

Buckyballs in water: structural characteristics and energetics

By

E. M. Kotsalis, R. L. Jaffe, J. H. Walther, T. Werder AND P. Koumoutsakos

1. Motivation and Objectives

The 1985 discovery by Curl, Kroto, and Smalley of the molecule C₆₀ (dubbed “buckminsterfullerene” and nicknamed the “buckyball”) marked the first time that elementary carbon was found to form stable molecules in which the atoms are arranged in closed shells. Ever since then, chemists have found numerous ways to produce variations on that theme, generically dubbed “fullerenes”. One such class of molecules is that of the carbon nanotubes, which are novel structures with unique mechanical and electrical properties (Odom *et al.* 2000). Applications of buckyballs have been proposed in fluidic sensor technology (Wang *et al.* 1996; Amao *et al.* 1999). The interaction of the buckyball with the surrounding fluid is therefore of great importance. In this study we consider the structural characteristics and energetics of buckyballs in water using molecular-dynamics simulations. Specifically, we report on the breathing frequency of a buckyball in water, and characterize the carbon-water interface through water density profiles and the orientation of the water molecules. Finally we consider the energetics involved in introducing a buckyball into water to study the hydrophobic-hydrophilic behaviour of the buckyball water interface.

2. Accomplishments

2.1. Method of calculation

The buckyball-water system is studied using molecular-dynamics simulations. The water molecules are modeled by the flexible SPC potential which features harmonic stretch and bend terms between the oxygen and hydrogen atoms. The non-bonded interactions involve a Coulomb term between the partial charges of the water, computed using a smooth truncation, and a Lennard-Jones term between the oxygens of the water (Walther *et al.* 2001). The buckyball is modeled by terms describing Morse bond stretch, harmonic cosine bending and a 2-fold torsion potentials. We also consider Lennard-Jones interactions between carbon-carbon (excluding 1-2 and 1-3 pairs) and oxygen-carbon atoms. The water molecules are initially placed on a regular cubic or rectangular lattice for the simulation of one or two buckyballs in water, respectively. The system is equilibrated to obtain the desired temperature of 300 K using velocity scaling. The timestep is 0.2 fs which has been proved sufficient for stability of the trajectory and conservation of energy. The initial placement of the water molecules does not allow a predetermined bulk water density in the vicinity of the buckyball. Therefore, during the equilibration we adjust the size of the computational box by re-positioning the periodic boundaries to match the target bulk density of water ρ_0 of 997 kg m^{-3} .

TABLE 1. Summary of cases considered. n_{WM} denotes the number of water molecules and n_B the number of buckyballs in the simulation. Case 12 corresponds to a simulation of the buckyball in vacuum and the cases with $n_B = 0$ correspond to a pure water simulation. r_C is the long-range cutoff we used and S is the initial wall-to-wall distance of the two buckyballs.

Case	n_{WM}	n_B	$r_C(\text{\AA})$	$S(\text{\AA})$
1	702	1	9.50	
2	702	1	12.66	
3	1304	1	15.83	
4	961	2	12.66	4.676
5	1018	2	12.66	6.676
6	1019	2	12.66	7.676
7	1123	2	12.66	8.676
8	1120	2	12.66	10.676
9	1120	2	12.66	12.676
10	729	0	9.50	
11	729	0	12.66	
12	0	1	12.66	

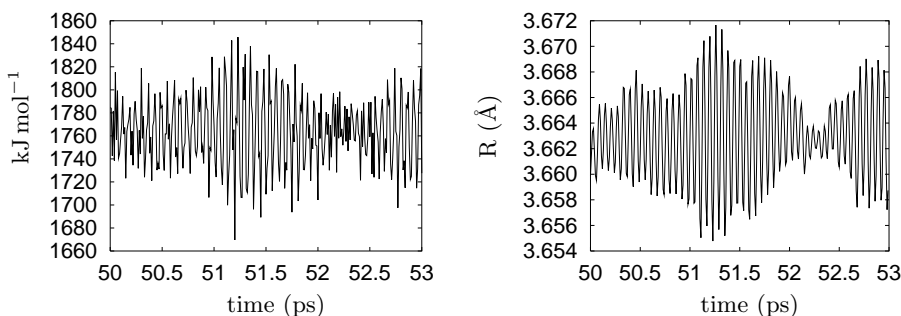


FIGURE 1. Left: The carbon-carbon Lennard-Jones interaction energy. Right: The oscillation of the radius of the buckyball.

2.2. Buckyball in vacuum

Previous studies of carbon nanotubes (CNT's) in vacuum and in water (Walther *et al.* 2001) indicated that the present CNT potentials provide an accurate description of the breathing mode of the CNT. The present studies extend the validation of the potentials by considering buckyballs in vacuum and in water. The simulation for the buckyball in vacuum was conducted for 6 ps with an initial 2 ps equilibration. The predicted breathing mode extracted from the time history of the radius of the buckyball is 542 cm^{-1} . This result is in good agreement with the experimental Raman spectroscopy value of 491 cm^{-1} (Venkateswaran *et al.* 1999). A useful observation is that the energy due to carbon-carbon Lennard-Jones interaction also oscillates with a frequency of 542 cm^{-1} . Introducing the buckyball in water increased the frequency of the breathing mode to 546 cm^{-1} and the Lennard-Jones potential oscillated with a frequency of 547 cm^{-1} (see also Fig. 1). A similar, small increase was also observed in the CNT case (Walther *et al.* 2001). The characteristics of all the MD trajectories are shown in Table 1.

2.3. Buckyball in water

Molecular-dynamics trajectories were computed for a buckyball in water. Three cases were considered: Case 1 with the buckyball surrounded by 702 water molecules and a cutoff of $3\sigma_{oo}$ (9.5Å); Case 2 with the buckyball surrounded by the same number of water molecules but with a cutoff of $4\sigma_{oo}$ (12.66Å); and Case 3 with a long-range cutoff of $5\sigma_{oo}$ and the buckyball surrounded this time by 1304 water molecules (Table 1). The size of the computational box in Cases 1 and 2 was $28 \times 28 \times 28$ Å and in Case 3 it was $34 \times 34 \times 34$ Å. We performed these three different simulations in order to get cutoff independent results. The choice of a cutoff length of $4\sigma_{oo}$ is sufficient because Cases 2 and 3 revealed no significant difference in the orientation of the water molecules and in the number of the hydrogen bonds that are built, and there was no noticeable distinction between their radial density profiles (see Fig. 2). We will present here the results from Case 2. The statistics are collected after the equilibration every 20 fs until 50 ps of the system with a total of 1500 samples.

2.3.1. Radial density profiles

The radial density profiles of the water for Case 2 shown in Fig. 2 are sampled in 60 spherical bins of constant spacing extending from the surface of the buckyball. The coincidence of the peaks in the oxygen and hydrogen profiles at a distance r^* of 3.2 Å measured from the surface of the buckyball indicates that the water molecules tend to be tangential to the buckyball surface. It is important to note that the closest oxygen-to-buckyball surface is detected at a distance of 2.3 Å and the closest hydrogen at distance of 1.3 Å. The difference in these distances corresponds to the OH bond length. From the plots (see also Fig. 2) we may conclude that the water molecules stand off approximately 3.2 Å from the surface of the buckyball.

2.3.2. Angle profiles

Let r_{BO} denote the line from the buckyball center to the oxygen atom of a water molecule. The spatial orientation of the water molecules is probed by considering the following three angles: (i) the angle ϕ formed by r_{BO} and the dipole moment, (ii) the angle ψ between r_{BO} and each of the OH-bonds and (iii) the angle α formed by r_{BO} and the normal to the plane of the water molecule (see Fig. 3). Because of the planar symmetry of water we compute the absolute value of α . The orientation of the water is computed at a distance of 2.8, 3.2, 3.9, 4.7, 5.9 and 7.4 Å from the buckyball surface to the oxygen of a water molecule, respectively. At a distance of 2.8 Å and 3.2 Å the plane of the water (α -angle) clearly shows the preference for an angle of about 180° (see Fig. 4) indicating that the HOH-plane is tangential to the surface of the buckyball. The peaks in the distributions become less pronounced, and the most probable angle shifts to 160° and 140° at distances of 3.9 and 4.7 Å, respectively. At a distance of 5.9 Å there is a slightly elevated probability for an angle of 90°. This distance corresponds to the second peak in the water density profile. Concerning the orientation of the dipole moment (ϕ -angle), at distances of 2.8 and 3.2 Å, the angles are distributed around 90° with an average of 88° (see Fig. 5). It can be seen that the distributions become broader as the distance increases. The profile for the orientation of the OH-bonds (ψ -angle: see Fig. 6) at 2.8 Å shows that the strongest preference is for an angle of about 95° which confirms, like the previous angle profiles, that the HOH-plane is tangential. As the distance is increased, the profile has its peaks at 100°, 110°, 123°, and finally 180° at a distance of 5.9 Å: this corresponds to a rotation of the plane around its normal. Finally, at a distance of 7.4 Å,

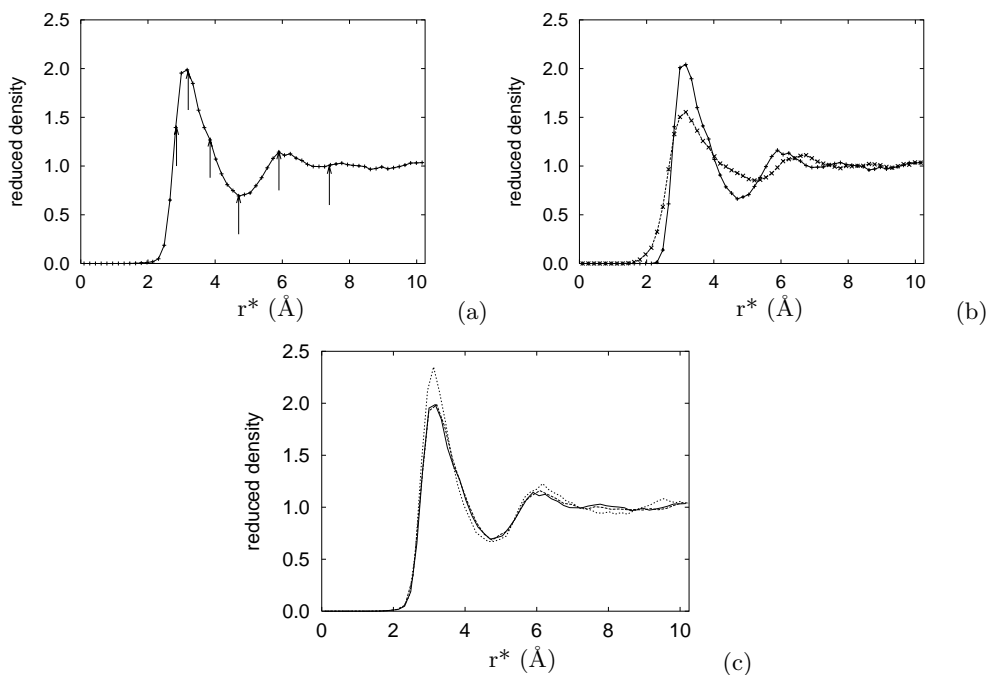


FIGURE 2. (a): The radial density profile of water for Case 2. The arrows indicate the center of the bins used for the profiles of the orientation of the water. (b): Oxygen density profile. —+—: (ρ_O/ρ_O^0) and hydrogen density profile - -x- -: (ρ_H/ρ_H^0) for Case 2 where ρ_O^0 and ρ_H^0 are the bulk densities of oxygen and hydrogen, respectively. r^* is the distance from the surface of the buckyball. c): The radial density profiles for Cases 1, 2 and 3. There is no noticeable distinction between the ones of the Cases 2 and 3. In Case 1 the value of the reduced density at the first peak is 17.5 % higher.

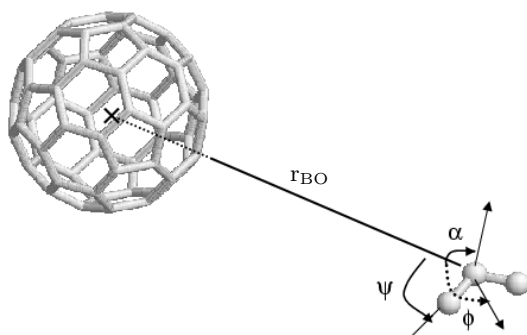


FIGURE 3. Definition of the dipole (ϕ), OH (ψ) and plane (α) angles.

bulk properties have been reached and all the angles are equally probable, as expected in bulk water.

2.3.3. Hydrogen-bond profile

It is well known that liquid water has a network of hydrogen bonds. The introduction of the buckyball into water results in a disruption of these hydrogen bonds. The number

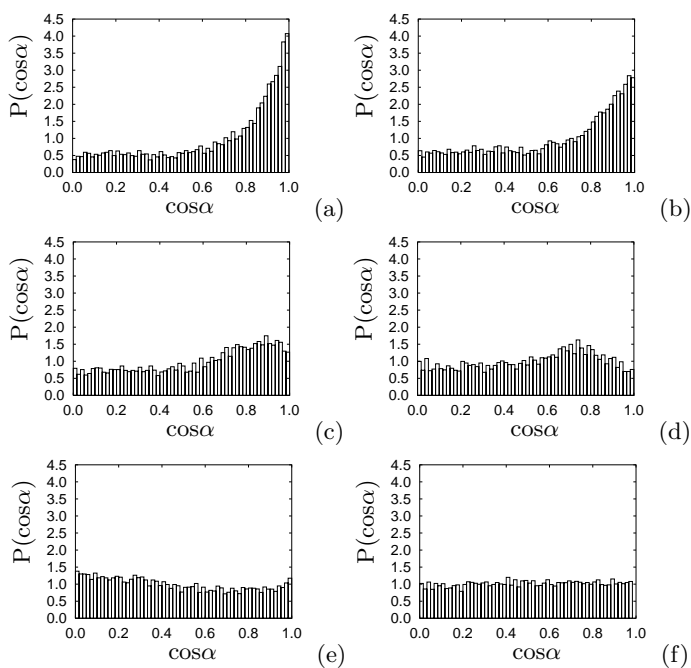


FIGURE 4. (a)-(f): The probability distributions show the orientation of the plane (α) for the distances of 2.8, 3.2, 3.9, 4.7, 5.9 and 7.4 Å from the surface of the buckyball, respectively. We compute the absolute value of the cosine because of the planar symmetry of water. (Case 2)

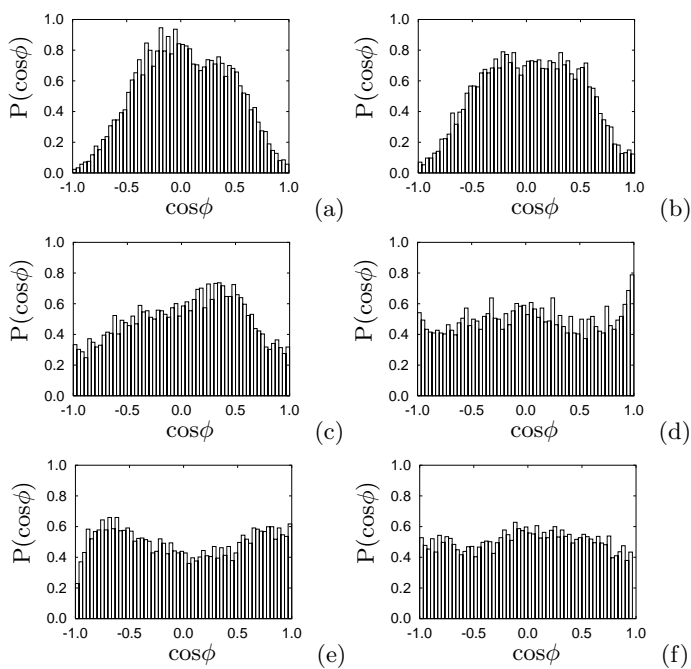


FIGURE 5. (a)-(f): The probability distributions show the orientation of the dipole moment (ϕ) for the distances of 2.8, 3.2, 3.9, 4.7, 5.9 and 7.4 Å from the surface of the buckyball, respectively. (Case 2)

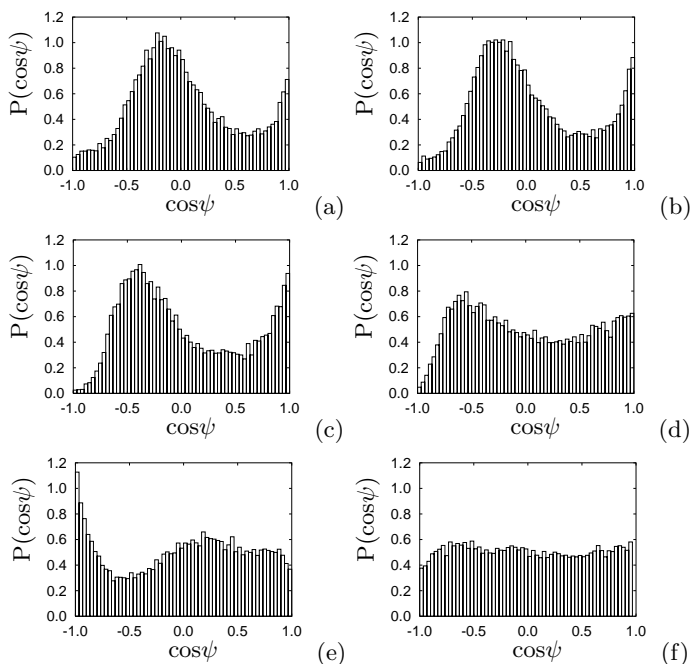


FIGURE 6. (a)-(f): The probability distributions show the orientation of the OH bonds (ψ) for the distances of 2.8, 3.2, 3.9, 4.7, 5.9 and 7.4 Å from the surface of the buckyball, respectively. (Case 2)

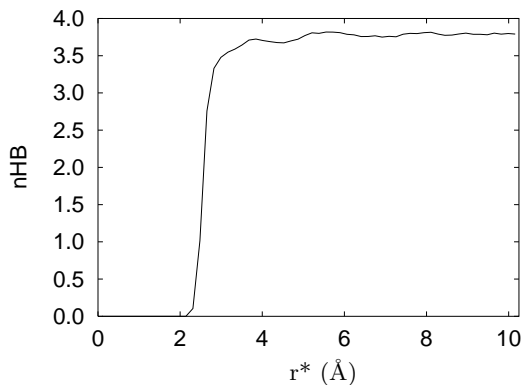


FIGURE 7. This figure shows the number of hydrogen bonds per water molecule in the vicinity of the buckyball. (Case 2)

of hydrogen bonds per water molecule (as shown in Fig. 7) decreases from 3.79 in the bulk to 2.75 at the buckyball water interface. A reduction to 3.67 is also observed at the lowest peak of the radial density profile at a distance of 4.7Å. The results are consistent with previous findings for the CNT case (Walther *et al.* 2001) and there are no noticeable curvature effects.

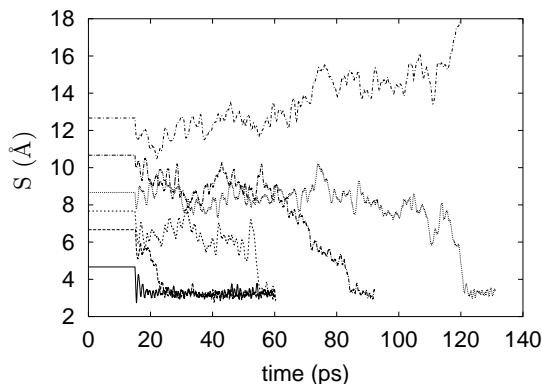


FIGURE 8. Time history of the minimum carbon-carbon (S) spacing between two buckyballs in water. The initial centre-of-mass (COM) spacing is: —: 12 Å; - - -: 14 Å; - - -: 15 Å; ···: 16 Å; ---: 18 Å; - - - -: 20 Å.

2.4. Two buckyballs in water

To study the hydrophobic interaction between buckyballs in water, we conduct simulations of two buckyballs initially placed at a center of mass distance of 12, 14, 15, 16, 18, and 20 Å, corresponding to a wall-to-wall distance of 4.676, 6.676, 7.676, 8.676, 10.676 and 12.676 Å, respectively (see Fig. 8). The center of mass of the buckyballs is fixed during the first 15 ps of the equilibration to allow the water to stabilize between the buckyballs. After the release of the buckyballs each system is equilibrated for another 10 ps and the simulations are continued to a maximum of 130 ps depending on the observed drying behaviour. A cutoff of $4\sigma_{oo}$ was used throughout (see Table 1 for the list of the simulations). The number of hydrogen bonds that the buckyballs will disrupt depends on the exposed surface between them and the water. That surface area is minimised when the buckyballs move close together (drying) so that there is no water between them. In this state their centers of mass will come to a distance of 10.5 Å as observed in the simulations and they will not allow the existence of water between them. For distances up to 15 Å drying takes place in less than 60 ps (Fig. 8). In Case 7 (16 Å) drying is completed at about 120 ps. The fact that in Case 8 (18 Å) the buckyballs came together in a time period smaller than in Case 7 is due to random motion of the system. When we placed the buckyballs at a distance of 20 Å, drying had not yet taken place at 120 ps. Snapshots of the atomic structure from the simulations are shown in Figs. 9, 10 and 11 for Cases 5 and 7.

2.5. Energetics

The introduction of (hydrophobic) fullerenes in water requires energy in order to create the accommodating cavity in the water. In a related study, the energy involved in solvating a (16,0) carbon nanotube was found to require approximately 29 kJ mol^{-1} (Walther *et al.* 2001). The corresponding surface tension of the curved CNT-water interface was found to be $127 \text{ dynes cm}^{-1}$, and similar to the value found for the planar liquid-vapour interface of $124 \text{ dynes cm}^{-1}$, indicating a negligible curvature effect.

The surface tension of the two-buckyball system considered in § 2.4 is computed for the dry, equilibrium state shown in Fig. 11. The surface area of the water is estimated as 1060.72 Å^2 . This corresponds to the surface of two intersecting spheres, with the radius of the buckyball plus the distance to the first peak of the radial density profile (3.2 Å). The surface energy is calculated from the difference between the average potential energy

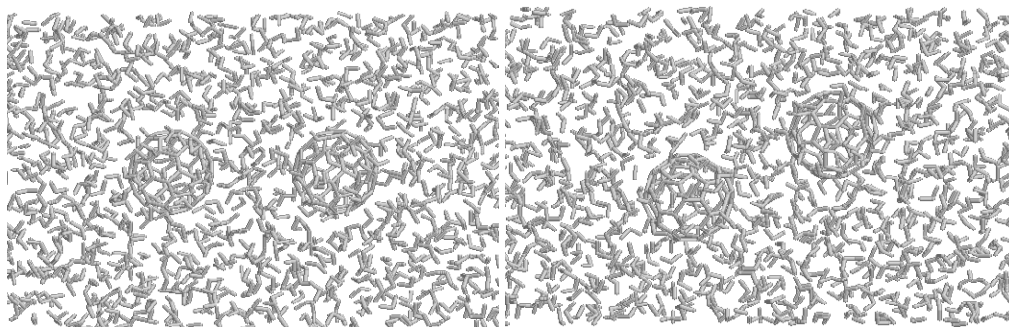


FIGURE 9. Left: The two buckyballs of Case 5 just before they are released at 15 ps. The water molecules are stable. Right: The two buckyballs of Case 7 at a center-of-mass spacing of 10.5 Å after 125 ps.

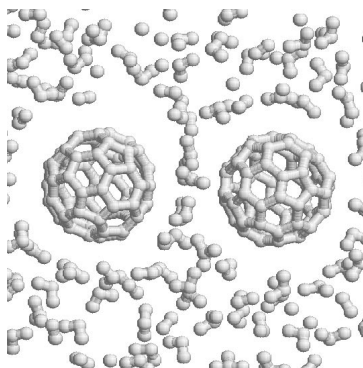


FIGURE 10. The two buckyballs of Case 5 at a center-of-mass spacing of 12.6 Å after 20 ps. The thickness of the water slab in the direction normal to the paper is 6 Å.

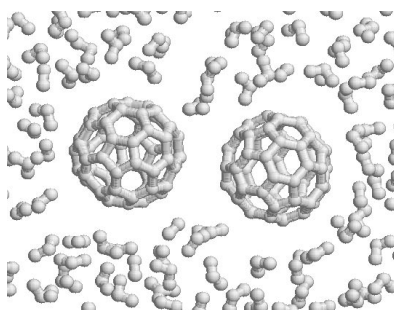


FIGURE 11. The two buckyballs of Case 5 at a center-of-mass of 10.5 Å after 60 ps. The thickness of the water slab in the direction normal to the paper is 6 Å.

(per water molecule) of bulk water, $-43.44 \pm 0.15 \text{ kJ mol}^{-1}$ (Case 11) and the elevated potential energy of the buckyball-water system, $-42.33 \pm 0.13 \text{ kJ mol}^{-1}$ (Case 5: 1018 water molecules). Thus the computed surface energy is $177 \text{ dynes cm}^{-1}$, which consists of a 40% increase compared to the CNT-water interface, indicating a significant curvature effect. However, further studies are being conducted to confirm this result. The systems consisting of a single buckyball in water did not allow an accurate extraction of the surface energy, due to the smallness of the surface area.

3. Conclusions and Future Work

We found that the water molecules stand approximately 3.2 Å from the buckyball, and their plane is oriented tangential to the buckyball surface at the buckyball-water interface. At the interface the number of hydrogen bonds per water molecule was found to be 2.75. We also found that the surrounding water did not affect the breathing mode of the buckyball. We showed that if we place two buckyballs in water the drying will take place within a time period of 60 ps for a distance between their centers of mass up to 15 Å. In the cases of 16 and 18 Å distance, the drying was complete within a period of 125 ps. For the case of 20 Å distance, drying did not occur at all. Also, we analysed in detail the energetics of the process of introducing two buckyballs into water. The surface energy in the case of introducing two buckyballs in water at an initial distance of 14 Å is large than in the case of carbon nanotubes (Walther *et al.* 2001), due to curvature effects. Future work will include further validation of the interacting potentials and the behaviour of functionalised buckyballs.

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