

New horizons in inner space

The voids inside fullerene molecules and their larger relatives offer a cosseted environment in which unusual physics and chemistry may be possible. Fundamental science, as well as applied research, should benefit.

THE old riddle has it that there are two sides to a sphere — inside and outside. From the outside, the closed carbon cages of fullerenes and 'nanotubes' are potential building blocks for chemistry and technology. From this perspective, C_{60} itself can be regarded as a kind of giant pseudo-atom. But from the inside, these carbon structures acquire a new character: that of a microcosm (or perhaps nanocosm).

The interior phase of fullerenes such as C_{60} , the realm of so-called endohedral chemistry, has been widely discussed. Formation of the hollow carbon clusters by laser ablation of a composite of graphite and lanthanum oxide creates fullerene-lanthanum complexes in which the metal atoms appear to be inside the fullerene cage. The stability of these complexes in solvents argues strongly that the metals are encapsulated as endohedral species.

But there is not much room inside the fullerenes known at present — C_{82} has an inside diameter of about five ångströms, enough to accommodate just three or four metal atoms. Sumio Iijima's discovery of carbon nanotubes in 1991 led Richard Smalley to predict potentially more interesting ways of exploiting their interior phase: for example, by trapping metal atoms "like peas in a pod". The tubes might thereby become 'nanowires'.

But how to get the atoms inside? As formed in the now-standard arc-discharge technique, the carbon tubes are capped at each end, presumably as a result of pentagonal defects in the hexagonal graphite-like sheets. These cause the sheets to curl up and close upon themselves, avoiding dangling bonds. These relatively high-energy caps are the most promising target for attempts to make an opening.

That seems to be borne out by experiments of Iijima and P. M. Ajayan reported on page 333 of this issue. Among samples of closed nanotubes, they deposit microscopic particles of lead from a laser-evaporated vapour. On annealing in air at 400 °C (above lead's melting point), the caps are destroyed and molten material is sucked inside the tubes by capillary action. The mechanism of cap destruction is not clear, although both the metal particles and air seem to be essential — some kind of metal-catalysed oxidation is a possibility.

Whether the material that fills the tube is pure lead or a compound is also unclear, although apparently it is not a simple oxide. Moreover, the filling is mostly amorphous, and so it may not be the ideal metallic nanowire that might have been hoped for. But it will be interesting to see what conductivity measurements reveal. Transmission electron microscopy shows some partially

contact angles remain well defined in the filled nanotubes, for instance), the character of phase transitions shows a pronounced dependence on the size and the dimensionality of the system. In cylindrical pores, correlation lengths can diverge only along the pore axis, so phase transitions should be pseudo-one-dimensional, quite unlike those in three-dimensional bulk materials. Liquid-vapour transitions (capillary condensation) and superfluid transitions in porous media have been studied in the past, but open, uniform cylindrical nanotubes might provide the ideal pores much needed in these investigations.

Solid-liquid transitions in nanometre-scale pores (capillary melting/freezing) have been investigated only theoretically (G. Navascués & P. Tarazona, *Mol. Phys.* **62**, 497; 1987), and it is here in particular that studies of filled nanotubes might bear fruit, as the change of phase in a single tube may be visible with electron microscopy. As with capillary condensation, the expectation is that the freezing or melting transition will be shifted in a narrow pore relative to the bulk; but in addition, constraints on packing in the interior phase may generate a rich subtlety in the phase diagram, and there is the intriguing possibility of a solid-liquid critical point, at which the two phases lose their distinct identity. Symmetry arguments appear to rule out this possibility for bulk materials.

Another potential approach to the generation of filled carbon nanostructures is to create them with the filling *in situ*, in the same way that endohedral fullerene complexes are formed. That is the very trick that has enabled Rodney Ruoff and colleagues (*Science* **259**, 346-347; 1993) and Yahachi Saito and co-workers (*Jap. J. appl. Phys.*, in the press) to create closed, concentric polyhedral carbon shells (like short, fat nanotubes) containing what appears to be crystalline lanthanum carbide (LaC_2). The encapsulated material (which is normally hygroscopic) is protected against several days' exposure to air. Here, then, is a new kind of airtight wrapping for readily degraded substances. Based on experience with synthetic, macrocyclic cages such as the hemicarcerands of Donald Cram, it may be that these structures will provide a protected environment for all manner of delicate chemistry.

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Lanthanum carbide crystal inside a 30-nm carbon polyhedron. (Courtesy Y. Saito.)

crystalline regions of filling. Perhaps this crystallinity will be improved if a way can be found to introduce the material more slowly into the tube — by controlling the wetting dynamics.

What applications this new nanocomposite might offer will not be apparent until its electronic and mechanical properties have been measured. The empty tubes are themselves predicted to have immense tensile strength along the axis and to be semiconducting or metallic, depending on the detailed structure of the cylindrical sheets.

Some of the most immediate benefits, however, may be for fundamental research. In particular, the opening and filling of nanotubes should cast new light on how matter behaves under confinement. Previous studies of this sort, aimed for example at understanding the effect of confinement on phase transitions, have relied on porous media such as Vycor silica glass, which can soak up simple liquids and gases. But the non-uniform pore sizes and shapes of these materials complicates interpretation of the results.

Although in many respects concepts relating to bulk matter remain surprisingly well suited to describing systems of nanometre dimensions (menisci and