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Unidirectional motion of a water nanodroplet subjected to a surface energy gradient

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We perform molecular dynamics simulations to demonstrate that when a nanodroplet is confined inside a carbon nanotube (CNT), unidirectional motion can be created by a nonzero surface energy gradient. It is found that the water nanodroplet moves along the direction of increasing surface energy. The transportation efficiency of the water nanodroplet is found to be dependent on the surface energy gradient; environmental temperature; and the flexibility, diameter, and defectiveness of the CNT. It is shown that higher surface energy gradient, the smaller diameter of the CNT, and fewer defects promote higher transportation efficiency. However, 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 is also found that the hydrogen bonds of water molecules play a role in the dynamic acceleration process with a wavelike feature. The present work provides insight for the development of CNT devices for applications such as drug delivery, nanopumps, chemical process control, and molecular medicine.

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I. INTRODUCTION

Carbon nanotubes (CNTs), which are small in size and have innate holes, possess a large surface area, high elastic modulus, remarkable electrical conductivity, and ultrahigh 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 [6]. 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 such as 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] and then demonstrated in experiments [18,19]. Such transportation characteristic is of great importance to designing novel molecular devices, machines, and sensors. Inspired by the charges in the biological water channels (aquaporins), 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 an 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. 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], it has been shown that a 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 a target area along the CNTs. Previous works have 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 transition 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 a different surface energy gradient, environmental temperature, flexibility, diameter, and number of defects of the CNT is discussed. In Sec. II we give a detailed description of the system and simulation methods. Results and a discussion are presented in Sec. III. Finally, a summary is given in Sec. IV.

II. SYSTEM AND METHOD

To study the transportation of water nanodroplets confined inside CNTs, a series of uncapped single-walled carbon

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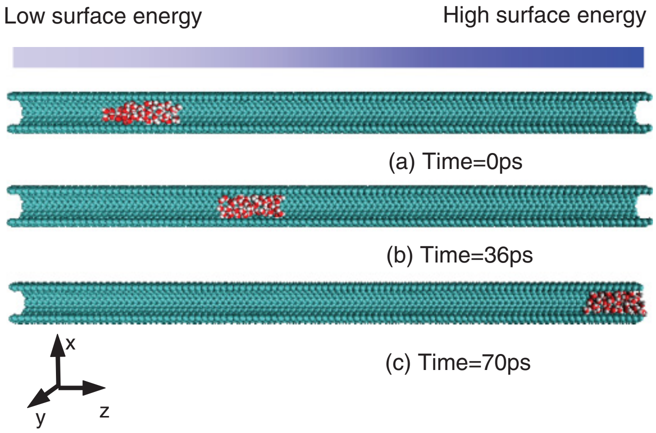


(a) Time=0ps

(b) Time=36ps

(c) Time=70ps

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 0.0145 kJ mol^{-1} nm^{-1} at temperature 300 K at (a) the initial equilibrium state, (b) 36 ps, and (c) 70 ps. The top strip shows the surface energy changing along the surface of the 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.

nanotubes, in each of which a nanodroplet is encapsulated, were prepared as shown in Fig. 1. A surface energy gradient was applied along the z-axis direction of the CNT. In reality, this can be altered through chemical modification or a dc or ac electric field [33–38]. For each set, after initially equilibrating the system at a specific temperature (200, 300, or 330 K) assuming a uniform surface energy along the CNT, the water nanodroplet was kept at 5 nm from the left end of the CNT. The initial position of the mass center of the droplet is set equal to 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 260, 300, or 330 K, which was maintained by using a velocity rescaling 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 water model [41] 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 $\sigma_{\mathrm{C,C}} = 0.34$ nm and $\sigma_{\mathrm{C,O}} = 0.3275$ nm. The depth of the potential well was $\varepsilon_{\mathrm{C,C}(l)} = 0.3612$ kJ mol^{-1} and $\varepsilon_{\mathrm{C,O}(l)} = 0.4802$ kJ mol^{-1} at the left end of CNT [31]; $\varepsilon_{\mathrm{C,C}(p)}$ was continuously and arbitrarily varied along the CNT in the simulations (the subscript p represents the position along the z direction of the CNT). The surface energy gradient λ was defined as the difference of adjacent layers of carbon atoms per nanometer, viz., $\lambda = (\varepsilon_{\mathrm{C,C}(p)} - \varepsilon_{\mathrm{C,C}(l)})/L_{p,l}$, where $L_{p,l}$ 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 the CNT [36]; it was greater than zero in the present simulations. It has been shown that the effective C-C interaction energy ($\varepsilon_{\mathrm{C,C}}$) can be tuned by applying a dc or ac electric field [33,34,36] or using different chemical modifications [35,37,38]. The interaction energy (binding energy) between the water molecules and the 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 0.04 ps. When investigating the effect of flexibility, carbon-carbon bond lengths of 0.142 nm and bond angles of 120° were maintained by harmonic potentials with spring constants of 393 960 kJ mol^{-1} nm^{-2} and 527 kJ 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 the unidirectional motion of a water nanodroplet induced by a surface energy gradient in a (10, 10) CNT. In Fig. 1(a) the water nanodroplet at the equilibrium state is composed of 53 molecules and confined in a 24.3 nm long CNT with a surface energy gradient of $\lambda = 0.0145$ kJ mol^{-1} nm^{-1}. From Fig. 1 (or refer to movie S1 in Ref. [44]) it can be observed that the water nanodroplet moves in the direction of increasing surface energy under the condition of room temperature (300 K). 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 Figs. 2(a)–2(c) the influence of surface energy gradient on the position of the mass center, the velocity, and the acceleration of the nanodroplet in the CNT. When the surface energy gradient was set equal to zero [see the magenta line in Fig. 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, the thermal motion or self-assembly of water molecules can lead to only random motion of the water nanodroplet within a very narrow range [11]. For a liquid droplet on a solid substrate, it was shown that the Marangoni effect can create spontaneous motion [45]. 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 in Fig. 2(b) is that the movement velocity is not invariant. It increases with a small fluctuation over the simulation time span. At a room temperature of 300 K and a surface energy gradient of 0.0145 kJ mol^{-1} nm^{-1}, the movement velocity of the nanodroplet can reach approximately 350 nm ns^{-1}. However, only 22 nm ns^{-1} was attained when a thermal gradient of 1.05 nm^{-1} was used [26]. Furthermore, it is observed in

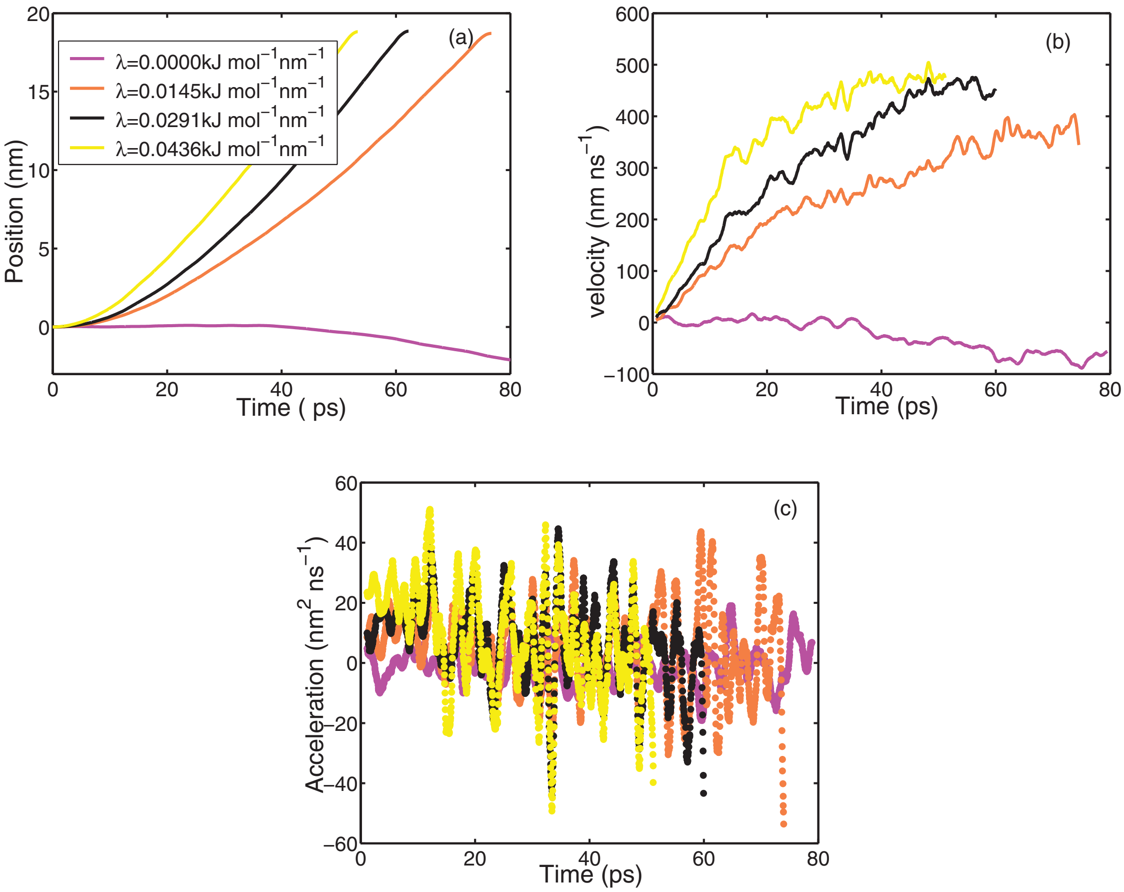


FIG. 2. (Color online) Parameters of (a) the position of the center of the nanodroplet, (b) the velocity of the nanodroplet, and (c) the acceleration of the nanodroplet as a function of the time for different surface energy gradients [0.0 kJ mol^{-1} nm^{-1}, magenta (bottom) lines; 0.0145 kJ mol^{-1}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

Fig. 2(c) that there is a movement acceleration and changes in a waveform 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 a water nanodroplet [31,46]. With unbalanced forces at the front and rear of the water nanodroplet, the hydrogen bonds exhibit an elastic characteristic. This is especially apparent when the hydrogen bond lengths are more than 3.4 Å, where a more regular fluctuation takes place. In comparing the upper part (acceleration greater than 0) with the lower part (acceleration less than 0) of Fig. 2(c) one can see that the 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 Figs. 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 in Fig. 2(c), there is a greater amplitude of fluctuation for a larger surface gradient. This is consistent with the above discussion of hydrogen bonds. This implies that a higher surface energy gradient can make the nanodroplet move faster.

Under the same surface energy gradient of $\lambda = 0.0145$ kJ mol^{-1} nm^{-1}, we conducted the simulation under different environmental temperatures, viz., 200, 300, and 330 K, respectively. The solid lines in Fig. 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 an environmental temperature of 300 K moves faster than that at a higher temperature of 330 K and a lower temperature of 200 K. This phenomenon can be explained as follows. A higher environmental temperature of 330 K can cause 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. In contrast, under a lower temperature, the initial velocity is inducted only 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 a too high and a too low temperature can reduce the transportation efficiency of a nanodroplet inside a CNT and an optimal transportation efficiency may exist under a certain appropriate temperature.

Furthermore, we investigated the effect of the flexibility of carbon atoms on the transportation efficiency. Figure 4 (see also movies S1 and S2 in Ref. [44]) shows the transportation

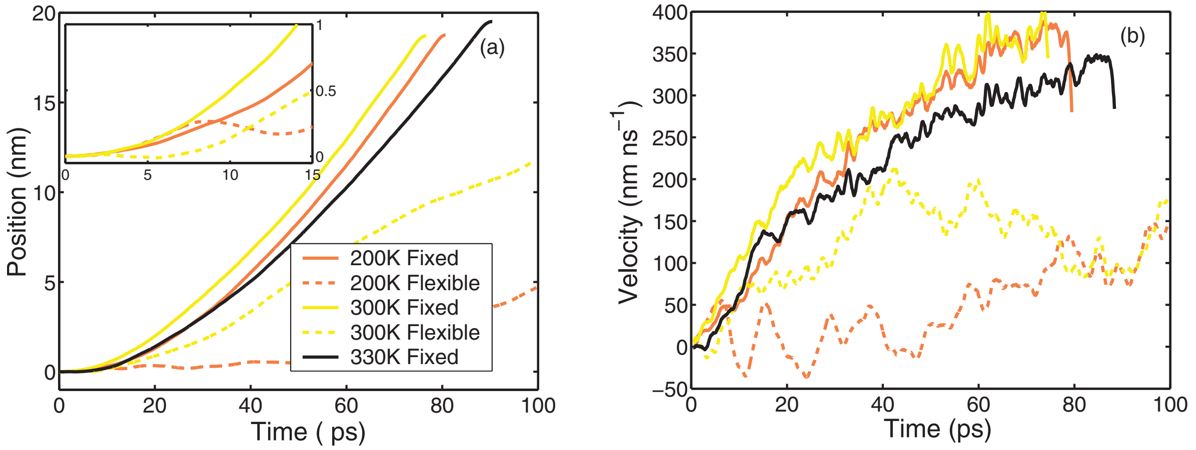
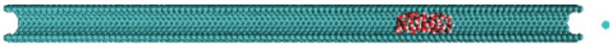


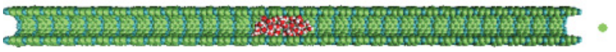
FIG. 3. (Color online) Parameters of (a) the center position of the nanodroplet and (inset) an enlarged drawing during the initial stage, (b) the velocity of the nanodroplet as a function of the time for a different temperature and flexible or fixed at a surface energy gradient of 0.0145 kJ mol^{-1}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

of a nanodroplet inside a CNT with fixed and flexible carbon atoms. For both cases, the temperature and surface energy gradient were the same. The CNT shown in Fig. 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 Fig. 4 [or in Fig. 3(a) (from the solid lines to the dashed lines)]. The flexibility of the CNT wall increases the 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 Fig. 3(a), the nanodroplet inside the flexible CNT can move faster than that inside the fixed CNT under the relatively low temperature of 200 K. This phenomenon cannot be observed under the temperature of 300 K. One explanation for this is that the movement of water molecules is weak under the low temperature and the flexibility of the 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 the 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 the CNT wall impedes water transport across the nanotube, but accelerates movement during the initial stage only at a relatively low environmental temperature.

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 a (6,6) CNT and a (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 56 ps are shown in Figs. 5(a) and 5(b). The position of mass center, the velocity, and the acceleration of the nanodroplet are shown in Figs. 6(a)–6(c). It can be seen that the water cluster inside the (6, 6) CNT can reach to the right end faster than that inside the (10, 10) CNT, as shown in Figs. 5 and 6. From a structural point of view, the water cluster in the (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

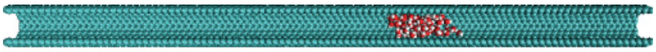


(a) Fixed; Temperature=300K, 60ps Fixed

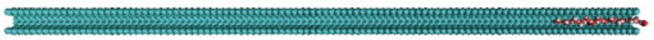


(b) Flexible; Temperature=300K, 60ps Flexible

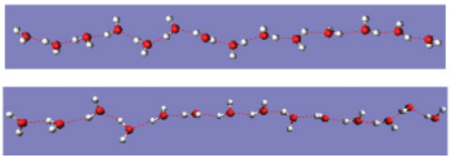
FIG. 4. (Color online) Comparison of snapshots between the (a) fixed CNT and (b) flexible CNT at a time of 60 ps and a temperature of 300 K. Fixed carbon atoms are shown as cyan and flexible carbon atoms are shown as lime.



(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 the transportation process of a water nanodroplet confined inside (a) a (10, 10) CNT and (b) a (6, 6) CNT with a surface energy gradient of 0.0145 kJ mol^{-1} nm^{-1} at a temperature of 300 K and a time of 56 ps. Also shown is a single-file water chain confined inside a (6, 6) CNT at (c) the initial equilibrium state and (d) the transportation process.

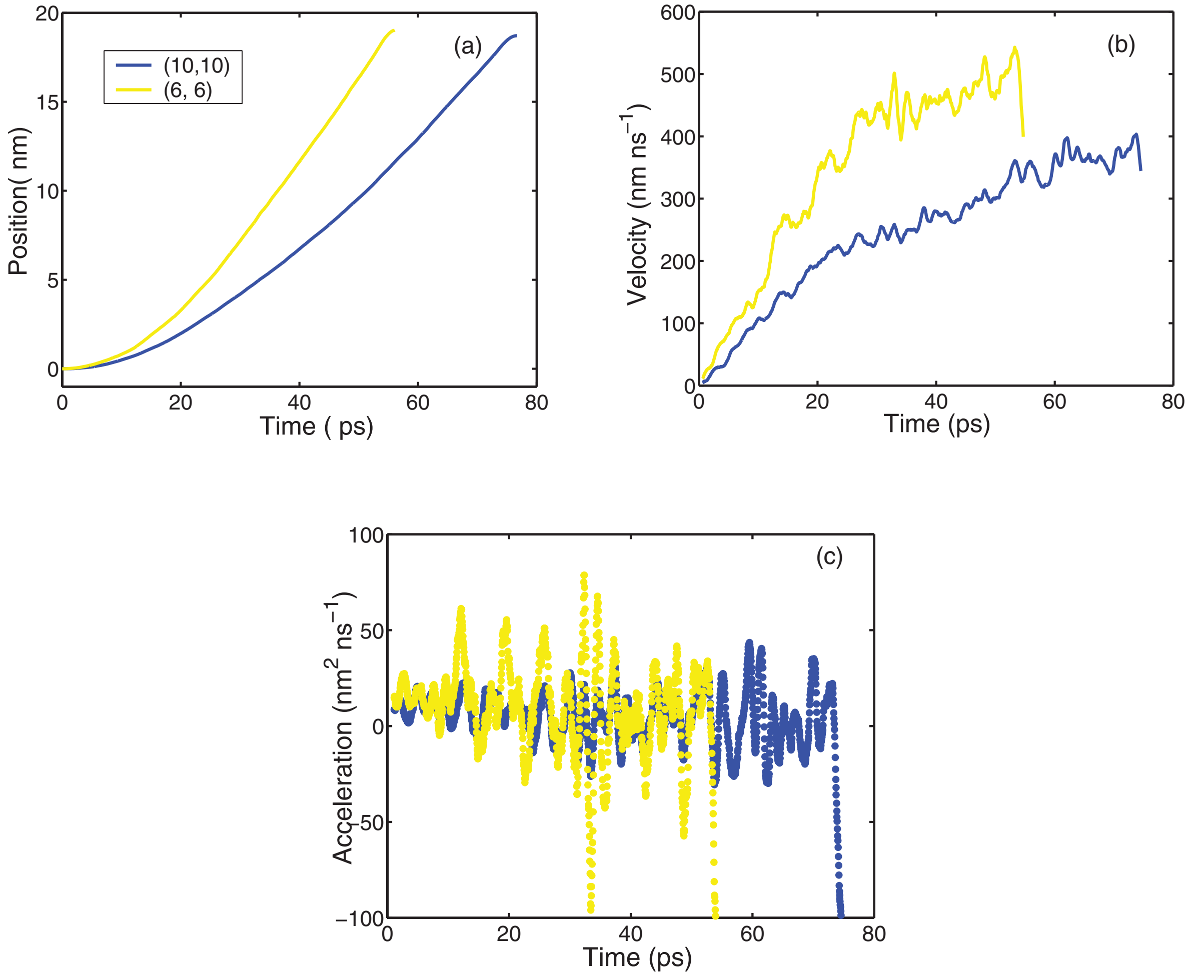
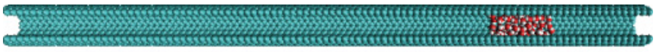
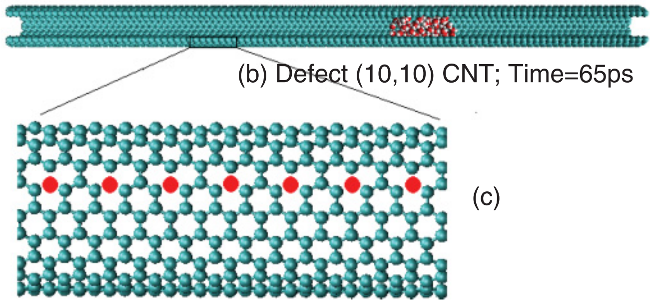


FIG. 6. (Color online) Parameters of (a) the position of the center of the nanodroplet, (b) the velocity of the nanodroplet, and (c) the acceleration of the nanodroplet as a function of the time for different diameters with the same surface energy gradient of 0.0145 kJ mol^{-1} nm^{-1} at a temperature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

molecules and the water nanodroplet may have complicated movement in the transverse and longitudinal directions. When inside the (6, 6) CNT the water molecules form a single-file structure [see Fig. 5(d)], each water molecule has maximally two interactions with another water molecule at the front and rear ends in addition to its interaction with the wall of the CNT. Further, the water molecules of the single-file chain only rotate in dipole orientation [21] around the axis of the CNT or move along the direction of the CNT [22,31]. As a result, the temperature can have a greater effect on the water cluster in the (10, 10) CNT than that on the single-file water chain in the (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 in Figs. 6(a) and 6(c) before 10 ps, where almost no difference is apparent between these two structures. Moreover, since the smaller CNT has a higher specific surface area, which produces a stronger interaction, the acceleration of water molecules in the (6, 6) CNT is observed to be greater than that in the (10, 10) CNT, as shown in Fig. 6(c). It is concluded in Figs. 5 and 6 that the dimension of CNTs is sensitive for the transportation of the water nanodroplet. The CNT with smaller dimension has



(a) Perfect (10,10) CNT; Time=65ps



(b) Defect (10,10) CNT; Time=65ps

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

a higher transportation efficiency of the water nanodroplet, especially for the (6, 6) CNT. Furthermore, we note in the (6, 6) CNT that the orientation of the water molecules is face to face [see Fig. 5(c)] at the initial state. The dynamics process begins after about 1.4 ps, when the orientation of the water molecules quickly flips and is maintained in one direction.

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 on a 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 present only the vacancy defects on the transportation efficiency, as shown in Fig. 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 the CNT. This implies a smaller interaction force between the CNT wall and the water nanodroplet, leading to a lower transportation efficiency.

IV. CONCLUSION

To summarize, we have shown that water nanodroplets confined inside carbon nanotubes can move unidirectionally by means of a 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 is dependent on the surface energy gradient; environmental temperature; and the flexibility, diameter, and defectiveness of the CNT. The present findings can have practical implications in the development of nanodevices for nanopumping and drug delivery.

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