

 PHASE TRANSITION

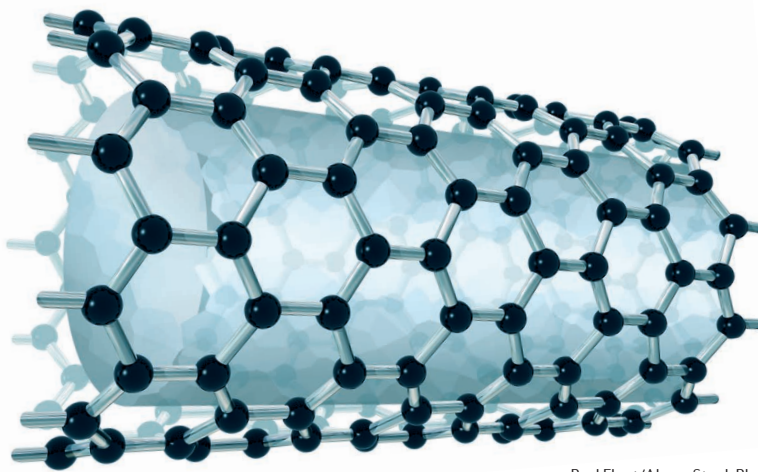
Cold as ice

“We like to think of a carbon nanotube as the smallest possible pipe. Understanding how the properties of liquids change when confined inside these tiny pipes is very interesting”

The physical properties of water change when it is confined in nanometre spaces, such as the interior of a carbon nanotube (CNT). Here, water can freeze at temperatures above 100 °C, as reported by Michael Strano and colleagues in *Nature Nanotechnology*.

Water behaving differently when confined in CNTs has already been predicted by computational studies. Furthermore, previous experiments by Strano *et al.* showed that ion transport rates within a CNT are dependent on tube diameter — an additional indication that a CNT can induce changes in water structure and, in turn, affect the ionic flow. However, the shift in melting temperature of pure water and its dependence on CNT diameter has not been measured until now. “These effects were much larger than anticipated,” says Jesse Benck, postdoctoral researcher in Strano’s group and expert in the field. “It was very surprising to find that the freezing point, which could be increased by more than 100 °C, is substantially affected by even small differences in tube diameter.”

The liquid–solid phase transition temperature of water was measured with molecules confined in six different single- and double-walled CNTs with internal diameters ranging from 1.05 to 1.52 nm. The small changes in CNT diameter greatly influenced the freezing/melting temperature. Water was found to freeze/melt in the range of 105–151 °C if confined in the smallest CNTs, whereas in the largest CNTs the phase transition occurs near ambient temperature (3–30 °C). Notably, opposite behaviour was observed for water in CNTs of intermediate size, in which the freezing



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point decreased to temperatures between –35 and 10 °C.

In this work, centimetre-long CNTs were grown on silicon through iron-catalysed methane decomposition. Following this chemical vapour deposition, the ends of the CNTs were opened by plasma etching to let water flow inside. The response of CNT-confined water to variations in temperature was analysed by monitoring a specific vibrational mode — the radial breathing mode — using Raman spectroscopy. Such vibrations involve concerted movement of carbon atoms, so that the tube contracts and expands radially. Importantly, the movement is restricted when the CNT is filled with water, an effect enhanced when water solidifies into ice. These changes can be observed by considering shifts of the radial breathing mode to higher frequencies. “A critical advantage of this approach is our ability to measure a single nanotube. This is crucial for observing and understanding how small changes in carbon nanotube diameter lead to significant changes in the water phase transition temperature,” explains Benck.

One natural extension of this work would consider the effects of

nanoconfinement on other liquids. “We like to think of a carbon nanotube as the smallest possible pipe. Understanding how the properties of liquids change when confined inside these tiny pipes is very interesting,” notes Benck. These studies could highlight new properties that might have important implications in many technological applications. For example, ice nanowires could be used as materials for thermal energy storage. Alternatively, the potentially high proton conductivities of ice nanowires might see them incorporated into electrochemical energy conversion devices. Benck further envisions that we will one day use these proton-conducting ice wires to make more efficient fuel cells, and concludes: “However, if this turns out to be possible, it will require many more years of research to achieve!”

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ORIGINAL ARTICLE Agrawal, K. V. *et al.* Observation of extreme phase transition temperatures of water confined inside isolated carbon nanotubes. *Nat. Nanotechnol.* <http://dx.doi.org/10.1038/nnano.2016.254> (2016)

FURTHER READING Choi, W. *et al.* Diameter-dependent ion transport through the interior of isolated single-walled carbon. *Nat. Commun.* **4**, 2397 (2013)

Subject categories:

Physical sciences / Materials science / Nanoscale materials / Carbon nanotubes and fullerenes

[URI /639/301/357/73]

Physical sciences / Materials science / Materials for energy and catalysis / Porous materials

[URI /639/301/299/1013]