Nanoscale High-Frequency Contact Mechanics Using an AFM Tip and a Quartz Crystal Resonator

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The transmission of high-frequency shear stress through a microscopic contact between an AFM tip and an oscillating quartz plate was measured as a function of vertical pressure, amplitude, and surface properties by monitoring the MHz component of the tip's deflection. For dry surfaces, the transmission of shear stress is proportional to the vertical load across the contact. This provides a measure of the forces of adhesion between the substrate and the tip. When stretching soft polymer fibers created by pulling on the surface of a pressure sensitive adhesive, the transmitted shear stress decreased linearly with extension over the entire range of pulling. This contrasts with the static adhesive force, which remained about constant until it discontinuously dropped at the point of rupture.

Introduction

The atomic force microscope (AFM) has in recent years evolved into a versatile tool to study the mechanical properties of soft surfaces on the nanoscale. Imaging of mechanical stiffness is possible with the “tapping mode” or the “pulsed force mode”, which performs a more sophisticated analysis of the cantilever’s trajectory and can extract the adhesive properties of the sample. Numerous workers have used AFM technology without lateral scanning to study mechanical properties on the nanoscale. For example, Rief and co-workers have shown that the mechanical properties of single polymer strands can be probed by pulling on the polymer surface. In another context, colloidal spheres have been attached to the tip and the forces between the sphere and a surface have been determined in detail. Overney et al. have emphasized that shear force modulation has certain advantages compared to normal force modulation for surface characterization. The displacement pattern is simpler, and the hydrodynamic coupling is weaker. Also, the force–displacement relation does not suffer from the strong nonlinearities associated with the jump into contact.

In principle, these measurements can be carried out with spectroscopic resolution: the effective spring constant can be measured as a complex function of frequency. However, this kind of local mechanical dynamical spectroscopy is not easy. One is either limited to frequencies much below the resonance frequency, or the raw data will be affected by the resonance properties of the cantilever and some scheme of correction has to be found. Burnham and co-workers have pointed out that quantitative dynamic measurements are also possible at frequencies much higher than the resonance frequency of the cantilever. If the wavelength of sound is much less than the length of the cantilever beam, the stiffness of the beam is of little importance. The force at the tip is governed by inertia, rather than the cantilever’s spring constant. There are again simple relations for analysis. Quartz crystal resonators are attractive in this context because they provide a simple and convenient source for shear excitation. Typical frequencies are in the range of a few MHz to a few hundred MHz, which is much above the typical resonance frequencies of cantilevers. The shear amplitude can be anywhere between 0.1 nm (or less) and 100 nm.

The behavior of contacts under high-frequency shear is interesting for a number of reasons. High-frequency tribology is an intermediate step between conventional, low-speed, low-frequency contact mechanics, such as typically performed with the AFM or the surface forces apparatus (SFA), and the practical world, wheresliding usually occurs at much higher speed. Quartz crystals perform an oscillatory motion, which is different from steady or rotary sliding. On the other hand, the oscillatory motion allows one to investigate a fixed location on the sample, which is impossible in steady sliding. Bureau et al. have recently applied low-frequency oscillatory stress to a multicontact interface between two rough polymer surfaces. Their work focuses on the transition from static friction to sliding friction. It turns out that the transition is not strictly discontinuous. As predicted by Mindlin, there is a range of partial slip, where the rim of the contact slips, while the center sticks. The in-phase component of the stress measured by Bureau et al. can be well explained with the Mindlin microslip model. The out-of-phase component, on the other hand, is at variance with...
In the MHz range, the force change induced by the deflection of the cantilever can be observed. The dynamic signal reflects the transmission of shear stress between the sample and the tip. The model. The authors conclude that the macroscopic laws of friction (and Coulomb's law, in particular) do not apply on the local scale.

Our work follows a similar concept but differs in two respects: a single-asperity contact (given by the AFM tip contacting a flat surface) is studied, and the frequency is in the MHz range. In principle, it would be desirable to infer the lateral force from the frequency shift of the quartz resonator induced by the contact with the AFM tip. Unfortunately, the lateral force is too small to induce a frequency shift large enough for quantitative analysis. Kim et al. have been able to acquire AFM images of an oscillating quartz surface and record the frequency shift in parallel to the scanning process, thereby providing a map of the frictional properties of the surface. A tribological contrast between patches of gold and poly-styrene could be observed. However, the variations in friction reflect the transmission of shear stress between the sample and the electrode. In contact, the motion of the tip is locked to the oscillation of the quartz plate. The signal has the same shape as the conductance curve. The resonance is measured by fitting resonance curves to the spectra of the complex admittance of the quartz. Note that the resonance parameters usually do not change upon contact because the tip is so small. Therefore, the experiments can be performed at one fixed frequency on the center of the resonance.

Figure 1 shows a sketch of the experimental setup. The sample is coated onto the upper electrode of the resonator. A laser beam is deflected from the back of the tip, passing a knife edge on the way to the detector. The signal from the detector is electronically amplified and displayed on a spectrum analyzer. We have occasionally checked for out-of-plane components of the motion by placing a droplet of water on the quartz surface and comparing the frequency shift and the half-band-half-width. For a pure shear motion in liquids, one expects the increase in the half-band-half-width to be the same as the decrease in frequency. That expectation was fulfilled within about 20%, whenever we checked. The possibility of a vertical contribution to the motion should be kept in mind.

The resonator plate can be coarsely positioned in three dimensions with micrometer screws and an x–y–z stage (OWIS, Stauffen, Germany). Fine approach of the quartz surface to the AFM tip in the z-direction occurs by means of a piezo actuator (P517.3CL, PI, Göttingen).

Results and Discussion

For a high-frequency lock-in amplifier (Stanford Research Systems, SR844) referenced to the quartz oscillation, the detection electronics was used to filter and amplify the raw signal. The analogue output of this amplifier was fed into a second, slower lock-in amplifier (Scitec, 500MC) referenced to the optical chopper. This second filtering stage proved necessary to eliminate capacitive crosstalk between the quartz plate and the detector. In most cases, the magnitude (R) from the first lock-in amplifier was used for further amplification. For a complex mode of measurement, the real and the imaginary part of the signal (X and Y) can be analyzed, as well. A third, slow lock-in amplifier (EG & G S109) was used to measure the low-frequency signal from the detector, referenced to the chopper. This is the "static signal", proportional to the static deflection.

The resonator (5 MHz blanks, Maxtek, CA) with gold electrodes was mounted in a commercial holder (CHT100, Maxtek), which allows for measurements in air or in liquid. A network analyzer (HP4396A, Agilent) is used to acquire the resonance curves. Resonance frequency and resonance bandwidth are determined by fitting resonance curves to the spectra of the complex admittance of the quartz.

Figure 3 shows the modulus of the dynamic signal acquired at a fixed distance between the cantilever and the tip while the frequency of the resonator is swept across the resonance. Out of contact, the tip does not respond to the frequency sweep, whereas in contact, the dynamic signal has the same shape as the conductance curve. The conductance is a measure of the shear amplitude: the shear strain is proportional to the current through the electrodes. In contact, the motion of the tip is locked to the motion of the quartz plate.
The shear oscillation of the quartz plate occurs along the crystallographic x-direction. The dynamic signal should therefore change when the resonator is rotated in the sample plane. Figure 4 shows that this is indeed the case. Three approaches of the tip to the sample are displayed. The round dots (○) correspond to a situation in which the deflection was perpendicular to the knife edge, whereas the triangles (△) show data for which the displacement is along the knife edge. In the latter case, the dynamic signal is much smaller. The residual variation is caused by a slight misalignment. When the displacement is perpendicular to the knife edge (○), the dynamic signal actually saturates for large deflection, resulting in a dip.

In Figure 5, we show the dependence of the dynamic signal on amplitude. The data were taken with a cantilever, where beads with a diameter of 10 μm were glued to the tip. The three approaches were done at different drive levels. The magnitude of the signal is about proportional to the driving voltage, which has been converted to an amplitude of lateral motion as explained in the text.
range of the detection system are reached. In this particular case, one finds a nonzero dynamical signal at a vertical position of the cantilever where the static signal still does not give evidence of contact. This result was only found when a sphere was glued to the tip. Presumably, there is a transmission of shear stress across the small air gap.

Having proven that the instrument in principle works well, we justify the approach on a more fundamental level. It is essential to realize that the quartz plate cannot bend the entire cantilever at a frequency of 5 MHz. Rather, the bending distortions have the character of elastic waves. The wavelength can be estimated from the length of the cantilever and the fundamental resonance frequency. At the fundamental, the length of the cantilever equals about a quarter of the wavelength. Regardless of the size and the shape of the cantilever, it can be assumed that the wavelength scales about inversely with frequency. Using a resonance frequency of the cantilever of 10 kHz, one finds that a resonance frequency of the quartz plate of 5 MHz corresponds to a wavelength of the bending waves which is 125 times less than the length of the lever. In principle, these waves may be reflected at the support of the lever, giving rise to standing waves or, equivalently, discrete modes of vibration. Note, however, that the Q-factor of a cantilever in air rarely exceeds 100. Applied to traveling waves, this means that the waves decay over a range of about 100 cycles and, as a consequence, do not return to the tip. In the frequency domain, this implies that the modes are overdamped to the extent that discrete resonances can no longer be seen. The spectrum of the mechanical susceptibility is a broad, featureless continuum. The waves launched by the shear excitation therefore just dissipate the energy; they do not contribute to the elastic stiffness. Far from the purpose of modeling, the tip can be regarded as a rigid mass in a “viscous” environment, where the dissipation is achieved by the bending waves traveling along the lever.

Having said that the elastic waves in most cases do not reach the mount of the cantilever, one may ask whether they reach the mirror. In other words, if the cantilever is too short to be considered a rigid object, is the pyramidal tip short enough? This question again comes down to a comparison of the dimensions of the tip and the wavelength of sound. Using a speed of sound, \(v\), equal to the speed of sound in a typical solid-state material (\(v \sim 3000 \text{ m/s}\)), a quick calculation shows that the size of the pyramid (\(\sim 10 \mu m\)) is indeed smaller than the wavelength at 5 MHz by a factor of about 60.

We now discuss the dependence of the dynamic signal on the vertical force in more detail. Figure 6 displays the dynamic and the static signal observed when approaching a silicon tip (CSC12, MikroMasch) to the resonator’s gold electrode. The static signal exhibits a strong adhesion hysteresis, presumably caused by capillary forces. The experiment was conducted at ambient conditions. We show two out of many more cycles of approach and retraction. The data are well reproducible. Changing the point of contact did not make a difference. Not surprisingly, the dynamic signal strongly increases when contact is being made. We attribute the leveling off at high vertical force to the limited dynamic range of the detection system. Upon retraction, the dynamic signal decreases linearly. It intersects the x-axis at the point of detachment. The linear dependence of the dynamic signal on the deflection suggests that the transmission of shear sound is proportional to the true vertical force at the contact, where the true vertical force is the sum of the external force (as given by the spring constant and the deflection of the cantilever) and the forces of adhesion.

A lateral stress proportional to a vertical load is reminiscent of Coulomb’s law for sliding friction. In the context of sliding friction, it is argued that the force is transmitted across many small asperities. The sliding force is proportional to the true contact area, which in turn is proportional to the load. Bureau et al. have shown that a similar argument can be applied to the elastic stress in oscillatory shear.\(^{12}\) They apply the Mindlin model of partial slip\(^1\) on the level of single asperities but extend it in order to take the statistical properties of the rough surface into account. Note, however, that Coulomb friction assumes plastic deformation of small asperities. The local stress is assumed to be so high that protrusions flatten out until the local stress is the same as the yield stress of the material. The fact that we do not observe aging gives evidence against plastic deformation. For a sphere—plate contact deforming elastically, one would expect the stiffness to be proportional to the contact radius, \(r_c\).\(^{20}\) In the Hertz model, the contact radius, in turn, is proportional to the cubic root of vertical load and the effective spring constant should therefore also scale as the cubic root of the vertical force. The Hertz model has been extended to account for forces of adhesion\(^{21}\) and long-range attraction.\(^{22}\) However, these extensions do not predict a contact radius proportional to the load.

In the following, we discuss different explanations of the fact that the transmission of shear sound is proportional to the vertical force. First, the tip and the surface might be so irregular that we in fact have a multicontact interface. This explanation does not seem plausible because thedependence of the dynamic signal on the vertical load should then be variable. Depending on the details of the geometry, a cubic-root dependence should sometimes be observed. On the contrary, the experiments for a silicon—gold contact are rather reproducible. We have never observed a dynamic signal proportional to the cubic root of the vertical load.

A second explanation might be that the tip slides on the surface and therefore samples the statistics of the surface.

\(^{20}\) The stiffness is not proportional to the contact area, \(\pi r_c^2\), because there is a stress concentration in the contact area which scales as \(r_c^{-1}\).\(^{21}\) Johnson, K. L.; Kendall, K.; Roberts, A. D. Proc. R. Soc. London, Ser. A 1971, 324, 301.\(^{22}\) Pollock, H. M.; Maugis, D.; Barquins, M. Appl. Phys. Lett. 1978, 33, 798.
over time. The Hertz model would not describe such a situation. However, an estimation of the ratio of the shear force and the normal force shows that sliding is unlikely. If we set the lateral force, \( F_r \), equal to the product of the mass of the tip and the acceleration \( (F_r \approx \omega^2 a m_{tip} \) with \( \omega \) being the shear amplitude) and use a mass of \( 10^{-9} \) g, a shear amplitude of 20 nm, and a frequency of 5 MHz, we arrive at a lateral force of 3 pN. (Note that inertia governs the high-frequency dynamics.) Typical normal forces, on the other hand, are in the nanonewton range. Assuming that the static friction coefficient is of the order of unity, it seems unlikely that sliding sets in.

Third, one could argue that the transmission of shear stress is affected by partial slip in the rim of the contact area. For a sphere–plate contact under oscillatory shear, there is an annulus close to the contact line, where the two contacting surfaces slide relative to each other. The width of this rim depends on the ratio of the lateral and the normal force. As the normal force increases, the partial slip in the rim of the contact area becomes appreciable, there is essentially no response at MHz frequencies. After a few approach/retraction cycles, the coupling between the surface and the tip sets in.

None of the above arguments can rigorously explain why the stiffness of the contact is proportional to the vertical force. Again, the absence of aging provides evidence against an interpretation in the frame of plastic deformation.

In the following, we present two applications of the technique to more complex situations. In a first example, we have examined the characteristic of a silicon chip with a Langmuir–Blodgett film of 19 layers of the polyamic acid PAAB. The details of the chemical structure are provided in ref. 23. Figure 7 shows the static deflection versus time. The tip has been approached 15 times. The curve displays neither a jump into contact nor capillary forces. Presumably, the adhesion is prevented by the fact that the sample is hydrophobic. A dynamic signal is hardly detectable for the first seven cycles of approach. Starting with the eighth cycle, the signal gradually increases. Clearly, there is wear. The static signal remains entirely unchanged. We interpret our finding in the sense that the tip penetrates the film after a few cycles, which increases the friction coefficient. In passing, we note that the friction coefficient must have been very low initially in order to allow for sliding. Possibly, the friction coefficients at high frequen-

\[
S = \frac{2 - \nu}{4Kr_c} \left(1 - F_{\parallel} \frac{F_{\perp}}{F_{\parallel}} \right)^{-1/3}
\]

where \( \nu \) is Poisson’s number, \( K \) is the modulus, \( r_c \) is the contact radius, \( F_{\parallel} \) is the friction coefficient in the Coulomb sense, and \( F_{\parallel} \) and \( F_{\perp} \) are the lateral and the normal force, respectively. Given that the lateral force is much smaller than the normal force, eq 1 predicts that the compliance scales about as \( r_c^{-4} \), which is in accordance with the Hertz model and at variance with our data.

Finally, the sphere–plate geometry may not be a good approximation for the contact between the tip and the surface. The Hertz model only applies as long as the contact radius is much smaller than the radius of the sphere. If the shape of the tip under large vertical force is closer to a flat punch than to a sphere, then there is no stress concentration at the point of contact and the transmitted stress is proportional to the contact area (as opposed to the contact radius). If the contact area would increase linearly with vertical load, this would explain our findings.

None of the above arguments can rigorously explain why the stiffness of the contact is proportional to the vertical force. Again, the absence of aging provides evidence against an interpretation in the frame of plastic deformation.

Figure 7. A demonstration of sliding and wear. The sample is covered with a Langmuir–Blodgett film of a polyamic acid. The tip was approached to the sample 15 times. The dynamic (top) and the static signal (bottom) are displayed versus time. Initially the tip slides. Even though the static normal force is appreciable, there is essentially no response at MHz frequencies. After a few approach/retraction cycles, the coupling between the surface and the tip sets in.

Figure 8. Static and dynamic deflection acquired during a contact between a Si tip and a sticky polymer surface. Upon retraction, fibers are pulled out of the surface. The transmission of shear stress through the fibers gradually decreases with extension. There is no discontinuity when the fibers finally rupture.

\( F_{\parallel} \) and \( F_{\perp} \) are the lateral and the normal force, respectively.

Figure 8. Static and dynamic deflection acquired during a contact between a Si tip and a sticky polymer surface. Upon retraction, fibers are pulled out of the surface. The transmission of shear stress through the fibers gradually decreases with extension. There is no discontinuity when the fibers finally rupture.

The static and the dynamic signal acquired while retracting the tip from the surface of a pressure sensitive adhesive (Figure 8). As we have shown previously, an AFM tip can pull fibers out the surface.24 The adhesive is a commercial product from BASF Aktiengesellschaft and mainly consists of a polyacrylate latex. A transmission of shear waves does occur through the fibers. It decreases with elongation, suggesting that the fiber’s shear stiffness decreases during stretching. The static force–distance curve displays a plateau. Both the static and the dynamic signal provide the rupture length, which varied between 300 and 1500 nm. For the first rupture event, there is a discontinuity in both curves, but for the latter two pulls the dynamic signal continuously approaches zero. This contrasts to the static signal, which displays a plateau and drops discontinuously at the point of rupture.

**Conclusions**

The transmission of high-frequency shear stress through nanoscale contacts has been measured by touching an

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oscillating quartz plate with an AFM tip and monitoring the MHz component of the tip's deflection. The transmission of shear stress is proportional to the true vertical load at the contact, which is the sum of the external load and the forces of adhesion.

We have shown two applications of the instrument to measurements of sliding friction and adhesion. The transmission of shear stress depends much more sensitively on the details of the contact than the normal force.

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