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Author(s)	Zhao, Yang; Ma, Chi Chiu; Wong, Lai Ho; Chen, Guan Hua; Xu, Zhiping; Zheng, Quan Shui; Jiang, Qing; Chwang, Allen T.
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Energy exchanges in carbon nanotube oscillators

Yang Zhao[1], Chi-Chiu Ma[1], Lai-Ho Wong[1], GuanHua Chen[1], ZhiPing Xu[2], QuanShui Zheng[2], Qing Jiang[3] and Allen T Chwang[4]

[1] Department of Chemistry, University of Hong Kong, Hong Kong, People's Republic of China

[2] Department of Engineering Mechanics, Tsinghua University, Beijing 100084, People's Republic of China

[3] Department of Mechanical Engineering, University of California, Riverside, USA

[4] Department of Mechanical Engineering, University of Hong Kong, Hong Kong, People's Republic of China

E-mail: ghc@everest.hku.hk and zhengqs@tsinghua.edu.cn

Abstract

Energy exchanges between orderly intertube axial motion and vibrational modes are studied for isolated systems of two coaxial carbon nanotubes at temperatures ranging from 300 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. This constitutes the first computer simulation of a nanomechanical device that exhibits negative friction.

Concentric cylindrical carbon nanotubes have been recently proposed, and intensively studied, as promising candidates for nanoscale molecular bearings, springs, and oscillators [1–5]. Performance and load-bearing properties of fundamental components of nanomachines have yet to be understood despite their unlimited application prospects. In addition, nanomachinery has also been suggested to serve as a test bed for ergodicity and equipartition on complex energy surfaces, and energy exchanges amongst various degrees of freedom [3]. In fact coupled oscillator systems have undergone a large number of investigations as model systems for such studies. Half a century ago, Fermi, Pasta, and Ulam (FPU) reported the first numerical study [6] on a chain of coupled oscillators with quartic anharmonicity. It was found in their celebrated FPU model that, if the energy is below a certain threshold and initially resides in a few low-frequency modes, equipartition of energies among all modes will take an extremely long time to be attained [6, 7]. Seemingly contrary to the equipartition hypothesis, a persistent recurrence to the initial conditions in the FPU chain is often found, and inadequate thermalization in FPU chain poses difficulties in defining quite a number of thermodynamic quantities including the temperature and the specific heat. Nano-oscillators composed of two coaxial carbon nanotubes extend the one- and two-dimensional Lennard-Jones model to a practical three-dimensional construct with additional bonded interparticle interactions, where intra-oscillator energy exchanges offer new avenues for

investigating equipartition processes in a realistic, nanoscale setting.

We report in this study 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. What makes this particular form of energy transfer 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 such a particular form of energy exchanges between the excess intertube van der Waals energy and DWNT low-frequency mechanical modes that allow energies to flow back and forth between them. In a macrosized machine, this would be entirely impossible since mechanical modes of interest have much lower frequencies and much larger amplitudes than modes comprising their dissipative thermal baths, and the energy flow is unidirectionally from mechanical modes to the bath. For nanosized 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 timescale 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.

Legoas *et al* run molecular dynamics (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 [8, 9]. 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 [10], and a similar approach is used by Servantie and Gaspard fixing T_i at 300 K [11]. Similar to the nano-oscillator set-up 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 an approach similar to that of Guo *et al* [10]. The geometry of the oscillator is optimized first, and the DWNT is then heated up to 300–600 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 centre-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 had 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 transferred 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 call the period between $t = 500$ (400) ps and 800 (750) ps the hibernation period, and the time after $t = 800$ (750) ps, the awakening period. Detailed examinations of the hibernated DWNT oscillator reveal the low-energy vibrational modes are peaked around 0.5 THz as will become clearer.

Figure 2 shows a frequency-domain analysis of the radial movements of a carbon atom in the centre portion of the outer tube before, during, and after the hibernation period of the intertube axial oscillation. The radial movements during the hibernation period are attributed to low-frequency vibrations of the DWNT with both tubes bending or waving. Such vibrations with resonance frequencies in the terahertz range have been previously reported [12]. The centre portion is found to experience larger radial motion than the end portion. In the centre portion of the outer nanotube, radial oscillations of carbon atoms with an approximate period of 2 ps can be found for all three time periods, 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 centre 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 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 DWNT oscillators [3, 11, 13]. For example, frictional forces can be derived from the time-dependent changes of the intertube centre-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 $t = 0$ to 450 ps is 1.9 Å ps^{-1}, 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/atom. 'Negative friction' is a direct result of the energy exchanges in the DWNT oscillator system. Such a perception of course rests on seeing the axial intertube oscillation as the sole useful mode in the nanodevice. Under alternative circumstances, such as in a carbon nanotube bearing, other forms of friction may be defined. Energy transfer between the intertube axial motion and low-frequency mechanical modes, such as the intratube bending–waving and rotational modes, reveals difficulties for a classical system of a miniature size relaxing 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 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 for 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 intermode 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, the energy exchange takes place between the oscillator and the bending–rotational modes. A sketch of the reduced phase space is shown in figure 4 depicting energy transfers amongst three quasi-stable regimes. The three quasi-stable regimes are linked to form a reduced system that allows energy exchanges amongst them but otherwise prohibits a rapid thermal equilibration from taking place. An interesting feature of this reduced system is that the energy exchanges amongst quasi-stable modes are statistical in nature, unlike those in an isolated mechanical system with a few degrees of freedom. The reduced system depicted in figure 4 can thus be a stable, yet flexible one with ample complexities. A (short for regime A) in figure 4 represents the phase space region corresponding to the axial oscillation, B for the bending–waving motion, and C for the rotational motion. The bending–waving motion that appears during the hibernation period consists of several collective bending and waving modes, while the rotational motion in the same period corresponds to modes with a continuous distribution of frequencies and includes also small-amplitude librations. Significant changes take place in energy transfer between different modes as one moves from macrosized to nanosized oscillators. For nanosized machines, the mechanical mode of interest, such as the axial oscillation of the DWNT oscillator,

becomes indistinguishable in both frequency and amplitude from modes considered to be part of the dissipative thermal bath. As a result of energy exchanges between the two, the mechanical mode of interest can be revived encountering the so-called negative frictional behaviour. For macrosized machines, however, mechanical modes of interest have much lower frequencies and much larger amplitudes than modes comprising dissipative thermal baths. Therefore, the back-and-forth energy flow between mechanically useful modes and dissipative bath modes does not occur in macrosized machines [14].

In the literature dynamical behaviour of identical particles interacting via the Lennard-Jones potential has been examined [15] with the aim of investigating the characteristics of the classical phase space of coupled oscillators. DWNTs discussed here are an extension of the Lennard-Jones model. Revelations and feedbacks from studies of statistical mechanics, in turn, can also help design nanoscale mechanical devices. As conjectured by Sokoloff [16], a transition from frictional behaviour 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 superefficient 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 a case intermediate between the macroscopic system in which ergodicity holds and a nanoscale system in which Sokoloff's conjecture can be realized.

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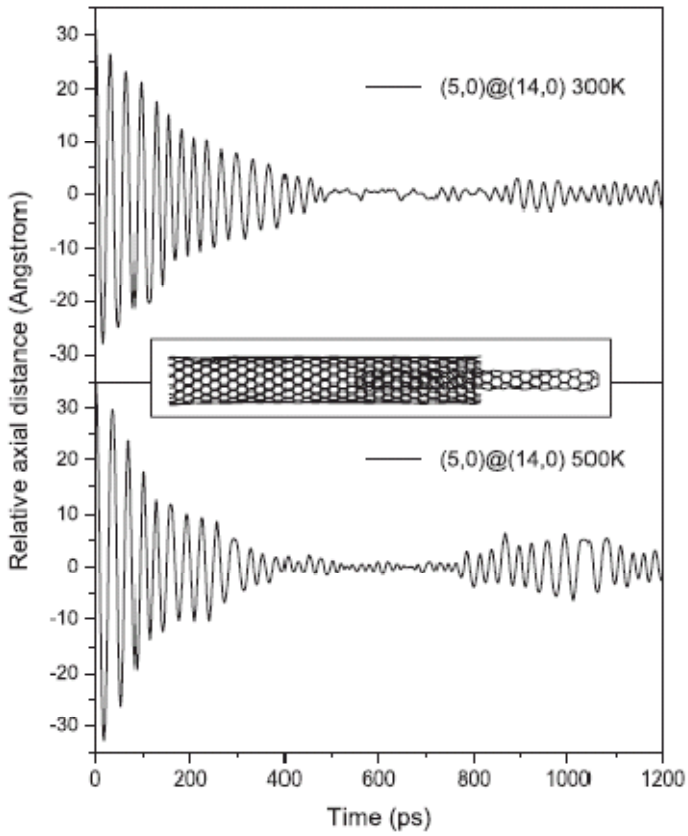
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(5,0)@(14,0) 500K
Relative axial distance (Angstrom)
Time (ps)
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20
10
0
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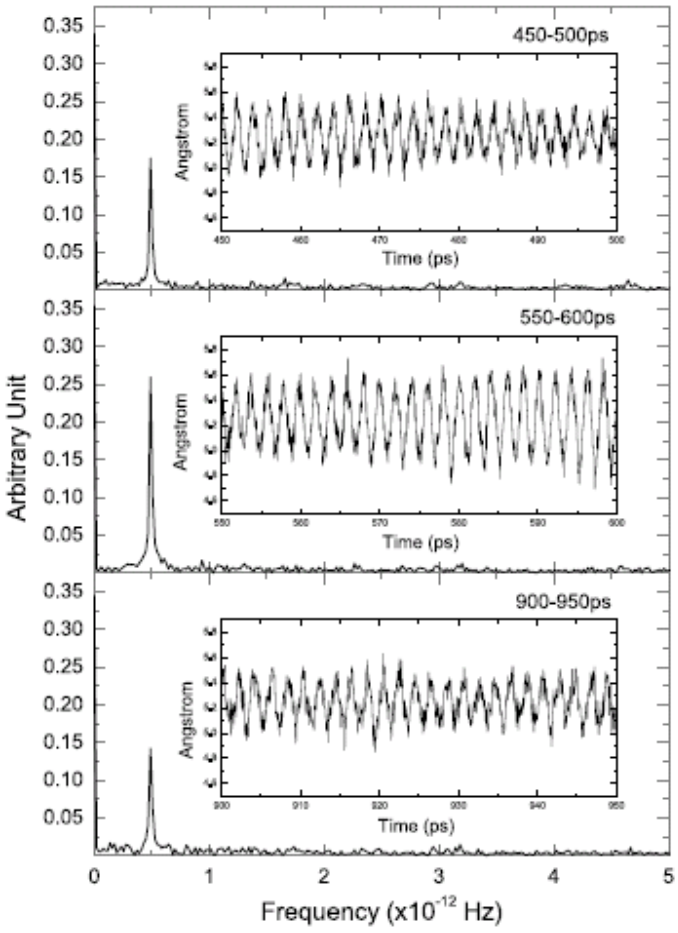
0
200
400
600
800
1000
1200

Fig. 1.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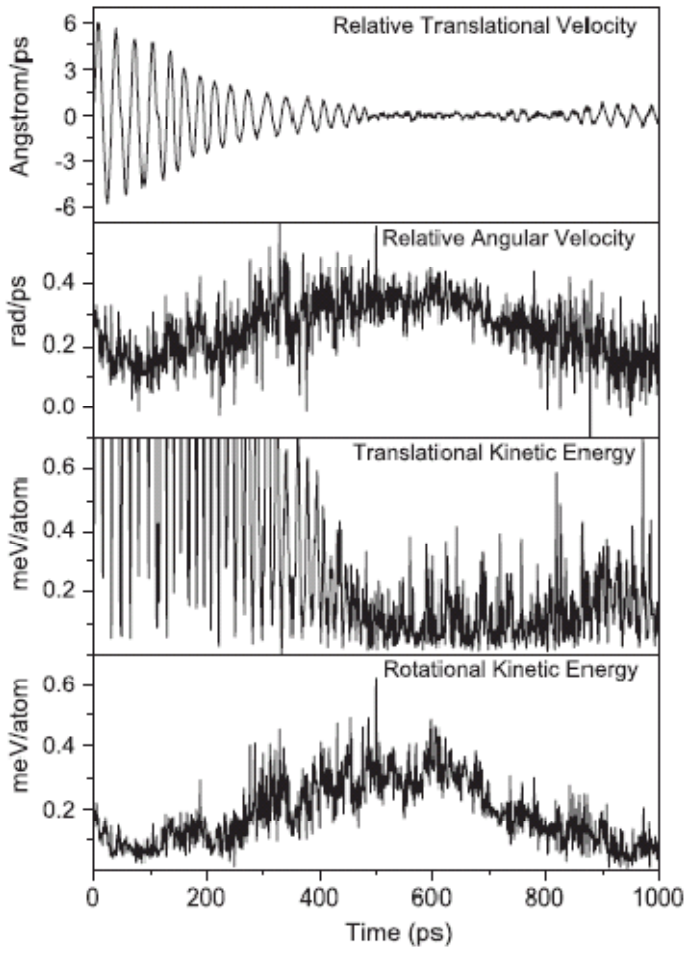
Angstrom
Time (ps)
Arbitrary Unit
Frequency (x10^{-12} Hz)

Fig. 2.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0
-3
-6
Relative Angular Velocity
rad/ps
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0.2
0.0
Translational Kinetic Energy
meV/atom
0.6
0.4
0.2
Rotational Kinetic Energy
meV/atom
0.6
0.4
0.2
0
200
400
600
800
1000
Time (ps)

Fig. 3.

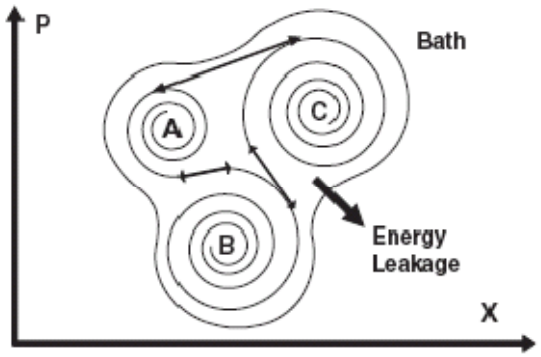

Fig. 4.