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Observation of Liquid Neck Formation with Scanning Force Microscopy Techniques

J. Colchero,* A. Storch, M. Luna, J. Gómez Herrero, and A. M. Baró

*Departamento de Física de la Materia Condensada, Facultad de Ciencias,
Universidad Autónoma de Madrid, 28049 Madrid, Spain*

In the present work, we describe a technique to measure the tip−sample interaction in a scanning force microscope setup with high precision. Essentially, the force exerted on the cantilever is acquired simultaneously with a spectrum of the cantilever. This technique is applied to study the behavior of the microscope setup as the tip approaches a sample surface in ambient conditions. The measured interaction can only be understood assuming the formation of a liquid neck and the presence of a thin liquid film on the tip as well as on the sample.

Scanning probe microscopy and particularly scanning force microscopy (SFM) have become a powerful tool to investigate surfaces on a nanometer scale. An important feature of this technique is that generally scanning probe microscopes can be operated not only in ultrahigh vacuum (UHV) but also in liquids and under ambient conditions. Although experimental conditions are best defined in UHV, most SFM experiments are performed in air. Operation in air is easy and for most applications sufficient. In air, it is well-known that a thin liquid film composed mostly of water adsorbs on all surfaces. Due to the presence of this film, the surface is not as well defined as in UHV. Consequently this film is usually seen as a disturbance in SFM and, quite often, simply ignored. On the other hand, it is well-known that adsorbed films can change the properties of surfaces dramatically. The physics and chemistry of these films are very rich and complex: they determine friction and adhesion of surfaces, chemical reactivity, optical properties, among others. Wetting and dewetting of the film itself are fascinating phenomena. Therefore, the characterization and investigation of adsorbed films are of fundamental interest, both for basic research as well as for technology. Application of SFM with its high spatial resolution to the study of these films will result in a new vision of this vast field.

The presence of this film has been detected with SFM techniques indirectly through the dependence of friction[1,2] and of adhesion[3] on the relative humidity. Liquid bridge formation has been observed by measuring discontinuity in force vs distance and oscillation amplitude vs distance curves.[4] Recently, scanning polarization microscopy[5] has been proposed to image liquid films on surfaces. However, the contrast observed with this technique seems to be mainly due to the ions in the liquid. In the present paper we describe a method to study tip−sample interaction by SFM techniques with high precision. We apply this method to detect the liquid film as well as the formation of a liquid neck between the surface and the tip of the SFM cantilever. Essentially, the cantilever is oscillated near resonance as the tip approaches the sample. Due to tip−sample interaction the force and the resonance frequency of the cantilever vary. In our experiments, the variation of both is recorded simultaneously. As will be explained in more detail, our measurements cannot be explained only in terms of van der Waals or electrostatic interaction between tip and sample. Our data are only consistent if the liquid films on the surfaces of tip and sample are taken into account and if the formation of a liquid neck between tip and sample is assumed.

Different techniques can be applied to study the interaction of a SFM tip with the sample. Mostly, this interaction is measured by acquiring a so-called force vs distance curve.[6] With this technique the deflection of the cantilever, which is proportional to the force exerted on the tip, is recorded as the tip approaches the sample surface (see Figure 2). Another way of determining the interaction is to study the variation of the resonance frequency of the tip−sample system as the tip approaches the sample.[7,8] To understand the latter technique in detail, we first recall that for most applications, a SFM setup can be approximated by a harmonic oscillator. If the tip feels no interaction, the resonance frequency of the cantilever is $\omega_{00} = c/m_{eff}$, where c is the force constant of the cantilever and $m_{eff} = m_{tip} + 0.24\ m_{lever}$ an effective mass[9] taking into account that the mass is distributed along the whole cantilever and not only at its free end. With an interaction potential $V(z)$, the resonance frequency of the free cantilever is modified according to[7]

$$\omega_0{}^2(z) = \frac{c + V''(z)}{m_{eff}} = \omega_{00}\left(1 + \frac{V''(z)}{c}\right) \qquad (1)$$

where ω_{00} is the free resonance frequency and $V''(z)$ the force gradient of the interaction potential. Essentially, the force gradient and the force constant of the cantilever add to an effective force constant of the system. For attractive potentials, that is, for potentials which induce forces that pull the tip toward the surface, this force gradient is negative and therefore the resonance frequency

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shifts toward lower values. An interesting feature of eq 1 is that for $V''(z) = -c$ the resonance frequency is zero and that for $V''(z) < -c$ it is imaginary and is therefore physically not defined. This is related to the instability which occurs in a SFM setup when the force gradient is more negative than the force constant of the cantilever. It is well-known in SFM that in this case the force constant of the cantilever is too low to keep the tip—sample system in a stable equilibrium. Instead, the tip snaps onto the surface until it is held by the strong repulsive forces that act when tip and sample are in mechanical contact.

Finally, we note that the oscillation amplitude of the system driven by a harmonic driving force $F(t) = F_0 e^{iwt}$ is described by a Lorenz function

$$a(\omega) = a_0 / \left(1 - \left(\frac{\omega}{\omega_0} \right)^2 + \frac{i}{Q} \left(\frac{\omega}{\omega_0} \right) \right) \qquad (2)$$

where Q is the quality factor of the oscillator and $a_0 = F_0/c$, the amplitude at zero frequency, that is, the deflection of the cantilever due to a dc force of magnitude F_0.

The resonance frequency of the tip—sample system can be measured in two different ways. On the one hand, a phase-locked loop can be used to keep the cantilever always at resonance,[7] even if this resonance frequency varies. This method has the advantage of speed and measuring range, but a precise and stable loop has to be implemented. On the other hand, the resonance frequency can also be determined by acquiring a spectrum of the cantilever, that is, either by measuring the spectrum of its thermal noise[8] or by recording the response of the cantilever to an excitation of variable frequency.[10,11] The resonance frequency of the tip—sample system can then be deduced from a fit to the resonance curve. This method is rather slow and needs data processing; therefore it cannot be used for imaging applications. However, it is easy to implement with a lock-in amplifier and it is very precise. We have chosen this second method for our present work.

The experiments were performed with a commercial SFM and the corresponding software[12] by slightly varying the classical setup for imaging applications. More precisely, the ramp which is normally used for the fast scan direction (typically "x"-axis) was fed into a voltage-controlled oscillator which then provided a frequency sweep of fixed voltage amplitude. This voltage was applied either to a small piezo on which the cantilever was mounted or directly between tip and sample. In the first case, the vibration of the cantilever was excited mechanically; in the second case, this oscillation was induced by the electrostatic force between tip and sample. Typical oscillation amplitudes of the cantilever were $0.1-0.2$ nm at resonance. Small oscillation amplitude is fundamental to avoid averaging the force gradient over the oscillation range of the cantilever.[13] Highly oriented pyrolytic graphite (HOPG) and gold were used as sample surfaces, but only data corresponding to the first are presented in the present paper. The potential between tip and sample was carefully controlled to avoid spurious electrostatic

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(13) Large oscillation amplitude will lead to nonlinearity of the cantilever motion and to frequency doubling. If this is the case, interpretation of data using linear response theory is not valid any more. We have not observed this effect in our experiments, which seems reasonable since the smallest tip—sample distance (about 3 nm) is large compared to the maximum oscillation amplitude (about 0.2 nm).
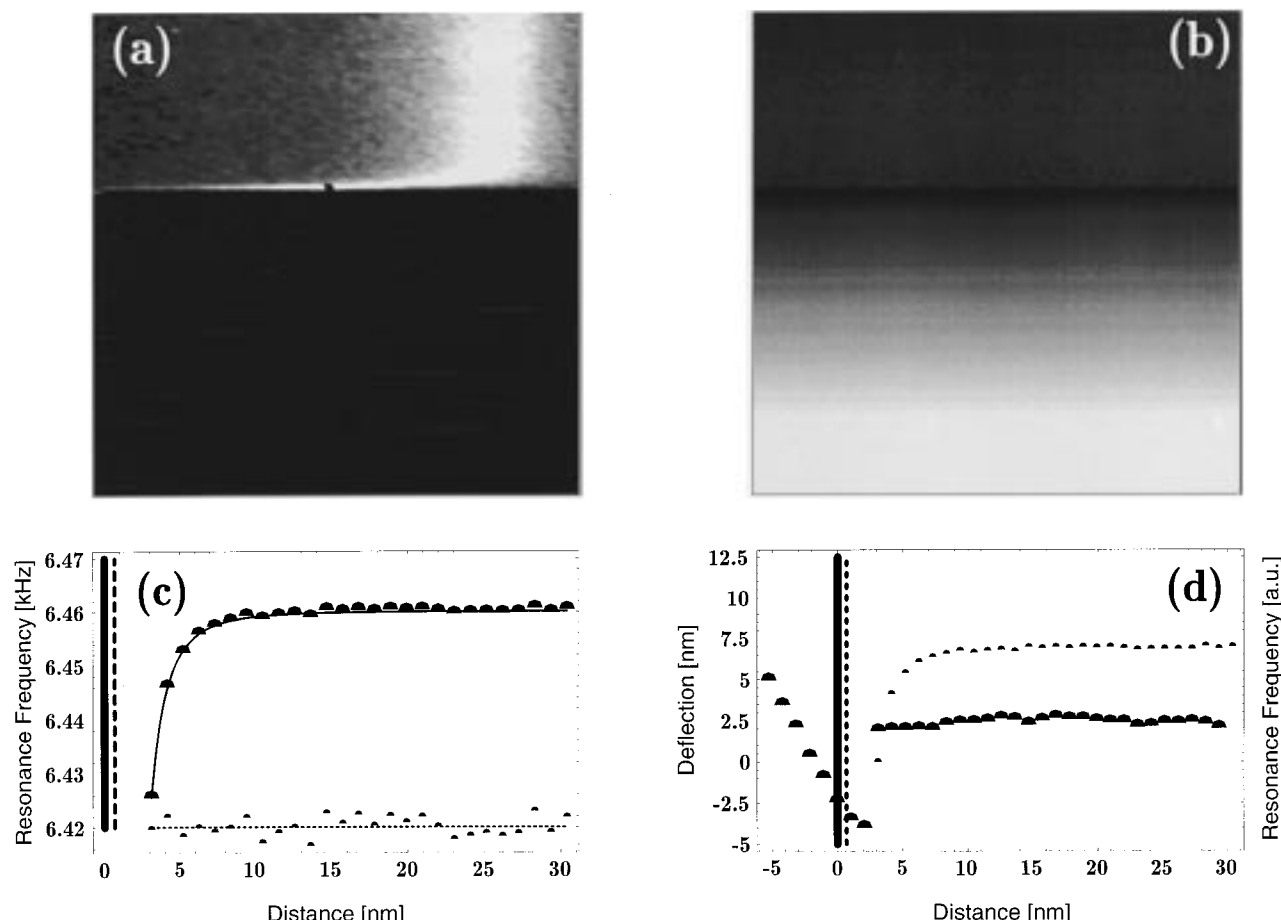
interaction. The slow scan signal which is used typically for varying the "y"-position of the tip in imaging applications was used in our setup to vary the tip—sample distance ("z"-axis). For each experiment, two "images" were taken simultaneously, one corresponding to the output of the lock-in amplifier, which is proportional to the oscillation amplitude of the cantilever (Figure 1a), and the other one corresponding to the normal force (Figure 1b). The first image reflects how the resonance frequency varies with the tip—sample distance. Every line of this image represents a spectrum of the cantilever at a fixed tip—sample distance. The image corresponding to the normal force on the other hand is essentially a force vs distance curve: apart from a small variation due to the oscillation, the normal force signal should be constant along each horizontal line. A vertical cut of the normal force image is simply a force vs distance curve. The two raw images are processed as follows: In the case of the normal force image, each line is averaged to give a single force value. The whole image therefore gives a typical force vs distance curve of high precision due to the averaging process. Each line of the image corresponding to the output of the lock-in amplifier is fitted to a Lorenz curve (eq 2) to give the three parameters a_0, Q, and ω_0. This image therefore results in three curves: a_0 vs distance, Q vs distance, and ω_0 vs distance. Only the latter will be considered here.

Parts a and b of Figure 1 show the raw images corresponding to a typical experiment. In this case the cantilever was excited mechanically and no voltage was applied between the tip and the HOPG sample. The HOPG sample was cleaved and introduced into an airtight microscope chamber. The experiment was started after about 2 h to allow thermal equilibration of the whole microscope setup. A homemade cantilever made from 25 μm Pt/Ir wire bent and electrochemically etched to form a sharp tip was used as SFM probe. Its force constant was estimated to be 6N/m and its free resonance frequency was 6.46 kHz. The frequency of the driving signal was varied between 6.38 and 6.48 kHz (x-axis of the images), and the total displacement of the sample toward the cantilever was about 100 nm. We observe that as the tip approaches the sample, the resonance peak of the system shifts toward lower frequencies (left), as is expected for an attractive potential. Approximately in the center of the images the oscillation suddenly vanishes. The corresponding line in the normal force image shows a discontinuous drop of the force indicating jump to contact. From the raw data shown, a resonance vs distance curve (Figure 1c) and a force vs distance curve (Figure 1d) is obtained as discussed above. The bigger points in Figure 1c correspond to the measured resonance frequency at the corresponding tip—sample distance. The solid line represents a least-squares fit to these points assuming a van der Waals interaction potential $V(z) = -AR/6z$, with A the Hamaker constant and R the tip radius. The tip radius is deduced from this fit. A value of about $R = 25$ nm is obtained using a van der Waals constant $A = 2 \times 10^{-19}$, which is typical for a low electron density conducting surface. The z-scale in this graph is adjusted so that $z = 0$ corresponds to the pole of the interaction potential, that is, to the position of the surface as predicted by the fit. To guide the eye, this position is marked by a vertical solid line. The significance of the dotted vertical line is discussed below. The smaller points scattered around the dotted horizontal line are proportional to the error between the data and the fit. Since this error is without tendency, we conclude that the fit and therefore the assumption of pure van der Waals interaction is essentially

Figure 1. (top) Images corresponding to the output of the lock-in amplifier (a, left) measured simultaneously with the force (b, right) as the tip−sample distance is reduced. For each line, the frequency which is used to oscillate the cantilever is swept between 6.38 and 6.48 kHz while the position of the piezo is kept constant. Different lines are taken at different piezo positions, tip−sample distance is reduced from top to bottom, and contact occurs approximately in the middle of the image. The total gray scale corresponds to about 0.2 nm oscillation amplitude (left) and 20 nm total deflection of the cantilever (right). (bottom left, c) Frequency vs distance data calculated as described in the text from the raw image shown above. The solid curve shows the least-squares fit to the data points assuming pure van der Waals interaction. The small points scattered around the horizontal dotted line (bottom of the graph) correspond to 5 times the error between the data points and the fit. (bottom right, d) Force vs distance data (black points) calculated from the corresponding raw image shown above. The small points in this graph show the measured resonance frequency which have been included to allow a direct comparison between the force vs distance curve and the resonance vs distance curve. The vertical lines correspond to the sample position ($z = 0$, solid line) and to the theoretical jump distance ($z = z_{jump}$, dotted line).

correct. The black points in Figure 1d correspond to the force vs distance curve obtained from the normal force image.

Before interpreting the experimental data, we would like to describe the type of data which is expected for an ideal surface without liquid layer (see Figure 2). As discussed above, if the attractive potential is strong enough, the resonance frequency of the system becomes zero at some tip−sample distance. At this distance, the tip jumps onto the surface. For pure van der Waals interaction this happens at a critical distance $z_{jump} = (AR/3c)^{1/3}$. In this case, the resonance frequency is

$$\omega_0{}^2(z) = \omega_{00} \left(1 - \left(\frac{z_{jump}}{z}\right)^3\right) \tag{3}$$

The critical distance z_{jump} is marked with a dotted vertical line in all the figures. We note that the jump to contact instability in a force vs distance curve should be at the same tip−sample position as the zero frequency point in the resonance vs distance curve (dotted line). Moreover, the (complex) pole at $z = 0$ of eq 3, which is marked by the black vertical line, should agree with the position of the surface as deduced from the force vs distance curve. This

position is deduced by tracing a horizontal line from the last point before the instability to the increasing linear part of the force vs distance curve corresponding to the tip−sample contact. The intersection of these lines defines the position of the sample.

In our experimental results (Figure 1c,d) we find a behavior different from the one described in the previous paragraph. The distance z_{jump} as predicted by the fit to the resonance vs distance curve is marked by the dotted vertical line and it is evident that the jump to contact occurs long before the resonance frequency of the system drops to zero. In fact, jump to contact occurs at a frequency shift of only $\Delta\omega \simeq 0.005\omega_{00}$, instead of $\Delta\omega = \omega_{00}$, and at a distance of about 3.5 nm, instead of the theoretical $z_{jump} = 0.7$ nm. Moreover, the $z = 0$ position calculated from the fit to the frequency data does not agree with the position of the surface as deduced from the force vs distance curve. The fit "sees" the surface (black line) about 4 nm above the position deduced from the force vs distance curve.

Figure 3 shows the result of a similar experiment performed with the same tip, but with an applied dc voltage of 1.5 V between tip and sample. The oscillation of the
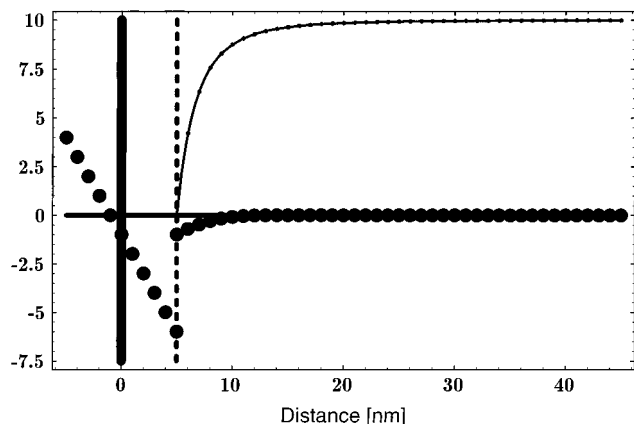
Figure 2. Force vs distance (points) and frequency vs distance curve (line) for an ideal surface without liquid layer. The force constant of the cantilever is supposed to be weak, therefore jump to contact occurs at a certain distance ($z = z_{jump}$, dotted line). For an ideal surface without liquid layer the pole of the frequency curve ($z = 0$, solid line) agrees with the position of the sample as deduced from the force vs distance curve, and the force vs distance curve shows an instability at the position where the resonance frequency of the tip–sample system becomes zero (dotted line). The scale on the vertical axis is arbitrary, but its zero corresponds to zero force and to zero frequency.

cantilever was induced by summing a small ac voltage ($U_{ac} = 4$ mV) to the applied tip–sample dc voltage. The frequency data were fitted with $V''(z) = -B/z^2$, which corresponds to an electrostatic interaction between a spherical tip and the sample.[14] In this case, $B = \pi\epsilon_0 R U_{dc}^2$, with R the tip radius and U_{dc} the applied voltage. The fit gives a tip radius $R = 30$ nm, in reasonably good agreement with the previous result ($R = 25$ nm). The points corresponding to the error between the fit and the data show a small but distinct tendency, indicating that the $1/z^2$ dependence assumed for the electrostatic interaction is not perfectly correct. In spite of this error, the two effects discussed above are again evident: the cantilever snaps long before the critical distance $z_{jump} = 0.6$ nm, and the position of the surface as "seen" by the fit and by the force vs distance curve does not agree. We note that these results were obtained consistently with different (hard) cantilevers on HOPG as well as on gold surfaces. Results which are consistent with an ideal surface without liquid layer as discussed above (see also Figure 2) were only obtained with soft cantilevers (<1 N/m) and by applying high voltages ($U_{dc} > 2$ V).

The experiments described are explained as follows: In ambient conditions—our experiments were performed at room temperature with a relative humidity of about

50%—the effect of relative humidity is 2-fold. On the one hand, a film of thickness

$$d = \left(\frac{A}{6\pi nkT}\frac{1}{\ln(x)}\right)^{1/3} \qquad (4)$$

with A the Hamaker constant of the tip–sample system, n the number density of the liquid, kT the thermal energy, and x the relative humidity, condenses on the tip as well as on the sample. On the other hand, a liquid meniscus of radius

$$\kappa = \frac{\gamma}{nkT}\frac{1}{\ln(x)} \qquad (5)$$

the so-called Kelvin radius, where γ is the surface energy of the liquid ($\gamma_{H_2O} \simeq 72$ mJ/m), is formed around the tip–sample contact. For typical ambient conditions ($x = 50\%$) eqs 4 and 5 give a film thickness of 0.4 nm and a Kelvin radius of about 2 nm.

We believe that the $z = 0$ position calculated from the frequency data corresponds to the liquid–vapor interface, while the $z = 0$ position deduced from force vs distance curve is the position of the solid surface, since the tip is pulled through the liquid film. The resonance data therefore "see" the liquid–vapor interface and the force vs distance curve "sees" the solid–liquid interface. Since this difference is as large as 4 nm, and therefore about an order of magnitude higher than what is expected for an adsorbed liquid film, we believe that a drop has formed on the sample or on the tip, or on both. Formation of nanosized liquid drops has in fact been observed by other groups after mechanical contact of tip and sample.[15] We should note that also in our experiments, tip and sample had been in contact prior to the acquisition of the data shown. Finally, when the tip is at a distance of the order of magnitude of twice the Kelvin radius, we believe that a liquid meniscus is formed spontaneously between tip and sample which then pulls the tip onto the sample because the force constant of the cantilever used in our experiment is not strong enough to hold the tip within the liquid neck. Similar results obtained previously by other groups have also been interpreted along these lines,[4] although the jump distance was determined with less precision. We therefore understand that the tip jumps onto the sample long before the critical jump distance is reached and that the resonance frequency does not drop to zero. With soft cantilevers and high voltages this effect is not observed since then the snapping distance is larger than twice the Kelvin radius (see eq 1); therefore jump to contact due to the instability caused by the surface
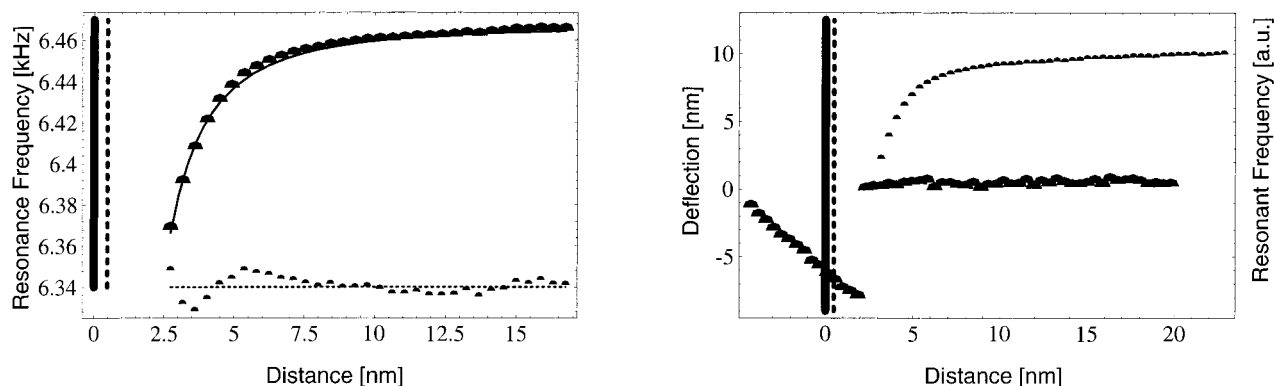

Figure 3. Frequency vs distance data (left) and force vs distance curve (right) similar to those shown in Figure 1. In this case, however, a voltage bias of 1.5 V was applied between tip and sample.

potential occurs before the meniscus can develop. Correspondingly neck formation is not observed.

In summary, we have presented a technique to study tip−sample interaction in SFM with great detail by simultaneously measuring the force and the resonance frequency of the tip−sample system. This method has allowed the observation of effects which are not compatible with the model of an ideal surface where the presence of an absorbed liquid film is neglected. We propose that as the SFM tip approaches the surface, a small liquid neck forms spontaneously pulling the tip onto the sample surface. This is in contrast to the general opinion that jump to contact is always due to the force gradient of the surface potential. Finally, we believe that the technique presented can be valuable also for the investigation of other phenomena related to tip−sample interaction. In particular, the so called "tapping mode" now widely used in SFM might well be strongly affected by the formation of the liquid neck.

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