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FRICTION BETWEEN POLYELECTROLYTE BRUSHES

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We develop a scaling model that quantitatively demonstrates how polyelectrolyte brushes provide more effective lubrication than bare charged surfaces or neutral brushes. We consider two planar substrates decorated with charged polymer brushes sliding over each other, and examine how the resulting shear and normal forces depend on length and degree of ionization of tethered polyelectrolytes, chain grafting density, and solvent quality. An increase in normal force upon compression of polyelectrolyte-decorated substrates is due to increase of counterion concentration in the mid-plane between them. Since most counterions are confined within the brushes, the sharpest increase of the normal force upon compression occurs at distance between grafting surfaces on the order of brush thickness H_0. At this distance the concentration of counterions at mid-plane changes from a very low value outside the brushes to a very high value inside the brushes.

Lateral force between brushes also increases upon compression, but to a lesser extent. The shear stress at larger separations is due to solvent slip layer friction. The thickness of this slip layer sharply decreases at distance on the order of H_0. The corresponding effective viscosity of the layer sharply increases from the solvent viscosity to a much higher value. At stronger compression there is a second sharp increase of shear stress corresponding to interpenetration of the chains from opposite brushes with resulting very high effective viscosity due to friction within semidilute interpenetration layer. In this regime the velocity-dependent friction coefficient between two partially interpenetrating polyelectrolyte brushes does not depend on the distance between substrates because both normal and shear forces have the same distance dependence. Although lateral forces between polyelectrolyte brushes are larger than between bare surfaces, the enhancement of normal forces upon compression of opposing polyelectrolyte brushes is much stronger resulting in lower friction coefficient in comparison to bare charged surfaces. The behavior of polyelectrolyte brushes in salt-free solutions is also retained in solutions with added salt as long as counterion concentration is higher than that of added salt ions. The mechanism of relatively low friction at high normal pressure maintained in polyelectrolyte brushes and gels sheds some light on lubrication phenomenon in biological systems, e.g., low friction at high load in synovial joints or between mucins tethered to airway surface cilia.