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MASS SENSORS

Weighing single atoms with a nanotube

Researchers have used a vibrating carbon nanotube to set a new record for nanomechanical mass sensing. Could this approach — currently being pursued by three independent groups — lead to a new type of mass spectrometer?

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An inertial balance measures the mass of an object by determining the acceleration produced by a known force and relying on Newton's second law of motion: force equals mass times acceleration. Such measurements usually involve determining the frequency at which a mass attached to a spring oscillates — the larger the mass, the lower the frequency. Of course, the spring itself always has some mass, so the addition of a very small amount of extra mass will cause only a negligible frequency change for most balances. Writing on page 533, Kenny Jensen, Kwanpyo Kim and Alex Zettl¹ from the University of California, Berkeley report that they have used a carbon nanotube to make the lightest inertial balance ever, and have gone on to make measurements with atomic mass sensitivity. In effect they have made a nanoscale mass spectrometer. Subsequently two other groups — Adrian Bachtold of the CIN2 laboratory in Spain and co-workers², and Marc Bockrath of Caltech and co-workers³ — have reported similar results.

Building such a mass spectrometer is one of the main goals in the burgeoning field of nanomechanics. Mass spectrometry typically involves ionizing an atom or molecule, accelerating it through an electric potential, and then separating the atomic or molecular species on the basis of their charge-to-mass ratio. Many sophisticated techniques have been used for the ionization and separation, but no current instrument works with uncharged atoms or molecules. An inertial balance relies only on the mass and does not, therefore, require the ionization or acceleration stages that might damage the molecules being measured. This means that a nanoscale inertial balance would be able to measure the mass of biological macromolecules that might be too fragile to be measured by conventional instruments⁴. To be useful, a mass spectrometer must

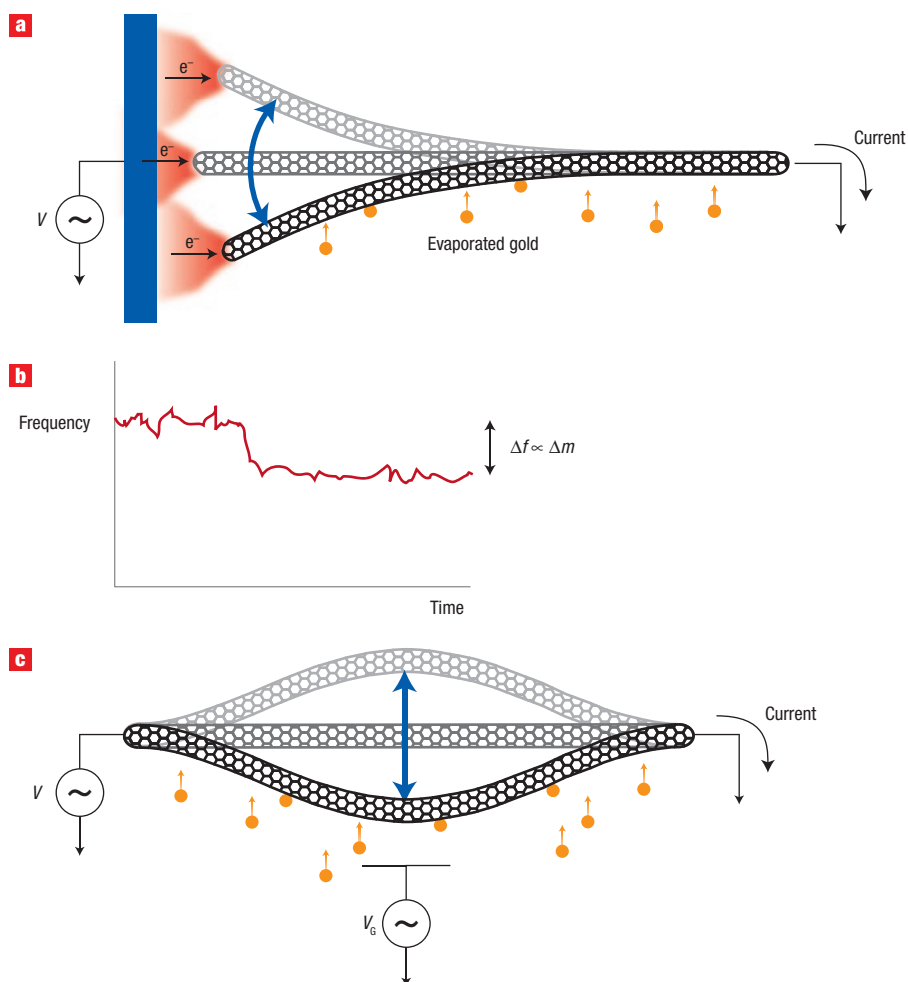


Figure 1 Three groups have shown that nanotube mass sensors are capable of atomic resolution. In all three experiments the resonant frequency of the nanotube changes when one or more atoms stick to it, and this change can be detected by measuring the current through the nanotube as a function of time. **a**, The Berkeley group¹ measure the field-emission current between the electrode on the left and the nanotube. **b**, The change in resonant frequency Δf of the nanotube is proportional to the change in mass Δm . **c**, The CIN2² and Caltech³ groups measure the current through a nanotube that is clamped at both ends and modulated by a gate voltage V_g .

have a resolution of 1 Dalton (1.66×10^{-24} g or 1.66 yoctogram) — in other words, it must be able to distinguish the mass of a single nucleon.

The sensitivity of nanomechanical mass sensors has been rapidly increasing

through a glossary of obscure metric prefixes: femtograms⁵ (10^{-15} g), attograms⁶ (10^{-18} g) and zeptograms⁷ (10^{-21} g). This dramatic improvement has been due to advances in three areas: smaller mechanical resonators, which mean that the fractional change in

mass is large; higher resonant frequencies (achieved by lowering the mass while keeping the resonator stiff), so that a small fractional change in frequency is still absolutely large; and improved readout techniques to detect the motion. These devices have all used top-down lithography and etching of metals and semiconductors to fabricate the devices, which limits their size to tens of nanometres at a minimum.

All three groups take advantage of the unique properties of carbon nanotubes. Nanotubes are exceptionally light, stiff and small, making them ideal for use in nanomechanical mass sensing. Several recent experiments have used nanotubes as mechanical resonators^{8,9,10}, with various techniques employed to measure the motion.

The Berkeley group exploits the very large field-emission current from a biased nanotube¹¹, which they previously used to demonstrate a 'nanotube radio'¹². In the nanoscale mass spectrometer a double-walled carbon nanotube is fixed to a negative electrode and aligned to point at a positive electrode in ultrahigh vacuum at room temperature (Fig. 1a,b). The extremely sharp nature of the nanotube concentrates the electric field near its tip, and a field-emission current flows between the nanotube and the positive electrode, depending very strongly on the separation between them. By modulating the voltage on the positive electrode, the nanotube can be forced to vibrate, which in turn changes the field-emission current¹³. Because of the nonlinearity of the current, the vibration signal (at several hundred megahertz) can be modulated down to audio frequencies, which was demonstrated by playing *Good Vibrations* by The Beach Boys on the nanotube radio.

The CIN2 and Caltech groups both use techniques that involve current flowing through a nanotube clamped at both ends (Fig. 1c). By applying a voltage to a capacitively coupled gate, the conductance

of the nanotube is changed, causing the current to modulate through it. The CIN2 group relies on the change in doping caused by the field effect of the gate at both room temperature and low temperature⁹. The Caltech group uses the fact that such a nanotube at low temperature can become a single-electron transistor — the charge on the nanotube is quantized and the gate voltage can cause dramatic changes in conductivity as the nanotube vibrates. Clamping the nanotube at both ends reduces the amplitude of the vibrations in these experiments, but it also makes it easier to align the devices.

In all three experiments atoms were directed towards the nanotube, with some of them hitting the nanotube and sticking to it. The atoms change the mass of the nanotube and slow it down, thus reducing its resonant frequency (Fig. 1b). All three groups have a resolution of approximately one atom in mass. This represents a record for sensitivity of an inertial balance, but is still a factor of about 100 from being useful as a mass spectrometer. However, by examining the noise spectrum of the frequency shifts, the Berkeley and Caltech teams can see the discrete nature of the atoms arriving at the nanotube ('atomic shot noise'), and the sizes of these shifts are consistent with the mass arriving in chunks of about the size of an atom.

As well as needing an improvement in resolution by a factor of about 100, there are still questions to be answered before a practical mass spectrometer can be made. Most important is the problem of determining where the atom lands on the nanotube. Because some parts of the tube vibrate much more than the base, an atom that lands near the fast-moving region has a much greater effect on the resonant frequency (equivalent to many atoms arriving at the base). Moreover, in addition to the lowest-order vibrational mode shown for the

cantilever (Fig. 1a) and the doubly clamped nanotube (Fig. 1c), higher-order modes in which the maximum displacement occurs at two or more positions along the nanotube are possible. These higher-order vibrational modes could be exploited in experiments because the change in the resonant frequency also depends on how much the nanotube moves at the absorbing point. This means that measurements made with higher-order modes could potentially allow both the mass and landing position to be determined¹⁴. Another problem is determining how well various species stick to the tube, and how floppy macromolecules interact with the moving nanotube. The assumption that adsorbing molecules change the mass of the nanotube, but not the stiffness, is certainly not true for all molecules, further complicating the analysis.

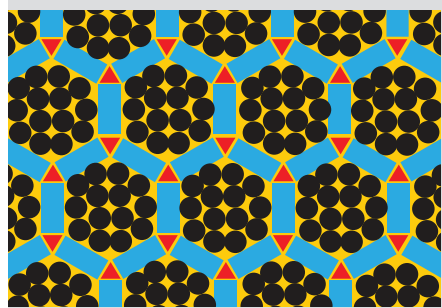
So do these advances pave the way for a new form of mass spectrometer? It remains to be seen, but with a new metric prefix before gram arriving every few years, the prospects look good. And it is tempting to imagine many of these sensors integrated on a chip, each gently shaking its molecules and coaxing out their secrets.

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PATTERNED SURFACES

An organized union



Self-assembly offers unique possibilities for creating ordered and functional surfaces. Using non-covalent interactions, researchers have constructed open networks that leave nanoscale areas of the surface uncovered. Alternatively, self-assembled monolayers offer a flexible route to tailoring the properties of an entire surface. Now, Rafael Madueno, Manfred Buck and colleagues at St Andrews University have combined these two approaches to form a

carefully designed and versatile surface (*Nature* **454**, 618–621; 2008).

The team formed a hexagonal network of hydrogen-bonded organic molecules with a period of 3.5 nm on a gold surface (left). Made of two-fold (blue) or three-fold (red) symmetric molecules, the network acted as a template for thiol molecules (black), with the self-assembled monolayers only forming in the open cavities.

Owain Vaughan