FLUID INTERFACE DYNAMICS AND PHASE TRANSITIONS INSIDE CARBON NANOTUBES

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A hydrothermal method of nanotube synthesis has produced high-aspect-ratio, multiwall, capped carbon nanotubes, which are hollow from tip to tail, mostly closed with some remaining open.[1] These tubes (see simplified schematic of Fig. 1) have typically 30–70 fringes per wall (wall thickness in the range 10–25 nm), an outer diameter of about 100 nm, and lengths varying from 1 to 10 μm. These nanotubes are at least by two orders of magnitude smaller than the finest capillaries used in other dynamic fluidic experiments so far. Many of the closed-end tubes contain a high-pressure encapsulated aqueous multicomponent fluid displaying clearly segregated liquid and gas by means of well-defined curved menisci. Figure 2 displays a transmission electron microscopy (TEM) image of a carbon nanotube with a representative fluid inclusion. The fluid is expected to include H_2O, CO_2 and CH_4, as based on thermodynamic equilibrium calculations performed for the hydrothermal synthesis conditions (700^{o}–$800^{o}C$, 100 MPa) using Gibbs energy minimization principles.[2]

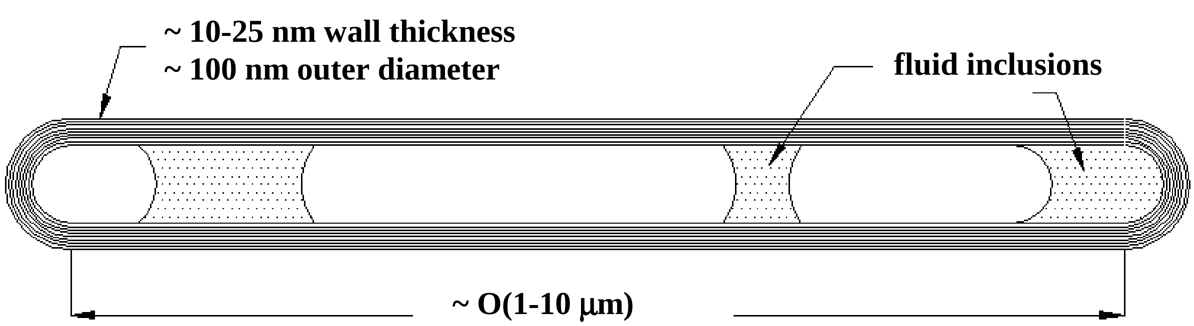

Fig. 1. Illustrative schematic of the nanoscale experimental system utilized in this work. Liquid inclusions are identified by the shaded areas. Pressures within the closed tubes at room temperature are estimated to be up to 30 MPa.

Thermal experiments were performed using electron irradiation as a means of heating the contents of *individual* nanotubes in the high vacuum of a TEM, where the multiphase fluid is thermally excited by expanding/contracting the electron beam. Figure 3 shows an experimental sequence where an aqueous membrane was subjected to gentle heating. The excellent wettability of the graphitic inner tube walls by the aqueous fluid and the mobility of this liquid in the nanotubes are observed with nanometer-scale resolution. Interface dynamic phenomena have been visualized, as driven by thermocapillary forces as well as evaporation/condensation.[3,4] Experimental evidence has been presented[4] of nanometer-scale liquid films rapidly transporting fluid within the nanochannel with velocities 0.5μm/s or higher. The hydrothermal nanotubes examined herein offer a promising platform for studying the behavior of multicomponent, multiphase fluids in nanosize channels at high-pressure conditions. The phenomena documented in this study demonstrate the potential of implementing such tubes in future nanofluidic devices.

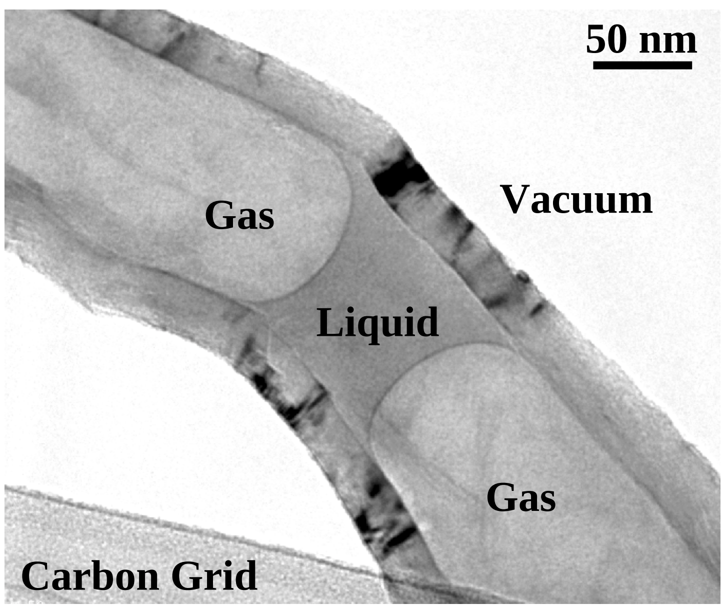

Fig. 2. TEM image of the elbow portion of a carbon nanotube. This tube is capped at both ends and contains a liquid inclusion constrained between two curved menisci separating the aqueous liquid from the adjoining gas. The nanotube rests on a holey carbon grid, a segment of which is visible in the lower left corner of the micrograph. The environment outside the nanotube is the high vacuum of the TEM column. The volume of the liquid inclusion is of the order of 10^{-18} (*atto*) liters. The contact angles varied between 0 and 25 degrees.

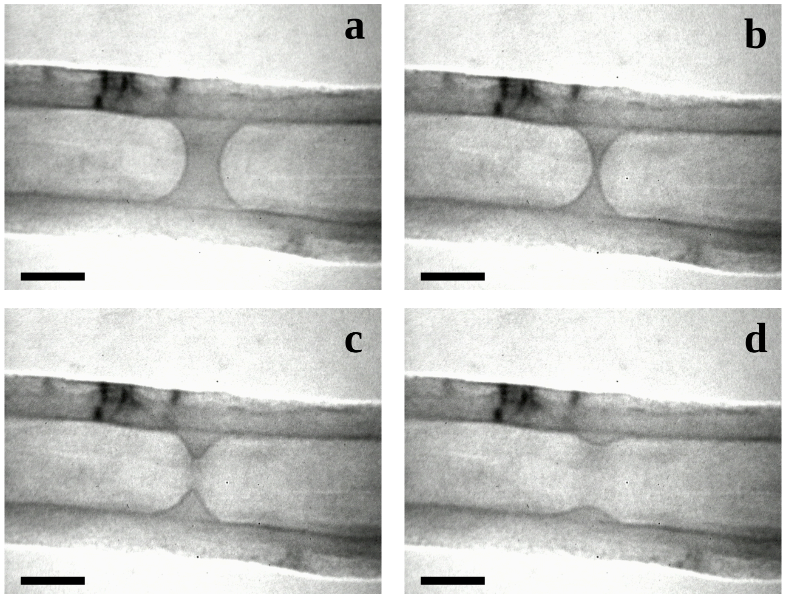

Fig. 3. TEM micrographs of a typical carbon nanotube with an aqueous inclusion subjected to continuous gentle heating using a contracted electron beam. (a-b) Reversible contraction. (c) Membrane pinches off near the center upon sustained heating. (d) Fluid gradually spreads along the tube walls forming a film few nanometers in thickness, and eventually disappears. Scale bar corresponds to 50 nm.

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