

Phase Behavior, Filling Dynamics, and Packing of Fluids inside Isolated Carbon Nanotubes

by
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Fluids behave differently inside nanoscale pores than they do in bulk solution. When confined inside so-called single digit nanopores – pores with diameters smaller than 10 nm – the atomic configuration, phase behavior, and dynamics of fluids vary markedly from bulk behavior and depend sensitively on pore diameter. Understanding fluid behavior at these scales is critical to the design of a wide variety of engineering systems, such as membranes for chemical separations and batteries for energy storage. The study of nanofluidics also informs our understanding of natural phenomena, including the single-file transport of water into biological cells and flow through nanoporous geologic media.

In this thesis, we develop experimental platforms to study confinement effects on fluid packing, filling, and phase behavior inside isolated, substrate-bound carbon nanotubes with diameters ranging from 0.8 nm to 3 nm. Through advances in carbon nanotube growth and nanofabrication, identical segments of the same diameter and chirality carbon nanotube are produced. This platform increases the number of replicable single-pore measurements by orders of magnitude compared to the previous state of the art. Using Raman spectroscopy, carbon nanotubes can be assigned as empty, fluid-filled, or partially fluid-filled as a function of location, time, temperature, and nanotube diameter with micrometer and second precision.

After building precision nanopore systems and developing techniques to characterize nanopore filling, we address several topics of interest to the field of nanofluidics, as explored in the sections of this thesis. First, we study the diameter dependence of fluid packing and filling inside carbon nanotubes, showing that the variation in the change of the Raman radial breathing mode upon fluid filling is indicative of configurational changes in water inside nanotubes of different sizes. Second, we develop continuum elastic shell theories to explain why double-walled nanotubes, but not single-walled nanotubes, can distinguish between interior fluid filling and exterior fluid adsorption by changes in radial vibrations alone. Third, we explore the thermodynamics of water phase transitions inside open and closed carbon nanotube systems, generating estimates of the enthalpy of vaporization of water inside 1.35 nm and 1.48 nm diameter carbon nanotubes of 25.0 kJ/mol and 22.1 kJ/mol, lower than the bulk value. Fourth, we observe dynamic changes in filling state with time, showing that nanotube filling occurs by nucleation and growth, not by monotonic filling from the pore mouth. Finally, as an applied example of transport in porous media, we demonstrate an innovative heated mask design to prevent transmission of respiratory viruses.

Spectroscopic measurement of water inside carbon nanotubes, as explored in this thesis, expands our view of the thermodynamic and dynamic properties of fluids under confinement and addresses key knowledge gaps in nanofluidics. These measurements can inform new theories, force fields, and mechanisms for fluids in nanoconfined regimes.

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