Effect of humidity on the surface adhesion force of inorganic crystals by the force spectrum method

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Abstract Effect of relative humidity on the surface adhesion force of several inorganic crystals of mica, CaF_2 and KCl was studied by atomic force microscopy (AFM). The results showed that the magnitude of surface adhesion force is mainly dependent on the surface free energy of the adsorbed liquid film, but almost independent of the thickness of the film. Furthermore, the deliquescence on the crystal surface was investigated, which demonstrated the capability of the force spectrum method to monitor changes in ionic concentrations of adsorbed liquid film in real-time.

Keywords: mica, CaF₂, KCl, adhesion force, relative humidity, AFM.

Since its invention in 1986^[1], AFM has become a powerful tool for investigation of surface on atomic scale. The morphology of a sample surface is obtained based on the interaction between the tip and sample. When the tip approaches or separates from the sample, the interaction between them can be detected by the deflection of the cantilever and thus comes out the force-distance curve or force spectrum. The force needed to separate the tip completely from the sample surface is called adhesion force. Using the force spectrum method to measure the adhesion force between the chemically or biologically modified tip or/and sample, we can get the relevant chemical or biological information. So far, much work has been done in this area^[2-7]. For example, Florin et al.^[2] have measured the adhesion force between individual ligand-receptor pairs such as avidin-biotin and iminobiotin-biotin, and Lee et al.^[3] have made a direct measurement of the forces between complementary strands of DNA. Using chemically modified tips, Werts et al.^[4] determined the local surface reaction conversion during a chemical surface modification.

One of the advantages of AFM is that it can be used in ambient conditions, and in ambient air, a thin film of water exists on most surfaces^[8]. For instance, using a scanning polarization force microscopy, Hu et al.^[9] directly observed the process of condensation and evaporation of water on mica at room temperature. They^[10] also studied the structure formed on the (100) cleavage surface of NaCl exposed to water vapor. Using ellisometry, Beaglehole et al.^[11] have determined the thickness of the adsorbed water film on mica as a function of the relative vapor pressure of water. When neither the tip nor the sample is modified, the adhesion force between the tip and the sample is a sum of all the attractive forces acting on the cantilever, including van der Waals attraction, electrostatic interactions and capillary force. In most cases, the van der Waals force and electrostatic interactions are very small and can be neglected without introducing serious errors. Therefore, the capillary force resulting from the condensation of water which forms a liquid bridge between the tip and sample is the dominating factor of the adhesion force, and this can be proved by the fact that the adhesion force in liquid can be drastically decreased. In 1989, Weisenhorn et al.^[12] found that the adhesion force between the tip and mica could decrease from about 100 imes 10^{-9} N in air to 1×10^{-9} N in water.

It is long supposed that under ambient conditions, the adhesion force between the tip and a sample is affected by temperature, the thickness, the surface free energy of the adsorbed water film, etc. To make this problem clear is of essential importance to the quantification of the force spectrum method. Yet up to now, disparity has been shown in different experiments. According to Thundat et al.^[13], when the relative humidity increased from 15% to 80%, the adhesion force between Si₃N₄ tip and mica increased from 4.5×10^{-9} N to about 10×10^{-9} N. In a more recent article of Eastman et al.^[14], it is reported that the adhesion forces between unmodified, hydrophilically and hydrophobically modified Si₃N₄ tips and mica were measured at different humidities. However, their results showed that for one tip, the magnitude of the adhesion force did not change with humidity, but the force increased as the hydrophilicity of the tip increased.

As stated above, to make certain what factors influence the adhesion force between the tip and sample is of significant help to investigations of other systems by the force spectrum method. In order to confirm if the thickness of adsorbed film and ions in the film affect the adhesion force, we selected three inorganic crystals mica, CaF_2 and KCl as our targets whose adsorbed water films have different qualities, and measured their adhesion forces as humidity changed.

1 Instruments and methods

The atomic force microscopy we used is commercially produced by Molecular Imaging Corporation, USA. It has a chamber which can be sealed and thereby makes it possible for us to monitor the environmental conditions (i.e. relative humidity and temperature). Relative humidity between 20% and 80% was controlled by mixing streams of dry nitrogen and wet nitrogen (prepared by bubbling nitrogen gas through distilled water) at an appropriate flow ratio and the relative humidity above 80% could be obtained by putting distilled water in the chamber. The humidity was monitored by a digital humidity-sensitive sensor (produt of the Beijing Kunlun Hai'an Center). The adhesion force at every humidity ($\pm 1\%$) is a statistical average of numerous measurements. Experiments were conducted at 25°C.

2 Results and discussion

From many repetitive experiments on mica, we obtained similar results as follows: as the relative humidity increased, the surface adhesion force on mica did not change; when we lowered the humidity, we could get almost completely reversible results. A representative group of data is shown in fig. 1 for specific illustration.



Fig. 1. Adhesion forces between AFM tip and mica surface under various relative humidities.

Beaglehole et al.^[11] have ellipsometrically determined the thickness of adsorbed water film on mica as a function of the relative vapor pressure of water at 18°C. Their results showed that the thickness of the water film on mica increased steadily from the relative humidity of 20%; especially after the humidity reached 80%, the thickness of water film increased more sharply and at 95%, the film was thicker than 1×10^{-9} m. The saturated vapor pressure of water at our experiment temperature 25°C is 1.5×10^3 Pa higher than that at $18^{\circ} C^{[15]}$, so at every relative humidity at 25°C, the thickness of the water film should be thicker than its counterpart at 18°C^[11]. However, as shown in fig. 1, the adhesion force did not change even when the humidity increased from 80% to 95%. Therefore, we conclude that the adhesion force is almost unaffected by the thickness of the water film and thus must be mainly dependent on the surface free energy of the film. This can be further proved by the following results from CaF₂ and KCl.

Figs. 2 and 3 respectively show the surface adhesion force on CaF_2 and KCl as a function of relative humidity. From fig. 2 we can see that just like mica, the adhesion force on CaF_2 remained almost constant as the relative humidity increased; while fig. 3 shows that the adhesion force on KCl changes with humidity. When the humidity increased from 20% to 60%, the adhesion force increased slightly, and above the humidity of 60%, the adhesion



Fig. 2. Adhesion forces between AFM tip and \mbox{CaF}_2 surface under various relative humidities.



Fig. 3. Adhesion forces between AFM tip and KCl surface under various relative humidities.

force increased dramatically with small increase in humidity. The different performances of CaF₂ and KCl are again due to the difference in the surface free energy of the adsorbed water film. CaF₂ hardly dissolves in water (at 18°C, the solubility in 100 g water is only 1.50 mg, and at 40 °C, 1.67 mg^[16]), and when the adsorbed water film grew thicker with the increasing humidity, almost no ions dissolved in the film. As the result, the surface free energy did not change with humidity and so did the adhesion force. Contrarily, KCl dissolves in water very easily (at 25 °C, the solubility in 100 g water is 35.98 $g^{[16]}$) and in air it deliquescences readily. Using the infrared spectroscopic photometry, Peters et al.^[17] provided the adsorption isotherm of water on the surface of NaCl(100). They found that at the humidity of 50%, there were ions dissolved in the adsorbed water film. Since KCl and NaCl are very similar in their solubility (at 25°C, the solubility of NaCl is $36.08 g^{[16]}$), we can infer the similar result for KCl. When the water film became thicker with humidity, more and more K^+ and Cl^- would dissolve in the film. Once there are ions in water, the ions will attract water molecules to the inner part of the solution and the extra energy to overcome the electrostatic interaction will increase the surface free energy, which in turn will lead to the increase in the adhesion force. Fig. 3 shows that when humidity was below 60%, since the amount of ions in the film is very small, the surface free energy increased very

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slightly and so did the adhesion force. After the humidity was raised to above 60%, ions dissolved in the film made the surface free energy increase much and hence the adhesion force increased dramatically.

The different effects of humidity on the adhesion force on CaF_2 and KCl showed again that in AFM, when the liquid film is continuous, the adhesion force between the tip and sample is mainly dependent on the surface free energy of the film, but almost independent of the thickness of the film.

The magnitude of the measured adhesion force may differ from one tip to another. This may be caused by two factors. (i) Different tips have different radii; and from the equation $F_{cap} = 4\pi R \gamma \cos\theta^{[19]}$ (F_{cap} , capillary force; R, radius of contact area; γ , surface tension or surface free energy of the liquid; θ , contact angle of the liquid-solid interface), we can know that this will make the capillary force between the tip and sample different and thus produces different adhesion forces. (ii) Different properties of tips such as contaminants adsorbed on the tip and the real value of the elastic constant can also result in different adhesion forces. Therefore, definite calibration of the properties of the tip is very important to the quantification of the force spectrum method.

3 Conclusion

In summary, by the force spectrum method, the surface adhesion force of mica, CaF_2 and KCl were measured as the relative humidity changed. It is concluded that when the adsorbed liquid film is continuous, the adhesion force between the tip and sample is mainly dependent on the surface free energy of the adsorbed liquid but almost unaffected by its thickness.

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