How the doors to the nanoworld were opened

CHRISTOPH GERBER AND HANS PETER LANG

are at the National Competence Center for Research in Nanoscale Science, Institute of Physics, University of Basel, Klingelbergstrasse 82, 4056 Basel, Switzerland.

e-mail: Christoph.Gerber@unibas.ch

The invention of the scanning tunnelling microscope 25 years ago, followed by the arrival of the atomic force microscope five years later, were crucial events in the history of nanoscience and nanotechnology. As the recent International Conference on Nanoscience and Technology in Basel made clear, scanning probe microscopes based on these discoveries are still having a tremendous impact on many areas of research.

In March 1981 a new type of microscope made its debut. Unlike traditional microscopes, however, the scanning tunnelling microscope (STM) did not use lenses. Instead, a sharp tip was moved close enough to a conductive surface for the electron wavefunctions of the atoms in the tip to overlap with the wavefunctions of the surface atoms. When a voltage was applied, electrons started to 'tunnel' through the vacuum gap, causing a current to flow from the foremost atom of the tip into the surface. Quantum tunnelling had been studied theoretically before, but had never been demonstrated so elegantly as in these experiments at the IBM Zurich Research Laboratory in Switzerland.

Moreover, the tunnelling current depended exponentially on the distance between the tip and the surface: changing this distance by just an atomic diameter changed the current by a factor of a thousand. Therefore, by scanning the tip over a sample in two dimensions and keeping the tunnelling current constant, it was possible to image surfaces on the atomic scale.

The initial results were written up in a manuscript entitled "Tunnelling through a controllable vacuum gap", which was submitted to a leading physics journal in June 1981. However, the paper was declined by the editors based on the following referee reports: one referee said that the exponential dependence of the tunnelling current on distance was well accepted, so the experiment would not give any new insight; the other report described the work as "extraordinary" and a "technical jewel", but this referee said that whether such technological work should be published in this particular physics journal was an editorial decision. Eventually the results were published in another leading journal, *Applied Physics Letters*, in January 1982[1].

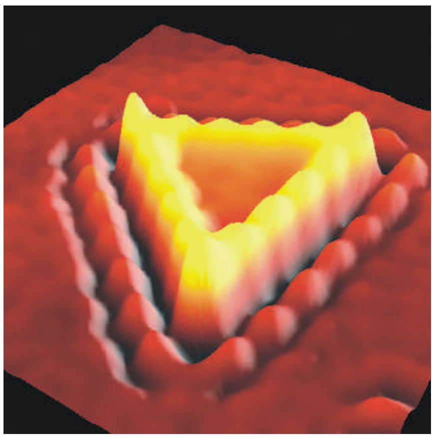

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Figure 1 **Keep it clean. Molybdenum disulphide nanocrystals are used as catalysts to remove sulphur impurities at oil refineries. Reducing harmful sulphur emissions from the combustion of transport fuel is a major environmental challenge. Recent STM studies of MoS_2 nanocrystals[6] — which are triangular — on gold surfaces have clarified how these catalysts work and lead to improvements in their performance.**

In terms of science, the real breakthrough for the STM came in 1983 with the experimental observation of one of the most intriguing phenomena in surface science at that time: atom-by-atom imaging of the 7×7 surface reconstruction in Si(111) (ref. 2). The STM images allowed the now widely accepted model of the reconstruction to be worked out from the models of the time[3]. For the first time it was possible to get up close and personal with individual atoms on surfaces in a three-dimensional representation.

It took the small but steadily growing community another two years to verify the initial results obtained in Zurich, and it was only at a workshop at Oberlech in the Austrian Alps in 1985 that researchers started to realize the potential of the new method. Devices such as the atomic force microscope (AFM) have their roots in this meeting, and during the last night of the workshop the Alps were buzzing with crazy new ideas for using such microscopes in many different areas of science and technology. People were eager to get back to their labs and start working right away, although some almost missed the bus to the airport the next morning because they were still caught up in the discussions. A year later, in 1986, Gerd Binnig and Heinrich Rohrer shared the Nobel Prize in Physics "for their design of the scanning tunneling microscope". A significant number of the protagonists in that meeting are still going strong in the field today.

In the years that followed the excitement of the mid-1980s, Don Eigler and co-workers at the IBM Research Lab in Almaden, California, used an STM to write the IBM logo with 35 xenon atoms on a nickel surface[4], and later moved iron atoms on a copper surface to make a quantum corral[5]. Some researchers discussed the possibility of using such structures for quantum teleportation, whereas others have tackled important environmental problems. Flemming Besenbacher and co-workers at the University of Aarhus in Denmark, for instance, have recently used STMs to understand how molybdenum disulphide nanoclusters act as catalysts to remove potentially harmful sulphur compounds from crude oil[6] (Fig. 1). These are just two of many examples that demonstrate the enormous potential of the STM.

MAY THE FORCE BE WITH YOU

This, however, is just half of the story. The encore came with the development of the AFM 20 years ago[7]. This work has now been cited more than 4,700 times, which makes it the second-most-cited paper published in *Physical Review Letters* in the last 25 years. As with the STM, the AFM relies on a sharp tip that is scanned over a surface. This tip is part of a cantilever that can measure forces down to the lower piconewton range. In a sense the AFM resembles a record player — the forces between the surface and the tip cause the cantilever to bend in the vertical direction, and by measuring this deflection, it is possible to produce an image of the surface with atomic resolution. The forces, which can be attractive or repulsive, depend on the nature of the interaction between the tip and the surface being investigated. Examples include chemical forces, van der Waals forces, electrostatic forces, capillary forces or friction forces.

Since 1986, the AFM has proved its suitability in various applications. First designed as an instrument to image the surfaces of non-conductive materials with high lateral and vertical resolution, the technique has been adapted to work in various environments (for example, in liquids, at low temperatures, in high magnetic fields and so on), and also for chemical and biological applications when the tip is suitably modified. Its ability to investigate surfaces with unprecedented resolution introduced a wealth of related techniques (see Fig. 2). For instance, local electric charges on the tip or surface lead to electrostatic forces that allow the distribution of electric charge on a surface to be visualized (electrostatic force microscopy). Similarly, magnetic forces can be imaged if the tip is coated with a magnetic material, such as cobalt, that has been magnetized along the tip axis (magnetic force microscopy).

Information on force gradients can be obtained if the cantilever is forced to oscillate. Depending on the amplitude of the oscillation we can operate the AFM in 'tapping' mode or perform dynamic force microscopy to provide true atomic resolution[8], which, in turn, allows us to perform force spectroscopy on specific sites. Material properties, especially differences in elasticity, can be locally discerned using ultrasonic force microscopy. But this is only the tip of the iceberg (Fig. 2).

In addition to imaging surfaces, the AFM can also be used to modify surfaces and manipulate individual atoms and molecules. By depositing, removing or modifying material from the tip and/or sample, it is possible to write and read information to and from the surface. Meanwhile, measuring forces as a function of the tip–sample separation (that is, measuring force–distance curves) allows us to draw conclusions regarding the material characteristics of surfaces and their chemical properties. It is also possible to tether one end of a molecule (such as DNA) to a surface, and the other end to the AFM tip, and investigate the mechanical and elastic properties of the molecule by stretching it (force–distance spectroscopy and single-molecule spectroscopy).

Magnetic resonance force microscopy — the mechanical detection of electron or nuclear spins — has shown great promise and may finally lead to a way of locally mapping the chemical structure of a surface[9]. Moreover, the development of chemical force microscopy[10] has shown that the cantilever itself is a very sensitive tool for observing chemical reactions and processes[11].

Another broad area of application is biological and chemical sensing. In this approach the absorption of molecules onto the cantilever allows them to be detected because they change the mass, and hence the resonance frequency, of the cantilever. However, in physiological environments, the absorption of biomolecules (such as DNA, proteins, peptides and antibodies) is detected by changes in surface stress in a way that could have advantages over standard biomolecular techniques. In general, the possibilities offered by coating the individual cantilevers in an array with layers to which only particular types of biomolecules can attach are enormous[11].

Indeed, even the sky is not the limit for AFM technology. The Rosetta mission to comet 67P launched by the European Space Agency in 2004 includes an AFM in its MIDAS (Micro-Imaging Dust Analysis System) instrument. The goal of this mission, which is expected to touch down on 67P in 2014, is to analyse particle size distributions in cometary material. The next NASA mission to Mars is also expected to include an AFM for similar studies.

OUTLOOK

With the emergence of scanning probe microscopy (SPM) and related techniques in the 1980s, the door to the nanoworld was pushed wide open. Today these methods are still making a tremendous impact on many disciplines that range from fundamental physics and chemistry through information technology, quantum computing, spintronics and molecular electronics, and all the way to life sciences. Indeed, some 4,000 AFM-related papers were published last year alone, bringing the total to 22,000 since it was invented, and the STM has inspired a total of 14,000 papers. There are also at least 500 patents related to the various forms of scanning probe microscopes.

Commercialization of the technology started in earnest at the end of the 1980s, and approximately 10,000 commercial systems have been sold so far to customers in areas as diverse as fundamental research, the car industry and even the fashion industry. There are also a significant number of home-built systems in operation. Today some 30–40 companies are involved in manufacturing SPM and related instruments, with an annual worldwide turnover of $250–300 million. Moreover, the market of SPMs is predicted to double over the next five years.

The state-of-the-art in nano was on display in August when more than 1,600 researchers gathered in Basel to mark the STM and AFM anniversaries at the International Conference on Nanoscience and Technology (www.icnt2006.ch). The breadth and scope of modern nanoscience and its technological potential was underlined by the 40 different topics covered at the conference[12]. There were also sessions on the impact of new nanomaterials on the environment and human health, and the teaching of nanoscience at universities.

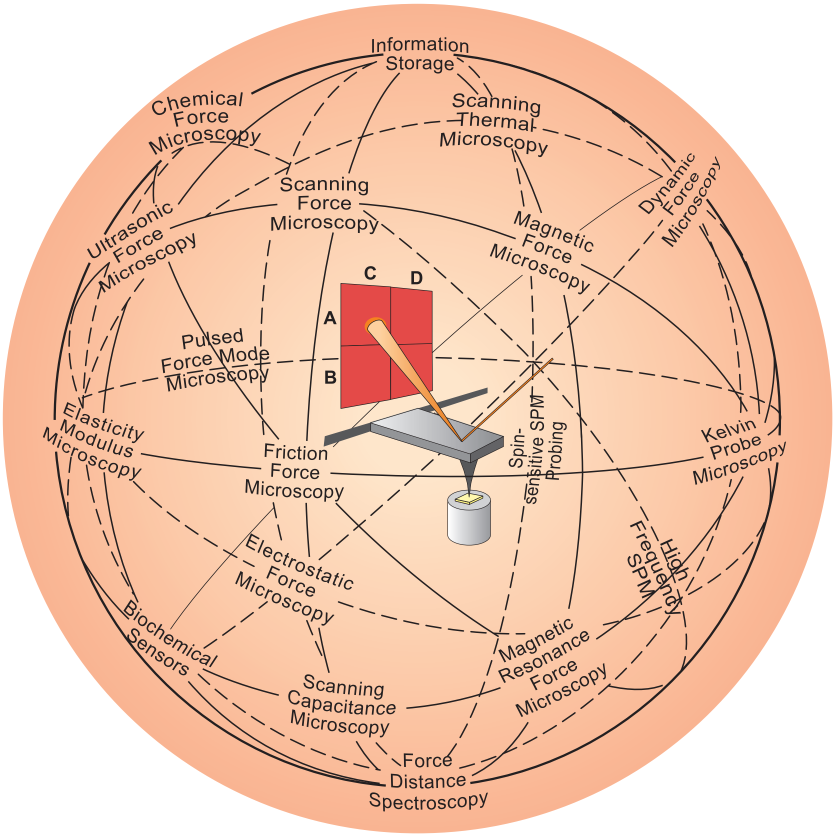

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Figure 2 **World of possibility. The AFM (centre) has inspired a variety of other scanning probe techniques. Originally the AFM was used to image the topography of surfaces, but by modifying the tip it is possible to measure other quantities (for example, electric and magnetic properties, chemical potentials, friction and so on), and also to perform various types of spectroscopy and analysis.**

Here we present just a few of the scientific highlights from this memorable meeting. Spin-polarized STM has been used to probe nanomagnetic states for the first time, with clear atomic-scale spin contrast being seen on NiO(001) surfaces. These results could have applications in nanomagnetism (R. Wiesendanger, Univ. Hamburg). In nano-optics the control of light propagation on length scales of a few nanometres by large periodic assemblies of identical nanostructures was reported, which could have applications in new optical approaches to information technology (B. Hecht and H.-J. Eisler, Univ. Basel). And for the first time it was shown that friction could be switched on and off on the atomic scale by modulating the normal force between the tip and surface (A. Socoliuc and E. Meyer, Univ Basel; see also ref. 13, and p20 of this issue[14]).

In other work, carbon and boron nitride nanotubes have been integrated in higher-order nanoelectromechanical systems such as motors, high-frequency resonators, and sensors (A. Zettl, Univ. California, Berkeley), and self-organization has been used to make well-defined functional molecular and supramolecular structures (J. M. Lehn, Univ. Strasbourg). New results on large-scale circuitry at densities that span the projections of the semiconductor industry roadmap for the period 2020–2030 were also presented (J. Heath, Caltech).

There has also been remarkable progress in the development of high-speed STM, AFM and scanning near-field optical microscopy. By using device resonances in the fast scanning direction, speeds of up to several tens of thousands of scan lines per second can be achieved (M. Miles, Univ. Bristol; J. W. M. Frenken, Univ. Leiden). Multiprobe microscopy is another area where progress has been rapid. STMs with up to four independent tips have been used to measure the electrical conductivity of nanostructures, and an AFM with four conductive probes has also been built (M. Aono, NIMS, Tsukuba).

So what does the future hold? The top-down approach that dominates in nanotechnology today is already, to a certain extent, meeting the bottom-up approach of self-assembly and self-organization that has been so successful in the natural world, to create a new generation of materials, devices and systems that will spectacularly outperform those that we have today in information technology, medicine, environmental technologies, the energy industry and beyond. But for this to happen we need to learn more about how atoms and molecules behave on the nanoscale, and we will therefore continue to rely on the STM, the AFM and their many offspring.

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