Journal of
Computational and Theoretical Nanoscience
Vol. 3, 1–5, 2006

Quasi-Reversible Energy Flows in Carbon-Nanotube-Based Oscillators

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Quasi-reversible energy flows between orderly intertube axial motion and vibrational modes are studied for isolated systems of two coaxial carbon nanotubes at temperatures ranging from 300 K to 500 K. It is found that the excess intertube van der Waals energy, depleted from the intertube axial motion, is primarily stored in low-frequency mechanical modes of the oscillator for an extended period of time.

Keywords:

Multi-walled carbon nanotubes (MWNTs) have recently emerged as promising candidates for nanoscale molecular bearings, springs, and oscillators.[1–8] However, much is to be learned on mechanical properties of carbon-nanotube-based devices despite their unlimited prospects in nanomechanical applications. In addition, nanomachinery has also been proposed as a testing ground to study ergodicity and equipartition on complex energy surfaces, and energy exchanges amongst various degrees of freedom.[3,4] In the literature, coupled oscillator systems including the Fermi-Pasta-Ulam chains[9] and the Lennard-Jones lattices[10] have undergone a large number of investigations as model systems for such studies, and MWNTs are a three-dimensional extension of the often-studied Lennard-Jones chains with additional bonded interactions. Also of great importance and interest is to explore dynamics of carbon nanotubes for nanoscopic implications to fundamental hypotheses in thermodynamics. For example, the second law of thermodynamics forbids entropy reduction in an isolated, macroscopic system, but a nanomechanical device such as a carbon nanotube oscillator or bearing might violate the second law for brief periods of time despite that the probablity of such occurrences is expected to decrease exponentially with the amount of entropy reduction.[11] That the second law of thermodynamics may break down for nanomachines was well stated by Boltzmann himself: "... as soon as one looks at bodies of such small dimension that they contain only very few molecules, the validity of this theorem (the second law of thermodynamics and its description of irreversibility) must cease." It has been recently suggested[11] that sub-micrometer mechanical devices can run thermodynamically in reverse as their sizes are further miniaturized. Understanding limits of thermodynamic laws in a nanoscopic setting therefore carries great practical as well as fundamental importance.

In this study we report an interesting, counterintuitive energy-exchange phenomenon, which takes place between the orderly intertube axial oscillatory motion and mechanical modes in double-walled nanotube (DWNT) oscillators, and which is found to be *quasi-reversible*. What makes this particular form of energy exchanges appealing is that the excess intertube van der Waals energy, created by the initial inner tube extrusion, is expected to be gradually, often irreversibly dissipated into various vibrational modes in the DWNT, and at the crossroads of the energy dissipation process we encounter this quasi-reversible energy-exchange phenomenon channelling the excess intertube van der Waals energy to and from the DWNT low-frequency mechanical modes. The apparent reversibility of this particular energy-exchange form is especially interesting as the intertube axial oscillatory motion is considered to be a form of orderly motion whose revival may point to a local loss of entropy, and thus, a possible microscopic violation of the second law of thermodynamics. In a macro-sized machine, this would be entirely impossible since mechanical modes of interest have much lower frequencies and much larger amplitudes than modes comprising their

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dissipative thermal baths, and the energy flow is unidirectionally from mechanical modes to the bath. For nano- sized machines, however, useful mechanical modes, defined by the functions of the machines, are no longer clear-cut from bath modes as the amplitudes of the two are analogous. Also note that the characteristic time scale of the axial motion in a DWNT oscillator is comparable to that of low-frequency mechanical modes in the DWNT, which renders energy transfer between the two more obtainable but nonetheless intriguing.

There have been quite a number of authors who have recently performed various molecular dynamics (MD) investigations on the DWNT oscillators. Legoas et al. run MD simulations with a canonical ensemble for a variety of temperatures up to 400 K, and Rivera et al., for a temperature range from 275 to 450 K.[12, 13] Guo et al. thermally equilibrate DWNT oscillators with a bath to reach an initial temperature T_i, then switch to a microcanonical ensemble for simulations,[14] and a similar approach is used by Servantie and Gaspard fixing T_i at 300 K.[15] Similar to the nano-oscillator setup in our previous work,[3] the system is chosen to be a DWNT, one of the most elementary realizations of a nanoscale oscillator. In this work we concentrate on one particular configuration: the outer and inner tubes both chosen to be of the zigzag type, specifically, the open-ended outer tube is $(14, 0)$ with a length of 70 Å, and the capped inner tube is $(5, 0)$ with a length of 55 Å. Here we take a similar approach as that of Guo et al.[14] The geometry of the oscillator is optimized first, and the DWNT is then heated up to 300 K $\sim$ 600 K for 20 ps, and thermally equilibrated for 200 ps, prior to performing MD runs in a microcanonical ensemble. After the thermal equilibration, the inner tube is displaced by 35 Å such that the initial extrusion length of the inner tube $s = 27.5$ Å. Simulation of the DWNT oscillation is then carried out using the CHARMM force field, and various energies are calculated as a function of time. A time step of 1 fs was used for simulations reported here. Much smaller time steps, such as 0.01 fs, however, have been tried to ensure qualitative features found in the simulations are robust.

In Figure 1, the intertube axial oscillation amplitude as represented by the center-of-mass distance between two nanotubes is displayed as a function of time for up to 1000 ps. As shown in the upper (lower) panel, at the start of intertube axial oscillations the inner tube was released from an initial extrusion length of $s = 27.5$ Å after the DWNT oscillator has been heated up to 300 K (500 K), and due to pre-simulation heating and dynamic intertube roughness at atomic scales, the axial oscillation amplitude is rapidly damped in the first 500 (400) ps. As displayed in the upper (lower) panel, from $t = 500$ (400) to 800 (750) ps, the intertube axial oscillation is virtually diminished, and the excess intertube van der Waals energy is transfered to other forms of energies that are to be identified. To our surprise, from $t = 800$ (750) ps the DWNT starts to oscillate again, albeit with reduced amplitudes. We

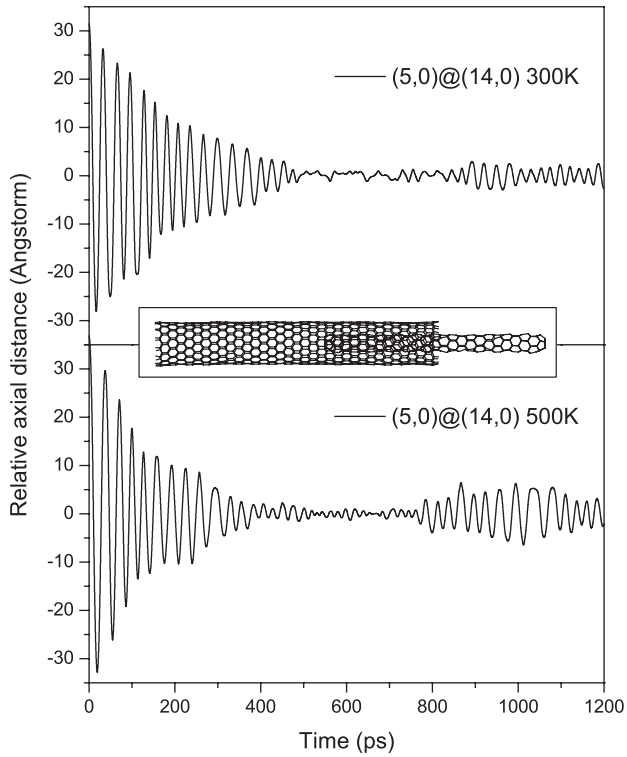

Fig. 1. The intertube axial oscillation amplitude as represented by the center-of-mass distance between two nanotubes as a function of time. Upper panel: $s = 27.5$ Å, $T_i = 300$ K. Lower panel: $s = 27.5$ Å, $T_i = 500$ K. Inset shows the DWNT oscillator.

call the period between $t = 500$ (400) ps and 800 (750) ps the hibernation period, and the time after $t = 800$ (750) ps, the revival period. Detailed examinations of the hibernated DWNT oscillator reveal the low-energy vibrational modes are peaked around 0.5 THz as shall become clearer.

Figure 2 shows a Frequency-domain analysis reveals that radial movements of a carbon atom in the center portion of the outer tube before, during, and after the hibernation period of the intertube axial oscillation. The radial movements during the hibernaion period are attributed to low-frequency vibrations of the DWNT with both tubes bending or waving. Such vibrations with resonance frequencies in the tera-hertz range have been previously reported.[16] The center portion is found to experience larger radial motion than the end portion. In the center portion of the outer nanotube, radial oscillations of carbon atoms with an approximate period of 2 ps can be found for all times, but their amplitude is most pronounced during the hibernation period implying a significant energy transfer into DWNT mechanical modes during that time period. In the insets of Figure 2, corresponding time-domain pictures are shown for the radial movements of the carbon atom located in the center portion of the outer nanotube before, during, and after the hibernation period.

In addition to the aforementioned bending-waving motion, intertube angular motion is also found in the DWNT oscillator prior to and during the hibernation

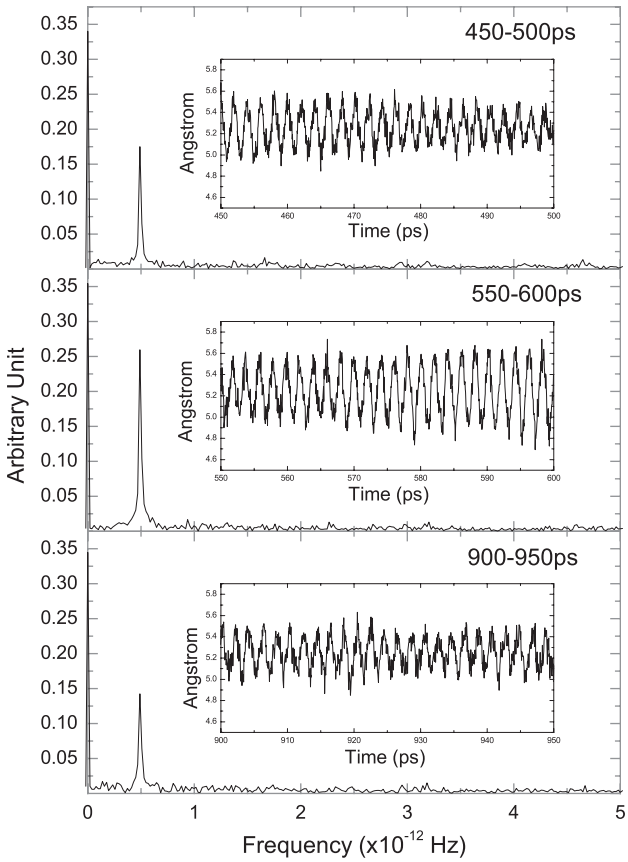

Fig. 2. Frequency-domain analysis of the radial movements of a carbon atom located in the center portion of the outer nanotube before (upper panel), during (middle panel), and after (lower panel) the hibernation period of the intertube axial oscillation. Initial extrusion $s = 27.5$ Å, and $T_i = 300$ K. Insets: corresponding time-domain pictures for the radial movements of the same carbon atom.

period. One cycle of the rotational motion lasts about 20 ps, and due to energy exchanges, the rotational speed also fluctuates. In the top panel of Figure 3, the velocity of intertube axial motion for the case of $s = 27.5$ Å and $T_i = 300$ K is shown for the first 1 ns. In comparison, the intertube relative angular velocity is displayed in the second panel in Figure 3. The relative angular velocity peaks when the hibernation period commences at $t = 500$ ps. Further proof is provided in the third and fourth panels in which the kinetic energies of the intertube axial motion and relative rotational motion are displayed, respectively. Therefore, in addition to bending-waving motion, the relative angular motion is also present in the hibernation period, and on a declining slope. At $t = 1$ ns, the intertube rotation comes to a near stop with the intertube axial motion and other low-frequency mechanical modes being the energetic beneficiaries. For longer times beyond $t = 1$ ns, our simulation shows that the hibernation period of the intertube axial motion can reappear as energies are again channelled back into the bending-waving motion and the rotational modes.

Quite different definitions of the intertube frictional force in the axial direction have been proposed for the

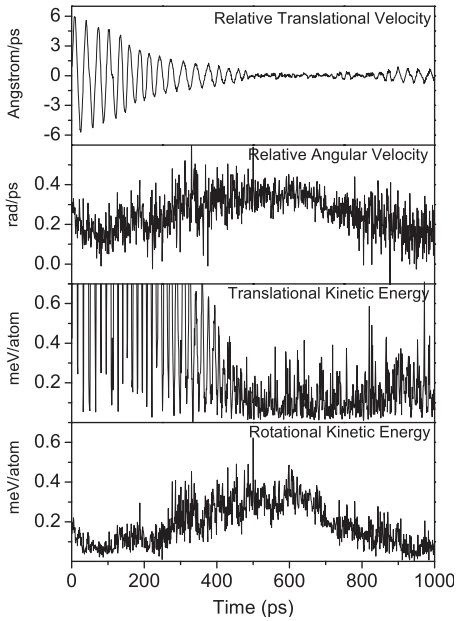

Fig. 3. The intertube axial velocity (first panel) and the corresponding kinetic energy (second panel), and the relative angular velocity (third panel) and the corresponding kinetic energy (fourth panel), are plotted for $s = 27.5$ Å, $T_i = 300$ K. The first 1000 ps of the simulation is shown.

DWNT oscillators.[3, 15, 17] For example, frictional forces can be derived from the time-dependent changes of the intertube center-of-mass velocity. Energetic considerations of the frictional force can also be contemplated in place of kinetic ones. Following our previous work,[3] here we estimate the frictional force per carbon atom from energy decay rates of the intertube axial oscillation. The outer tube has a much larger mass than the inner tube, and therefore, by the conservation of the system momentum, the speed of the inner tube can be a rough estimate of the intertube speed. For $s = 27.5$Å and $T_i = 300$ K, the average velocity of the inner tube from $t = 0$ ps to 450 ps is 1.9 Å/ps, and the frictional force estimated for the same time period is about 1.8×10^{-14} N per atom. However, starting from the hibernation period, due to the transfer of energy stored in the vibrational-rotational modes back to the intertube axial oscillation, the frictional force thus estimated between 600 and 1000 ps is -1.7×10^{-17} N per atom. "Negative friction" is a direct result of quasi-reversible energy exchange in the DWNT oscillator system. Such a perception of course rests on seeing the axial intertube oscillation as the sole useful mode in the nano device. Under alternative circumstances, such as in a carbon nanotube bearing, other forms of friction may be defined. Reversible energy transfers between the intertube axial motion and low-frequency mechanical modes, such as the intratube bending-waving and rotational modes, reveal difficulties for a classical system of a miniature size to relax expeditiously to an equipartition state.

Simulations on an armchair DWNT oscillator with a $(7, 7)$ inner tube and a $(12, 12)$ outer tube have also been

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performed. Incomplete hibernation of the intertube axial motion has been found in which the oscillatory translational motion is significantly reduced while its energies are transferred into various low-energy mechanical modes in the armchair DWNT oscillator. But unlike in the zigzag DWNT oscillator, for the armchair DWNT oscillator energies have largely gone into relative rotational modes from the partially hibernated intertube axial motion. As the oscillator recovers from the partial hibernation of its intertube axial motion, the relative rotation slows down and is depleted of energies. Efforts have also been made to study DWNT oscillators of other chirality combinations, and similar results are found. This points to the universality of the inter-mode energy transfers amongst low-frequency mechanical modes of the DWNT oscillators, intertube axial motion included, regardless of chiralities of their composing SWNTs.

Our calculations on $(5,0)/(14,0)$, $(7,7)/(12,12)$ and other DWNT oscillators reveal that a DWNT oscillator with thousands of degrees of freedom can be reduced to a simple system with a few most relevant degrees of freedom in the presence of a thermal bath. Those few degrees of freedom correspond to several important low-frequency mechanical modes such as intertube axial oscillation, intertube rotation and bending-waving modes while the thermal bath is made of other higher-frequency vibrations of the nanotube. When the energy leakage from the reduced system to the bath is slow enough, quasi-reversible energy exchanges take place between the oscillator and the bending-rotational modes.

Orderly intertube axial movements of the DWNT oscillator are supposedly dissipated by frictional effects into disorderly phonons. Evoking the second law of thermodynamics, this process irreversibly increases the system entropy. However, what has been witnessed here is that it may be possible that carbon nanotube oscillators can go thermodynamically in reverse, and at the crossroad of the dissipation process, quasi-reversible energy exchanges can take place between the orderly intertube axial oscillation and low-frequency DWNT mechanical modes. To extend the thermodynamic description to the nanooscillator, we choose the DWNT oscillation amplitude as the thermodynamic quantity that defines the state of the system. Other degrees of freedom specify thus the detailed microscopic states of the oscillator. For a given oscillation amplitude, the number of the accessible microscopic states provides a measure of the system entropy. A quantitative analysis of the DWNT entropy may be carried out following an established method of Goddard and coworkers.[18] The velocity autocorrelation functions during and after the hibernation period have been computed[19] after removing the cente-of-mass velocities of both nanotubes. For instance, at $T_i = 500$ K, the velocity autocorrelation fucntions are evaluated for the periods between 500 ps and 700 ps and between 800 ps and 1000 ps. The Fourier transformations of the two autocorrelation functions are found to be strickingly similar, i.e., the accessible states during the two periods are almost the same. This shows that the degrees of freedom inside the nanotube oscillator minus the intertube axial oscillation can be treated in a quasi thermal equilibrium, and their contribution to the DWNT entropy can be evaluated by partitioning the DWNT into a solid phase and a gas phase[18] and by taking into account the minute temperature difference, about 1.36 K, between the two time periods. Excluding the intertube axial motion, the DWNT oscillator possesses an entropy of $2456.7k_B$ ($2449.7k_B$) during (after) the hibernation period. The entropy contribution from the remaining degree of freedom, the axial motion, can be calculated by employing the particle-in-a-box model

$$S_{\text{axial}} = \frac{k_B}{2} + k_B \ln \frac{L}{\Lambda} \tag{1}$$

where k_B is the Boltzmann constant, L is the maximum separation between centers of mass of the two nanotubes during oscillation, and $\Lambda = h(2\pi\mu k_B T)^{-1/2}$ with h the Planck constant and μ the reduced mass of two nanotubes. The oscillation amplitudes for the hibernation period and revival period are 1.0 Å. and 7.9 Å, respectively, giving an entropy increase of about $2.0k_B$ from the axial motion. Summing up the two contributions, the DWNT oscillator is found to undergo an entroy reduction of $5.0k_B$ as its axial oscillation reemerges after the hibernation period.

In the literature dynamical behavior of identical particles interacting via the Lennard-Jones potential has been examined[20] with the aim of investigating the characteristics of the classical phase space of coupled oscillators. DWNTs are in fact an extension of the two-dimensional Lennard-Jones model to a practical, three-dimensional construct with additional bonded interparticle interactions. Revelations and feedbacks from studies of statistical mechanics, in turn, can also help design nanoscale mechanical devices. As conjectured by Sokoloff,[21] a transition from frictional behavior to nearly frictionless sliding would occur as the size of the system decreases beyond a critical value. This opens up the possibility of nearly frictionless and super-efficient nanoscale molecular oscillators with practically no dissipation of the oscillator energies for a prolonged period of time. What has been witnessed in this work is an intermediate case between the macroscopic system in which ergodicity holds and a nanoscale system in which Sokoloff's conjecture can be realized.

Acknowledgments: Authors thank Bill Goddard, Martin Grant, and David Ronis for stimulating discussions. Support from the Hong Kong Research Grant Council (HKU 7012/04P and HKU 7056/01E), the Committee for Research and Conference Grants (CRCG) of University of Hong Kong, the China National Science Foundation and the China 973 Project, and US National Science Foundation through Grant No. CMS-0140568, is gratefully acknowledged.

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Received: 28 January 2006. Accepted: 1 March 2006.