Thermally driven large-amplitude fluctuations in carbon-nanotube-based devices: Molecular dynamics simulations

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Thermally driven devices based on double-walled carbon nanotubes are proposed in this paper. Molecular dynamics simulations show that large-amplitude axial oscillation can be effectively excited for the local van der Waals potential barrier, V_{loc}, accessible by the thermal fluctuation. Besides the axial oscillation, the angular and transverse motion are observed and discussed. It is further found that severe structure distortion can terribly disturb the motion at high temperature. The great intertube mobility observed here implies the possibility of building a nanoscale Brownian machine or molecular transport channel, with broad applications.

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Nanoelectromechanical systems (NEMS), which can measure and drive mechanical motions at a molecular level, have great potential in engineering applications. Numerous studies, both experimental[1,2] and theoretical,[3,4] have been devoted to this field. Carbon nanotubes (CNTs), comprising nanoscale concentric graphene shells, have been shown to possess exceptional mechanical and electronic properties, thus hold the promise of building blocks for the next-generation NEMS and have attracted many research interests recently.[5] For example, the strong intrashell sp^2 bonding leads to extremely high axial Youngs modulus and tensile strength, however the weak van der Waals interactions between neighboring shells results in ultralow intershell shear strength on the order of 0.08–0.3 MPa.[6,7] This high anisotropy provides CNT-based nanodevices with great intershell mobility without losing their structural stability. Inspired by this feature, Zheng and Jiang[8] proposed the first CNT-based mechanical oscillator with an operating frequency in the gigahertz range. Since then, extensive theoretical and experimental studies on gigahertz oscillators and related physical and mechanical problems have been carried out. Fennimore *et al.*[9] fabricated nanorotators which is controllable by electrical field. Jensen *et al.*[10] synthesized tunable nanoactuators based on telescoping carbon nanotubes. Moreover, a large amount of work investigating the CNT-based oscillator using molecular simulations[11–15] have been reported, which have predicted its gigahertz frequency[8] and examined the mechanism of energy dissipation and transformation there.

Previous molecular simulation results[11–15] have shown that, through coupling with the internal vibration of a lattice such as waving, rocking, and intershell rotation, the axial oscillation decays quickly within a few nanoseconds. In principle, these devices are supposed to be driven by mechanical manipulators,[7] electrical[2] or optical sources.[4] However, the need for precise control down to the molecular level poses great technical challenges. In particular, the energy supplement and signal detection in nanoseconds time scale evolved in the GHz oscillators are inaccessible now. On the other hand, at a length scale down to a nanometer, the thermal fluctuation is relatively large and comparable with the mechanical energy of translation or rotation. With the recently developed nanotechnology and inspiration from the biological world, people are now trying to construct small devices working at a molecular level and activated by the thermal fluctuation. One example is the so-called Brownian ratchet, where a particle moves unidirectionally over a switchable anisotropic potential.[16] Thus we wonder if a specific CNT-based device could be actuated by the thermal coupling, i.e., in the Fokker-Planck mode,[17] where kinetic energy can be pumped from internal lattice vibrations into some directed motion.[3]

At first we examine some energy aspects of the possible thermally driven motion. We consider the relative axial sliding motion of a free double-walled carbon nanotube (DWNT) as a vibration mode. Thus kinetic energy of this mode is $E_{kin}=\mu v^2/2$, where $\mu=m_{in}m_{out}/(m_{in}+m_{out})$ is the reduced mass, with m_{out} and m_{in} denoting masses of the outer and inner tubes. The average kinetic energy E_{kin} should be equal to the equipartition thermal energy of the mode, $k_BT/2$. Thus we see that a higher average axial velocity v could be excited for a smaller system under a certain temperature T. For example, for a C_{60} molecule inside a long carbon nanotube, the average axial speed $v=(k_BT/m_{in})1/2$ (because $m_{in}/m_{out}\ll 1$) could be 15 m/s at $T=20$ K. On the other hand, the interaction energy between the inner and outer tubes is not constant but corrugated as they are sliding relatively. In view of this, the thermal energy $k_BT/2$ must exceed the local energy barrier V_{loc} to actuate an axial oscillation, which corresponds to a critical speed $v_{loc}=\sqrt{2V_{loc}/\mu}$. Previous calculations based on DFT have found that the height of energy barrier depends upon the combination of the nanotube chiralities of the DWNT[17] and incommensurate combinations or combinations with shorter commensurate length have higher barriers. In this work, we choose an incommensurate armchair-zigzag DWNT (7,7)@(21,0) with a regular intershell spacing of 0.34 nm to realize a much smoother intershell resistance. The lengths of the inner and outer tubes are 2.5 nm and 20 nm, respectively (see the inset in Fig. 1). A very short length is chosen for the inner tube here to lower reduced mass and enhance the possibility of intershell diffusion.

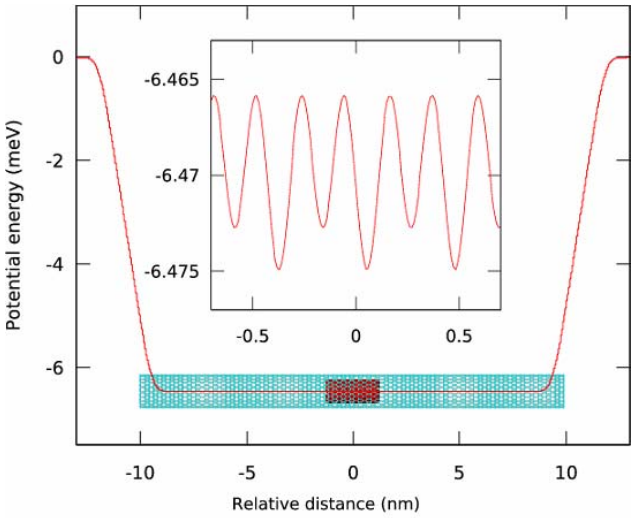


FIG. 1. (Color online) The atomic structure of DWNT (7,7)@(21,0) with a typical intershell distance of 0.34 nm and intertube interaction energy against axial sliding. The 2.5 nm long inner core (red), is confined by the ends repulsion potential well of 6.47 meV/atom and a corrugation of 0.009 meV is formed by the interaction with the 20 nm long outer tube (gray).

The intertube van der Waals interaction energy surface is calculated using Lennard-Jones formula and the result is depicted in Fig. 1. It can be seen that the core tube is confined within a potential well with the depth $V_{\text{ends}}=6.47$ meV per atom, while its local corrugation against sliding, $V_{\text{loc}}=0.009$ meV/atom, is three orders smaller. The high length ratio of the outer to inner tubes leads to the U-shaped potential-well profile with an almost flat region inside. The axial motion of the DWNT thus can be considered as a confined Brownian particle in one-dimensional periodic potential. Following the analysis on such a problem of diffusion over V_{loc} (Refs. 17 and 18) and supposing the fluctuation of intertube motion can be described by the Fokker-Planck equation, we can obtain the diffusion coefficient $D=\omega W^2 \exp(-V_{\text{loc}}/k_BT)/2$ and mobility $B=\omega W^2 \exp(-V_{\text{loc}}/k_BT)/2k_BT$. $W=0.21$ nm and $\omega=\sqrt{k}/\mu$ in the expression denote the width and the oscillation frequency near the minimum of V_{loc}, respectively. In our (7,7)@(21,0) system, by using harmonic approximation we can obtain the effective stiffness $k=1.87$ N/m which is on the same order as Servantie and Gaspard's result,[19] however unlike the V-shape potential well with width of several nanometers in their system, the subnanometer width of local barriers here leads to the possibility of diffusing over them. Following the Arrhenius formula, we can finally obtain the diffusion coefficients 1.22×10^{-10} and 2.76×10^{-9} m^2/s at $T=100$ and 300 K, respectively. These results of great mobilities are consistent with the results obtained for $C_{60}@C_{240}$ (Ref. 20) and (8,2)@(16,4) systems.[17]

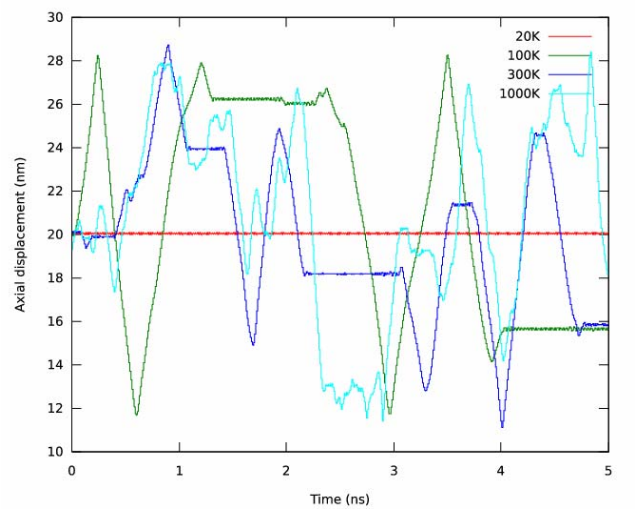
To examine the thermally excited motion of the DWNT, we have carried out molecular dynamics simulations using Dreiding force field.[21,22] The system is first equilibrated with Nosé-Hoover thermostat at a specific temperature for 200 ps. After that the whole system is investigated within a *NVT* ensemble. In our simulation, the thermal coupling is only applied to the outer tube to avoid the effects of thermostat on the intertube motion. The inner tube feels the thermal bath through interatomic interaction with the outer tube only.

The key issue of the thermal motion of the DWNT is the environmental temperature which contributes to the kinetic energy of the atoms. To explore this, we carried out simulations at various temperatures from $T=10$ to 1500 K. Typical results are presented in Fig. 2. As can be seen from the axial displacement, when the temperature is low, $T=20$ K, for example, the intertube sliding is confined inside the 0.21 nm wide local barrier V_{loc}, with maximal speed at $v_{20\text{ K}}\sim10$ m/s. However, at a temperature higher than 60 K, such as $T=100$ or 300 K, large amplitude sliding has been activated, extending to the whole range ($\sim$20 nm) of the outer shell. The critical temperature $T_c=60$ K observed here is close to the orientational melting temperature 70 K for the $C_{60}@C_{240}$ system.[20] Because of the presence of the wall due to the tubes ends repulsion, the DWNT can oscillate subsequently. The sliding speed to access the local barriers is estimated as 50 m/s [Fig. 2(b)], which corresponds to an oscillation frequency $f\sim2.5$ GHz.

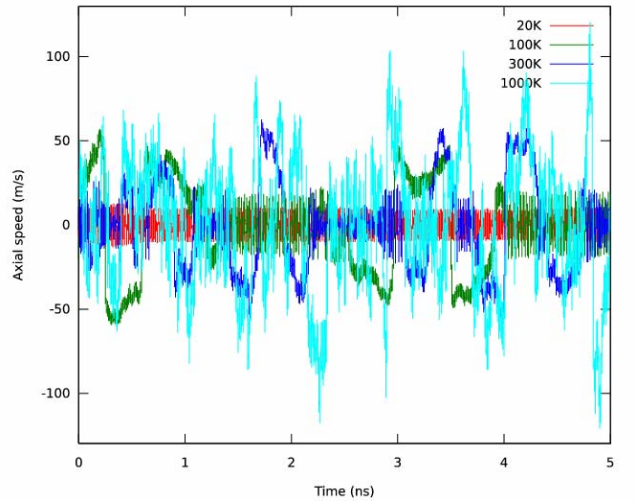
The above observations of thermodynamic fluctuation can be explained as diffusion over one-dimensional barriers and can be resolved into two different behaviors: (1) local fluctuating state (LFS) bounded by V_{loc} and (2) global sliding state (GSS) beyond V_{loc} but confined by V_{ends}. Transition from LFS to GSS occurs when the axial speed exceeds v_{loc}, the critical value to overcome V_{loc}. In our system, v_{loc} is 50 m/s calculated from $V_{\text{loc}}=\mu v_{\text{loc}}^2/2$ as mentioned above. The simulation results shown in Fig. 2 present the confined LFS at $T=20$ K when the axial speed does not exceed v_{loc} and GSS activated at $T=100$ and 300 K when the axial speed fluctuates beyond v_{loc}.

The simulation results of intertube oscillation also show nonperiodic behavior. Sometimes the GSS pauses and switches to the trapped LFS. The pause time intervals are random too. To understand where this anomaly comes from, we have examined the trapped state of the DWNT at 300 K from 4.7 to 5 ns in details. The atomic configuration of the DWNT at 4.8 ns is extracted from the simulation and plotted as the inset in Fig. 3. Localized lattice distortion is observed along the whole outer tube, which causes it to deviate from its cylindrical geometry. This deformation significantly strengthens the interaction potential barrier height to 0.025 meV per atom. The enhanced barrier corresponds to a remarkably larger critical speed $v_{\text{loc}}=83$ m/s which cannot be exceeded by the fluctuating speed at 300 K. As a result, the global sliding is then trapped and will not restart until the local distortion is released by the thermal fluctuation.

To eliminate the distortion of a graphite lattice which interrupts the regular oscillation behavior of the DWNT, we apply constraints to part of the outer tube atoms. However, the trapping behavior is still observed. Detailed analysis reveals that intertube rotation is activated in the trapping events and causes the sliding to pause (see Fig. 4). In fact, coupling of sliding with lattice distortion or rotation can hardly be avoided in principle. As argued previously,[12] in a molecular system such as a DWNT, the typical mechanical modes, such as sliding, rotation, bending, and rocking, interact with each other and exchange energies all the time. Simu-



(a)



(b)

FIG. 2. (Color online) (a) Intertube axial displacement at 20 K (red), 100 K (green), 300 K (blue), and 1000 K (cyan), respectively. The axial oscillation at low temperature is confined by the local potential barrier of 0.21 nm wide (as shown in Fig. 1), while at higher temperature than the critical value ($T_c \sim 60$ K) large amplitude sliding is excited. In addition to the regular (or uniform) sliding across the local barrier, some trapped regions can also be seen from the displacement data, where the axial sliding is temporarily trapped due to the thermal-fluctuation-induced structural distortion. At a very high temperature such as 1000 K, the nanotube deformation is very severe and causes frequent trapping. (b) Corresponding axial speeds of the DWNT. There exists a critical sliding speed ~50 m/s, agreeing well with the estimation from V_{loc}. The global sliding areas [seen from (a)] correspond to sliding speeds higher than v_{loc}, and the trapped regions correspond to speeds lower than v_{loc}.

lations at higher temperatures such as 1000 and 1500 K show that the structural deformations are so severe that the sliding can hardly exceed a few nanometers, even though high axial speeds (over 100 m/s) are excited.

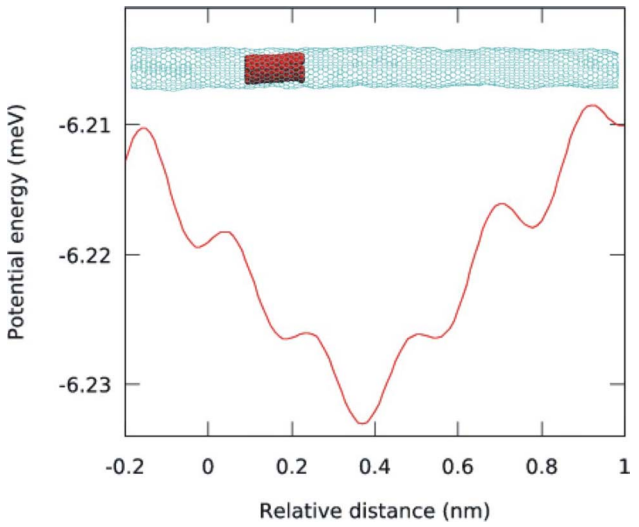


FIG. 3. (Color online) The trapped state at time $t=4.8$ ns for 300 K taken from the flat region of the displacement curve plotted in Fig. 2(a). The cylindrical lattice of the outer tube is distorted, causing an enhanced local potential well of 0.025 meV per atom against sliding, which requires a larger axial speed (83 m/s) to overcome. The radial deformation of a carbon nanotube is magnified 3 times for visualization.

Besides the incommensurate DWNT (7,7)@(21,0) discussed above, some kinds of commensurate nanotubes, such as (4,4)@(20,20) and (8,2)@(16,4), also provide smooth intertube potential surface. In (4,4)@(20,20) where $V_{\mathrm{loc}} = 4.5 \times 10^{-4}$ meV/atom, the intershell spacing 1.08 nm is much larger than the equilibrium value 0.34 nm, thus besides the large amplitude diffusion along the axial direction, transverse oscillation is also observed with an amplitude of 1.7 nm. In the (8,2)@(16,4) system, where $V_{\mathrm{loc}} = 1.4 \times 10^{-4}$ meV/atom, similar phenomena as in the (7,7)@(21,0) studied are present, including both LFS and GSS. In addition, the phenomenon reported here is not specific to the carbon nanotubes. We have also investigated other systems, such as a C_{60} molecule confined inside a car-

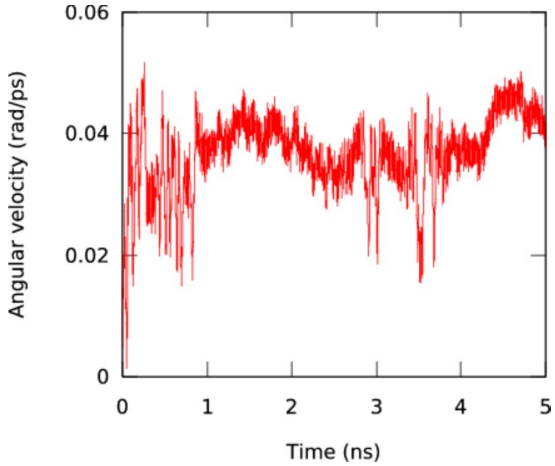


FIG. 4. (Color online) Intertube angular speed at 100 K. The angular motion of (7,7)@(21,0) is very easy to be excited because the loss of angular symmetry results in a negligible energy barrier.

bon nanotube, where similar behavior has been observed.

The large diffusion coefficient and quasi-one-dimensional nature of the DWNT system provide an approach to build nanoscale devices which can perform useful functions through intertube translation or rotation. By introducing some mechanism to offer energy, such as the time-dependent asymmetric field in the Brownian ratchet, the devices can transform kinetic energy from internal lattice vibrations into directed motion. Especially, the atomic-precision positioning and large-amplitude motion observed here satisfies the requirements[3] as a good Brownian machine well.

In summary, thermal fluctuation in DWNT-based device is investigated using molecular dynamics simulation. The atomistically smooth intertube potential surface, low mass, and thermal coupling at a certain temperature range make it possible to excite large-amplitude intertube oscillation. The oscillation observed here can operate with nanoscale precision and at high frequency on the order of 10^9 Hz. This model system has great potential in applications such as optical, medical, and memory storage devices or molecule transport channels assisted by thermal fluctuation, it may also be interesting for studies on nanoscale thermodynamics. However, experimental control and detection of the dynamical process still remain challenges.

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