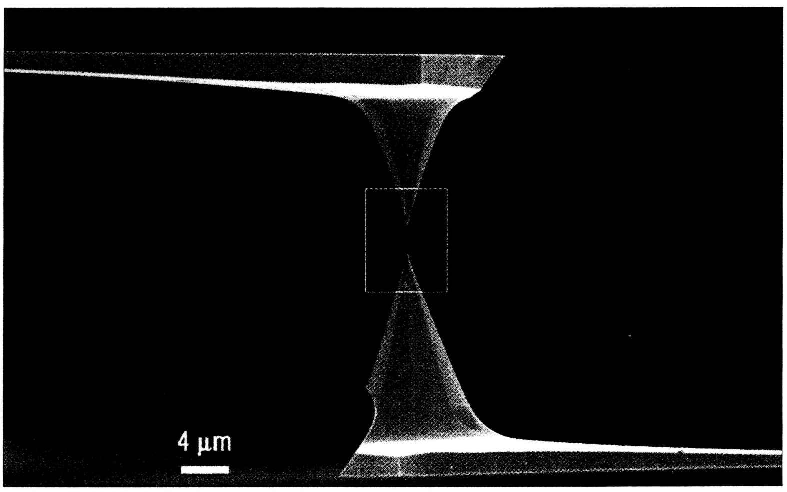
Vacuum experiments reveal the nanoworld

Atomic force microscopy in vacuum is providing new insights into the structural, frictional and mechanical properties of materials at the atomic scale. Robert Carpick surveys the latest advances that have been enabled by this versatile tool



Amazing grace – a multiwalled carbon nanotube held between two AFM tips inside a scanning electron microscope

The atomic force microscope has revolutionized surface imaging since its invention in 1986 by Gerd Binnig and Christophe Gerber at IBM's Zurich Research Laboratory in Switzerland and Calvin Quate at Stanford University in the US. The atomic force microscope (AFM) has been used to study an array of materials with resolution at the atomic scale, and is compatible with almost any environment, including air, gases, liquids and ultrahigh vacuum. This flexibility allows all types of materials to be studied, ranging from insulators through to semiconductors, metals and organic materials.

The AFM has acquired stunning images of crystal surface lattices, measured forces between individual DNA strands, imaged the deposition of atoms in real-time, and allowed scientists to manipulate and position individual molecules. It has provided insights into problems that have vexed scientists for years, and has enabled discoveries of phenomena that were previously unimagined.

The AFM is now firmly established as a critical tool in the rapidly expanding field of nanotechnology. Structures with a size approaching the scale of their atomic constituents have novel optical, electronic and mechanical properties. These can be exploited in a range of applications, including ultrahigh density data storage, ultrafast nanoscale transistors, photonic materials that steer light just as semiconductors guide electrons, and assembled molecules and structures that are otherwise impossible to create.

With these new opportunities come new challenges. As devices get smaller it becomes essential to control surface properties on the atomic scale. This is a difficult challenge, however, as our understanding of surface atomic properties is far from complete. And an interface between two materials is even more complicated than two separate surfaces.

Materials at the atomic scale

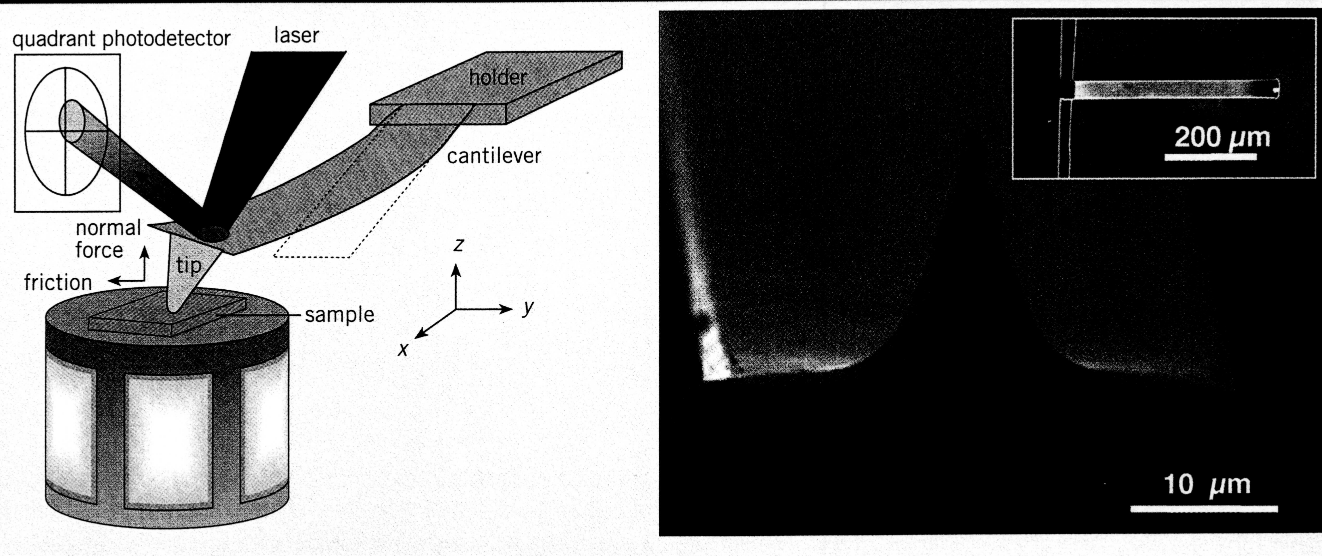
An ultrahigh vacuum environment is essential for studying surfaces at the atomic scale. After several years of progress AFM vacuum applications have matured to the point where they can provide quantitative information on material properties. One area of interest has been the frictional, structural and mechanical properties of materials at the atomic scale. Recent experiments in this field show that vacuum AFM is uniquely capable of discovering the knowledge needed to enable nanotechnology.

At the heart of an AFM is a sensor that measures atomic scale forces and displacements. A number of sensor configurations can be used, but the most popular is the cantilever sensor. It is composed of a tip, 10–100 nm wide, that is integrated with a compliant cantilever beam (figure 1). Various vendors produce microfabricated cantilevers with different force constants, sizes and tip materials.

Forces acting on the tip cause the cantilever to move, with the resulting deflections usually recorded by optical means. This approach routinely measures forces in the 10^{-10} N range or better, although Dan Rugar from IBM's Almaden Research Center in the US has recently used ultra-sensitive cantilevers in vacuum to measure forces approaching 10^{-18} N.

The relative positions of the sample and cantilever must be precisely controlled in all three directions to acquire data in terms of both applied force and position. This is achieved by using scanning elements made from piezoelectric materials, which deform

Inside an atomic force microscope



1 In an AFM normal and lateral forces are measured by using a laser and a photodetector to determine the deflections of a cantilever. A piezoelectric scanner moves the sample in all three directions with sub-nanometre precision. In contact mode the AFM tip interacts directly with a sample. The contact region is typically a few nanometres in diameter or less, while the cantilever is typically between 100–200 μm in length. Also shown are electron micrographs of a microfabricated silicon AFM cantilever with an integrated tip.

in a controlled way in an applied electric field. Measurements can be carried out at a single point, over an extended image region, or even over a prescribed pattern traced out over the surface.

Two of the most common operating schemes are the contact and non-contact modes. In contact mode the tip is placed in direct mechanical contact with the sample. A net force results from both repulsive and attractive forces acting on the tip: the repulsive force is due to the interaction between electrons in the tip and sample, while attractive forces arise from chemical bonds, van der Waals' forces and electrostatic interactions. The net force or "load" is controlled using the piezoelectric scanner, and at low loads the tip can probe a surface with no damage to either the tip or sample. At higher loads the tip can rearrange the surface and tip atoms, sometimes with extremely precise control.

In the non-contact regime the tip is prevented from making any sustained contact with the sample. Interaction forces attract the tip to the sample, and the spatial variation of these forces can be mapped to provide a high resolution image of the surface. Operation in vacuum is critical for achieving the best resolution.

An AFM can be built to work in vacuum at temperatures ranging from cryogenic to hundreds of degrees Celsius. Several commercial vendors offer variable temperature ultrahigh vacuum AFM systems, including Omicron Vakuumphysik, JEOL and RHK Technology, a new arrival to the market. These instruments owe their existence to brilliant early design innovations from research groups such as those lead by Hans-Joachim Güntherodt at the University of Basel in Switzerland and Miquel Salmeron at Lawrence Berkeley National Laboratory in the US. Gerd Binnig also pioneered cryogenic vacuum work after his invention of the AFM, and several groups have developed customized vacuum AFM systems that are yielding impressive results.

After several years of progress, AFM vacuum applications have matured to the point where they can provide quantitative information on material properties

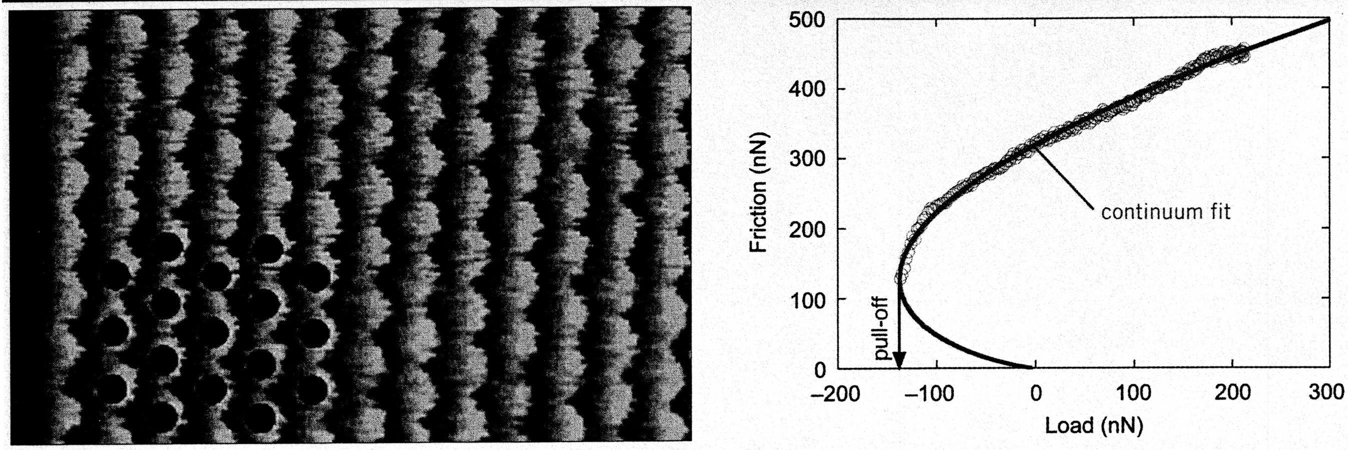
Friction at the atomic scale

The AFM in contact mode has become an important tool in nanotribology – the study of friction, lubrication and wear at the atomic scale. These phenomena are not well understood at a fundamental level, and it is hoped that the AFM's ability to resolve both normal and lateral forces with extremely high resolution will help to reveal the complex processes that occur at sliding interfaces. It is important to carry out experiments in vacuum because friction is strongly affected by both contamination and the chemical composition of the interface.

A dramatic example is the phenomenon of atomic "stick–slip" friction. Stick–slip usually refers to the behaviour of large sliding interfaces such as a creaking door hinge, a bowed violin string and geological faults. But in AFM experiments the tip is often observed to stick and slip at each atomic site or unit cell on a crystalline sample. For example, the lateral force measured between an AFM tip and a muscovite mica sample varies with the same period as the surface crystal lattice of the mica, indicating that the force repeatedly builds up before the tip slips by one unit cell (figure 2a).

Atomic stick–slip behaviour is due to the collective interaction of a large number of atoms. Theories that

Atomic "stick–slip" behaviour



2 The lateral force between a platinum coated tip and a muscovite mica surface (left) repeatedly builds up and then quickly slips by one mica unit cell. The black dots show the mica crystal lattice sites, which have a periodicity of 0.52 nm. A graph of friction against load (right) shows a non-linear relationship. In this case friction is proportional to the contact area as predicted by continuum mechanics (green line).

fully explain this phenomenon are still being developed, although it is clear that strong interfacial interactions are at play. For the mica surface described above, the force at which slip occurs was measured as the load is increased (figure 2b). Friction forces in macroscopic systems usually have a linear dependence on the load, but this law seems to break down at the atomic scale. Instead friction is proportional to the actual contact area between the tip and sample, which increases with the load due to elastic deformations of the sample and tip.

Remarkably, the variation is closely fit by a continuum theory of adhering elastic contacts, with the accuracy and reproducibility of this fit largely due to the cleanliness of the ultrahigh vacuum environment. Ken Johnson of Cambridge University in the UK – one of the great pioneers of continuum contact mechanics – said he was "gobsmacked" to see that models he had developed for macroscopic contacts can be applied to ones only a few nanometres in diameter. Even a few hundred atoms at an interface are enough to render a continuum description reasonably valid, even though atomic-scale variations of the friction force are also present.

Chemical contributions to friction can also be quantified by AFM experiments in vacuum. Scott Perry at the University of Houston in the US recently showed that a monolayer of oxygen adsorbed on the surface of a vanadium carbide crystal caused a reduction in friction of around 40%. Vanadium carbide is an emerging material for hard coatings, and the result provides an insight into the coupling between friction and environmental effects such as oxidation. It also shows that the frictional properties of surfaces can be controlled by tailoring the surface chemistry at the atomic scale, a critical finding for materials that are to be deployed in nanoscale devices.

Vacuum operation has also enhanced the resolution of images produced with the AFM. In contact mode the contact area between the tip and sample inevitably exceeds the scale of a single atom, which meant that some creative thinking was required to achieve true atomic resolution.

Franz Giessibl of Augsburg University in Germany provided the breakthrough while working with Park Scientific Instruments. It is well known that the resonance frequency of an oscillating structure shifts when a force is applied, and Giessibl showed that atomic interaction forces in the non-contact regime caused a small but observable shift in the cantilever's resonance frequency. The key is to operate in vacuum, where the lack of air damping gives the cantilever an extremely high quality factor and therefore allows the frequency shift to be measured precisely.

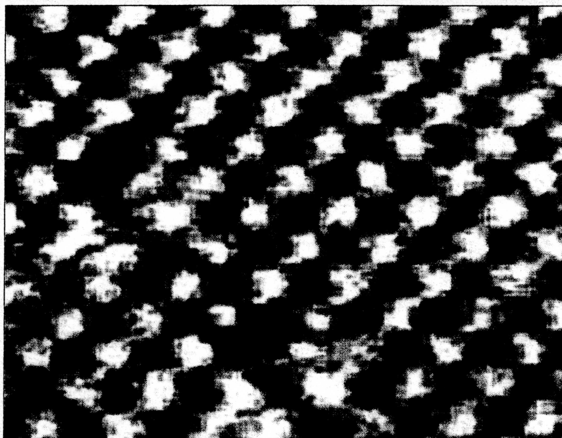
By carefully controlling the tip–sample distance, Giessibl was able to produce an atom-by-atom image of a silicon surface. While the scanning tunnelling microscope has provided such images for years, it is limited to conducting or semiconducting materials. This new technique – known as frequency-modulation AFM – takes advantage of the vacuum environment to extend single-atom imaging to insulators.

Unprecedented resolution

Since then spectacular advances have been made by several groups. Güntherodt's group at the University of Basel unambiguously demonstrated atomic resolution for an insulator, with images of a sodium chloride surface clearly revealing the atomic lattice, as well as single vacancy defects (figure 3). Insulators, metals, semiconductors, polymers, organic films and even DNA have now been imaged at high resolution.

The Basel group recently used the technique at low temperatures to image the "beautiful" surface

Imaging atomic resolution



3 A frequency modulation image of the sodium chloride surface shows one bump for every unit cell of the surface lattice. Two isolated vacancy defects can also be seen.

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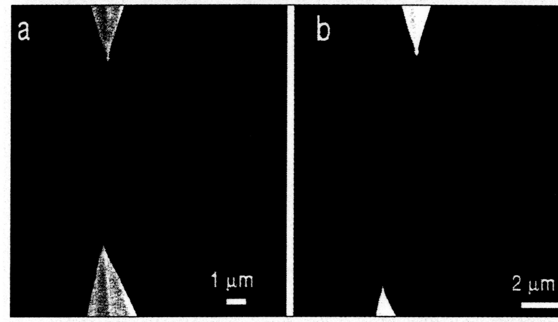
Breaking nanotubes



4 Electron microscope images reveal the fracture of a multiwalled carbon nanotube. The left image shows the nanotube just before breaking. In the right-hand picture the nanotube has broken due to tensile loading. In this case the upper fragment has been pulled out from the lower one, and the length of fragments on the upper and lower tips indicate that the inner set of tubes was pulled from the outer tube.

of silicon – the reconstructed 7×7 surface – with unprecedented resolution. For the first time these images resolved not only the top-most layer of adatoms, but also the interstitial sub-layer of rest atoms in the silicon structure. The strength of the tip–sample chemical interaction was also determined for distinct atomic sites.

Meanwhile, Sugawara and colleagues at Hiroshima University in Japan examined aluminium adsorbates on the same silicon surface. The atomic arrangement of the aluminium adatoms was clearly resolved, and the enhanced strength of the tip–sample interaction was consistent with the dangling bond that is typical of aluminium adatoms. The group also used the technique to observe the motion of individual vacancy defects on the indium phosphide surface.

These examples illustrate that the development of nanoscale devices will require detailed knowledge and precise control of surface atomic properties. Vacuum measurements provide critical data that may ultimately be used for device design.

Manipulation on the atomic scale

Vacuum operation allows the structure of materials to be visualized at the nanometre scale. But the tip also exerts forces on materials, acting as a nanoscale actuator that, under human control, can manipulate the position of nanostructures. The Basel group, for example, has used an AFM tip in ultrahigh vacuum to push nanoscale islands of carbon-60 across a sodium chloride surface. The experiments were able to determine the shear forces required to initiate and maintain sliding, and such studies show that it is feasible to assemble and transport materials at the nanoscale.

Rod Ruoff's group at Washington University in the US recently demonstrated an extension of nanomanipulation that allowed the mechanical properties of carbon nanotubes to be observed and measured directly. The researchers developed a miniature tensile test system that could operate inside a scanning electron microscope (SEM). They placed a pair of AFM tips inside the SEM, and between the two tips they attached a multiwalled carbon nanotube – essentially a "Russian doll" nesting of several individual nanotubes. One tip was used to deform the multiwalled nanotube while the other measured the applied force, all the while using the SEM to watch the tube stretch and eventually break (figure 4).

The experiments measured the force required to break the tube – indicating a strength close to diamond – and also identified the breaking mechanism. This turned out to be a "sword-in-sheath" process in which the outermost tube breaks and the inner tubes pull out from it. These types of measurements are needed to determine how to exploit the mechanical properties of nanotubes and other nanostructures for future applications.

The building blocks of nanotechnology are nanostructured materials, and one of the key testing and construction tools is the AFM. While nanotechnology has some way to go before a set of reliable applications are developed, vacuum AFM studies are uncovering the frictional, structural and mechanical properties of materials at the nanoscale.

Vacuum AFM applications will continue to multiply as new materials and devices are developed. And while the road leading to mature nanotechnology applications remains long and far from clear, the results discussed here prove that the trip will indeed be beautiful.

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