

FORCE MICROSCOPY

Magnetic tips probe the nanoworld

A new approach to magnetic resonance force microscopy has demonstrated a resolution of 90 nm, and with further improvements it may be possible to determine the chemical compositions of single molecules.

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Nuclear magnetic resonance is one of the most important tools available for determining various types of structures in chemistry and biology, and the related technique of magnetic resonance imaging is widely used in medicine. So far, however, the resolution of these techniques has been limited to a few micrometres at best. Now, on page 301 of this issue, John Mamin, Dan Rugar and co-workers at IBM's Almaden Research Center and Stanford University demonstrate an alternative approach to magnetic resonance imaging that is capable of achieving a spatial resolution of better than 100 nm (ref. 1). Ultimately, it may be possible to reach single-nucleus resolution with these techniques, which would allow researchers to determine the chemical composition of individual molecules.

As its name suggests, nuclear magnetic resonance involves manipulating and measuring nuclei that have magnetic moments or 'spins', such as the protons in water molecules. In a conventional magnetic resonance experiment the sample is placed in a magnetic field, which aligns all the magnetic moments so that they point in the same direction as the magnetic field. A radio frequency (RF) pulse is then used to 'flip' the spins so that they point in the opposite direction: the RF photons have an energy that is close to (or equal to) the energy difference between these two spin states — hence the word resonance.

Over time the spins flip back again, emitting an RF signal that is detected with induction coils. By carefully measuring this signal it is possible to extract a great deal of information about the sample. And if the magnetic field varies with position (that is, if it has a gradient), different parts of the sample will have different resonant frequencies, which makes it possible to actually image the sample.

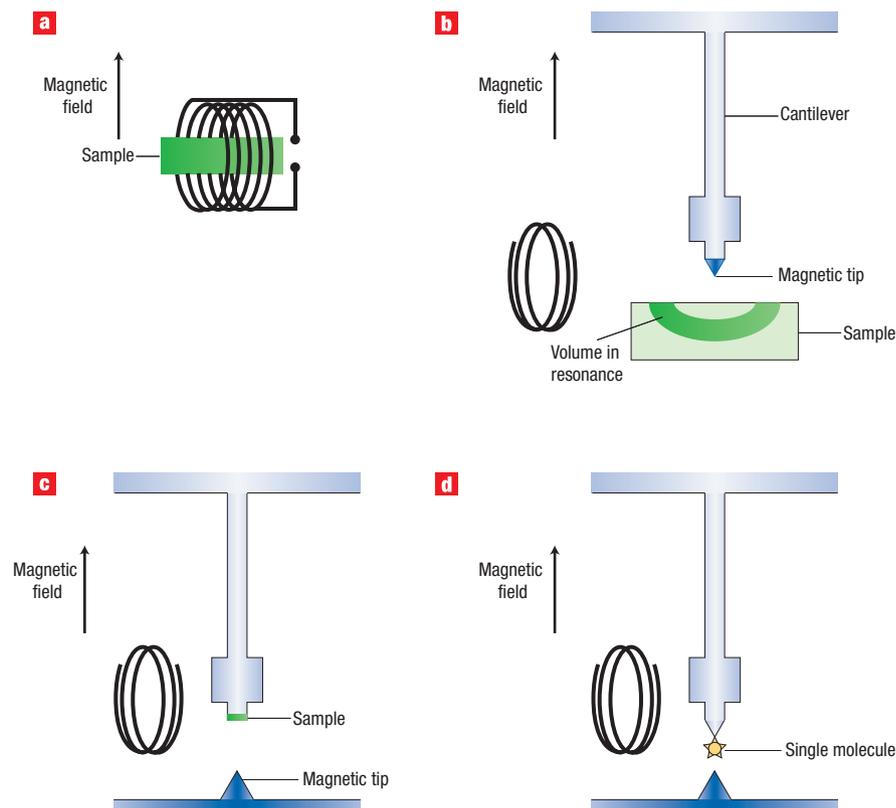


Figure 1 Different approaches to magnetic resonance. **a**, In conventional nuclear magnetic resonance, the sample (green) is placed in a magnetic field (black arrow) and an induction coil is used to both excite the spins and detect the signal. **b**, In magnetic resonance force microscopy (MRFM) a coil is used to excite the spins, while a magnetic tip (blue) on a cantilever oscillates just above the sample. The interaction between the tip and the resonant volume in the sample changes the resonant frequency of the cantilever. **c**, In the inverted MRFM geometry used by Mamin and co-workers the magnetic tip is fixed and the sample is attached to the cantilever. **d**, Ultimately, it might be possible to perform such experiments on single molecules.

However, the induction signal is proportional to the diameter of the coil so there is limited scope for miniaturization (Fig. 1a). Mamin and co-workers overcome this problem by using an approach called magnetic resonance force microscopy (MRFM; refs. 2 and 3), which allows them to make their system smaller without losing sensitivity. In this approach, which is similar to magnetic force microscopy (itself

a variation on atomic force microscopy), the sample is probed by a sharp magnetic tip on a mechanical cantilever with a very low spring constant.

The forces between the tip and the resonant region can be determined by measuring how they influence the oscillations of the cantilever, notably by measuring how they change the resonance frequency. These forces are extremely

small, of the order of attoNewtons (10^{-18} N), so the associated frequency shifts are also very small. One advantage of using sharp magnetic tips is that the magnetic field gradient, which plays a central role in imaging, increases as the radius of curvature of the tip gets smaller.

Mamin and co-workers used a vertical alignment for the cantilever, which stopped it 'jumping' into contact with the sample (Fig. 1b). They also developed a novel way to probe the magnetic resonance of volumes as small as 650 zeptolitres (650×10^{-21} litres). This is 60,000 times smaller than the previous record for nuclear magnetic resonance, and corresponds to about 30 million spins. However, the signal is proportional to the square root of the number of spins, and as only a small fraction of the spins contributes to the signal, the effective number of spins they detect is about 3,200. The authors estimate that they are able to detect as few as 1,200 nuclear spins at a temperature of 650 mK.

In modern magnetic resonance experiments, complex sequences of RF fields (known as protocols) are applied to the sample. The cyclic-CERMIT protocol developed by Mamin and co-workers was based on the CERMIT (cantilever

enabled readout of magnetization inversion transients) protocol created by Sean Garner, John Marohn and co-workers^{4,5} at Cornell University. An essential part of the new protocol is that the RF pulses are synchronized to the oscillations of the cantilever. Another important ingredient of the IBM experiment is the development of magnetic tips with field gradients as high as 10^6 Tesla per metre. To make these tips, a multilayer film of Fe/CoFe/Ru was grown on micromachined silicon, which resulted in a magnetization of 2.3 T combined with a radius of curvature of less than 20 nm.

Mamin and co-workers also decided to use an inverted geometry in which the sample is attached to the cantilever and the magnetic tip is fixed (Fig. 1c). This geometry has the advantage that the oscillations of the cantilever are less affected by the magnetic field, which ensures that the required force sensitivity is maintained at high magnetic fields. To demonstrate the resolution of the technique, a 100 nm CaF_2 film was grown on the end of the silicon cantilever and patterned with a focused ion beam. Signals from the ^{19}F nuclei were then detected in two dimensions, revealing a resolution of 90 nm. (Three-dimensional

imaging was not possible owing to the thinness of the film.)

There is still room for improvement: for example, the magnetic field gradient could be increased to 10^7 Tesla per metre; the tip-sample separation could be reduced; and the thermal vibration of the cantilevers could be minimized by further reducing the temperature. Ultimately, it might be possible to attach a single molecule to the cantilever (Fig. 1d) and determine its chemical composition, because each nucleus in the molecule that has a magnetic moment will give a different response, depending on its place in the periodic table. More than half the elements in the periodic table have a magnetic moment, which means that MRFM is potentially a very powerful technique for this sort of analysis. And as there is no instrument that can determine the chemical composition of single molecules at present, this is a challenge that is well worth taking on.

References

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DEVICE PHYSICS

Will fluidic electronics take off?

For decades semiconductors have formed the core of microelectronic circuits. Although nanofluidics may not put silicon out of business, it will likely open a host of new applications.

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With applications ranging from molecular detection to the control of chemical reactions, synthetic nanochannels and nanopores are the focus of growing scientific interest¹. Now, two groups of researchers have shown that nanochannels filled with an electrolyte behave like the electrical diodes that regulate the direction of current in power supplies and surge protectors. Writing in *Nano Letters*, Ivan Vlasiouk and Zuzanna Siwy² of the University of California, Irvine, and

Arun Majumdar and co-workers³ at the University of California, Berkeley, the University of Tokyo and the Lawrence Berkeley National Laboratory report that when a positive voltage is applied to a nanofluidic diode, the ion current is several hundred times larger than with the corresponding negative voltage.

The finding that these devices work like diodes confirms a theoretical prediction made by Hirofumi Daiguji and colleagues at the University of Tokyo in 2005 (ref. 4). The diode operation results from the interaction between permanent surface charges inside the nanochannel with ions in the electrolyte solution, and the work demonstrates that the enormous surface to volume ratio of these objects leads to new phenomena at

the nanoscale that do not occur at the microscale.

The 'heart' of a typical diode is the interface between an n-type semiconductor, in which the majority of the charge carriers are electrons, and a p-type semiconductor, in which the majority of the carriers are holes. Fixed donor atoms contribute the electrons and holes in the n- or p-type semiconductors, so both sides of the device are electrically neutral far from the interface. The electrons and holes want to spread out as much as possible, so electrons will move from the n-type to the p-type side and vice versa for the holes, leaving behind a zone of static charge from the fixed dopant atoms. The build up of negative charge on the p-type side and