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Surfactant-nanotube interactions in water and nanotube separation by diameter: atomistic simulations

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Abstract. A non-destructive sorting method to separate single-walled carbon nanotubes (SWNTs) by diameter was recently proposed. By this method, SWNTs are suspended in water by surfactant encapsulation and the separation is carried out by ultracentrifugation in a density gradient. SWNTs of different diameters are distributed according to their densities along the centrifuge tube. A mixture of two anionic surfactants, namely sodium dodecylsulfate (SDS) and sodium cholate (SC), presented the best performance in discriminating nanotubes by diameter. Unexpectedly, small diameter nanotubes are found at the low density part of the centrifuge tube. We present molecular dynamics studies of the water-surfactant-SWNT system to investigate the role of surfactants in the sorting process. We found that surfactants can actually be attracted towards the interior of the nanotube cage, depending on the relationship between the surfactant radius of gyration and the nanotube diameter. The dynamics at room temperature showed that, as the amphiphile moves to the hollow cage, water molecules are dragged together, thereby promoting the nanotube filling. The resulting densities of filled SWNT are in agreement with measured densities.

1 Introduction

Carbon nanotubes are promising materials for use in nanotechnology due to their outstanding properties. One of these is the geometry dependent electronic structure: given the chiral indices (n, m) [1], single-walled carbon nanotubes (SWNTs) are found to be metallic or semiconducting. Applications have been proposed for both types. Presently the synthetic methods to produce nanotubes yield samples formed by nanotube bundles containing a mixture of species of several diameters and electronic structures. The effective use of carbon nanotubes in many technological applications relies either on the availability of large scale sorting methods or selective growth methods [2].

Among several sorting methods developed in recent years, the non-destructive method reported by Arnold and collaborators [3] appears as a powerful tool to prepare monodisperse samples. The idea, first used by O'Connel [4], relies on the dispersion of nanotubes in aqueous detergent solutions. Ultrasound treatment is needed to break the bundles and allow the surfactants to wrap on the tubes and effectively suspend them in water. The isolation of particular nanotubes is carried out by ultracentrifugation inside a density gradient. The sorting process was successful when SC was used to suspend nanotubes and co-surfactant mixtures, when used, were added just before ultracentrifugation. It seems that the specific way surfactants bind to the nanotube walls is relevant to the ultracentrifugation outcome. Experimentally, it was found that the solubility of nanotubes in SDS solutions decreases with increasing centrifugation force [5]. Recent molecular dynamics studies of the nanotube/SDS system in water showed that, even at high surfactant density, the amphiphiles do not cover the nanotube surface evenly but rather form aggregates over the molecules adsorbed on the walls [6].

The density of surfactant-encapsulated nanotubes was considered to decrease with increasing nanotube diameter, when the nanotubes are empty. As a consequence, larger diameter tubes were expected to be found at the low density part of the centrifuge tube. Surprisinly, nanotube distribution in the density gradient occurs in the opposite order: small diameter SWNTs lie at the low density part. Similar experiments were carried out by Wenseleers and collaborators [7]. They have shown that the ultrasound waves provoke the breaking of the tubes. Spectroscopic characterization of samples treated by sonication is consistent with the open tubes being filled with water. A molecular dynamics study was carried out by Hennrich et al. [8] to determine the density of water filled SWNTs. Water was allowed to enter SWNTs of several diameters in MD simulations. A layered structure of water molecules was obtained inside the tubes and the filled tube density still decreased with tube diameter.

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In the present work we studied the interaction of surfactant molecules with SWNTs. Molecular Dynamics (MD) with a suitable force field was used to investigate the interaction of the nanotube-surfactant systems, both isolated and surrounded by water. We found that surfactant molecules, when approaching the tube open end, are attracted to the nanotube cavity and drag water with them. The calculated densities showed that tubes filled with water or water-surfactant mixtures, provided that they carry a hydrated surfactant layer at the external surface, are in agreement with experimentally measured densities. Besides, our calculations showed why specific co-surfactant mixtures can discriminate small diameter/large diameter SWNTs. We present the methodology in Section 2, and results and discussion follow in Section 3.

2 Computational details

To study the structure of the SWNT/surfactant system we considered three amphiphiles: sodium dodecylsulfate (SDS) and sodium cholate (SC), the most commonly used surfactants in experiments, and an aromatic amphiphile, 2,3-bis[2-methoxyethoxy] – naphthalene (MEN). The latter surfactant is non-ionic and has an aromatic segment that should increase the adhesion to the nanotube surface [9]. All MD calculations and structure optimizations were carried out using the CVFF-950 [10] force field as implemented in Cerius2 [11] package. Bonding parameters for water molecules were taken from CVFF force field and atomic charges from the SPC [12] water model. Calculations included valence terms (bond stretch, bond angle, torsion angle), as well as van der Waals and Coulomb terms. Charge distributions in surfactant molecules were calculated via Rappé-Goddard [14] charge equilibration scheme of the isolated molecule at the equilibrium geometry and kept frozen during energy minimization procedures and solvated MD. Ionic surfactant molecules were treated as pairs of organic anion separated from sodium cation in MD simulations.

Constant volume (NVT) and constant pressure (NPT) MD simulations were performed at 300 K, with a time step of 1 fs. The temperature control was made by the Nosé-Hoover algorithm [15]. The water filling of the simulation box measuring 35 × 35 × 90 Å started by the hexagonal ice crystalline structure. The system was driven to thermal equilibrium, that is, until the radial distribution of water oxygen atoms reproduced that of the literature [16], after around 20 ps. A cylindrical void of an appropriate diameter was created in the center of the box to accommodate the nanotube. After this process, the periodic box contained of the order of 3300 water molecules and 700 carbon atoms from the SWNT. A second void was created to include the surfactant, when needed.

In some cases we calculated potential energy averages and standard errors. We proceeded an energy minimization of the simulation box, considering the water molecules as rigid bodies, until the average force dropped below 0.5 Kcal/mol Å. The energy-minimized box was then thermalized for 10 ps at 300 K. The initial atom velocities were randomly assigned from a 600 K Maxwell-Boltzmann distribution. The atomic positions and velocities from the last frame of the thermalization run were used as initial conditions for the production, average-taking run, which lasted 5 ps and data were recorded every 10 time steps (10 fs), resulting in 500 data points for potential energy average and standard errors evaluation.

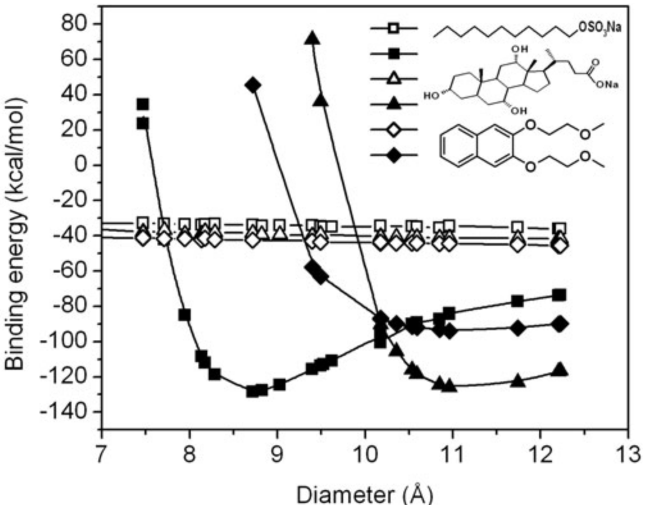

Fig. 1. Binding energies (kcal/mol) as a function of nanotube diameter (Å). Open symbols: surfactant adhered to the outer nanotube surface. Full symbols: surfactant inside the nanotube cavity. The surfactant molecular structures are sketched beside the labels: squares, SDS; triangles, SC; diamonds, MEN.

3 Results and discussion

3.1 Surfactant binding energy to SWNTs

We first studied isolated pairs of one nanotube and one surfactant molecule. The amphiphiles were allowed to interact with nanotubes in two distinct situations: at the outer tube surface (open symbols in Fig. 1), and inside the tube (full symbols in Fig. 1). The binding energy of the SWNT-surfactant system was calculated as:

$$BE = E_{SWNT+surf} - (E_{SWNT} + E_{surf}), \qquad (1)$$

where $E_{SWNT+surf}$ is the minimum energy of the SWNT + surfactant system and E_{SWNT} and E_{surf} are the minimum energies of the isolated molecules. By this definition, more negative BE values imply more stable configurations.

We notice that these molecules present similar binding energies at the outer nanotube surface, although a preference for more planar surfactant structure can be deduced. As expected, the evolution is toward stronger binding as the tube diameter increases, in all three cases. The nanotube cavity discriminates among these amphiphiles, as demonstrated by the curves with full symbols. Due to geometrical constraints, these surfactants are not allowed inside tubes whose diameters are smaller than a

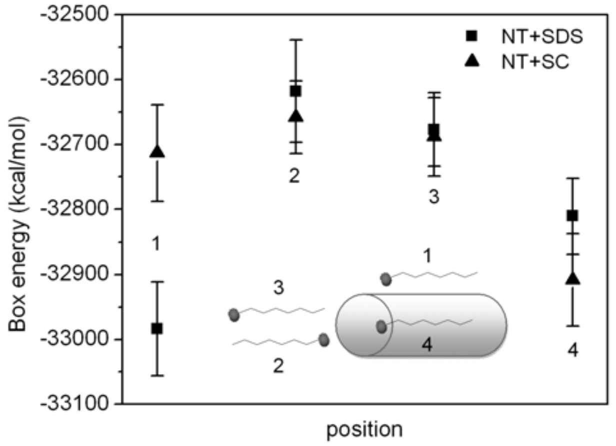

Fig. 2. Average potential energy (kcal/mol) of the simulation box, at 300 K, of the solvated (14, 0) nanotube-surfactant system in four configurations: (1) surfactant at the outer nanotube surface; (2) surfactant close to the nanotube open end, polar head first; (3) surfactant close to the nanotube end, apolar tail first; (4) surfactant inside the nanotube cavity. Error bars are the standard errors. Squares, SDS; triangles, SC.

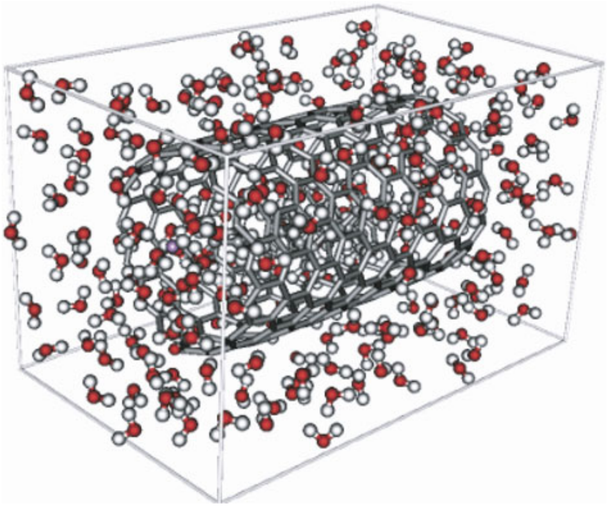

Fig. 3. (Color online) NPT simulation box, at 300 K, used to calculate the average number of molecules (water or surfactant or both) inside nanotubes.

critical diameter, which depends on the radius of gyration of each molecule. Assuming that this critical diameter corresponds to zero *BE*, one obtains 7.5 Å for SDS, 9.0 Å for MEN and 9.7 Å for SC. MD simulations were then carried out in order to verify whether the surfactant molecule could be attracted to the tube interior or not, in case any barrier would prevent it to happen. These simulations were run in a canonical NVT ensemble at 300 K. The open-end $(14, 0)$ nanotube, which has a diameter of 10.7 Å, was used. All surfactants, when approached the open end, where attracted to the internal region. It is interesting to note that the surfactant travels inside the tube until the opposite open end is reached, when it is attracted back to the interior of the tube. The surfactant kinetic energy is gradually transferred to the SWNT's vibrational modes, via the van der Waals interactions, such that the oscillatory motion is damped. This friction leads to the surfactant eventually coming to rest inside the SWNT.

Water molecules can change the binding of amphiphiles to the nanotubes. Water effects were accounted for using NVT dynamics. Typical results are displayed in Figure 2. Here we show time averages of the total box potential energy, as well as the standard deviation, in several configurations of the SWNT-surfactant system, as indicated in the sketch included in Figure 2. Results are for the (14, 0) nanotube interacting with SDS and SC. During the simulations at 300 K, water molecules did not enter the tube. We recall that this tube has a diameter of 10.7 Å. According to the data in Figure 1, SC inside this tube has larger binding energy than SDS. Although the isolated pair SDS-SWNT has the lowest energy when SDS lies inside the tube, the possibility of interacting with water changes the relative stability and favours SDS binding at the outer SWNT surface. The solvated SC-SWNT, on the other hand, has SC inside the tube as the lowest potential energy configuration. Similar calculations were performed for SDS interacting with the (7, 5) nanotube (diameter 8.2 Å). This tube diameter is close to the largest binding energy for SDS inside the tube. In this case the potential energy averages resulted similar to those obtained for SC-SWNT, with SDS inside the tube having the smallest potential energy.

The above results suggest that SDS preferentially fills smaller diameter tubes while SC only enters tubes larger than 9.7 Å of diameter. In the experiments, Arnold et al. [3] reported an enhanced isolation of larger diameter SWNTs when SC was used alone, and an enhanced isolation of smaller diameter SWNTs in a mixture of SDS and SC with the weight ratio 1:4.

3.2 Density of suspended nanotubes

Calculating the density of an object of molecular dimensions inside a liquid is not an easy task. A model for the layer attached to the external SWNT surface has to be assumed. We allowed SC to pack around nanotubes of several diameters and measured the thickness of the resulting layer. Then we obtained the solid state density of nanotubes in hexagonal packing by energy minimization adopting the same force field used in the MD simulations.

The evaluation of the number of species inside a nanotube in equilibrium with water involved NPT calculations in a box of similar dimensions as above, shown in Figure 3, that contains enough water molecules to reproduce a density of 1 g/cc. A nanotube open at both ends was inserted, such that the distance between the nanotube replicas was 10 Å along the nanotube axis. Water or water + surfactant molecules were then inserted inside the nanotube and the MD simulations were run until the equilibrium number of molecules inside the tubes was achieved, at the same pressure of the water box. These were used as unit cells for the solid state calculations.

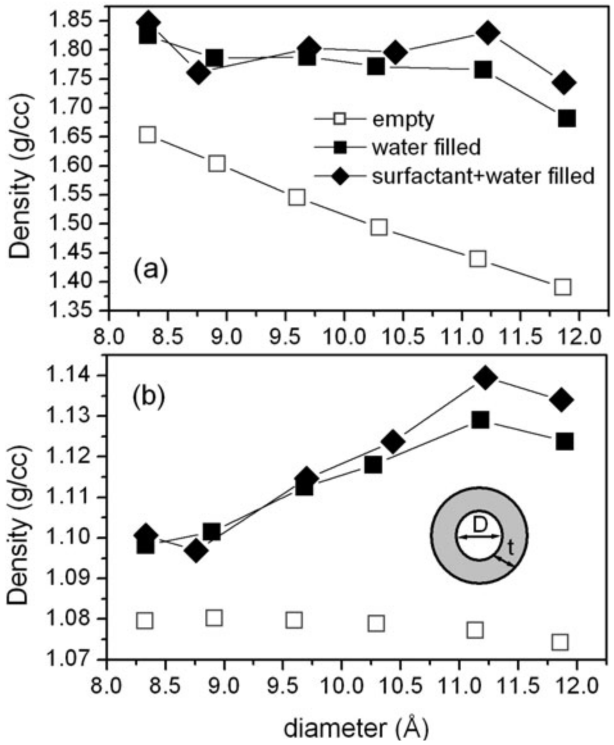

Fig. 4. (Color online) (a) Densities of nanotubes in the solid state and (b) densities of suspended nanotubes including a surfactant shell, calculated from equation (2). The inset shows the geometry assumed to calculate densities with a surfactant shell. Empty squares, empty nanotubes; full squares, water-filled SWNT; full diamonds, water+surfactant filled SWNT.

The density of suspended nanotubes was considered to depend upon a SC shell of thickness t and density ρ_{shell} that covers the outer nanotube surface according to the formula

$$\rho = \frac{\rho_{solid} D^2 + \rho_{shell}[(D+2t)^2 - D^2]}{(D+2t)^2} \qquad (2)$$

where ρ_{solid} is the nanotube density obtained in the solid state minimization and D is the corresponding diameter. The measured surfactant shell was $2t \approx 17$ Å, and a shell density close to that of water, $\rho_{shell} \approx 1.01$ g/cc was assumed. The results are displayed in Figure 4.

The calculated densities of empty, water-filled and water + surfactant-filled nanotubes show that there is not a density differentiation for empty nanotubes. Those filled with water have densities that increase with increasing diameter. However, as amphiphiles are in the solutions they necessarily enter the nanotube cavity as well, and the densities increase further. These densities should be considered as the largest possible, so that a more realistic picture would consider that some tubes are empty, some partially filled and some other with the largest possible amount of molecules in the cavity, giving a continuous variation of the density as a function of diameter.

In summary, we proposed a model, based on molecular dynamics calculations, by which carbon nanotubes are separated by diameter in surfactant solutions due to the ability of SWNTs in encapsulating molecules of appropriate size. The optimal internal adsorption depends on the relationship between the radius of gyration of the surfactant and the tube diameter. Given a surfactant layer attached to the external surface, these non-uniform objects have densities varying in the interval 1.08 to 1.15 g/cc, in agreement with experiment.

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