Low-Friction Surfaces Achieved Through Polymer Brush Layers

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ChE210D Final Project, June 15, 2012

Abstract: Polymers that are end-grafted to a substrate, as known as a polymer brushes, are commonly used to modify surface properties. Polymer brush systems have many practical applications including as a way to create low-friction surfaces. This remarkable property can be observed using simple coarse-graining models in computational efforts. Molecular dynamics simulations of a polymer brush system were conducted and the friction coefficient was subsequently calculated. The movie shows two surfaces functionalized with polymer brushes that are brought in contact before a shear velocity is applied to the upper wall.

Introduction: Tethering polymer chains to a surface has been shown to be an effective way to modify surface properties by carefully altering the chemistry and morphology of the macromolecules. Polymers tethered to a surface in this way are often referred to as a polymer brushes. Polymer brushes have been demonstrated to be useful ways of achieving low-friction surfaces, though the reason for this reduction in friction is still uncertain. Experimental and computational efforts are currently ongoing to attempt to decompose the exact mechanism by which polymer brushes achieve these lubricating properties.[1]-[3] This report describes the results from a molecular dynamics simulation used to inspect the low-friction behavior of polymer brushes.

Model and Methodology: The system being studied consists of evenly spaced polymer brushes tethered to two opposing walls. In this work, 160 beads are distributed into polymers consisting of 5 beads each, resulting in 32 total polymers, 16 per wall. The system is initialized with the end of each polymer chain residing at either the top or the bottom wall. Periodic boundary conditions are imposed in the directions that lie in the plane of the walls, but not along the direction perpendicular to the walls. For simplicity we can say that periodic boundaries are enforced in the x and y directions but not in the z direction.

The individual beads interact by two potentials, a harmonic potential for bonded beads, and a shifted Lennard-Jones potential. Both potentials are shown below, where r is the distance vector between two beads in three dimensions.

$$U_{LJ}(r) = \begin{cases} 4\epsilon\left[\left(\frac{r}{\sigma}\right)^{-12} - \left(\frac{r}{\sigma}\right)^{-6} - \left(\frac{r_c}{\sigma}\right)^{-12} + \left(\frac{r_c}{\sigma}\right)^{-6}\right] & if\ r \le r_c \\ 0 & if\ r > r_c \end{cases}$$

$$U_{harmonic}(r) = \epsilon\frac{k}{2}(r - r_0)^2$$

The LJ potential is cut and shifted at a cutoff distance $r_c=2^{(1/6)}$. This value for the cutoff distance was chosen to only include repulsive forces between unbounded beads, which simulates a good solvent environment.[4]

In addition, a wall potential was introduced to keep the polymer beads from collapsing onto, or moving through the supporting surface. A common way to implemented is to integrate

the LJ 6-12 potential over the x and y coordinates to derive an effective potential that depends only on z, the distance from the wall.[5] The result is a Lennard-Jones 3-9 potential as shown below. In this equation, z is the position of a bead in the z-direction, and z_0 is the location of the wall in the z-direction.

$$U(z) = \frac{4\pi\epsilon\rho_s{\sigma_{surf}}^3}{3}\left[\frac{1}{15}\left(\frac{z-z_0}{\sigma}\right)^{-9} - \frac{1}{2}\left(\frac{z-z_0}{\sigma}\right)^{-3}\right]$$

For the purposes of the current simulation, the value of $\rho_s{\sigma_{surf}}^3$ was set at 0.74, which is typical for a close-packed surface.[5] For simplicity, only the term raised to the -9 power was included in the simulation, since only the repulsive part of the potential is necessary to prevent the collapse of the polymer brushes.

Once initialized, conjugate gradient and successive line searches are conducted to minimize the energy of the brush system. After energy minimization, the walls are brought closer together. At this point the system was evolved in time using a Velocity-Verlet algorithm. The system undergoes a preliminary equilibration run to stabilize the system. During this equilibration, velocity rescaling is used to impose a constant temperature on the system. This was done using a Berendsen thermostat. Periodically throughout the equilibration, the walls were moved closer or further apart depending on the desired distance between walls. This was done slowly to avoid large spikes in the force and energy calculations. Once the walls reached the desired distance, a second equilibration began but this time without velocity rescaling. After allowing this system to equilibrate again, a production run began. During production, a shear velocity was applied to the beads at the upper wall. As the system underwent shear, the potential energy and the forces in the system were tracked.

Results and Discussion: During the production run the normal force and the shear force was measured periodically. The average of each force was used in computing a friction coefficient. The friction coefficient μ was taken as the ratio of shear force to normal force. The simulation was repeated for a total of 5 times to gain a sense of variation between runs. This procedure was followed for 4 different separation distances between plates. Figure 1 is an example of the normal forces measured throughout a production run. The force was normalized by the value (ε/σ). Similar data was collected for the force in the direction of shear. There was a lot of fluctuation in both forces about their average value, which contributed in large error bars when computing the friction coefficient. Figure 2 shows the average friction coefficient μ versus the separation distance between plates D, normalized by the characteristic length scale σ. The friction coefficient ranged between 0.08 and 0.04, with error bars that indicate the uncertainty in these values.

This system was significantly more complicated to implement than expected. The model used was quite simplified, and resulted in less than ideal statistics. The simulation would benefit from a more detailed atomistic model, for example, one that included explicit solvent particles. That being said, this simple model does confirm the expected low-friction behavior of polymer brushes with friction coefficients comparable to those found in the literature.[2],[4]

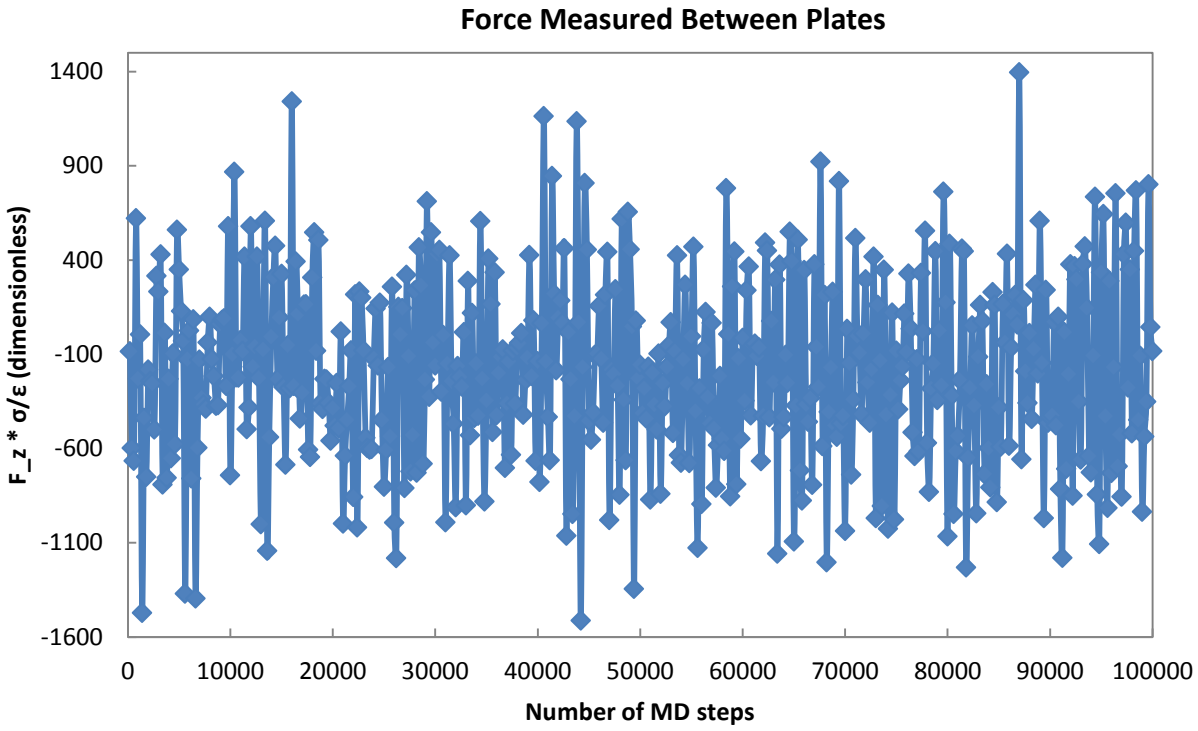

Figure 1: Normal force measured over the course of a production run.

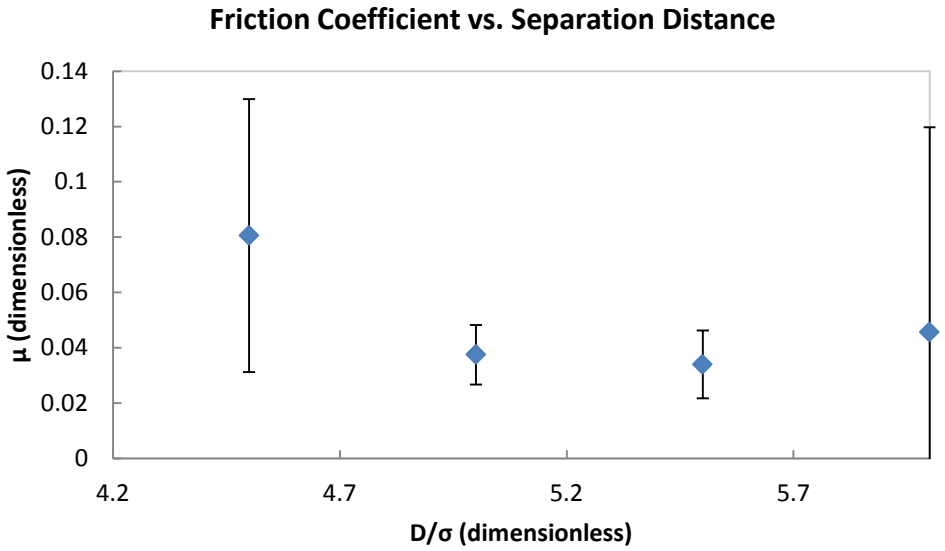

Figure 2: Friction coefficient as a function of distance between walls.

Movie: A movie was recorded from a representative trajectory. The movie file shows the initial energy minimization, followed by wall moves and equilibration, and ends with the shearing of the walls.

References:

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[3] Spirin, L., A., G., Kreer, T., Binder, K., & Baschnagel, J. (2011). Polymer-Brush Lubricated Surfaces With Colloidal Inclusions Under Shear Inversion. *Physical Review Letters*, 106, 168301.

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[5] Shell, S. (2012) Classical Force Fields. http://www.engr.ucsb.edu/~shell/che210d/Classical_force_fields.pdf