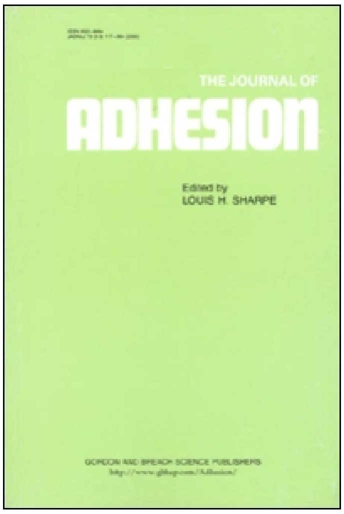

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The Effect of Adhesion on the Rheological and Frictional Behavior of a Confined Lubricant Film*

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We investigated the rheological and frictional behavior of a model system of lubricated, atomically-smooth, solid surfaces at zero and negative external normal load. The measurements were performed with a surface forces apparatus modified for oscillatory shear. For low deflection amplitudes, and negative loads up to the point when the surfaces jumped apart, the confined liquid layer (0.7 ± 0.2 nm perfluorinated heptaglyme) showed a highly elastic behavior independent of load. In the sliding regime at large amplitudes, the behavior was mostly dissipative but also independent of normal load. The force necessary to separate the surfaces was not affected by any sliding conditions. However, the friction force showed a very pronounced decrease as a consequence of sliding at large amplitudes. Thus, for our system, friction and adhesion are decoupled. We propose a mechanism of in-plane rearrangements of the molecules and explain the shear-induced reduction of friction by the formation of shear-bands.

KEY WORDS: surfaces forces; confinement; van der Waals attraction; friction; lubrication; shear induced effects; hysteresis; adhesion

INTRODUCTION

Is the strength of adhesion at rest altered if the two adhering surfaces are in sliding motion relative to each other? Are changes in the frictional behavior reflected in changes in adhesion? In other words, is there a direct correlation between adhesion and friction? These questions have been of interest for a long time.[1,2] Naively, one may think that both quantities are determined by the same intermolecular interactions and, therefore, should be directly related. Neglecting any structural details of the molecules, one may theoretically derive a relation for the effect of van der Waals interactions on friction.[3] On the other hand, experiments comparing the behavior of fluorinated and hydrogenated molecules showed quite convincingly that a decrease in adhesion can, nonetheless, result in an increase of friction.[4,5] Recently, it was shown that there exists a correlation between adhesion *hysteresis* and friction.[6,7] In a molecular picture, this is attributed to the degree of interdigitation and mobility (characterized by the Deborah number) of the molecules at the interacting surfaces.[7] In order to allow for sliding,

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[*] One of a Collection of papers honoring Jacques Schultz, the recipient in February 1995 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M.*

opposing molecules have to separate by moving normal to the direction of sliding first, otherwise they would "bump" into each other. This idea has been expressed very graphically, *e.g.* in the cobblestone model.[8] For a thin lubricant layer one can imagine an alternative possibility. The molecules may squeeze past each other within a plane parallel to the sliding surfaces, a process which will not involve any movement normal to the sliding direction.

In the present article we want to show that such a possibility exists and that, in such a case, friction and adhesion are decoupled. We will concentrate on the effect of negative load. If adhesion during sliding would be reduced, one would expect that these surfaces under tension would jump apart. In previous studies, the reduction of the friction force with increasing negative load was attributed to a decrease of the "true area of contact".[9,10] However, as rough surfaces were used in those experiments the true area of contact was not accessible to measurement. In this study, we will show, for a model system consisting of a lubricant film confined between two atomically-smooth surfaces (geometry of a single asperity), that even under negative load the rheological behavior of the lubricant and adhesion are unchanged, while the friction force can vary dramatically depending on sliding history.

EXPERIMENTAL

The Apparatus

The measurements were performed with a surface forces apparatus[11] modified for oscillatory shear. A detailed description of this apparatus can be found elsewhere.[12,13] In brief, two atomically-smooth mica sheets are glued (using 1,5-diphenylcarbazide) onto cylindrical glass supports. A schematic view of this geometry is presented in Figure 1. The lower glass lens was mounted onto a cantilever spring which acted as a force gauge. The surfaces are brought in close proximity by mechanical motor movements. The separation between the two mica surfaces is measured optically based on interference effects,[14] allowing a resolution of about 0.1–0.2 nm.

Shear was applied by the voltage-induced bending of a piezoelectric bimorph which induced a deformation of the lubricant layer. Part of the force was needed to bend a second bimorph used as deformation sensor. Therefore, the applied force (F) was split into two contributions,[15] one which acted on the confined liquid and a second whose magnitude is related to the compliance of the sensor bimorph.

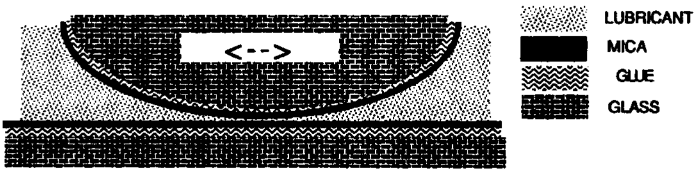

FIGURE 1 Schematic representation of a cross-section of the experiment. The separation of the two mica surfaces is exaggerated. Due to attractive forces the contact point is flattened out. In reality, the ratio between the diameter of the area of contact and the separation of the two mica surfaces is of the order of 10^4.

$$F = (Z_1 + Z_2) \cdot d \tag{1}$$

where Z_1, Z_2 are the complex spring constants of the confined lubricant and the sensor bimorph, respectively. d is the deflection distance.

The response signal was picked up by a lock-in amplifier which was set to yield the amplitude and the phase of the fundamental component of the response to applied sinusoidal shear forces. Thus, we neglected the small contributions of higher harmonic components in the sliding regime. Except for real-time measurements, amplitude and phase were averaged over about 100 sec. The time constant of the lock-in amplifier was 1 sec for the frequencies used and the data were sampled with a frequency of 1 Hz.

If the two mica surfaces were in direct contact or if the layer of confined molecules was thinner than a few nanometers, the underlying glue layers were deformed, a result of intermolecular interaction (mostly due to van der Waals forces).[16] The actual geometry of the contact area could then be represented by two parallel plates. The separation of the plates was about 10^4 times smaller than the diameter of the contact area. The contact diameter at zero load was typically about $10 \pm 5\,\mu m$. It has to be noted that although we measured this area of contact, the uncertainties were comparatively large due to resolution limits of the optical technique employed. Thus, we did not use these results to normalize the measured friction forces.

The Lubricants

For the present study we focused on fluorinated model lubricants. Perfluorinated heptaglyme (PFG) (CF_3O-$(CF_2CF_2O)_7$-CF_3) and perfluoro- 4,9-dioxododecane ($CF_3CF_2CF_2OCF_2CF_2CF_2CF_2OCF_2CF_2CF_3$). Both lubricants showed similar results. Several other lubricants were investigated previously.[13, 17, 18]

Data Analysis

The shear response of the confined lubricant layer was decomposed into an out-of-phase and an in-phase component.[19] The in-phase component represents the elastic response which we express by force divided by deflection amplitude (denoted by κ in units of N/m). The out-of-phase component represents dissipative losses which we denote by μ, defined in analogy to κ, also in units of N/m. κ and μ are closely related to a spring- constant and a dashpot-coefficient of the lubricant layer. Contributions to the shear response due to deformation of the glue layers are subtracted.[13]

RESULTS AND DISCUSSION

The two mica surfaces were brought to a separation of a few 100 nm. The system was kept at this separation until thermal drifts and mechanical relaxations had died out. Then the surfaces were slowly brought closer in steps of a few nanometers. When a separation of about 10 nm was reached, usually no additional motor movement was necessary to reach the final separation of 0.7 ± 0.2 nm. Due to relaxations of the mechanical parts, the surfaces slowly approached a separation of about 5-7 nm. From that point they were pulled together within less than a second to 0.7 ± 0.2 nm. This final distance was stable and did not change even at applied external normal loads up to 1 mN. Thus, our model system can be considered as a film of constant thickness consisting of probably one or two layers of molecules between two atomically-smooth solid surfaces of about 10 μm in diameter.

The rheological response of the confined lubricant layer changed dramatically when the two mica surfaces moved into adhesive contact (from ~10 nm to 0.7 ± 0.2 nm), as can be seen from Figure 2 for a typical experiment. There, κ and μ are plotted as a function of time (t) for a 1Hz oscillation with an amplitude of about 1 nm up to $t = 34$ sec, and 0.1 nm afterwards. At $t = 0$ sec the surfaces have been moved to a separation of about 10 nm. After about 34 sec the separation was about 5–7 nm. At that point the surfaces were visibly pulled together probably due to van der Waals forces between the two mica sheets across the lubricant. Taking into account the time-constant of 1 sec of the lock-in amplifier,[20] one can conclude from Figure 2 that the confined lubricant layer almost instantaneously behaved like an elastic solid as soon as the separation of 0.7 nm was reached. This can be seen more convincingly if one takes the ratio of μ/κ as shown in the inset of Figure 2. A value of 0.1 for μ/κ expresses that the response is 10 times more elastic than viscous. For times $t < 34$ sec no elastic component could be detected and, therefore, μ/κ could not be determined.

In order to separate the surfaces again, they were put under tension (a negative load was applied to the surface mounted onto the cantilever spring). When the applied load exceeded the attractive force between the mica surfaces the two surfaces jumped apart. In Figure 3 we show the behavior of κ and μ (for a 250 Hz oscillation with an amplitude of about 0.1 nm) as the system was under tension and, due to relaxation of the mechanical parts, slowly approached the point where the surfaces jumped apart. At $t = 0$, a negative load of about − 450 μN was applied by continuous motor movement. After the surfaces jumped apart, we needed + 500 μN to bring the surfaces back to a

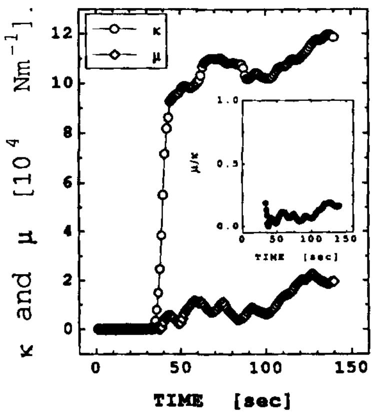

FIGURE 2 Shear response expressed by κ and μ (similar to spring-constant and dashpot-coefficient) as a function of time for PFG between two mica sheets. The surfaces drifted together ($t < 34$ sec) and jumped into adhesive contact. The frequency of oscillation was 1 Hz and the deflection amplitude changed from 1 nm ($t < 34$ sec) to 0.1 nm ($t > 34$ sec). In the inset, the ratio of μ/κ is shown which indicates spontaneous solid-like behavior after adhesive contact was established.

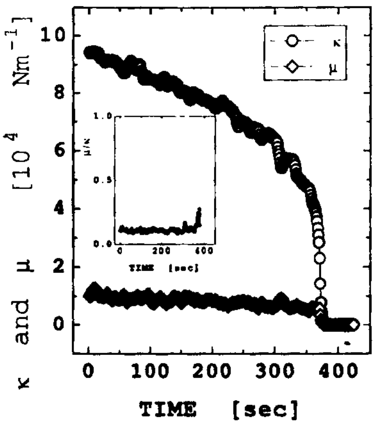

FIGURE 3 Response to shear (250 Hz oscillation and 0.1 nm amplitude) of a confined, 0.7 ± 0.2 nm thick, PFG layer under negative load, expressed by κ and μ. A $-450\,\mu$N force was applied at $t = 0$. Due to relaxations of mechanical parts of the apparatus the load increased to $-500\,\mu$N at $t = 370$ sec when the surfaces jumped apart. In the inset, the ratio of μ/κ is shown indicating that the confined layer behaved highly elastically as long as the two mica surfaces were in adhesive contact.

separation of 0.7 nm. Hence, we concluded that due to relaxations an additional load of $-50\,\mu$N was added. Both κ and μ decreased with time (see Fig. 3), which can be attributed to a decrease of the elastic deformation of the glue layers which caused a decrease of the contact area (S). Taking the ratio μ/κ eliminates the dependence on S, as both parameters depend on S equally. As can be seen in the inset of Figure 3, μ/κ was not affected by this reduction of S. Only close to the point where the surfaces jumped apart (around $t = 370$sec) μ/κ increased slightly. However, even then the response was highly elastic. For $t > 370$ sec no elastic component in the shear response could be detected.

It is instructive to compare the force needed to separate the two mica sheets in contact with the lubricant (pull-off force $F_{po} = 500\,\mu$N) and the bare van der Waals force acting between two mica surfaces in air. According to the JKR-approach,[21, 22] the work of adhesion, W_a, is related to the pull-off force, F_{po}, by:

$$W_a = 2/3\pi F_{po}/R = 9.3\,\text{mJ/m}^2 \tag{2}$$

Here we have used the experimentally-determined value $R = 1.15$ cm for the mean radius of curvature of the crossed cylindrical glass lenses.

For the geometry of our experiment (= parallel plates) the van der Waals interaction energy is given by the following equation:[23, 24]

$$W_{\text{vdW}} = -A/12\pi D^2 = 7.3\,\text{mJ/m}^2 \tag{3}$$

For the Hamaker constant, A, we have used[24] $A = 13.5 \times 10^{-20}$ J, $D = 0.7$ nm for the separation of the two mica sheets. As D can only be resolved with an accuracy of 0.1 nm at best, W_{vdW} can vary between 9.9 and 5.6 mJ/m^2 for D between 0.6 and 0.8 nm. We conclude that the major part of the pull-off force has to be attributed to van der Waals interaction between the mica sheets. The lubricant layer is neither contributing to, nor reducing significantly, the adhesion.

It is also notable that the shear behavior of the lubricant layer (expressed by μ/κ) is not affected by negative load. Close to the point where the surfaces jump apart, there is effectively no normal force acting on the liquid. Consequently, the observed elastic behavior of the lubricant has to be attributed to the influence of confinement- resulting from adhesion between the mica sheets- on the mobility of these molecules. In particular, this shows that external load does not lead to increased ordering of the molecules, which would result in a measurably-increased elasticity and decreased dissipation of the lubricant layer. The reduction with negative load of either μ or κ, separately, is a consequence of the reduction in deformation of the contact asperity.

The question concerning the effect of sliding motion on adhesion was approached, a) by measuring friction as a function of (increasing and decreasing) deflection amplitude for various loads and, b) by checking if there exists a deflection amplitude (as a function of negative load) at which the surfaces under tension (but still in contact at rest) jump apart.

In Figure 4 we plotted the force acting on the confined lubricant (necessary to achieve a deflection amplitude d_0) *versus* d_0, for stepwise increasing (solid symbols) and decreasing (open symbols) deflection amplitude at an oscillation frequency of 250 Hz. We show two cases, the response at zero external normal load and at a negative load of −350 μN, about 70% of F_{po}. On the left side of the dotted line the behavior was solid-like and this branch corresponds to static friction – highly elastic behavior of the lubricant. On the right side, the surfaces were sliding and the energy put into the system was mostly dissipated. Each point represents the response after equilibration for several minutes. Besides the fact that friction forces were lower for the case of negative load (attributed in part to a smaller area of contact) both cases exhibited similar characteristics. The most remarkable features are that sliding induces significant

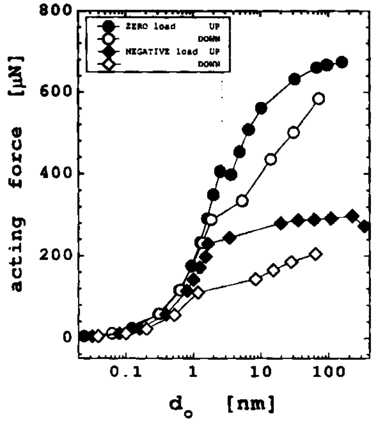

FIGURE 4 Force acting on a confined PFG layer (0.7 ± 0.2 nm) as a function of deflection amplitude d_0 for an oscillation frequency of 250 Hz for two different values of external normal load: circles, zero load and diamonds, −350 μN negative load. The full and open symbols represent results obtained in the direction of increasing and decreasing d_0, respectively. The dotted line separates the regime of highly elastic response from the regime of mostly dissipative response.

hysteresis (*i.e.* the force necessary to move the surface became history-dependent), that the onset of sliding occurred at a deflection amplitude nearly independent of load[25] and that the friction force tended to become independent of deflection amplitude at large amplitudes.[26] Under negative load the system relaxed faster towards stable values. The difference between the friction force in the upward and downward direction for a given d_0 value, and for approximately the same history, was larger under negative load.

In Figures 5a and b we show how the response to the acting force was split up into an elastic and a dissipative component. Again, negative load did not result in a qualitative change in behavior. The only significant difference was an increase of the mobility of the molecules as expressed by faster relaxations in response to steps in the applied force. This effect may be correlated with an increased hysteresis during a cycle of increasing and decreasing deflection amplitude.

Surprisingly, the ratio μ/κ was only very weakly affected by negative load as can be seen in Figure 6. Although the absolute values for the friction forces were different for the two investigated cases (see Fig. 5) the curves of μ/κ for zero and negative load are more or less identical. This indicates that negative *normal* load did not affect the rheological properties of the confined lubricant layer and suggests that the observed changes in the absolute values of responding forces in the static friction regime were due to a change in the area of contact. In the representation of μ/κ (for the same data as in Figs. 4 and 5) one clearly can observe the two distinctly-different regimes-highly elastic at low deflection amplitudes and mostly dissipative at larger amplitudes. While in the elastic regime the response was independent of deflection amplitude d_0, μ/κ increased almost linearly with d_0 in the dissipative regime. The longer the sliding distance, the lower was the relative amount of (recoverable) elastic energy. It is remarkable that almost *no* hysteresis was observed for μ/κ.

After sliding at large amplitudes, the friction force was up to a factor of two lower than before (see Fig. 4). If this reduction in friction force were (linearly) correlated with

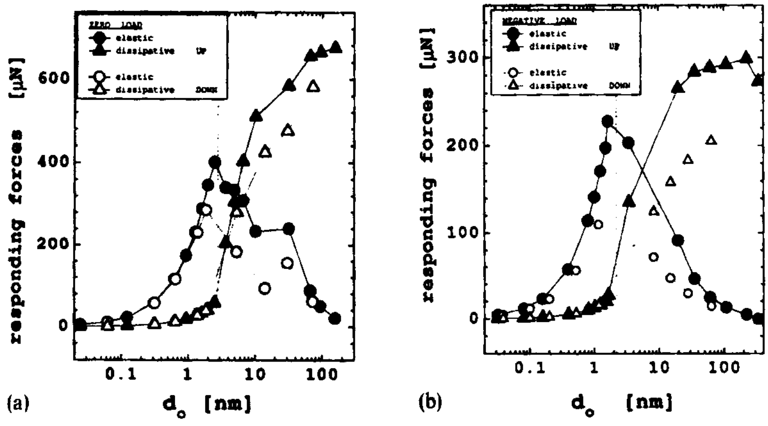

FIGURE 5 Responding elastic (circles) and dissipative (triangles) forces are shown as a function of d_0 for the data in Figure 4 as deduced from the in-phase and out-of-phase component of the response; a) Zero load, b) −350 μN negative external normal load. Full and open symbols and the dotted line have the same meaning as in Figure 4.

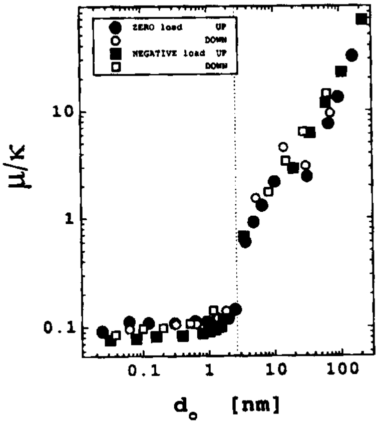

FIGURE 6 The ratio of elastic and dissipative forces expressed by μ/κ as a function of d_0 for the data of Figure 5. Full and open symbols and the dotted line have the same meaning as in Figure 4. Circles, zero load and squares, $-350\ \mu N$ negative external normal load.

adhesion, the surfaces under tension (about 70% F_{po}) should have jumped apart. However, such an effect was never observed, even if the negative load was about 95% of F_{po}. The friction force, on the contrary, was always quite dramatically reduced after sliding at large amplitudes.

In contrast to other systems,[27] the fluorinated lubricants investigated in this study did not show any effect of sliding amplitude, nor velocity, on the force necessary to pull the surfaces apart during sliding. This, together with the fact that there was no effect of negative load on the dependence of friction on d_0 (see in particular μ/κ *versus* d_0), leads to the conclusion that during sliding no (or at least no measurable) normal forces were created. Thus, the sliding mechanism cannot involve significant movements of molecules normal to the shear direction. We propose a mechanism where the molecules are moving only within a plane parallel to the direction of shear and they squeeze past each other. As the lubricant layers were very thin, all molecules were interacting with the mica sheets. It is reasonable to assume that the molecules were not in a crystalline state (the observed stiffness of the layer is comparatively low) and, thus, were randomly distributed. Each molecule interacted strongest with the mica sheet that it was closest to. This assumption essentially leads to a distinction between two populations of molecules opposing each other. That is, molecules more strongly interacting with the top surface are opposing molecules that are more strongly interacting with the bottom mica sheet. In order to pass past each other, these two populations have to rearrange and the formation of shear bands seems to be very probable. A schematic representation of these ideas is given in Figure 7.

The observed hysteresis can probably be attributed to some kind of shear-alignment of the molecules which was not completely lost even when reducing d_0. The higher degree of order may explain the lower value of the friction force, as aligned bands of molecules will experience a lower number of interactions (fewer molecules are "bumping" into each other) and, thus, lower friction when sliding past each other, than a random distribution of molecules. As the thickness of the lubricant layer is not affected

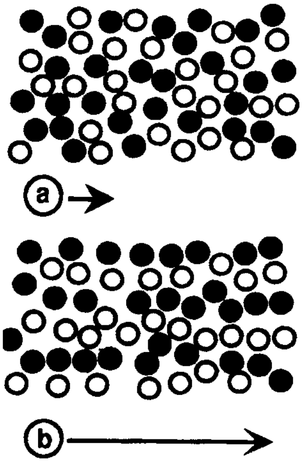

FIGURE 7 Schematic representation of the in-plane distribution of molecules more strongly interacting with the top (full circles) and bottom (open circles) mica surface, respectively. a) situation at rest or small deflection amplitude (random distribution) and, b) during sliding at large amplitudes (shear bands). The sliding direction is indicated by the arrows.

by such a rearrangement process, and the number of molecules interacting with the mica surfaces is not changed, no effect on the force necessary to separate the two mica surfaces is expected.

CONCLUSIONS

Our experiments clearly show that adhesion and friction are not necessarily directly correlated. The friction force due to intermolecular interactions preventing lateral motions can be varied without affecting adhesion. If sliding does not create normal forces, applied normal load, on the other hand, will not affect friction. The absence of any change in the pull-off force as a function of deflection amplitude (or velocity) demands a mechanism for sliding different from, *e.g.*, the cobblestone model where the molecules move across each other. The comparatively weak interaction of the fluorinated lubricant molecules with the mica sheets[28] facilitates local rearrangements without significant efforts. This possibility of rearranging the molecules allows the formation of shear bands which may be responsible for the observed reduction (hysteresis) of friction after sliding at large amplitudes. The highly elastic behavior of the confined lubricant layer at rest (or at deflection amplitudes smaller than the size of the molecules), which persists even at large negative loads, indicates that confinement (or consequently steric hindrance) plays a dominant role. This idea can be extended and analogously applied to the case of sliding motion. Sliding is prevented as long as the molecules can resist being pushed aside or cannot pass each other as long as the acting force cannot compete with the forces induced by space restrictions. The mechanism of in-plane movements proposed above is expected for lubricants which are not strongly adsorbing onto the solid surfaces, and, thus, may occur also for non-wettable surfaces.

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References

1. J. M. Georges, Ed., *Microscopic Aspects of Adhesion and Lubrication* (Elsevier, New York, 1982).
2. I. L. Singer and H. M. Pollock, Eds. *Fundamentals of Friction* (Kluwer Academic Publishers, Dordrecht, 1992).
3. L. S. Levitov, *Europhys. Lett.*, **8**, 499 (1989).
4. B. J. Briscoe and D. C. B. Evans, *Proc. R. Soc., London*, **A380**, 389 (1982).
5. R. M. Overney *et al.*, *Nature*, **359**, 133 (1992).
6. M. J. Chaudhury, M. J. Owen, *Langmuir*, **9**, 29 (1993), *Langmuir*, **9**, 29 (1993); *J. Phys. Chem.*, **97**, 5722 (1993).
7. H. Yoshizawa, Y.-I. Chen, J.N. Israelachvili, *J. Phys. Chem.*, **97**, 4128 (1993); J. N. Israelachvili, Y.-L. Chen, H. Yoshizawa, *J. Adhesion Sci. Technol.*, **8**, 1231 (1994).
8. see *e.g.*: J. N. Israelacvili, in Ref. 2, p. 351.
9. J. Skinner, N. Gane, *J. Phys. D: Appl. Phys.*, **5**, 2087 (1972).
10. B. V. Derjaguin, Yu. P. Toporov, in Ref. 1, p. 343.
11. J. N. Israelachvili, G. E. Adams, *Nature*, **262**, 774 (1976).
12. J. Van Alsten, S. Granick, *Phys. Rev. Lett.*, **61**, 2570 (1988); J. Peachey, J. Van Alsten, S. Granick, *Rev. Sci. Inst.*, **62**, 463 (1991).
13. G. Reiter, A. L. Demirel, J. Peanasky, L. Cai, S. Granick, *J. Chem. Phys.*, **101**, 2606 (1994).
14. J. N. Israelachvili, *J. Coll. Interf. Sci.*, **44**, 259 (1973).
15. We distinguish between the force applied to the whole system and the force acting on the confined lubricant layer only. This acting force is balanced by the responding friction force consisting of an elastic and a dissipative component.
16. J. L. Parker, P. Attard, *J. Phys. Chem.*, **96**, 10398 (1992).
17. G. Reiter, A. L. Demirel, S. Granick, *Science*, **263**, 1741 (1994).
18. J. N. Israelachvili, P. M. McGuiggan, *Science*, **241**, 795 (1988); M. L. Gee, P. M. McGuiggan, J. N. Israelachvili, A. M. Homola, *J. Chem. Phys.*, **93**, 1895 (1990).
19. J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd Ed. (Wiley, New York, 1980).
20. A time constant of 1 sec leads to a smearing (averaging) of the signal over several seconds.
21. K. L. Johnson, K. Kendall, A. D. Roberts, *Proc. R. Soc. London*, **A 324**, 301 (1971).
22. K. Kendall, *Science*, **263**, 1720 (1994).
23. J. N. Israelachvili, *Intermolecular and Surface Forces*, 2nd ed. (Academic Press, London, San Diego, 1992).
24. H. K. Christenson, *J. Phys. Chem.*, **97**, 12034 (1993).
25. The importance of a critical deformation distance in the context of sliding was discussed in: T. Baumberger, F. Heslot, B. Perrin, *Nature*, **367**, 544 (1994); F. Heslot, T. Baumberger, B. Perrin, B. Caroli, C. Caroli, *Phys. Rev. E*, **49**, 4973 (1994).
26. For a discussion of the independence of sliding amplitude see Ref. 13.
27. Such a reduction of the pull-off force has been observed for self-assembled monolayers (see Ref. 13) and confined alkane films (unpublished).
28. This is indicated by the low resistance against van der Waals attraction of the two mica sheets and also by the negligible contribution of the lubricant layer to the total pull-off force.