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Controllable transport of water through nanochannel by rachet-like mechanism

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By using molecular dynamics simulation, we have investigated systematically the feasibility of continuous unidirectional water flux across a deformed single-walled carbon nanotube (SWNT) driven by an oscillating charge outside without osmotic pressure or hydrostatic drop. Simulation results indicate that the flux is dependent sensitively on the oscillating frequency of the charge, the distance of the charge from the SWNT, and the asymmetry of the water-SWNT system. A resonance-like phenomenon is found that the water flux is enhanced significantly when the period of the oscillation is close to twice the average hopping time of water molecules inside the SWNT. These findings are helpful in developing a novel design of efficient functional nanofluidic devices. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4707744]

I. INTRODUCTION

Recently, growing attention has been paid to pumping of water through carbon nanotubes (CNTs). There are two main reasons behind it. One is due to the unique properties and behaviors of water confined inside those CNTs, such as the ordered water structure,[1,2] non-Fickian-type diffusion,[3] extrafast motion of water molecules,[4] and excellent on-off gating behavior.[5,6] The other reason is wide technical applications of water-CNT systems,[7–14] such as in hydroelectric power converters, fluid separation, and drug delivery.

It is important to develop suitable nanoscale water pump devices. Conventionally, pumping in nanofluidic systems is accomplished mainly using osmotic or hydrostatic pressure gradient, or chemical or thermal gradient.[15–18] Recently, various novel concepts and blueprints for nanoscale pump have been proposed.[19–29] In 1999, Král and Tománek[19] proposed a laser-driven pump. They used laser to excite an electric current in the carbon nanotube, which drives intercalated atoms by the wind force. The experiments that followed have demonstrated that nanoparticles of iron inside the hollow core of multiwalled carbon nanotubes can be driven in the direction of the electron flow by electromigration force.[20] Insepov *et al.*[21] used molecular dynamics (MD) simulation to show that the gas inside the carbon nanotube can be driven by the Rayleigh surface wave. Wang and Král[22] introduced nanoscale propellers to pump solvent molecules. Duan and Wang[24] used a small portion of the initially twisted wall of a carbon nanotube to function as an energy pump for the transportation of water molecules. About two years before the experiment by Ghosh *et al.*,[11] Král and Shapiro predicted that electric current can be generated in metallic carbon nanotubes immersed in liquids flowing along them, which was consis-

tent with the following experimental results of Ghosh *et al.*[13] In 2008, Sun *et al.*[10] demonstrated experimentally that a water flow can also be driven by the applied current of a single-walled carbon nanotube (SWNT). In the meantime, Joseph and Aluru's[25] simulation results showed that confined water in carbon nanotubes can be driven by external electric field. A little later, Bonthuis's work showed that static electric fields do not induce fluid flow in the planar geometry.[26] This discord has stirred fierce discussions.[27,28,30]

Though progress in moving material inside the carbon nanotubes has been made, but it is still difficult to make a controllable continuous unidirectional water flow. Interestingly, the cellular membrane contains channel proteins as passive and active transporters, possessing an elegant protein super-structure, that have a remarkable ability to transport or pump them in and out of the cell interior. In 2004, by means of an stochastic model, Kosztin and Schulten[31] suggested that in an active plasma membrane, even passive channel proteins can act as active transporters by consuming energy from nonequilibrium fluctuations fueled by cell metabolism. Furthermore, on the basis of molecular dynamic simulations, Gong *et al.*[32] proposed an intriguing concept for a molecular water pump, with three charges being asymmetrically positioned adjacent to a SWNT, which was inspired by the charge distribution in aquaporins (AQPs), and showed a continuous unidirectional flow resulting from an asymmetric water-charge potential between two ends of the tube. However, very recently, Guo and co-workers[33] argued that AQPs can facilitate highly efficient and selectively passive permeation of water in response to osmotic gradient across cell membranes, but cannot act as pumps or conduct water unidirectionally. In our recent work,[34] we investigated the influence of the position of the narrow region on water transportation through carbon nanotube using MD simulation. We found that for an asymmetric nanotube, the flux through it and through the inverted one are different even under the same osmotic pressure, presenting a

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kind of ratchet mechanism. Therefore, it is of current of interest in this field to create suitable nano water pumps (or nano energy conversion devices) for converting electrical power into the transport of the charge-neutral water molecules. And there is a great need to grasp the basic mechanism by which molecules can flow through nanochannels.

The ratchet motion is a fascinating phenomenon. Previously, researchers study ratchet phenomena mostly by means of one-body Langevin (or Fokker-Planck) descriptions. The many-body features of molecular motion are characterized as 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 Fokker-Planck equation.[29]

In this work, we propose a new methodology for the continuous pumping of single-file water molecules through a deformed SWNT by ratchet-like mechanism, in which an extra oscillating charge serves as an "engine". The nano pump can convert the energy of the oscillating charge into the transport of the water molecules efficiently and conveniently. The water flux obtained by the new methodology even exceeds the measured value for aquaporin-1 (AQP-1) (Ref. [38]) when the period of the oscillating charge is close to twice the average hopping time of water molecules inside the SWNT. The direction and magnitude of the water flux can be controlled conveniently by the oscillation period of the charge, the distance of the charge from the SWNT, and the symmetry property of the water-SWNT system. There are many ways to the generate asymmetry, but we choose to change the geometrical deformation to break the symmetry of the carbon nanotube, as it is easy to achieve the key points in analyzing the ratchet phenomenon by using this simple model.

II. METHODOLOGY

The MD simulation system are shown in Fig. 1. An uncapped armchair SWNT was embedded in the membranes along the z direction. The membrane atoms are located in a face centered cubic fashion in the xy plane and held fixed in the simulation. The SWNT is 22.14 Å in length and 8.14 Å in diameter. By the same method used in Refs. [6] and [34], a carbon atom of the SWNT was pushed inwardly by an external force (hereafter, we refer to this atom as the forced atom), leading to a 2 Å radial displacement of the forced atom. Consequently, the neighboring atoms will be pushed away from their initial positions forming a narrow region. For the convenience of analysis, we number the prospective forced atom and choose the fifth prospective forced atom as the origin point of the z axis, as shown in Fig. 1. A positive charge with a quantity of $1.0e$, which can vibrate along the z direction, is placed outside the SWNT. The radial distance of the imposed charge from the carbon atoms of the nanotube is denoted by d. The charge oscillates around the middle of the tube and the oscillation pattern is $z = A\cos 2\pi t/T$, where $A = 2.5$ Å is the amplitude and T is the oscillation period. To keep the whole
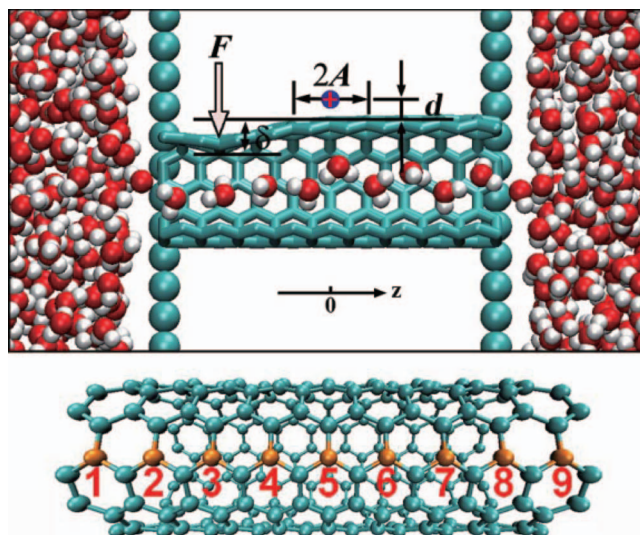

FIG. 1. Snapshot of a typical simulation system. One atom (labeled atom 2) of the SWNT was pushed δ deeply. The charge oscillates around the middle of the tube. The radial distance of the charge from the carbon atoms of the nanotube is denoted by d.

system electrically neutral, a counter charge was introduced close to the boundary of the system.

All the simulations were carried out using GROMACS 4.0.7[35,36] at a constant volume with initial box size dimensions of $Lx = 5.0$ nm, $Ly = 5.0$ nm, $Lz = 6.0$ nm, and a temperature of 300 K for 105 ns. Periodic boundary conditions were applied in all directions. A time step of 2 fs was adopted, and data were collected every 0.1 ps. The last 100 ns were collected for analysis. The carbon nanotube is regarded as a large molecule consisting of carbon atoms. The atom can be regarded as material points. The total potential energy function of SWNT is made up of a sum of many terms, such as van der Waals interactions (Lennard-Jones interaction), bond stretching (2-body), bond angle (3-body), and proper and improper dihedral angle (4-body) interactions. It can be expressed in the form

$$V_{total} = \sum_{VDW} 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + \sum_{bond} \frac{1}{2}k_b(r - r_0)^2$$
$$+ \sum_{angles} \frac{1}{2}k_\theta(\theta - \theta_0)^2 + \sum_{dihedrals} \frac{1}{2}k_\xi(\xi - \xi_0)^2.$$
$$(1)$$

All the parameters were taken from Ref. [37]: $\sigma_{CC} = 0.34$ nm, $\varepsilon_{CC} = 0.3612$ kJ mol^{-1}, carbon-carbon bond lengths of $r_0 = 0.142$ nm, bond angles of $\theta_0 = 120°$, spring constants of $k_b = 393\,960$ kJ mol^{-1} nm^{-2} and $k_\theta = 527$ kJ mol^{-1} deg^{-2}, $k_\xi = 52.718$ kJ mol^{-1} deg^{-2}. Water is modeled by using the TIP3P model. The water-carbon interaction is Van der Waals interactions with cross section of $\sigma_{CO} = 0.3275$ nm, $\varepsilon_{CO} = 0.4802$ kJ mol^{-1}. The particle-mesh Ewald method[35] was used to handle the long-range electrostatic interactions with a cutoff for real space of 1.4 nm. In order to fix the SWNT in the simulation, each carbon atom in the bottom is held at its initial position by a restraining force.

TABLE I. Simulation systems.

Scenarios	Charge	The number of the forced atom	Symmetry property	System name
1	Static, $T = \infty$	5	Symmetrical	S-S
2	Static, $T = \infty$	2	Asymmetrical	S-AS
3	Oscillating, $T = 2$ ps	5	Symmetrical	O-S
4	Oscillating, $T = 2$ ps	2	Asymmetrical	O-AS

III. RESULTS AND DISCUSSION

Firstly, four scenarios (as shown in Table I) are prepared to investigate the feasibility of continuous water transportation driven by the charge outside the SWNT. In these four simulations, the radial distance of the charge from the SWNT is $d = 1.4$ Å and the oscillation period of the charge, T, is 2 ps. It is noted that the simulation system is symmetrical when the 5th forced atom is pressed, and the symmetry is broken when the 2nd forced atom is pressed (see simulation system in Fig. 1).

For easy discussion about directional transportation of water across the SWNT, the flow and the flux are defined by means of the expression

$$flow(t) = \frac{N_{right}(t) + N_{left}(t)}{t}, \qquad (2)$$

$$flux(t) = \frac{N_{right}(t) - N_{left}(t)}{t}, \qquad (3)$$

where $N_{right}(t)$ is the number of water molecules that have crossed the SWNT from the left end to right end during the time t. By contraries, $N_{left}(t)$ is the number of water molecules that have crossed the SWNT from the right end to the left end during the time t. The flow is the total of N_{right} and N_{left} per nanosecond, and the flux is the difference of N_{right} and N_{left} per nanosecond.

Fig. 2 shows the variation of averaged water flux with time for different systems. For each system, five simulations were carried out for 105 ns with different preliminary states.
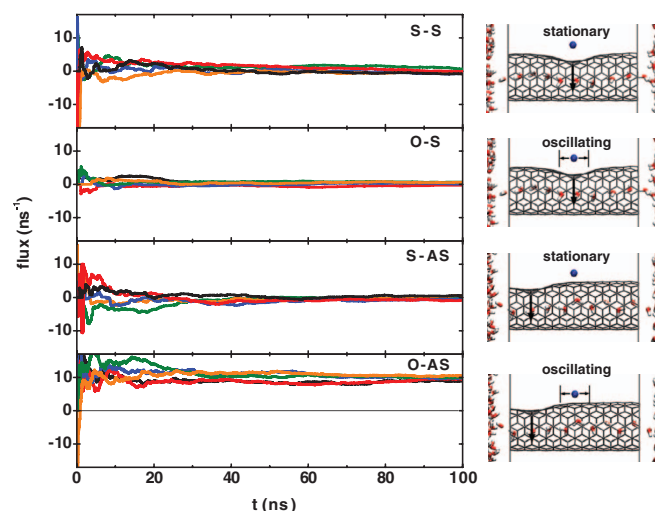
Unlike the macroscopic case, water molecules could penetrate through the SWNT by the thermal fluctuation even without external osmotic pressure; therefore, the water flux fluctuates with time. It is remarkable to find out continuous directional water flux through the SWNT in O-AS system, resulting in a water flux of 9.86 water molecules per nanosecond. This value is more than twice the measured 3.9 ± 0.6 ns^{-1} for aquaporin-1.[38] It should be noted that there is no external hydrostatic pressure or osmotic pressure. The unidirectional water flux is driven by the oscillating external charge. However, the flux of S-S, O-S, and S-AS systems is close to zero, respectively.

Furthermore, the motions $z(t)$ of individual water molecules inside the SWNT as a function of time are analyzed, as shown in Fig. 3. Water molecules form a single-file water chain and permeate through the SWNT synchronously. The distance between two neighboring water molecules is about 0.34 nm. Single-file water conduction occurs in pulses through the nanotube. The burst-like water conduction follows from the vibration of the charge and the tight hydrogen-bond chain inside the nanotube. When the charge vibrates periodically, the single-file water vibrates approximately synchronously due to electronic interaction between charge and water molecules. The obvious drift motion of the water molecules along the nanotube unidirectionally can be found.

We also calculated the potential of mean force (PMF) along the nanotube by $G(z) = -k_B \ln[\rho(z)/\rho_0]$, which is often used to characterize the motion of the single-file water inside the carbon nanotube. Here, $\rho(z)$ is the water density distribution along the carbon nanotube, and ρ_0 is the bulk water density. The PMFs are wavelike (see Fig. 4). Since the left portion of the nanotube is deformed, the symmetry of the PMF is broken. It is obvious that the part of the PMF locating

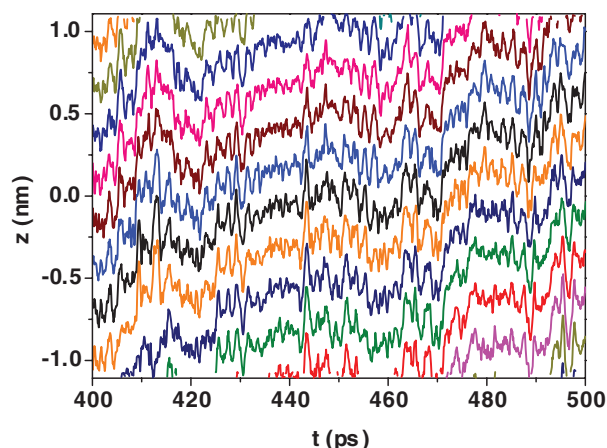FIG. 2. The water flux averaged with respect to time for four types of systems.

FIG. 3. Motions $z(t)$ of individual water molecules inside the SWNT shown as colored lines for the 4th scenario.
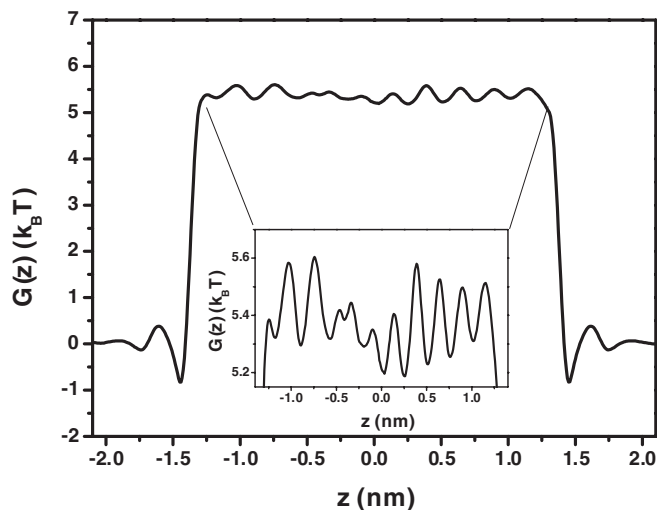
FIG. 4. Potential of mean force (PMF) along the carbon nanotube. Inset is the amplified view of PMF in the range of the SWNT.

in the narrow portion of the SWNT is lifted. When the charge oscillates (i.e., O-AS system), the nano device can work like a "ratchet and pawl" engine, which Feynman used to illustrate the meaning of the second law.[39] The oscillating charge drives the system far away from the equilibrium, so to overcome the restrictions imposed by the second law of thermodynamics. It has been known that the different implementations of the ratchet effect can be traced back to two main elements: first, the system has to be driven out of equilibrium; second, the symmetry of the system has to be broken. The O-AS system just meets the above two conditions, which is generically sufficient for the emergence of directed transport.

   To understand the mechanism behind the remarkable pumping phenomenon for the O-AS system, we calculated the forces acted on the single-file water inside the SWNT, such as charge's force (f_{WC}), carbon nanotube's force (f_{WSWNT}), and bulk water's force (f_{WB}). Then, the resultant force (f_{total}) on the water chain is the overall effect of them. We take the average of these interaction forces according to the below formula (we only consider the z component of these forces):

$$F_z(t) = \frac{1}{N} \sum_{n=0}^{N-1} f_z(t + nT), 0 \le t < T; \qquad (4)$$

$$\langle F_z(t) \rangle = \frac{1}{T} \int_0^T F_z(t)dt. \qquad (5)$$

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

   We find that charge-water, SWNT-water, and bulk-water forces are sinusoidal functions of time t approximately (Fig. 5). 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. The charge oscillates periodically and pumps the water chain through the SWNT. The average charge's force, $\langle F_{WC} \rangle$, on water chain is about -8.15 kJ mol^{-1}nm^{-1} (see Fig. 5(a)), indicating that the water chain feels larger resisting force when it moves toward the left than

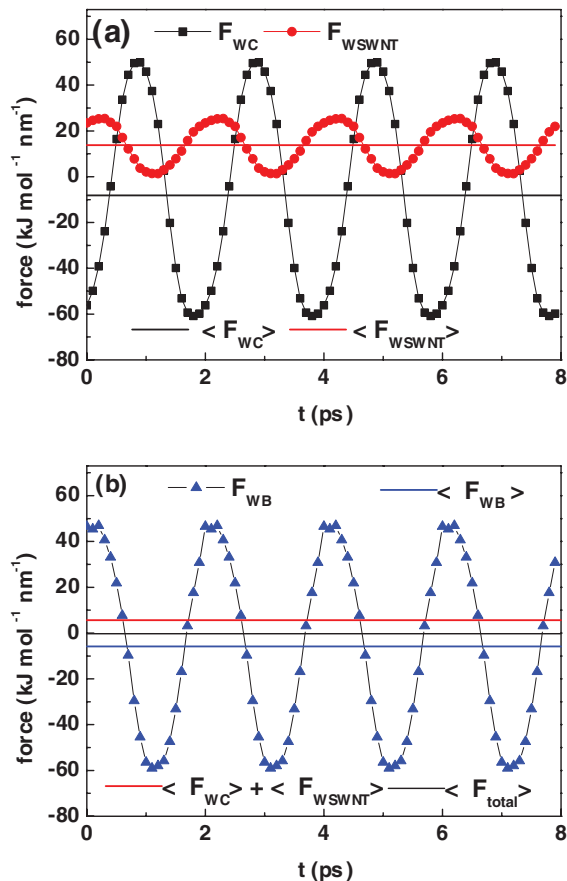FIG. 5. (a) The interaction force between the external charge and the water chain inside the SWNT (F_{WC}) and its average value $\langle F_{WC} \rangle$; the interaction between the SWNT and the water chain (F_{WSWNT}) and its average value $\langle F_{WSWNT} \rangle$. (b) Bulk water and the water chain interaction force (F_{WB}) and its average value $\langle F_{WB} \rangle$.

toward the right. Correspondingly, the average SWNT's force, $\langle F_{WSWNT} \rangle$, on the water chain is about 13.75 kJ mol^{-1}nm^{-1}. And the resultant force of them, $\langle F_{WC} \rangle + \langle F_{WSWNT} \rangle$, is positive (about 5.60 kJ mol^{-1} nm^{-1}), so the net water flux is toward the right direction.

   When the single-file water chain permeates through the SWNT, it feels resistance force by the bulk water. It is approximately proportional to the velocity of the single-file water ($F_{bulk} \approx -\gamma_{bulk}v$), where γ_{bulk} is resistance coefficient. From Fig. 5(b), we can see that the average bulk water's force ($\langle F_{WC} \rangle$) on the water chain is just equal to $-(\langle F_{WC} \rangle + \langle F_{WSWNT} \rangle)$ approximately. So, the resultant force ($\langle F_{total} \rangle$) on water chain inside the SWNT is about zero.

   Furthermore, the influence of charge oscillation period and spacing on the water transportation through the SWNT is investigated. Fig. 6 shows the strong dependence of flux and flow on the oscillation period. We can see that the flow decreases monotonically with the oscillation period of the charge. However, the flux is different. It has a resonant-like maximum as the oscillation period of the charge approaches to 2 ps, just approximately equaling twice the noise-induced escape time of the water-SWNT system.[40] For the current simulation system, the average hopping time of water molecules inside the SWNT is about 0.97 ps.
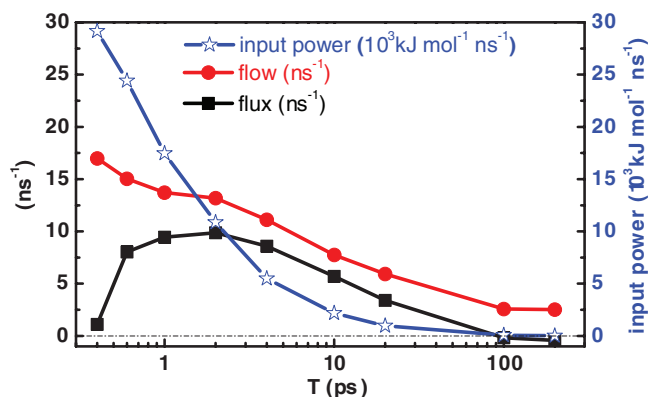
FIG. 6. The flux, flow, and input power vs. the oscillation period of the charge for $d = 1.4$ Å.

FIG. 8. Flux and flow as a function of the distance (d) between the charge and the SWNT for $T = 2$ ps. (Inset) The Coulomb force between the oscillating charge and single-file water inside the SWNT for different d.

We calculated the input power shown in Fig. 6, which is defined as the rate at which work is done by the charge. As the oscillation frequency increases, the input power increases as well which would increase the kinetics of water molecules inside the SWNT. When the kinetics of water molecules increases to a certain level, the N_{right} and N_{left} approach to each other. The flux would decrease with further increasing charge oscillation frequency.

The forces acted on the single-file water inside the SWNT rely on the oscillation period of the charge. Herein, we focused on the charge's force (F_{WC}) on water molecules inside the SWNT. The amplitude of F_{WC} (here we denote by A_{WC}) reflects the magnitude of driving force on water molecules inside the nanotube, which is proportional to flux approximatively. Fig. 7 shows A_{WC} as a function of the oscillation period of the charge for $d = 1.4$ Å. When $T = 2$ ps, the charge resonates with the water molecules, so the amplitude of driving force A_{WC} reaches to maximum. It becomes hard to pump the water molecules when T is too large or too small. The A_{WC} curve is basically in agreement with the flux curve of Fig. 6 in shape. The liner fit of A_{WC} and flux is shown in the inset of Fig. 7.

Since the average charge-water interaction force would be inversely proportional to the squared distance between the charge and the SWNT (see inset in Fig. 8), this distance would affect the water transportation through the SWNT as well. To study the effect of the spacing between charge and SWNT on water transportation, the distance d is varied from 0.6 Å to 4.6 Å by moving the charge away from the SWNT. As shown in Fig. 8, the flux decreases with increasing the distance d. When $d > 3$ Å, the flux is almost zero and the flow remains at a stable values (about 10 ns^{-1}). The explanation of this phenomenon is that, at this distance, the interactions between the charge and the water molecules are much weaker than the water-water interactions, and the effect of charge oscillation can be negligible (see inset in Fig. 8). When the distance is smaller, the Coulomb interaction becomes stronger, it is easier for the energy of the oscillating charge to be transformed into single-file water molecules. Consequently, the water transportation through the SWNT is enhanced.

The asymmetry of the channel plays a key role in pumping capability too. In this study, five different systems with different forced atom (see Fig. 9) in the SWNT are constructed to investigate the effect of asymmetry on water transportation through the SWNT. As shown in Fig. 9, when the
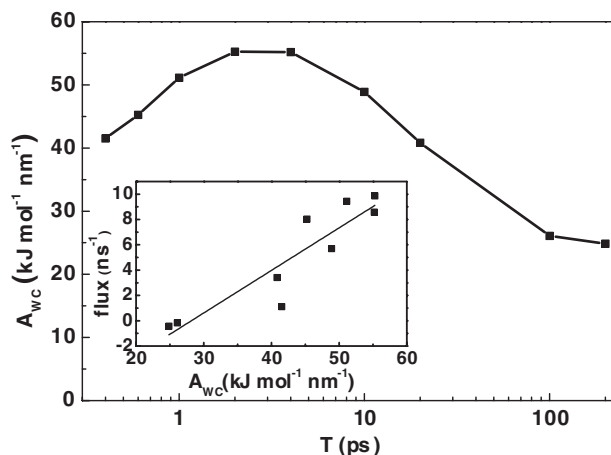

FIG. 7. The amplitude of F_{WC} as a function of the oscillation period of the charge for $d = 1.4$ Å. (Inset) The relationship between A_{WC} and the net water flux for different oscillation period of the charge. The solid line is a linear fit.
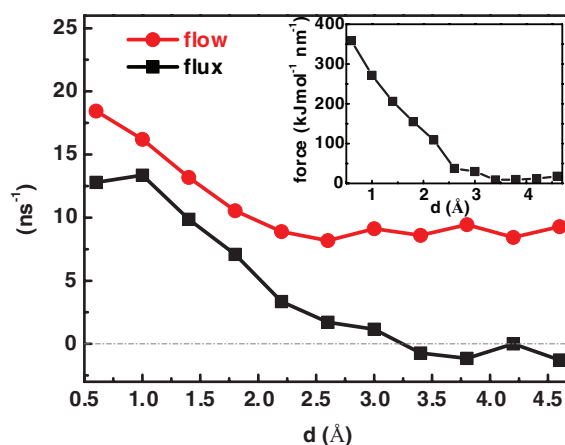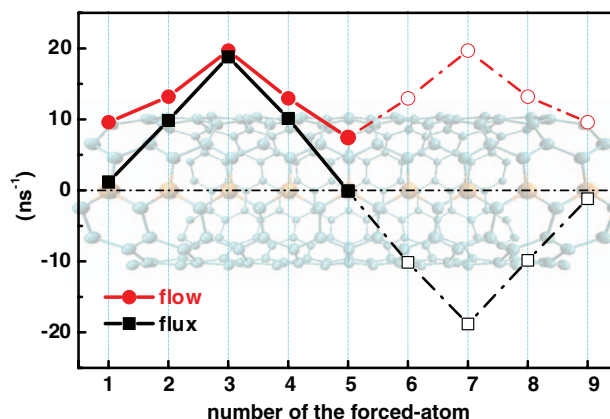

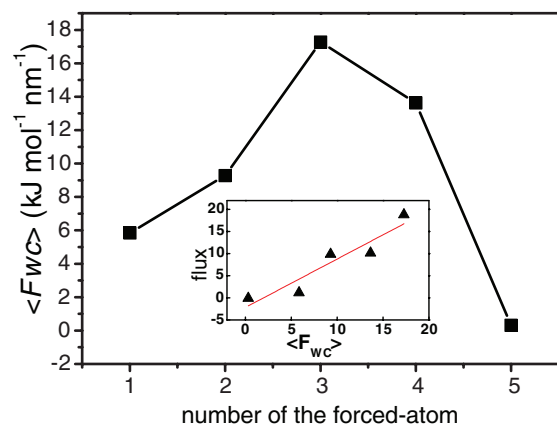FIG. 9. The flux and flow as a function of the number of the forced atom for $T = 2$ ps, $d = 1.4$ Å.

FIG. 10. The average force ($\langle F_{WC} \rangle$) between the external charge and the water chain inside the SWNT for $T = 2$ ps, $d = 1.4$ Å. (Inset) The relationship between the flux and $\langle F_{WC} \rangle$ for these five systems with different symmetries. The solid line is a linear fit.

5th forced atom is pressed, the simulation system is completely symmetrical, and the flux is obviously to be zero. When either forced atom from 1st to 4th atom is pressed, the system becomes asymmetrical, and the oscillating charge induces the non-zero net flux across the SWNT. The flux increases when the pressed forced atom is away from the center of the SWNT, and reaches the maximum as the 3rd forced atom is pressed. The flux decreases rapidly when the forced atom moves to the end of the SWNT. As mentioned previously, due to the unsymmetrical shape of the deformed SWNT, the narrower portion of the SWNT resistance to water molecules is different from the other portion. Our simulation results indicate that the SWNT resistance to water molecules is larger when the water molecules move toward the narrow portion direction than toward the wide portion direction.

We calculated $\langle F_{WC} \rangle$ for different systems with different forced atom in the SWNT. Fig. 10 shows that the profile of $\langle F_{WC} \rangle$ is similar to that of the flux curve. $\langle F_{WC} \rangle$ approaches to the maximum as the 3rd forced atom is pressed. When the 5th forced atom is pressed, the simulation system is symmetrical. So, $\langle F_{WC} \rangle$ is close to zero. In fact, the oscillating charge drives water molecules inside the SWNT to move fast. And the asymmetrical shape of the deformed SWNT induces to that $\langle F_{WC} \rangle$ is not zero, resulting in the non-zero net flux. Generally, the net flux is proportion to $\langle F_{WC} \rangle$. When the 3rd forced atom is pressed, $\langle F_{WC} \rangle$ reaches to the maximum and the flux approaches to the maximum too. In this situation, the energy of oscillating charge is transformed into single-file water inside the SWNT effectively.

IV. CONCLUSIONS

Here, by using dynamics simulations, we have demonstrated a novel design, which can be potentially used as a nano water pump. The nano water pump can convert the energy of the oscillating charge into the transport of the water molecules efficiently and conveniently. The direction and magnitude of the flow can be easily regulated. The net flux exceeds the measured value in Ref. 4 and the measured 3.9 ± 0.6 ns^{-1} for

AQP-1.[38] The osmotic pressure needed to create such a water flux is about 18.5 MPa if by using traditional method. Interestingly, we found that the water flux increases significantly when the oscillation period is close to twice the average hopping time of water molecules inside the SWNT. This is an intriguing phenomenon similar to stochastic resonance. Similar simulation results can also be obtained using the parameters suggested by Karttunen and co-workers[41] This study helps to understand the molecular mechanism of water transportation through biological water channels efficiently and develops a novel method of producing water flux differing from the traditional techniques such as applying osmotic pressure or hydrostatic pressure gradient.

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