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Attoliter fluid experiments in individual closed-end carbon nanotubes: Liquid film and fluid interface dynamics

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A hydrothermal method of catalytic nanotube synthesis has been shown to produce high-aspect-ratio, multiwall, capped carbon nanotubes, which are hollow and contain a high-pressure encapsulated aqueous multicomponent fluid displaying clearly segregated liquid and gas by means of well-defined curved menisci. Thermal experiments are performed using electron irradiation as a means of heating the contents of individual nanotubes in the high vacuum of a transmission electron microscope (TEM). The experiments clearly demonstrate that TEM can be used to resolve fluid interface motion in nanochannels. Good wettability of the inner carbon walls by the water-based fluid is shown. Fully reversible interface dynamic phenomena are visualized, and an attempt is made to explain the origin of this fine-scale motion. Experimental evidence is presented of nanometer-scale liquid films rapidly moving fluid along the nanochannel walls with velocities 0.5 μm/s or higher. © 2002 American Institute of Physics. [DOI: 10.1063/1.1429249]

Since their official discovery in 1991, nanotubes (NTs) have been the target of a rapidly growing number of investigations, mainly due to their great promise for a wide range of potential applications, from nanowires and molecular containers to biosensors. The greatest percentage of NT studies have concentrated on the structure and electronic properties of these unique carbon forms, with only limited attention given to the thermal fluid aspects of their existence or their potential thermal fluid applications.

Multiwall hollow carbon NTs possess extremely high mechanical strength, which, when combined with their ability to provide a conduit for fluid transport at near-molecular length scales, makes them attractive candidates for implementation in future micro- or nanofluidic devices. To this end, understanding fluid behavior in nanochannels is important for the proper design and efficient operation of such devices.

A natural complication in this area is the underlying fundamental question of whether fluids behave as continua at these ultrafine length scales, typically down to a nanometer or less. Sobolev et al. employed conventional experimental techniques using cylindrical capillaries with radii in the range 40–200 nm to reach the conclusion that the surface tension of water at these scales does not differ from the bulk values in the temperature range 8–70 °C. Other experimental studies of capillary phenomena in subnanometer channels have also been performed, but the reported results were based primarily on bulk-type measurements. In some cases, carbon NTs have been filled, at least partially, with molten materials (liquid metals, salts, or oxides) through capillary action, but little has been reported on the dynamic aspects of fluid transport during or after the NT filling process.

The NT samples in the present study were synthesized using a hydrothermal method, at a pressure of 100 MPa and temperature 700 to 800 °C in the presence of Ni catalysts; see equipment and procedures described in Refs. 11 and 12. The procedure produces multiwall carbon NTs, which are hollow from tip to tail, mostly closed with some remaining open. The tubes of approximately circular cross section have typically 30–70 fringes per wall (wall thickness ~10–25 nm), an outer diameter of about 100 nm, and lengths varying from 1 to 10 μm. Many of the closed-end tubes contain a high-pressure encapsulated aqueous fluid, which displays clearly segregated liquid and gas separated by well-defined curved interfaces. None of the open-end NTs display any apparent fluid inclusions. It is noted that pure, single-phase fluids have been previously trapped within hollow carbon tubes by post-treating them at high pressures (~60 MPa) after their production. However, fluid interfaces were lacking from the samples examined in Ref. 14.

Based on thermodynamic equilibrium calculations, the encapsulated fluid is expected to contain H2O, CO2, CH4, H2, and CO at the synthesis pressure and temperature. The
presence of water and gases was confirmed in the sealed synthesis capsule (along with the formed NTs) after the completion of each experiment. Thus, it is logical to assume that the composition of the fluid trapped inside the tubes is approximately the same (aqueous) as that in the host environment of the sealed capsule contents. If one considers that a closed tube was sealed at 750 °C and the hydrothermal fluid was trapped at this temperature, the pressure of the tube contents cooled at room temperature may be up to ~30 MPa. The fluid at these conditions is expected to consist only of H2O, CO2, and CH4. Naturally, the inner NT pressure could be conceivably lower than 30 MPa, if the tube was sealed at a temperature below 750 °C. It is important to note that the critical pressures of the possible fluid components are 22.1 MPa (H2O), 3.5 MPa (CO2), 7.4 MPa (CO), 1.3 MPa (H2), and 4.64 MPa (CH4). Most of these pressures are considerably lower than the estimated maximum pressure in the NT interior (30 MPa); it is therefore likely that the pressure of the trapped fluid mixture may exceed its critical value.

The ability of closed hydrothermal NTs 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), makes them very attractive for fluid studies possibly approaching the continuum limit. Furthermore, the lack of defects on their inner surface makes these NTs an appealing system for contact line–wetting studies. The experiments reported herein expand the work reported in Ref. 13 and were performed using electron irradiation as a means of gently heating the contents of individual NTs in the electron microscope column. High-resolution TEM was used for imaging at the midplane of individual NTs, where the image has maximum contrast.

The TEM photomicrograph of Fig. 1, an image typical of NT samples made in the hydrothermal process, shows an elbow portion of a carbon NT containing a liquid bridge inclusion constrained between two clearly-defined menisci. The fluid between the menisci is less transparent to the electron beam, consequently it has a higher mass density than the remaining fluid. Energy dispersive spectrometry (EDS) measurements performed on either side of these interfaces with a probe size of O(10 nm) revealed the intensity of the oxygen signal on the darker-fluid side to be substantially higher, presumably due to the presence of water molecules in that fluid. Thus, it has been concluded that the interfaces seen in Fig. 1 separate a liquid from a gas phase; see markings on this image. Despite the possibly supercritical pressure of the NT contents, the clear presence of interfaces in Fig. 1 suggests that the visualized fluid is in a subcritical state. It is also worth noting that the volume of the liquid inclusion seen in Fig. 1 is of the order of 10^-18 l (attoliters).

The two menisci bordering the liquid in Fig. 1 show good wettability of the inner carbon walls by the water-based fluid. Wetting of multiwall NTs (2–20 nm diameter) has been examined by Dujardin et al.17 As reported therein, there exists an upper limit for the surface tension of the liquid (~180 mN/m) beyond which wetting of multiwall NTs is no longer favorable. In a follow-up study,18 single-wall NTs (1.4–2.4 nm diameter), despite their much higher curvatures, were found to shift from wetting to nonwetting between 130 and 190 mN/m.

As suggested by the analysis of Zisman,19 carbon NTs can be filled with aqueous solutions (γ~72 mN/m). Zisman deduced a phenomenological parameter, the critical surface tension γc, which is characteristic of the solid and independent of the wetting substance. He used contact angle θ measurements of various liquids with surface tension γ on low-energy solid surfaces and found that for most surfaces a linear relation holds, namely

$$\cos \theta = 1 + b(\gamma_c - \gamma).$$

Zisman generalized the above concept to high-energy surfaces, such as graphite. To this end, Dujardin et al.18 used Zisman’s approach to determine γc for single-wall carbon NTs wetted by sulfur, cesium, vanadium oxide, selenium, or lead oxide. On a plot of cos θ vs γ for all these substances, the value of γc was found to be in the interval 40–80 mJ/m². On the same plot, the maximum value γmax of surface tension for wettableness was found to be in the interval 130–170 mN/m. The practical implications of these two important phenomenological parameters, γc and γmax, are that for liquids with γ<γc, complete wetting is expected with formation of a thin film (θ~0°). Nonwetting is expected for γ>γmax and partial wetting (θ<90°) is expected for γc < γ<γmax.

Dujardin et al.18 concluded that the wetting properties of single-wall and multiwall tubes are not different. This conclusion supports the validity of Eq. (1) for the current multiwall NT system. This equation was used herein to produce an estimate of γ for the encapsulated liquid of Fig. 1. The measured values of θ were in the range 10–25 deg. Using the range of γc reported in Dujardin et al.18 for carbon NTs and the value of b=0.011 corresponding to Fig. 3 of that work, Eq. (1) infers a range of γ~30–80 mN/m for the liquid of Fig. 1. Although it is recognized that the above procedure produces only an approximate estimate of γ, it is intriguing to note that the calculated range includes the surface tension of pure water at room temperature (γ~72 mN/m), thus supporting the assumed aqueous nature of the trapped liquid.
Using the above estimate of surface tension of the liquid (30–80 mN/m), a radius of curvature $r$ equal to the inner diameter of the tube 50 nm, the measured liquid–solid contact angle range 10–25 deg, and the Young–Laplace equation

$$\Delta p = p_{\text{gas}} - p_{\text{liq}} = 2 \gamma \cos \theta / r,$$

the pressure difference across the meniscus was found to be in the range 1–3 MPa, being less than 10% of the maximum equilibrium pressure of the NT contents at room temperature.

Figure 2 depicts two images of a liquid inclusion (plug), which is typical of those encountered in straight sections of the closed NTs. The two micrographs of Fig. 2 show the same liquid plug, but correspond to different times in an experimental sequence during which the liquid was subjected to modest heating by focusing the illuminating electron beam. The liquid is bounded on either side by two nearly identical curved interfaces, which again indicate almost perfect wetting of the inner carbon wall by the aqueous liquid. As heating proceeds from Fig. 2(a) to Fig. 2(b), the apparent volume of the liquid is reduced. Three independent mechanisms could be responsible for the liquid volume reduction documented in this figure. The first mechanism is liquid displacement due to adjoining bubble expansion, the second is liquid evaporation, and the third is thermocapillary motion. As the temperature of the liquid is raised upon heating, its surface tension should decrease, possibly causing liquid migration (by means of a thin wall film) towards cooler portions of the NT away from the illuminated heated region in Fig. 2. When the electron beam was re-expanded from its contracted state [Fig. 2(b)], the liquid rapidly returned to its initial shape [Fig. 2(a)].

Figure 3(a) depicts the equilibrium (unheated) state of a gas bubble confined between two well-defined menisci and the NT walls. The upper meniscus separates the gas bubble from a liquid plug directly above it, while the lower meniscus separates the bubble from a liquid mass trapped by an interstitial cap (seen in lower right end) blocking access to the rest of the NT below. The area marked by the dashed rectangle was further interrogated by being subjected to modest heating/cooling by focusing/expanding the incident electron beam. The image in (b) corresponds to an instant during a heating sequence, while (c) corresponds to an instant in the subsequent cooling sequence. The black arrows in (b) and (c) indicate motion of the meniscus interface, while the white arrow in (b) indicates the presence of a thin film on the inner wall.

Figure 3(a) depicts the equilibrium (unheated) state of a gas bubble confined between two well-defined menisci and the surrounding NT walls. The upper meniscus separates the bubble from a liquid plug directly above it [similar to the one seen in Fig. 2(a)], while the lower meniscus separates the bubble from a liquid mass trapped by an interstitial cap blocking access to the rest of the NT below. The bubble was subjected to gentle heating/cooling by contracting/expanding the TEM beam. When heated, the gas bubble was seen to expand along its two axial ends. In that process, the liquid in the vicinity of the end cap was gradually displaced by the expanding gas above it. Upon sustained heating, all of the liquid by the cap could be driven off that region. When the electron beam was expanded back to its original size, i.e.,
heating was ceased, the bubble was seen to revert to its original size seen in Fig. 3(a). In order to resolve the mechanism driving liquid transport under these conditions, the TEM beam was moved lower to cover the area indicated by the dashed rectangle in Fig. 3(a). When the liquid near the interstitial cap was heated [Fig. 3(b)], the adjoining gas bubble also expanded, in turn displacing the liquid below the meniscus [see dark arrow in Fig. 3(b)] to higher locations off the field of view in Fig. 3(b). It is worth noting that liquid heating promotes evaporation, which could further enhance the meniscus downward motion seen in Fig. 3(b). The specific micrograph seen in Fig. 3(b) represents an instantaneous image from a recorded video sequence that documented the dynamic phenomena at a rate of 30 frames per second. This image reveals the presence of a thin wall film [see white arrow in Fig. 3(b)], which swells rapidly as the meniscus moves lower displacing the liquid away from the cap. This TEM observation is consistent with the hypothesis that the rapid drainage of liquid from the lower end of the bubble occurs primarily through a thin layer, and not evaporation. When the electron beam intensity was lowered immediately after beam contraction, thus allowing the illuminated area to cool locally, the lateral wall film was seen to thin out rapidly as it re-supplied the liquid volume below the bubble near the cap. In that process, the meniscus moved upward once again (the gas bubble also contracted during this cooling period) as shown by the arrow in Fig. 3(c).

The above observations offer experimental evidence that nm-scale liquid films can be quite effective in rapidly moving fluid within nanochannels. In Fig. 3, the wall film thickness was combined with the measured liquid-volume displacement rates to produce an estimate of the film spreading velocities. These velocities were of the order of 0.5 μm/s, but may be appreciably higher if nonaxisymmetric transport occurs.

A simple calculation was performed to examine whether thermocapillary forces alone could account for the liquid transport rates seen in Fig. 3. Considering Marangoni-driven transport, and following the approach of Mazouchi and Homsy, the volume flux of the liquid pumped along the walls is

$$Q = \pi a w U_T,$$

where $a$ is the tube radius, $w$ the wall film thickness, and $U_T$ the maximum thermocapillary velocity corresponding to a temperature gradient $\beta = dT/dx$ along the tube wall. It is

$$U_T = -d\gamma/dT\beta w/\mu,$$

where $\gamma$, $\mu$ are, respectively, the surface tension coefficient and viscosity of the liquid. The quantities $Q$, $a$, $w$ were measured in the present experiments, while $\mu$ was estimated by the bulk value for water. Furthermore, an estimate of $\beta$ was made, using the length scale of the problem and considering that the liquid remains at subcritical temperatures, as revealed by the sustained presence of fluid interfaces. This analysis led to values of $|d\gamma/dT|$ at least three orders of magnitude lower than the bulk water value (10$^{-3}$ N/m/K). This, in turn, suggests that thermocapillary motion alone cannot be solely responsible for the liquid transport rates visualized in this work.

In summary, the hydrothermal NTs examined herein offer a promising platform for studying the behavior of multicomponent, multiphase fluids in nanosize channels at high-pressure conditions. It is plausible that under intense heating rates, near-critical transitions may occur, thus providing an opportunity to interrogate fluid behavior in regimes of the thermodynamic diagram that have not been readily accessible before.

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20. The units of $\gamma$ are in energy per unit area—since it is characteristic of the solid surface—while the surface tension of a liquid is in units of force per unit length.