# New Design Principles for Biomimetic Mechanical Contacts by Computer Simulation

An important function of lubricants is to keep two surfaces from touching directly so that not only friction but also undesired wear is minimal. This is not easy to achieve, because even highly polished surfaces are rough at the microscopic scale so that most fluids are squeezed out quickly when asperities from opposite surfaces approach each other. Nature and technology have so far pursued different avenues to keep a lubricating fluid within the contact [1]: commercial lubricants are based on oils that quickly increase their viscosity when the local pressure goes up. This gives oils the ability to remain between two colliding asperities and to sustain locally a normal load over a non-negligible time. In contrast to this solution, biological lubrication is based on aqueous liquids that maintain highly fluid at all times. The lubricants yet remain in the contact, because surfaces in biological joints, specifically their cartilage, carry long, end-anchored sugar chains. These polymers are strongly hydrophilic and thus exert a large osmotic pressure up to a few 100 Mega Pascal on the aqueous lubricants giving them the ability to sustain large normal pressures in a sliding contact while remaining slippery.

Porting the principles of bio-lubrication into technological applications has been pursued for many decades [2], albeit with little success. The reason is that end-anchored polymers whose chain termini and loops penetrate the opposing "polymer brush" are prone to scission and detachment [3]. A biological system can regrow the lost end-anchored chains. However, in technical systems only oligomers, i.e., relatively short chains with chemically active head groups can be dissolved as additives that replenish lost material on rubbing surfaces [4]. These molecules are not long enough to form soft, solvated polymer brushes.

To avoid chain scission and detachment in a biomimetic frictional contact, we recently proposed to decorate one surface with hydrophilic polymers and the counter surface with hydrophobic polymers [5]. If the lubricant is a mixture of two liquids so that each liquid dissolves its own favorite polymer, a fluid-fluid interface will be created. The idea is that polymers belonging to one brush cannot pass through the fluid-fluid interface so that chain scission and detachment no longer occur. Here, we review computer simulations [5,6] in which we examined if the envisioned lubrication mechanism can be achieved in practical applications. We also present comparisons to experiment, which were motivated by the computer simulations.

## Simulation Method

To mimic the thermodynamic and non-equilibrium behaviour of polymers, it has become common practice to simulate coarse-grained models of polymers with molecular dynamics (MD) methods. Kremer and Grest [7] proposed one of the most successful coarse-grained polymer models more than two decades ago.
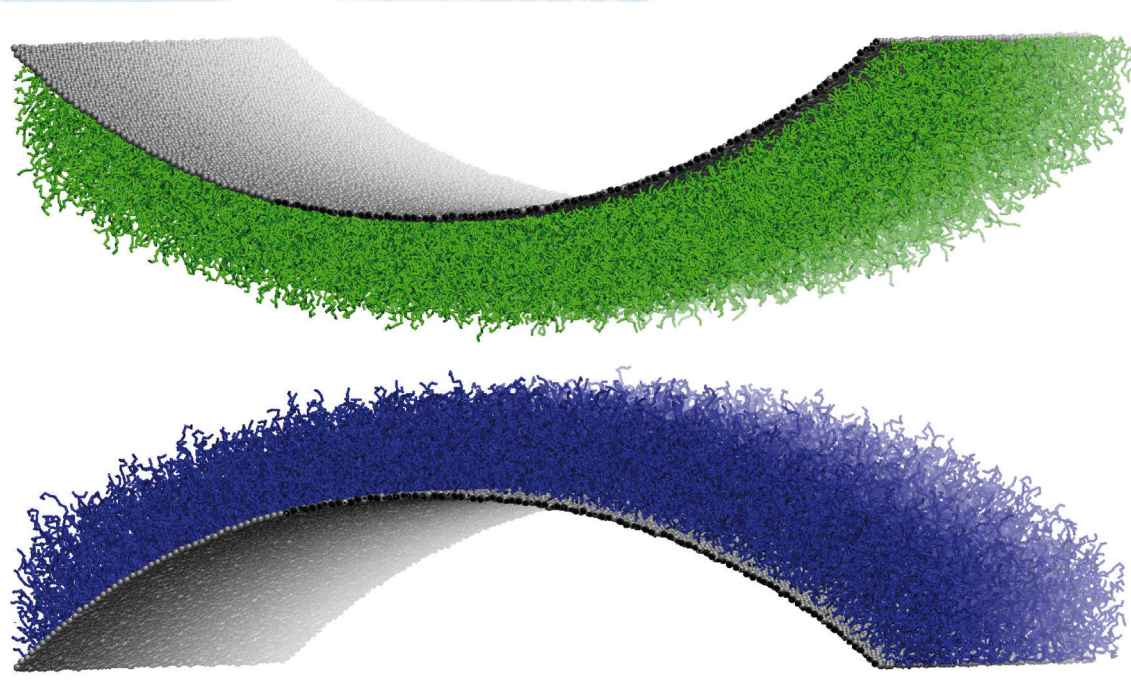


Figure 1: Set up of a typical simulation cell showing the configurations of the polymers before the two surfaces come into contact. Solvent particles are removed for clarity. The system is repeated periodically in the in-plane direction. Motion can occur parallel to the cylinders, normal to the interface, and in transverse direction, which allows one to simulate asperity collisions. In some cases, we also consider a tip on a flat surface to simulate geometries realized in the surface-force apparatus or in atomic-force microscopy experiments.
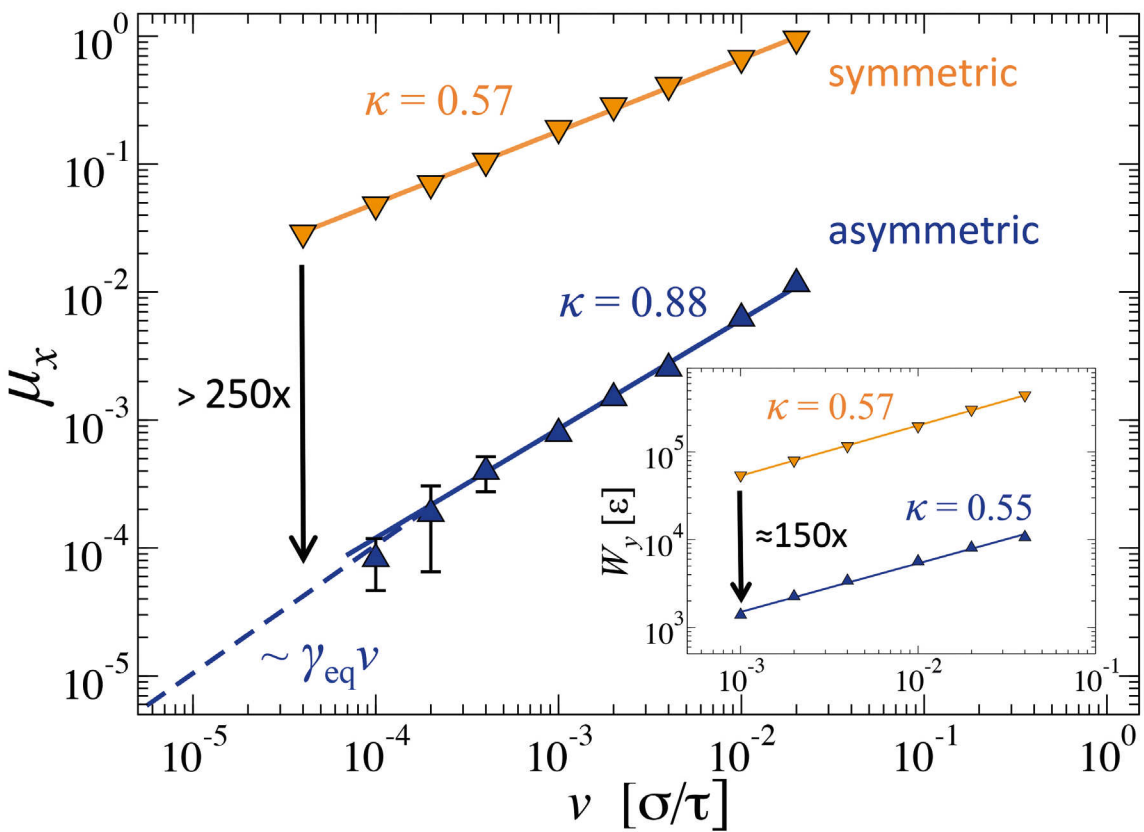


Figure 2: Friction coefficient as a function of velocity for a symmetric (orange) and an asymmetric (blue) brush contact for a tip on a surface geometry. The inset shows energy losses that occur in asperity collision mode, i.e., when the cylinders are moved in the transverse direction. Adopted from Ref. [5].

It represents polymers as bead-spring chains, in which the springs are finitely extensible and nonlinearly elastic. The parameters are designed such that crossing of two chains is extremely unlikely, even though the springs remain sufficiently flexible to allow for reasonably large MD time steps. In addition to the elastic potential between two adjacent beads in a chain, Lennard Jones (LJ) interactions act between all monomers as long as they are within a predefined interaction radius. In our simulations, LJ interactions also act between polymers and solvent particles as well as between different solvent particles. We refer to the literature for details and content ourselves with stating that the fine-tuning of LJ parameters allows one to determine if two fluids or polymer systems want to mix or to segregate. As such, the employed model has successfully reproduced the generic tribological behaviour of adsorbed [8] and end-tethered [9] hydrocarbon films.

Specific to our simulations is the use of an explicit solvent and curved surfaces. We found this to be necessary for mainly two reasons: First, the lubrication mechanism that we attempt to simulate lives from polymers not wanting to pass through a fluid-fluid interface and there would be no such repelling interface without explicit solvents. Second, in contrast to the long-held believe that friction between polymer brushes is dominated by the direct or fluid-mediated interactions occurring due to brush overlap [9], we noticed that many other dissipation mechanisms are relevant for polymers grafted to more realistic, that is, rough surfaces [10]: these are, in particular, viscoelastic deformation of the brushes in non-conformal contact geometries, squeeze-out/re-adsorption dynamics of the solvent, and

capillary hysteresis for partially solvated brushes. A setup characteristic for our simulations is shown in Fig. 1. Typical system sizes comprise 0.5 million polymer beads and a similar number of solvent particles. Simulations were run with the LAMMPS software package [11], which is a highly scalable molecular dynamics package.

## Results

In a first study [10], we demonstrated that there is no universal friction-velocity dependence $F(v)$ for polymer brush systems, although all systems showed a power-law dependence $F \sim v^\kappa$. In particular, we found the exponent $\kappa$ to depend on the sliding direction. For example, when moving parallel to the symmetry direction in Fig. 1, the exponent turned out to be $\kappa=0.57$. This is in agreement with previous simulations [12] and experiments [13] employing effectively plane-plate geometries. In this case, energy losses can be rationalized as dissipation resulting from the overlap between two opposing brushes [12]. For motion in the two orthogonal directions, by which we mimic asperity collisions, we found smaller exponents, that – unlike for the motion in the symmetry direction – varied with the details of the set-up, i.e., the precise exponents depended on the degree of polymerization, the amount of solvent, and force-field parameters. The reason why exponents do not have to be universal is that different dissipation mechanisms mix and that there is no clear time-scale separation between different types of dissipation processes (viscoelastic relaxation, capillary formation, and interdigitation can all have a broad and overlapping distribution of relaxation times). Since we found a relatively small shear-thinning exponent $\kappa$ for motion in the normal and transverse directions, one
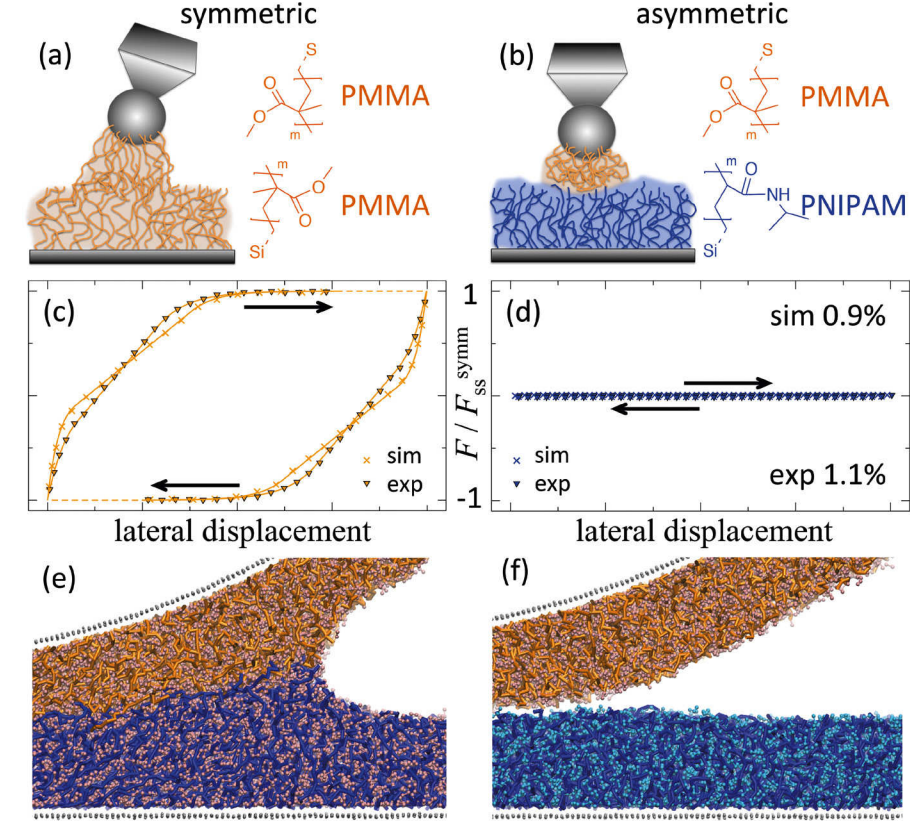


Figure 3: Set up of the experimental system in the symmetric case, (a), in which both sides are hydrophobic (acetophenone-solvated PMMA) and the asymmetric case, (b), where one side is made hydrophilic (water-immersed PNIPAM). The sphere represents a colloid, which carried the hydrophobic brush while being glued to an atomic-force microscope cantilever. Friction traces, normalized to the steady-state friction of the symmetric contact are shown in (c) and (d) for the symmetric and asymmetric system. Simulation and experiments show the same trends when represented in terms of appropriate dimensionless variables. Snapshots of the simulations are shown in (e) and (f). They reveal that polymer brushes overlap in the symmetric case, while a slick fluid-fluid interface is formed when the two brush systems are immiscible. Adopted from Ref. [5].

must expect (technically relevant) small-velocity friction between rough surfaces to be dominated by processes other than those related to brush overlap.

It remains to be investigated if it is possible to reduce friction and wear between solids by decorating them with two mutually immiscible polymer brush systems. To answer this question we conducted simulations of two polymer brush systems, which we designed such that one surface was decorated with polymers of type "P", which was soluble in a solvent "S" but not in another solvent "$\bar{S}$", while the other surface carried end-anchored polymers of type $\bar{P}$, which were soluble in $\bar{S}$ but not in S.

Moreover S and $\bar{S}$ were immiscible. In all simulations that were set-up according to this scheme, we found friction to be much reduced in comparison to those where the components were mutually miscible, except at extremely large sliding velocities, where solubility no longer plays a prominent role. At the smallest velocities that we could approach in the simulations (which would roughly correspond to 1 mm/s in real-time units), the friction reduction was as big as two orders of magnitude. Results for the amount of dissipation are shown in Fig. 2. The important insight is that the exponent, with which friction becomes smaller as the sliding velocity goes down, is noticeably larger for the

asymmetric case than the one typical for overlapping brushes, revealed by the asymmetric brushes. Moreover, when going into "asperity collision mode", that is, when the cylinders are moved in the transverse direction, dissipation is again much smaller in the asymmetric than in the symmetric system. This time, however, the exponents appear to be identical. Since the time is too short for the polymers to interdigitate, even for the symmetric system, we attribute the energy losses in collision mode to be dominated by viscoelastic deformation. Interestingly, the exponent is close to that of "friction-by-interdigitation" so that it might not be possible to discriminate between the two friction mechanisms experimentally in a straightforward fashion.

To confirm the validity of our simulations, we conducted experiments mimicking the set-up of our simulations [5]. Polymers were end-anchored to a substrate as well as to a colloid, which itself was glued to an atomic-force-microscopy cantilever. The experimental system and typical force traces are presented in Fig. 3. By choosing an appropriate unit system, experimental and simulation results can almost be superimposed. This is also true for measurements not shown here explicitly, such as the normal motion of the tip after velocity inversion. We thus see it as legitimate to exploit the data obtained in MD simulations to rationalize not only the simulations themselves but also the experiments.

We can use simulations to investigate a broader range of sliding velocities and normal pressures than possible with current experimental techniques. In addition, one can investigate to what degree friction reduction persists if polymers are fully solvated and the two solvents are miscible with each other while retaining a clear preference for one of the two brushes. A two-component miscible solvent would be preferential from a practical point of view. In Ref. [6], we demonstrate that one still has a well-defined fluid-fluid interface in those situations even if the friction is no longer reduced quite as much as in the case of partially solvated brushes, in which the two solvents are immiscible. The important aspect remains the formation of a sharp interface that prevents chain termini and loops of one side to penetrate the other side, as this prevents the scission and pulling out of polymers, thereby prolonging the lifetime of the sliding bodies. Preliminary experimental results [5] indicate a reduction of not only friction but also wear when a conventional symmetric brush system is replaced with an asymmetric one.

## Outlook

While our MD simulations have very successfully predicted that friction and wear can be strongly reduced when a conventional, i.e., symmetric brush interface (found, for example, in biological joints) is converted into one where opposing brushes are immiscible, quite a few unanswered questions persist. In particular, two issues remain challenging to address: First, there are some crucial experimental differences in the rheological response of hydrophobic and hydrophilic, in particular, zwitterion-based brush systems, whose explanation certainly requires one to go beyond generic bead-spring/Lennard-Jones models. To describe zwitterion-based brushes realistically, it might be necessary to embed the properties of real water, including its ability to participate in proton transfer reactions, into the force fields. Second, simulations of the dissipation of brushes always indicate that a power-law relation between friction and velocity is followed by a linear response when the shear rate is decreased to extremely small values. Experimentally, friction often becomes a logarithmic function of velocity at very small v, akin of solid or Coulomb friction. To obtain such a velocity-dependence, there must be instabilities at very small length scales. The nature of such instabilities remains to be identified, before simulations can assist a material-specific design of a frictional system.

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