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Research Article

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Vibrating Carbon Nanotubes as Water Pumps

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ABSTRACT

Nanopumps conducting fluids directionally through nanopores and nanochannels have attracted considerable interest for their potential applications in nanofiltration, water purification, and hydroelectric power generation. Here, we demonstrate by molecular dynamics simulations that an excited vibrating carbon nanotube (CNT) cantilever can act as an efficient and simple nanopump. Water molecules inside the vibrating cantilever are driven by centrifugal forces and can undergo a continuous flow from the fixed to free ends of the CNT. Further extensive simulations show that the pumping function holds good not only for a single-file water chain in a narrow (6,6) CNT, but also for bulk-like water columns inside wider CNTs, and that the water flux increases monotonically with increasing diameter of the nanotube.

KEYWORDS

Nanopump, carbon nanotube, nanofluidics, centrifugal forces, water dynamics

1. Introduction

Making a continuous unidirectional water flow is of significant importance in many applications including nanofiltration, water purification, and hydroelectric power generation [1–3]. A widely used approach to drive water inside nanochannels is to create an osmotic or hydrostatic pressure gradient [4]. In recent years, a number of alternatives have been proposed to move fluids or nanoparticles inside nanochannels. Molecular dynamics (MD) simulations have shown that temperature differences can transport water inside carbon nanotubes (CNTs) from the hot end to the cold end [5, 6]. It has also been shown that a positively charged nanotube can drive out a neutral CNT or fullerene ball inside it at an extremely high speed [7]. In addition, it has been suggested that the transportation of nanoparticles including water molecules encapsulated in a CNT could be induced by mechanical torsion and sequential collapse of the CNT [8–10], or by a sustained mechanical actuation on the CNT excited by two oscillating tips [11]. More recently, the possibility to produce a unidirectional water flow through a short CNT by asymmetrically positioned point charges adjacent to the tube, mimicking the charge distributions in conserved regions of water channels in cellular membranes (aquaporins), was also discussed [12, 13].

The mechanical vibration of a CNT can be excited by environmental vibration, external fields [14–16], or absorption of ambient or waste thermal fluctuations [17, 18]. Such a vibrating nanotube holds promise for numerous potential technical applications, such as ultrasensitive mass detection [19] and radiofrequency

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signal processing [20]. Here, we demonstrate that a vibrating CNT cantilever can also function as an efficient molecular water pump, in which water molecules are pushed by centrifugal forces, due to their circle-like motions along the nanotube. This intriguing pumping ability holds good not only for a single-file water chain formed in a narrow-diameter CNT, but also for bulk-like water columns inside wider nanotubes. Moreover, flowing water through CNTs has been shown to be capable of producing bias voltages along the nanotubes [2, 3], and thus, may provide us with the possibility to transport water and produce electricity simultaneously using vibrating CNTs.

2. Modeling and simulations

We used an uncapped CNT solvated in a water reservoir as the model system (Fig. 1(a)). To create a cantilever, the carbon atoms at the left end of the nanotube were fixed, while each of the remaining atoms was subjected to a periodic force $F_{ij}(t) = F_i\sin(2\pi f_j t)$ vertical to the tube axis in order to force the CNT into periodic vibration, where F_i and f_j denote the amplitude and frequency of the applied force, respectively. As a model of a pump, a fixed graphene sheet was attached to the fixed end of the CNT to separate it from the reservoir. All MD simulations were performed at a constant temperature of 300 K with NAMD2 [21] and visualized using visual molecular dynamics (VMD) [22]. Periodic boundary conditions were imposed in all directions. The carbon atoms were treated as aromatic carbons (CA) in the CHARMM27 force field [23] and water was modeled with the TIP3P model [24]. The particle mesh Ewald (PME) method [25] was employed to treat the long-range electrostatic interactions. A time step of 2 fs was used and coordinate data were collected every 1 ps. After 1000 steps of energy minimization, the system was initially equilibrated for 0.2 ns. Inside a (6,6) CNT with diameter of ~8.1 Å, water molecules form a single hydrogen-bonded chain in the equilibrium state (see Fig. 1(a)), consistent with previous studies [26] and similar to the water chains inside the biological water channel aquaporins [27, 28]. This water arrangement has been suggested to be largely responsible for the rapid water transport inside CNTs [29].

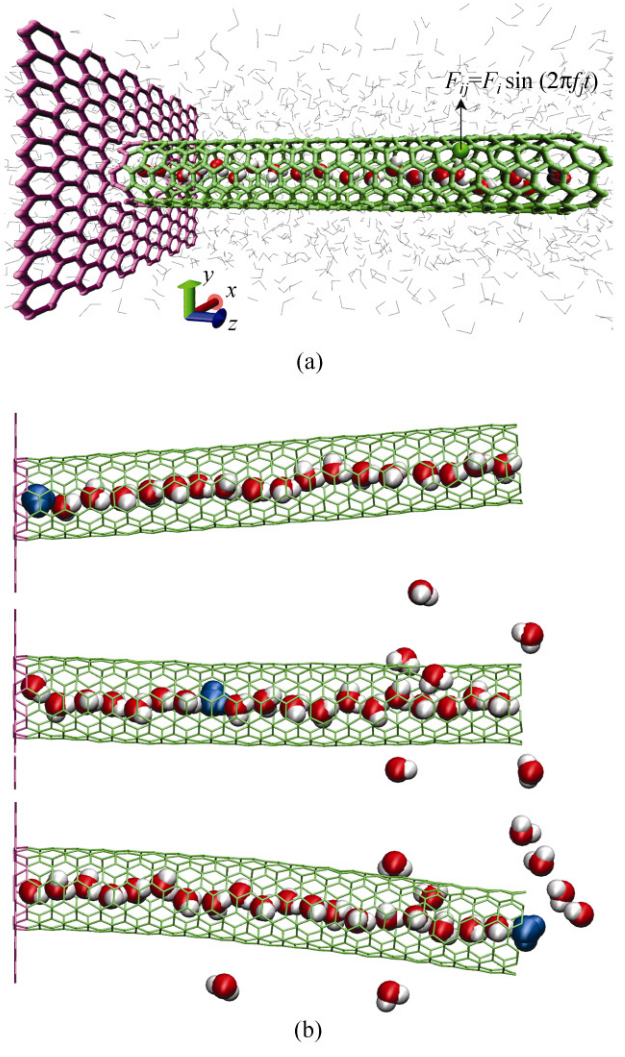

Figure 1 The model system of the (6,6) vibrating carbon nanotube cantilever pump. (a) The pump system consisting of a (6,6) nanotube with length of 50 Å in a water reservoir (represented by lines) separated by a fixed graphene sheet (colored magenta). Water molecules inside the CNT channel are shown in sphere representation with oxygen in red and hydrogen in grey. The nanotube is fixed to the graphene sheet at the left end and subjected to a periodic external force $F_{ij}(t) = F_i\sin(2\pi f_j t)$ per atom along the y direction. A typical carbon atom subjected to the force is shown as a green sphere. (b) Snapshots showing the molecular dynamics process for a water molecule (highlighted in blue) moving from the fixed end to the free end under a vibrating force of $F_i = 30$ pN and $f_j = 100$ GHz (see also Movie S-1 in the Electronic Supplementary Material (ESM))

3. Results and discussion

To investigate water movement inside a vibrating CNT cantilever, we conducted further 64 ns MD simulations

and collected the results from the last 60 ns for analysis. We first applied a periodic force $F_{ij}(t)$ with F_i = 30 pN and f_j = 100 GHz to each atom of the (6,6) CNT to force it into vibration. Surprisingly, it was found that when water molecules inside the CNT were forced to move transversely in a tangential direction to the vibrating nanotube, they started to move along the tube from the fixed end to the free end (Fig. 1(b)), leading to a net water flux through the vibrating CNT. We define the net flux as the difference between the number of water molecules per nanosecond leaving the CNT from one end and from the other, having entered the nanotube from the opposite end [13]. Remarkably, during the last 60 ns, 1,550 water molecules flowed out of the nanotube from the free end with no opposing water permeation being observed, resulting in a net flux of ~25.8 ns^{-1} crossing the CNT. This net flux is more than one order of magnitude larger than the experimentally measured water flux through a CNT with diameter of less than 2 nm under a pressure gradient of 1 atm [30].

A continuous hydrogen-bonded water chain has been suggested to be critical for water transport in nanochannels such as biological aquaporins and CNTs [26–29]. Can the continuity of a water chain still exist inside a vibrating CNT channel? To address this issue, we monitored the number $N(t)$ of water molecules inside a vibrating (6,6) CNT during a 60 ns MD simulation, as shown in Fig. 2(a). It was found that the CNT channel was always occupied by about 19 water molecules during the entire simulation, suggesting that the water chain inside the nanotube is continuous during its vibration. To further characterize the water chain continuity inside the CNT, we calculated the distribution of disruption probability $P(z)$ of the single-file water chain. Along the channel axis, the CNT channel was divided into 0.5 Å-thick equidistant sections. Given a position z, $P(z)$ was obtained by calculating the ratio of the disrupted number $N_d(z)$ and the total number $N_t(z)$ of water pairs (i.e., two neighboring water molecules) within the section during the 60 ns MD simulation, as $P(z) = N_d(z)/N_t(z)$. If the spacing of a water pair was longer than 3.75 Å, the water pair was considered disrupted [31]. As shown in Fig. 2(b), the disruption probability was below 0.003 throughout the CNT channel, further confirming that the single hydrogen-bonded water chain inside the CNT channel is continuous during its vibration and showing the possibility of making a continuous water flow using vibrating CNTs.

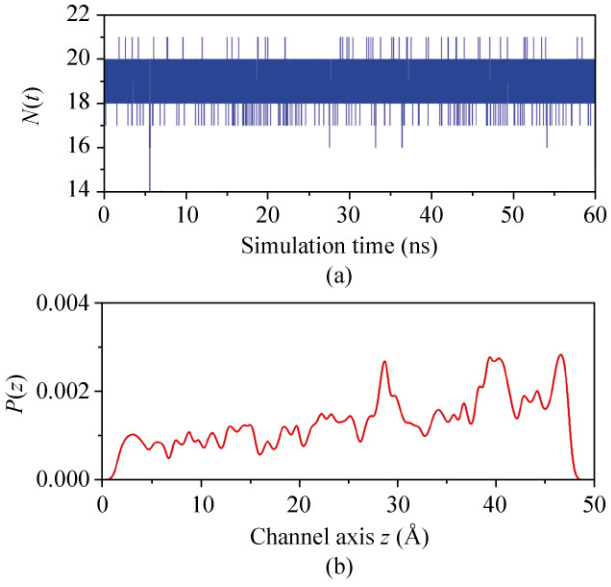

Figure 2 Water chain continuity during CNT vibration under a external force of F_i = 30 pN and f_j = 100 GHz. (a) Number $N(t)$ of water molecules inside the vibrating CNT as a function of simulation time. (b) Distribution of disruption probability $P(z)$ of the water chain inside the vibrating CNT along the channel axis z. The origin corresponds to the center of the fixed end of the CNT

The velocity of a water molecule inside the vibrating nanotube cantilever consists of a transverse component v perpendicular to the nanotube axis and a longitudinal component u along the nanotube caused by the centrifugal force due to its circular-like tangential motion with the nanotube around the fixed end of the tube (Fig. 3(a)). According to Newton's second law of motion, an object with mass m moving in a circular path with radius r at a tangential velocity v requires a centripetal force with magnitude mv^2/r to keep it in the circular orbit. Similarly, a water molecule within a vibrating CNT also needs such a centripetal force to keep it in the moving CNT. However, as the friction between water and the CNT is so weak that it can be neglected [32], a centrifugal force F_c equal and opposite to the centripetal force will pull the water molecule outward from the fixed end along the longitudinal direction of the tube. Note that the tangential velocity v of a water molecule inside the vibrating CNT depends not only on the angular velocity of the CNT that is related to the deviation from its equilibrium position,

but also on the longitudinal position of the water molecule inside the CNT. Consequently, water molecules within a vibrating CNT should be driven by distinct centrifugal forces at different positions, but hydrogen bonding interactions between neighboring water molecules can keep them as a continuous chain.

To examine the dependence of the water flux on external force, a series of simulations were performed on the (6,6) CNT subjected to distinct external forces. For larger forces over 90 pN the tube structure broke down, and below 90 pN the pumping flux was proportional to the value of F_i at a constant frequency f_j = 100 GHz, as shown in Fig. 3(b). This proportional flux was also seen for a shorter nanotube of 25 Å in length, although it exhibited a lower water flux (Fig. 3(b) inset). This observation can be explained by computing the vibration properties of the nanotube under different loadings. It was found that larger force amplitude F_i leads to larger vibration amplitude of the CNT (Fig. 3(c)). We also calculated the average tangential

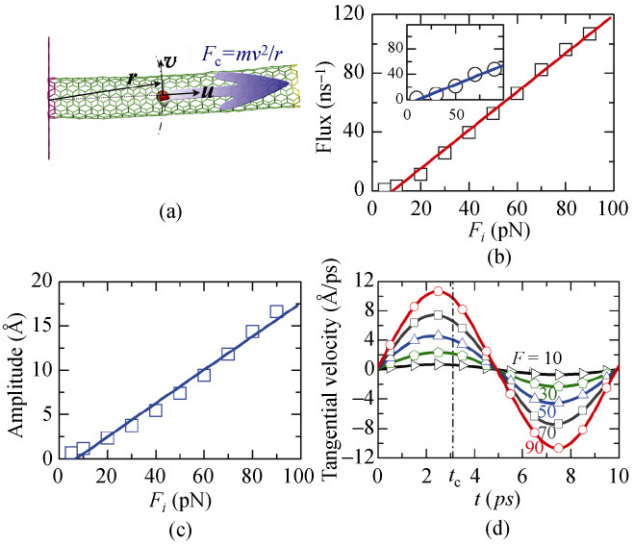

Figure 3 Forced movement of water molecules in the vibrating (6,6) CNT at a constant frequency f_j = 100 GHz. (a) Schematic illustration of centrifugal force F_c (blue arrow) acting on a water molecule with mass m, tangential velocity v, and longitudinal velocity u. (b) Pumping flux through the vibrating CNT with a length of 50 Å as a function of the amplitude F_i of the applied force. Inset: Variation of the flux in a shorter CNT with length of 25 Å as a function of F_i. (c) Plot showing the increase in moving amplitude of the free end (colored yellow in panel a) of the CNT with increasing force amplitude F_i. (d) Periodic change of the tangential velocity v at the free end of the CNT with time

velocity v of the free end of the CNT within a vibration period of 10 ps at f_j = 100 GHz. At a given time (e.g., t_c in Fig. 3(d)), it is clear that a stronger applied force F_i leads to larger absolute value of v. Consequently, larger vibration amplitude and higher tangential velocity of the CNT will certainly lead to a stronger centrifugal force acting on water, which moves the water more rapidly and leads to higher water flux through CNTs. In addition, further extensive simulations show that the net water flux remains constant when the frequency f_j of the external force is below ~100 GHz, but decreases monotonically with increasing frequency beyond ~100 GHz, while changing the chirality of CNT has little effect on its pumping ability (see Figs. S-1 and S-2 in the ESM).

As the CNTs employed in previous experimental studies were usually of larger diameters, one may wonder whether the pumping behavior described here is also observed for wider CNTs. To address this issue, we calculated the pumping fluxes inside vibrating CNTs with diameters from 10.9 Å to 13.6 Å, as shown in Fig. 4(a). It was found that directional water flow can also be produced by these vibrating CNTs, but with larger flux, still proportional to force amplitude F_i. Moreover, when subject to the same external force, the net water flux increases monotonically with increasing CNT diameter (Fig. 4(a), inset). Figure 4(b) shows the different water structures inside CNTs with various diameters: single-file water chain (8.1 Å), stacked pentagonal rings (10.9 Å), stacked hexagonal rings (12.2 Å), and disordered bulk-like water (13.6 Å). These different water structures remain approximately constant during vibration of CNTs, and resemble those inside a fixed CNT [33, 34]. This is because the unidirectional water flow inside vibrating nanotubes is steered by centrifugal forces acting on water molecules, which, combined with interactions between neighbouring water molecules in the tubes, can move the water columns collectively towards the free ends of the vibrating CNTs, and thus, would not disturb the internal water structures. Furthermore, it is to be expected that for vibrating CNTs with even larger diameters the pumping function would also exist, which should have more practical importance for future applications.

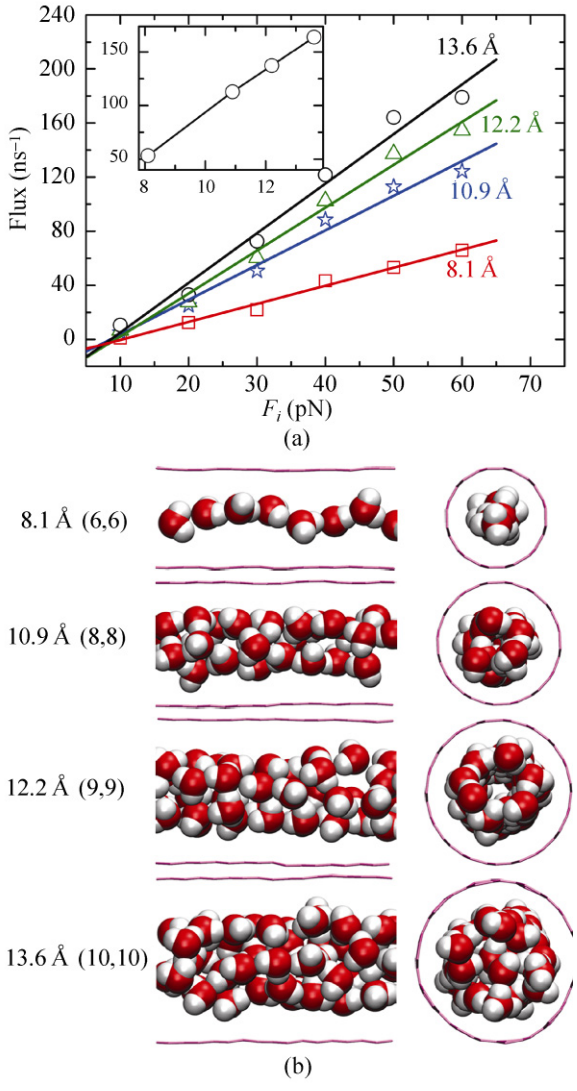

Figure 4 Water conduction in larger carbon nanotubes with diameters ranging from 10.9 Å to 13.6 Å. (a) Water flux as a function of F_i at f_j = 100 GHz. The inset shows that the water flux increases with tube diameter (in Å) at F_i = 50 pN. (b) Water structures inside the tubes

Finally, we note that the decrease in vibration frequency does not significantly lower the pumping flux (see Fig. S-1 in the ESM), such that further work can be devoted into powering the nanopump with low frequency environmental energy such as waste heat and external fields. In addition, as flowing water can produce bias voltages in CNTs [2, 3], further efforts should be made to detect the possibility of using an array of nanotube cantilevers to pump water and to generate electricity simultaneously, as summarized in Fig. 5.

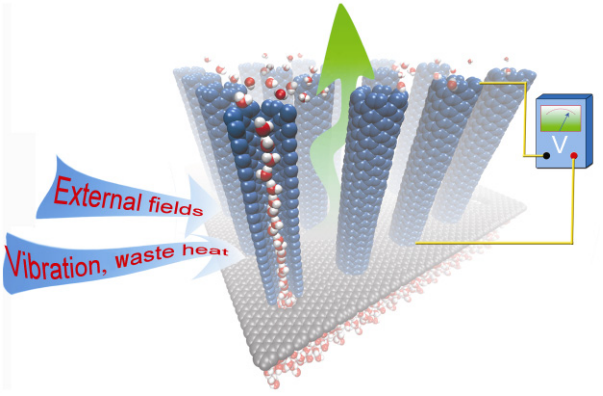

Figure 5 Schematic illustration showing energy harvesting and conversion of the pumping system. The green arrow indicates the direction of water flow through the vibrating nanotubes

4. Conclusion

We have shown that vibrating CNT cantilevers can serve as efficient water pumps. Water movement inside the vibrating CNT is driven by centrifugal force due to its forced vibration with the nanotube. The resulting pumping flux increases with increasing vibration amplitude, while a change of chirality of the nanotube has little effect on the interior water flux. It is also found that the water chain inside the vibrating CNT channel is continuous during its vibration, showing the robustness of the pumping ability. Furthermore, this effect was also demonstrated in wider nanotubes, which may have more practical importance for future applications.

Acknowledgements

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Electronic Supplementary Material: A video showing the water pumping process of a vibrating CNT and further details of effect of the frequency of external force and CNT chirality on water flux are available in the online version of this article at http://dx.doi.org/10.1007/s12274-010-0080-y.

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