because it can occupy any region of the parameter space depending on the degree of saturation of calcium carbonate: undersaturated water will dissolve limestone (which is how a limestone cave is formed) depending on flow rate[3].

On a more applied level, limestone precipitation under flow is a process of great industrial significance; being responsible for scaling in pipes and boilers it creates considerable financial losses. Moreover, travertine terracing is far from the only example of this class of system. We see almost identical patterns in systems where precipitation is connected with heat flux away from a flowing sheet of water, such as terraces of water ice on sloping surfaces (Fig. 2) and silica terraces around hot springs. In other situations, the association between flow rate and surface growth may be due to consolidation of the surface under ballistic deposition, such as in the so-called litter dams forming from leaves and pine needles on forest paths after a heavy rainfall.

So next time you go to a hot spring, limestone cave, a forest, or anywhere icy, watch out for those steps. Not only are they strange and beautiful — they represent a phenomenon of general significance, and after reading the article of Veysey and Goldenfeld you will also know something about how they form.

Published online: 16 March 2008.

References
1. Veysey, J. II & Goldenfeld, N. *Nature Phys.* **4**, 310–313 (2008).
2. Hammer, Ø. *et al. Earth Planet. Sci. Lett.* **256**, 258–263 (2007).
3. Buhmann, D. & Dreybrodt, W. *Chem. Geol.* **48**, 189–211 (1985).

CARBON NANOTUBES

Old nanotubes, new tricks

Despite more than a decade of study, single-wall carbon nanotubes still have the ability to surprise. One recent study finds that in ultraclean nanotubes an unexpectedly strong spin–orbit coupling arises; another demonstrates their ability to support one-dimensional Wigner crystals.

Jesper Nygård
is at the Niels Bohr Institute and Nano-Science Center, University of Copenhagen, DK-2100 Copenhagen, Denmark.
e-mail: nygard@nbi.dk

Nanoscale conductors are excellent laboratories for studying how fermions interact. Although the quantum mechanical nature of electrons — the best known of the fermions — is well established, an accurate description of their behaviour when confined within nanoscale structures can challenge even the most advanced of theoretical approaches. Consequently, the construction of model electron systems whose properties can be reliably controlled is vital to understanding them. Carbon nanotubes are perhaps the most popular of such systems. But after a decade of study, they still have the potential to surprise. On page 314 of this issue[1], Deshpande and Bockrath observe the ability of nanotubes to support a one-dimensional Wigner crystal — an unusual structure consisting of a spontaneously formed array of highly localized electronic states. And in a report in *Nature*[2], Kuemmeth and colleagues demonstrate that the spin and orbital motions of electrons in nanotubes are coupled, disproving the widespread expectation that these degrees of freedom should be independent.

Even at the very low temperatures, most of the electrons in a solid will have high kinetic energies. This is because, being fermions, they are forced to successively fill a ladder-like sequence of energy states up to the Fermi energy, which is typically of the order of 1 eV. In most instances, this kinetic energy has a more important role in governing the behaviour of individual electrons than the repulsive coulombic interaction between them. Only at a very low electron density does this interaction become dominant. In 1934, Wigner predicted that at such a density, an electron gas should freeze into an ordered state where its individual electrons become strongly localized to form an ordered array[3]. Unlike the periodic electronic structure of a conventional semiconducting crystal, this 'Wigner crystal' forms spontaneously with a structure that is independent of the positive ions of the atomic crystal in which it resides.

The formation of a Wigner crystal requires an exceptionally clean system to support it, with minimal disorder. One place in which such conditions are met is at a liquid helium surface, on which electrons can float freely, hovering some ten nanometres above. The emergence of 2D Wigner crystals were observed in this type of system in 1979 (ref. 4). Wigner crystallization can also occur in solid-state semiconductors where sufficiently low electron densities can be achieved. Quantum dots, typically made from group III–V semiconductors, provide versatile systems whose characteristics (such as their electron density, coupling strength, spin states, energy levels and so on) can be tuned either electrically or with external magnetic fields[5,6]. In such systems, stable structures of just a few electrons, known as 'Wigner molecules', can form[7]. But to support enough electrons for forming a canonical crystal, things get more difficult.

More than a decade ago it was shown that single-wall carbon nanotubes could act as quantum dots[8,9], and have since been shown to behave as ideal 1D conductors. Carbon nanotubes enable a variety of intriguing quantum transport phenomena to be studied with arguably greater clarity and control than is possible in other quantum dot systems. The behaviour of a finite nanotube can be modelled reasonably well by simple 1D particle-in-a-box models, and many experiments have suggested that the electronic spectrum of an ideal nanotube can be fully described by a structure whose energy states are four-fold degenerate (Fig. 1a). This four-fold degeneracy arises from the expectation that the spin of an electron (which can be either 'up' or 'down') and its orbital motion within a nanotube (which can be either clockwise or anticlockwise) are independent (Fig. 1b). Both the present studies[1,2], however, reveal crucial shortcomings in this otherwise attractive model, and discover some surprising new features.

In their study, Deshpande and Bockrath[1] investigate electronic transport in semiconducting nanotubes grown with particular care to avoid lattice defects and impurities. This was achieved by growing

the carbon nanotubes directly on the chip as the very last step of the fabrication sequence — an approach that has previously been shown to provide cleaner nanotube devices than those produced following post-growth processing[10]. They control the gate voltage of the devices so that its Fermi level lies near the edge of the nanotube bandgap, and map how the first few tens of charge carriers (holes in their case) occupy the nanotubes. By determining the spin orientation of the charges from the response to an external magnetic field, they find that, surprisingly, around a dozen enter the nanotube all with the same spin. Such behaviour is highly unlikely to occur in the case of conventional filling of its electronic states, in which one would expect to observe a sequence of alternating spin orientations (Fig 1a). This is because the Pauli exclusion principle dictates that the two electrons that occupy a given energy level must have opposite spin. Therefore, for electrons of the same spin to fill a given electronic structure, they would have to occupy a series of different levels of increasing energy, leaving these levels only half filled, which is costly in terms of energy and thereby thermodynamically unfavourable. This, however, is for a case where the electron wavefunctions occupy essentially the same region of space, in extended quantum states. If the parallel-spin-oriented electrons are strongly localized to occupy different points in space, they can all occupy low-lying energy states — a situation that is satisfied by the formation of a Wigner-crystal-like arrangement of electrons (Fig. 1c).

Kuemmeth and colleagues[2] find in their study that the orbital motion of the electrons in a nanotube also has a role, and demonstrate that the expectation, from the simple model of Fig. 1a, that their spin and orbital degrees of freedom be independent is wrong. By mapping the magnetic field behaviour of transport in a quantum dot containing just a single electron, they resolve the electronic structure of a nanotube with unprecedented resolution and clarity. Earlier experiments have used nanotubes where interactions due to disorder or multiple electrons have masked this effect. But by allowing just a single electron to be trapped on the nanotube, effects of electron–electron interactions that might otherwise confuse the picture are avoided. In doing so, Kuemmeth and colleagues observe a pattern in the nanotube's electronic spectrum that exactly matches that expected for a system that includes spin–orbit interactions. The authors argue that this arises from a nanotube's cylindrical geometry, which induces a significant spin–orbit coupling that is not simply adopted from its underlying hexagonal (graphene) crystal structure. As a result, the four-fold degeneracy, and even the electron–hole symmetry, is broken.

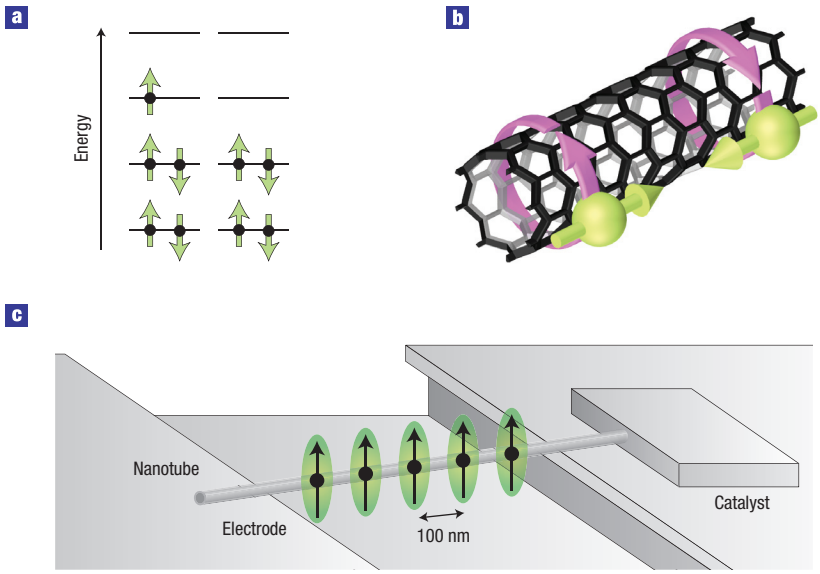

Figure 1 Electrons in carbon nanotubes. **a**, The widely expected energy-level spectrum for a finite, defect-free carbon nanotube (arrows indicate the spin directions). The Pauli exclusion principle dictates that for two electrons to occupy the same energy level they must have antiparallel spin. **b**, Four-electron shells are anticipated due to the two possible degeneracies for electronic states in tubes; spin direction up or down (green arrows), and clockwise or anticlockwise orbital motion (purple). An experiment using ultraclean nanotubes demonstrates the unexpected result that these spin and orbital degrees of freedom are strongly coupled[2]. **c**, Wigner crystal in a carbon nanotube. The nanotube originates from the catalyst materials and is suspended between the two metal electrodes on the banks of the trench. In the Wigner-crystal regime, a few charge carriers are confined to the nanotube and organize into an array of localized states[1].

The result will come as a surprise to most researchers, not only because it seems to contradict a large number of earlier experiments, but for the fact that its proposed mechanism was unexpected. It is well known that in other carbon-based materials the spin–orbit interaction is very weak and the same was expected to be the case for nanotubes. In fact, together with the absence of nuclear magnetic moments in carbon (^{12}C), a weak spin–orbit coupling was expected to lead to long spin-relaxation times in carbon nanotubes — often emphasized as a major reason for envisaging spin-based information processing based on nanotubes.

The reported experiments exemplify the richness of the physics to be found in nanotubes with few electrons, and demonstrate how much still remains to be understood, such as how spin–orbit interactions[2] affect the Wigner-crystal picture[1]. Such interactions could enable much easier and more localized electric-field-mediated control over spin states than is possible with a magnetic field[11] — control that could be useful for spintronics. And given that the spacing between charges in a nanotube Wigner crystal could reach up to the order of hundreds of nanometres, one could even conceive of it as a ready-made array of 'qubits'. On this scale, arrays of gate electrodes might readily be able to address each of these carriers individually as well as control the coupling between them. Whether the Wigner crystal would survive such a perturbation, though, is not clear. Certainly, more work needs to be done to answer such questions. But important avenues have certainly been opened for exploring new physics and electronics based on carbon nanotubes in the quantum regime.

References

1. Deshpande, V. & Bockrath, M. *Nature Phys.* **4,** 314–318 (2008).
2. Kuemmeth, F., Ilani, S., Ralph, D. C. & McEuen, P. L. *Nature* **452,** 448–452 (2008).
3. Wigner, E. *Phys. Rev.* **46,** 1002–1011 (1934).
4. Grimes, C. C. & Adams, G. *Phys. Rev. Lett.* **42,** 795–798 (1979).
5. Kouwenhoven, L. P. & Marcus, C. M. *Phys. World* **11,** 35–39 (June 1998).
6. McEuen, P. L. *Science* **278,** 1729–1930 (1997).
7. Reimann, S. M. & Manninen, M. *Rev. Mod. Phys.* **74,** 1283–1342 (2002).
8. Tans, S. J. *et al. Nature* **386,** 474–477 (1997).
9. Bockrath, M. *et al. Science* **275,** 1922–1925 (1997).
10. Cao, J., Wang, Q. & Dai, H. *Nature Mater.* **4,** 745–749 (2005).
11. Nowack, K. C., Koppens, F. H. L., Nazarov, Yu. V. & Vandersypen, L. M. K. *Science* **318,** 1430–1433 (2007).