Behaviour of water at the nanoscale

Ujjal Kumar Sur

It is often found that physics, chemistry, biology do not scale down. Scaling means that the rules that hold true at macroscopic scale, may not be true at microscopic scale. It has been found from the literature that confinement of matter on the nanometer scale can induce phase transitions[1], which are not observed in the bulk systems. Many fluids behave abnormally as a result of confinement in a space of nanometer dimensions[2]. Klein and Kumacheva[3] have shown that simple organic liquids become solid-like, when squeezed between two smooth surfaces into a film of few molecular layer thickness. Simulation studies[4] have shown that nano-ice is formed by water in nanotubes of different dimensions. Hummer *et al*.[5] have shown water conduction due to density fluctuations through the hydrophobic channels of carbon nanotubes from their molecular dynamics simulation studies; such conduction is not possible in a macroscopic bulk system. By designing a single-walled, uncapped carbon nanotube of 13.4 Å length, 8.1 Å diameter and simulating for 66 ns in a water reservoir containing about 1000 water molecules, the central channel of carbon nanotubes was occupied by about five water molecules forming a hydrogen-bonded chain. Figure 1 shows the hydrogen-bonded water chain inside hydrophobic carbon nanotube. The main feature of their simulation study is that water molecules are not just confined within the nanotube, but during 66 ns about 1000 water molecules can enter and leave the tube freely. The weak van der Waals' interaction between carbon atoms of nanotubes and water plays a crucial role in the conduction of water molecules through hydrophobic nanotubes. Thus when the carbon–water attraction was made less favourable by reducing the depth of Lennard–Jones energy well from -0.114 kcal mol^{-1} to -0.065 kcal mol^{-1}, the pore remains empty of water molecules for most of the time. So a small change in carbon–water interaction potential can induce wet–dry transition at the nanometer scale. The energetics of hydrogen bonding acts as the driving force in the entry of water into hydrophobic carbon nanotubes. The energy loss due to loss of two hydrogen bonds, on average, for each water molecule entering the hydrophobic channel can be partially compensated by the weak van der Waals' interaction with carbon atoms of carbon nanotubes. But this is not enough for allowing the water to enter inside the carbon nanotubes. Fluctuations in the number of hydrogen bonds per water molecule in the bulk aqueous phase make a large fraction of water incompletely hydrogen bonded possessing low binding energy. The water molecules present inside nanotubes have higher binding energy providing large difference in chemical potential to drive water inside it and water inside the nanotubes is shielded from fluctuations. Water inside the hydrophobic carbon nanotubes moves through the tube with little hindrance in bursts. An average of about 17 water molecules move through the nanotube per nanosecond. However water transmission through the nanotubes occurs in pulses with peaks of about 30 water molecules per nanosecond. This kind of simulation study on the behaviour of water inside carbon nanotubes may also provide important clues in the understanding of biological pores and ion channels which have almost same dimensions as carbon nanotubes. Aquaporins are an important class of biological pores present in cell membranes. Beckstein *et al*.[6] have shown that changing the dimension of membrane pore by a small amount can induce such wet-dry transition. They have also shown that entry and exit of water can also be controlled by the presence or absence of a small dipole provided by a polar side chain in the biological channels in a membrane. Jensen *et al*.[7] have studied the mechanism of glycerol conduction in Aquaglyceroporins present in *Escherichia coli*. Their molecular dynamics simulations revealed spontaneous glycerol and water conduction driven, on nanosecond time scale, by thermal fluctuations. From the technological application point of view, such emptying/filling transitions in functionalized nanotubes conducted by light-induced excitation of dye molecules, can be potentially used in light-sensors as single molecule 'FET'. The simulation study by Hummer *et al*.[5] supports the predictions of Lum, Chandler, Weeks (LCW) theory[8] of hydrophobic effect at small and large length scale. This theory provides a quantitative understanding of multifaceted nature of hydrophobicity. The LCW theory[8] predicts that for an extended hydrophobic surface (> 1 nm) in water, presence of hydrogen-bonded water structure near the hydrophobic surface is geometrically impossible. The loss of hydrogen bonds near the extended hydrophobic surface expelled the liquid water producing a thin water vapour layer separating the hydrophobic surface from bulk liquid water. This kind of phase

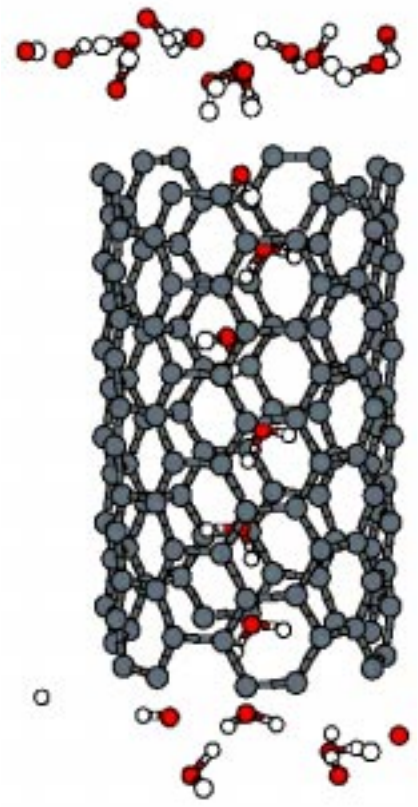

Figure 1. Structure of the hydrogen-bonded water chain inside carbon nanotube (Courtesy: Susanne Hahn).

transition is known as 'drying transition'. However for a hydrophobic surface consisting of small apolar molecules, water molecules can still reorganize near the hydrophobic surface without sacrificing their hydrogen bonds and as a result 'drying transition' cannot occur. The former is relevant to the solvation of macromolecules like proteins, whereas the latter is relevant to aqueous solvation of a butane or butanol molecule. The LCW theory may provide a better understanding of the phenomena of 'protein folding' and the stability of protein assemblies. Finally this paper by Hummer *et al*.[5] is interesting not only to the field of biophysics, but also to the field of both physics and chemistry.

For further reading please visit the following websites: http://www.sciam.com/news/110801/1.html; http://www.nature.com/nature/links/011108/011108-4.html; http://gold.cchem.berkeley.edu/~susanne/

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Ujjal Kumar Sur is in Raman Research Institute, Bangalore 560 080, India.
e-mail: uks@rri.res.in

Random selections

Nuclear Power: A Special Report
IEEE Spectrum 38, 2001, **11**, 32–51.

Increasing power blackouts (possibly undependable future), supplies of oil, confirmed global warming contributed by (some) power generation technologies, have made people sit up and take a second look at a cleaner and abundant source of power, namely, nuclear power. With more and more operating experience, life time extensions of aged reactors are increasingly being sanctioned.

In the special report on 'Nuclear Power' cited here, there are eight articles. Four of these may be of universal interest and the rest are essentially US-centered. In 'Pragmatic concerns fuel nuclear support', Steve Miller discusses how the 'pendulum of public opinion' has swung over the past three decades. There is still no clear-cut, perceptible positive swing in US, thanks to concerns like thermal pollution, radioactive waste management, fears of core melt down and weaponization in other countries, etc. In the article 'Canned heat', Glenn Zorpette states that 'consensus over a temporary fix has finally emerged in US, Europe and Japan (for dealing with radioactive waste)'. The solution is based on the technique known as 'dry-cask storage', although it is not a new approach. He concludes, however, 'no one really expects spent fuel to sit on those pads, monitored and guarded and with periodic changes of the cask, until it is twice as old as the Sphinx in Egypt is now. But it is probably just as well as that the casks can apparently hold the waste for a century or more'. Then the article 'Extending life by half' by David P. Amber, deals with the process of some dozen or more 40-year-old nuclear power plants in US getting a fresh lease of their licenses for another 20 years or more, by taking care of age-related safety and other problems. The September 11 terrorist attack has led to focusing attention on protecting nuclear plants and waste from terrorist 'repurposing' in the article, 'Unconventional nuclear weapons'. The Special Report skirts several issues dealing with nuclear technologies being pushed in several countries, other than USA.

Male mate choice selects for female colouration in a fish: By Trond Amundsen and Elisabet Forsgren
Proc. Natl. Acad. Sci. USA, 2001, **98**, 13155–13160.

Sexual selection has proved successful in explaining a wide variety of male ornaments. It has been known traditionally that female ornaments are considered non-functional. In this paper, the authors have carried out two experiments to test whether males preferred to mate with more colourful females. In the first experiment (two-spotted gobees (*Gobisculus flavescens*)) female species with natural colouration and in the second experiment females with a manipulated belly colouration were introduced. It was found that males preferred to spend more time with coloured females than the naturally coloured ones, leading thereby to the conclusion that female ornaments are sexually selected.