Water conduction through carbon nanotubes

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ABSTRACT

In molecular dynamics simulations we found that water can form hydrogen-bonded water chains in the interior of carbon nanotubes. Water penetration is sensitive to details of thermodynamic conditions and interaction potentials, resulting in sharp, first-order like transitions between filled and empty states. Under wetting conditions, water molecules are transported efficiently through nanotubes. Implications on the design of nanotube channels for small molecules and protons will be discussed.

Keywords: carbon nanotubes; water transport; one-dimensional fluids

1 INTRODUCTION

Water exclusion from the hydrophobic core is a paradigm of protein stability. Protein function, in contrast, often requires water penetration into the nonpolar interior. Biomolecular proton conduction occurs through transiently solvated hydrophobic channels, as in the proton pumps cytochrome c oxidase and bacteriorhodopsin, or in the mono-oxygenase cytochrome P450 [1]–[3]. Water itself can be selectively transported across biological membranes through predominantly hydrophobic, not hydrophilic channels, as demonstrated by the structure of aquaporin-1 [4], [5]. Why do water molecules occupy hydrophobic channels where they are, at best, able to form two hydrogen bonds, and thus lose several $k_{\rm B}T$ in energy compared to bulk solution? How do water molecules get into, through, and out of such hydrophobic channels?

To address these questions, we studied the water transport through the simplest molecular hydrophobic channel, a solvated carbon nanotube, by molecular dynamics simulation [6]. With their rigid nonpolar structures [7], carbon nanotubes offer unique possibilities as molecular channels, tunable through variations in diameter and length, and by chemical modifications. Remarkably, the smallest nanotubes [8] have diameters similar to the hydrophobic, water-conducting channel of aquaporin-1 [4]. We designed a short [9] 144-carbon uncapped, single-wall nanotube by folding a graphite sheet of 5×12 six-carbon rings into a 13.4-Å long cylinder with a diameter of 8.1 Å. The dynamics of the solvated nanotube was simulated for 66 ns, showing pulse-like transmission of water molecules across the channel. Small changes in the magnitude of the carbon-water interactions led to sharp emptying transitions of the nanotube interior [6].

2 METHODS

In the simulation, the nanotube was surrounded by a bath of about 1000 water molecules in which the tube was free to translate and rotate. The cubic simulation cell was periodically replicated. The interior of the nanotube was thus effectively simulated in a grand-canonical ensemble with respect to water exchange. The carbon nanotube and its interactions with TIP3P water [10] are described with a classical force field [11]. For the carbon atoms, parameters of sp^2 carbons were used. In addition, we conducted a simulation with modified carbon-water Lennard-Jones interactions to weaken the water-nanotube van-der-Waals attractions by about a factor of two. For comparison, we also performed a simulation of bulk TIP3P water.

The number N of water molecules in a volume ΔV inside the nanotube is determined by the difference of the local excess chemical potential μ_{nt}^{ex} relative to that of the bulk fluid, μ_w^{ex}:

$$N \;=\; \rho\Delta V e^{-\beta(\mu_{nt}^{ex}-\mu_w^{ex})}\;, \qquad (1)$$

where ρ is the bulk water density. Excess chemical potentials μ^{ex} are directly related to the distributions $p_{\rm bind}(u)$ of binding energies of individual molecules:

$$e^{\beta\mu^{ex}} \;=\; \langle e^{\beta u}\rangle = \int p_{\rm bind}(u)e^{\beta u}du\;, \qquad (2)$$

where $\beta^{-1}=k_{\rm B}T$, with $k_{\rm B}$ Boltzmann's constant and T the temperature. The binding energy u of a given water molecule is the potential energy difference of the system with and without that molecule. The distribution $p_{\rm bind}(u)$ of binding energies is related to the distribution $p_{\rm ins}(u)$, where u is the potential energy of a water molecule randomly inserted into the volume ΔV, averaged over equilibrium configurations of the unperturbed

system [12]:

$$\frac{p_{\rm bind}(u)}{p_{\rm ins}(u)} \quad = \quad e^{\beta(\mu^{ex}-u)} \ . \qquad (3)$$

Histograms $p_{\rm bind}(u)$ and $p_{\rm ins}(u)$ for energies of water molecule removal and insertion, respectively, were determined for bulk water, and for the central channel of the nanotube. Excess chemical potentials of water in the nanotube channel were then determined from a histogram analysis [12]. A slope of -1 with respect to βu indicates that the water molecules inside the channel are at thermal equilibrium with the outside water.

3 THERMODYNAMICS OF WATER FILLING

Despite its strongly hydrophobic character, the initially empty central channel of the nanotube rapidly filled with water from the surrounding reservoir, and remained occupied during the entire 66 ns [6]. On average, five water molecules occupy the pore region. These water molecules form a hydrogen bonded chain. The number of water molecules N fluctuates between 2 and 7, with $N = 2$ occurring only once in 66 ns, and never drops to zero. Remarkably, the local water density inside the cylinder exceeded the bulk density.

Water molecules inside the nanotube lose on average two out of four hydrogen bonds. Only a fraction of the lost energy is recovered through van-der-Waals interactions with the carbon atoms of the nanotube, while electrostatic interactions with water molecules beyond the nanotube wall are found to be negligible. Considering this loss of hydrogen bonding, and the weak attraction of water to the nanotube carbon atoms, this persistent hydration of the nanotube interior may seem surprising, but is consistent with the experimentally inferred adsorption of water onto nanotubes [13].

The water occupancy of the channel is determined by the local excess chemical potential, μ_{nt}^{ex}, defined as the negative free energy of removing a water molecule from the channel in Eq. **2**. The average $\langle \exp(\beta u) \rangle$ of the Boltzmann factor of the interaction energy u of water molecules in the channel is dominated not by how strongly bound a water molecule typically is, but by how populated unbound states ($u > 0$) are. Even though the average binding energy u of water molecules inside the nanotube is unfavorable compared to bulk water, u is more sharply distributed, and in particular, high energy states dominating the $\langle \exp(\beta u) \rangle$ average are less frequently occupied. As a consequence, while water molecules at the center of the nanotube lose energy on average, their excess chemical potential was found to be lower by more than 1 $k_{\rm B}T$, in agreement with the estimate from the average occupancy number via Eq. **1**. A larger fraction of weakly bound and unbound water molecules ($u > 0$) in the bulk fluid is already manifest at the level of water contact pairs. 15 % of water molecules in contact (within 3.5 Å oxygen distance) are unbound in the bulk fluid (pair interaction energy $u_{ij} > 0$). In contrast, water molecules inside the nanotube have a much smaller fraction of unbound contact pairs of 2×10^{-4}, and optimize their pair interactions by forming a nearly linear chain of hydrogen bonds. Inside the nanotube, hydrogen bonds were found to be highly oriented. Nevertheless, water molecules could rotate almost freely about their aligned hydrogen bonds to retain entropy despite the quasi-one-dimensional order. Interestingly, a recent simulation study showed that ions of a potassium iodide melt are similarly sucked into carbon nanotubes to form quasi-one-dimensional crystallites [14].

4 WATER CONDUCTION

Water molecules not only penetrate into, but are conducted through the nanotube. During the 66 ns, more than 1000 water molecules entered the nanotube on one side and left on the other side [6]. The resulting flow of about 17 water molecules per nanosecond is comparable to that measured for the transmembrane protein aquaporin-1 [15]. Interestingly, the flow occurred in sharp pulses with peaks of about 30 water molecules per nanosecond, reminiscent of single ion channel activity [16]. However, in the simulation, the water flow is not driven by a pressure or chemical potential gradient, and therefore the net water flow (with upward and downward conduction subtracted rather than added) is about zero.

The tight hydrogen bond network inside the nanotube is responsible for the efficient water conduction. A lack of competition inside the nanotube strongly enhances the average life time of a hydrogen bond. As a consequence, rupturing the water wire is energetically costly and thus rare. This leads to the highly concerted and persistent motion of the water molecules inside the nanotube, resulting in bursts in the water flow. The water wire moves with little resistance through the "greasy" nanotube in the absence of hydrogen-bond interactions with the hydrophobic wall [6].

5 DRYING THE NANOTUBE

Water occupancy of hydrophobic channels can easily be tuned or modulated by tilting the subtle balance between loss of hydrogen bonds, elimination of energetic fluctuations, and van-der-Waals attractions. A comparably small change in, e.g., the van-der-Waals interactions was sufficient to empty a previously occupied cavity [6]. We changed the carbon-water Lennard-Jones interactions by weakening the attraction. The nanotube then fluctuated in sharp transitions between empty and

filled states [6], reflecting the energetic cost of fragmenting the water wire during transitions. Emptying of the space between nonpolar ellipsoids was observed by Wallqvist and Berne [17]. Drying transitions induced by nonpolar molecular surfaces were predicted by Lum, Chandler and Weeks based on a theory that incorporates fluctuations between the liquid and vapor phases of water [18]. Drying of the space between plates was studied by using lattice models [19]. In the nanotube, "drying" occurred for a quasi-one-dimensional microscopic volume without incurring a significant free energy cost for forming a water-vapor interface [6].

6 APPLICATIONS

Normally, sensitivity to the potential parameters interferes with the quantitative interpretation of molecular simulations. Here, sensitivity is an important observation: Small changes in the nanotube water interactions can lead to large changes in the water occupancy of the channel. This might have biological significance, and offer an explanation for the crystallographically empty, yet functionally filled hydrophobic channels in proton-transferring proteins. In cytochrome c oxidase, a simulation study showed that transient water molecules in the active site can rapidly form a hydrogen bonded water wire anchored by a hydrogen bond donor at the Glu-242 site (bovine numbering) [20]. In bacteriorhodopsin, the increased polarity of the de-protonated Asp-96, located in a relatively hydrophobic environment of the cytoplasmic half-channel, could trigger water influx to establish proton connectivity to the solvent. This would lead to re-protonation of Asp-96 [21] which would in turn lower the polarity of the channel and cause drying to prevent proton back leakage. The hydrophobic channels in cytochrome c oxidase and bacteriorhodopsin would thus act as "field-effect transistors" for protonic currents, with rotational isomerization of Glu-242 [2], [22] and the charge state of Asp-96 providing the "gate voltage", respectively, by increasing the local polarity. It is conceivable that emptying/filling transitions in membrane-inserted, functionalized nanotubes (controlled, for instance, by light induced excitation of covalently bound dye molecules), could potentially be used to design single-molecule "transistors" for protonic currents [6].

7 CONCLUSIONS

We conclude that, counter to intuition, hydrophobic channels can have significant water occupancy despite a reduction in the number hydrogen bonds [6]. Water molecules inside such channels are shielded from competing interactions, permitting tight and long-lived hydrogen bonds. So why do water molecules not normally penetrate into membranes [23] or the hydrophobic core of proteins? To reconcile conflicting conclusions from NMR [24], [25], X-ray crystallography [26], and simulation [27], we find that isolated water molecules in small hydrophobic cavities are unlikely since that would require van-der-Waals interactions comparable to the excess chemical potential in the bulk fluid, $\mu_w^{ex} \sim -10\ k_{\rm B}T$. Essential factors for high water occupancy appear to be (1) cavity size and shape, permitting multiple water molecules to form hydrogen bonds, as seen [24] in interleukin 1β; (2) rigidity of the cavity wall to shield those hydrogen bonds; and (3) strong van-der-Waals attractions, often to polarizable aromatic residues, as in the hydrophobic cavities of interleukin 1β, bacteriorhodopsin, and cytochrome c oxidase [1], [24].

Appropriately functionalized carbon nanotubes could be used to transport water and other small molecules, even polymers, across membranes. By regulating the water occupancy, for instance by applying an electric field or by changing the solvent conditions (polarity, salt concentration, etc.), nanotubes could be switched between filled and dry states, opening up possibilities for their use as single-molecule "transistors" for mass and proton-current flow.

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