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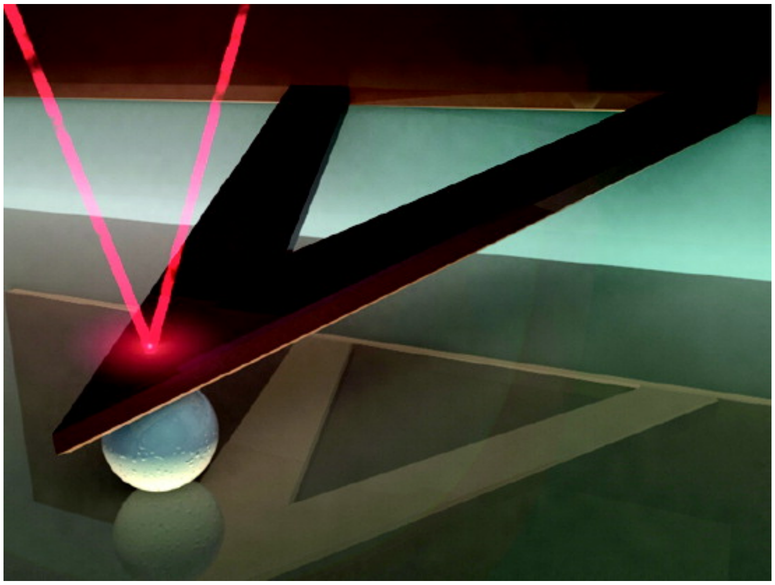

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Superlubricity Using Repulsive van der Waals Forces

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Using colloid probe atomic force microscopy, we show that if repulsive van der Waals forces exist between two surfaces prior to their contact then friction is essentially precluded and supersliding is achieved. The friction measurements presented here are of the same order as the lowest ever recorded friction coefficients in liquid, though they are achieved by a completely different approach. A gold sphere attached to an AFM cantilever is forced to interact with a smooth Teflon surface (templated on mica). In cyclohexane, a repulsive van der Waals force is observed that diverges at short separations. The friction coefficient associated with this system is on the order of 0.0003. When the refractive index of the liquid is changed, the force can be tuned from repulsive to attractive and adhesive. The friction coefficient increases as the Hamaker constant becomes more positive and the divergent repulsive force, which prevents solid−solid contact, gets switched off.

Using colloid probe atomic force microscopy[1−3] (CP-AFM), we show that if repulsive van der Waals forces exist between two surfaces prior to their contact then friction is essentially precluded and supersliding is achieved. The friction measurements presented here are of the same order as the lowest ever recorded friction coefficients in liquid,[4,5] though achieved by a completely different approach.

The nanotribology approach, where friction is measured directly between micro- or nanosized contacts,[4−910,11] has made it possible to relate the observed friction either directly to the surface chemistry or to the nature of the surface forces between the contacts. It has recently been shown that low friction is very well correlated with steeply repulsive surface forces.[4,5] The repulsion between the interacting surfaces, originating, for example, from hydrated counterions[12] bound to surfaces immersed in an aqueous medium, prevents intimate surface contact and thus minimizes the energy dissipation during sliding.[5] Similarly, (charged) polymers that have been adsorbed or grafted to the sliding surfaces give rise to low-friction systems where the frictional forces correlate well with the conformations of the surface molecules.[4,11] With grafted so-called polymer brushes, a well-defined sliding plane combined with a stiff, load-bearing layer, resulting from the parallel alignment of well-solvated polymers, leads to low friction. Adsorbed biomolecules can also give steeply repulsive interactions, which probably accounts for their friction-reducing capability in joints and the oral cavity.[13 14]

It is not only the magnitude but also the distance dependence of the repulsion that is of importance in friction elimination. If friction is predominantly due to energy dissipation within the solid surfaces as a result of their physical contact, then it should not be observed in a system where the precontact forces preclude the attainment of contact. A divergent surface force (i.e., a force that increases asymptotically with decreasing separation) would be ideal for this purpose. The surface force that meets this criterion is the van der Waals force.

The van der Waals interaction has an electrodynamic origin because it arises from the interactions between oscillating or rotating electrical dipoles within the interacting media.[15,16] In the vast majority of systems, the force is attractive and always so if two like media interact across a third. It was recognized early, however, that a repulsive interaction may arise when the electric fields interact destructively and not constructively as in the normal attractive case.[17] Hence, certain combinations of media (the two surfaces and the intervening fluid) will lead to a repulsive force; for condensed media, these systems are so rare and esoteric that they have generally been ignored as scientific oddities (although we note that for solid−liquid−air interfaces they are not uncommon; for example, they are present in froth flotation[18]). Recent force measurements using AFM (atomic force microscopy)[19−22] have verified that it is possible to observe such repulsive forces and indeed that the gradient of the force diverges at short separations. At short separations $D \ll a$, where the radius (of a sphere interacting with a flat surface), a, is much larger than the

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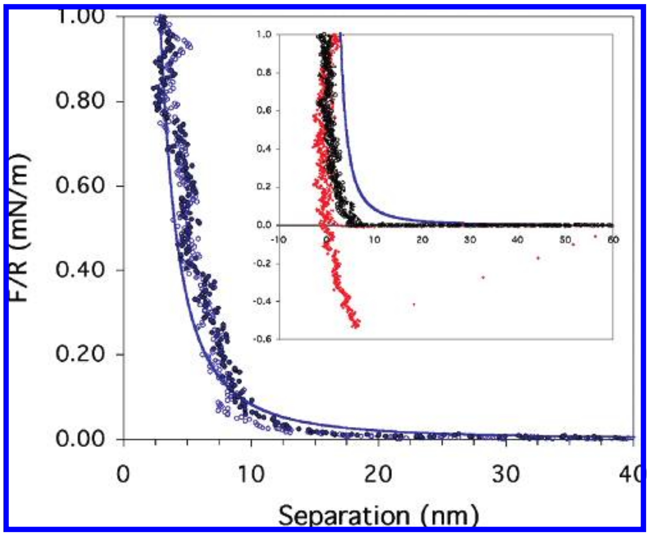

Figure 1. Surface forces between a thiolated gold sphere and a flat PTFE surface in cyclohexane. Filled symbols correspond to approach, and open symbols correspond to separation. The line is a fit of eq 1 to the data with a Hamaker coefficient of -5×10^{-20} J. (Inset) Forces in ethanol. The force (black symbols, anhydrous) is more short-ranged than in cyclohexane. On addition of water (10%), the force becomes weakly attractive with a measurable adhesion (red symbols). The line is the fit from the main plot. Forces are scaled by the radius of the gold sphere used.

separation distance, D, the van der Waals force, F_{vdW}, can be expressed as

$$F_{\mathrm{vdW}}(D) = -\frac{Aa}{6D^2} \tag{1}$$

where A is the Hamaker constant that depends on the dielectric and optical properties of the three media involved (in this case, the sphere, the fluid medium, and the surface) and may be either positive (attractive forces) or negative (repulsive forces). Hamaker constants for different material combinations can be estimated using Lifshitz theory[23] using optical data of both the material and the media.[15,24]

Figure 1 shows that the normal surface forces are repulsive when cyclohexane is chosen as the intervening liquid beyween a gold sphere and a PTFE surface. Simple estimates using Lifshitz theory suggest that this combination of a liquid with a dielectric response intermediate to that of the gold and PTFE, which respectively have very high and very low dielectric responses, should result in a large, negative Hamaker constant and hence a strong repulsive van der Waals force. (Calculations performed by Milling et al.[19] show that, depending on the type of PTFE, the Hamaker constant will be in the range of $+1.5 \times 10^{-20}$ to -5.5×10^{-20} J) The distance dependence of the measured normal forces follows a behavior predicted by eq 1 with a fitted Hamaker constant of -5×10^{-20} J and divergence at small separations. (Although the fit for the three-layer equation is clearly good, we note that the presence of the thiol layer means that a four- or five-layer model should be strictly applied.[24,25])

However, as discussed below, the effect of deformation is likely to be at least as important as the spatial variation of the Hamaker constant at very short separations. No evidence of attraction or adhesion between the surfaces is observed either on approach or separation of the surfaces. At larger separations, the equation overestimates the actual force due to retardation effects, which is related to the finite time taken for the respective electric fields to travel between media. The results are entirely consistent with those of Milling et al.[19] Because the thiol layer on the gold surface is a hydrocarbon, its dielectric properties are similar to those of the solvent and thus will only marginally affect the van der Waals interaction.[26] The quality of the fit in Figure 1 confirms this, and the separation in this Figure is thus that between the gold surface and the Teflon surface. The length of the (fully extended) thiol molecule is estimated to be 2.0 nm, and thus the thiol and Teflon surfaces are short of contact even at the highest applied load.

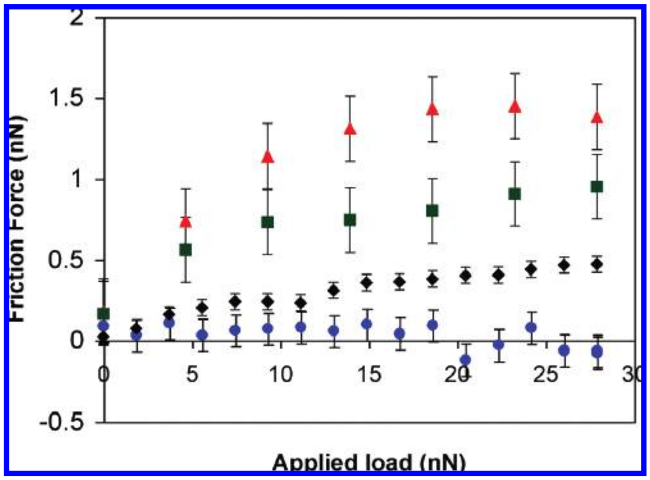

Figure 2. Friction forces. (Circles) Friction as a function of increasing load between a spherical thiolated gold particle and a flat PTFE substrate in anhydrous cyclohexane. The frictional forces are essentially below the resolution of the instrument, and the friction coefficient is thus <0.0003. The diamonds, squares, and triangles are the equivalent measurements in ethanol with 0, 5, and 10% added water, respectively. The nonlinear behavior is characteristic of adhesive systems.

Exchanging the solvent for ethanol is predicted to lead to a Hamaker constant of approximately zero and thus no precontact force. In fact, a slight repulsion was observed (inset of Figure 1) that was of much shorter range, which may be due to a slight van der Waals force and/or compression of the contact. When water was added to the system in small quantities, changing both the dielectric constant and refractive index, the force became adhesive. A range of water/ethanol mixtures were thus used to tune the nature of the interaction between the extremes of 0 and 10% added water shown in the inset.

Measurements of the frictional force (Figure 2) show that a gold particle slides on PTFE in cyclohexane with essentially no resistance. Within our resolution, we effectively have a friction coefficient of zero. The coefficient of friction, μ, is the conventional means of quantifying friction and is defined as the constant of proportionality between the measured friction and applied load. In fact, we can say that the resolution of the frictional force using the AFM is on the order of 10 pN, which gives an upper bound for the friction coefficient of 0.0003 because the maximum applied load is 30 nN in Figure 2. In fact, it is likely that the value is even less than this because higher loads could be applied with no apparent change in the behavior. (A linear least-squares fit constrained to the origin gives a coefficient of 0.0002.) Note that negative friction values are impossible and

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that the apparent negative values are a result of the low signal-to-noise ratio. The low friction is clearly a result of the "untouchable" nature of the interaction. In fact, under the repulsive force the gold sphere is expected to deform and flatten over an area on the order of tens of square nanometers, even though the surfaces do not achieve contact. Because the force between parallel flat surfaces has an even stronger distance dependence than predicted by eq 1 (a dependence on D^{-3}), such a deformation would cause the forces to diverge even more steeply at smaller separations. At the maximum force applied in Figure 1, the surfaces are 2.9 nm from one another, well short of contact. Implicit in this result is that the liquid retains a low viscosity even for nanometer-thick films; it is also suggestive of wall slip by the fluid (i.e., that the fluid in contact with the solid surfaces is not immobilized), in line with recent observations.[27] The forces applied here are sufficiently small that no significant deformation of either the PTFE or thiol layer is expected. For realistic tribological pressures, these effects become important and are the subject of current study.

The friction measurements in ethanol/water exhibit a small but measurable sliding resistance, and the friction increases systematically with the amount of water added. This effect is clearly a consequence of the transition to an attractive interaction and the resultant attainment of intimate contact. The gradual increase of the adhesion with water content, as shown by the inset in Figure 1, shows that we are indeed able to tune the interaction and thus the sliding resistance by the deliberate addition of water.

This work clearly shows that two surfaces experiencing a repulsive surface force, which diverges at small separations, can slide essentially without friction. The number of systems in which repulsive van der Waals forces could occur is limited but includes metal bearings in a PTFE housing with an organic lubricant and certain combinations of technically interesting ceramic materials. Recent proposals concerning the control of van der Waals forces[28] and the fact that van der Waals forces can be enhanced by electromagnetic radiation in the microwave[29] and visible[30] ranges also open up the possibility of achieving friction-free sliding in a much wider range of systems.

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Supporting Information Available: Methodology, a description of the analysis of force curves, and the determination of zero separation. This material is available free of charge via the Internet at http://pubs.acs.org.

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