, σ_{br} relaxes almost instantly, that is to say, $C_{\sigma_{br}}$ becomes essentially zero within once or twice the time necessary for a sound wave to travel from one wall to the other wall and back. For longer polymers, where entanglements are possible, the situation might be different. The fast relaxation of σ_{br} is nevertheless unexpected, because even for our unentangled polymers, structural relaxation times are rather large. It is interesting to note that as far as the relaxation of the end-to-end radius is concerned, the relaxation process is almost logarithmic in time (see Fig. 4), while the relaxation

of the inclination, which is not shown here, can be approximated much better by a single exponential.

In the inset of Fig. 4, the half-life period τ_R of the relaxation $C_{R_c^2}(t)$ is shown. For large sliding velocities, where the system is far from equilibrium, the (apparent) relaxation times τ_R are roughly proportional to the degree of polymerization. At smaller velocities, the apparent relaxation times increase significantly, but, as stressed before, we have no means to estimate the linear-response values of τ_R .

The relaxation process is also described in the inset of Fig. 2, where neighbored symbols denote data that are equidistant in time. In all cases, the brushes swell slightly during the relaxation within the time window accessible. The regime above the solid line, which reflects the theory by Rabin and Alexander [4] of unperturbed brush heights, indicates a brush swelling with respect to zero sliding velocity, while the regime below the line indicates brush shrinking. Despite relatively long waiting times, one can see that the system is still far away from equilibrium and it is also remarkable how strongly the relaxation slows down as equilibrium is approached. While the shear stress relaxes almost instantly in our simulations, there can be noticeable differences in the σ_{br} signal when sliding is re-initiated in the direction opposite to the initial sliding direction. In that case, we find an increasing maximum in σ_{br} with increasing waiting time. At present, the statistical quality of that data does not yet allow us to make more quantitative statements. In our case of good solvent conditions and degrees of polymerization slightly below the entanglement length, we can conclude that the shear stress relaxation does not couple strongly to the slowest relaxation processes, while the re-initiation of sliding is much more susceptible to the structural relaxation of the brushes.

In a different set of simulations, the solvent quality was altered to poor solvent conditions, where interactions do not only consist of entropic like excluded-volume potentials, but they can also be of energetic nature. This alteration leads to *qualitatively* different behavior concerning the brush shear stress relaxation, which now decays on much longer time scales than in good solvent conditions. The reason for this discrepancy could be that thermal activation is required in order to release the shear stress in poor solvent conditions.

5. Discussion and conclusions

In this paper, we report molecular dynamics simulations of two polymer brushes in relative sliding motion and good solvent conditions. In most of our calculations, we neglect the coupling of the brushes to the solvent flow in sliding direction, which we believe to be a justified approximation of the experimental situation characterized by large degrees of polymerization and small sliding velocities. While the shear stress σ_{br} must increase linearly with sliding velocity if v_0 is sufficiently small so that linear response theory is applicable, we obtain a logarithmic *decrease* with increasing v_0

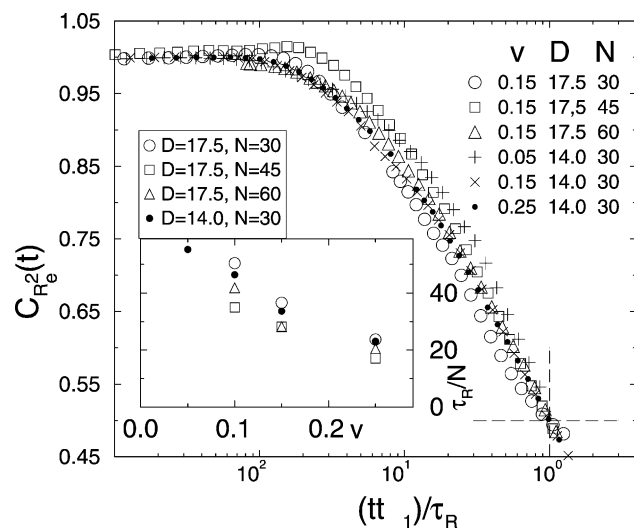


Fig. 4. Relaxation $C_{R_c^2}(t)$ of average squared end-to-end radius R_c^2 as a function of time for different systems and sliding velocities. The time axis is rescaled such that all curves coincide at the half-time τ_R of the relaxation. Inset: τ_R divided by chain length N for different realizations as a function of initial sliding velocity.

within the limited velocity window accessible to us. We argue that the shear stresses are due to *entropic* forces that attempt to drive the system back into equilibrium, where the interdigitation of the brushes is distinctly larger than during steady-state sliding and where polymers are not shear aligned. However, when friction is due to *energetic* forces (for instance, due to mechanical instabilities [13–15]), the picture is qualitatively different: The number of instabilities per slid distance and hence the friction force becomes constant plus corrections in the order of $\ln v_0$ with a *positive* prefactor.

Similar entropic arguments that concern arm retraction for chains much longer than the entanglement length have recently been suggested by Tadmor et al. [11]. They propose that friction and structural relaxation of opposing brushes bears analogy to that of long dangling ends in branched polymer networks. Close to thermal equilibrium, the number of entanglements is large and thus a large force is needed to maintain relative sliding motion, while at large velocities the formation of entanglements is kinetically suppressed. de Gennes predicted that dangling ends relax logarithmically and that a similar time-dependence should be found for the decay of mechanical stress [16]. Although our chains are relatively short and no entanglement effects can be expected, we observe that the end-to-end radius of the stretched polymers relax almost logarithmically in time in agreement with de Gennes' prediction. However, in our case, the shear stress drops to zero almost instantly after sliding is stopped.

Our results must be discussed further in light of the experimental results reported by Tadmor et al. [11]. While our conclusions are to a large degree in agreement, two of their observations seem to be in contradiction with our findings: first, their shear stress σ_s relaxed on large time scales after sliding stopped, and second σ_s was almost independent of the sliding velocity v_0 or possibly even *increased* logarithmically with v_0 . However, these two points do not necessarily contradict our findings, if one considers that: (i) the solvent quality encountered in experiments is certainly not as good as the pure excluded volume interactions that one can impose artificially in computer simulations; and (ii) experiments are closer to thermal equilibrium for sliding velocities as small as in [11].

We now discuss these two differences in more detail. (i) For less ideal good solvent conditions, energetics will play a more important role and the occurrence of mechanical instabilities (fast pops of certain microscopic degrees of freedom) might become unavoidable. This would be a rather generic scenario for $\ln v_0$ type corrections to the friction force [13–15]; see also the nice discussion by Charitat and Joanny [17] incorporating details of polymer dynamics into the picture of mechanical instabilities leading to $(\ln v_0)^{2/3}$ corrections. (ii) One may yet speculate that energetically

driven instabilities would become less important if experiments were done at larger values of v_0 , in which case the experimental situation would better resemble the circumstances of our MD simulations. In particular, it was estimated that the chain elongation was at most 20% of the fully stretched chain, which is much less than in our typical runs. We therefore expect σ_{br} to decrease eventually with increasing v_0 , although the coupling to the solvent might camouflage a decrease in the direct interactions between the brushes.

In our simulations, we found that energetics play a crucial role for the relaxation of the shear stress. As soon as the solvent property was changed from good to poor, we observed strongly increased relaxation times, indicating that thermal fluctuations became necessary to release the shear stress with time. While we do not claim thermal relaxation to be the main mechanism in Tadmor et al.'s experiments, it is yet a plausible scenario leading to the observed effects in addition to the entanglement mechanism discussed by Tadmor et al. [11].

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