

# Hydrodynamics of Carbon Nanotubes - Contact Angle and Hydrophobic Hydration

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## ABSTRACT

Molecular dynamics simulations are used to study the hydrophobic-hydrophilic behavior of carbon nanotubes in water. We report contact angles for tube diameters ranging from 25 to 75 Å and for droplets containing up to 4632 water molecules. Furthermore, we investigate the interaction between two carbon nanotubes immersed in water and we extract the hydration acting between the tubes. We find that two (16,0) carbon nanotubes in water exhibit drying of the interstitial water for an initial minimal carbon-carbon distance of 10-12 Å. Finally, a tentative study of a cluster of sixteen carbon nanotubes in water reveals interesting self arranging behavior into carbon nanotube ropes.

**Keywords:** Contact Angle, Hydrophobic Hydration, Nanofluidics, Carbon Nanotubes, Self Organization

## 1 INTRODUCTION

Whether and how carbon nanotubes can be used as fundamental engineering entities in nanofluidic devices such as AFM tips (1), biosensors (2) and others, depends critically on their wetting behavior. There is experimental evidence (3) that liquids with surface tension exceeding a limit of  $\approx 130 - 170$  mN/m do not wet single-wall CNT bundles and thus water should wet a CNT since its surface tension is 72 mN/m at room temperature. Direct observations of aqueous inclusions in multiwall CNT (4; 5) show wetting of the CNT, but the fluid in these experiments contains substantial amounts of carbon dioxide and methane which may result in a different surface tension. Here, we characterize the interaction of pure water with CNTs in two canonical problems using molecular dynamics simulations. The first problem is the determination of the contact angle of nano-size water droplets inside CNT of diameters in the range from 25 to 75 Å. The second problem involves the study of capillary cavitation between two CNTs in water leading to a hydrophobic force with a range of. The information gained is a possible starting point for developing a meso-scopic model of the CNT - water system. It is expected that the long range hydrophobic force between multiple CNTs in water results in self-assembly of the latter. As an outlook, we present a fully atomistic study

of sixteen (16,0) CNT in water initially arranged on a four by four lattice.

## 2 COMPUTATIONAL MODEL

The molecular dynamics simulation technique and the force field we use in the present study were introduced in earlier works, cf. (6; 7). The water-water interaction is modeled by the flexible SPC water model (8). It represents the O-H bond stretching and the H-O-H bending by harmonic potentials. The intermolecular interaction of the water is modeled by an O-O Lennard-Jones (LJ) potential and by a Coulomb potential between the point charges residing on the atom sites. The force field describing the CNT consists of a Morse potential, a harmonic angle potential, and a torsion potential. A LJ interaction between carbon atoms is added with the standard 1-2 and 1-3 nearest neighbor exclusion rules applied. The carbon-water interaction is also modeled by a LJ potential, with the parameters  $\epsilon_{CO} = 0.3135$  kJ mol<sup>-1</sup> and  $\sigma_{CO} = 3.19$  Å obtained from experimental data (9). The Lennard-Jones and the Coulomb potentials are considered within a cutoff distance  $r_c$  of 10 Å using smooth truncation of the potentials (10). The equations of motion are integrated using the leapfrog scheme with a time step of 0.2 fs.

Table 1: Overview of the CNT-water systems. All systems are periodic in the direction of the tube axis. The length of the tubes is 138.9 Å (periodic in the direction of the tube axis) and the chirality corresponds to a zig-zag CNT.  $D$  denotes the diameter of the CNT.  $N_{H_2O}$  is the number of water molecules in one periodic image of the system.

Case	Chirality	$D$ [Å]	$N_{H_2O}$	Contact Angle
A	(32, 0)	25.0	360	$103.3^\circ \pm 2.2^\circ$
B	(64, 0)	50.0	1872	$105.9^\circ \pm 1.4^\circ$
C	(96, 0)	75.0	4632	$106.9^\circ \pm 1.6^\circ$

### 3 RESULTS AND DISCUSSION

#### 3.1 Contact Angles of Water Droplets in Carbon Nanotubes

We determine the contact angle of nanometer-size water droplets in carbon nanotubes of diameters 25 Å, 50 Å, and 75 Å, corresponding to the cases A, B, and C in Table 1, respectively. The initially flat drops (having a density of  $1 \text{ g cm}^{-3}$ ) are composed of twelve layers of randomly oriented water molecules. The CNT-water system is equilibrated during 30 ps and afterward samples are taken every 0.04 ps for 170 ps. From these samples we construct isochore profiles of the water droplets. The contact angle is then determined by fitting a circle to the spherical water-vapor interface as illustrated in Figure 1 and Figure 2.

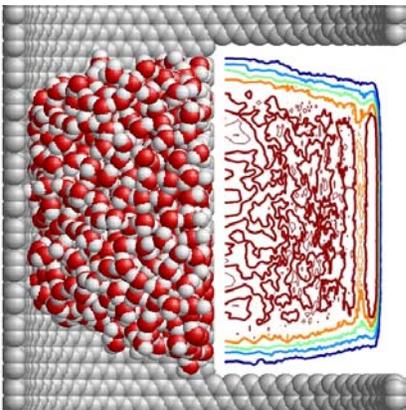


Figure 1: Water droplet confined in a CNT (case B in Table 1). On the right hand side of the tube we display a circumferentially averaged isochore line plot which is extracted from a 170 ps simulation. The isochore lines correspond to 0.2, 0.4, 0.6, 0.8 and  $1.0 \text{ g cm}^{-3}$  (labels are omitted for clarity). One can clearly observe a non-wetting behavior of the water.

We apply this procedure to the isochores at 0.45, 0.55, 0.65, and  $0.75 \text{ g cm}^{-3}$  for the cases A, B, and C, and obtain an average contact angle of the confined water droplets of  $103.3^\circ \pm 2.2^\circ$ ,  $105.9^\circ \pm 1.4^\circ$ , and  $106.9^\circ \pm 1.6^\circ$ , respectively. These results indicate that pure water is not wetting CNT which is in contrast to the experimental findings and predictions by Gogotsi *et al.* (4; 5) and by Dujardin *et al.* (3). It should be emphasized that the above mentioned experiments do not include pure water but aqueous solutions which may exhibit considerably different surface tension and could thus lead to the observed differences. On the simulation side, one has to keep in mind that both the validation for the CNT force field (6) and for the water model (11) yielded satisfactory results but that there is still a need to test

the CNT-water interaction. However, a persistent non-wetting behavior was observed even for a 20% increase in the interaction parameter  $\epsilon_{CO}$  (cf. Werder *et al.* (7)).

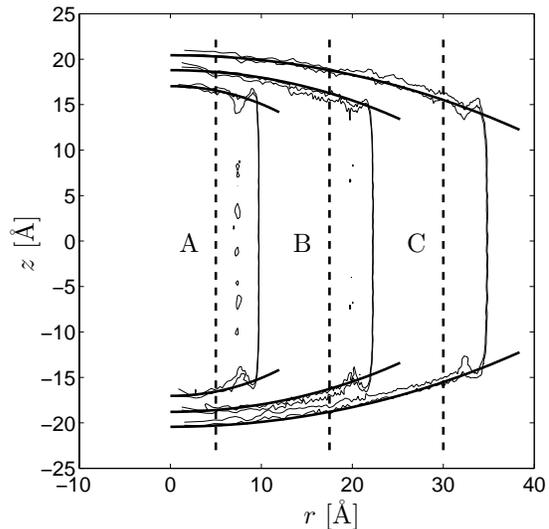


Figure 2: Plot of the isochore lines  $0.6$  and  $0.7 \text{ g cm}^{-3}$  for the cases A, B, and C. The least squares fit of the  $0.65 \text{ g cm}^{-3}$  isochore line is super-posed. For the fit only the part of the isochore lines that lies outside the CNT-water interface is considered (as indicated by the dashed vertical lines).

#### 3.2 Hydrophobic Hydration of Carbon Nanotubes

We study the hydrophobic-hydrophilic behavior of two (16,0) carbon nanotubes surrounded by water at atmospheric pressure and room temperature (300 K). The simulations involve 4536 water molecules and 832 carbon atoms for each CNT. The methodology to determine the potential of mean force between the two CNT is as follows. First the systems (differing in their initial tube spacing  $S$ ) are equilibrated for 4 ps. During the simulation a control mechanism is applied to smoothly constrain the tube spacing to its initial value. At equilibrium, the force needed to maintain this spacing  $S$  balances the hydration force and we are thus enabled to extract the constraining force as a function of the spacing  $S$  and in consequence the potential of mean force, cf. Figure 4. The first equilibrium of the drying transition is found at the point of contact where the minimum distance between the CNT is approximately  $3.5 \text{ Å}$  (the LJ equilibrium distance between two carbon atoms is  $3.2 \text{ Å}$ ). The attractive part of the force reaches its maximum at a tube spacing of  $5.2 \text{ Å}$ . This is approximately  $1 \text{ Å}$  less than the spacing required to host one layer of

water. The force decreases rapidly at larger distances and reaches a low, but positive value at a tube spacing of  $6.5 \text{ \AA}$  which allows the accommodation of an unstable layer of water molecules. The second equilibrium is finally reached at a carbon-carbon distance of approximately  $9.2 \text{ \AA}$  coinciding with the thickness of two layers of water. An extended and more thorough study of the hydrophobic hydration of buckyballs and CNT is in preparation (12).

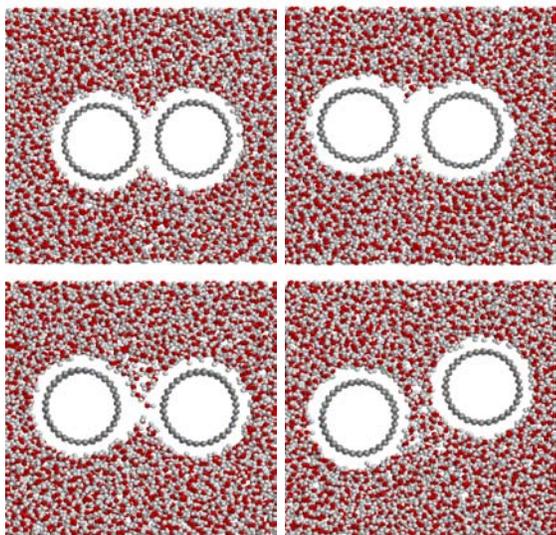


Figure 3: Snapshots of the simulations of two carbon nanotubes in water. The center of mass distance (and the minimum carbon-carbon distance) are  $16.0$  ( $3.48$ ),  $19.5$  ( $6.98$ ),  $20.5$  ( $7.98$ ),  $22.0$  ( $9.48$ )  $\text{\AA}$ .

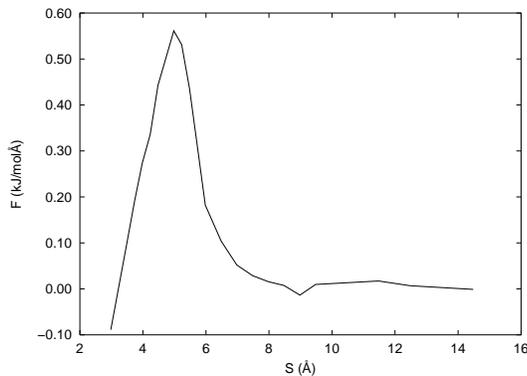


Figure 4: Hydration force between two  $(16,0)$  CNT immersed in water as a function of the tube spacing  $S$ .

### 3.3 Self Organizing Behavior of Carbon Nanotubes in Water

The long range hydrophobic force is expected to result in a self-assembly and alignment of multiple carbon nanotubes suspended in water. In a preliminary study of this effect we consider sixteen unconstrained  $(16,0)$  CNT in water ( $12'400$  water molecules and  $16 \times 832$  carbon atoms). The center of mass (COM) of the CNT are initially placed on a regular four by four lattice with a lattice constant of  $20 \text{ \AA}$ , allowing a single layer of interstitial water. The chosen COM spacing results in a minimum carbon-carbon distance of  $7.48 \text{ \AA}$ . The tubes are only constrained to remain at their respective position during the  $4 \text{ ps}$  equilibration time, afterward they are released. Due to the periodicity of the system, water can be trapped between the tubes as can be observed in Figure 5.

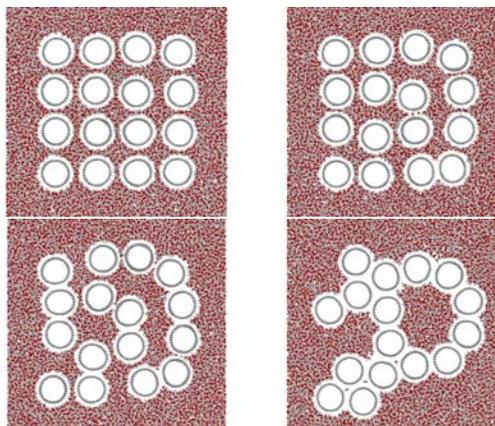


Figure 5: Snapshots of the simulation of 16 carbon nanotubes in water. From an initial regular four by four arrangement the system evolves into a bundle of closely packed tubes with occasionally trapped water pockets. The periodicity of the system prevents these pockets to empty. Top row:  $4 \text{ ps} - 10 \text{ ps}$ , bottom row:  $16 \text{ ps} - 120 \text{ ps}$ .

## 4 CONCLUSIONS

We have conducted molecular dynamics simulations to characterize the interaction between CNT and water. It was shown, that for the described model potentials, wetting of the CNT by water droplets does not occur. This is in contradiction to the wetting behavior observed experimentally (13; 5).

Furthermore, we presented a tentative simulation on the behavior of clusters of CNT.

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