

Four years later Estermann and Stern recorded the diffraction patterns produced by helium atoms and hydrogen molecules scattering off the surface of a sodium chloride crystal<sup>2</sup>.

The first double-slit experiment with electrons was performed 30 years later, by Jönsson, using a copper grating with a period of 1  $\mu\text{m}$  (Fig. 1a)<sup>3,4</sup>, and the build up of the interference pattern when there was only one electron in the apparatus at a time was first recorded by a group in Bologna in 1976<sup>5</sup> and later by a group at Hitachi in 1989<sup>6</sup>. Both the Bologna and Hitachi groups also made movies<sup>7,8</sup> showing how the wave-like diffraction pattern gradually builds up in the spatial distribution of a large number of stochastically arriving single particles.

The diffraction of atomic and molecular beams from crystal surfaces proved to be a useful and versatile tool for surface science. However, this approach does not work if the molecules are fragile (because they will break up if they hit the surface) or if they interact too strongly with the surface (because they will undergo inelastic scattering processes that wipe out the coherence needed to form the interference pattern).

The angle through which particles are diffracted by a grating scales as the ratio of the de Broglie wavelength to the period of the grating. The de Broglie wavelength in an atomic or molecular beam is typically on the order of 100 pm or less, and for the heavy molecules used in the Vienna experiment it can be as short as  $\sim 5$  pm. Therefore, the grating period needs to be of the order of 100 nm or less to make the diffraction angle large enough to allow the diffraction peaks to be resolved. In a pioneering experiment in 1988, Dave Pritchard and co-workers at MIT observed the diffraction of a beam of sodium atoms by a gold grating with a period of 200 nm (ref. 9). This was the first time that a beam of atoms had

been diffracted by a fabricated structure. Subsequently, free-standing gratings with a period of 100 nm have routinely been made by Tim Savas and Hank Smith, also of MIT<sup>10</sup>, and have been used by groups around the world in matter-wave experiments<sup>11</sup>.

In 1999, the Vienna group used such a grating (Fig. 1b) to observe the diffraction of  $\text{C}_{60}$  molecules<sup>12</sup>, which have a mass of 720 AMU, and in 2011 they observed the diffraction of  $\text{C}_{60}[\text{C}_{12}\text{F}_{25}]_{10}$  molecules, which contain 430 atoms and have a mass of 6,910 AMU, making them the largest molecules ever to demonstrate wave-like behaviour<sup>13</sup>. However, they did not use a conventional grating in that experiment, instead they used a laser to create a standing light wave, which acted as a grating, and they observed the near-field diffraction patterns that were produced when beams of various large molecules were scattered by this optical grating. Observing far-field diffraction patterns for such large molecules is not possible with gratings of the type shown in Fig. 1b because the interactions between the molecules and the grating material would diminish the effective width of the slits in the grating too much<sup>14</sup>. Now Arndt and co-workers have laid the groundwork for studying the diffraction of large molecules by conventional gratings by taking advantage of advances in nanofabrication and nano-imaging.

First, they have made a new generation of free-standing 100-nm-period gratings with an unprecedented thickness of 10 nm (Fig. 1c). The interactions between the molecules and the grating material are reduced to a tolerable level in such a thin grating. Second, they have implemented a laser-desorption molecular-beam source that allows them to produce a beam of large, complex organic molecules; such beams cannot be prepared by a conventional oven source as the molecules would fragment because of the heat. Third, they have

been able to use a form of fluorescence microscopy that offers resolution beyond the diffraction limit<sup>15</sup> to detect diffraction patterns with single-molecule sensitivity and with a spatial resolution of 10 nm. This detection scheme is at least four orders of magnitude more sensitive than conventional electron-impact ionization methods.

The results obtained by Arndt and co-workers demonstrate how nanotechnologies will enable matter-wave diffraction experiments to be performed with molecules that are larger, more massive or more complex than at present. Moreover, these experiments should provide new insights into the differences between the quantum and classical worlds.  $\square$

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## MASS SENSING

# Devices reach single-proton limit

An ultrasensitive nanomechanical mass sensor based on a single carbon nanotube could have applications in mass spectrometry and surface science.

Wayne Hiebert

**M**icrocantilevers have been used to measure small masses<sup>1,2</sup> since the 1990s, and around a decade ago it became clear that if these cantilevers could be made small enough,

their sensitivity would approach the mass of a single proton. A race to the bottom ensued with demonstrations of ever better levels of sensitivity — from femtogram<sup>3</sup> ( $10^{-15}$  g) through attogram<sup>4</sup> ( $10^{-18}$  g) and

zeptogram<sup>5</sup> ( $10^{-21}$  g) to sub-zeptogram<sup>6–8</sup>. Writing in *Nature Nanotechnology*, Adrian Bachtold and co-workers now report that they have passed another milestone in this race by demonstrating yoctogram

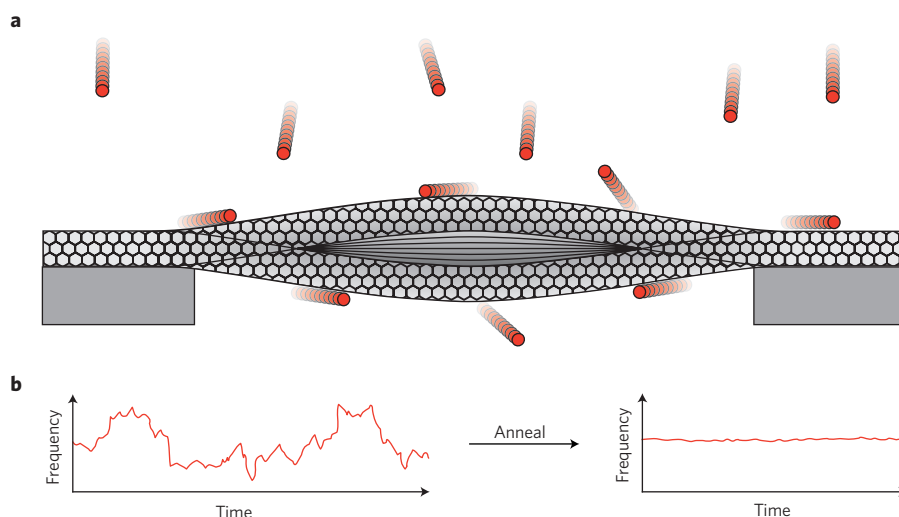
( $10^{-24}$  g) sensitivity with a nanotube-based mass sensor<sup>9</sup>.

This is exciting because the ability to distinguish masses that differ by one proton mass (1.67 yoctograms) could lead to mass spectrometers based on nanotubes or other nanomechanical resonators<sup>10</sup> that would have several advantages over existing mass spectrometers. Conventional mass spectrometry involves three stages: ionization, separation and detection. Mechanical mass spectrometry could eliminate the need for the first two stages because it works with neutral species (thus removing the need for the ionization stage) and because it measures the mass of particles directly (thus removing the need for distinct separation and detection stages). Moreover, nanomechanical mass spectrometers would be much smaller than mass spectrometers (chip-scale compared with table-top or larger).

But this is not the only reason to be excited. Existing surface-science techniques tend either to observe molecules that have been 'frozen' into place by the use of low temperatures, or to treat diffusing atoms in ensembles. The sensitivity offered by nanomechanical-based mass sensors could be used to study the adsorption, desorption and diffusion of individual atoms and molecules on surfaces<sup>11</sup>. Figure 1a illustrates how atoms often move around constantly after landing on a surface.

Mass sensors based on nanotubes are inertial: the nanotube behaves like a spring, which means that it has a characteristic resonance frequency that is inversely proportional to the square root of its effective mass. Therefore, if you make the effective mass extremely small to start with (by, for example, using a carbon nanotube as the spring), and ensure that the frequency is very stable (one part per billion is not unheard of), you will be able to measure exquisitely small masses, and even register individual atoms or molecules landing on the nanoresonator<sup>6–10</sup>, by monitoring changes in its resonance frequency.

Bachtold and co-workers — who are based at the Catalan Institute of Nanotechnology in Barcelona and the ICMAB-CSIC laboratory, also in Barcelona — start by observing the behaviour of atoms and molecules indirectly. As they cool their mass sensor in vacuum, a few gas molecules adsorb onto the device. Monitoring the resonance frequency of the nanotube as a function of time (using an electrical frequency modulation mixing method<sup>12</sup>), they observe more abrupt jumps in the signal than expected (Fig. 1b, left). This happens, they argue, because of the presence and migration of the adsorbates acquired during cooling (Fig. 1a). The frequency shift



**Figure 1** | Nanomechanical mass sensing. **a**, The mass sensor developed by Bachtold and co-workers contains a single carbon nanotube suspended over a trench in a silicon or silicon dioxide substrate and attached to metal electrodes at both ends<sup>9</sup>. This nanotube vibrates with a characteristic resonance frequency, which changes as atoms and/or molecules (shown in red) land on and migrate along the nanotube. **b**, Schematic graphs showing the resonance frequency versus time before (left) and after (right) the nanotube is annealed by passing an electric current through it. Before annealing, the diffusion of atoms or molecules along the nanotube leads to frequency fluctuations that limit the performance of the device as a mass sensor. These fluctuations are dramatically reduced by annealing, which allows very small changes in frequency (and, therefore, very small changes in mass) to be detectable. The thickness of the red line can be thought of as roughly equivalent to the frequency change associated with one proton mass. These devices also allow the interplay between the adsorption, desorption and diffusion of single atoms or molecules to be studied.

depends on both the mass of the molecule and its position on the nanoresonator (with molecules adsorbed near the centre of the nanoresonator leading to a larger frequency shift than molecules adsorbed near the ends): therefore, the resonance frequency will change as molecules diffuse back and forth along the surface of the nanotube. Moreover, the frequency response becomes much more stable after an electric current is run through the nanotube, which is consistent with the molecules being 'boiled off' the surface via local Joule heating (Fig. 1b, right). This 'reset' function will be important for application in mass spectrometry.

The resolution of a nanomechanical mass sensor is limited by the level of the fluctuations in the measurement of the resonance frequency, and the Barcelona team demonstrates a mass resolution of 1.7 yoctograms (which is very close to the mass of the proton). The team uses this record sensitivity to track the adsorption of two species — xenon atoms and naphthalene ( $C_{10}H_8$ ) molecules — in separate experimental runs. They also employ two different methods for tracking the resonance frequency. The first method involves taking repeated snapshots of the resonance curve and can handle larger fluctuations without resetting. The second method, which involves

a computer-controlled open feedback loop, offers better resolution, but suffers from dead time during large jumps in frequency.

In the experiments, a stream of atoms or molecules is directed at the sample from a room-temperature reservoir. In the experiments with naphthalene, the feedback system detects clear downward steps in frequency (Fig. 3b in ref. 9). These are the hallmark of individual adsorption events, and this experiment constitutes a demonstration of nanomechanical mass spectrometry with the smallest molecules so far.

The xenon experiments are even more interesting because of what they don't see — despite the record sensitivity of their device, Bachtold and co-workers do not see clear evidence for single xenon adsorption events. This is probably because the xenon binding energy on the nanotube surface is too low to keep the atoms in place, so they move about between local energy minima, diffusing on and off the ends of the nanotube or desorbing (Fig. 1a). A wealth of information about the surface dynamics is hidden in the fluctuations<sup>11</sup> observed by Bachtold and co-workers (Fig. 3a in ref. 9) and longer data runs will surely bear statistical fruit. To illustrate this potential, the authors extract the xenon binding energy and confirm that desorption is a thermal process, with more

atoms accumulating at lower temperatures. They find that the binding energy for xenon on a nanotube is 30% lower than for xenon on graphite, and explain this difference in terms of reduced van der Waals interactions (due to the surface of the nanotube being curved and containing only one layer of carbon atoms, whereas graphite is flat and contains several layers of carbon atoms).

The movement of atoms and molecules along the nanotube is a double-edged sword. For researchers building mechanical mass spectrometers it is one more potential source of noise and error (although it might be possible to modify the carbon lattice to create trapping sites that will stop this

movement and improve performance). However, the fact that atoms can move on the surface, combined with the extraordinary mass resolution that is available, means that surface scientists will be able to study a wide variety of processes and phenomena — such as nucleation processes in thin-film growth and the dynamics of monolayer formation — at the level of single atoms and single-adsorption sites. □

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## NANOELECTRONICS

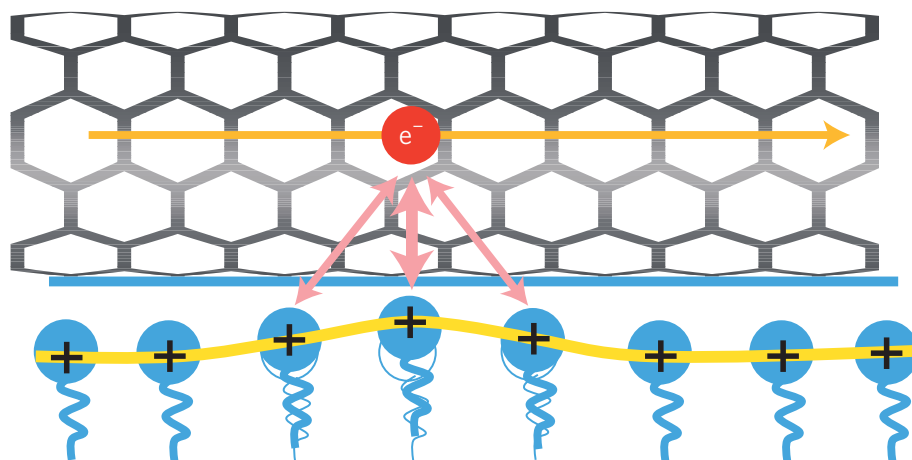
# Nanotubes throw their heat around

A direct current flowing through a carbon nanotube on a substrate heats the substrate but not the nanotube, and it may be possible to exploit this phenomenon in the thermal management of nanoelectronic devices.

Amin Salehi-Khojin, Wei Zhu and Richard I. Masel

When carbon nanotubes and graphene are described as attractive electronic materials, it is usually because of their high carrier mobilities<sup>1,2</sup> and atomic-scale dimensions, which are characteristics expected to aid efforts to reduce the size of electronics<sup>3,4</sup>. However, the potential impact of such carbon nanostructures for thermal management — arguably an equally important challenge facing the electronics community — is less clear. Writing in *Nature Nanotechnology*, John Cumings and co-workers at the University of Maryland, College Park report that they have discovered a surprising new facet of charge transport in one dimension: a direct current passing through a carbon nanotube can heat the substrate under the nanotube, but leave the nanotube itself cool<sup>5</sup>.

The Maryland researchers overcame significant experimental difficulties to prove that this effect, which they call remote Joule heating, was occurring. First they prepared and deposited pristine nanotubes, to avoid defects that would otherwise create thermal hotspots. Second, they minimized the effect of contact resistance by increasing the area of overlap between the nanotube and the metal contact relative to that between the nanotube and the substrate. This was important because the low thermal and electrical resistivities of carbon nanotubes would cause the electrode contacts to dominate resistivity data. Finally, the researchers used a technique called electron thermal microscopy (ETM) to



**Figure 1** | A possible model for substrate heating by a direct current flowing through a nanotube. Atoms at the surface of the substrate (blue) experience a time-varying electric field with each electron (red) passing through a nanotube (grey). Because of their close proximity to the electron, the atoms are displaced from their equilibrium positions (outlines) even though they are neutral, and are subject to a spring-like restoring force (blue wavy lines). This interaction also slows the electron down.

measure the temperatures of their nanotube, substrate and contacts. This technique overcomes the spatial resolution limits of infrared imaging techniques by using an electron microscope to monitor nanoscale metallic indium islands as they change from solid to liquid (and back again) in response to local temperature fluctuations<sup>6</sup>. The key result of this careful experimentation and analysis was the observation that the substrate

underneath the nanotube and between the metallic contacts heated up before the nanotube or the contacts, suggesting extremely effective thermal transport from the nanotube to the substrate.

This means that most of the energy dissipation in electronic devices based on carbon nanotubes can be made to occur in the substrate, opening new possibilities for thermal management in these systems.