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Unidirectional Motion of Water Nanodroplet Subjected to a Surface Energy Gradient

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Abstract

We performed molecular dynamics simulations to demonstrate that, when a nanodroplet is confined inside a carbon nanotube (CNT), unidirectional motion can be created by nonzero surface energy gradient. It was found that the water nanodroplet moves along the direction of increasing surface energy. The transportation efficiency of the water nanodroplet was found to be dependent on the surface energy gradient, environmental temperature and the flexibility, diameter and defectiveness of the CNT. It was shown that higher surface energy gradient, smaller diameter of the CNT, and less number of defects promote higher transportation efficiency. But when the temperature is too high or too low, the water transport across the CNT is impeded. Except for the initial stage at the relatively low environmental temperature, higher flexibility of the CNT wall reduces the transportation efficiency. It was also found that the hydrogen bonds of water molecules play a role in the dynamic acceleration process with a wave-like feature. Present work provides an insight for the development of CNT devices for applications such as drug delivery, nanopumps, chemical process control, molecular medicine, etc.

Keywords: water transport, carbon nanotube, molecular dynamics simulation

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I. INTRODUCTION

Carbon nanotubes (CNTs), which are small in size and have innate holes, possess large surface area, high elastic modulus, remarkable electrical conductivity and ultra-high thermal conductivity [1–3]. These physical characteristics make them potentially useful in many micro- and nano- electromechanical devices. For example, the conventional strategy for drug delivery to a target area is chemotherapy, which can be harmful to surrounding organic tissues, because of the inadequate and nonspecific delivery of therapeutic concentrations to the tumor tissue [4, 5]. Recently, one experimental report showed that CNTs are so small that they have the ability to penetrate across the cell membrane and reach the nucleus of the cell in a harmless manner, and therefore, the CNTs can be a very promising carrier system in target therapy for drug, protein, and gene delivery [6, 7].

Water transport inside CNTs is also important to the understanding of the flow behavior of fluids at very small length scales and the design of nanofluidic devices [8, 9]. The confinement of water molecules inside CNTs can present many interesting properties and behaviors, like the ordered water structure [10–12], non-Fickian-type diffusion [13], and excellent on-off gating behavior [14, 15]. Fast transport of gas and water through CNTs membranes was first predicted by means of Molecular Dynamics simulation [16, 17], then demonstrated in experiments [18, 19]. Such transportation characteristic is of great importance to designing novel molecular devices/machines/sensors. Inspired by the charges in the biological water channels (AQPs), Gong *et al.* [20] proposed a molecular water pump by using a combination of charges positioned adjacent to a CNT. This molecular pump provides a possibility to develop water transport devices without osmotic or hydrostatic pressure gradient. When the orientation of water molecules confined inside CNTs is maintained along one direction, a net flux along that direction can be attained due to the coupling between rotational and translational motions [21]. If water molecules are confined in a specially sized nanochannel (6, 6) CNT, they can form a single-file structure with concerted dipole orientations. And along the dipole-orientation, a net flux can be observed without any external electric field or pressure difference [22]. Recently, interesting results were reported that the unidirectional flow of water molecules confined inside CNTs can induce current [23, 24]. By using capillary force to draw molecules into CNTs [25], one study has shown that temperature difference can make a water droplet moving from the hot end to the cold end inside CNTs [25, 26]. In addition, the water nanodroplet can also be controlled by charges or ions in space and time [27, 28]. This means that drug molecules dissolved in a water droplet and can be delivered to target area along the CNTs. Previous work has shown that the boundary condition is a critical issue in nanoscale systems [29, 30]. Hummer *et al.* [31] and Wu *et al* [32] have shown that a minute change in the attraction between the tube wall and water can dramatically affect pore hydration, leading to a sharp transitions between empty and filled states within a nanosecond time scale.

In the present work, based on Molecular Dynamics simulations, we investigate the transport of a water nanodroplet confined inside a CNT with surface energy gradient. The transportation efficiency of the water nanodroplet with respect to different surface energy gradient, environmental temperature, flexibility, diameter, and number of defects of the CNT is discussed. In Section II, we give detailed description of system and simulation methods, and results and discussion are presented in Section III. Lastly, some concluding remarks are given in Section IV.

II. SYSTEM AND METHODS

To study the transportation of water nanodroplet confined inside CNTs, a series of uncapped single-walled carbon nanotubes, in each of which a nanodroplet is encapsulated, were prepared as shown in Figure 1. A surface energy gradient was applied along z-axis direction of the CNT. In reality, this can be altered through chemical modification or DC/AC electric field [33–38]. For each set, after initially equilibrating the system at a specific temperature (200K, 300K or 330K) assuming a uniform surface energy along the CNT, the water nanodroplet was kept at 5nm from the left end of CNT. The initial position of the mass center of the droplet is set to be zero.

All Molecular Dynamics simulations in this work were performed by using Gromacs 4.0.7 [39] in the NVT ensemble. The dynamics process was conducted to allow the system to exchange heat with the environment at a constant temperature of 260K, 300K or 330K, which was maintained by using a V-rescale thermostat [40]. The simulation system was sufficiently large to avoid direct interaction between the CNTs and the periodic surfaces, the periodic boundary conditions were applied in all directions. The TIP3P [41] water model was applied. The particle-mesh Ewald method [42] was used to treat the long-range electrostatic interactions. The carbon atoms were modeled as uncharged Lennard-Jones particles with a cross section of $\sigma_{C,C}$=0.34nm, $\sigma_{C,O}$=0.3275nm. The depth of the potential well was of $\varepsilon_{C,C(l)}$=0.3612kJ mol^{-1}, $\varepsilon_{C,O(l)}$=0.4802kJ mol^{-1} at the left end of CNT [31], $\varepsilon_{C,C(p)}$ was continuously and arbitrarily varied along the CNT in the simulations, the subscript p represents the position along z director of the CNT. The surface energy gradient (λ) was defined as the difference of adjacent layers of carbon atoms per nanometer, viz., $\lambda = (\varepsilon_{C,C(p)} - \varepsilon_{C,C(l)})/L_{p,l}$, where the $L_{p,l}$ represents the distance between the left end and the position of p along the CNT. The value of λ was used to vary the surface energy gradient of CNT [36]) and it was bigger than zero in present simulations. It has been shown that the effective C-C interaction energy ($\varepsilon_{C,C}$) can be tuned by applying *dc/ac* the electric field [33, 34, 36] or using different chemical modifications [35, 37, 38]. The interaction energy(binding energy) between the water molecules and CNT wall is much stronger with the increase of surface energy gradient [43]. A time step of 2 fs was used, and data were collected every 0.04ps. When investigating the effect of flexibility, carbon-carbon bond lengths of 0.142nm and bond angles of 120° were maintained by harmonic potentials with spring constants of 393 960 kJ mol^{-1}nm^{-2} and 527kJ mol^{-1}deg^{-2} before relaxation [31]. In addition, a weak dihedral angle potential was applied to bonded carbon atoms [31].

III. RESULTS AND DISCUSSION

Figure 1 shows three typical snapshots of unidirectional motion of a water nanodroplet induced by a surface energy gradient in a (10, 10) CNT. In Figure 1(a), the water nanodroplet at the equilibrium state is composed of 53 molecules and confined in a 24.3nm long CNT with a surface energy gradient of $\lambda = 0.0145$kJ mol^{-1}nm^{-1}. From Figure 1(or refer to Supporting Information (SI) Movie S1 [46]), it can be observed that the water nanodroplet moves in the direction of increasing surface energy under the condition of room temperature (300K). It is therefore expected that, under the room temperature, a resultant force is induced between the CNT wall and the water molecules, which is strong enough to drive the molecular. In other words, a surface energy gradient can result in unidirectional motion for a water nanodroplet inside CNTs.

A series of transportation conditions were simulated to investigate their effects on the transportation efficiency of water nanodroplet. We show in Figures 2(a)∼2(c), the influence

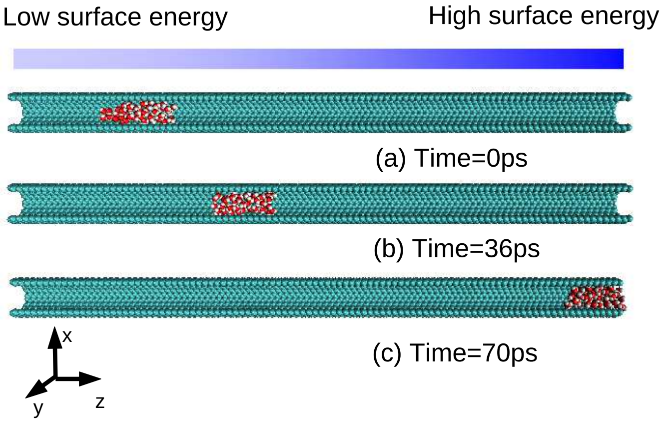


FIG. 1: (Color online) Snapshots of a successful transportation process of a nanodroplet of 53 water molecules confined inside a (10, 10) CNT subjected to a surface energy gradient of 0.0145kJ mol^{-1}nm^{-1} at temperature 300K at (a) the initial equilibrium state, (b) 36ps, and (c) 70ps. Top inkle shows surface energy changing along the surface of CNT. The cyan spheres are the carbon atoms of the CNT. The water molecules are described by spheres with oxygen in red and hydrogen in white.

of surface energy gradient on the position of the mass center, the velocity and the acceleration of the nanodroplet in CNT. When the surface energy gradient was set to be zero (see magenta line in Figure 2(a)), the water nanodroplet was found to swing around the original position(Figure 2 shows the change of the nanodroplet position in a short time span. Over a long time span, little net movement of nanodroplet was apparent). This is reasonable as, without any external force, thermal motion or self-assembly of water molecules can only lead to random motion of the water nanodroplet within a very narrow range [11]. For a liquid droplet on a solid substrate, it was shown that Marangoni effect can create spontaneous motion [44]. When a nonzero surface energy gradient was applied to the CNT, the water nanodroplet can quickly move from one end to the other inside the CNT. One interpretation for this is that, thermal motion makes the water nanodroplet confined inside CNTs to become more unstable, and the surface energy gradient generates unbalanced forces at the front and rear of the water nanodroplet, leading to the continuous unidirectional motion of a water nanodroplet. Another important phenomenon observed from Figure 2(b) is that the movement velocity is not invariant. It increases with a small fluctuation over the simulation time span. At the room temperature of 300K and the surface energy gradient of 0.0145kJ

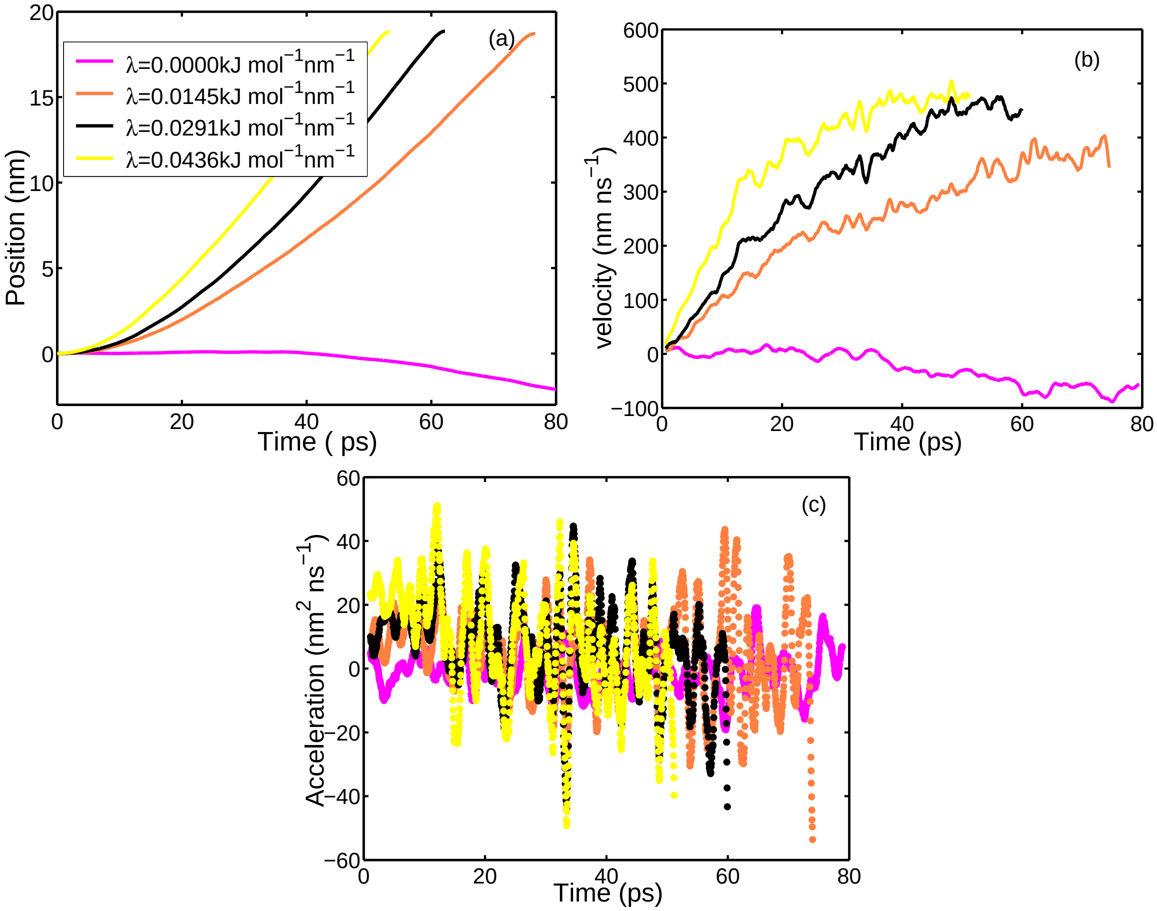


FIG. 2: (Color online) Parameters of (a) position of the center of the nanodroplet, (b)velocity of the nanodroplet, and (c) acceleration of the nanodroplet, as a function of the time for different surface energy gradients (0.0 kJ mol^{-1}nm^{-1}(magenta lines), 0.0145kJ mol^{-1}nm^{-1}(black yellow lines), 0.0291kJ mol^{-1}nm^{-1}(black lines) and 0.0436kJ mol^{-1}nm^{-1}(yellow lines)) at temperature 300K.

mol^{-1}nm^{-1}, the movement velocity of the nanodroplet can reach approximately 350nm ns^{-1}. However only 22nm ns^{-1} was attained when a thermal gradient of 1.05 nm^{-1} was used [26]. Furthermore, it is observed from Figure 2(c) that, there is a movement acceleration, while changes in a wave form with a degree of fluctuation. It is well known that the hydrogen bonds of two neighboring water molecules play an important role in the formation of water nanodroplet [31, 45]. With unbalanced forces at the front and rear of the water nanodroplet, the hydrogen bonds exhibits an elastic characteristic. This is especially apparent when the hydrogen bonds length are more than 3.4Å, where more regular fluctuation takes place.

Comparing the upper part(acceleration>0) with the lower part(acceleration<0) of Figure 2(c), total acceleration of the upper part is greater than that of the lower part. This means that it is in general an acceleration process. The apparent results in Figure 2(a) and 2(b) show that the larger the surface energy gradient, the quicker the water nanodroplet reaches the end of the CNT. With regard to acceleration, as can be seen from Figure 2(c), there is a greater amplitude of fluctuation for a larger surface gradient. This is consistent with the above discussion on hydrogen bonds. This implies that higher surface energy gradient can make nanodroplet move faster.

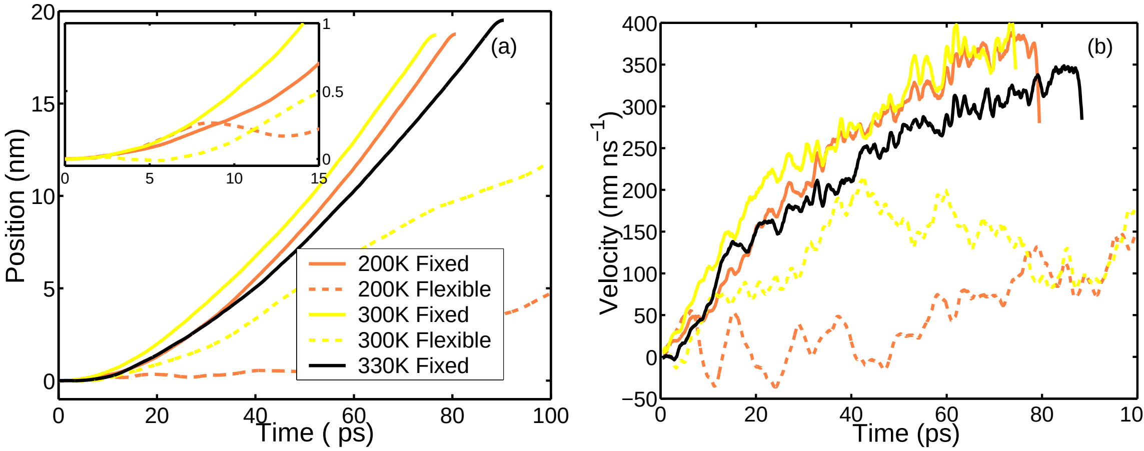
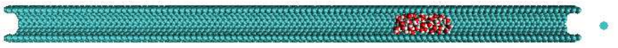
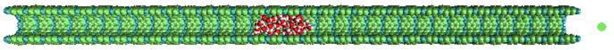


FIG. 3: (Color online) Parameters of (a) center position of the nanodroplet and (inset) enlarged drawing during initial stage, (b) velocity of the nanodroplet, as a function of the time for different temperature and whether flexible at surface energy gradient of 0.0145kJ mol^{-1}nm^{-1}.

Under the same surface energy gradient of λ=0.0145kJ mol^{-1}nm^{-1}, we conducted the simulation under different environmental temperatures, viz. 200K, 300K and 330K, respectively. The solid lines in Figure 3 show the position and velocity of the nanodroplet during the process under different environmental temperatures. It is clear that the relationship between the environmental temperature and the transportation efficiency of the water nanodroplet is not linear. A water nanodroplet at the environmental temperature of 300K moves faster than that at a higher temperature of 330K and a lower temperature of 200K. This phenomenon can be explained as follows. A higher environmental temperature of 330K can create in faster motion of a water molecule, which results in more violent collisions among the water molecules and between the water molecules and the CNT wall. This stronger collision leads to more unstable motion in the transverse direction, and slows down the movement of the water nanodroplet. On the contrary, under a lower temperature, initial velocity is only inducted by self-assembly. If the temperature is very low, the water molecules will be frozen. This means that a lower temperature will slow down the transport. This means that both too high and too low temperature can reduce transportation efficiency of a nanodroplet inside a CNT, and an optimal transportation efficiency may exist under certain appropriate temperature.



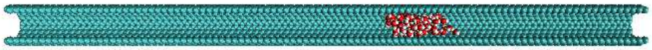
(a) Fixed; Temperature=300K, 60ps



(b) Flexible; Temperature=300K, 60ps

FIG. 4: (Color online) Comparison of snapshots between the fixed CNT and flexible CNT at time of 60ps and temperature of 300K, (a) is fixed, (b) is flexible. In figure, fixed carbon atoms are shown in color of cyan, flexible carbon atoms are shown in color of lime.

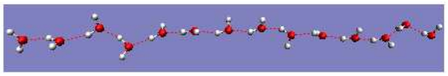
Furthermore, we investigated the effect of flexibility of carbon atoms on the transportation efficiency. Figure 4 (Moves S1, S2 [46]) shows the transportation of a nanodroplet inside a CNT with fixed and flexible carbon atoms. For both cases, the temperature and surface energy gradient were the same. For the CNT shown in Figure 4(b), the fixed carbon atoms and flexible carbon atoms are arranged intermittently (viz. two rings of 40 fixed carbon atoms followed by four rings of 80 flexible carbon atoms). A nanodroplet in the CNT containing flexible carbon atoms requires a longer time to complete the transportation process, as shown in Figure 4 or in Figure 3(a)(from the solid lines to the dashed lines). The flexibility of CNT wall increases free-energy barriers to such motion, which impedes the water transport across the CNT [47]. It is noteworthy that, during the initial stage of dynamic process as shown in the inset of Figure 3(a), the nanodroplet inside the flexible CNT can move faster than that inside the fixed CNT under the relatively low temperature of 200K. This phenomenon cannot be observed under the temperature of 300K. One explanation for this is that the movement of water molecules is weak under the low temperature, and the flexibility of CNT wall provides kinetic energy for the initial movement of the water nanodroplet [48]. When under a relatively high temperature, the water molecules possess higher energy and exhibit free motion. If flexibility is added in CNT wall, it is difficult to control the free motion by the surface energy gradient. Therefore, this leads to a lower velocity. It is concluded from the foregoing discussion that the flexibility of CNT wall impedes water transport across the nanotube, but accelerates movement during initial stage only at a relatively low environmental temperature.



(a) (10,10) CNT; Time=56ps

(b) (6,6) CNT; Time=56ps

(c) Time=0ps



(d) Time>1.5ps

FIG. 5: (Color online) Snapshots of transportation process of water nanodroplet confined inside (a) (10, 10) CNT, (b) (6, 6) CNT with surface energy gradient of 0.0145kJ $\mathrm{mol}^{-1}\mathrm{nm}^{-1}$ at temperature of 300K and time of 56ps. A single-file water chain confined inside a (6, 6) CNT, at (c) the initial equilibrium state, (d) the transportation process.

Hummer *et al.* [31] proposed that single-walled carbon nanotubes can be designed as molecular channels, especially for (6,6) CNTs which possess the major characteristics of transportation that are shared by the biological channels. Here, we compare the transportation efficiency of water nanodroplets in (6,6) CNT and (10,10) CNT. A water cluster composed of 14 water molecules is confined in the (6,6) CNT, whose length and surface energy gradient are the same as the (10,10) CNT. Snapshots of the molecular dynamics process at 56ps are shown in Figures 5(a) and 5(b). The position of mass center, the velocity and the acceleration of the nanodroplet are shown in Figures 6(a)∼6(c). It can be seen that the water cluster inside (6, 6) CNT can reach to the right end faster than that inside the (10, 10) CNT as shown in Figures 5 and 6. From a structural point of view, the water cluster in (10, 10) CNT is of a self-assembled distribution [11]. This means there is not only an interaction between the water molecules and the wall of the CNT, but also a strong interaction among the water molecules and the water nanodroplet may have complicated movement in

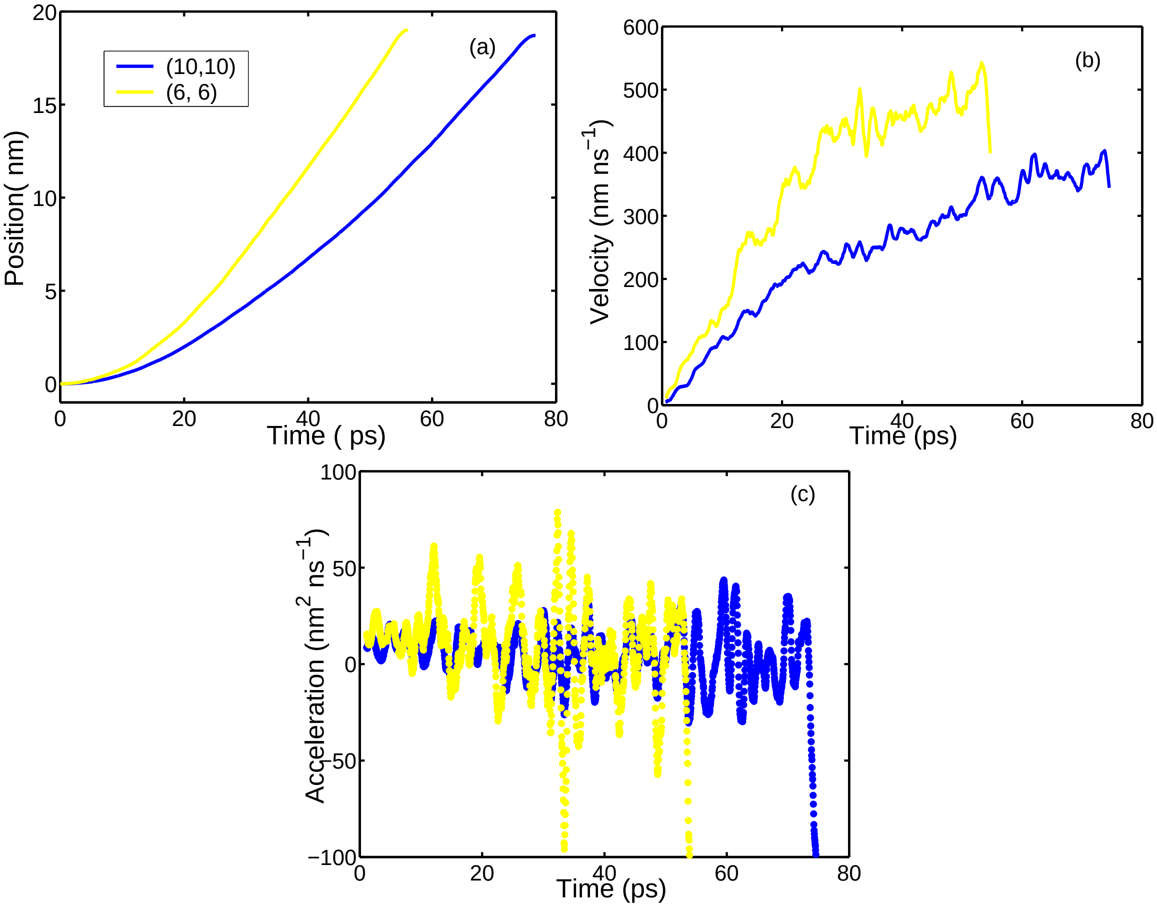


FIG. 6: (Color online) Parameters of (a) position of the center of the nanodroplet, (b)velocity of the nanodroplet, and (c) acceleration of the nanodroplet, as a function of the time for different diameters with the same surface energy gradient of 0.0145kJ mol^{-1}nm^{-1} at temperature of 300K.

transverse and longitudinal directions. When inside (6, 6) CNT, the water molecules form a single-file structure (see Figure 5(d)), each water molecule has maximally two interactions with another water molecule at the front and rear end in addition to its interaction with the wall of the CNT. And the water molecules of single-file chain only rotate in dipole orientation [21] around the axis of CNT or move along the direction of CNT [22, 31]. As a result, the temperature can have a greater effect on the water cluster in (10, 10) CNT than that on the single-file water chain in (6, 6) CNT [10] when the water molecules begin to move. A higher environmental temperature causes stronger motion of a water molecule, which results in increased collisions between water molecules and the CNT channel. Therefore, this leads to a more severely fluctuating unstable force in the transverse direction of the tube. These can also be seen from Figures 6(a) and 6(c) before 10ps, where almost no difference is apparent between these two structures . Moreover, since every water molecule in the smaller CNT is subjected to stronger interaction due to higher specific surface area. Acceleration of water molecules in (6, 6) CNT is observed to be greater than those in (10, 10) CNT as shown in Figure 6(c). It is concluded in Figures 5 and 6 that, the dimension of CNTs is sensitive for the transportation of water nanodroplet. The CNT with smaller dimension has a higher transportation efficiency of a water nanodroplet, especially for (6, 6) CNT. Furthermore, we note in (6, 6) CNT that the orientation of the water molecules is face to face (see Figure 5(c)) at the initial state. The dynamics process begins after about 1.4ps, when the orientation of the water molecules quickly flips and was maintained in one direction.

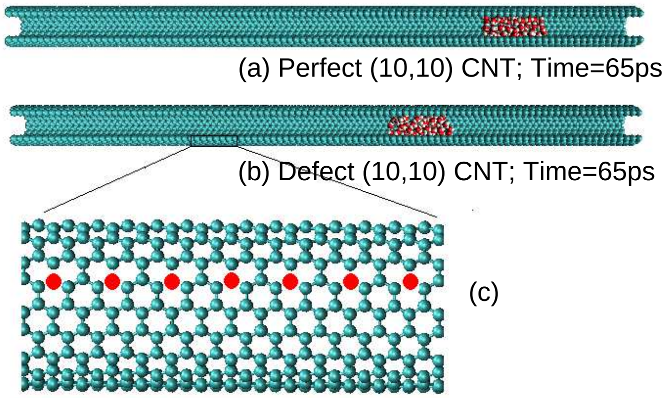


FIG. 7: (Color online) Snapshots of transportation process of water nanodroplet confined inside (a) perfect (10, 10) CNT, (b) defect (10, 10) CNT with surface energy gradient of 0.0145kJ mol^{-1}nm^{-1} at temperature of 300K and time of 65ps, and (c) is a enlarged schematic with vacancy defects. The red filled circles denote the locations of the vacancy defect.

In practically fabricated nanochannels, defects are common [49, 50]. There are mainly two types of defects, Stone-Wales (SW) defects and vacancy defects. To explore the effect of defects on transportation, we performed Molecular Dynamics simulations were carried out on CNT with defects. It was found that there is little effect of SW defects on the transportation efficiency because of the characteristics of SW defects. We therefore only present the of the vacancy defects on the transportation efficiency, as shown in Figure 7. It can be seen that the transportation efficiency is greatly impeded by the presence of vacancy defects. The reduction in transportation efficiency is attributed to the decreased number of carbon atoms of CNT. This implies a smaller interaction force between the CNT wall and the water nanodroplet, leading to a lower transportation efficiency.

IV. CONCLUSIONS

In conclusion, we have shown that water nanodroplets confined inside carbon nanotubes can move unidirectionally by surface energy gradient. Water nanodroplets move from the low surface energy region to the high energy region in CNTs. It was found that the transportation efficiency of the water nanodroplets are dependent on the surface energy gradient, environmental temperature, as well as the flexibility, diameter, and defectiveness of the CNT. Present findings can have practical implications in the development of nano-devices for nanopumping and drug delivery.

Acknowledgments

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[1] B. Peng, M. Locascio, P. Zapol, S. Li, S. L. Mielke, G. C. Schatz, and H. D. Espinosa, Measurements of near-ultimate strength for multiwalled carbon nanotubes and irradiation-induced crosslinking improvements. Nat. Nanotechnol. **3**, 626 (2008).

[2] S. H. Hong and S. Myung, Nanotube electronics: A flexible approach to mobility. Nat. Nanotechnol. **2**, 207 (2007).

[3] M. S. Dresselhaus, G. Dresselhaus, and P. Avouris, Carbon nanotubes: synthesis, structure, properties and applications; Springer: New York, (2000).

[4] P. Couvruer and C. Vauthier, Nanotechnology: intelligent design to treat complex disease. Pharm. Res. **23**, 1417 (2006).

[5] T. A. Hilder and J. M. Hill, Modeling the Loading and Unloading of Drugs into Nanotubes. Small **5**, 300 (2009).

[6] D. Pantarotto, J. P. Briand, M. Prato, and A. Bianco, Translocation of bioactive peptides across cell membranes by carbon nanotubes. Chem. Commun. **1**, 16 (2004).

[7] Z. Liu, J. T. Robinson, S. M. Tabakman, K. Yang, and H. J. Dai, Carbon materials for drug delivery at cancer therapy. Mater. Today **14**, 316 (2011).

[8] A. Noy, H. G. Park, F. Fornasiero, J. K. Holt, C. P. Grigoropoulos, and O. Bakajin, Nanofluidics in carbon nanotubes. Nano Tody **2**, 22 (2007).

[9] M. Whitby and N. Quirke, Fluid flow in carbon nanotubes and nanopipes. Nat. Nanotechnol. **2**, 87 (2007).

[10] K. Koga, G. T. Gao, H. Tanaka, and X. C. Zeng, Formation of ordered ice nanotubes inside carbon nanotubes. Nature **412**, 802 (2001).

[11] W. H. Noon, K. D. Ausman, R. E. Smalley, and J. P. Ma, Helical ice-sheets inside carbon nanotubes in the physiological condition. Chem. Phys. Lett. **355**, 445 (2002).

[12] R. J. Mashl, S. Joseph, N. R. Aluru, and E. Jakobsson, Anomalously Immobilized Water- A New Water Phase Induced by Confinement in Nanotubes. Nano Lett. **3**, 589 (2003).

[13] A. Striolo, The Mechanism of Water Diffusion in Narrow Carbon Nanotubes. Nano Lett. **6**, 633 (2006).

[14] R. Z. Wan, J. Y. Li, H. J. Lu, and H. P. Fang, Controllable water channel gating of nanometer dimensions. J. Am. Chem. Soc. **127**, 7166 (2005).

[15] J. Y. Li, X. J. Gong, H. J. Lu, D. Li, H. P. Fang, and R. H. Zhou, Electrostatic gating of a nanometer water channel. Proc. Natl. Acad. Sci. U.S.A. **104**, 3687 (2007).

[16] A. I. Skoulidas, D. M. Ackerman, J. K. Johnson, and D. S. Sholl, Rapid Transport of Gases in Carbon Nanotubes. Phys. Rev. Lett. **89**, 185901 (2002).

[17] T. M. Truskett, The subtleties of water in small spaces. Proc. Natl. Acad. Sci. USA **100**, 10175 (2003).

[18] M. Majumder, N. Chopra, R. Andrews, and B. J. Hinds, Enhanced flow in carbon nanotubes. Nature **438**, 44 (2005).

[19] J. K. Holt, H. G. Park, Y. Wang, M. Stadermann, A. B. Artyukhin, C. P. Grigoropoulos, A. Noy, and O. Bakajin, Fast Mass Transport Through Sub-2-Nanometer Carbon Nanotubes. Science **312**, 1034 (2006).

[20] X. J. Gong, J. Y. Li, H. J. Lu, R. Z. Wan, J. C. Li, J. Hu, and H. P. Fang, A charge-driven molecular water pump. Nat. Nanotechnol. **2**, 709 (2007).

[21] S. Joseph and N. R. Aluru, Pumping of Confined Water in Carbon Nanotubes by Rotation-Translation Coupling, Phys. Rev. Lett. **101**, 064502 (2008).

[22] R. Z. Wan, H. J. Lu, J. Y. Li, J. D. Bao, J. Hu, and H. P. Fang, Concerted orientation induced unidirectional water transport nanochannels through. Phys. Chem. Chem. Phys. **11**, 9898 (2009).

[23] Y. C. Zhao, L. Song, K. Deng, Z. Liu, Z. X. Zhang, Y. L. Yang, C. Wang, H. F. Yang, A. Z. Jin, Q. Luo, C. Z. Gu, S. S. Xie, and L. F. Sun, Individual water-filled single-walled carbon nanotubes as hydroelectric power converters. Adv. Mater. **20**, 1772 (2008).

[24] Q. Z. Yuan and Y. P. Zhao, Hydroelectric Voltage Generation Based on Water-Filled Single-Walled Carbon Nanotubes. J. Am. Chem. Soc. **131**, 6374 (2009).

[25] M. J. Longhurst and N. Quirke, Temperature-Driven Pumping of Fluid through Single-Walled Carbon Nanotubes. Nano Lett. **7**, 3324 (2007).

[26] H. A. Zambrano, J. H. Walther, P. Koumoutsakos, and I. F. Sbalzarini, Thermophoretic Motion of Water Nanodroplets Confined inside Carbon Nanotubes. Nano Lett. **9**, 66 (2009).

[27] B. Y. Wang and P. Kr*á*l, Dragging of Polarizable Nanodroplets by Distantly Solvated Ions. Phys. Rev. Lett. **101**, 046103 (2008).

[28] P. Xiu, B. Zhou, W. P. Qi, H. J. Lu, Y. S. Tu, and H. P. Fang, Manipulating Biomolecules with Aqueous Liquids Confined within Single-Walled Nanotubes. J. Am. Chem. Soc. **131**, 2840 (2009).

[29] C. Liu and Z. G. Li, Flow regimes and parameter dependence in nanochannel flows. Phys. Rev. E **80**, 036302 (2009).

[30] C. Liu and Z. G. Li, Molecular Dynamics Simulation of Composite Nanochannels as Nanopumps Driven by Symmetric Temperature Gradients. Phys. Rev. Lett. **105**, 174501 (2010).

[31] G. Hummer, J. C. Rasaiah, and J. P. Noworyta, Water conduction through the hydrophobic channel of a carbon nanotube. Nature **414**, 188 (2001).

[32] K. F. Wu, B. Zhou, P. Xiu, W P. Qi, R. Z. Wan, and H. P. Fang, Kinetics of water filling the hydrophobic channels of narrow carbon nanotubes studied by molecular dynamics simulations. J. Chem. Phys. **133**, 204702 (2010)

[33] R. Maheshwari, R. P. arthasarathi, and A. Dhathathreyan, Molecular dipoles at substrate-

film interfaces influencing surface energy of Langmuir-Blodgett films. J. Col. Int. Sci. **271**, 419 (2004).

[34] R. Langlet, M. Devel, and P. H. Lambin, Computation of the static polarizabilities of multiwall carbon nanotubes and fullerites using a Gaussian regularized point dipole interaction model. Carbon **44**, 2883 (2006).

[35] S. Morgenthaler, C. Zink, and N. D. Spencer, Surface-chemical and -morphological gradients. Soft Matter **4**, 419 (2008).

[36] X. Shi, Y. Cheng, N. M. Pugno, and H. Gao, Tunable Water Channels with Carbon Nanoscrolls. Small **6**, 739 (2010).

[37] X. Hou, W. Guo, and L. Jiang, Biomimetic smart nanopores and nanochannels. Chem. Soc. Rev. **40**, 2385 (2011).

[38] C. J. Shearer, A. V. Ellis, J. G. Shapter, and N. H. Voelcker, Chemically Grafted Carbon Nanotube Surface Coverage Gradients. Langmuir **26**, 18468 (2010).

[39] B. Hess, C. Kutzner, D. V. D. Spoel, and E. Lindahl, GROMACS 4: Algorithms for Highly Efficient, Load-Balanced, and Scalable Molecular Simulation. J. Chem. Theory Comput. **4**, 435 (2008).

[40] G. Bussi, D. Donadio, and M. Parrinello, Canonical sampling through velocity rescaling. J. Chem. Phys. **126**, 014101 (2007).

[41] W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, and M. L. Klein, Comparison of simple potential functions for simulating liquid water. J. Chem. Phys. **79**, 926 (1983).

[42] U. Essman, L. Perela, M. L. Berkowitz, T. Darden, H. Lee, and L. G. Pedersen, A smooth particle mesh Ewald method. J. Chem. Phys. **103**, 8577 (1995).

[43] T. Koishi, K. J. Yasuoka, S. Fujikawa, T. Ebisuzaki, and X. C. Zeng, Coexistence and Transition between Cassie and Wenzel State on Pillared Hydrophobic Surface. Proc. Natl. Acad. Sci. U.S.A. **106**, 8435 (2009).

[44] A. W. Adamson, *Physical Chemistry of surfaces* (Wiley, New York, Ed.3. (1976))

[45] R. Kumar, J. R. Schmidt, and J. L. Skinner, Hydrogen bonding definitions and dynamics in liquid water. J. Chem. Phys. **126**, 204107 (2007).

[46] Transportation process of 53 water molecule is provided with and without fixed (flexible) of carbon atoms in two movies. Some of them were picked up and shown in Figure 1 and Figure 4. Movie S1 Movie S2

[47] S. Andreev, D. Reichman, and G. Hummer, Effect of flexibility on hydrophobic behavior of nanotube water channels. J. Chem. Phys. **123**, 194502 (2005).

[48] J. L. Kou, H. J. Lu, F. M. Wu, and J. T. Fan, Toward the hydrophobic state transition by the appropriate vibration of substrate, EPL **96**, 56008 (2011).

[49] M. B. Nardelli, J. L. Fattebert, D. Orlikowski, C. Roland, Q. Zhao, and J. Bernholc, Mechanical properties, defects and electronic behavior of carbon nanotubes, Carbon **38** 1703 (2000).

[50] A. Hashimoto, K. Suenaga, A. Gloter, K. Urita, and S Iijima, Direct evidence for atomic defects in graphene layers. Nature **430**, 870 (2004).