In situ multiphase fluid experiments in hydrothermal carbon nanotubes

Yury Gogotsi
Department of Materials Engineering, Drexel University, Philadelphia, Pennsylvania 19104

Joseph A. Libera, Almila Güvenç-Yazıcıoğlu, and Constantine M. Megaridis
Department of Mechanical Engineering, University of Illinois at Chicago, Chicago, Illinois 60607-7022

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Hydrothermal multiwall closed carbon nanotubes are shown to contain an encapsulated multiphase aqueous fluid, thus offering an attractive test platform for unique in situ nanofluidic experiments in the vacuum of a transmission electron microscope. The excellent wettability of the graphitic inner tube walls by the aqueous liquid and the mobility of this liquid in the nanotube channels are observed. Complex interface dynamic behavior is induced by means of electron irradiation. Strong atomic-scale interactions between the entrapped liquid phase and the wetted terminated graphite layers are revealed by means of high-resolution electron microscopy. The documented phenomena in this study demonstrate the potential of implementing such tubes in future nanofluidic devices.


Understanding the behavior of fluids in nanochannels is important for the efficient design and operation of micro- and nanofluidic devices. In micron-thick channels, interaction with walls and surface tension makes axial movement of the fluid difficult. Multiwall carbon nanotubes show great potential for use in nanofluidic devices. Nanotubes would provide cylindrical channels similar to pipes used in the macroscopic world. Typically, the inner diameter of carbon nanotubes is less than 10 nm and the wall thickness exceeds the inner diameter. As a consequence, only a small part of the cross section is available to serve as a fluidic channel. The interaction of fluid molecules with the nanotube walls could be conceivably so strong, as to prevent throughflow. Nanotubes with inner diameter of <4 nm could not be filled with a salt melt. On the other hand, capillary forces can facilitate filling of thin channels in case of good wettability of the solid wall surface by the fluid. The capillarity action is only possible in the presence of wetting. Filling of nanotubes by liquid metals, salts, oxides, and HNO3 has been studied and it has been shown that some liquids could be sucked into nanotubes due to capillary forces. Studies of the wetting and capillarity of carbon nanotubes demonstrate that only relatively low-surface-tension materials can be drawn inside nanotubes. The reported cutoff value of surface tension of 100–200 mN/m is sufficiently high to allow water and organic solvents to wet and fill the interior of carbon nanotubes. Simple experiments of placing a water droplet (surface tension 73 mN/m) on the surface of a carbon nanotube bundle showed the water to be readily sucked into the capillary channels, eventually leaving a dry surface. Although the behavior of fluids in nanotubes may differ fundamentally from that in macroscopic pipes or even microcapillaries, no in situ studies of fluid transport and/or phase transition in nanotubes or nanosize channels have been reported yet.

Fluid mechanics at the nanoscale is in its infancy and experimental data are scarce. Despite the critical need for improved knowledge of fluid phenomena at these extreme length scales, there is hardly any information available on the behavior of even abundant fluids, such as water, in nanosize channels. Such studies could greatly facilitate the development and validation of modeling tools which, so far, have concentrated on single-component nonpolar fluids flowing axially in nanotubes.

The major obstacle to in situ experimental studies of fluid behavior in nanotubes has been the rarity of such systems filled, at least partially, with fluids. A recently suggested hydrothermal method of nanotube synthesis has produced nanotubes with an encapsulated aqueous fluid, which includes segregated liquid and gas, and well-defined interfaces. The nanotubes were synthesized using Tuttle-type tube autoclaves at pressure up to 100 MPa and temperature 700–800 °C in the presence of Ni catalyst, using the equipment and process described in Refs. 18 and 19. The tubes are hollow from tip to tail, being mostly closed with some remaining open. Based on thermodynamic equilibrium calculations performed for the hydrothermal synthesis conditions using the ChemSage-3.1 Gibbs energy minimization code, the predicted composition of the trapped fluid at room temperature is 85.2% H2O, 7.4% CO2, and 7.4% CH4 (mole). This composition was found to be almost independent of pressure. If we consider that a closed tube was sealed at 750 °C and the hydrothermal fluid was captured at this temperature, the pressure in the tube contents at room temperature may be up to ~30 MPa. The inner pressure could be conceivably lower if the tube was sealed at a temperature below 750 °C. High pressures are known to facilitate increased solubility of gases in liquids. This possibility must be taken into account in the interpretation of the observed phenomena. The demonstrated ability of closed hydrothermal nanotubes to act as miniature pressure vessels and maintain the pressurized fluid, even when heated under the high vacuum of the transmission electron microscope (TEM) column (10−8 Torr), confirms their high strength and wall perfection.

Portions of hydrothermal tubes produced in our experiments (Fig. 1) look like pipes used in the macroscopic world,
just being many orders of magnitude smaller. These tubes have typically 30–70 lattice fringes of graphite per wall with an interplanar distance of \( \sim 0.34 \) nm (wall thickness \( \sim 10–25 \) nm). As described in this letter, these nanotubes offer a unique opportunity to study the behavior of aqueous fluids in nanosize channels, and visualize a variety of chemical and physical phenomena in the TEM. It should be emphasized, however, that chemical interactions in the nanotube interior are not within the scope of this letter.

As Fig. 1 demonstrates, the trapped fluid phase showed variations in mass density; see curved fluid interfaces bounding a liquid membrane (plug) in this figure. The amount of the dense phase (called liquid hereon) varied with location within the tube (compare Figs. 1 and 2). Each carbon nanotube contained several of these inclusions at random locations along its protracted length. The clear visual definition of the interfaces in Fig. 1 suggests that this fluid is at sub-critical conditions.

The TEM observations (Fig. 1) demonstrated excellent wettablity of the graphite walls by the liquid. The sequence of frames (a) and (b) in Fig. 1 shows how the liquid inclusion shrinks upon heating via electron irradiation. When cycling was done by expanding and focusing the electron beam, the same behavior was repeatedly observed [see frames (c) and (d) in Fig. 1]. The contraction/thinning of the liquid inclusion seen in Fig. 1 was reversible in the early stages of heating. Shrinkage of the liquid volume may result from liquid evaporation within the tube, while volume recovery could occur via condensation/dissolution from the gas phase. Another possibility is offered by thin-film fluid transfer along the tube walls. Such transfer may be triggered by either wetting or thermocapillary forces, the latter developing when temperature gradients form along the fluid interface or along the tube walls. It is important to note that heating of the fluid with the electron beam elevates both pressure and temperature, thus having the potential to create near-critical conditions for the fluid in the closed tube. If that occurred, the liquid and gas densities would become less disparate, thus allowing for rapid interface movement during phase transition. However, the sustained clear definition of interfaces between gas and liquid confirms that the critical point of the fluid mixture was not reached in our experiments.

In some cases, liquid was constrained from one side either by the tube end or an internal compartment closure. In the initial stages of heating, such liquid inclusions (Fig. 2) behaved similar to a freestanding inclusion (Fig. 1) demonstrating expansion/contraction upon heating/cooling. However, when such liquid inclusions were heated for a prolonged period of time, thus reaching higher temperatures, vapor nucleation at the liquid/solid interface led to the formation of bubbles, ranging in size from 10 to 50 nm, near the blocked end (Fig. 2). It is important to note that all phenomena seen in Figs. 1 and 2 can be explained by the conventional fluid continuum theory and suggest that transport of liquids in sub-100 nm capillaries is possible, at least in response to external thermal stimuli.

When some of the liquid inclusions that were sufficiently large (axial length exceeded one diameter) were heated for a prolonged time period under the electron beam, a complex behavior was observed reproducibly (Fig. 3). Instead of volume contraction (as seen in Fig. 1), the heating caused severe interface deformation and liquid expansion along the axis of the tube [Figs. 3(b)–3(c)], while the contact line near the
TEM images of a water-carbon interface. Lattice fringe imaging of tube walls in the area of the liquid meniscus [Fig. 4(a)] showed a very strong interaction between the carbon tube inner walls and the adjacent liquid. When a liquid inclusion was present in the area where some graphite planes terminated within the tube (for example, at an inner diameter change or occasional bending of the tube), swelling of the inner tube walls was observed and the wetted graphite layers turned away from the wall toward the tube axis (see arrows in Fig. 4). It is plausible that water penetrated between the bent carbon layers, thus causing this behavior. This strong interaction between the liquid and tube walls appears to be of chemical nature, and may account for the low mobility of the liquid/carbon interface near the wall [Fig. 3(d)]. In conclusion, hydrothermal nanotubes open new horizons in investigating a variety of challenging scientific problems at the nanoscale.

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