

Orientation Requirements for Successful Entry of Water into a Nanotube

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Abstract

Carbon nanotubes are likely to form an integral part of future nanofluidic and biological devices. An understanding of fluid-interaction on a molecular scale is essential to the successful design and efficient operation of such devices, particularly concerning important liquids such as water. We demonstrate through first-principles density-functional theory (DFT) that the energies at which individual water molecules are able to enter the nanotube depends very strongly on their orientation. This has a number of implications for the flow of water through the nanotube at different temperatures and densities, particularly when considering low-density water vapour.

Introduction

The applications of nanotubes are expected to be wide-ranging and far-reaching. They are likely to form an integral part of future nanofluidic devices, with applications both in biology and industry. Some potential applications include nanopipettes [Melle-Franco2006], chemical sensing [Ghosh2003] and even nano-thermometers [Li2003].

Crucial in the successful design and optimisation of such devices is the understanding of molecular interaction with nanotubes at different energies, since this strongly dictates the nature of the flow dynamics in and around the nanotube. In particular, studies concerning water are especially important, not only due to the ubiquitous nature of water in its many forms, but also because it displays highly unusual phenomena such as an incredibly high flow rate through the nanotube [Majumder2005], as well as unusual flow dynamics such as pulsated flow [Hummer2001] and ballistic transport [Striolo2006].

The successful utilisation of nanotubes in commercial applications requires an understanding of these flow properties at different temperatures and densities. In the past, such phenomena have primarily been examined through molecular dynamics (MD) simulations based on assumed inter-atomic potentials. A detailed study of the individual interaction between water and a nanotube is required however, in order to gain an insight into the fundamental underlying physics involved and to understand the flow dynamics through and around the nanotube. We report about ongoing work to make such a study.

Calculation method

System design

The interaction between a nanotube and a water molecule has been studied using first-principles density-functional theory (DFT), using the commercial software DMol³ as part of the Modelling Studio package developed by Accelrys Inc [Delley1998, Delley2000]. All calculations were performed with a generalised gradient approximation (GGA) using the density functional by Perdew and Wang (PW91) [Perdew1991]. A double-numerical polarised basis set was used and the electron orbital cut-off was set at 4Å [Maiti2000]. The self-consistent field tolerance parameter during the iteration was set to 10⁻⁶, and convergence occurred in under 50 iterations. The calculations were performed with a (10,0) armchair nanotube, with 80 carbon atoms. The length of the nanotube was deliberately kept short for computational reasons, although the results at the entrance of the nanotube may also be applied to a longer nanotube, too. The dangling bonds of the nanotube were terminated with hydrogen atoms to reduce their strength and to ensure convergence of the calculation within a reasonable time period.

Energy calculation

Calculations of the energy of the isolated nanotube and isolated water molecule were performed, yielding energies of -83.3 keV and -2.1 keV respectively. These energies can be understood as the energy required to remove every atom within the molecule to infinity. The binding energy of the system is calculated as the difference of the combined system, to that of the sum of the isolated nanotube and water (equation 1). Therefore the more negative the binding energy, the greater the strength of the binding, and the more favourable the system configuration is. The position of the water molecule was considered to be the position of the mass-weighted average of the 3 atoms.

$$E_{bind} = E_{system} - (E_{NT} + E_{water}) \quad (1)$$

Results

Approaching the outside wall

Initial calculations were performed for a water molecule outside the nanotube, over a carbon atom, bond, and a hexagonal mid-point, approaching the wall as shown in figure 1. Figure 2 shows the relative orientations of the water molecule to the nanotube. The results of the binding-energy calculations are shown in figure 3, and demonstrate the substantial influence of the orientation of the water molecule on the strength of the binding energy when the molecule is placed over the carbon atom indicated by arrow 1 in figure 1. The depth of the potential reaches around -90meV, which clearly indicates a substantial binding at temperatures even above room temperature. Although the actual numbers must be taken with some reservation due to the inherent difficulties of DFT to reproduce van der Waals dispersion forces, it is clear that the different orientations give rise to substantially different binding energies, and that the extent of these energies is sufficient to cause a significant orientation dependence on the ability of the water to approach and remain at the nanotube wall.

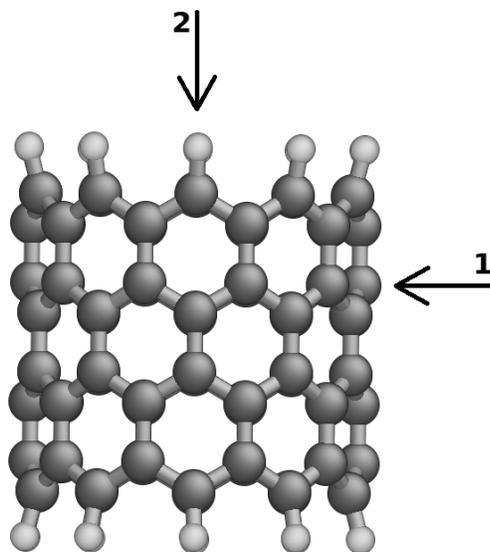


Figure 1. Directions of approach of the water molecule: The outside wall (arrow 1) and entering the nanotube through the central axis (arrow 2).

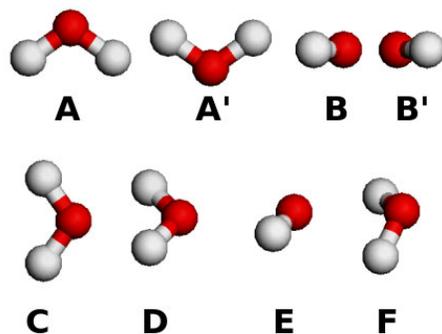


Figure 2. The different orientations of the water molecule relative to the nanotube orientation shown in figure 1.

In bound orientations, using an ideal-gas approximation, the substantial variation in the depth of the potential well of around 19 meV represents a temperature range of about 150K. Therefore, on approach to a nanotube, water molecules with different orientations may gather a wide variation in energy. This not only has implications for the flow dynamics around the nanotube, but also the stability of water at equilibrium near the wall.

Most significant however is the observation of orientation *B'*, with the oxygen pointing directly towards the nanotube. In this configuration there is no distance at which the molecule is favourably bound, agreeing with other published results (eg, [Peng2000]). At approximately 3.6Å there exists a flat minimum which is characteristic of the behaviour exhibited by the other orientations of the water molecules. The binding energy then rises to around 15meV, reaching a peak around 5.5Å before tending to zero as the distance increases. These short and long-range barriers can be explained by the following: The sharp short-range repulsion is characteristic of the repulsion experienced by the other orientations, and is clearly van der Waals repulsion. The other, longer-range repulsion, comes about due to the electrostatic repulsion between the molecules due to the slightly negative charge of the oxygen and the pi-orbitals of the nanotube. If all the energy of the water molecule is

considered to be translational kinetic energy, then the long-range barrier of 15meV requires a minimum temperature of around 115K to be overcome. In addition, any vibrational or rotational motion which keeps the oxygen facing the nanotube will effectively raise this minimum temperature. The dynamics of liquid water and the structure of ice may be significantly altered around such a transition temperature.

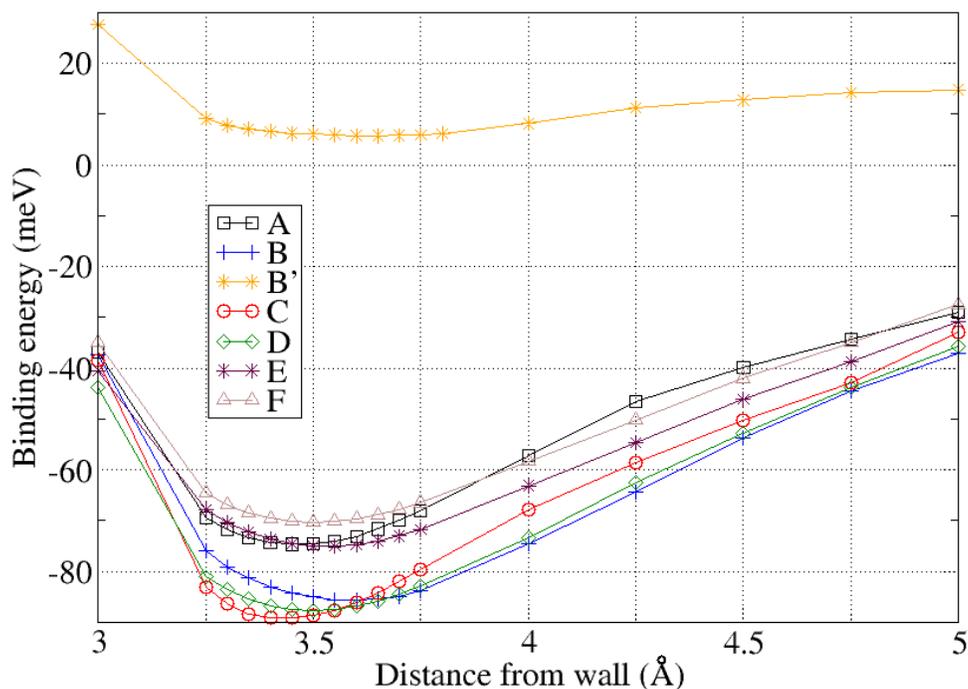


Figure 3. Variation of binding energy on approach to the nanotube wall (figure 1, arrow 1) based on the water-molecule orientations shown in figure 2. Lines are used as a guide to the eye.

Entering the nanotube

The results described so far offer a fascinating insight into the effect of orientation on the flow properties and structure of water around a nanotube. Of crucial interest however in areas such as energy transfer through nanotubes and applications such as filtration [Sholl2006], is the appreciation of the flow dynamics of water-entry into the nanotube. There have already been a number of MD studies concerning flow entry into a nanotube, however they all rely on broad assumptions about the binding energy between a nanotube and water molecule. Figure 4 shows the results from our DFT calculations and demonstrates that the binding energy is strongly dependent on the water molecule's orientation.

What is paramount to note in figure 4 is how the most favourable orientation of the water molecule changes as it enters the nanotube. Outside the nanotube, when the oxygen of the water molecule is facing the entrance, there is actually a barrier to entry of around 15meV which is similar in magnitude to that found with the interaction outside the wall. For other orientations however, entry of the water is quite energetically favourable. The most favourable orientation changes however with the hydrogens of the water molecule pointing at the level of the 1st row of carbon atoms, causing a full 180° rotation. The effect of these different orientations is reflected in the substantial range of energy at the entrance of the nanotube.

It is also clear that if the kinetic energy is too low, water molecules that are easily able to rotate will assume an orientation like that of *A* and will collect at the entrance of the nanotube, rather than penetrating to the centre. Once within this well there is an effective barrier between positions 1 and 3 in figure 4 of around 50meV, which translates to a temperature of around 390K (17°C) for water. This implies that there is an opposition to water entry below 17°C which is not significant at higher temperatures, giving an important variation in the flow dynamics at liquid temperatures. Considering however as before that some of the energy of the molecule will go into vibrational and rotational motion, this suggested temperature indeed represents a minimum, indicating that this barrier may also have significant implications for higher-temperature water-entry too.

There may however be an additional method of overcoming such a barrier, without the need for additional kinetic energy. Hydrogen bonding between water molecules is known to be between typically 150-200meV in strength [Schuster1976], which is comparable to the range of energies observed at the nanotube entrance. Therefore if an approaching water molecule is part of an extended hydrogen-bonded network, it may be restricted in its ability to rotate and therefore maintain an orientation like that of *D* allowing penetration to the centre. This suggests therefore that there is an important density dependence on the ability of water to enter the nanotube which has not been explicitly examined before, with low-density water molecules being easily rotated, and high-density molecules being part of an extended hydrogen-bonded network, unable to easily rotate.

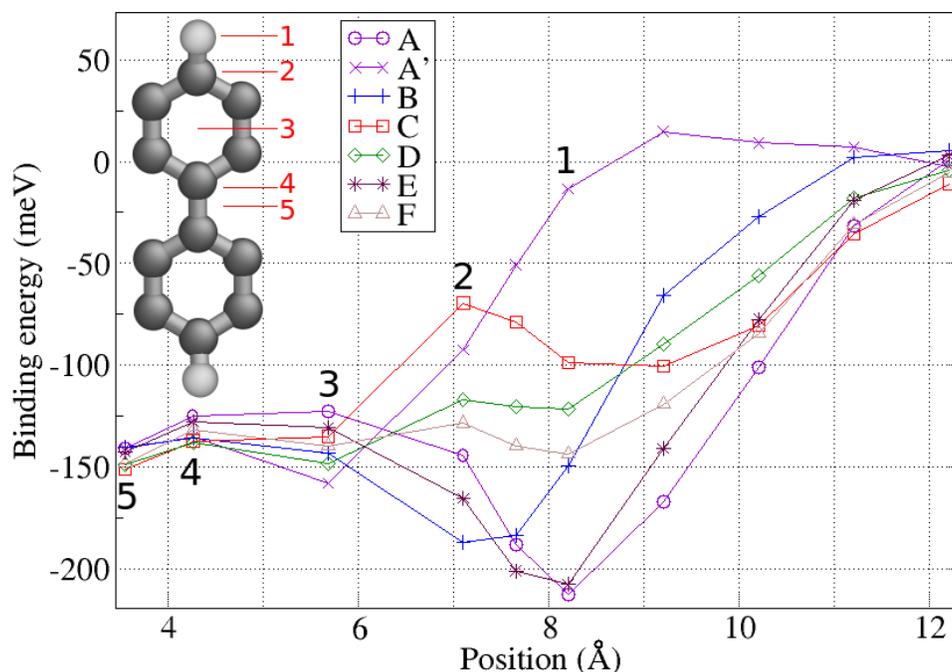


Figure 4. Variation of the binding energy as the water molecule enters the nanotube down the central axis (figure 1, arrow 2) based on the water-molecule orientations shown in figure 2. The numbers on the graph correspond to the nanotube locations denoted on the segment in the top-left of the graph. Lines are used as a guide to the eye.

Conclusion

In summary, we have demonstrated that the orientation of the individual water molecule plays a crucial role in the dynamics of entry into a nanotube, by defining the energy (and hence the temperature) at which entry can occur. Our results have suggested that a water molecule is likely to undergo a full 180° rotation as it enters the nanotube. It has been shown that the freedom or restriction of this rotation will have an influence on the ability of the water to penetrate to the centre of the nanotube, indicating an additional density dependence on the flow dynamics, at and above room temperature.

In addition, the flow dynamics and structure of water at the side of the nanotube is highly important. It has been shown that there is a transition temperature, about which there may be a variation in the structure of water and ice around a nanotube, with the implications for the stability of water around a nanotube that this brings.

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