Molecular dynamics of zigzag single walled carbon nanotube immersion in water†

Piotr A. Gauden, Artur P. Terzyk,* Rafael Pieńkowski, Sylwester Furmaniak, Radosław P. Wesołowski and Piotr Kowalczyk†

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The results of enthalpy of immersion in water for finite single-walled carbon nanotubes are reported. Using molecular dynamics simulation, we discuss the relation between the value of this enthalpy and tube diameters showing that the obtained plot can be divided into three regions. The structure of water inside tubes in all three regions is discussed and it is shown that the existence of the strong maximum of enthalpy observed for tube diameter ca. 1.17 nm is due to freezing of water under confinement. The calculations of hydrogen bond statistics and water density profiles inside tubes are additionally reported to confirm the obtained results. Next, we show the results of calculation for the same tubes but containing surface carbonyl oxygen groups at pore entrances. A remarkable rise in the value of enthalpy of immersion in comparison to the initial tubes is observed. We also discuss the influence of charge distribution between oxygen and carbon atom forming surface carbonyls on the structure of confined water. It is concluded for the first time that the presence of surface oxygen atoms at the pore entrances remarkably influences the structure and stability of ice created inside nanotubes, and surface carbonyls appear to be chaotropic (i.e. structure breaking) for confined water. This effect is explained by the pore blocking leading to a decrease (compared to initial structure) in the number of confined water molecules after introduction of surface oxygen groups at pore entrances.

1. Introduction

The heat of immersion (or heat of wetting) is defined as the amount of heat evolved when a known mass of an outgassed solid is completely immersed (but not dissolved) in a given liquid.1 When determined at constant pressure and temperature it can be regarded as the enthalpy of immersion, which is (by simple integral) directly related to the integral enthalpy of adsorption for the equivalent gas-solid system2,3 (in fact, since there is very small pressure-volume work during the immersion experiment, the enthalpy change is essentially the same as the change in internal energy4). In our recent study we showed the results of this enthalpy calculation for a system: virtual activated carbon–water.5 The influence of carbon porosity and the concentration (and location) of surface oxygen groups on the enthalpy of immersion in water was studied using molecular dynamics simulation. The origin of relationship between enthalpy of immersion and the concentration of surface oxygen groups was explained.

The major aim of the current study is the extension of the previous approach and to use molecular dynamics to study the process of immersion of single walled zigzag carbon nanotubes in water. As it was mentioned by Alexiadis and Kassinos6 in their review (see also references therein) devoted to water in nanotubes “water in CNTs undergoes structural transition from liquid-like (disordered) to solid-like (ordered) state depending on the pressure, temperature and the CNT geometry”. Therefore it is interesting to check to what extent this transition influences the value of enthalpy of immersion. One of the most important papers where authors studied the behaviour of water inside infinite single-walled carbon nanotubes was published by Takaiwa et al.7 The authors reported the phase diagram of confined water. The major conclusions are: there exists at least nine ice phases of water confined in a cylindrical space, each ice has a structure that maximizes the number of hydrogen bonds under confinement and that the global maximum in the melting curve is located at ca. 1.1 nm where water freezes in a square ice nanotube.

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‡ Present address: Nanochemistry Research Institute, Curtin University, PO Box U1987, Perth WA 6845, Australia
2. Method

The models of the following zigzag single wall carbon nanotubes (described by the chiral indices \((n,m)\)): (10,0), (11,0), (12,0), (13,0), (14,0), (15,0), (16,0), (17,0), (18,0), (20,0), (22,0), and (26,0) were constructed using the Nanotube Modeller software.\(^5\) The applied methodology of representative structure creation (initial and modified, respectively), together with used nomenclature, are shown in Fig. 1 (note that some figures were created using the VMD program\(^6\),\(^7\)). The diameters of the cylinders \((D)\) were calculated from the well-known formula\(^6\) relating this diameter to the length of the carbon–carbon bond (assumed equal to 0.141 nm) and with chiral indices. The values of \(D\) were collected in the caption of Fig. 1. To check the influence of tube length on obtained results the simulations were performed for three different tube lengths (see Fig. 1). Only the longest initial structures were modified using the so called “virtual oxidation” procedure proposed by us previously.\(^5\),\(^12\)–\(^16\) In this procedure we introduced carbonyl surface groups at the edges of the initial structures. To do this, all two-bonded terminal carbon atoms in the structure were saturated \((\text{C}=\text{O} = 0.1233 \text{ nm})\).\(^5\),\(^12\)–\(^17\) The direction of a bond between a carbon atom in the structure and an oxygen atom in the carbonyl groups was determined by the seant of an angle \(\text{C–C–C}\) (the middle \(\text{C}\) denotes an atom where the group is bonding; the remaining atoms are those in the structure and bonded with this carbon). Using the “virtual oxidation” procedure of the tube with chiral indices \((n,0)\), \(2n\) carbonyl groups were attached \((i.e.\text{ mass percentage of oxygen for all oxidized systems is equal to 3.31\%})\). The charges of carbon and oxygen atoms were equal to \(+0.50\) and \(-0.50\), respectively.\(^5\),\(^12\)–\(^17\) Moreover, we also studied the influence of the charge distribution (between oxygen and carbon atoms forming surface carboxyls) performing simulations for oxidized tubes where the charges of oxygen ranged from 0.00 up to −0.75 (see Fig. 1).

All simulations were performed using Gromacs Molecular Dynamics package.\(^8\) Simulations were performed in the isobaric–isothermal ensemble with Berendsen thermostat and barostat (298.15 K, 1 atm). For arbitrarily chosen systems, we also performed simulation for different temperatures to check the temperature dependence of pore blocking mechanism (see ESI (Electronic Supplementary Information))). Water was modelled using the TIP4P model\(^9\) and dispersion interactions were taken into account using the Lennard-Jones (LJ) potential with respective parameters for carbon\(^20\) (see ESI Table 1 for details;\(^\dagger\) carbon structures are treated as rigid during simulations). Periodic boundary conditions were applied in all three directions. The method for calculation of electrostatics and van der Waals interactions was based on cut-offs and these cut-offs were located at 0.90 nm.\(^5\) The starting configuration of the cubicoid box containing carbon nanotube and water was prepared using the Genbox procedure, \(i.e.\) the standard procedure adopted in Gromacs package for preparation of simulation boxes (it was described in detail previously).\(^5\) However, this procedure does not imitate the immersion experiment exactly. To overcome this, we prepared a second series of simulation boxes containing water molecules located only outside the tubes \((i.e.\text{ the water molecules placed during Genbox procedure\(^5\) inside the tubes and those located at the vicinity of terminal atoms and carbonyl groups were deleted from initial configurations). Moreover, it should be noted that for the given \((n,0)_{\text{max}}\) and \(ox(n,0)_{\text{max}}\) the same number of water molecules in simulation boxes was studied. Since we use the barostat, one can observe after equilibration a tube fully immersed in water. After calculations the density of water far from the structure was always close to 0.997 g cm\(^{-3}\) (experimental value) and the distance between nanotubes (atom–atom) is close to 3 nm (in periodic boundary conditions).

Simulations were performed for 10 000 ps. All equilibrium properties were calculated from the last 1500 ps. The enthalpy of immersion \((\Delta H)\) was calculated from the simple relation proposed previously:\(^5\)

\[
\Delta E_i = E_{\text{ws}} - (E_w + E_s) \equiv \Delta H \tag{1}
\]

where \(\Delta E_i\) is the change in energy during immersion process, \(E_{\text{ws}}\) is the energy of equilibrated structure immersed in water, \(E_w\) is the energy of respective number of equilibrated water molecules, and \(E_s\) is the energy of the equilibrated structure without water. The values of energy were calculated in a box with the same dimension as the box containing a structure immersed in water.

To obtain the information concerning the structure of confined water, we calculated the statistics of hydrogen bonds for water confined inside tubes. During this calculation we considered only the molecules present in a central part of a tube \((i.e.\text{ the molecules located at distances smaller than 0.5 nm from the end of an edge carbon atom})\) using the procedure proposed by Gordillo and Martí\(^{21}\) (the results were also averaged from the last 1500 ps). Density profiles of water were determined assuming that the centers of molecules are

![Fig. 1](https://example.com/fig1.png)

**Fig. 1** Upper panel shows schematic representation of arbitrarily chosen initial and modified carbon nanotubes (red balls—oxygen atoms). Bottom panel shows the lengths \((l)\) of tubes. The following diameters \((D [\text{nm}]\) are studied (from (10,0) up to (26,0), respectively): 0.777, 0.855, 0.933, 1.011, 1.088, 1.166, 1.244, 1.322, 1.399, 1.555, 1.710, and 2.021.
located on an oxygen atom (it was also calculated from last 1500 ps). This density was studied as a function of the distance from the tube axis (r) and as a function of the distance in the direction of the tube axis (z). We also calculated the density of water molecules in different slices dividing the simulation box into 300 slices perpendicular to the tube axis (z axis).

Finally, to check the orientation of the water dipole moment vector with respect to the surface of a tube, we determined the angle between this vector and the vector being the lengthening of the tube radius passing by a centre of oxygen atom (i.e. a normal to the surface). We analyzed the molecules inside and outside the tube and placed at the vicinity of the tube surface (the distance between oxygen atom and tube surface no greater than 0.4 nm). The values of angles equal to 0° and 180° denote water molecules with perpendicular orientation to the tube surface and with oxygen atom (0°) or with hydrogen atoms (180°) pointed towards the tube axis. If we consider the molecules inside tubes, the first case describes the molecules with hydrogen, and the second case with oxygen atoms, directed at the tube surface. If one considers water molecules outside the nanotube the reverse situation occurs. The value of this angle equal to 90° denotes the parallel orientation of a molecule with respect to the tube surface. Similar calculations were performed by Thomas and McGaughey.\(^2\)

### 3. Results and discussion

Fig. 2a shows the relation between calculated (eqn (1)) enthalpy of immersion and tube diameter. One can see that (for the studied tube length range) there are small differences between the enthalpy calculated for tubes with different lengths (i.e. denoted as min, med and max—see Fig. 1). On the obtained plots (Fig. 2a) at least three different regions can be observed. In the regions marked as I and III (Fig. 2a) the enthalpy of immersion is almost constant (and slightly more negative in range III than in range I), and a maximum in range II is recorded. This maximum is observed for tube (15,0), i.e. with a diameter equal to 1.17 nm. As was suggested by Takaiwa et al.\(^7\) in this range of tube diameters one can observe the creation of (5,0) ice inside nanotubes. This is the most stable of the nine ices created inside single walled carbon nanotubes. The studies performed by mentioned authors shows that this type of ice melts around 290 K, and the melting process is connected with breaking into clusters upon heating (note that we observe some small differences in physicochemical properties of ices compared to those described by Takaiwa et al. and this is caused by differences in simulation procedures). From the results shown in Fig. 2a it can also be concluded that the enthalpy for tubes containing oxygen is shifted upward (i.e. to more negative values), and the maximum is not as strongly pronounced as for the case of hydrophobic nanotubes. Therefore, the major conclusion of this part of the study is that for the case of isolated nanotubes, one should observe the dependence of immersion enthalpy on the tube diameter. Fig. 2b shows selected snapshots of water confined in both types (i.e. hydrophobic and hydrophilic) of nanotubes. As one can see, sometimes ice structures are present, but what is more important is that the appearance of oxygen groups at the pore entrances strongly changes the structure of confined water. In this figure we show some examples for tubes from the range marked in Fig. 2a as II. Thus, inside the oxidised (13,0) tube, due to pore blocking effect (discussed by us previously\(^13,16\)), water is almost absent inside, and one can observe only some clusters at the pore entrances. For the hydrophobic tube (16,0) (with diameter equal to 1.24 nm) we observe the creation of (6,0) ice, and this is in accordance with previously published results.\(^7\) However, as it is observed in Fig. 2b, after introduction of the edge oxygen atoms, this ice melts. Therefore, it will be interesting to check how the oxidation of tube entrances changes the phase diagram of water in nanotubes. Based on the preliminary results obtained in this study, it can be concluded that a remarkable influence should be observed. Moreover, our results (together with the results presented below) show that surface carbonyls can be called chaotropic\(^23\) for confined water molecules since they destroy the structure of ice.

We also tried to check how the distribution of charges between oxygen and carbon atoms (formed attached to tube entrance carbonyl groups) changes the enthalpy of immersion. The results are shown in Fig. 3a. Since, as was mentioned above, the influence of tube length on obtained enthalpy of immersion values is small (see Fig. 2a), we checked the influence of charge distributions by performing simulations only for the longest tubes (i.e. labeled as max—see Fig. 1). As
the charge of carbon atom more positive), the enthalpy of oxygen atom becomes more negative (and consequently interactions (and this is obvious). However, if the charge of mainly determined by the value of the energy of electrostatic potentials, in Fig. 3 show that the shift in enthalpy curves is times larger LJ potential energy well depth, but the results slightly smaller collision diameter than carbon, and has a three results as for initial (i.e., unmodified) tubes. Oxygen atom has a slightly smaller collision diameter than carbon, and has a three times larger LJ potential energy well depth, but the results collected in Fig. 3 show that the shift in enthalpy curves is mainly determined by the value of the energy of electrostatic interactions (and this is obvious). However, if the charge of oxygen atom becomes more negative (and consequently the charge of carbon atom more positive), the enthalphy of immersion becomes also more negative (i.e., a more exothermic effect is observed). The snapshots collected in Fig. 3b show that the charge located on oxygen and carbon atoms forming the edge carbonyl groups has a remarkable influence on the structure of confined water. Thus, for example in the oxidized tube (13,0), the more negative the charge of the oxygen atom, the less stable the structure of confined water, i.e. water clusters break creating smaller fragments. Finally, water is not present inside nanotubes due to pore blocking effect (this is observed for charges more negative than \( \text{ca.} -0.25 \)). A similar situation occurs in the tube (14,0) with a diameter equal to 1.088 nm (where, for charge equal to zero, the ice (4,0) is formed\(^7\)) and one can observe the melting and even breaking of ice structure with the rise in charge of oxygen atom. For larger tubes, i.e., (15,0) and (16,0), the influence of this charge is similar; however we observe only melting of structures inside (i.e., the structures do not break). It is interesting to mention that for all studied tubes one can observe the rise in the enthalpy of immersion after oxidation of nanotubes by comparing with the value observed for initial structures (see Fig. 3a). This rise is observed even for the tubes where water clusters present inside break into smaller parts. It means that the major contribution to the rise in the enthalpy of immersion value after carbon oxidation originates from the energy of electrostatic interactions between carbonyl oxygen atoms and water. The profiles shown in Fig. 4 demonstrate that a remarkable rise in the density of water around surface groups is observed. As was deduced from the observation of the snapshots discussed above, the appearance of surface oxygen groups changes the density (and structure) of confined water. Moreover, it also has influence on the density of water adsorbed in the layers at the vicinity of tube walls outside a nanotube. This is shown more precisely in Fig. 5, where density profiles for a slice containing a carbonyl oxygen atom (located at a distance 1.6 nm from the origin of \(z\) axis) are plotted (note that the location of this slice is labelled as a solid line in Fig. ESI1–ESI4). As one can observe, the rise in the charge of surface oxygen atom causes at least two interesting phenomena. First is the rise or decrease in density of water around oxygen atoms, strongly pronounced for the case of (13,0)\(_\text{max}\) and (14,0)\(_\text{max}\). The next effect is the creation of high density water at the pore centre—visible for larger tubes, i.e., (15,0)\(_\text{max}\) and (16,0)\(_\text{max}\). The influence of carbonyl group charge distribution on the density of water can also be observed in Fig. ESI1–ESI4.\(^\dagger\)

Finally, we discuss the structure of water inside nanotubes using the results of hydrogen bond statistics calculations (and the average number of confined water molecules). The results presented in Fig. 6a clearly confirm that (in the range of studied tube lengths), we do not observe a remarkable influence of the tube length on the average number of hydrogen bonds formed inside. As one can also observe in this figure, after oxidation of tube entrances the average number of hydrogen bonds decreases in the whole range of studied tube diameters. As was discussed by Takaiwa et al.,\(^7\) the number of hydrogen bonds in different types of ices found inside single walled carbon nanotubes is ranged between 3 (found for (2,0) ice) and 4 (this number occurs for so called TL ice). This is generally in agreement with our results. The differences can be caused by different criteria used during calculation of hydrogen bond statistics. Takaiwa et al.,\(^7\) applied an energy criterion (i.e., \(-12\) kJ/mole). However they mentioned that use of an alternative geometrical criterion does not change the hydrogen-bond network structures. Contrarily, in our calculation, we use the geometric criterion, i.e., the distance \(R_{30}\) between the

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**Fig. 3** The comparison of enthalpy vs. tube diameter for different charges of carbon and oxygen groups forming surface carbonyls (a) and selected snapshots showing the structure of water confined inside nanotubes—the influence of charge distribution (b).
oxygens of both water molecules has to be smaller than 0.36 nm, the distance $R_{OH}$ between the oxygen of the acceptor molecule and the hydrogen of the donor has to be smaller than 0.24 nm, the bond angle between the $R_{OO}$ direction and the molecular $R_{OH}$ direction of the donor, where H is the hydrogen which forms the bond, has to be smaller than 30°. The major differences are observed for very small nanotubes and they are caused by differences in simulation procedures (i.e. in our calculations nanotubes are finite, contrary to Takaiwa et al.). Fig. 6b shows that the number of confined water molecules increases with the tube length. However, it is still smaller after oxidation of tube entrances. The percentage difference is plotted in Fig. 6c and the obtained results clearly demonstrate that the role of so called “pore blocking effect” vanishes with the rise in tube diameter. The results of similar considerations shown in Fig. 7 clearly demonstrate that with the rise in the negative charge of the oxygen atom of surface carbonyl we observe a decrease in the number of hydrogen bonds formed inside as well as a decrease in the number of confined water molecules. As in Fig. 6 we see that the differences in a number of confined water molecules decrease with the rise in a tube diameter.

Fig. 4 Density profiles (g cm$^{-3}$) determined for selected tubes and assuming that the centre of the molecules is located on oxygen atom, $r$ is the distance from the tube axis and $z$ is the direction of tube axis.
Fig. 5  The comparison of water density profiles calculated for the slice containing carbonyl surface atom (i.e. at the slice marked with a horizontal line in Fig. ESI1–ESI4†).

Fig. 6  Average number of hydrogen bonds (∥N_{H\text{H}}∥) (a) formed between water molecules inside tubes, the influence of the diameters of the cylinders on the average number of water molecules confined inside (b) and on the average percentage difference between the amount of water inside initial and oxidised structures (c).
We also tried to check if the changes in structure of confined water caused by the appearance of surface carbonyl groups at the pore mouth are due to additional contribution to adsorption potential (electrostatic forces between water and surface carbonyls) and/or maybe they are caused by decreasing number of water molecules inside pores. The results presented in Fig. 8 answer this question. In this figure, we show the dependence between the decrease in the average number of hydrogen bonds (calculated per one water molecule) confined inside initial and oxidised tubes, and the average number of confined water molecules. It can be clearly seen that the differences in the structure of confined water molecules between initial and oxidized tubes are not caused by the appearance of electrostatic potential between water and surface carbonyls. They are due to the decrease in the number of confined water molecules after oxidation of tube entrances.

The obtained histograms of the orientation of water dipole moment vector with respect to the surface of selected tubes are presented in Fig. ESI5. One can see that the situation is especially interesting for the case of molecules confined inside three tubes i.e. (14,0), (15,0) and (16,0) (i.e. the tubes where the enthalpy of immersion is the largest—see Fig. 2). For tubes that do not contain oxygen groups, a majority of water molecules has a parallel orientation with respect to the tube surface, and a small amount of water molecules has a perpendicular orientation. We practically do not observe the molecules with intermediate orientation. The appearance of oxygen at tube entrances and the rise in the value of its charge causes that this ordered orientation is disturbed. We still see perpendicular orientation but also intermediate orientations appear. This is in accordance with our observations given above. In the case of the remaining tubes (containing or not containing oxygen) the obtained curves do not show the ordered orientation. In the case of molecules outside the orientation is practically independent of the type of the tube (and of the presence or absence of oxygen). The curves show two maxima responsible for parallel and angular orientations, respectively.

Finally we tried to check the dependence of pore blocking on temperature. Density profiles and selected snapshots for one of studied systems are collected in Fig. ESI6–ESI9. The obtained data suggest that for hydrophobic nanotube (Fig. ESI6) we observe a decrease in density of water inside as well as outside with a rise in temperature. The structure becomes less ordered as temperature increases. Similar effects of drop in density are observed for oxidised nanotubes (Fig. ESI7–ESI9). As one can observe in the studied temperature range the pore blocking effect does not vanish. However, we should to point out that this problem needs further calculations and the results will be published in future.
Conclusions

We report the first results of molecular dynamics simulation showing the effect of carbon surface oxygen groups on the behaviour of the enthalpy of immersion. The major conclusions of this paper are as follows: there is a maximum on the plot of relation between the value of enthalpy of immersion and tube diameter. This maximum is observed for tube (15,0), i.e. with a diameter equal to 1.17 nm. As it was suggested by Takaiwa et al. this is the range of tube diameters where one can observe the creation of (5,0) ice inside nanotubes. We show that the oxidation of tube entrances strongly changes the structure of water inside and generally leads to decrease in stability of the formed ice structures, and remarkable rise in the value of the enthalpy of immersion (i.e. the process is more exothermic). It is concluded that the changes in a structure of confined water molecules after oxidation of tubes are due to pore blocking effect, i.e. the decrease in a number of confined water molecules caused by interactions with surface oxygen groups. It is also shown that the power of this effect increases with the rise in the value of a negative charge located on a surface carbonyl oxygen atom.

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Fig. 8 The dependence between the decrease in the average number of hydrogen bonds (calculated per one water molecule) confined inside initial and oxidised tubes, and the average number of confined water molecules. Tubes from the range of chiral indices (13,0)–(16,0) were studied. Moreover, the results for different charges are also presented.