Nanotube mystery

Science typically works through the slow accumulation of evidence. Experiments and observations grow more extensive and accurate; methods more precise, consistent and controllable; and errors and spurious dead ends become recognized as such. No one may be able to define the scientific method, but it somehow rests on a stubborn unwillingness to be fooled — and a continuing suspicion that we might be.

The process is often messier than textbook histories of science suggest. Single experiments rarely lead to the sharp rejection of a theory or hypothesis; there are too many other possibilities. Fields routinely labour onward through clouds of seemingly contradictory experimental results, yet they get somewhere in the end. One recent example involves theoretical and experimental efforts to pin down the nature of heat conduction in simple systems of low dimension — in one-dimensional wires, for example. Two decades of research has apparently clarified some basic issues, but others still persist.

In three dimensions, we know empirically — from literally millions of engineering applications — that heat in most materials flows in keeping with Fourier's law, first written down by Joseph Fourier nearly two centuries ago. Energy spreads through a material by diffusive motion. It's intriguing that there still exists no strict derivation of this equation from a microscopic Hamiltonian, but the equation works. That's not generally true in lower dimensions, though.

Twenty years ago, physicists widely expected heat transfer in low dimensions to show some strangeness, though much was unknown. In the late 1990s, theorists analysing simple models of conductors in one dimension found evidence for a deviation from Fourier's law. Results implied that the thermal conductivity of a one-dimensional system of length L would actually grow as L^{α}, with $\alpha > 0$. As a system grows longer, its thermal conductivity also grows, in principle without bound.

Yet, as it so often goes, not all one-dimensional models gave similar results. In particular, some models devised to explore systems without momentum conservation did turn out to follow the intuitive relation described by Fourier. As of 2005 or so, the theoretical picture was mixed.

Naturally, some physicists turned to experiments with real systems, using carbon nanotubes as approximate or quasi-one-dimensional conductors. Here, calculations based on phonon transport predicted that — for ideal, defect-free nanotubes up to about 1 mm in length — conductivity should grow with length as L^{α}, with α between 1/3 and 1/2. In 2008, experiments using these thin wires with lengths up to 3 μm showed conductivity increasing with length, although the exponent α was in the range between 0.6 and 0.8 (C. W. Chang *et al.*, *Phys. Rev. Lett.* **101,** 075903; 2008). Not quite as expected.

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Since then, experiments have been held back by a host of problems in fabricating nanomaterials with extreme aspect ratios, for example, or in measuring conductivity with the required sensitivity. Other complications have come from natural defects and disorder. Aside from experimental inconsistencies, theoretical issues also remain, with some theorists arguing that a nanotube should in fact pass through an anomalous phase of behaviour with increasing length, but then return back to normal thermal conduction at some point.

But we may be getting somewhere, in the usual erratic and gradual way. Very recent experiments have now probed nanotubes with lengths reaching up to 1 mm. Victor Lee and colleagues at the National Taiwan University synthesized these ultralong, single-wall nanotubes using chemical vapour deposition, then picked up samples using a special manipulator and placed them on a grid of parallel suspended microscopic beams in order to measure their thermal conductivity (*Phys. Rev. Lett.* **118,** 135901; 2017). The idea was to apply heat precisely to the beams, on the understanding that a small portion of the power would flow through the nanotube and raise the temperature of a microscale sensor. Using the geometry of the beam setup, the team could then calculate the effective thermal conductivity of the nanotube.

The sample nanowires examined in these experiments ranged in length over three orders of magnitude, from a few micrometres up to 1.039 mm. Again, measurements of the associated thermal conductivity showed a consistent trend of increasing conductivity as length L grows. But estimating the actual exponent α — to make a definitive comparison with theory — required some further work. Due to radiative heat loss from the nanowire surfaces, the measurements actually only reflect a lower bound of the actual conductivities. The authors had to correct for this radiative effect. Doing so, they found in the end anomalous behaviour in all cases, with the exponent α between 0.1 and 0.5. For the longer wires, α fell into the narrower range of 0.2 to 0.5, suggesting that these wires come closer to an ideal, quasi-one-dimensional system.

So, after quite some time and lots of confusion, the experimental results now agree fairly well with the original theoretical predictions for nanotubes. One interesting point — the exponents measured here are smaller than previous results determined by the micrometre-long nanotubes, which fell into the range 0.6 to 0.8. Why is not clear, although the authors suggest that, given the wires' short length, some phonons travelling through ballistically (that is, without scattering) could have contaminated the results. Ballistic thermal conduction would have an exponent $\alpha = 1$. It will take further work to verify this.

All in all, these experiments give a satisfying resolution to confusion over heat conduction in one dimension. But more remains to be settled: as Lee and colleagues point out, the nanotubes in their experiments are actually anything but ideal and defect free. About 1% of the carbon atoms in the nanotubes are the isotopic ^{13}C, and these long wires also have many impurities and defects. The divergence of conductivity emerges nonetheless, and this observation conflicts with theories predicting that defects should destroy the divergent behaviour. For some reason, in these wires, it persists for much longer distances than theoretically anticipated.

That's another puzzle for the future, as is learning if insight into the one-dimensional problem can help find a theoretical basis for Fourier's law in three dimensions. There are likely to be many more surprises to come. ❐

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