CHANGES IN SURFACE STRESS MEASURED WITH AN ATOMIC FORCE MICROSCOPE

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Abstract

The bending of microfabricated silicon nitride cantilevers was used to determine surface stress changes at solid-liquid interfaces. The bending radius of curvature is directly proportional to changes of the differential surface stress. To demonstrate the possibilities and limitations of the technique, cantilevers coated on both sides with gold and densely packed monolayers of different thiols were put in a constant flow of aqueous electrolyte solution, and the bending was measured with an atomic force microscope. Changes in the surface stress for the different thiol monolayers due to specific proton adsorption are presented. Possible applications and improvements of this technique are discussed.

Key Words: Atomic force microscopy, AFM, surface stress, cantilevers, biosensors, surface energy of solids.

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Introduction

For liquids, surface tension is one of the most important parameters which characterize the surface. Several methods are available to measure it accurately and reliably. For solids, however, it is difficult to measure the equivalent quantity, the surface stress σ (Adamson, 1990). Most methods have some drawbacks, e.g., they are technically demanding, they cannot be used to monitor changes of the surface stress, they are semiempirical and depend on further assumptions, or they are not generally applicable.

We and others have recently improved the bending-plate technique to measure changes in the surface stress of solids by using microcantilevers as sensors (Raiteri and Butt, 1995; Thundat et al., 1994, 1995; Chen et al., 1995; Butt, 1996). The princip of the experimental technique is straightforward (Fig. 1). A microcantilever, prepared with different opposite faces, bends as a result of changes of surface stress. If, for instance, the surface stress on one side changes, say it increases, then that side tends to contract. Hence, changes of the surface stress cause the cantilever to bend. The radius of curvature, R, is given by (Stoney, 1909; Hoffman, 1966).

$$\frac{1}{R} = 6\frac{1-\nu}{E t_s^2}(\Delta\sigma_1 - \Delta\sigma_2) \tag{1}$$

E is the elasticity of the basic cantilever material, ν denotes the Poisson ratio, t_s is the thickness of the cantilever. $\Delta\sigma_1$ and $\Delta\sigma_2$ are the surface stress changes of the top and bottom side respectively. The applicability of Equation 1 has been thoroughly discussed in (Preissig, 1989; Müller and Kern, 1994).

Measuring the bending of a thin plate to determine sur-face stress changes was already used by several au-thors (Cahn and Hanneman, 1964, Martinez et al. 1990), e.g., to measure electrocapillary curves of gold and platinum (Fredlein et al., 1971; Fredlein and Bockris, 1974), or to measure adsorbate-induced surface stress changes in vacuum (Sander and Ibach, 1991; Sander et al., 1992). In a variation of the bending plate method, the deformation of a circular plate was measured (Lewis et al., 1993; Haiss and Sass, 1995; Láng and Heusler, 1995).

All these measurements were facilitated by the fact that surface stress changes were relatively high, typically 0.1-1 J/m², and these changes could be induced quickly, usually in few seconds. In contrast, measuring generally surface stresses, especially at solid-liquid interfaces, is more demanding: first, the sensitivity needs to be one order of magnitude higher because changes in surface stress caused by different concentrations of solutes are usually much smaller than 0.1 J/m². Second, changes in surface stress have to be induced by changing the medium around the cantilever. Preferably, this should be done in a flow-through experiment because then surface reactions could be continuously monitored. Changing the medium causes turbulences.

Using microfabricated cantilevers instead of thin, but still macroscopic plates (typically 0.1 mm thick and 1-10 cm long) (Fredlein *et al.*, 1971; Fredlein and Bockris, 1974; Martinez *et al.*, 1990; Sander and Ibach, 1991; Sander *et al.*, 1992), enabled us to monitor changes in surface stress induced by changing the pH or the concentrations of various substances. Microfabricated cantilevers, which are 100-400 mm long and 0.3-0.6 mm thick, are ideally suited because they fulfill two requirements: first, for a given change in surface stresses $\Delta\sigma_1$ and $\Delta\sigma_2$, of the two opposite surfaces 1 and 2, the deflection of the cantilever, z, is proportional to $(L/t)(\Delta\sigma_1 - \Delta\sigma_2)$ {see Eqs. 1 and 4 (below)} where L is the length of the cantilever. Hence, the sensitivity of the measurement increases with the ratio of cantilever length to thickness. To achieve a high sensitivity cantilevers should be long and thin. Second, resonance frequency,

$$\nu = 0.163 \frac{t}{L^2} \sqrt{\frac{E}{\rho}}$$

should be as high as possible to prevent external vibrations from interfering with the measurement (Rugar and Hansma, 1990). ρ is the density of the cantilever material. High sensitivity, and at the same time, low noise can be achieved by using small cantilevers. Small cantilevers also have the advantage of being relatively insensitive to turbulences in a flow-through experiment.

Thundat *et al.* (Thundat *et al.*, 1994, 1995; Chen *et al.*, 1995) already used microcantilevers and a sensitive deflection detection to measure changes in the resonance frequency of cantilevers upon adsorption of chemicals in the gas phase. They also observed a bending due to hydration or dehydration of the cantilever at different humidities.

As a consequence of the mentioned improvements, not only electrocapillary curves (Raiteri and Butt, 1995; Brunt *et al.*, 1996), but generally changes in surface stress could be measured in flow-through experiments. The feasibility of the technique was demonstrated by measuring changes of the surface stress of silicon nitride upon varying the pH (Butt,

1996). Also, the unspecific binding of protein in aqueous electrolyte was monitored by observing changes in the surface stress.

A possible application of the technique is to use micro-cantilevers as sensors for specific substances. One possible way of achieving this is to coat one side of the cantilever with a receptor while keeping the other side relatively inert. A first step in this direction is described in this paper. One side of the cantilever was coated with carboxylic groups. We could detect the proton adsorption to these carboxylic groups in aqueous electrolyte solution.

Materials and Methods

Commercially available silicon nitride cantilevers (Nano-probes, Digital Instruments, Santa Barbara, CA) were used. They are V-shaped to minimize lateral de-flec-tion. They were L = 190 μm long, and each arm was 40 μm wide and 0.6 μm thick. We approximated their elastic behavior with to parallel beams (Albrecht *et al.*, 1990; Butt *et al.*, 1992; Sader and White, 1993; Sader, 1995). The calculated spring constant is 0.09 N/m. The commercial cantilevers are coated on one side with a 20-30 nm layer of gold in order to enhance their reflectivity.

Cantilevers were treated in the following way: first they were immersed overnight in 1 mM octadecanethiol ethanolic solution. The octadecanethiol formed a stable, dense, and highly structured monolayer on the gold originally present on the upper surface (Dubois and Nuzzo, 1992; Xie and Li, 1995). After eliminating all excess of alkane-thiols by rinsing with ethanol, 3-5 nm of chromium and 30-40 nm of gold were evaporated onto the other side. The temperature during evaporation did not rise above 100°C. 100°C is a temperature thiol mono-layers can stand. It is known that above that temperature they start to desorb (Schönherr *et al.*, 1996). Then we immersed the freshly coated cantilever into a 1 mM ethanolic solution of thiols with a different side group. In particular, we used 3 mercaptopropionic acid ($HS(CH_2)_3COOH$), 2 amminoethanthiol ($HS(CH_2)_2NH_2$) and 2 mercaptoethanol ($HS(CH_2)_3OH$); all were from Fluka Chemie AG (Buch, Switzerland), purissium. The new thiol solution could not remove the previously bound octadecanethiol since the thiol-gold bond is relatively strong (binding energy 120 kJ/mol). Before use, each cantilever was thoroughly rinsed in ethanol and water. We assumed that the deposited layers did not change the elastic properties of the cantilevers.
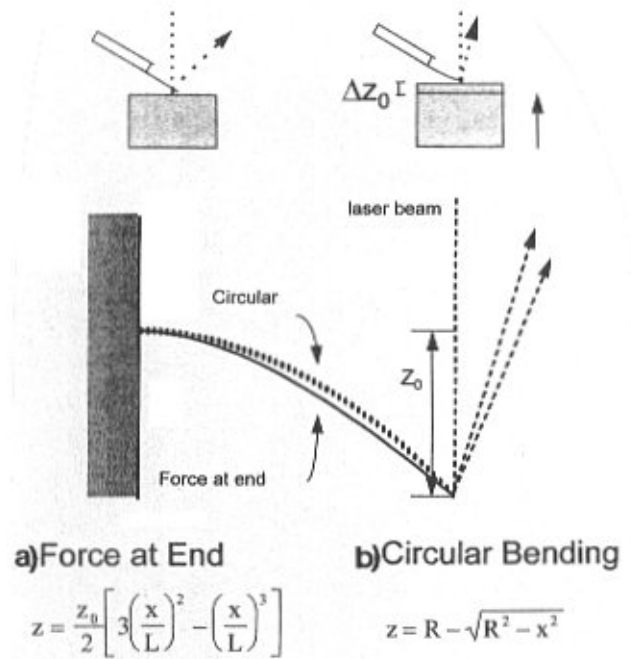
Deflection detection and calibration

The radius of curvature of the cantilever was measured with the detection system of the head of a commercially available atomic force microscope (AFM) (Nanoscope II, Digital Instruments, Santa Barbara, CA). Light from a laser diode was focused onto the end of the cantilever. The reflected laser spot hit a two-segment photodiode, and the difference in intensity measured by the two segments was used as the
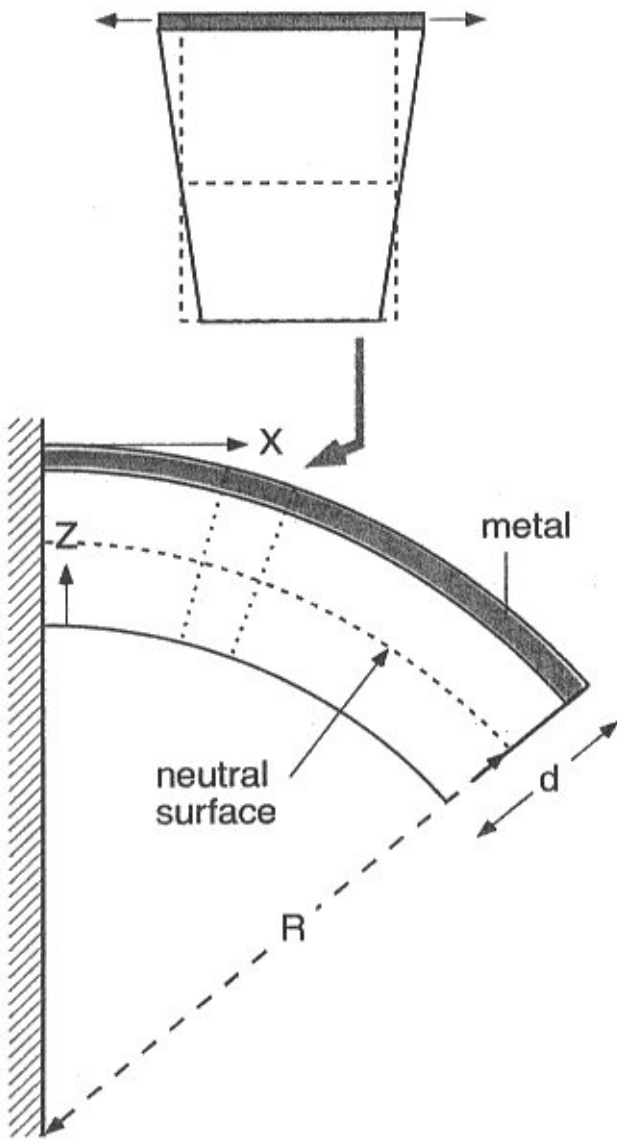
Figure 1. Schematic side view of a silicon nitride can-ti-lever of thickness t_s, with a t_f thick layer on one side. Top: an increase/decrease of the surface stress on the coated side causes the area of that side to contract/expand around a neutral plane. For uniform surface stress and isotropic material, the resulting bending over the whole length is circular with a constant radius of curvature R.

a)**Force at End**

$$z = \frac{z_0}{2}\left[3\left(\frac{x}{L}\right)^2 - \left(\frac{x}{L}\right)^3 \right]$$

b)**Circular Bending**

$$z = R - \sqrt{R^2 - x^2}$$

Figure 2. (**a**) Standard cantilever deflection calibration procedure to relate cantilever deflection to changes in the photodiode signal. Sample is displaced a known distance z_0, and the corresponding change in reflected spot (dotted line) is recorded. (**b**) Comparison between different bending shapes of a thin beam clamped on one side (zero deflection and zero slope) for a given deflection z_0 at its free end. Dotted line is circular, while continuous line is originated by a load applied at the free end. Equations describing the shape for the two cases are given. The two shapes give rise to two different reflected spots and, eventually, photodiode signals.

deflection signal. This signal is not a measure of the cantilever displacement z. Rather, it is proportional to the slope of its free end. For a circular bending, the slope at distance L is related to the radius of curvature R, by:

$$\frac{dz(x)}{dx}\Big/_{x=L} = \frac{L}{\sqrt{R^2 - L^2}} \tag{2}$$

The usual way to calibrate the deflection, typically before each measurement, is to push the cantilever a known distance z_0 against a hard surface and to measure the corresponding change in the photodiode signal. In this case the bending (Fig. 2) is not circular, and the measured signal is related to the displacement z_0 by:

$$\frac{dz(x)}{dx}\Big/_{x=L} = \frac{3}{2L}z_0 \tag{3}$$

Equation 3 is strictly valid only in the case of a rectangular

beam. Detailed calculations showed that the V-shaped cantilevers deviate at most 15% from the predicted behavior (Sader, 1995).

Equations 2 and 3 imply that different cantilever displacements correspond to the same measured signal. Therefore, to obtain the radius of curvature R as a function of the calibrated cantilever displacement, z_{cal}, one has to equate Equations 2 and 3. This leads to:

$$\frac{1}{R} = \frac{3 z_{cal}}{L \sqrt{4L^2 + 9 z_{cal}^2}} \tag{4}$$

Equation 4, together with Equation 1, allowed us to calculate the differential surface stress from the calibrated deflection signal z_{cal}.

To continuously monitor stress changes induced by changes in the medium we used a fluid-flow set-up (Fig. 3). A commercial AFM head and a sealed fluid cell were used. The top part of the cell was the standard commercial fluid cell, while the bottom plastic part and the flexible silicon sealing were homemade. The need for a homemade fluid cell arose for several reasons: reliable sealing is needed since even small leakages over long periods can seriously damage the AFM head electronics and piezo scanners, moreover, the cantilever needed to be far away from the bottom surface to avoid any interactions with it and to limit flow turbulences. Liquid flowed into the cell through an inlet via silicon and Teflon tubing from a reservoir flask. The liquid flow was driven by gravity and was kept constant during the whole measurement. Typical flow rates were 0.5-0.8 ml/min. Since the volume of the cell is » 0.3 ml, the liquid in the cell was exchanged twice in about 1 minute.

An experiment consisted in starting the flow with a neu-tral solution and letting the system stabilize for at least half an hour. We continuously monitored the pH value in the external reservoir and the deflection signal from the photodiode. Without stopping the flow, we then added into the external reservoir small quantities of a strong acid or base in order to vary the pH. After approximately 30 seconds, the new solution entered the cell, and the cantilever started to deflect, reaching a new steady state in 2-3 minutes.

The flow induced a static bending of the cantilever which is function of the flow rate. Therefore great care was taken to maintain a constant flow rate both by maintaining a constant pressure in the input Teflon tube and by preventing drop formation at the output.

Drift in cantilever deflection was reduced when cantilevers were allowed to equilibrate in solution used for the measurement for few days before doing the actual experiment. However, there was usually a residual drift which could not be eliminated and limited the minimum speed at which changes in surface stress could be monitored.

The pH of the solution and cantilever deflection were recorded via an A/D (analog/digital) board connected to a personal computer. Force curves (Burnham *et al.*, 1993; Butt *et al.*, 1995) were recorded before and after each experiment against the hard bottom of the cell. From the slope of the constant compliance region, we could relate measured deflection with cantilever displacement.

Results and Discussion

The results presented in this paper were obtained by coat-ing both sides of a cantilever first with gold and then putting different thiol monolayers onto the gold. In this way, each side presents two interfaces: gold/thiol and thiol/liquid. We expect that the liquid, and especially the ions, cannot reach the gold/thiol interface. Therefore we attribute the whole effect to the thiol/liquid interface (i.e., the "thiol surface").
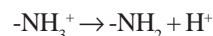
Surface stress changes measured with a cantilever coated on one side with octadecanethiols and on the other side with 3 mercaptopropionic acid (sketched in Fig. 4) are shown in Figure 5. When referring to the carboxylic side the surface stress showed a minimum around pH 4-5. When the pH was increased to above pH 5 or decreased to below pH 4, the cantilever bent toward the mercaptopropionic acid side, that is, its surface stress increased.

For the interpretation, the proton dissociation of the carboxyl group

$$-COOH \rightarrow -COO + H^+$$
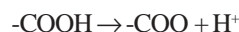
is probably important. For propionic acid, the dissociation has a pK between 4 and 5. Binding of a proton to a carboxylate group lowers the free enthalpy of that group by $\Delta G = kT\log(K)$, where K is the binding constant ($K = 10^{-pK}$), T is temperature in Kelvins, and k is Boltzman's constant. This could explain the increase in surface stress with increasing pH, as shown in Figure 5. Protons dissociate and leave high energy carboxylate groups behind. The fact that the increase in surface stress looks "smeared" (i.e., without an abrupt change) and shifted to higher pH values than would be indicated by this dissociation mechanism can be explained in terms of local mutual interactions among the densely packed carboxyl groups on the surface. This mechanism, however, cannot explain the small but significant increase of surface stress when reducing the pH below 4. We have yet no interpretation for this observation.

In experiments with 2 aminoethanthiol and 2 mercaptoethanol instead of the mercaptopropionic acid, only the increase of surface stress with increasing pH was observed. The side groups of these molecules can dissociate according to

$$-NH_3^+ \rightarrow -NH_2 + H^+$$
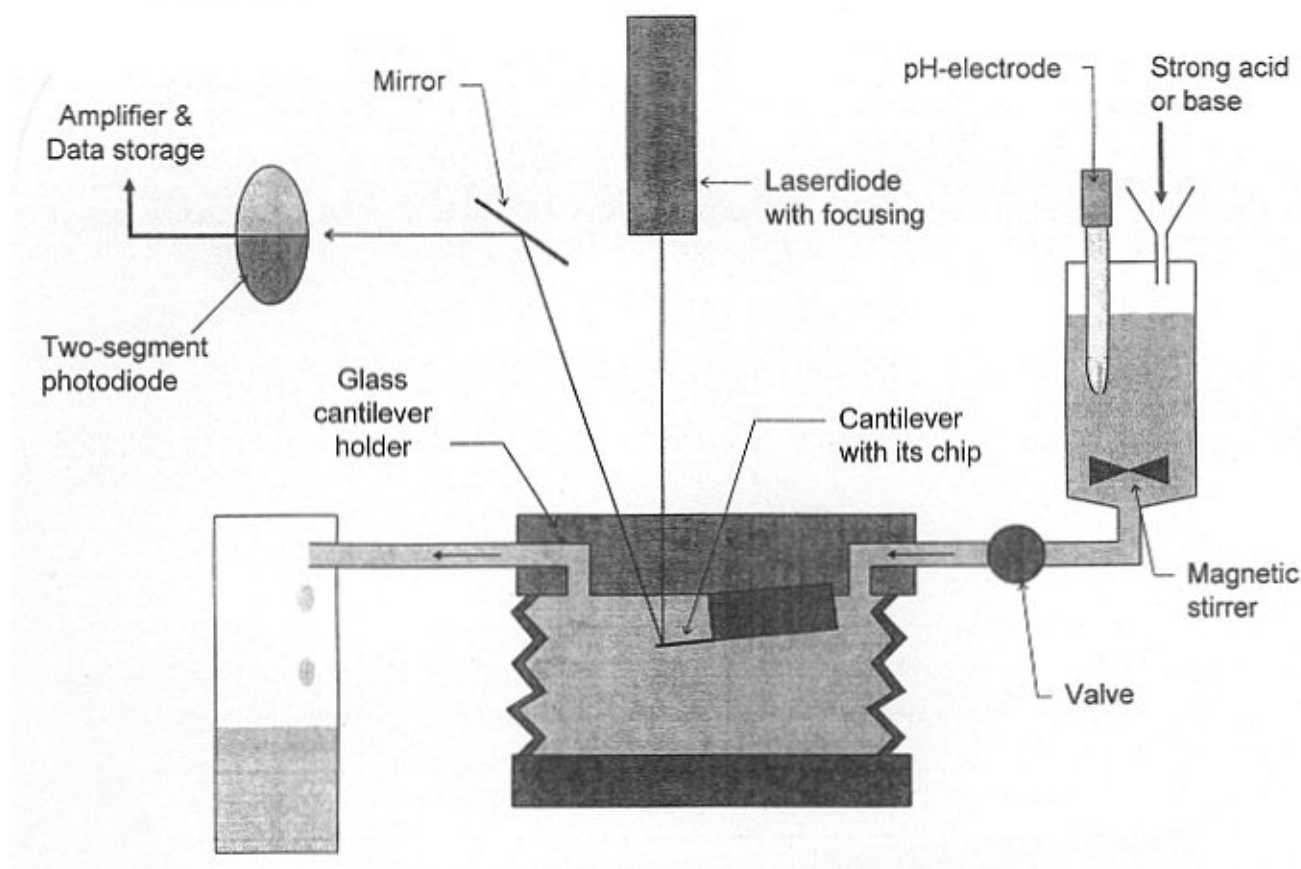
Figure 3. Schematic of the experimental set-up. We used a commercial AFM head with its optical lever detection system. The cell was sealed with a homemade flexible silicon ring. Solutions flowed into the cell from an external reservoir and from the cell to a waste. Gravity drove the flow. By putting the external reservoir more than one meter higher than the cell and clamping the input tubing, we could obtain a rather constant flow rate. The pH was adjusted by adding the corresponding acid or base of the salt used while continuously stirring. The pH was also monitored with a glass electrode, used as an external pH-meter.

$$-OH \rightarrow -O + H^+$$
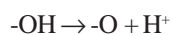
with pK values of 10 and > 10, respectively. Results of these experiments are presented in Figure 6. With both substances, small changes in surface stress were observed compared with surface stress changes observed with mercaptopropionic acid. This is reasonable since the degree of dissociation should be relatively small. However, we did not detect any steep increase in surface stress in the case of 2 aminoethanthiol, not even for pH 11-12, where proton dissociation should already have taken place. A possible explanation is the interaction between the amino or hydroxyl groups. The thiols typically occupy an

area of 20-25 Å², which corresponds to a distance between the functional groups of 4-5 Å. At such small distances, the groups influence each other and the effective pK is smeared out.

For a test, both sides of the cantilever were coated with the same thiol monolayer. No deflection was observed varying the pH of the electrolyte solution. We therefore assumed that the measured deflections were to ascribe to changes in surface stress only.

The method proposed measures changes in surface stress, $\Delta\sigma$. Sometimes it is useful to speak in terms of surface free energy, γ. They are related through the Suttleworth equation (Suttleworth, 1950; Couchman *et al.*, 1972, 1975, Láng
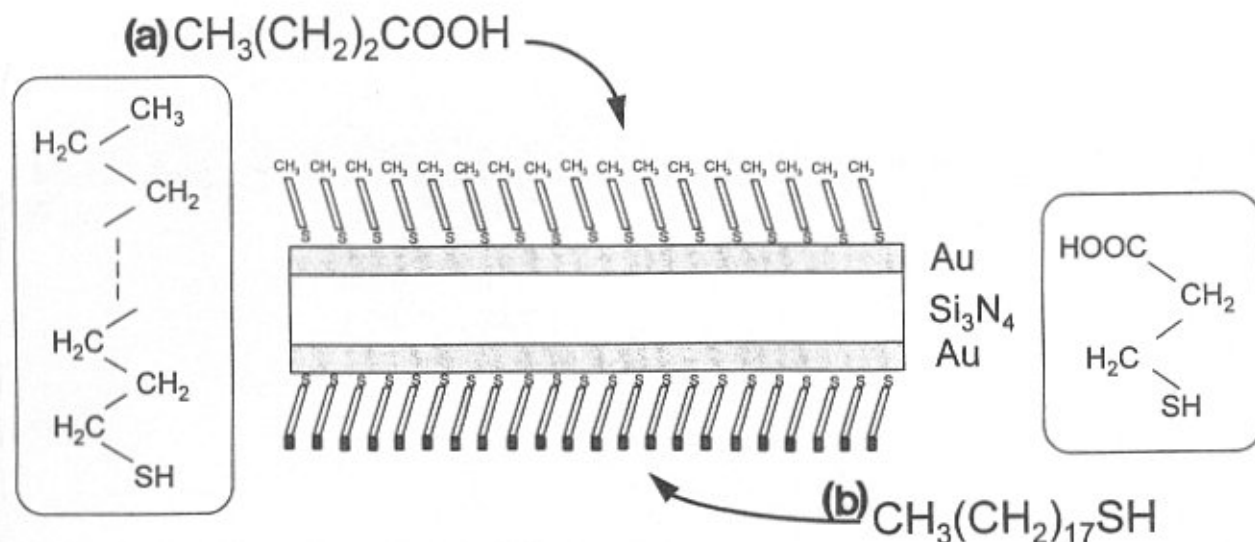
Figure 4. Schematic of a cantilever used in the exper-i-ments (side view). The upper part was coated with a thin (30 nm) film of gold and a monolayer of octadecanethiols, $CH_3(CH_2)_{17}SH$, whose structure is depicted in inset a). The lower side was also coated with gold, and a monolayer of 3 mercaptopropionic acid, $CH_3(CH_2)_2COOH$, whose structure is depicted in inset (**b**). Thiols covalently bind to gold forming self-assembled densely packed monolayers. Carboxyl groups, facing the solution at the bottom side, can loose a proton charging themselves and increasing the surface energy. On the other side, hydrocarbons are relatively inert to pH variations.

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and Heusler, 1994)

$$\sigma = \gamma + \frac{d\gamma}{d\varepsilon} \qquad (5)$$

The surface strain, ε, is defined as $d\varepsilon = dA/A$, where A is the surface area. First, one can note that both surface stress and surface energy have the same units of N/m (or J/m²). For liquids, the second term of Equation 5 is zero, and therefore surface stress and surface free energy correspond. For solids, the second term takes into account the fact that when the surface is elastically strained the interatomic distance is changed from the value which would minimize γ, and it therefore requires more energy to form a unit area of the strained surface than of the unstrained one. In analogy with Moliner and Beck (1979), we estimated the value of $d\gamma/d\varepsilon$ for a crystalline gold structure, and we found that, for a given $\Delta\gamma$, the corresponding value of $d(\Delta\gamma)/d\varepsilon$ is less than 1%. We are confident that also in the case of other surfaces, such as thiol monolayers, the second term of Equation 5 is much smaller than the first one, and therefore the measured values can be considered very close to surface free energy changes. Such values represent an integral quantity over the whole cantilever surface. From knowledge of the density of the thiols in the layer and the area of the surface, it would be possible to estimate the free energy change for a single molecular interaction.

Conclusion

The use of microfabricated cantilevers allowed several improvements compared to the previous bending-plate techniques using macroscopic plates: measurements can now be done in a relatively simple and reliable (commercial) set-up; the method is generally applicable to thin deposited films; it is now possible to monitor *in situ* processes changing the surface stress; and the sensitivity achievable is much higher due to the low noise sensitivity. Commercially available cantilevers are made of silicon nitride, silicon, and polymers with dimensions ranging from 50 to 400 nm, and resonant frequencies ranging, in air, from 10 to 300 kHz. The principle of the method implies the preparation of different opposite surfaces. This can be achieved in several ways, like evaporating, sputtering, or spraying a thin layer of material on one side. Thiols, available with different possible rest groups, are well suited to form highly ordered monolayers with different properties {for a review, see Dubois and Nuzzo (1992) and Xie and Li (1995)}. They bind covalently onto gold and show a high stability under AFM scanning (Dürig *et al.*, 1993; Thomas
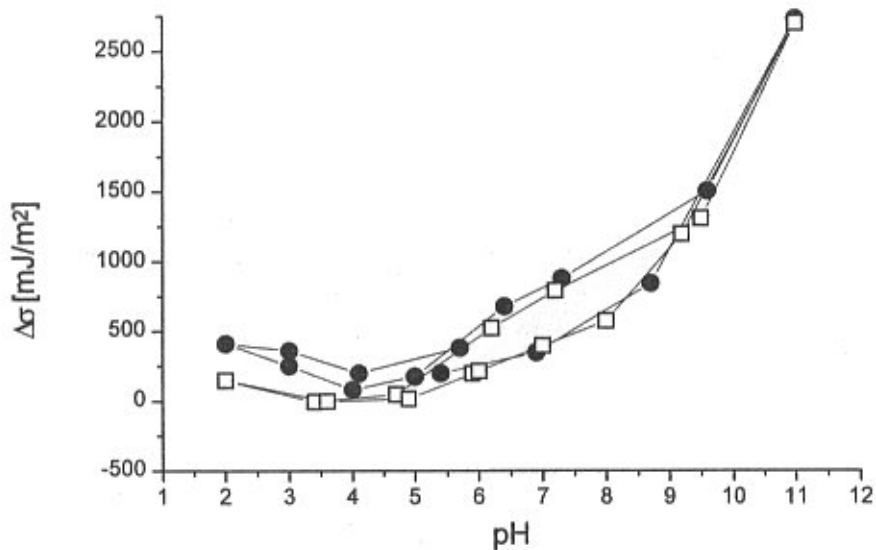
Figure 5. Relative surface stress values for a cantilever coated as in Figure 4, as a function of pH in a 0.1 M KNO$_3$ solution. pH was varied while continuously flow-ing, by adding 0.1 M KOH or 0.1 M HNO$_3$. Dots and squares represent results from two different experiments with two different coated cantilevers. We always let the system stabilize at least for five minutes after a pH change before considering the reported deflection/ surface stress value. Positive values correspond to deflections toward the 3 mercaptopropionic acid monolayer. Higher stress values correspond to higher surface energy.
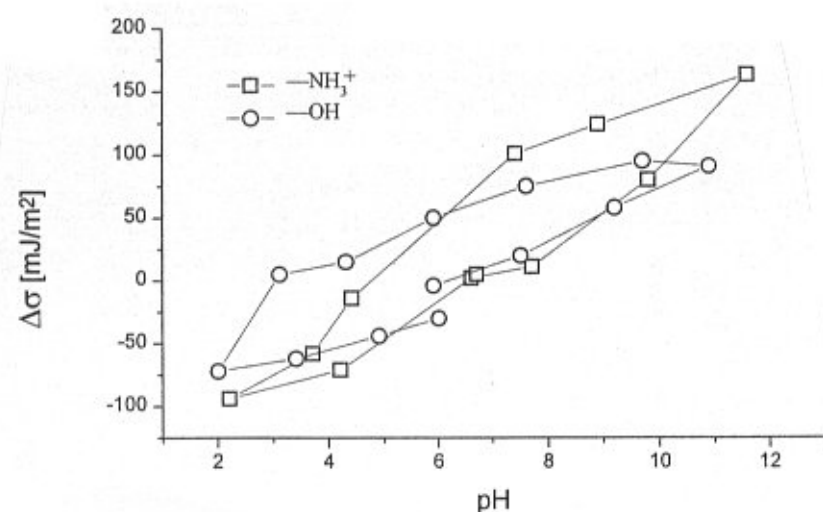
Figure 6. Relative surface stress as a function of pH for cysteamine (squares) and 2 mercaptoethanol (circles) in 0.1 M KNO$_3$. pH was adjusted by adding 0.1 M KOH and 0.1 M HNO$_3$. Cantilevers where prepared as in the experiments with 3 mercaptopropionic acid, coating first one side with octadecanethiols and then the other side with the thiol under study (see Fig. 4).

et al., 1993; Liu and Salmeron, 1994) and to potentials applied to the gold substrate in electrochemical cells (Li and Weaver, 1984, Porter *et al.*, 1987; Miller and Grätzel, 1991; Sondag-Huethorst and Fokkink, 1992).

The possibilities offered by this technique directly involve AFM operation. Changes in the static cantilever deflection are a fundamental matter to take into account in the interpretation of force-distance curves in AFM operation. Moreover, surface stress measurements can help in the characterization of the cantilever material (e.g., estimation of the surface charge both of metal coated or silicon nitride cantilevers).

A number of different applications not directly related to AFM can be foreseen:
• chemical sensors to monitor the concentration of substances in a solution or gas around the cantilever
• sensors to measure specific binding of ligands to cantilevers which are coated on one side with a receptor
• sensors to monitor chemical surface reactions occurring on one side of the cantilever. Gimzewski *et al.* (1994) measured the bending due to the bimetallic effect of the cantilever caused by the heat generated from a chemical reaction; Oden *et al.* (1998) monitored the electro-chemical deposition of Pb onto gold coated cantilevers.

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Editor's Note: All of the reviewer's concerns were appropriately addressed by text changes, hence there is no **Discussion with Reviewers**.