Interactions between Carbon Nanotubes and Liquids: Imbibition and Wetting

A. Cuenat*, M. Whitby**, M. Cain*, D. Mendels* and N. Quirke**

*National Physical Laboratory, Division of Engineering and Process Control,
Hampton Road, Teddington, TW11 0LW UK, alexandre.cuenat@npl.co.uk,
**Department of Chemistry, Imperial College, London SW7 2AY, UK, m.whitby@imperial.ac.uk

ABSTRACT

We report on our progress to extend the current experimental measurements of interactions between fluid and materials to times and length scales characteristic of nanomaterials. The rapid imbibition of decane and non-polar fluids by carbon nanotubes is investigated to confirm recent theoretical results obtained using MD simulations. The wetting dynamics of carbon nanotubes and larger carbon fibres (~200 nm) are studied as a function of the liquid. We outline the main experimental challenges both in terms of time resolution and force sensitivity necessary for reliable experiments at these scales and present the first result of in-situ TEM observations of wetting of carbon nanotubes.

Keywords: carbon nanotube, wetting, imbibition, nano-fluidic

1 INTRODUCTION

Nano-tubular structures, and especially carbon nanotubes (CNT), have a large set of potential applications in nanofluidic devices. Most microfluidic devices have been fabricated in silicon or glass and are often limited to the micrometric range due to lithographic constrains. Recently, the capillary filling speed of water in nanochannels around 100 nm high has been measured [1] and the meniscus position qualitatively follows the Washburn model.

However, so far, no efficient design for 3D nanofluidic devices has been found and we may have to resort to manipulating “natural” nano-pipes. CNT provide a test platform that is smaller than capillaries used in fluid experiments and are thus the perfect tool to study confinement and fluid behavior at the nanoscale. In order to make use of these potential nanofluidic applications, it is necessary to understand the flow in a CNT channel and the influence of confinement.

Carbon nanotubes are already in use in composites where their combination of high aspect ratio, small size, high strength and stiffness, low density and high conductivity makes them perfect for improving the mechanical, thermal, and electrical properties of the materials. The three major problems in nanocomposite applications: dispersion, alignment and bonding of carbon nanotubes in the composite matrix, all require a better understanding of the wetting behavior of the nanotube surface.

In summary, CNT interactions with fluids, such as wetting, imbibition and solution rheology are critical in both nano-fluidic and composite applications. Furthermore, this interest extends to the many engineering applications where the wetting dynamics of homogeneous and structured surfaces is critical and to the physico-chemical properties of confined fluids. The present research aims at examining experimentally the interactions of carbon nanotubes with various types of fluids. Fluids filling the inside and surrounding the outside of nanotubes are being examined using a combination of scanning probe microscopy (SPM) and transmission electron microscopy (TEM).

2 FLUID-NANOTUBE INTERACTION

Capillary filling of nanotubes was first reported by Ajayan and Iijima [2] back in 1993. They observed, a very low filling efficiency. Ugarte et al [3] used TEM observation to show the filling of carbon nanotubes by a range of molten metal salts., but again for the smaller tubes (< 5 nm), the filling efficiency was poor.

Interaction of CNT with fluid was also probed by Barber et al [4] using carbon nanotubes attached to an AFM tip. They studied the dipping of the CNT into various organic liquids and measured the vertical forces as the probe was withdrawn from the surface. The diameter of the MWNT was 20 nm with a 2 µm length. They found that with polydimethyl-soloxane (PDMS) catastrophic flooding of the cantilever occurs with jump to contact; this indicated complete wetting of the nanotube. Using other liquids, similar flooding occurred where the nanotube tip was smaller than 0.5 µm. With a longer probe, an equilibrium meniscus was established below the attachment point on the cantilever and force measurements were successfully carried out.

2.1 Molecular Dynamics Simulations

In 2003, N. Quirke et al reported MD simulations of carbon nanotube imbibition [5]. Their key finding was a rapid filling of the pore with a velocity of about 445 ms-1. The filling did not follow the Washburn equation, but instead the filled length dependence was linear with time (rather than proportional to the square root).

In a second paper, N. Quirke et al [6] found that decane molecules were also attracted to the outside of the nanotube and wetted this surface. The velocity of the external wetting was much less than in the pore: 30 times slower in the case of the (13,13) nanotube.

3 EXPERIMENTS

The main objective of this research is to provide experimental evidence of rapid filling of CNT with inner diameter smaller than 5 nm in order to confirm the recent MD simulations [5,6]. The second objective is to provide quantitative data for the interactions between CNT and wetting fluids. The main experimental approach is based on the immersion into fluid of an open nanotube attached to the tip of an AFM. The resulting forces on the nanotube are measured as the probe is advanced, equilibrates and is withdrawn from the surface.

3.1 Sample preparation

The nanotubes are opened using standard chemical and physical treatment [3], so that their central channels are accessible for filling. The tubes are heated in air and oxygen at 700 ^{o}C to open the pores by oxidation of the tips. A further high temperature heating step at 2000 to 2100 ^{o}C in vacuum to graphitise amorphous carbon residues and to remove dangling bonds is done. This annealing step reduces the number of defects in the tubes, which may be important for unimpeded capillary flow. The opening of the tube and the quality of the inner wall are measured using TEM.

For SPM measurement, the open nanotubes are manipulated for attachment to the AFM tip by using a SEM based nano-manipulator (Zyvex Corp, Austin, TX, USA).

3.2 TEM observation

A first set of experiments is carried out to confirm imbibition. This involves immersing open carbon nanotubes into suitable liquids, such as decane and measuring the filling of the nanopore by direct TEM observation. These simple experiments determine that imbibition has taken place, but they do not allow for a precise determination of the timescale and of the force involved. TEM observations show liquid nonadecane droplets mixed with MWNT. The inner diameter of the nanotubes are around 5 nm with a 30 nm external diameter.

3.3 Experimental issues

A considerable number of questions and uncertainties surround these experiments. The first issue is the time resolution needed to measure the imbibition and capillary forces wetting the nanotube. It is clear that as soon as the CNT come into contact with the surface of the liquid, capillary forces cause spontaneous wetting of the entire nanotube. A way to solve this problem is to use a long enough carbon nanotube. The imbibition speed being an order of magnitude larger than the wetting speed, this should increase the time delay between the imbibition and the wetting signal. It may be necessary to functionalize the outside of the nanotube to reduce its wettability.

Regarding the comparison between the MD simulations and the experiments, the MD simulations are made for CNT without defects and with perfect openings at the end. Real nanotubes may have a variety of dangling bonds, irregularities, lattice defects and attached functional groups. Annealing of CNT is used to reduce these imperfections, but the possibility remains that they may hinder imbibition. It is interesting to note that only 1 in 30 of the open carbon nanotubes used by Ugarte et al were successfully filled [4].

Trapped air molecules inside the carbon nanotube may eventually impede the filling due to the fact that the top end of the nanopore is closed. In the existing MD simulations a vacuum is assumed inside the tube. Hopefully the pressure-build up effect will be small or only comes in to play after imbibition can be detected. It is however not clear whether the fluid dynamics associated with an open nanotube penetrating a thin layer of molecules allows imbibition to occurs spontaneously, or if a driving force is needed.

4 CONCLUSION

These results will be used to make the most of CNT properties and to explore their possible use as nano-test tubes filled with different fluids. We envisage the use of CNT nanotubes for fluid transport applications in the near future.

5 ACKNOWLEDGEMENT

The authors whish to acknowledge the contribution of Milo Schaffer and Mathhew Longhurst from Imperial College to this project.

REFERENCES

[1] N.R. Tas et al., "Capillary filling of water in nanochannels". Appl. Phys. Lett.,85, 3274, 2004.
[2] P.M. Ajayan et al., "Opening Carbon Nanotubes with Oxygen and Implications for Filling". Nature, 362, 522, 1993.
[3] Ugarte, D., et al., "Filling carbon nanotubes." Applied Physics a-Materials Science & Processing, 67, 101, 1998.
[4] A. H. Barber, S.R. Cohen and H. D. Wagner, "Static and DynamicWetting Measurements of Single Carbon Nanotubes," Phys. Rev. Lett, 92, 186103, 2004.
[5] S. Supple and N. Quirke, "Rapid Imbibition of Fluids in Carbon Nanotubes," Phys. Rev. Lett, 90, 214501, 2003.
[6] S. Supple and N. Quirke, "Molecular dynamics of transient oil flows in nanopores I: Imbibition speeds for single wall carbon nanotubes." J. Chem Phys., 121, 8571, 2004.