

Sliding-induced non-equilibrium in confined systems

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ABSTRACT

When two solids are in relative sliding motion, the intervening layer separating the two surfaces (for example the boundary lubricant) is typically far from thermal equilibrium. With the help of a generic model reflecting the boundary lubricant, it will be shown that it is often not possible to characterize a sliding contact by means of a single effective temperature. The reason is that the probability distribution (PD) of microscopic variables differs in a characteristic fashion from equilibrium PDs. Non-equilibrium velocity PDs are not Gaussian but tend to be exponential, thus favoring rare events. Leaving dynamic equilibrium by non-uniform sliding conditions leads to yet additional effects, in particular to enhanced dissipation. This is shown in a model describing rubbing polymer brushes in good solvent conditions. Shortly after returning the sliding velocity, the brush interdigitation is distinctly larger than during steady-state sliding. Based on this observation, predictions can be made at what amplitude the loss is maximum for a given driving frequency.

INTRODUCTION

An important issue in tribology is the question what the mechanisms are that lead to energy dissipation [1] and how we can characterize the microscopic state of a sliding contact. Of particular interest are those sliding contacts in which the friction force does not vanish linearly with the shear rate for mainly two reasons. First, from a practical point of view, this behaviour is typically observed between virtually every pair of macroscopic bodies. Secondly, non-linear friction-velocity relationships clearly indicate that the systems cannot be treated within linear-response theory. This makes them interesting to study from a theoretical point of view. Many different scenarios have been suggested that result in non-linear friction-velocity relationships. A non-exhaustive list includes plastic deformation, self-healing cracks, elastic and mixing instabilities, as well as instabilities in boundary lubricants [2]. All these mechanisms have in common that the system is pushed far away from thermal equilibrium and that energy is lost as heat when the system relaxes or is trying to relax towards equilibrium.

While all above-mentioned processes are relevant to many different tribological aspects (i.e. wear), it is tempting to hypothesize that most of the energy gets dissipated in the boundary lubricant. First, it has been known since the works by W.B. Hardy in the early 20'th century that the application of a molecular thin layer of lubricant can change the friction forces between metals by almost an order of magnitude [3]. Second, a contact 'breaks' and hence dissipates energy at its weakest link, which is the boundary lubricant (BL). The reason for this is that interaction between the BL particles are physical, while the

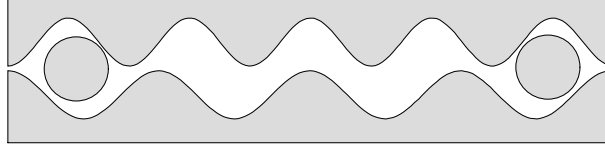


Figure 1. Schematic drawing of the mechanism by which a boundary lubricant locks two surfaces together, whose intrinsic corrugations do not match. From reference [7].

interactions in the confining solids are much stronger, because the intrabulk forces are due to either metallic, covalent, or ionic bonds or a combination thereof. Thus, the yield stress of the (solidified) BL should be smaller than that of the two surrounding solids.

Since Hardy, experimental techniques have made it possible to study the response of molecularly thin films to mechanical forces under ever better-controlled conditions [4,5]. It has yet remained an unsolved challenge to measure the atomistic structure of lubricants and to visualize the processes that cause Amontons's and Coulomb's laws of friction. New insights into the atomistic structure of mechanical interfaces could nevertheless be gained with the help of computer simulations. In particular, it could be shown that a BL is able to conform to the atomistic surface corrugation of both walls simultaneously. For this reason, two solids can lock at an atomic scale [6,7], see also figure 1. This 'locking-together' explains static friction. However, does this mechanism necessarily lead to 'typical' kinetic friction, i.e., to a law in which the kinetic friction F_k is *not* linear in the sliding velocity v_0 ? In the first half of this contribution, I intend to address this question, among other issues. For that purpose, I will discuss a generic model for a boundary lubricant in which a mechanical contact is mimicked by means of two confining crystalline walls plus the embedded boundary lubricant. One of the central questions will be how one can characterize the microscopic state of an embedded system under constant sliding velocity.

If deviations from thermal equilibrium lead to non-linear friction-velocity relationships under steady-state sliding conditions, what are the consequences if we go even further and consider sliding conditions that are unsteady? I will address this question in the second part of the present contribution. In that discussion, a different model system will be studied. It consists of two solids, which both have polymers chemically grafted onto their surfaces. The polymers are immersed in a good solvent and form so-called brushes, which will then slide against one another. The simulations of the friction between such polymer bearing surfaces were also motivated by experimental studies by Granick, Cai and coworkers [8,9], who found enhanced dissipation between polymer brushes for certain driving amplitudes at fixed frequency or alternatively, enhanced dissipation for certain frequencies at fixed amplitudes. The origins of this increased friction were discussed controversially in the literature [10,11].

The main part of the remainder of this contribution will consist of two parts. In the first part, the kinetic friction due to boundary lubricants will be discussed, in order to understand how the deviation from thermal equilibrium can effect the frictional forces between two solids. In the second part, the kinetic friction between polymer brushes will be reviewed with an emphasis on the effects of non-uniform driving. Finally, we will conclude with a general discussion.

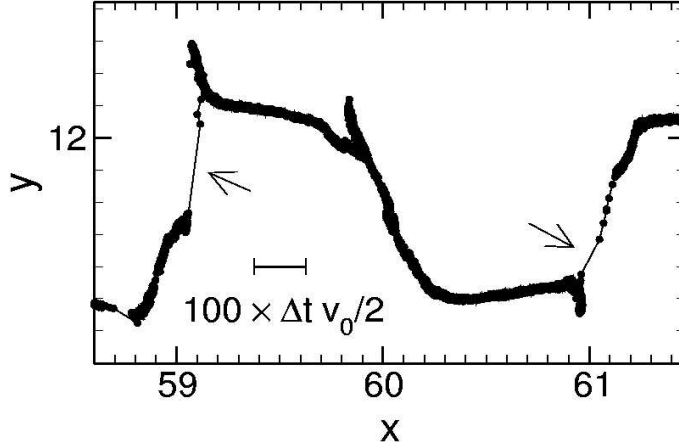


Figure 2. Trajectory of a lubricant impurity in the xy -plane tagged between two incommensurate surfaces. The relative velocities of the walls in Lennard Jones units is $v_0 = 10^{-3}$. The positions are plotted every $\Delta t = 0.5$. The unit of length would translate to approximately 3 \AA and that of time to 3 ps . The bar denotes 100 times the average drift distance per time interval Δt . The arrows indicate dynamical instabilities. From reference [12].

KINETIC FRICTION DUE TO BOUNDARY LUBRICANTS

General comments

As argued in the first paragraph of the introduction, deviations from thermal equilibrium result in friction that is in contradiction with Stokes' law $F \propto v$. A model which illustrates non-linear friction very nicely is the model by Prandtl and Tomlinson [2]. They considered a surface atom that is pulled over a corrugated substrate via a compliant spring. If the spring is sufficiently weak, then at some instances in time, the atom becomes unstable and 'pops' into the next available potential energy minimum. This process occurs in regular intervals, for example (but not necessarily) each time the spring has moved by one lattice constant. Each time an atom pops, (the same amount of) energy is lost. This produces a kinetic friction force that is (essentially) independent of v as the lost energy would be proportional to the covered distance. For a review of this process, including the role of thermal fluctuations invoking logarithmic corrections, I refer the reader to reference [2].

From the discussion of the Prandtl model in the previous paragraph one can learn that instabilities (or plucking motion) leads to laws that can deviate strongly from regular linear response. However, the detailed dynamics of realistic systems may be very different from that in the Prandtl model. For instance, if we consider the motion of adsorbed atoms between two incommensurate walls that slide past each other, we cannot expect trajectories as periodic as those in the Prandtl model. Indeed, the motion of atoms that are confined between two incommensurate walls is rather erratic [12], as can be seen in figure 2.

Each time an instability occurs, potential energy is first converted into kinetic energy, which ultimately will be dissipated into heat. While figure 2 shows that confined boundary lubricant can show the necessary plugging motion similar to that in the Prandtl Tomlinson model, it has been noted that plugging motion does not necessarily take place in boundary

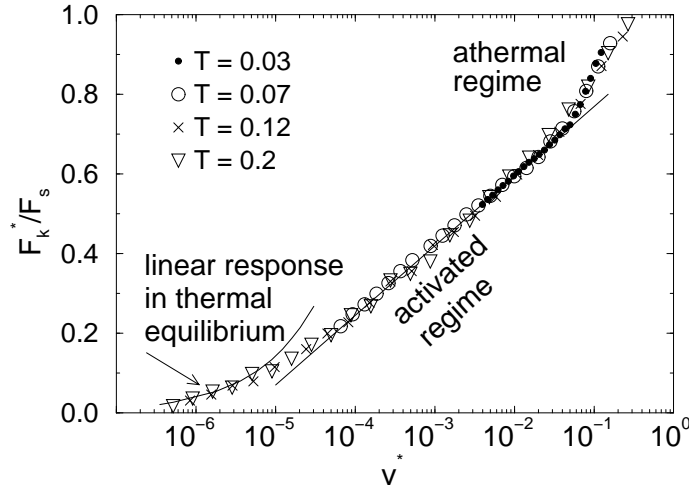


Figure 3. General tribological behaviour of an extreme boundary lubricant as shown by the scaled kinetic friction $F_k^*(v)$ normalized by the athermal zero-velocity limit $F_s = F_k(v = 0, T = 0)$ as a function of renormalized velocity v^* . The reference temperature in this plot is $T = 0.07$. A linear law $F_k(v) \propto v$ corresponding to the linear-response theory is included for comparison. In order to achieve superposition of the rescaled curves, the contribution $F_k(v, T = 0) - F_k(v = 0, T = 0)$ had to be subtracted from the friction forces. From reference [13].

lubricants [13]. For instance, if only few boundary lubricant (BL) atoms are present between two commensurate surfaces, there will be barely any instabilities. (Details depend on whether or not the walls are allowed to move transversally.) Also one-dimensional walls, as shown in figure 1, often do not invoke plucking motion, because the adsorbed atoms may be dragged along with one of the two moving walls, namely that which has the large surface corrugation. This effect can also occur in two dimensions, but only if the lubricant particles interact distinctly stronger with one wall than with the other wall [14]. If, however, pops do occur, then the behavior is rather generic, i.e., linear in velocity v_0 with which the walls slide past each other at very small v_0 , followed by a regime in which the dependence of F_k on v_0 is only logarithmic. At very large v_0 , the friction force reaches the same value as that at zero temperature [13].

It is worth noting that a logarithmic velocity dependence of F_k on v_0 is not only obtained with only a few impurities keeping the two opposing surfaces from getting into contact. Similar behavior, in particular the logarithmic velocity corrections, was also observed in large-scale molecular dynamics simulation by He and Robbins [15]. While often observed experimentally, logarithmic velocity correction to F_k are nevertheless by no means universal. For instance, the Prandtl model - as well as the dry friction between an atomic force microscope tip and a substrate - show corrections in the order of $(\ln v)^{2/3}$ in the intermediate or activated velocity regime [16,17].

The reason why the friction-velocity relationship becomes linear at extremely small velocities is due to the fact that the number of instabilities invoked through sliding is less than the number of pops that occur via equilibrium thermal fluctuations. Thus, sliding-induced plucking motion is only a small perturbation to the overall dynamics. As v_0 is increased,

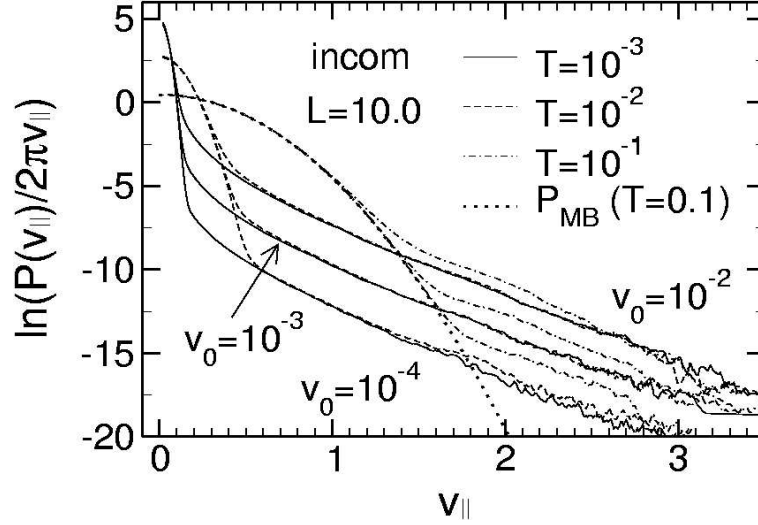


Figure 4. *Logarithm of the (in-plane) velocity distribution $P(v)$ of boundary lubricant atoms at various temperatures T and relative sliding velocity v_0 of the confining walls. The Maxwell Boltzmann distribution P_{MB} at the smallest temperature is inserted for comparison. The non-equilibrium tails decay exponentially. The slope of the tails in the logarithmic representation is independent of both v_0 and T . From reference [12]*

the sliding-induced pops become much more numerous than those in thermal equilibrium. Thermal fluctuations help atoms to leave energetically unfavourable positions, thus enabling the atoms to jump prematurely before the true instability point is reached. At large v_0 , temperature becomes irrelevant and F_k saturates, because the number of instabilities and the energy released only depends on the slid distance. At very large v_0 , dynamical resonance effects are starting to set in, because v_0 divided by a characteristic distance (i.e. the lattice constant) becomes comparable to intrinsic time scales in the system.

Velocity distributions

The jumps discussed in the last section will alter the atomistic velocity distribution $P(v)$ of the adsorbed atoms. Each time, an instability of a certain type occurs, there will be a characteristic deviation $\Delta P(v)$ of $P(v)$ from the Maxwell-Boltzmann equilibrium distribution $P_{MB}(v)$. During a jump, the plucking motion and its associated non-equilibrium velocity distribution will neither be sensitive to the temperature nor to the sliding velocities of the confining walls. The reason is that the duration of a pop is much shorter than both the time for the system to reach local thermodynamic equilibrium and the time for the walls to move by one lattice constant. Hence, the faster the walls slide past each other, the larger the deviation between $P(v)$ and $P_{eq}(v)$, and we would expect $\Delta P(v)$ to be proportional to v_0 . Moreover, one should not expect a significant temperature dependence in the tails of $\Delta P(v)$. These simple expectations can be confirmed by computer simulations, as shown in figure [4], which shows that the non-equilibrium tails of $P(v)$ are proportional in height with v_0 and relatively independent of temperature. Given the shape of $P(v)$ in figure 4, it is obvious that it would not be possible to reproduce that distribution in terms of a single effective

temperature, but if anything, as a distribution of temperatures.

What can we learn from the velocity distributions shown in figure 4? First, the excess kinetic energy will be dissipated into the walls as heat. In steady state, conservation of energy requires that the heat flow per time unit must correspond to the external power necessary to maintain motion. It is therefore possible to relate $\Delta P(v)$ and the related excess kinetic energy to the friction force, as done quantitatively in reference [12]. Second, one can learn that even though the net kinetic energy is barely increased with respect to the equilibrium kinetic energy at, let's say $T = 10^{-2}$ and $v_0 = 10^{-3}$, the probability to have exceedingly fast particles of velocities of let's say $v > 3$, is increased dramatically. This indicates that rare events are favoured considerably in non-equilibrium with respect to equilibrium, even when both have the same fixed kinetic energy. In our case, it is possible to describe the non-equilibrium distribution with two parameters in addition to the equilibrium parameters. The additional parameters are the slope of the exponential tails and the prefactor or alternatively slope of the tails and the area below them.

The slope B of the exponential tails such as those shown in figure 4 was found to be dependent on the normal pressure p_{\perp} . For our extreme BLs (from the impurity limit to up to two layers of lubricant confined between the surfaces), a power law $B \propto p_{\perp}^{0.4}$ was identified, although the exponent 0.4 is not expected to be universal. In particular, when the number of layers between the walls is increased very strongly, the tails in $P(v)$ seem to disappear altogether, perhaps due to more collective motion [18]. Nevertheless, in the case of extreme boundary lubrication, when everything is squeezed out but the last one or two layers, one can see the trend that higher loads lead to more extreme velocity distributions. One may speculate that this effect is relevant to tribochemistry, because extreme velocities favor chemical reactions.

KINETIC FRICTION BETWEEN POLYMER BRUSHES

In the previous part of this chapter, it was discussed how sliding makes a boundary lubricant deviate from thermal equilibrium and how this leads to dissipation. Now, we will be concerned with the effects of leaving not only thermal equilibrium but also uniform sliding. As mentioned in the introduction, Granick, Cai and coworkers [8,9] found enhanced dissipation when they employed oscillatory shear between polymer brushes. In linear response, such increased losses can be related to an (approximate) coincidence of relaxation times and inverse driving frequencies [10]. However, at the given driving amplitudes, the brushes must have already been far removed from linear response, so that this explanation does not seem apply to the mentioned experiments. Zaloj *et al.* suggested an alternative mechanism for the occurrence of enhanced dissipation [11]. Taking into consideration the elastic coupling of the driving device to an embedded (frictional) system, they showed that stick-slip motion can occur at intermediate driving amplitudes \mathcal{A} , which would then explain the observed enhanced dissipation. Both, at small \mathcal{A} and at large \mathcal{A} , friction would be smaller, because the embedded particle's motion is smooth in either limit. Zaloj *et al.* supported their claim by studying a simple linear molecule, embedded between two shearing plates. While this scenario for increased loss is certainly legitimate, it is not necessarily the relevant mechanism for the system of interest and a more accurate model is needed to clarify the mechanism. One may argue in support of Zaloj *et al.*'s scenario that computer simulations indicated a

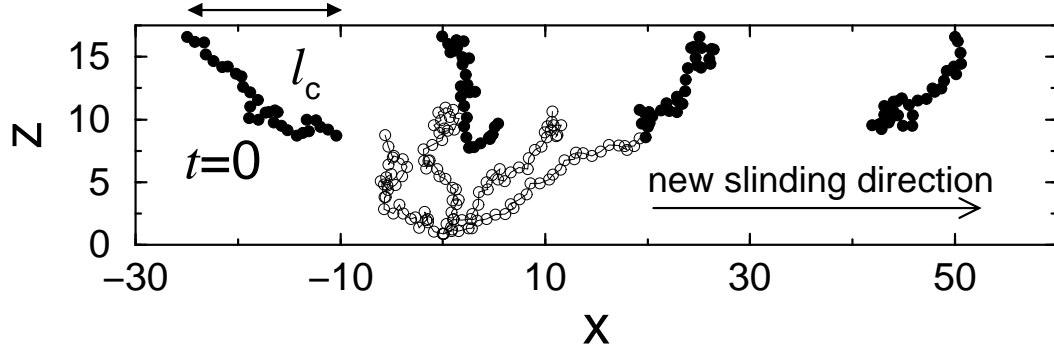


Figure 5. Time evolution of two randomly picked chains; the polymer represented with open symbols is attached to the upper wall, the other one to the lower wall. On the left-hand side, the brushes are shown in their uniform sliding state, at time $t = 0$, just before the sliding direction is inverted. l_c and the arrow above denote a characteristic length of the polymer in steady-state sliding. After reference [20].

decreasing shear force with increasing shear rate [19]. Nevertheless, the bead-spring polymers do not show stick-slip motion, even at weak coupling and small v_0 . Therefore it seems that this explanation does not seem to explain the enhanced friction either.

Another reason might be more convincing: When the sliding direction is returned, the interdigitation of the polymers will be much larger than during steady-state sliding. Thus, energetically unfavorable configurations are produced and the relative excess energy will be lost as heat. Indeed, this is what one can see from snapshots of computer simulation as shown in figure 5. The simulation underlying figure 5 will be discussed in the following [20].

Model and normal forces

Over the last decade, many computer simulations of polymer bearing surfaces have employed a simple bead spring model [19-22]. Using simple but generic models makes it possible to access much longer chains and timescales than it would be with chemically accurate potentials. This makes it possible to study the universal behavior of polymers. The main ingredient of the present model is that the interaction between non-bonded segments is purely repulsive, thus mimicking good solvent conditions. Furthermore, neighbored segments on a chain are sufficiently close so that bond crossing does not occur. More details on the model potential are given in references [19] and [22].

All simulations discussed here, have been carried out in the semi-dilute regime, which is characterized by a grafting or anchoring density $1 \gg \alpha_g \gg \alpha_g^* := 1/\pi R_{\text{gyr}}^2$, where α_g^* denotes the critical grafting density and R_{gyr} the radius of gyration of an untethered single chain. At α_g^* , chains are starting to overlap which leads to stretching of the polymers perpendicular to the walls. Although our model does not capture any chemical details and even though our polymers are much shorter than those studies in many experiments, it is possible to reproduce semi-quantitatively characteristic experimental features. For example,

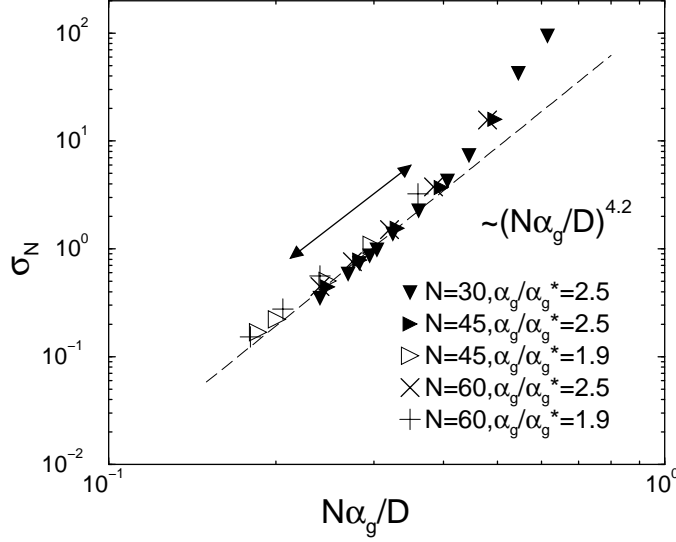


Figure 6. Normal stress σ_N as a function of an effective density $N\alpha_g/D$ between the two confining walls for different degrees of polymerization N and grafting densities α_g . The arrow encompasses the regime of the shear simulations presented below. The dashed line reflects a power law $D^{-4.2}$, where D is the separation between the walls. From reference [20].

it is possible to superimpose scaled force-distance curves rather accurately even when various parameters are altered, such as the degree of polymerization or the ratio of grafting density α_g and critical grafting density α_g^* . To be specific, we observe a power law dependence $\sigma_N \propto D^{-4.2}$ of the normal shear pressure σ_N as a function of the separation D . Comparison with experimental data, such as that presented in Ref. [23], is difficult, because flat confining surfaces were used in the simulations, while crossed curved surfaces with grafted polymers were employed in the experiments.

Steady-state sliding

When two polymer brushes are sheared against each other at constant sliding velocity, the mutual interdigitation decreases with increasing sliding velocity v_0 , even though the brush height remains almost unaltered [19]. The reduction of the brush overlap with increasing shear rate leads to a logarithmic reduction in the friction force F_k for simple bead spring models [21]. It was argued, however, that the friction-velocity relationship would also contain *positive* $\ln v_0$ corrections to F_k , if energetic processes and instabilities (plucking motion) were starting to play a role. These are absent in the purely entropic bead-spring polymers. Indeed, experiments indicate that F_k is essentially independent of v_0 or perhaps has small net positive corrections which are logarithmic in v_0 [24].

The purely entropic brushes shows some more interesting behaviour: F_k and the overlap between the brushes is highly correlated, i.e., at fixed reduced grafting density α_g/α_g^* all measured curves, F_k as a function of the overlap, superimpose, even when the degree of polymerization N , the sliding velocity v_0 , and the thermostat (reflecting the viscosity of the solvent) are changed [20]. Given the brush overlap, one might have expected higher drag

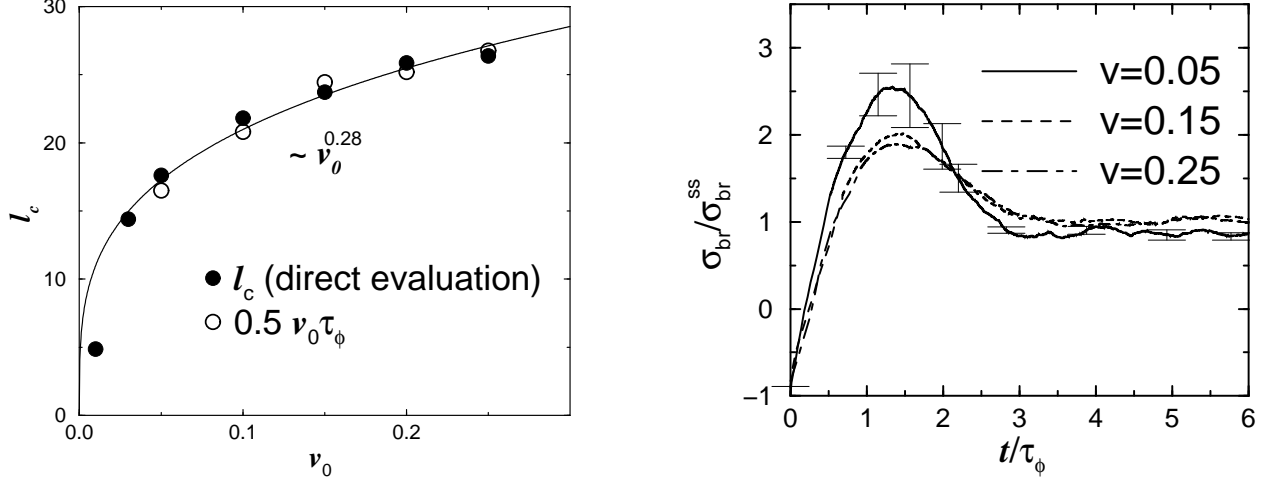


Figure 7. *Left: Direct and indirect evaluation of the characteristic lateral length l_c as a function of sliding velocity v_0 . τ_ϕ denotes the time necessary for the polymer brushes to pass through a 90° configuration after the sliding direction has been returned. Right: Shear stress σ_{br} normalized by steady-state shear stress σ_{br}^{ss} as a function of time in units of τ_ϕ . Adapted after reference [20].*

between the brushes at higher velocities. However, the better shear alignment at higher v_0 reduces the friction and compensates the velocity effect. A measure for the shear alignment is the characteristic lateral length l_c , which is introduced in figure 6. It was found that it depends like a power law $l_c \propto v_0^{0.3}$ on the sliding velocity.

Non-uniform sliding

The most simple non-uniform sliding mode, accessible to simulations, is to set the sliding velocity suddenly to zero. The opposite protocol, namely to abruptly increase the sliding velocity from zero to finite v_0 cannot be done as easily in a meaningful manner, because the system at rest needs too much time to equilibrate. The 'slide and stop' protocol was investigated in detail in Ref. [21]. It was found that the shear stress relaxes much more quickly than the structure. One should thus be careful when drawing conclusions on the rheology of polymer brushes, when only tribological data is available. The relaxation of the end-to-end radius of the polymers was found to be logarithmic in time, which perhaps explains the logarithmic dependence of F_k on velocity. It was also observed that the brush height remained essentially constant during the relaxation.

Non-uniform sliding that can best be described as 'slide-stop-return' was analysed in Ref. [20] and new qualitative behaviour was observed. In particular, the polymers were found to swell, as can be seen in figure 6. The swelling is most pronounced after the relative motion of the two surfaces is twice the characteristic length l_c , which was defined for steady-state flow. Also the shear stress, evaluated directly between the brushes, is maximum after the two surfaces have slid approximately twice the distance l_c , which can be seen on the right-hand side of figure 7. On the left-hand side of figure 7, the direct measurement of l_c in steady state flow is compared to the indirect estimate, which is the length necessary to slide

the upper wall so long that the inclination of the polymer is 90° on average.

These results allow a new interpretation of the shear stress maxima of polymer brushes under oscillatory shear that were mentioned in the introduction. At very small amplitudes \mathcal{A} and fixed driving frequency Ω , the system will be in linear response and thus dissipation is small. At very large \mathcal{A} , the brushes will be in smooth sliding most of the time, because brush swelling and interdigitation is only significant during a small initial fraction after the sliding direction was reversed. If, however, \mathcal{A} and Ω are chosen such that the exploration of the shear stress maxima shown in figure 7 is a significant fraction per cycle, then dissipation will be large. This enhanced friction can neither be explained with stick-slip motion nor with a coincidence of intrinsic relaxation times and driving frequency, because the configurations responsible for the large friction occur neither in thermal equilibrium nor in uni-directional sliding. From the steady-state law $l_c \propto v_0^{0.3}$ predictions can be made how the 'optimum' frequency Ω_{opt} scales with the driving amplitude \mathcal{A} , i.e., by replacing v_0 with $l_c \Omega_{\text{opt}}$ times some geometric factor. Equating l_c with \mathcal{A} , one would obtain $\mathcal{A}^{0.7} \propto \Omega_{\text{opt}}^{0.3}$. It would be interesting to see an experimental test of this prediction. Of course, one may not expect the exponent to be exact, but seeing a powerlaw relationship $\mathcal{A} \propto \Omega_{\text{opt}}^\gamma$ with an exponent γ close to $3/7$ could certainly be considered strong support for the suggested picture.

CONCLUSIONS

We discussed two tribological systems, a simple boundary lubricant (BL) confined between two surfaces that move at a constant relative velocity, and two polymer brushes that rub against each other in good solvent conditions under non-uniform sliding. Due to the externally imposed motion, the BL is constantly pushed away from thermal equilibrium and the energy released in the subsequent relaxation process gets lost as heat. At small sliding velocities when the system is still close to thermal equilibrium, the lost energy is proportional to the velocity. At large sliding velocity, however, the number of sliding induced instabilities or 'micro pops' is proportional to the distance slid, so that the friction force becomes insensitive to the sliding velocity. The distribution of velocities $P(v)$ in the high-velocity regime is different from the Maxwell Boltzmann distribution, i.e., there are tails that decay only exponentially with v rather than exponentially with v^2 . One can speculate that effects of this kind play a role in tribochemistry.

Imposing non-uniform sliding conditions in complex systems, such as the above-mentioned polymer brushes, leads to additional losses. In particular, when the sliding direction gets suddenly inverted, the brushes deeply penetrate into each other. This produces energetically unfavorable micro-configurations and ultimately leads to even larger losses than those that occur under uni-directional sliding. One may speculate that this is a generic feature of non-uniform sliding.

ACKNOWLEDGMENTS

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