

Improved atomic force microscopy resolution using an electric double layer

I. Yu. Sokolov^{a)}

Department of Physics, Department of Geology, University of Toronto, Toronto, Ontario M5S 1A7, Canada

G. S. Henderson

Department of Geology, University of Toronto, Toronto, Ontario, M5S 3B1, Canada

F. J. Wicks

Department of Mineralogy, Royal Ontario Museum, Toronto, Ontario, M5S 2C6, Canada

G. A. Ozin

MCR Group, Department of Chemistry, University of Toronto, Toronto, Ontario, M5S 3H6, Canada

(Received 20 September 1996; accepted for publication 20 December 1996)

High resolution (“atomic”) images of clinocllore and muscovite have been obtained in aqueous solution by inducing an electric double layer between the atomic force microscope tip and the sample surface. The electric double layer is created by the addition of a surfactant to water and greatly improves image resolution. A theoretical model is proposed to explain the improved resolution. © 1997 American Institute of Physics. [S0003-6951(97)04007-2]

The electric double layer (EDL) is a well-known phenomenon, and occurs commonly on surfaces at the interface between the solid and liquid phases. Each EDL consists of a layer of charged molecules on one side, and a layer of molecules with opposite charge on the other side. The development of an EDL on a surface has been used in studies of soft self-organized micellar thin films by atomic force microscope (AFM) (cf. Refs. 1–3). The micellar film of interest is created in a surfactant solution and develops the EDL on both the film and AFM tip. It results in an additional force of repulsion between the tip and the film. The EDL mimics the underlying film topography and scanning along the boundary of the EDL provides an indirect image of the film itself. This mode of scanning is called “pre-contact” because the AFM tip does not touch the rigid substrate.^{1,2} However, if one increases the scanning force, the repulsion due to the induced EDL is overcome and the tip jumps through the film.

Here we show that the use of a low concentration surfactant solution is very helpful for improving “atomic” resolution by eliminating the attractive van der Waals forces between the tip and the sample. The reduction of van der Waals forces to improve AFM resolution has been achieved previously by choosing appropriate media between the tip and the sample,^{4,5} and via active force compensation techniques.⁶ However, using the EDL to compensate for the attractive van der Waals force has not been proposed until now. This method is experimentally simpler than the one suggested in Ref. 6 and should give better results than in Refs. 4 and 5.

Muscovite and clinocllore, used in an earlier study,⁷ were mounted on magnetized stainless steel AFM substrates by means of either double-sticky tape or epoxy. Both the clinocllore and muscovite surfaces were cleaned by removing the upper cleavage layers with scotch tape.

The surfactant used was a water solution of C₁₆TACl (manufactured by Alridge, Inc.) at a concentration between 0.5 and 3 mM. After addition of surfactant solution, the fluid

cell was left standing for at least 2–3 min or more, prior to engaging the tip. Images without the surfactant were obtained after washing the tip and cell in distilled water for 10 min, then drying. The substrate and the fluid cell were reassembled and distilled water added instead of surfactant solution.

All the images were obtained using a Digital Instruments NanoScope III operating in contact deflection mode. The $A+B$ signal of the feedback was about 3 V while the $A-B$ signal was set at around -0.5 V and setpoint of 0 V (or less). Standard silicon nitride integrated pyramidal tips fixed on 200 μm cantilevers (spring constant $k \sim 0.06$ N/m) were used throughout the study. The radius of curvature of the tips was estimated at ~ 50 – 100 nm by scanning a cleavage step on a muscovite surface or strands of DNA. The D scan head (maximum scan area is $12.5 \times 12.5 \mu\text{m}^2$, z sensitivity is 9 nm/V) and A scan head ($1.0 \times 1.0 \mu\text{m}^2$, z sensitivity is 1 nm/V) were employed throughout the study.

In Fig. 1(a), a $4 \times 4 \text{ nm}^2$ unfiltered (as recorded) image of clinocllore is shown that was obtained in water [Fig. 1(a)] and in surfactant solution [Fig. 1(b)] using the same tip. Figure 2 shows the results of the same kind of experiment on a $4 \times 4 \text{ nm}^2$ area of muscovite. All images were collected in deflection mode and are the best images we were able to obtain. It is obvious that scanning in surfactant solution greatly improves the resolution. In Figs. 1(c) and 1(d) the scan force (tip deflection) is plotted versus the vertical position of the tip above the clinocllore surface in water and the surfactant solution, respectively. When scanning in water, an attractive force is observed [Fig. 1(c)]. However, when the surfactant solution is added the attractive force is clearly compensated [Fig. 1(c) does not show any deflection of the cantilever towards the sample]. The force of scanning (load force) in water that gave the best result did not exceed ~ 1 nN while the load force in the surfactant solution was at least a factor of 10 less than in water. Image resolution is consequently improved substantially due to the presence of the surfactant. Similar results were obtained for muscovite (Fig. 2).

^{a)}Electronic mail: sokolov@medb.physics.utoronto.ca

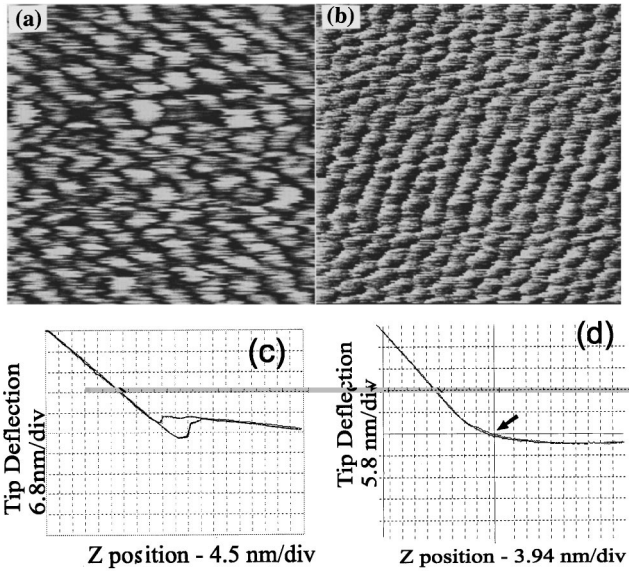


FIG. 1. Some $4 \times 4 \text{ nm}^2$ unfiltered clinoclchlore images (as recorded) collected in (a) water and (b) 0.5 mM surfactant solution. Force curves are shown during scanning in (c) water and (d) surfactant. The arrow indicates the region in which the electrical double layer force modifies the force curve in comparison with scanning in water. The observed interatomic distances indicate that the surface being images is the brucitelike layer of the 1:1 layer structure (cf. Ref. 7).

The improved image quality in the presence of an aqueous solution of surfactant can be explained by the presence of an EDL. A schematic picture of an EDL in the AFM-tip-sample configuration is presented in Fig. 3. As can be seen in the force curves of Figs. 1 and 2, the cantilever does not deflect towards the sample when scanning in the surfactant solution. This implies that the total force between the AFM tip and sample when scanning in surfactant is repulsive in nature, and the *long-range* attractive force (e.g., van der Waals) is being compensated by the *long-range* electrical double layer force. Moreover, this compensation takes place *before* the tip-sample contact [contact is the beginning of the straight line of the force curve, Figs. 1(c) and 2(c)]. Without an EDL, such a compensation takes place by means of a highly *short-range* repulsive force (Fermi force of interatomic overlapping) (e.g., Refs. 8 and 12), which leads to the development of high pressures at the surface and the possible breakage of the sharp apex of the tip, consequently preventing true atomic resolution from being achieved.

In considering this mechanism in more detail, the interaction potential between two atoms can be described by a Lennard-Jones potential

$$v(r) = \epsilon \left[\left(\frac{r_0}{r} \right)^{12} - \left(\frac{r_0}{r} \right)^6 \right], \quad (1)$$

where ϵ is the energy of binding between atoms, r_0 is the approximate equilibrium distance between bound atoms, and r is the interatomic distance.

To find the force of interaction between an AFM tip and a sample, one needs to integrate the potential (1) over the volumes of the sample and tip followed by some renormalization (e.g., Refs. 8 and 9). This results in

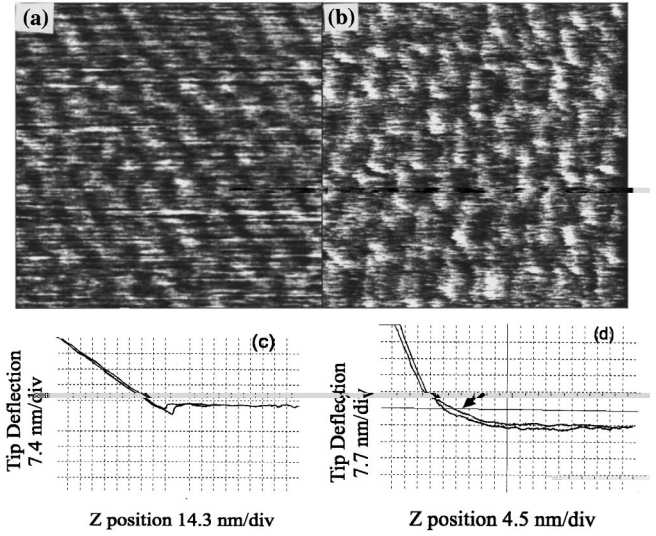


FIG. 2. Some $4 \times 4 \text{ nm}^2$ unfiltered muscovite images (as recorded) collected in (a) water and (b) 1 mM surfactant solution. Force curves are shown during scanning in (c) water and (d) surfactant. The arrow indicates the region in which the electrical double layer force modifies the force curve in comparison with scanning in water.

$$F(d) = \frac{\alpha N}{d^{13}} - \frac{AR}{6d^2}, \quad (2)$$

where F is the tip-sample force, α is a repulsion constant, N is the number of atoms at the apex of the tip, A is Hamaker constant, R is the radius of curvature of the tip, and d is the tip-sample distance.

A typical value of the Hamaker constant A (in air) for clinoclchlore/muscovite is about $2-3 \times 10^{-19} \text{ J}$ (see e.g., Ref. 11). Our estimated radius of tip curvature is 50–100 nm and the separation distance between tip and surface for contact scanning is $\sim 0.3-0.4 \text{ nm}$. Consequently the force of attraction due to the second term in Eq. (2) can reach 56 nN. In addition, the attraction force may not be reduced significantly in water. The Hamaker constant, and consequently the attractive force, is, for example, effectively reduced by only a factor of 1.4 (for gold–gold) and 3.4 (for gold–muscovite)^{10,11} in water relative to air. If we consider a

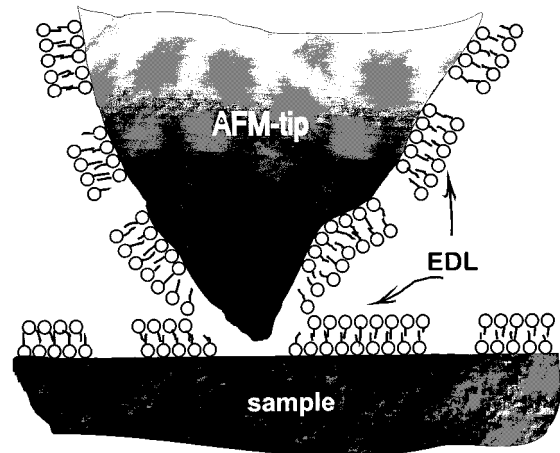


FIG. 3. Schematic of electrical double layer on the surface of the AFM tip and the sample.

scan without an EDL present and with load and attractive forces of 1 and 10 nN, respectively, then the real force acting on the tip/surface is 1+10=11 nN. This force is large enough to induce deformation and/or damage to the tip.

However, in the presence of an EDL, the attractive forces can be eliminated in a more gentle manner because the EDL repulsion acts, due to its long-range nature, on a much larger area. The detailed molecular EDL theory is rather complex and depends on the local structure of the EDL and the degree of dissociation, as well as the microtopography of the tip apex in contact with the sample. Fortunately, a qualitative understanding of these parameters is sufficient to understand the origin of the improved AFM resolution. By analogy with Eq. (2), one now has for the load force

$$F(d) = \frac{\alpha N}{d^{13}} - \frac{AR}{6d^2} + F_{\text{EDL}}, \quad (3)$$

where F_{EDL} is the force due to the EDL.

Because the scans were done when the load force was in the region marked by the arrow in Fig. 1(d), the F_{EDL} was greater than the attractive force. If this were not the case, one would see a straight line of contact in the force curve. If we return to our example above with 1 nN load force, one can see from the force curve [Fig. 1(d)] that long-range attraction is now overcompensated by the long-range F_{EDL} (this is because the total force is repulsive everywhere). This means that the real force acting on the tip apex atoms is equal to 1 nN minus $F_{\text{EDL}} - AR/6d^2$. Consequently, the tip apex will remain sharp and surface deformation will be reduced as a result of the eliminated attractive force. This is the reason why the resolution is improved in the presence of the surfactant solution.

There is a further advantage when using an EDL to exclude the attractive force as opposed to simply reducing the van der Waals force by addition of a specific medium.⁵ The presence of the EDL enhances tip stability during the image scan. This is because the tip is essentially between a relatively large EDL repulsion and a large attractive force, i.e., the tip is effectively trapped near the surface and lies in a potential well that is smooth in the lateral direction because of the long-range character of both forces. This results in a very stable imaging environment at the tip and does not lead to image artifacts.

It is worth noting that in this study we worked with surfactant concentrations that were small, below the critical micelle concentration (cmc). When the concentration is higher than the cmc, depending on the hydrophilicity or hydrophobicity of the substrate, a layer of micelle or hemimi-

celle cylinders, respectively, can be formed on the surface of the sample. These micellar structures were imaged in the pre-contact mode.¹⁻³ We found that even when the concentration is near the cmc, improvement of the clinochlore and muscovite image resolution is not apparent. The nature of this phenomenon can be understood through the analysis of the force curves. If the concentration of the surfactant is sufficiently high, the surface charge of the EDL is high as well, and, in order to image the surface, the AFM tip must overcome this high repulsion and contact the surface. As we observed in the force curves at our tip-sample distance, the attractive force gradient became high enough to make the tip jump to the sample. Under these conditions, any resolution advantage from the presence of the EDL appears to be lost. Thus, we found that an optimum concentration of the surfactant solution was about 0.5–1 mM for clinochlore and muscovite. However, this value will depend on the nature of the surfactant, the materials of the tip and sample, and cantilever rigidity.

In conclusion, we described a method for improving AFM image resolution which uses the presence of an electric double layer to compensate the attractive forces between the tip and sample. The EDL is created in the presence of a surfactant solution. In addition, the EDL also provides a stable scanning environment between the tip and sample being scanned.

The authors thank the Natural Science and Engineering Research Council of Canada for providing financial support in the form of research and equipment grants. Hong Yang is thanked for preparation of surfactant solutions.

¹T. J. Senden, C. J. Drummond, and P. Kekicheff, *Langmuir* **10**, 358 (1994).

²S. Manne, J. P. Cleveland, H. E. Gaub, G. D. Stucky, and P. K. Hansma, *Langmuir* **10**, 4409 (1994).

³S. Manne and H. E. Gaub, *Science* **270**, 1480 (1995).

⁴A. L. Weisenhom, P. K. Hansma, T. R. Albrecht, and F. Quate, *Appl. Phys. Lett.* **54**, 2651 (1989).

⁵J. L. Hutter and J. Bechhoefer, *J. Appl. Phys.* **73**, 4123 (1993).

⁶S. A. Joyce and J. E. Houston, *Rev. Sci. Instrum.* **62**, 710 (1991).

⁷G. A. Vrdoljak, G. S. Henderson, J. J. Fawcett, and F. J. Wicks, *Am. Mineral.* **79**, 107 (1994).

⁸I. Yu. Sokolov, *Surf. Sci.* **311**, 287 (1994).

⁹V. M. Mostepanenko, V. I. Panov, and I. Yu. Sokolov, *Sov. Tech. Phys. Lett.* **19**, 251 (1993).

¹⁰Yu. N. Moiseev, V. M. Mostepanenko, V. I. Panov, and I. Yu. Sokolov, *Phys. Lett. A* **132**, 354 (1988).

¹¹H. Krupp, W. Schovabel, and G. Walfer, *J. Colloid Interface Sci.* **39**, 421 (1972).

¹²J. N. Israelachvili, *Intermolecular and Surface Forces*, 2nd ed. (Academic, San Diego, 1991).