

## Nanomechanics using an ultra-small amplitude AFM

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### ABSTRACT

A new type of AFM is presented which allows for direct measurements of nanomechanical properties in ultra-high vacuum and liquid environments. The AFM is also capable of atomic-scale imaging of force gradients. This is achieved by vibrating a stiff lever at very small amplitudes of less than 1 Å (peak-to-peak) at a sub-resonance amplitude. This linearizes the measurement and makes the interpretation of the data straight-forward. At the atomic scale, interaction force gradients are measured which are consistent with the observation of single atomic bonds. Also, atomic scale damping is observed which rapidly rises with the tip-sample separation. A mechanism is proposed to explain this damping in terms of atomic relaxation in the tip. We also present recent results in water where we were able to measure the mechanical response due to the molecular ordering of water close to an atomically flat surface.

### INTRODUCTION

Atomic Force Microscopy (AFM) holds tremendous promise as a tool to explore and map the mechanics of matter at the nano- and atomic scale. However, current limitations in the techniques has slowed progress in advancing this important technique. Most commonly used AFM techniques suffer from a variety of problems which either limit resolution or make quantitative interpretation of the obtained data very difficult. These problems include snap-to-contact (contact AFM, intermittent contact AFM) or inherent non-linearities (most dynamic AFM modes) [1,2]. Here we present a new AFM technique which avoids these problems by using ultra-small amplitudes (linearization of the measurement), stiff levers (avoids snap-to-contact), and off-resonance operation (easy interpretation of the results, no need for high Q and thus useful in liquids). Using this new AFM technique we were able to map atomic bonding curves, measure atomic scale dissipation, and look at the mechanical properties of molecular ordering in water.

### EXPERIMENTAL

The two AFM used in this study were entirely home-built and incorporated a variety of new features not generally present in commercial AFM. One of the instruments is located in an ultra-high vacuum system (base pressure  $4 \times 10^{-11}$  mbar), while the other is designed to operate in air or liquids. Both AFM use levers of sufficient stiffness to avoid instabilities ( $> 100$  N/m in the ultra-high vacuum experiments) and sub-Ångstrom amplitudes. This requires

a very high sensitivity sensor to accurately measure lever deflection and amplitude. In our case, we used a fiber interferometer which can be tuned to give a sensitivity up to  $2 \times 10^{-4} \text{ \AA Hz}^{-1/2}$ . The levers were typically vibrated far below their lowest resonance at amplitudes of less than  $1 \text{ \AA}$  (peak-to-peak). As the lever moved towards the surface, the amplitude changed due to interactions with the surface. The amplitude was measured using a lock-in amplifier which also supplied the dithering signal for the lever vibration.

Assuming that the measurement is linear and that the lever frequency is far below the resonance frequency of the lever it can be shown that:

$$k_{ts} = k_L \left( \frac{A_0}{A} \cos \mathbf{f} - 1 \right) = - \frac{dF_{ts}}{dz} \quad (1a)$$

$$\mathbf{g}_{ts} = \frac{k_L A_0 \tan^2 \mathbf{f}}{A \omega \sqrt{1 + \tan^2 \mathbf{f}}} - \mathbf{g}_i \quad (1b)$$

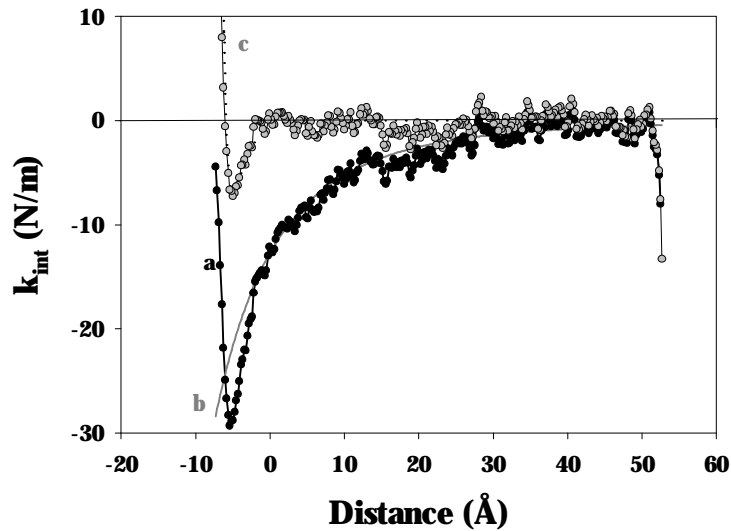
where  $k_{ts}$  is the measured interaction stiffness (negative of force gradient,  $dF_{ts}/dz$ ),  $k_L$  is the stiffness of the lever,  $A_0$  is the free lever amplitude far away from the surface,  $A$  is the measured amplitude,  $\mathbf{f}$  is the phase between the dither signal and the actual motion of the lever,  $\omega$  is the drive frequency,  $\gamma_{ts}$  is the damping associated with tip-surface interactions, and  $\gamma_i$  is the intrinsic damping due to the lever structure and the surrounding medium.

## RESULTS AND DISCUSSION

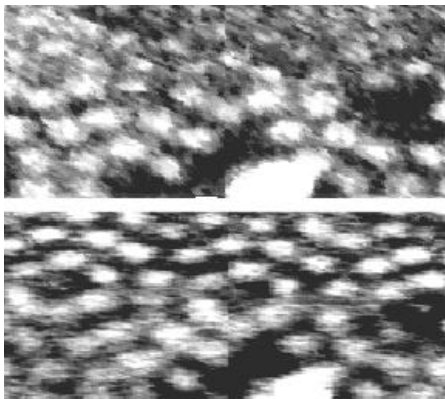
### A. Atomic force gradients and imaging on silicon

Figure 1 shows the measured interaction stiffness versus separation curve for a W tip approaching a clean Si(111) 7x7 surface. It should be noted that this curve was obtained by a continuous measurement of the amplitude of the lever (which never exceeded  $0.8 \text{ \AA}$  peak-to-peak during the measurement). The interaction stiffness was calculated using the simple formula (1a) where the phase was very small during the entire measurement (and thus  $\cos \mathbf{f} = 1$ ). This should be contrasted to measurements using large amplitude AFM where a frequency shift is measured and a careful deconvolution of the essentially integrated force data is needed to extract any meaningful mechanical information. The snap-to-contact was avoided by simply using a lever with a stiffness larger than the maximum attractive force gradient ( $k_L = 120 \text{ N/m}$ ). In the analysis of the raw stiffness data we took the bending of the lever and the relaxation of the tip and surface atoms into account. The van-der-Waals background was subtracted using a simple power-law fitted to the long range force gradient data. The remaining stiffness is due to short range forces associated with covalent bonding. This can be fitted to an empirical potential and yields length ranges of  $0.5 - 1.3 \text{ \AA}$  and binding energies of  $2 - 4 \text{ eV}$ , which are characteristic of single atomic bonds [3].

Using STM feedback we also simultaneously recorded the topography and the atomic force gradients at a 7x7 reconstructed Si(111) surface. We found that there is no simple relationship between the tunneling contour and the contrast obtained in the force gradient. This is shown in Figure 2 which shows STM and simultaneously recorded force gradient data on Si(111) using a W lever. Halfway through the image a tip change occurred



**Figure 1.** Interaction stiffness measured between a sharp W tip and a clean  $7 \times 7$  reconstructed Si(111) surface. Curve (a) shows the total stiffness measured (taking the cantilever bending into account). Curve (b) shows a fit of the long range van-der-Waals background. Curve (c) is the short range interaction stiffness due to covalent bonding obtained by subtracting the van-der-Waals background and adjusting for atomic relaxation of the tip and surface.



**Figure 2.** Simultaneously recorded STM topography (top) and force gradient (bottom) of a Si(111)  $7 \times 7$  surface. In the center of the image a change in contrast is observed which is due to an atomic scale tip change. In the case of the STM topography, the contrast was diminished, while the force gradient contrast was improved as a result of the uncontrolled tip change.

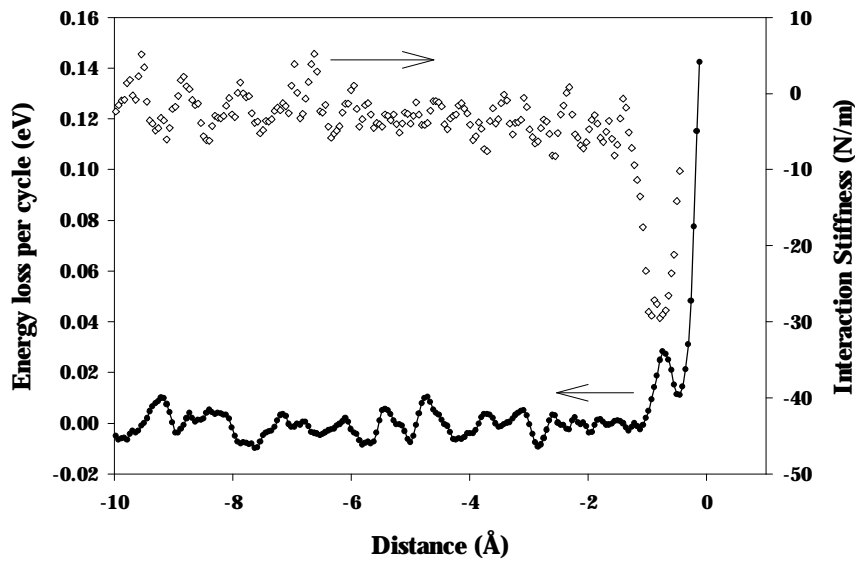
which in the case of the STM images reduced the contrast severely, but seemed to enhance the contrast of the force gradient image.

## B. Atomic scale damping

We also performed simultaneous STM and AFM experiments on Cu(100) surfaces. In particular we measured the damping associated with tip-sample interactions. In order to obtain the dissipated energy we used the model proposed by Anczykowski et al. [4]. In our case ( $\omega \ll \omega_0$ ) we arrive at the following expression for the dissipated energy per cycle:

$$E_{diss} = \frac{P}{4} k_L A_0 A \sin f \quad (2)$$

Figure 3 shows the dissipated energy as a function of separation. It can be seen that it increases sharply with separation and that it is of the order of a few 10 meV. It is an interesting question to speculate about the microscopic origin of this dissipation. Since it rises steeply in the vicinity of the surface it has to be related to tip-surface interactions. The frequency of the lever oscillation is very low (1 kHz) and thus the mechanism responsible for



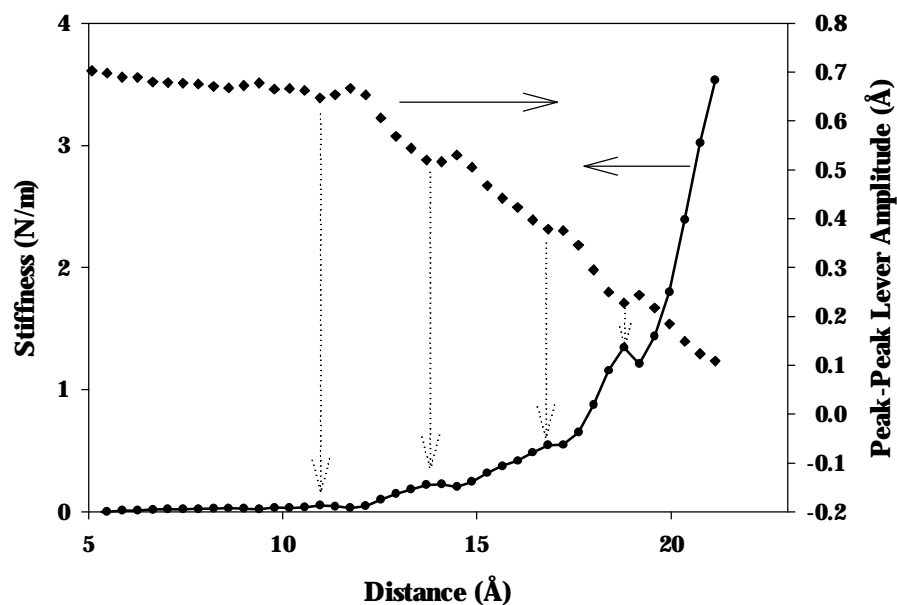
**Figure 3.** Interaction Stiffness (open diamonds) and dissipated energy (circles with connecting line) for a Pt/Ir tip approaching a clean Cu(100) surface. The free amplitude of the lever was 0.3 Å (peak-to-peak).

the dissipation needs to operate at a comparably slow time scale. Further, since we can achieve atomic resolution under these conditions, it needs to be structurally reversible. We should also note that due to the relatively large forces (of the order of a few nN) acting over a very short range ( $\sim 1\text{Å}$ ), the induced strains in the tip-surface interaction region must be

quite high. This leads us to the proposal that the dissipation is due to (geometrically) reversible but energetically irreversible atomic movement in the tip-surface region.

### C. Molecular layering in water

A final example of the utility of our new AFM technique is the measurement of molecular ordering of water close to a flat surface [5,6,7]. Figure 4 shows stiffness variations associated with liquid layering in water, measured directly from the change of oscillation amplitude of the lever. The stiffer regions correspond to tip-surface separations that are (on average) more commensurate with the natural layering of water molecules. As the tip moves slightly closer, the separation becomes increasingly incommensurate with the layering and the stiffness decreases. The stiffness oscillations observed are thus associated with commensurate and incommensurate tip-surface separations. This, to our knowledge, is the first time that these oscillations have been unambiguously and directly measured in an AFM.



**Figure 4.** Peak-to-peak amplitude (diamonds) and stiffness (circles with connecting line) measured during an approach of an atomically flat mica surface immersed in water. Regular spaced oscillations (mean spacing about 2.5 Å) are observed in the amplitude which translate into a stiffness variation. The increase in stiffness is associated with increased ordering of the water molecules into layers close to the mica surface.

## CONCLUSIONS

A powerful new AFM technique is presented, which allows for the direct measurement of force gradients (stiffnesses) in a variety of situations ranging from atomic bonding and atomic scale dissipation to molecular layering in liquids. The technique is based on a linear dynamic measurement using ultra-small amplitudes and off-resonance frequencies to excite the measuring lever. Snap-to-contact is avoided by use of sufficiently stiff levers.

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