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Vibrating-Charge-Driven Water Pump Controlled by the Deformation of the Carbon Nanotube

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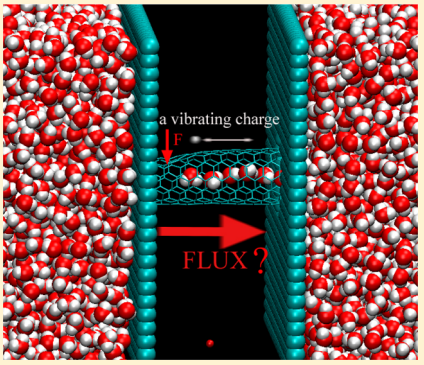
ABSTRACT: The directed transport of water molecules in a single-walled carbon nanotube (SWNT) based on a ratchet effect is investigated by molecular dynamics simulations. The system is driven far away from thermal equilibrium by an additional deterministic perturbation of a vibrating charge, and the spatial inversion symmetry is broken by the continuous deformations of the SWNT. It is well-known that the water flux across a circular channel decreases when the channel is narrowed or deformed. However, our simulation results show that the water flux almost increases linearly within a deformation of 1.9 Å. There exists an optimized value of deformation at which the pumping capacity takes its maximum value. Moreover, the direction of transport even exhibits a change of sign with narrowing the carbon nanotube.



I. INTRODUCTION

Understanding and controlling the transport of water through nanochannels is of great importance for designing novel molecular devices, machines, and sensors, which have wide applications in fields as diverse as chemical process control, cell biology, medical delivery, and nanorobotics.[1−9] The behavior of water confined in nanoscale channels usually exhibits dynamics different from that of the bulk system, as the characteristic dimensions of the confining volume reduce to the nanometer scale.[10,11] Microscopic fluctuations play a key role, and it no longer makes sense to describe the fluid as a continuum.[12,13] This is a gray area where our understanding of the transport of fluid through nanochannels is clouded by controversy.[13−15]

With the miniaturization of flow devices, it becomes hard to pump fluid across nanoconfined geometries, where the large surface volume ratio presents a step dissipative barrier to fluid motion. Though progress in moving material inside the carbon naotubes has been made, it is difficult to develop a suitable nanoscale water pump device which can make a continuous unidirectional water flow on nanoscale.[15,16] Conventionally, transporting water directionally through a nanochannel is driven by an osmotic or hydrostatic pressure gradient.[17] Such a method would involve a large reservoir of solution on one side of the nanochannel to produce the pressure gradient. In additional, chemical and thermal gradients are also applied to drive fluid through nanochannels.[18,19] Recently, different from the conversional methods, various novel blueprints for a nanopump have been proposed.[20−22] In 1999, Král et al. proposed a laser-driven pump for atomic transport through carbon nanotubes,[20] while Insepov et al., using numerical simulations, showed that the gas inside the carbon nanotube can be driven by the Rayleigh surface wave.[2] The experiments that followed have confirmed that nanoparticles inside the hollow core of multiwalled carbon nanotubes can be driven in the direction of the electron flow.[22] Later, Duan et al. proposed an energy pump for activating axial water molecules flow inside a carbon nanotube by setting up a small portion of the initially twisted wall of the carbon nanotube.[21] Interestingly, the theoretical work of Král and Shapiro showed that an electric current is generated along a metallic SWNT immersed in a liquid flowing along them,[23] which was demonstrated by the following experimental work of Ghosh et al.[24] Inspired by this result, Sun et al. also demonstrated experimentally that a water flow can also be driven by the applied current on a single walled carbon nanotube (SWNT).[25] In 2008, Joseph and Aluru's simulation results showed that confined water in carbon nanotubes can be driven by static electric field.[26] However, Bonthuis' work showed that static electric fields do not induce fluid flow in the planar geometry.[27] Later, Huang et al. proposed a design for pumping water molecules in a single-walled carbon nanotube in the presence of a linearly gradient electric field.[28] Very recently, Klaus F. Rinne et al. demonstrated pumping of water through a carbon nanotube by time-dependent electric fields by using molecular dynamics simulations.[29] In our previous work, we have proposed a novel nanoscale water pump (or nanoenergy conversion devices) for converting electrical power into the transport of the charge-neutral water molecules.[6,15] A continuous unidirectional water flow can be attained by a ratchet-like mechanism without osmotic pressure or hydrostatic drop.

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The ratchet motion is a fascinating phenomenon which has been widely studied.[30−33] In previous work, researchers studied ratchet phenomena mostly by means of one-body Langevin (or Fokker−Planck) descriptions, in which the many-body features of molecular motion are conveyed into an effective drag coefficient, representing the systematic interaction with the surrounding fluid, and a noise term, surrogating the collective motion of the molecules with a source of randomness. Assessing the robustness of ratchet phenomena toward many-body effects is thus of great interest, and it is different to solve the problem by the Fokker−Planck equation.[34] In this work, we made a step forward in this field by means of MD simulations of confined asymmetric nanoflows.

The transport of water molecules through nanochannels can be controlled by narrowing the channels conveniently. It is well-known that the water flux across a circular channel decreases when the channel is narrowed or deformed. However, in this paper, different from the conversional water pump, we find that the water flux driven by a vibrating charge increases linearly solely due to the narrowing of the carbon nanotube within a deformation of 1.9 Å. The water flux reaches the maximum when displacement of the forced atom reaches a critical value of 1.9 Å. Also, it decreases sharply for a further deformation of 0.6 Å. Moreover, the direction of transport even exhibits a change of sign when the displacement reaches 2.4 Å. The mechanism behind these interesting phenomena is discussed in detail.

This paper is organized as follows. The simulation model and parameters are introduced in section II. Section III is devoted to the simulation results and discussions. Our conclusions are presented in section IV.

II. METHODOLOGY

The simulation framework is shown in Figure 1. An uncapped armchair SWNT with 22.14 Å in length and 8.14 Å in diameter

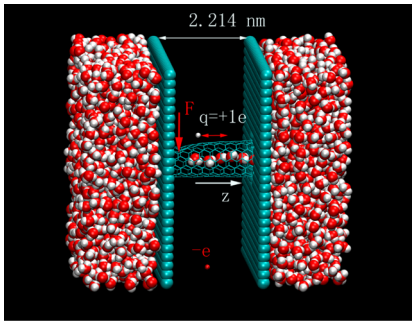

Figure 1. Snapshot of a typical simulation system. One atom in the left side of the SWNT was pushed away from the original position by the external force F, resulting in a radial displacement of δ deeply. A positive charge vibrates around the middle of the nanotube. The radial distance of the charge from the carbon atom of the nanotube is d = 1.4 Å.

was embedded in the membranes along the z direction. The membrane atoms were located in a face centered cubic fashion in the xy plane and were fixed during the simulations. In order to explore the effect of deformation on the water transport through the carbon nanotube driven by a vibrating charge, one carbon atom in the left side of the SWNT is pushed away from the original position by an external force F, resulting in a radial displacement denoted by δ. Consequently, the neighboring carbon atoms were pushed away from their initial position to form a narrow region due to the bond interaction among carbon atoms. For each radial displacement δ, an equilibrium state of a SWNT could be obtained by relaxation. To prevent the SWNT from being swept away, each carbon atom in the bottom part of the carbon nanotube was fixed by a restraining force. An imposed charge with value of 1.0 e was placed outside the SWNT. The radial distance of this imposed charge from the carbon atoms of the SWNT is d = 1.4 Å. The charge can vibrate around the origin point along the z direction. The oscillation pattern is $z = A\cos(2\pi t/T)$, where A = 2.5 Å is the amplitude and T = 2 ps is the oscillation period. A count charge was introduced close to boundary of the system to keep the whole simulation system electrically neutral.

All the molecule dynamics simulations were carried out at a constant volume (initial box size: L_x = 5.0 nm, L_y = 5.0 nm, L_z = 6.0 nm) and temperature (300 K) with GROMACS 4.0.7.[35] Period boundary conditions were applied in all directions. Here, water is modeled by using the TIP3P model.[36] The carbon nanotube is regarded as a whole molecule consisting of many carbon atoms which can be regarded as material points. The time for each simulation is 105 ns with a time step of 2 fs, and data were collected every 0.1 ps. Simulation data of the last 100 ns were collected for analysis. The Lennard-Jones parameters for the interaction among carbon atoms are the cross section of σ_{CC} = 0.34 nm, the depth of the potential well of ε_{CC} = 0.3612 kJ mol^{-1}, carbon−carbon bond lengths of r_0 = 0.142 nm, bond angles of θ_0 = 120°, and spring constants of k_b = 393 960 kJ mol^{-1} nm^{-2}, k_θ = 527 kJ mol^{-1} deg^{-2}, and k_ξ = 52.718 kJ mol^{-1} deg^{-2}.[15,37] The water−carbon interaction is van der Waals interactions with cross section of σ_{CO} = 0.3275 nm, ε_{CO} = 0.4802 kJ mol^{-1}. The long-range Coulombic interactions are handled by using the particle mesh Ewald (PME) summation with a cutoff of 1.4 nm, the FFT grid spacing of 0.12 nm, and the fourth-order interpolation.[38] The short-range van der Walls forces are calculated by applying a cutoff scheme with a cutoff distance of 1.4 nm.

III. RESULTS AND DISCUSSION

The average water flux and the average number of water molecules N for different δ are shown in Figure 2. For the unperturbed nanotube, the average number of water molecules inside the nanotube is about 8.5, and the water flux is zero because the system is completely symmetric. When the carbon nanotube is deformed, the spatial symmetry of the system is

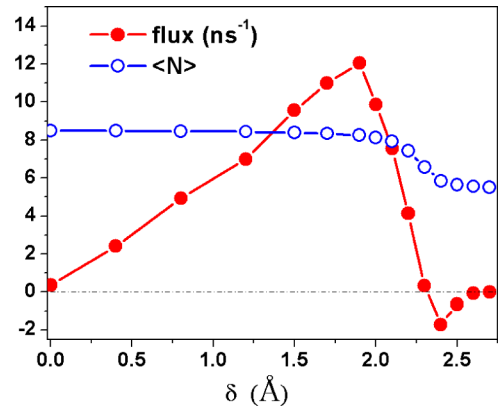

Figure 2. Average water flux and average number of N for different δ for T = 2 ps.

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broken, so the directed transport of water molecules is attained. It is remarkable to find that the water flux increases with δ linearly when $0 < \delta < 1.9$ Å and reaches the maximum value (about 12 ns^{-1}) at $\delta = 1.9$ Å. This maximum value is about three times the measured 3.9 ± 0.6 ns^{-1} for aquaporin-1. The average number of water molecules inside the tube is almost unchanged when $0 < \delta < 1.9$ Å. However, the flux decreases sharply when 2.0 Å$< \delta <$2.3 Å. Furthermore, the direction of the flux even reverses when $\delta > 2.3$ Å. Naturally, the water flux decreases to zero when further increasing δ to 2.6 Å, consistent with our previous work[39] and not affected by the length of the nanotube. The nanotube is functionally closed. We also calculated the input power in the typical cases. The input power is defined as the rate at which work is done by the charge. For $\delta = 1.9$ Å, the input power is about $P_0 = 10.86 \times 10^3$ kJ mol^{-1} ns^{-1} (also see ref 15). From our simulation results, we found that the input power is almost constant as $\delta <$2.0 Å. However, it decrease to about $^2/_3P_0$ as δ increases to 2.6 Å.

Figure 3 exhibits the distribution of water molecules inside the nanotube along the z direction under different values of δ.

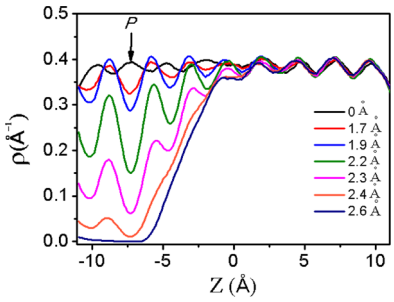

Figure 3. Water distribution along the nanotube axis for different δ. The arrow marked by P is the position of the pushed atom.

It is interesting to find that, in the right part of the tube, the water distribution is almost unchanged in the whole δ range. However, the water distribution in the left part (deformation part) changed greatly as δ increases. In the case of $\delta = 0$ Å the distribution has a wavelike structure with minimal values at the openings. As δ increases, the peaks (dips) move rightward, the left opening is no longer in the position for the minimal distribution, and the distribution at P becomes to the lowest dip from a peak. For $0 < \delta <$1.9 Å, the amplitude of the wave pattern shows a clear increase. But for $\delta > 1.9$ Å, the water distribution at the left part decreases obviously. Likewise, the average number of water molecules $\langle N \rangle$ also decreases from about 8.5 to 5.6 (see Figure 2). The water distribution at P, the location facing the forced atom, becomes the lowest dip and decreases gradually, corresponding to the narrowing of the nanotube at this position. Also, the water distribution at P is very close to zero when $\delta > 2.4$ Å. In this left region, the wavelike pattern almost disappears.

Figure 4 displays the probability of finding exactly N water molecules inside the tube for different δ. When $\delta = 0$, the probabilities of $N = 8, 9$ are 45.7% and 49.0%, respectively. For $\delta \leq 1.9$ Å, the total probability for the situations of $N = 8, 9$ is about 90%. And the probabilities of the other situations are very low. This indicates that the single file water chain keeps well with δ in the interval of 0−1.9 Å. The probability of $N = 9$ decreases greatly as δ further increases. Also, the probability of $N = 6, 5$ increases obviously. When $\delta = 2.4$ Å, the situations of $N = 5, 6, 7$ have a total probability of about 80%. On the

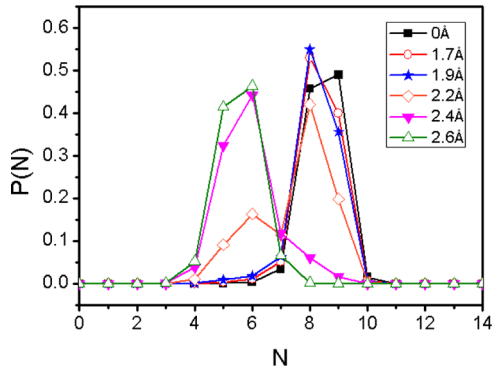

Figure 4. Probability of finding exactly N water molecules inside the tube for different δ.

contrary, the probabilities of $N = 8, 9$ decrease correspondingly and are very close to zero as δ further increases to 2.6 Å. From the simulation data, we observed that the right side of the position P was occupied most probably by about 5 water molecules and the left side of P was often occupied by one water molecule in most of time. These results are consistent with the average number of water inside the tube shown in Figure 2.

Figure 5 shows the average number of hydrogen bonds connecting with the water molecules inside the SWNT. In this

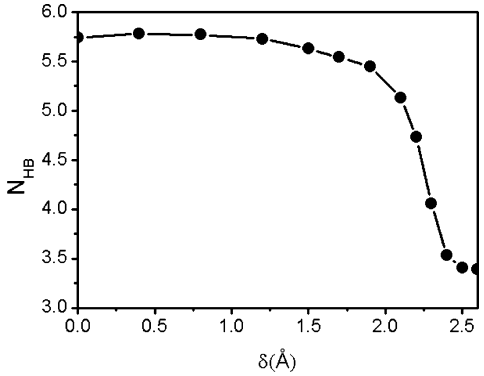

Figure 5. Average number of the hydrogen bonds inside the nanotube for different δ.

paper, we adopt a geometric definition of hydrogen bonds according to which water pair is hydrogen-bonded if the O−O distance is less than 3.5 Å and simultaneously the bonded O−H···O angle is less than 30°.[40] Here, we focus on the water molecules inside the SWNT, so the hydrogen bonds between water molecules both at openings and outside SWNT are beyond our consideration. For the unperturbed SWNT, the number of the hydrogen bond is about 5.7. It almost keeps constant when $\delta \leq 1.9$ Å. However, it decreases from 5.5 to 3.4 sharply for $\delta > 1.9$ Å, indicating that the structure of the single water chain is disturbed by the deformation of the SWNT. When $\delta = 2.6$ Å, the number of the hydrogen bond is about 3.4. From our simulation results, we can conclude that the single water chain is disrupted by the deformation. Correspondingly, the water flux decreases to zero. The nanotube is gated.

To understand the mechanism behind the effect of the asymmetry on the pumping for this nanoscale pump, we calculated the forces acted on the single-file water inside the SWNT under different value of δ: the force from the charge, denoted by F_{WC}; the force from the SWNT, denoted by

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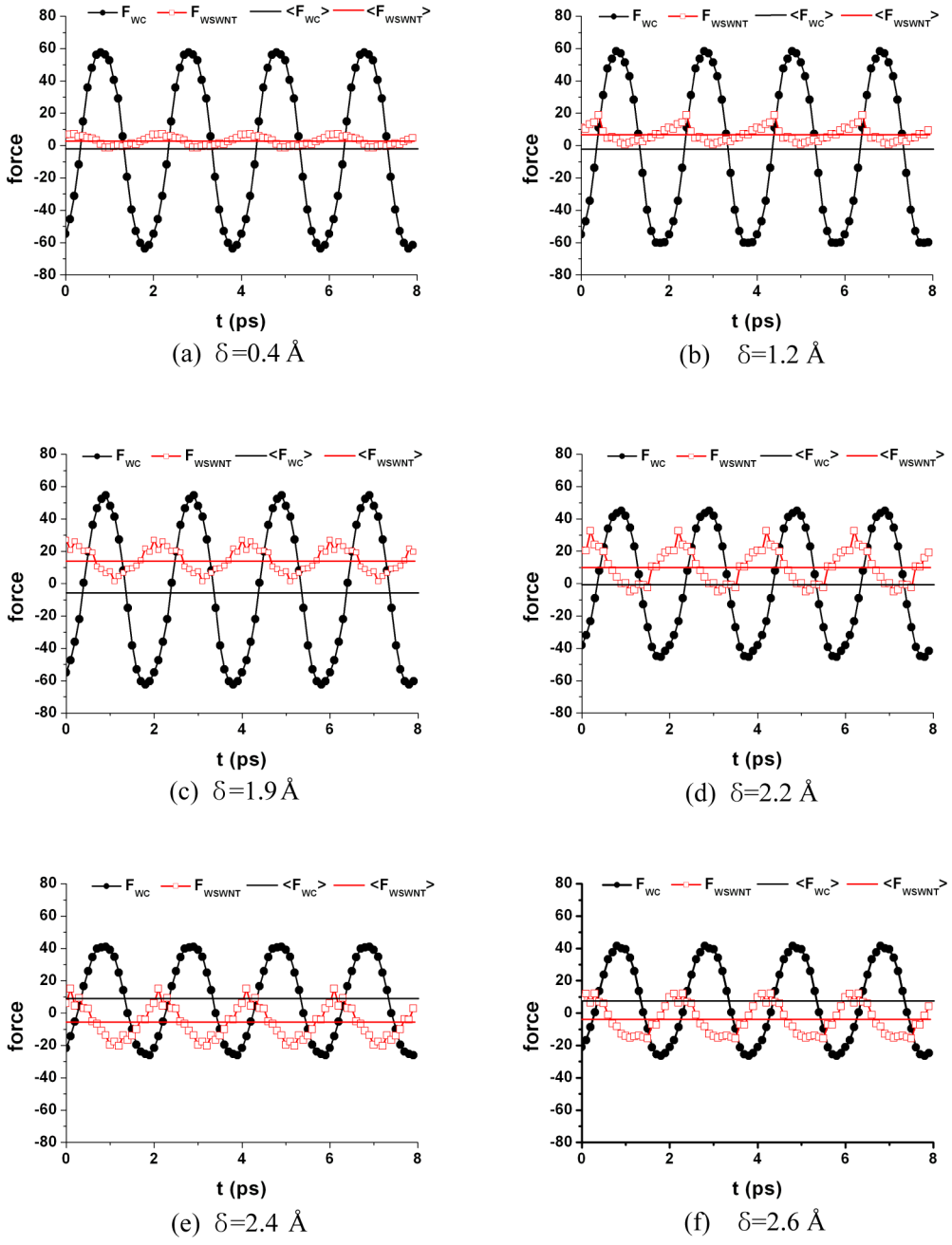

Figure 6. Interaction force between the external charge and the water chain inside the SWNT (F_{WC}) and its average value $\langle F_{WC}\rangle$; the interaction force between the SWNT and the water chain (F_{WSWNT}) and its average value $\langle F_{WSWNT}\rangle$ for different δ.

F_{WSWNT}. We also computed the average value of these forces. We take the average of these interaction forces according to the same formula as our previous work:

$$F_z(t) = \frac{1}{N}\sum_{n=0}^{N-1} f_z(t + nT) \qquad 0 \le t \le T \tag{1}$$

$$\langle F_z(t)\rangle = \frac{1}{T}\int_0^T F_z(t)\,\mathrm{d}t \tag{2}$$

T is the period of the oscillation of the charge, and total time of the simulation is $N{\cdot}T$.

The results are shown in Figure 6. It is clear that the charge−water, SWNT−water forces for each system are sinusoidal functions of time t approximately. In each simulation, the initial location of the charge is at the left position ($z = -$A). Due to the inertia of the water chain inside the SWNT, the charge's motion and the water chain's motion are out of step. For $0 < \delta < 1.9$ Å, the interactions of the SWNT and water chain inside the tube increase obviously due to the deformation of nanotube. The average value of the charge's force, $\langle F_{WC}\rangle$, decreases slowly, corresponding to the distributions of water molecules inside the left part of the tube changing gradually. We note that the single-file water chain keeps well in this δ range. The total effect of these two interactions is that the water chain feels larger resisting force when it moves toward the left than toward the right; the water flow to the right increases, and that to the left decreases with the δ increases. Thus, the water flux increases gradually in this δ range. As δ further increases (δ

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> 1.9 Å), the distance between those two water molecules neighboring P further increases, which leads to a smaller probability of a hydrogen bond between them and the decreasing of the average number of water molecules inside the nanotube. The average number of water molecules inside the nanotube decreases to about 5.6 when δ > 2.4 Å. The amplitude of the F_{WC} decreases for the decreasing of the water molecules inside the nanotube. And the water flux decreases sharply. As δ = 2.4 Å, the water molecule to the left of P (just at the left side of the tube) feels weak attraction from the charge, and also feels weak dragging effect from its right neighboring water molecule at right of P when the OH bond between them is broken. Thus, it is difficult for this water molecule to enter from the left side and then leave on the right side. On the contrary, the water molecule at the right side of the P has a certain probability to pass the narrowest region at P and leave on the left side. This probability becomes almost zero when δ = 2.6 Å. So, there is a value about 2 ns^{-1} of the reverse flux at δ = 2.4 Å, and then it decreases to zero at δ = 2.6 Å.

IV. CONCLUSIONS

In summary, we have demonstrated a blueprint of a water nanopump driven by a vibrating charge using MD simulation. Especially, we have studied the effects of the deformations of the nanopump system on the directional transport of water molecules by continuous deformations of the SWNT. Simulation results show that the deformation plays a key role in pumping water molecules through the carbon nanotube. The critical value of the deformation depth, δ_c = 1.9 Å, is found. The water flux almost increases linearly within a deformation of δ_c but decreases sharply for a further deformation of 0.6 Å. Flux reaches the maximum value (about 12 ns^{-1}) at $\delta = \delta_c$, about three times the measured 3.9 ± 0.6 ns^{-1} for aquaporin-1. For $\delta \leq \delta_c$, the number of water molecules inside the carbon nanotube and the number of the hydrogen bonds both almost keep constant, indicating that the structure of the whole single file water chain not disturbed by the deformation of the SWNT. However, the symmetry of the pump system is broken by the deformation, resulting in the difference of resisting forces when the water chain moves to the left and right. The difference of resisting forces increases with the deformation, so the water flux increases linearly. But when $\delta > \delta_c$, the number of water molecules inside the carbon nanotube and the number of the hydrogen bonds both decrease sharply. It is noted that the hydrogen bond connecting two water molecules in two sides of the deformed region is usually disrupted. So, the resisting force of the SWNT on the water chain increases sharply. The water transport is mainly prevented by the deformation region. So, the flux decreases sharply. Interestingly, the direction of water flux reverses when 2.3 < δ < 2.5 Å. In this case, the water molecules entering from the left end (left to the deformation region) are very difficult to enter the narrowed region. However, the water molecules in the right side can still transport through the narrow region with the help of the external vibrating charge. Our findings may have implications for water treatment, circulation without a pressure gradient, lab-on-a-chip technology.

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Notes

The authors declare no competing financial interest.

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