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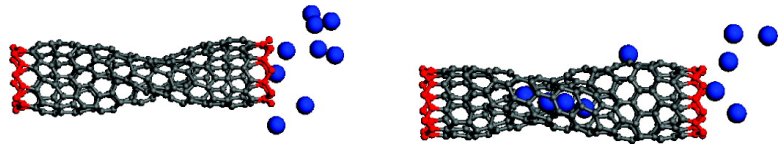

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Atomic Transportation via Carbon Nanotubes

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ABSTRACT

The transportation of helium atoms in a single-walled carbon nanotube is reported via molecular dynamics simulations. The efficiency of the atomic transportation is found to be dependent on the type of the applied loading and the loading rate as well as the temperature in the process. Simulations show the transportation is a result of the van der Waals force between the nanotube and the helium atoms through a kink propagation initiated in the nanotube.

Carbon nanotubes (CNTs) are macromolecules of carbon in a periodic hexagonal arrangement with a cylindrical shell shape.[1] Their remarkable electrical, mechanical, and thermal properties[2,3] enable them to be used for the development of devices for microelectromechanical and nanoelectromechanical system applications. In addition, the morphology of their hollow tubes and the specific large surface area provide an excellent opportunity to create nanopumping devices for atomic transportation.[4] Microflow in microcapillaries has great potential in the areas of nanorobotices, helium energetics, medical drug delivery, micropumps, microarays, atom optics, chemical process control, and molecular medicine.[5−7] A nanopipette action for metals using multiwalled CNTs was demonstrated experimentally.[8] The electro-migration forces, created at high electron current densities, were found to enable the transport of material inside the hollow core of CNT. A recent experimental report was on the gas and water flow measurements through microfabricated membranes in which aligned CNTs serve as pores.[9] The gas and water permeabilities of these nanotube-based membranes were observed to be several orders of magnitude higher than those of commercial polycarbonate membranes. Since small length and time scales associated with atomic level dynamics limit the ability of experiments to study atom-CNT interaction, molecular dynamics simulation has emerged as another efficient way to study atomic transportation through CNTs. The effects of CNTs diameter on mass density, molecular distribution, and molecular orientation of water molecules inside and outside of CNTs were identified for both confined and unconfined fluids via molecular dynamics.[10] Atomistic simulations for both self- and transport diffusivities of light gases in CNTs and in two zeolites with comparable pore sizes were reported.[11] Dynamics analysis of fluid transportation in CNTs was investigated, and it was found that the behavior of the fluid strongly depends on the rigidity of the tube.[12] A novel nanopumping effect on the activation of an axial gas flow in a CNT by actuating Rayleigh traveling waves on the nanotube surface was simulated.[5] Measurement of the flow of hydrogen and helium gases lighter than carbon through the CNT was reported in the research. The activation of atomic transportation via CNTs via traveling wave is normally accomplished through generating either thermoacoustic wave or sending ultrasound wave through media to the nanotubes. The effectiveness and the manipulation of the two ways for gases or liquid transportation in CNTs need further endeavors. On the other hand, since CNTs have been found to be manipulated by facilities, such as the tip of an atomic force microscope, to study their electronic and mechanical properties,[13] effective application of the deformed CNTs could have potential on atomic transportation, which has been rarely reported. The wall of a CNT subjected to compression or torsion loading beyond a critical value will deform transversely, or become unstable.[14,15] Such a transverse deformation, in turn, induces the change of van der Walls potential between the tube and the encapsulated atoms, and thus the possible pumping of atoms via CNTs could be fulfilled.

In this work, we examine the transportation of helium atoms encapsulated in a zigzag (8,0) CNT subjected to both compression and torsion loading via molecular dynamics simulations. Dependence of the type of loading and the loading rate on the effectiveness and efficiency of transportation of the encapsulated atoms in the CNT is investigated. In addition, the effect of the temperature used in the dynamic process on the atomic transportation is also explored. Van

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der Waals potential is calculated to measure the driving force for the transportation.

The transportation of ten helium atoms encapsulated in a zigzag (8,0) CNT with the length of about 23.5 Å is investigated via molecular dynamics. The interatomic interactions are described by the force field of condensed-phased optimized molecular potential for atomistic simulation studies.[16] This is the first ab initio force field that was parametrized and validated using condensed-phase properties, and it has been proven to be applicable in describing the mechanical properties of CNTs.[15] The dynamics process is conducted to allow the system to exchange heat with environment at a constant temperature. The Andersen method[17] is employed in the thermostat to control the thermodynamic temperature and generate the correct statistical ensemble. For a temperature control, the thermodynamic temperature is kept constant by allowing the simulated system to exchange energy with a "heat bath".[17] The force field is expressed as a sum of valence (or bond), cross-terms, and nonbond interactions: $E_{\text{total}} = E_{\text{valence}} + E_{\text{crossterm}} + E_{\text{nonbond}}$. The energy of valence, E_{valence}, is generally accounted for by terms including bond stretching, valence angle bending, dihedral angle torsion, and inversion. The cross terms, $E_{\text{crossterm}}$, account for factors such as bond or angle distortions caused by nearby atoms to accurately reproduce the dynamic properties of molecules. The energy of interactions, E_{nonbond}, between nonbonded atoms is primarily accounted for by van der Waals effect. In the simulations, torsion or compression loading is applied through subjecting torsion angle or axial displacement to one of the two ends of the CNT, which are clamped to restrain their motion.

Elastic torsional response and compression of CNTs encapsulating molecules and atoms have been investigated to study the change of mechanical properties of CNTs.[18,19] The effects of temperature and the filled molecules and atoms were examined using molecular dynamics simulations. The instability of CNTs encapsulating various foreign atoms subjected to compression and torsion loading has also been discussed via molecular mechanics process[20,21] in which only a final static buckling equilibrium of the system was of concern. Such a static buckling equilibrium cannot provide a driving force strong enough for an atomic transportation through CNTs at all. Therefore, in the following studies, the effect of dynamic loadings applied to CNTs with various loading rates is investigated to study the effectiveness and efficiency of a dynamic transportation process of the encapsulated atoms. Nanotube behavior at a tensile rate of the order of megahertz was ever studied by molecular dynamics to discuss the breaking pattern of CNTs.[22] We will apply loading rate equivalent to megahertz $\sim$ terahertz in the simulations.

The transportation process of 10 helium atoms in the CNT subjected to torsion loading at 1500 K is illustrated in Figure 1 first. The equilibrium state of the CNT with the encapsulated atoms is shown in Figure 1a in which a chain configuration of helium atoms is found, similar to the one also revealed in a number of studies.[20,21,23] The slippery nanotube surface and the chain configuration of the encapsulated atoms will generate the phenomenon of ultrafast flow through CNTs. The CNT keeps the stable state when a torsion angle,1.05 rad, is applied at first. At this torsional angle, the helium atoms remain almost undisturbed as the van der Waals potential between the tube wall and the helium atoms has a slight change owing to the unchanged circular wall of the CNT. Prerequisite instability analysis shows that at 2.40 rad the tube undergoes an obvious torsional instability process, and the severely crippled wall induces a strong reduction of the area of the cross section leading to the corresponding van der Waals force for the possible pumping. Therefore, we further apply additional torsion angle, 1.40 rad, at the left clamped end of the CNT with a rate of 2.79 rad/ps and display the morphology of the structure at the end of the loading process, $t = 0.5$ ps, in Figure 1b. During the loading process, the time step in the molecular dynamics is chosen to be 0.01 fs to make the simulations more reliable and accurate. At the moment of the end of the loading process, a clear local kink initiates at the left end. The initiation of the local kink breaks the balanced stable state of the structure and in turn accelerates the motion of the

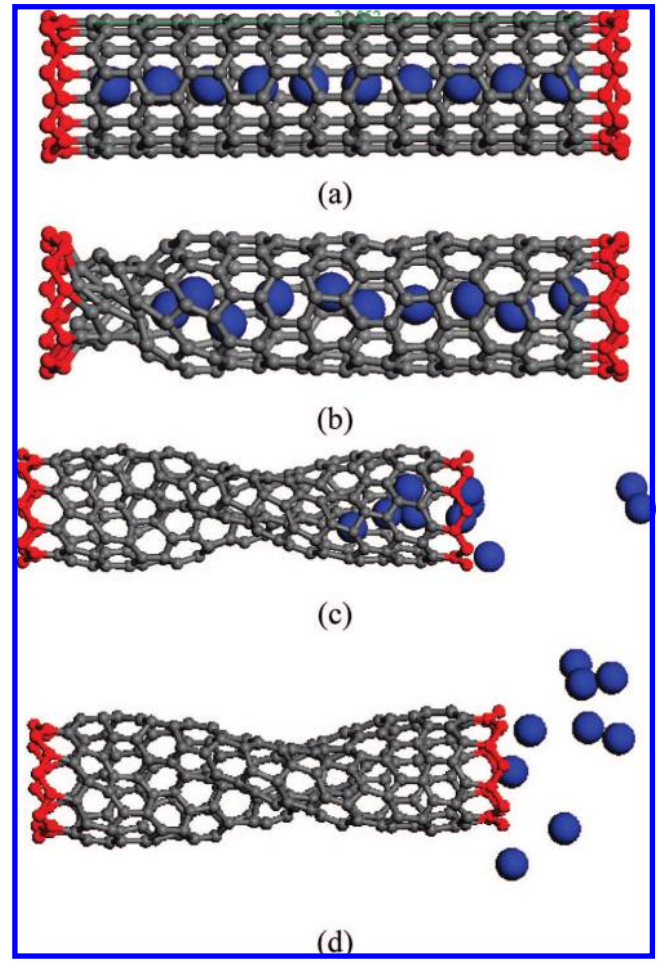

Figure 1. Molecular dynamics simulations of 10 encapsulated helium atoms and the (8,0) CNT subjected to torsion with a rate of 2.79 rad/ps at temperature 1500 K at (a) the initial equilibrium state; (b) the end of the loading process, $t = 0.5$ ps with all atoms in the tube; (c) $t = 10$ ps with half of the atoms outside of the tube; and (d) $t = 25$ ps with all atoms pumped outside of the tube successfully.

Table 1. van der Waals Potentials and the Corresponding Changes at Various Instants of the (8,0) CNT Subjected to Torsion Loadings with Three Different Loading Rates

torsion loading rate	instants	van der Waals potential (kcal/mol)	change of van der Waals potential (kcal/mol)	change in percentage
	0.5 ps	4522.19		
2.79 rad/ps	25 ps	663.68	3858.51	85%
	2 ps	1103.42		
0.70 rad/ps	20 ps	550.31	553.11	50%
	4 ps	892.06		
0.35 rad/ps	20 ps	571.15	320.91	36%

atoms and pushes them to move rightward due to the change of the van der Waals force owing to the tube wall crimpling. However, the driving force is not strong enough to drive any helium atoms out of the CNT at the moment since the kink is only distributed locally around the left end, and the major portion of the tube still keeps a circular shape, as seen clearly in Figure 1b. To investigate the motion of the structure after the loading is applied, the morphology of the CNT and helium atoms at $t = 10$ ps is provided in Figure 1c, in which three helium atoms are pumped outside of the CNT, three are at the edge of the tube, and the other four are still inside the tube. In the dynamic process after the loading is applied, the time step is chosen to be 0.1 ps in all the simulations to efficiently describe longer processes, while still satisfying the precision of calculations. Because the CNT is subjected to torsion with a high rate, a transverse deformation of the tube wall propagates along the tube and initiates motion of the filled atoms toward the direction of the propagation. On the other hand, since the torsion angel is beyond the buckling capacity of the tube, the kink starts to expand consequently along the tube from the left edge of CNT. As a result, some helium atoms are squeezed out of the CNT. Therefore, it is concluded that the driving force for atomic transportation is from the kink propagation or expansion that induces motions of the encapsulated atoms toward the direction of the kink propagation. On the other hand, it is noted that at the moment the kink only arrives around the center of the tube, and atoms are accelerated only within a shorter time. Thus four helium atoms are still inside the tube and could not be pumped out due to limited driving force. To further look into nature of the atomic motion via the kink propagation, the morphology of the structure at $t =$ 25 ps, a sufficiently long time after the loading impact is applied, is illustrated in Figure 1d. It is clearly seen that the kink propagation has arrived at the right edge of the CNT. As a consequence, all the remaining helium atoms, which have been accelerated after a longer time, are pushed out of the CNT owing to the strong van der Waals force. Finally, after the restriction on the two clamped ends of the CNT is released, the CNT recovers its original straight shape via a minimization process to calculate the optimal shape of the tube with minimal potential, showing a great recovery characteristic of the material. In the calculations, it is seen that the driving force for the transportation is mainly from the van der Waals force between the crippled tube wall and helium atoms due to the kink propagation or expansion along the tube.

To investigate the efficiency of the atomic transportation, we conduct the same process of applying torsion loading to the tube but with two lower rates, 0.70 rad/ps and 0.35 rad/ps. Figure 2a,b shows the morphologies of the atomic transportation with the two rates at the end of the dynamic process, $t = 20$ ps, respectively. Seven and six helium atoms are finally found to be pumped outside of the tube in the two panels because the buckling kink expands to the right direction similar to the process illustrated in Figure 1. However, since the kinks propagate slower in the tube with lower loading rates, the accelerations of helium atoms are observed to be smaller than those of the atoms in the tube subjected to a higher loading rate in Figure 1. As a result, some encapsulated atoms are locked inside the tube after the kinks propagation arrive at the right edge of the tube. On the other hand, the current lower impulse rates apparently lead to a combined nature of local and global buckling response of the tube, which will slow down the motion of the encapsulated atoms in the tube. A static torsional buckling process would provide an illustration of a special dynamic process with the smallest loading rate. In static torsional analysis via the minimization process, the onset of the kink occurs globally on the whole portion of the tube wall. Therefore, no possible propagation of the kink could be initiated. On the other hand, since there is not any wave

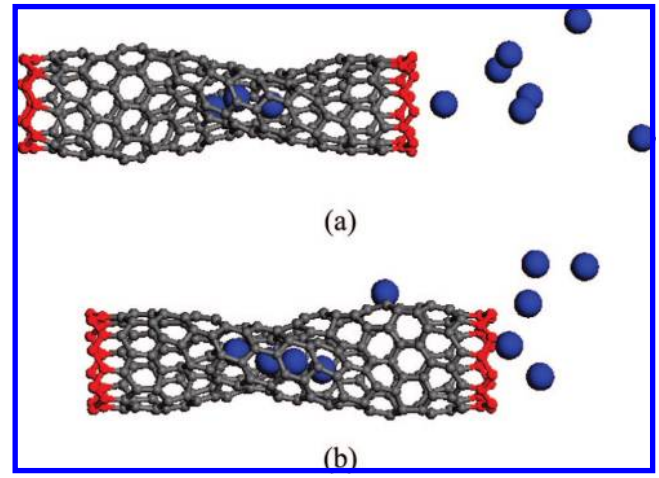

Figure 2. Molecular dynamics simulations at temperature 1500 K of 10 encapsulated helium atoms and the (8,0) CNT (a) subjected to torsion with a rate of 0.70 rad/ps at $t = 20$ ps with seven helium atoms outside of the tube; and (b) subjected to torsion with a rate of 0.35 rad/ps at $t = 20$ ps with six atoms pumped outside of the tube.

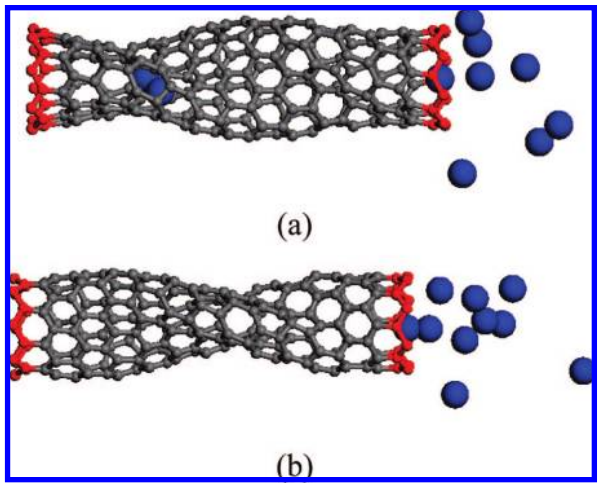

Figure 3. Molecular dynamics simulations at temperature 800 K of 10 encapsulated helium atoms and the (8,0) CNT (a) subjected to torsion with a rate of 2.79 rad/ps at $t = 20$ ps, with eight helium atoms pumped outside of the tube; and (b) subjected to torsion with a rate of 17.4 rad/ps at $t = 20$ ps with all atoms pumped outside of the tube.

propagation in the tube due to the globally distributed kink along the tube, the encapsulated atoms could not be accelerated to move along a fixed flowing direction. As a result, atomic transportation could not be fulfilled via a static buckling of CNTs, which is also indicated through simulations.[20,21] It is concluded from the simulations in Figure 2a,b that the efficiency of the transportation of foreign atoms depends on the impact loading rate subjected to the CNT. The lower the loading rate, the lower efficiency of the atomic transportation. Next, the change of van der Waals is employed to calculate the driving force for the transportation. Table 1 shows the calculations of the van der Waals potential at two moments respectively, that is, the end of the loading and the end of the dynamic process, for the CNT subjected to torsion loadings with three loading rates. It can be estimated that the total changes of van der Waals potentials from the end of the loading process to the end of the dynamic process are about 858.3, 553.1, and 320.9 kcal/mol, respectively, with the corresponding changes in percentage 85, 50, and 36% for the three loading rates. From the calculations, it is seen that the driving forces are higher used for the CNT subjected to torsion with higher rate, leading to a more efficient and complete atomic transportation via the CNT.

To visualize the effect of temperature in the molecular dynamics, the transportation of ten helium atoms at 800 K with the loading rate 2.79 rad/ps at $t = 20$ ps is shown in Figure 3a. It is clearly seen that seven atoms are successfully pumped outside of the tube, while three are locked in the tube in the end. With this loading rate, a complete transportation has been accomplished for the tube at 1500 K. To fulfill a complete transportation of the tube at the lower temperature necessitates a higher loading rate, say 17.4 rad/ps, which is clearly displayed in Figure 3b. Additional simulations for the tube subjected to the loading rates, 2.79 and 17.4 rad/ps, at 500 K are also listed in Figure 4a,b from which it is seen that six and two atoms are finally locked in the tube separately. Our simulations and observations show

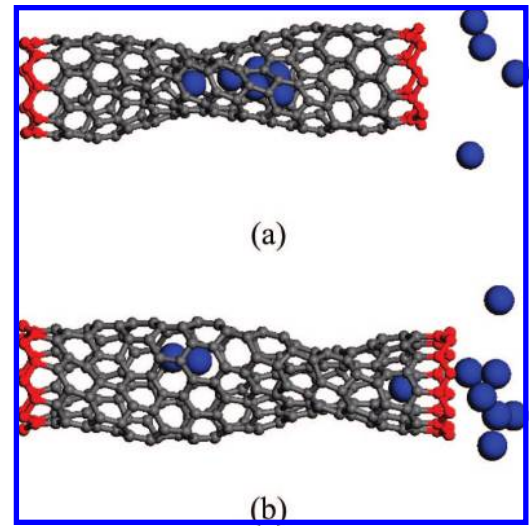

Figure 4. Molecular dynamics simulations at temperature 500 K of 10 encapsulated helium atoms and the (8,0) CNT (a) subjected to torsion with a rate of 2.79 rad/ps at $t = 20$ ps with four helium atoms outside of the tube; and (b) subjected to torsion with a rate of 17.4 rad/ps at $t = 20$ ps with seven atoms pumped outside of the tube.

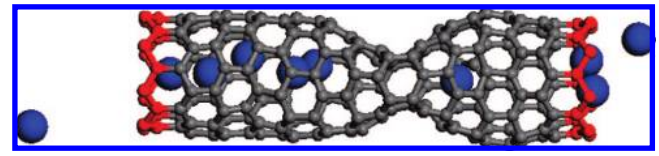

Figure 5. Molecular dynamics simulation at temperature 500 K of 10 encapsulated helium atoms and the (8,0) CNT subjected to a compression with a rate of 1.0 nm/ps at $t = 11$ ps with most atoms locked inside the tube.

that helium atoms tend to vibrate and are prone to move in the tube along the kink propagation direction more efficiently at higher temperatures. Therefore, it is concluded that higher environmental temperatures will lead to more effective atomic transportations via CNT.

We finally conduct the investigation of atomic transportation via the CNT in Figure 5 subjected to a compression loading with a very high rate, 1.0 nm/ps at temperature 1500 K. In the dynamic molecular simulations, the time step is chosen to be 0.1 fs. We first find that the tube remains its stable state after a compression of 1.0 Å. Figure 5 shows the morphology, at the moment $t = 11$ ps, of the tube subjected to further 1.0 Å with the rate of 1.0 nm/ps. A notable observation in this figure is that the kink in the CNT subjected to compression always propagates locally. Different from the kink in the CNT subjected to torsion that distributes or expands helically from the left to the right edge of CNT shown in Figure 1, it does not expand along the tube but only locally distributes in the longitudinal direction and thus can only induce lower change of van der Waals potential. As a result, most of the helium atoms finally remain in the tube due to the smaller driving force, which can be seen from the morphology. Therefore, applying compression, even with a very high rate, cannot effectively transport foreign atoms through CNTs.

In summary, our molecular dynamics simulations show that applying torsion or compression to CNTs provides an alternative approach for atomic transportation. The transportation is realized through the kink propagation induced by the applied impact loading to CNTs. Since kink always propagates locally along a CNT subjected to compression, transportation cannot be fulfilled effectively even when a very high loading rate is applied to the CNT. On the other hand, a complete atomic transportation is possible when torsion loading with a high rate is applied to the CNT as the kink expands along the tube to induce more van der Waals driving force. In addition, it is found that a higher environmental temperature will promote the atomic transportation through CNTs.

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Supporting Information Available: Video of the dynamic process of the CNT encapsulating helium atoms in Figure 1 from the moment, $t = 2$ ps, to the end of the molecular dynamics process, $t = 25$ ps, is available. This material is available free of charge via the Internet at http://pubs.acs.org.

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