Microscopic manipulation of materials by atomic force microscopy

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Atomic force microscopy (AFM) (1) developed as an alternative technique to scanning tunneling microscopy (STM) for scanning the topology of a surface with atomic resolution, is emerging as a new tool for probing mechanical properties of a material. AFM, unlike STM, which images by means of the tunneling current between the surface and scanning probe, does not require the samples to be conducting. Images of the sample surface are obtained by measuring the force between atoms at the surface and atoms at the microscopic tip of the probe. The resolution of the technique can be as good as 10^{-11} Newtons (2). The ability of AFM to scan the topography of a sample on an atomic scale is possible because the probe is attached to a cantilever with a spring constant weaker than that corresponding to the typical forces between atoms (3). The atomic force microscope is essentially a force balance (4) with a pictorial output. In the contact mode, short range, interatomic forces are measured. By positioning the tip tens of nm from the surface, long range magnetic, electrostatic, and attractive van der Waals forces are resolvable. In addition to mapping out topographical features of the sample, the frictional properties of a surface can be studied using the lateral forces on the cantilever (5), and the elastic properties studied by indenting the sample with the tip (6).

The paper by Brandow, Turner, Ratna, and Gaber in this issue demonstrates the use of AFM as a microscopic peel tester. They use the tip to ablate a lipid bilayer from its substrate, thereby measuring adhesion between the two surfaces on a microscopic scale. Brandow and her colleagues are among the first investigators to modify an organic surface in a controlled manner by varying the force of the microscope tip on the atoms at the surface (7). Their results, on bilayers formed from lipid tubules collapsed onto graphite substrates, teach us about the adhesion of lipid bilayers to a graphite surface and the fluidity of the lipids on that surface. Beyond fundamental material properties of lipids, their work is one of the first attempts to use AFM for lithographic definition of a pattern in an organic film.

"Soft" samples such as organic and biomolecules, because of their viscoelastic properties, are more difficult to image than hard, inorganic surfaces. The tip, for example, can push atoms out of position and, at forces greater than 10 nN, even damage the sample. This is particularly true for AFM done in air where there is a large contribution to the signal from wetting forces. Surfaces exposed to air easily adsorb hydrocarbon contaminants and condensed water; these form a meniscus pulling on the tip. Effects of wetting can be eliminated so that forces down to hundredths of nN are measurable by doing AFM in an aqueous environment. The better resolution in water and the ability to control the pH of the environment make it attractive to measure biomolecules under water (2, 3).

Brandow and her colleagues have demonstrated lipid bilayers fabricated from tubules, that are rigid enough to be imaged by AFM in air. The lipid bilayers are fabricated by self-assembly of lipid tubules followed by deposition from solution on the graphite substrates. This is important because the images of soft materials are easily blurred by effects of the probe on the molecules. Biomembranes have been investigated by AFM of membrane fragments (8), collapsed vesicles (9), and lipid bilayers deposited by the Langmuir-Blodgett technique (10, 11). Langmuir-Blodgett (LB) films are ideal for the study of lipids and fatty acids because of the density and rigidity of the film. Lipid bilayers of dimyristoyl phosphatidylcholine, for example, have been imaged under water (10). The tubule bilayers may be a very promising alternative to LB films for AFM studies; this is indicated by the observation that below the threshold force for damage the lipids are not affected by the applied force, even though it is a relatively large force. It would be very interesting to study the tubule bilayers in water and compare the ordering and structure to that observed on Langmuir-Blodgett films in water.

Brandow and colleagues have used AFM in the constant force mode to remove lipid material from the graphite surface. The force between the tip and the sample is kept constant, and the position of the tip measured as it scans the surface. The tubule derived bilayers were scanned with a force on the order of 10 nN, roughly a factor of 1,000 greater than the force used to image Langmuir-Blodgett layers under water. The exciting aspect of these AFM experiments is the use of the probe to "ablate" the bilayer material of the unpolymerized tubules. The force applied by the tip to the surface is increased until a threshold ($\sim$13 nN for this sample) for removal of material is reached. The tip is held at this force and scanned repetitively across the tubule until the graphite surface is reached. This "cutting" process is repeated, defining the perimeter of the area to be removed. The paper notes that the threshold force for cutting is the same for directions parallel and perpendicular to the tubule. Cutting through the bilayer requires over 2,000

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cuts. Since the layer is ~60 angstroms thick, each cut is removing less than one complete layer of atoms. One exciting possibility is that the threshold force could vary with the depth of the sample as the adhesion of the atomic layer at the surface changes. This has been observed, for example in a similar work on multilayer Langmuir-Blodgett films (12).

Lipid material is not removable from the polymerized tubules, even under applied forces up to 49 nN. This demonstrates that the AFM technique can be used to measure relative adhesion of different materials. Understanding adhesion is central to studies of material interfaces and critical to the numerous applications, where one material is spread on another. In addition to adhesion, it may be possible to measure anisotropy of the structure by measuring the cutting threshold along different directions. The ablated areas can even be repaired by the tip: a force 14% lower than the cutting force can be used to drive viscous flow of lipid into the cut. This technique should be explored further as a way of studying the fluid dynamics properties of molecules.

Brandow and co-workers present a novel use of the AFM to study "soft" materials. One might say that they have only scratched the surface. Although this demonstration is on lipid bilayers, the potential of this technique as a probe of adhesion, structure, and fluid dynamics should be explored with other material systems. One approach, for example, is to use well-characterized materials to test the technique. Materials that exhibit structural anisotropy in the plane, i.e., the higher ordered liquid crystals or polymers under shear, may be ideal model systems for developing AFM as a tool for probing in-plane asymmetric ordering. These techniques, if explored further with other materials and surfaces, could enhance our understanding of adhesion on a molecular level.

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REFERENCES

1. Binnig, G., C. F. Quate, and C. Gerber. 1986. Atomic force microscope. *Phys. Rev. Lett.* 56:930–933.
2. Rugar, D., and P. Hansma. 1990. Atomic force microscopy. *Physics Today.* 23–30.
3. Radmacher, M., R. W. Tillmann, M. Fritz, and H. E. Gaub. 1992. From molecules to cells: imaging soft samples with the atomic force microscope. *Science* (Wash. DC). 257:1900–1905.
4. Israelachvili, J. N. 1992. Intermolecular and Surface Forces, 2nd ed. Academic Press, New York.
5. Overney, R. M., E. Meyer, J. Frommer, D. Brodbeck, R. Luthi, L. Howald, H. J. Guntherodt, M. Fujihira, H. Takano, and Y. Gotoh. 1992. Friction measurements on phase-separated thin films with a modified atomic force microscope. *Nature (Lond.).* 359:133–135.
6. Maivald, P., H. J. Butt, S. A. C. Gould, C. B. Prater, B. Drake, J. A. Gurley, V. B. Elings, and P. K. Hansma. 1991. Using force modulation to image surface elasticities with the atomic force microscope. *Nanotechnology.* 2:103–106.
7. Weisenhorn, A. L., B. Drake, C. B. Prater, S. A. C. Gould, P. K. Hansma, F. Ohnesorge, M. Egger, S. P. Heyn, and H. E. Gaub. 1990. Immobilized proteins in buffer imaged at molecular resolution by atomic force microscopy. *Biophys. J.* 58:1251–1256.
8. Worcester, D. L., R. G. Miller, and P. J. Bryant. *J. Microsc.* 1988. Atomic force microscopy of purple membranes. 152:817–821.
9. Singh, S., and D. J. Keller. 1990. Atomic force microscopy of supported planar membrane bilayers. *Biophys. J.* 60:1401–1410.
10. Zasadzinski, J. A. N., C. A. Helm, M. L. Longo, A. L. Weisenhorn, S. A. C. Gould, and P. K. Hansma. 1991. Atomic force microscopy of hydrated phosphatidylethanolamine bilayers. *Biophys. J.* 59:755–760.
11. Meyer, E., L. Howald, R. M. Overney, H. Heinzelmann, J. Frommer, H. J. Guntherodt, T. Wagner, H. Schier, and S. Roth. 1991. Molecular resolution images of Langmuir-Blodgett films using atomic force microscopy. *Nature (Lond.).* 349:398–400.
12. Meyer, E. 1992. Atomic force microscopy. *Prog. Surface Sci.* 41:3–49.