

Direct measurement of interatomic force gradients using an ultra-low amplitude AFM

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Interatomic force gradients between a W tip and a 7x7 reconstructed Si(111) surface were measured using an off-resonance, ultra-low amplitude AFM technique. The amplitudes used were less than 1 Å (peak-to-peak) which allowed direct measurement of the interaction force gradients as a function of separation. The force gradient curves are shown to consist of an attractive van-der-Waals part and short-range attractive and repulsive interactions. The van-der-Waals background can be subtracted, leaving a short range interaction with an energy parameter of 1.9–3.4 eV and an interaction length scale of 0.54–1.26 Å characteristic of a single atomic bond. This correlates well with our observation of single atom resolved force gradient images. In general, the interaction is reversible up to the zero-intercept of the force gradient (inflection point of the energy). Beyond this point hysteresis tends to be observed and the onset of inelastic deformation can be clearly discerned. An analysis of the atomic scale contact gives reasonable values for the interfacial energy, yield strength, and the energy per atom needed to initiate plastic deformation.

Keywords: atomic force microscopy; interatomic potentials; nanomechanics; contact mechanics; atomic scale imaging

1. Introduction

Scanning probe microscopies are at the heart of nanoscience. Especially the Atomic Force Microscope (AFM) promises to be a key technique for measurement and manipulation of nanoscale volumes of matter down to the atomic scale. However, true atomic resolution in the AFM has only been achieved recently, so far by use of large amplitude, frequency modulation techniques (Giessibl 1995; Kitamura & Iwatsaku 1995; Ueyama et al. 1995). While providing high resolution images these techniques are limited as a quantitative spectroscopic tool, in atomic manipulation experiments and in measuring the nature of dissipative processes which lie at the heart of much of nanotechnology. This is because the measured parameter (frequency shift Δf) is not related in a simple manner to either the interaction energy or the force. Mathematical deconvolution is needed in order to extract the force (Giessibl 1997; Gotsmann et al. 1999a; Dürig 1999; Hölscher et al. 1999; Ke et al. 1999) which relies on a number of assumptions such as the harmonic motion of the lever, a conservative interaction potential and general reversibility of

the interaction. However, imaging with large amplitude AFM consistently involves a site dependent damping (Molitor et al. 1999; Gotsmann et al. 1999b) which is associated with non-conservative interactions and hysteresis of the energy curve.

In this paper we report a non-contact atomic force microscopy technique that directly measures the force gradient of the tip-sample interaction using very small oscillation amplitudes of less than 1 Å peak-to-peak (p-p) and sub-resonance oscillation frequencies. In this limit the measurement is linear and quasi-static. This enables us to directly measure complete force gradient curves up to the contact regime. In our technique the dynamic energy of the vibrating lever, and thus the maximum possible energy input into the tip/ sample interaction region, is < 0.1 eV per cycle as opposed to 10–100 eV in the case of large amplitude, resonance enhanced techniques (Anczykowski et al. 1999; Gotsmann et al. 1999b).

Since we measure the interaction directly we can separate contributions due to van-der-Waals, electrostatic and short-range interactions without the need of any deconvolution in terms of frequency shifts (Guggisberg et al. 2000). This way we can gain insight into the differences in interaction ranges that have been reported in the literature (Jarvis et al. 1996; Cross et al. 1998; Gotsmann et al. 1999b; Guggisberg et al. 2000) and the influence of tip geometry on high resolution imaging. Moreover, we can quantify the effect of the relaxation of tip and surface and also the behavior in the contact regime where we can clearly see the onset of plastic deformation and hysteresis in the force gradient curve. Inelastic deformation is observed when the inflection point of the interaction energy is surpassed. Therefore, in the non-contact region, the second derivative of the energy curve (the interaction stiffness) provides the most clear information since it passes through its minimum and intercept before contact is established. In our technique, the interaction stiffness is measured directly. The determination of the interaction length scale then only involves a suitable subtraction of the long-range interaction terms, while in large amplitude methods the length scale has to be inferred from taking the derivative of the deconvoluted frequency shift data after such a subtraction (Lantz et al. 2000).

2. Experimental

Our AFM technique relies on vibrating a stiff lever at sub-Ångstrom amplitudes, A_0 , and sub-resonance frequencies and monitoring the changes in vibration amplitude of the lever that result from interactions. Since in this small amplitude limit the measurement is linear and quasi-static, a force balance readily shows that the interaction stiffness (negative of the force gradient) can be measured directly from the change in vibration amplitude (Jarvis et al. 1993) and is given by:

$$k_{\text{total}} = -\frac{\partial F_{\text{total}}}{\partial z} = \sum_j k_i^{(j)} = k_{\text{Lever}} \left(\frac{A_0}{A} - 1 \right) \quad (2.1)$$

where A_0 is the amplitude in the absence of tip-surface interactions, A is the measured amplitude, k_{total} is the total measured tip-surface interaction stiffness, and k_{Lever} is the lever stiffness. The total interaction stiffness, k_{total} , is typically a sum of several contributions, $k_i^{(j)}$. The linearity of the measurements was confirmed by the fact that higher harmonics of the driving frequency were extremely small even

in the presence of rapidly varying force gradients and by comparing to numerical models of the equation of motion (Hoffmann & Pethica 2000).

To avoid snap to contact high stiffness tungsten levers were used (typically about 100 N/m). This necessitates the use of an ultra-high sensitivity displacement sensor which has been achieved by the use of a fibre interferometer with a sensitivity of better than $2 \times 10^{-4} \text{ \AA} / \sqrt{\text{Hz}}$. The details of the technique will be presented elsewhere (Oral et al. 2000). The lever stiffnesses were characterized by applying a known force via a calibrated test lever and monitoring the deflection of both the test and the measured lever by high resolution laser interferometric techniques.

Atomic scale imaging was obtained using the (averaged) tunnelling current as the feedback parameter. The oscillation period of the lever was much faster than the time constant of the feedback loop, thus causing no problems while imaging. All measurements were performed in ultra-high vacuum ($< 10^{-10}$ mbar) on clean 7×7 reconstructed Si(111) surfaces. The W tips were cleaned by baking at 160 °C and field emitting at ± 10 V while the tip was fully retracted (by about 1 micron). Care was taken to move the tip a large lateral distance after field emitting and before commencing any imaging.

3. Atomic and van-der-Waals force gradients

Figures 1a,b show measurements of the interaction stiffness between a W tip and a clean 7×7 reconstructed Si(111) surface as a function of distance for two different tips (1 and 2) and simultaneously measured tunnelling currents (which will be discussed later). The free oscillation amplitude was 0.42 Å (p-p) and 0.49 Å (p-p), respectively, and the amplitude did not exceed 0.7 Å (p-p) at any time during the measurement. The stiffnesses of the levers were 120 N/m and 180 N/m, respectively.

Now, the displacements of the piezo actuator are not identical to the local displacements of the tip. First of all, the bending of the cantilever structure has to be taken into account (Burnham 1993). Secondly, the relaxation of tip and surface needs to be considered more carefully, since it depends not only on the magnitude of the force but also on its range. Longer range forces act on a larger part of the tip and thus encounter a potentially larger stiffness. Van-der-Waals and electrostatic interactions are slowly varying on the scale of typical atomic bond distances and thus the correct stiffness to use is that of the macroscopic tip which is quite large. The total deflection due to van-der-Waals forces can be calculated if we consider that the displacement is a function of the force acting on each layer of the tip, dF , and the stiffness of the tip above each layer, $k_{\text{tip}}(h)$. For a van-der-Waals interaction acting on a tip we can write the total displacement in the following way (Israelachvili 1991):

$$\Delta L = \int_0^\infty \frac{dF}{k_{\text{tip}}(h)} = \int_0^\infty \frac{A_{\text{H}} R^2(h)}{2(h+d)^4} \frac{dh}{k_{\text{tip}}(h)} \quad (3.1)$$

Here A_{H} is the Hamaker constant (taken to be 3×10^{-19} J), h is the height along the tip, d is the tip-surface distance, and $R(h)$ is the tip radius at tip height, h . The geometry used in equations (3.1) – (3.3) is illustrated in figure 2. The stiffness

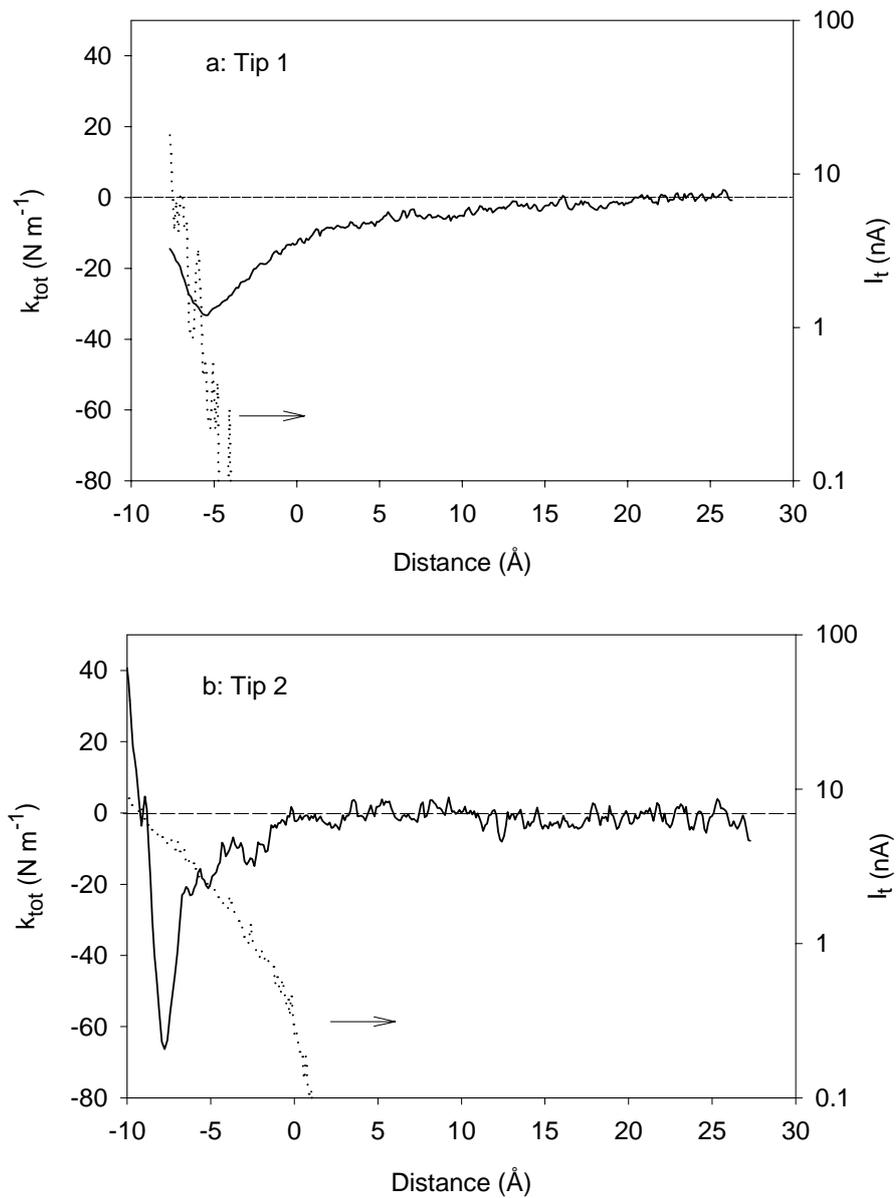


Figure 1. Measured interaction stiffness curves and simultaneously measured tunnelling currents versus distance for two different W levers and clean Si(111) 7x7 surfaces in ultra-high vacuum. Tip bias was -2V in both cases. The distance axis was corrected for the cantilever bending. a. Measurement using cantilever/ tip 1: Stiffness of the lever was 120 N/m, $\nu_0 = 9.8$ kHz, $\nu_{\text{applied}} = 4.7$ kHz, free oscillation amplitude was 0.42 Å (peak-peak). B. Measurement using cantilever/ tip 2: Stiffness of the lever was 180 N/m, $\nu_0 = 16.2$ kHz, $\nu_{\text{applied}} = 4.7$ kHz, and the free oscillation amplitude was 0.49 Å (peak-peak). The total acquisition time was of the order of 10 seconds.

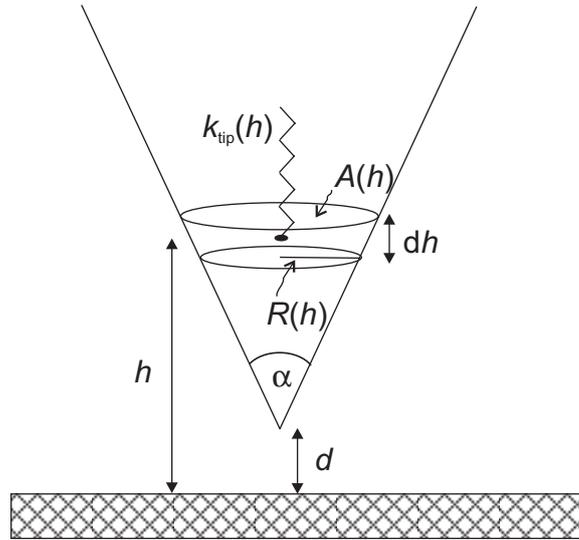


Figure 2. Geometry used in equations (3.1) – (3.3) to calculate the total tip relaxation due to long range forces.

above each layer, k_{tip} , for a cone shaped tip with cone angle α is given by:

$$k_{\text{tip}}(h) = c_{\text{tip}}^{-1}(h) = \left(\int_h^\infty \frac{dh}{A(h)E} \right)^{-1} = \left(\int_h^\infty \frac{dh}{E\pi h^2 \tan^2 \alpha} \right)^{-1} = E\pi h \tan^2 \alpha \quad (3.2)$$

where $c_{\text{tip}}(h)$ is the tip compliance, $A(h)$ is the cross-sectional area at height h , and E is Young's modulus of the tip. Plugging (3.2) into (3.1) and integrating, we obtain for the total tip displacement:

$$\Delta L = \frac{A_H}{12\pi E d^2} \quad (3.3)$$

For a cone-shaped W tip we arrive at a displacement of 0.02 \AA at a typical equilibrium distance of 2 \AA and less for larger separations. The corresponding displacement of the surface can be estimated to be about 0.04 \AA taking the lower modulus of silicon into account. This shows that the total surface-tip relaxation due to van-der-Waals interactions is unlikely to exceed 0.1 \AA and consequently will be neglected in the following analysis. The chosen geometry has little effect on these conclusions and similar results can be obtained for the similarly slowly varying electrostatic interactions which act on the surface of the conducting tip.

Long range forces can be electrostatic and van-der-Waals. Electrostatic forces are expected to be dependent on the square of the bias voltage between tip and sample, V_{bias}^2 (Jeffery et al. 1999; Guggisberg et al. 2000). We analyzed a variety of experimental force curves obtained at different voltages in the range -0.25 V to -2 V and found that the long-range interaction does not show any systematic dependence on V_{bias}^2 and is therefore mostly due to van-der-Waals interactions. This does not mean, however, that electrostatic forces are not present, only that they are much weaker or more slowly varying than the van-der-Waals forces.

Now, in order to separate out the van-der-Waals contribution it is necessary to determine the power-law dependence of the measured stiffness on the separation. A 4th order power law (for the force gradient) corresponds to a truncated (circular) rod geometry for the macroscopic part of the tip, a third order law indicates a spherical tip, and a cone shaped truncated or spherically capped tip corresponds to mixed 2nd to 4th order terms. In our case, we found that an exponent of 3.5–4 gave the best fit to the long-range data and we therefore chose a 4th order power law. Real tip structures can be expected to be highly irregular and thus any attempt to model the background in such simple terms has to be an idealization. However, the shape of the modeled long-range interaction curve is essentially independent of the particular model as the both the distance offset and curvature of the curve are determined by the measured data. The van-der-Waals stiffness for a truncated, circular rod is given by:

$$k_{\text{vdW}} = -\frac{A_{\text{H}}}{2} \frac{R^2}{(d - d_0)^4} \quad (3.4)$$

where R is the radius at the (macroscopic) tip end and d_0 is a distance offset which allows for the fact that the absolute zero of the distance axis is unknown. Analyzing the data shown in figure 1 we found $R = 65.5 \pm 5.6$ nm for tip 1 and $R = 17.8 \pm 3.5$ nm for tip 2. Averaged over several measured force curves obtained with the same two tips we found radii in the range of 52 ± 13 nm and 32 ± 18 nm for tips 1 and 2, respectively. In the case of tip 1 the radius did not change much between measurements, while in the case of tip 2 we observed a slow but marked increase of the radius with the number of measurements (some of which included full contact and indentation of the tip). Figure 1b shows a measurement that was obtained rather early in the life of tip 2. It became blunter later on. In general, the obtained values for R were reproducible between measurements performed with the same tip. Thus this seems to be a stable and reproducible process which gives mesoscopic geometric parameters which are physically realistic. The exact geometry is, of course, unknown.

Having subtracted the van-der-Waals background as described above, we are always left with a short range attractive/repulsive interaction. We now need to take the relaxation of the outermost tip atoms into account (Pérez et al. 1998). This is done by rescaling the distance axis and the measured short range stiffness according to (Burnham 1993, 1994):

$$k_{\text{sr}} = k_{\text{m}} \left(1 - \frac{k_{\text{m}}}{k_{\text{ts}}} \right)^{-1} \quad (3.5a)$$

$$z_{\text{sr}} = z_{\text{m},\infty} + \int_{\infty}^{z_{\text{m}}} \left(1 + \frac{k_{\text{sr}}}{k_{\text{ts}}} \right)^{-1} dz \quad (3.5b)$$

where z_{sr} is relaxation corrected distance (not the actual gap separation as there is always an arbitrary offset), z_{m} is the measured distance (after correcting for the lever movement), k_{sr} is the actual short-range interaction stiffness, k_{m} the measured short-range stiffness, and k_{ts} the combined tip/surface stiffness. Here we use stiffness values, k_{ts} , obtained from the study of Si/Si interactions by Pérez et al. (Pérez et al. 1998), but correcting for the fact that tungsten has a higher modulus. In particular, we took the stiffness of the Si surface to be 110 N/m and the stiffness

of the W tip to be 300 N/m. This gives a combined tip/surface stiffness, k_{ts} , of 80.5 N/m. It should be noted that values for the tip stiffness depend on the atomic configuration at the end of tip and therefore variations are possible. However, the values given by Pérez et al. are generally in agreement with other studies (Clarke et al. 1996).

The corrected short-range interactions are shown in figure 3. To model the short range interaction we used a semi-empirical short range interaction potential (Rose et al. 1984; Sutton 1993) given by:

$$k_{\text{int}} = \frac{d^2U}{dz^2} = \frac{|E_b|}{\lambda^2} (1 - 1.3a + 0.3a^2 - 0.05a^3) e^{-a} \quad (3.6)$$

where E_b is the minimum of the interaction potential, λ is the characteristic length scale (roughly the distance between the minimum of the interaction potential and its inflection point), and a is the normalized distance given by:

$$a = \frac{z - z_0}{\lambda} \quad (3.7)$$

where z_0 is a distance offset which results from the fact that the true zero of the distance axis is unknown. Fitting this potential to the short-range part of the force gradient (figure 3), the average length scales were determined to be 1.14 Å for tip 1 and 0.53 Å for tip 2. The energy parameter, $|E_b|$, was found to be 2.41 eV or 3.18 eV, respectively. Averaged over several measurements performed with the same tips we found $\lambda = 1.26 \pm 0.20$ Å, $|E_b| = 1.9 \pm 1.0$ eV for tip 1 and $\lambda = 0.54 \pm 0.08$ Å, $|E_b| = 3.4 \pm 1.4$ eV for tip 2. The measured values for the interaction range and energy compare well with theoretical values (Pérez et al. 1998). Although these measurements were done at room temperature, a thermally induced broadening of the interaction curve, as recently suggested, was not observed (Lantz et al. 2000). We conclude that we are directly measuring single bonds mechanical properties. The measured parameters for tips 1 and 2 are summarized in table 1. We now consider the relation of these observations to atomic scale imaging.

4. Imaging and the relative contribution of short-range interactions

The attractive length range and the relative strength of the van-der-Waals interaction greatly influences the lateral resolution while imaging. An indicator for the attractive length range of the interaction is the position of the onset of the simultaneously measured tunnelling current. As seen in figure 1a, the current onset in the case of tip 1 (large R , blunt) only occurred after the onset of the attractive force gradient. Now, a key observation is that only in cases where we observed the onset of the tunnelling current before a significant attractive force gradient (tip 2), were we able to achieve atomic resolution imaging. The relatively large difference between the onset of the tunnelling current in figures 1a and b is quite surprising. At this point, we can only speculate about its origin, but it should be noted that not only the onset but also the apparent barrier height (slope of the tunnelling current) is quite different in the two figures. A possible explanation might involve the detailed chemical nature of the tip, i.e. the type of atom interacting with the surface.

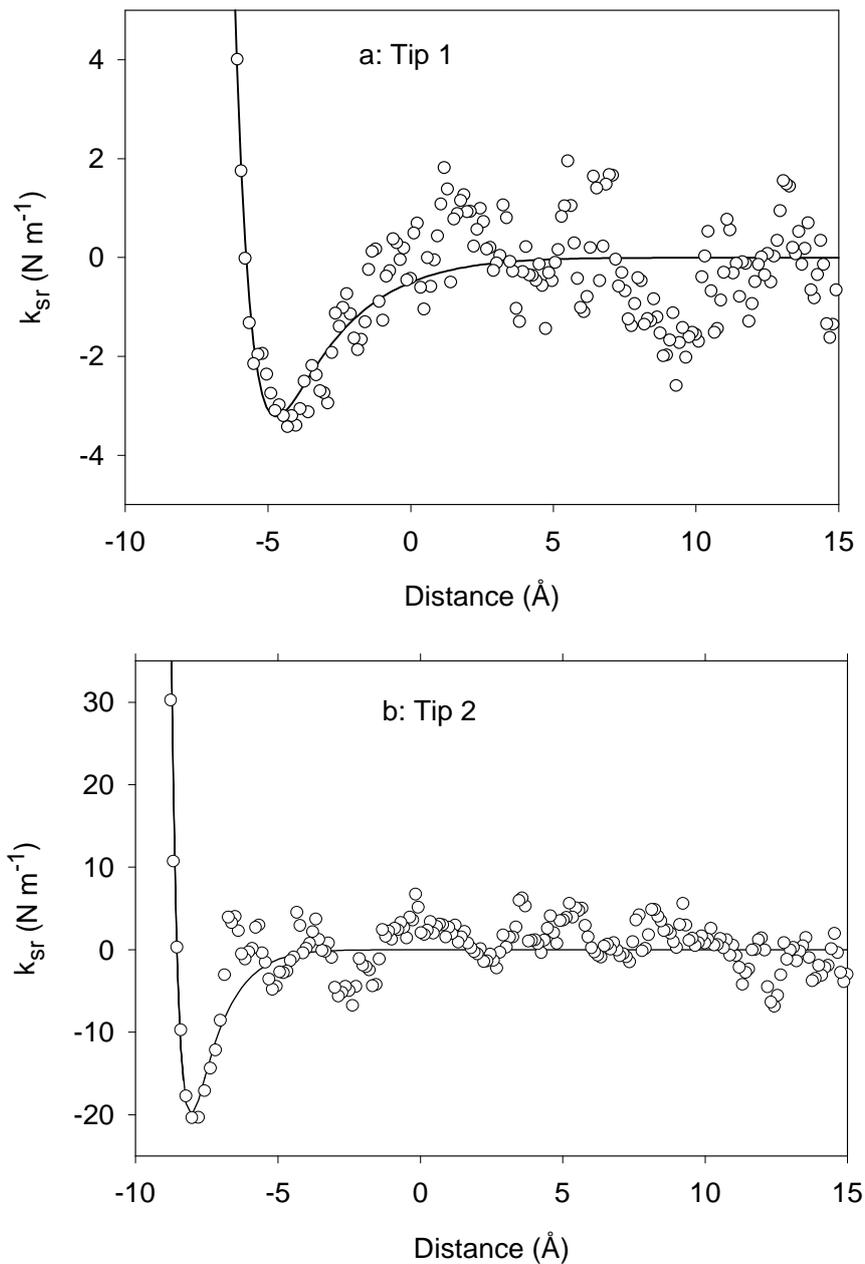


Figure 3. Interaction stiffness due to short-range covalent bonding interactions obtained by subtracting the long-range van-der-Waals background and correcting for the relaxation of tip and surface. a. Tip 1: Interaction energy $|E_b| = 1.9 \pm 1.0$ eV, characteristic length scale $\lambda = 1.26 \pm 0.20 \text{\AA}$. b. Tip2: $|E_b| = 3.4 \pm 1.4$ eV, $\lambda = 0.54 \pm 0.08 \text{\AA}$.

Table 1. Parameters obtained from measurements using tips 1 and 2

	cantilever/tip 1	cantilever/tip 2
Lever stiffness (N/m)	120	180
Resonance frequency ν_0 (kHz)	9.8	16.2
Applied frequency ν_{applied} (kHz)	4.7	4.7
Free amplitude (\AA)(p-p)	0.42	0.49
Van-der-Waals radius from figure 1 (nm)	65.5 ± 5.6	17.8 ± 3.5
Average van-der-Waals radius (nm)	52 ± 13	32 ± 18
Short range energy parameter $ E_b $ (eV)	1.9 ± 1.0	3.4 ± 1.4
Short range length scale λ (\AA)	1.26 ± 0.20	0.54 ± 0.08

Figure 4 shows topographic (STM) and simultaneously acquired force gradient images of Si(111)7x7. Averaged over several images obtained under identical conditions, the average topographical (STM) and force gradient corrugations between adatom and cornerhole for tip 2 were $1.07 \pm 0.18 \text{ \AA}$ and $8.4 \pm 3.1 \text{ N/m}$, respectively, while in the case of tip 1 no atomic resolution could be achieved. An important aspect in imaging is evidently the need for a relatively strong short range part to the total interaction to give significant contrast at atomic resolution. In the case of tip 1 only a very small fraction of the total force gradient ($< 10\%$) was due to short range interactions and therefore the force gradient imaging resolution can be expected to be seriously diminished.

The geometry of the tip and thus the relative contribution of van-der-Waals interactions and short-range interactions greatly influences the overall apparent interaction length scales (Buldum et al. 1999), the energies of the total measured force gradient, and the contrast in atomic scale imaging. It is clearly an essential factor in explaining the wide variability seen in the earlier literature. Using the measured parameters for tips 1 and 2 ($R = 17.8 \text{ nm}$ and 65.5 nm), we investigated this influence by calculating theoretical interaction stiffness curves composed of a short range covalent interaction (equation (3.6)) and a van-der-Waals interaction (given by equation (3.4)). In figure 5, the ratio between the short range stiffness minimum and the total stiffness minimum (given as a percentage) is plotted versus the relative strength of the van-der-Waals interaction at the tip-end, s . The relative strength is given by $s = R^2/\Delta d^4$, where $\Delta d = d_0 - z_0$ is a measure for the distance between the mesoscopic (van-der-Waals) tip and the actual (covalent) tip-end. The deflection of the lever and the relaxation of tip and surface were also taken into account. At large offsets or small radii (small s), the short-range interaction dominates the stiffness minimum. As the offset decreases or the radius increases (and thus s increases), the van-der-Waals contribution becomes more dominant. The relative strength of the short range interaction depends on its length range and energy. In the case of tip 2, the short range interaction continues to dominate the total stiffness much longer than in the case of tip 1 due to its much shorter length range and thus larger maximum force gradient. This is expected to have consequences for the contrast obtained when using these tips in imaging.

The inset to figure 5 shows the influence of the relative strength, s , on the apparent attractive length scale of the total force gradient. The attractive range, l_{attr} , is here given by the distance away from the surface over which the force gradient has decayed to $1/e$ of the maximum. For a purely short-range interaction (equation (3.6)) with a repulsive range of $\lambda = 1.26 \text{ \AA}$ acting on lever/tip 1 we would

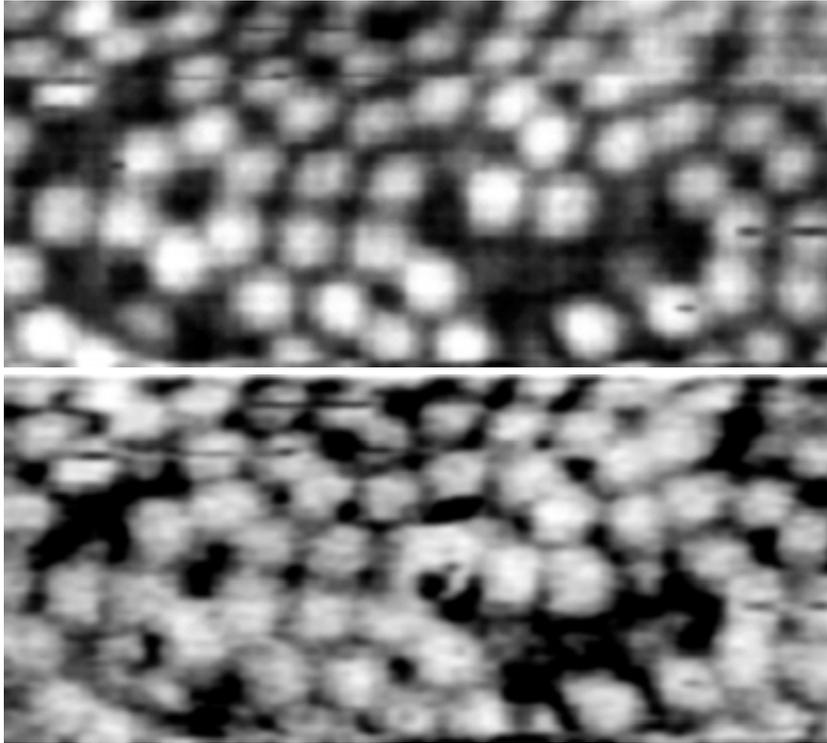


Figure 4. Simultaneously acquired STM topography (top) and force gradient image (bottom) of Si(111)7x7 using a free amplitude of 0.4 Å (peak-peak). Image size is 70×32 Å, acquisition time was 10 minutes.

expect an apparent attractive range of 3.00 Å and for lever/tip 2 with $\lambda = 0.54$ Å we would expect $l_{\text{attr}} = 0.85$ Å. It is interesting to note that for very small offsets (and thus strong influence of the van-der-Waals forces, large s), the apparent length range begins to shorten again. This is due to the high curvature of the van-der-Waals interaction stiffness when the offset is quite low. However, we should note that at very small separations between tip and surface, the van-der-Waals force may be reduced and the usual power law will not apply (Heinrichs 1973, Heinrichs 1975, Buhl 1976, Hartmann 1990), so that the observation of a very short interaction range can generally be attributed to covalent interactions.

5. Atomic scale contact and inelasticity

Using our AFM technique it is also possible to continue the tip-surface approach until repulsion terms become significant. We can thus measure and analyze contact stiffnesses. Figure 6 shows forward (moving toward the surface) and reverse (moving away from the surface) scans using tip 2 which were measured up to the contact regime. These scans were obtained in the early stages of the tip's use, when it was still rather sharp. The forward and reverse scans are significantly different and greatly displaced with respect to each other. In general, we observed hysteresis between forward and reverse scans when the zero intercept of the force gradient

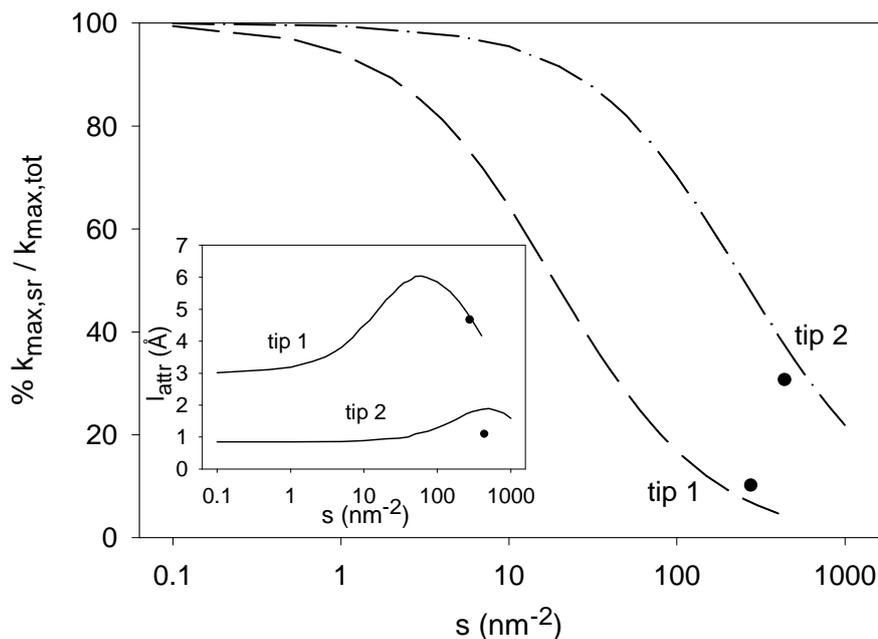


Figure 5. Proportion of the total measured interaction stiffness that is due to short-range interactions plotted versus the strength of van-der-Waals interaction, s (explanation see text). Lower curve (tip 1): $R = 65.5$ nm, $\lambda = 1.26$ Å, $|E_b| = 1.90$ eV. Upper curve (tip 2): $R = 17.8$ nm, $\lambda = 0.54$ Å, $|E_b| = 3.42$ eV. Dots indicate measurements taken from Figures 1 and 3. Inset: Apparent attractive length range l_{attr} versus s for the same parameters R , λ , and $|E_b|$.

(inflection point of the energy or minimum of the force) was exceeded. Once this point is passed, inelastic processes are taking place. In contrast, if the measurement is reversed before the inflection point of the energy the forward and reverse scans coincide except for a very small displacement due to drift. These observations put a severe limitation on large amplitude, frequency shift based AFM methods since their interpretation relies on a single valued and reversible interaction curve. Thus meaningful results can only be obtained with these techniques if the minimum of the force curve is not passed at any time during the motion of the cantilever.

Even closer to the surface the force gradient curve starts to bend over and the curve is interrupted by distinct jumps, i.e. sudden changes in stiffness without a large change in the tip-surface separation. In this region the positive (repulsive) stiffness exceeds the intrinsic stiffness of the tip and the overall stiffness is no longer dominated by interfacial interactions but by deformation of the bulk. This latter region can be analyzed by continuum contact stiffness models and in the context of this section of the paper we define this region as the contact region. Since we measure the interaction directly, we can analyze the contact stiffness to provide a quantitative picture of the contact mechanics of a sharp tip. As seen in figure 6, there is a slow increase of the stiffness once contact has been established interrupted by sudden upward jumps. These jumps could be associated with atomic rearrangement in the tip region resulting in a more stable (higher intrinsic stiffness)

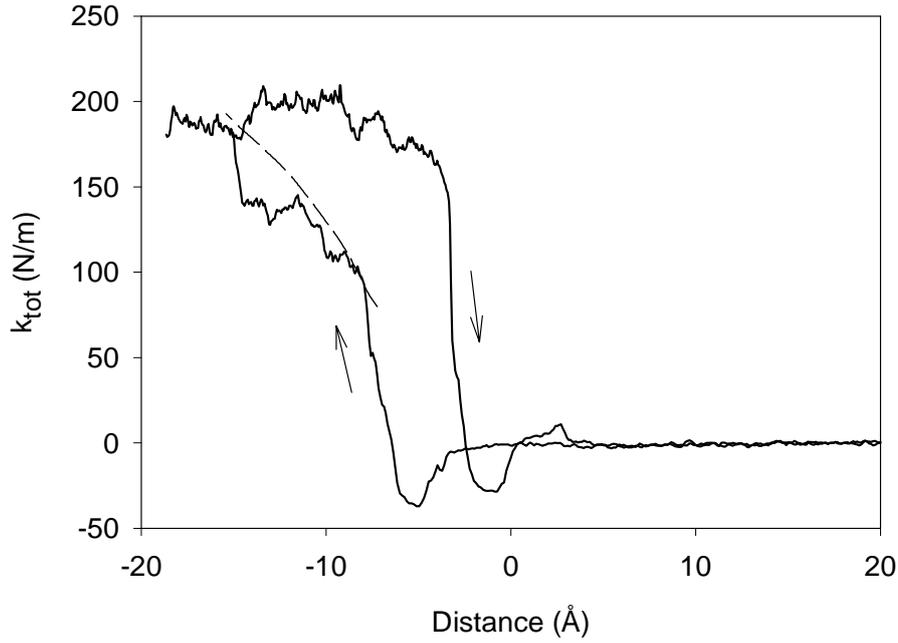


Figure 6. Forward and reverse scans measuring the interaction/contact stiffness between a W tip and a Si(111)7x7 surface in UHV. There is large hysteresis between the two scans due to non-conservative processes in the contact region. The dashed line shows a fit according to equations (5.1) – (5.4) with $E^* = 105$ GPa, $F_c = 24$ nN, $R = 1$ nm and $\gamma = 1.9$ J m⁻².

tip configuration. The slow increase before each jump can be analyzed using the JKR/DMT (Derjaguin et al. 1975, Johnson 1985) model of contact with adhesion. In this model there are two unknowns, the tip radius, R , and the interfacial energy, γ , which are related to the pull-off force via (Derjaguin et al. 1975; Israelachvili et al. 1980 ; Israelachvili 1991):

$$F_c = 4\pi\gamma R \quad (5.1)$$

The contact radius, r_c , can be calculated from (Johnson 1985):

$$\left(F - \frac{4E^*r_c^3}{3R}\right)^2 = 16\pi\gamma E^*r_c^3 \quad (5.2)$$

where E^* is given by:

$$\frac{1}{E^*} = \frac{1 - \nu_{\text{Si}}^2}{E_{\text{Si}}} + \frac{1 - \nu_{\text{W}}^2}{E_{\text{W}}} \quad (5.3)$$

Here, E_{Si} , E_{W} are the Young's moduli, and ν_{Si} , ν_{W} are the Poisson ratios of silicon and tungsten, respectively. The contact stiffness, k_c , is given by:

$$k_c = 2E^*r_c - \frac{4(\gamma E^* \pi)^{1/2} r_c}{(2/R)r_c^{3/2} - (\pi\gamma/E^*)^{1/2}} \quad (5.4)$$

The first term on the right-hand side of equation (5.4) is the Hertzian contact stiffness, whereas the second term represents a correction due to adhesion.

In order to analyse the experimental data, we first obtained a value for F_c from the tip retraction scan by measuring the size of the jump of the cantilever as it snapped off the surface. In this case we measured $F_c = 24$ nN. This determined the product γR (equation (5.1)). The force, F , was calculated as a function of distance by integrating the force gradient curve. Then, starting with a trial value for either γ or R , equation (5.2) provided a value for r_c for every point along the curve, which was used in equation (5.4) to calculate k_c as a function of distance. Thus all parameters are determined from the measured data and there is only one adjustable parameter (either γ or R). The resulting fit shown in figure 6 is very sensitive to the choice of γ (and thus R): even a 10 % change in γ leads to a visibly worse fit of the experimental data. The best fit (dashed line in figure 6) gives $\gamma = 1.9 \text{ Jm}^{-2}$ and $R = 1$ nm. Integrating over the stiffness the elastic energy stored in the contact can be calculated. The initial number of atoms in contact with the surface can be estimated from the contact radius to be about 25 which increases to about 65 at the reversal point. It is found that the elastic energy per atom increases to about 0.2–0.6 eV per tip atom before a jump in the stiffness occurs. The contact pressure at the first jump is of the order of 7–10 GPa which is comparable to the yield strength of silicon or tungsten. This model yields very reasonable values, despite the fact that the contact radius is of the same order as the tip radius (about 1 nm) and the number of atoms in the contact is very small.

6. Conclusions

We have demonstrated that an off-resonance, sub-Ångstrom amplitude AFM technique can be used to directly measure short and long-range interactions including hard contact. In addition, true atomic resolution can be achieved with this technique in force gradient imaging. The separation of different contributions to the total interaction stiffness is straight-forward as no deconvolution of frequency shifts is needed. In addition, the energy input into the tip/surface region is minimal and non-conservative processes can be measured easily. This opens up a large number of application in tribology, plasticity, and atomic manipulation which is not accessible with large amplitude methods. Analyzing the data we obtained, reasonable values for a number of physical parameters were obtained. These include the energy parameter and length range of covalent short-range interactions between W and Si, the interfacial energy between W and Si, and the elastic energies and pressures needed to initiate plastic deformation in small volumes of atoms. All of these measured values compare well with theoretical or known values.

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