Molecular Foundry Research Highlight

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Structural transformations of carbon nanotubes under pressure

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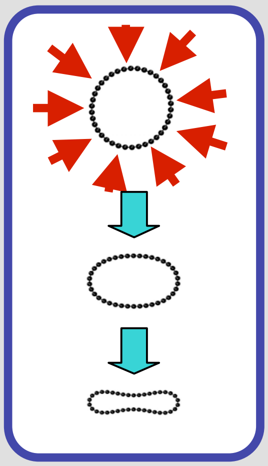
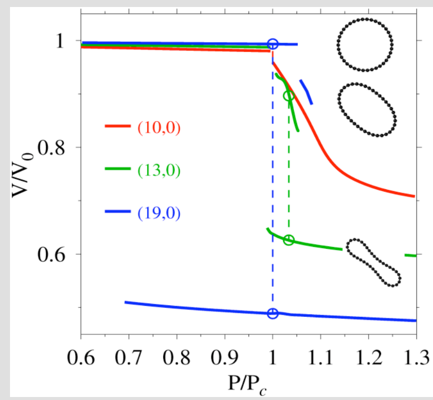
The response of carbon nanotubes to pressure depends qualitatively on diameter

Using atomistic simulations we can understand how and why nanotubes of different sizes deform and use this information to guide the interpretation of experiments.



All single-walled carbon nanotubes deform under pressure, but how they deform depends on their diameters. Small nanotubes gradually change their shapes whereas larger tubes abruptly collapse.

Right panel: Volume (relative to volume at zero pressure) vs pressure (relative to the pressure at which structural transformations begin) for **small**, **medium**, and **large** diameter nanotubes. Dashed vertical lines indicate pressures an which an abrupt collapse is predicted to occur.



A mechanical property of fundamental importance for any material is its response to pressure, and how the physical properties of carbon nanotubes change when pressure is applied has been intensively studied both experimentally and theoretically. While experimental evidence suggested that nanotubes deform under hydrostatic pressure, there was no consensus on the nature and mechanism of this deformation or on the pressures at which nanotubes begin to deform.

In the Theory Facility we have developed computational techniques to study nanotubes under pressure and discovered that their behavior depends qualitatively on their diameters: As pressure increases, the cross-sectional shape of a small-diameter tube deforms continuously from a circle to an oval and then a fully-collapsed or "peanut" shape. Large diameter tubes, on the other hand, remain circular until a critical pressure is reached at which point they suddenly collapse to a peanut shape. Nanotubes with intermediate diameters deform continuously from a circular to an ovular cross-section before abruptly collapsing. This diameter dependence is explained by the changing proportions in the total energy of the wall-curvature energy and the van der Waals attraction between opposite walls of the tube.

In a related Foundry user project, experimentalists from U.C. Berkeley and Chung-Ang University are working with the Theory Facility to interpret Raman scattering measurements under pressure. Raman scattering is an important tool for determining the structures of nanotubes. The disappearance of a Raman peak associated with the radial breathing of the nanotube at high pressures has frequently been attributed to the onset of structural deformation. However, by combining experiments and simulations we have shown that the disappearance of this resonance occurs at pressures much lower than the deformation pressure. The reason for this is that pressure lowers the frequency of one of the tubes' vibrational modes – the "squashing" mode – and, as a result, large symmetry-breaking thermal fluctuations destroy the Raman resonance responsible for the signature of the radial breathing mode. Our collaboration explains the lack of agreement on the observed pressures at which nanotubes deform and provide important guidance for the interpretation of Raman spectra [2].

[1] P. Tangney, R. B. Capaz, C. D. Spataru, M. L. Cohen, and S. G. Louie, "Structural transformations of carbon nanotubes under hydrostatic pressure," Nano Lett. **5**, 2268 (2005).
[2] I-H Choi, P. Y. Yu, P. Tangney, and S. G. Louie, "Vibrational properties of single walled carbon nanotubes under pressure from Raman scattering experiments and molecular dynamics simulations," *phys. stat. sol.* **244**, 121 (2007).