Rapid Imbibition of Fluids in Carbon Nanotubes

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Carbon nanotubes are potential building blocks for nanofluidic devices. The way fluids flow into and fill nanotubes is therefore of wide interest; however, there are currently no experimental data or theoretical models for this nanoscale process. We have carried out molecular dynamics simulations of nanotubes imbibing oil at an oil/vapor interface at 298 K. We find that nanotubes imbibe very rapidly (≤ 445 m/s) via complex imbibition dynamics. The filling does not obey the macroscopic Washburn equation; the penetration length is a linear function of time.

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Our understanding of the static properties of capillaries filled by a wetting liquid is based on the 19th century work of Laplace, Poisson, and Young [1]. The dynamics of capillary flow were elucidated much later by Washburn [2] using the Poiseuille equation with the driving force for flow described by the Laplace equation for the pressure difference across the invading liquid meniscus. More recently Kalliadasis and Chang [3,4] have reanalyzed the classical problem using a scaling law for the dynamic contact angle of the liquid phase and find agreement with the classic experimental results of Blake *et al.* [5]. There is extensive literature on the wetting dynamics of homogeneous and structured surfaces [6]. In this Letter we extend the research to times and lengths characteristic of nanomaterials by examining, using molecular dynamics, the imbibition of oil into a nanoscale capillary formed by a single wall carbon nanotube (SWNT).

The simulation [7] geometry is shown in Fig. 1. A liquid-vapor interface of 507 decane molecules was brought to equilibrium at 298 K. The decane model potential is a short range united atom chain model with intramolecular bond bending and torsion terms, but bond lengths are fixed at 0.153 nm. The bond bending is described by a harmonic Van der Ploeg and Berendsen [8] potential

$$u^{\mathrm{bend}}(\theta) = \tfrac{1}{2}k_\theta(\theta - \theta_0)^2, \tag{1}$$

where $k_\theta = 519.66\ \mathrm{kJ\,mol^{-1}\,rad^{-2}}$, and the equilibrium angle, $\theta_0 = 114°$. For the torsion a triple cosine potential was used

$$\begin{aligned} u^{\mathrm{tors}}(\phi) =& \tfrac{1}{2}A_1(1 + \cos\phi) + \tfrac{1}{2}A_2[1 - \cos(2\phi)] \\ &+ \tfrac{1}{2}A_3[1 + \cos(3\phi)], \end{aligned} \tag{2}$$

where ϕ is the angle between the planes ijk and jkn (where i, j, k, and n are consecutive adjacent atoms), $A_1 = 2.9517\ \mathrm{kJ\,mol^{-1}}$, $A_2 = -0.56697\ \mathrm{kJ\,mol^{-1}}$, and $A_3 = 6.5793\ \mathrm{kJ\,mol^{-1}}$. The forces, F_{ij}, due to nonbonded interactions were modeled using the Lennard-Jones (12-6) potential, with $F_{ij} = -\partial u^{\mathrm{LJ}}(r_{ij})/\partial r_{ij}$, $r < r_{\mathrm{cut}} = 0$, $r \geq r_{\mathrm{cut}}$ corresponding to

$$u^{\mathrm{LJ}}(r_{ij}) = 4\varepsilon_{ij}[(\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^6] - u^{\mathrm{LJ}}(r_{\mathrm{cut}}). \tag{3}$$

Parameter values were $\varepsilon_{\mathrm{CH_2}} = 0.55666$, $\varepsilon_{\mathrm{CH_3}} = 1.35020$, $\varepsilon_{\mathrm{CH_2/CH_3}} = 0.86695\ \mathrm{kJ\,mol^{-1}}$, and $\sigma_{ij} = 0.393$ nm, $r_{\mathrm{cut}} = 0.8$ nm. Our potential [9] reproduces the experimental coexisting fluid densities of decane between 298 and 500 K to an accuracy of better than 1%. At 298 K the model interface has a surface tension of 20.53 mN/m (experiment 23.37 mN/m).

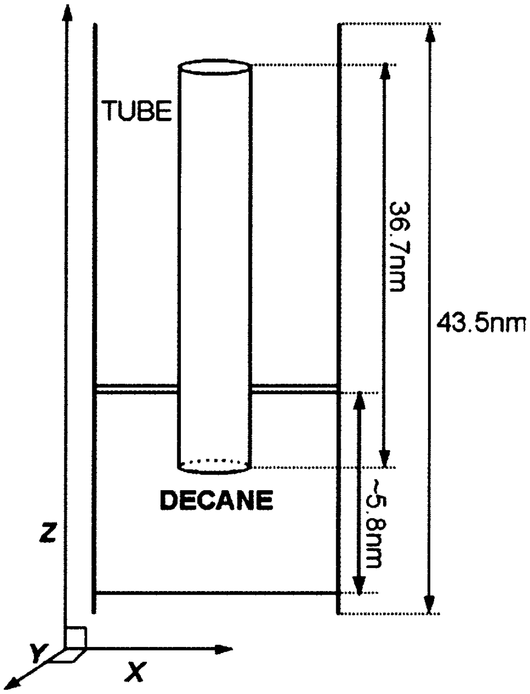

FIG. 1. Simulation cell for fluid imbibition, dimensions 5.7 nm by 5.7 nm by 43.5 nm. Periodic in X and Y, not in Z. Note that a short range repulsive wall was placed just above the liquid vapor interface in order to prevent the fluid from wetting the outside of the tube. This phenomenon is of interest in its own right but is secondary to the imbibition process described in this Letter.

The carbon nanotube was modeled as a rigid rolled graphene sheet, each carbon atom interacting with the decane molecules via an atom-atom Lennard-Jones potential using Lorenz-Bertholot mixing rules with $\sigma_{C/C} = 0.34$ nm, $\varepsilon_{C/C} = 0.233$ kJ mol^{-1}. Rouquerol *et al.* [10] report (zero coverage) energies of adsorption of alkanes up to *n*-octane on vulcan, a nonporous graphitized carbon. These data show a linear dependence on carbon number which allows an extrapolation to *n*-decane (~ 68 kJ/mol). Our decane-carbon potential gives an energy of adsorption of 59 ± 3 kJ/mol, 13% lower in energy corresponding to one graphene layer of carbon atoms as required for SWNT's instead of a sum over all layers as for a graphitic surface like vulcan (if we use the Steele potential [11]). Experiments on oil/nanotube systems are planned to provide data which will allow further refinement of the nanotube-oil potentials. In order to look at the effect of lowering the interaction strength we reduced the potential by another 13% and find no difference in the t^1 power law but a reduction in speed of filling (cf. Fig. 2) of the lower density *vapor* of approximately 30% with, however, the higher density liquid filling speeds not reduced. Since this reduced potential is lower than we expect for graphene, this gives us confidence that the qualitative results presented here for the (13, 13) nanotube are correct.

Following equilibration of the liquid-vapor interface, a (13, 13) armchair (diameter = 1.764 nm, length = 36.7 nm) single wall carbon nanotube was inserted to a depth of 1.8 nm. During a further period of equilibration the entrance to the nanotube was blocked by a short range repulsive wall. Throughout the simulation the simulation cell was maintained at 298 K using an Evans [12] thermostat, and qualitatively similar results to those presented below were obtained using the microcanonical ensemble and with a fully flexible tube [13].

At time zero the entrance to the nanotube was opened and the fluid allowed to enter the tube.

Figure 2 reports the (normalized) density in the tube as a function of time and distance along the tube, averaged over 100 numerical experiments (100 separate realizations of the tube filling process each started from a different equilibrated liquid-vapor interface). The tube first fills rapidly with low density fluid whose leading edge (at the capillary penetration length, L) reaches the top of the tube in 82.5 ps (a filling speed of 445 m/s), followed by higher density fluid at lower speeds tending to ~150 m/s for $\rho > 0.2$. These speeds can be compared to that of sound in air of 340 m/s and the root mean square speed of the decane molecules of 230 m/s (at 300 K). The effect of a finite tube length can be seen in the density "overhang" after 200 ps in which fluid collects at the top of the open tube. Within the tube the fluid flows along the walls in the deep potential well close to the cylindrical walls that terminates at the end of the tube. Therefore although open, the end of the tube acts as a barrier to further flow.

Figure 3 is a log plot of penetration length against time for the lower density contours (before the fluid collecting at the tube end influences the filling). The early stage flow is dominated by the rapid acceleration of the molecules on the inner surface of the tube by the attractive force due to the molecule-tube interactions within the range of the potential (first 1 nm of the tube) and this leads naturally to a linear time dependence. We note that simulations [13,14] of spreading drops which completely wet the

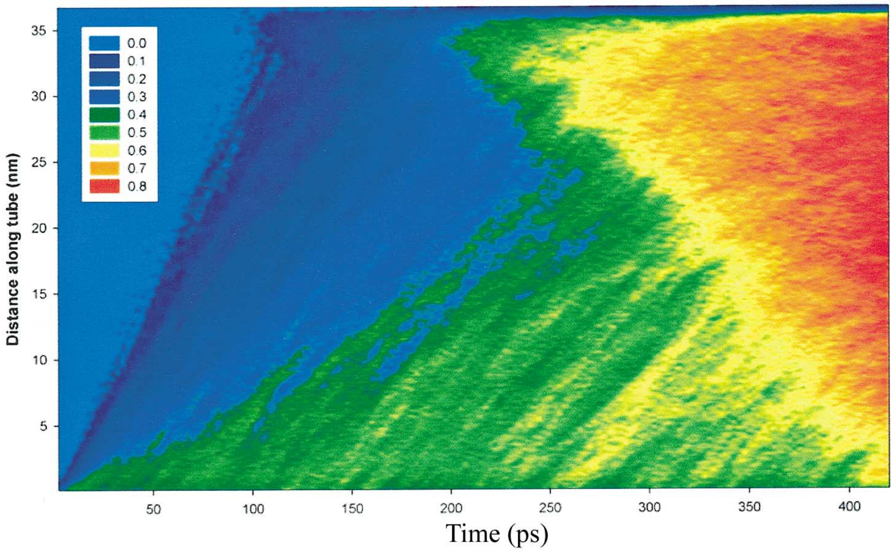

FIG. 2 (color). (normalized) Density ρ as a function of time and height for imbibition of decane at room temperature by a (13, 13) nanotube averaged over 100 imbibition simulations. The density is normalized with respect to the density inside a completely full tube.

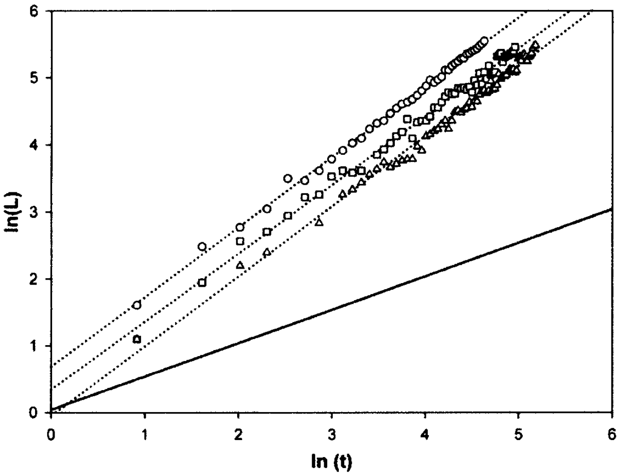

FIG. 3. Natural log plots of the leading edge contours for three normalized densities: 0.11 (○), 0.21 (□), 0.32 (△). The dotted lines are linear fits to the power law $L = bt^x$, $x = 1.0$. The solid line is a plot of the Washburn equation.

surface predict the formation of a very rapidly spreading precursor film in advance of the main wetting line, spreading as t^1 at short times. For our simulations the main flow is along the inner surface [13], and it is possible that for narrow tubes the filling process is analogous to the spreading of the precusor film on a flat surface, albeit at much greater speed due to the increased driving force arising from the convex geometry. Details of the flow front will be published elsewhere [13].

If the nanotube were a macroscopic capillary, filling by laminar flow of a wetting fluid ($\cos\theta = 1$) would be described by the Washburn equation [2]

$$L^2 = (R\gamma/(2\eta))t, \tag{4}$$

where L is the penetration length, R the radius, γ the surface tension, and t the time (see Fig. 3 for the expected behavior of a fluid obeying the Washburn equation with the experimental surface tension and viscosity for decane). Clearly for $R = 0.882$ nm, nanotube imbibition is much faster than expected from the Washburn equation (except for very short times at liquid densities > 0.32) with a linear rather than square root time dependence, although our simulations show imbibing liquid approaches this limit as the capillary radius increases [13]. Reducing the viscosity to take account of either the lower density of the imbibing fluid or the reduction in shear viscosity in a (13, 13) SWNT due to its small radius [15] shifts the intercept of the Washburn curve in Fig. 3 but not the slope.

The processes we describe in this Letter are of both fundamental and applied interest; nanotubes have a regular geometry for which theories can be unambiguously tested, for example, the equations of macroscopic hydrodynamics for steady state flow [16] . SWNT's have been filled with water [17] to act as flow sensors as well as with metals to form nanowires [18–20], and are envisaged as parts in electronic and/or nanofluidic devices [21–25]. Our data indicate that carbon nanotubes may fill and transmit wetting fluids such as oils very rapidly and motivate experimental studies of these fascinating systems [26].

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