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Energy Dissipation Mechanisms in Carbon Nanotube Oscillators

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Energy transfer from the translational degrees of freedom to phonon modes is studied for isolated systems of two coaxial carbon nanotubes, which may serve as a nearly frictionless nano-oscillator. It is found that for oscillators with short nanotubes (less than 30 Å) a rocking motion, occurring when the inner tube is pulled about 1/3 out of the outer tube, is responsible for significant phonon energy acquisitions. For oscillators with long nanotubes translational energies are mainly dissipated via a wavy deformation in the outer tube undergoing radial vibrations. Frictional forces between 10^{-17} and 10^{-14} N per atom are found for various dissipative mechanisms.

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Multiwalled carbon nanotubes (MWNTs) have been proposed as candidates for nanoscale molecular bearings, springs, and oscillators [1–3]. Zheng and Jiang have estimated that these nano-oscillators can have frequencies far beyond 1 GHz, pointing to a path for creating nanomachines operating in the gigahertz range [3], which has been viewed as one of the milestones on the road map of molecular manufacturing [4,5]. Despite unlimited prospects of applications for low-friction nanobearings, nanosprings, and nano-oscillators, performance, wear and load-bearing properties of fundamental components of nanomachines are largely not understood. We investigate in this Letter possible scenarios for realizing nearly frictionless and superefficient nano-oscillators. Our aim is to provide an understanding of nanoscale motion-induced heating mechanisms and to propose means for reducing frictional effects that hinder oscillator performance and efficiency.

The friction phenomenon, or the energy dissipation between two contacting parties which slide with respect to each other, is in general taken to denote the conversion of orderly translational energies into disorderly vibrational energies. In this Letter, using molecular dynamics (MD), double-walled carbon nanotube (DWNT) oscillators of various lengths and constructions are compared for their oscillation resilience under motion-induced self-heating. We show that friction in these oscillators is primarily associated with an off-axial rocking motion of the inner nanotube and a wavy deformation of the outer nanotube, which may or may not occur, depending upon both configurations of individual oscillators and initial system energies, and that oscillation is nearly frictionless in the absence of the rocking motion and the wavy deformation.

Our model DWNT has an inner tube and an outer tube of chiralities $(5, 0)$ and $(8, 8)$, respectively, and an intertube spacing ~ 3.4 Å, which is also the spacing between adjacent sheets in graphite. Both ends of the outer wall are open and those of the inner wall are closed. Structure optimization and simulation of the two-tube oscillators

are carried out using the CHARMM force field [6]. A time step of 1 fs is used for all simulations. A precise description of interactions between graphene sheets may include interlayer electronic delocalization [7], although the van der Waals forces are dominant for our purpose here. To check the accuracy of the force field, the radial breathing mode frequency of an $(8, 8)$ carbon nanotube is calculated to be 232 cm^{-1} in good agreement with that from observed Raman lines, 211 cm^{-1} [8]. We define the relative kinetic energy of two tubes

$$K_{\mathrm{rel}}(t) \equiv \sum_i \frac{1}{2} m_i |\mathbf{v}_i^{\mathrm{in}} - \mathbf{v}_{\mathrm{ave}}^{\mathrm{in}}|^2 + \sum_j \frac{1}{2} m_j |\mathbf{v}_j^{\mathrm{out}} - \mathbf{v}_{\mathrm{ave}}^{\mathrm{out}}|^2,$$

where $\mathbf{v}_i^{\mathrm{in}}$ ($\mathbf{v}_j^{\mathrm{out}}$) and m_i (m_j) are the velocity and the mass of the ith (jth) atom in the inner (outer) tube, respectively; $\mathbf{v}_{\mathrm{ave}}^{\mathrm{in}}$ ($\mathbf{v}_{\mathrm{ave}}^{\mathrm{out}}$) is the average atomic speed of the inner (outer) tube. $K_{\mathrm{rel}}(t)$ is a direct measure of the intratube temperature, i.e., an indicator of heat transfer from the orderly translational motion.

In the optimized structure the inner and outer tubes share a common center of mass. At the beginning of the simulation, $t = 0$, the inner tube is pulled out of the outer tube along their common axis, with an initial extrusion length s. The inner tube is then released with zero initial speed. We first simulate a configuration, in which the inner and outer tubes are of the same length 14.5 Å, referred to as the short-tube combination, and the calculated $K_{\mathrm{rel}}(t)$ is shown in Fig. 1(a) for three initial extrusion lengths, $s = 5$, 10, and 12 Å.

For $s = 12$ Å, about 0.17 eV of energy is transferred into $K_{\mathrm{rel}}(t)$ within initial 5 ps which coincides with the time it takes for the inner tube to travel from one side to the other, and the inner tube follows then a stable axial trajectory as shown in inset (A) of Fig. 1(a). The high-frequency oscillations of $K_{\mathrm{rel}}(t)$ correspond to the phonon frequencies in the two tubes. During the time period from the 20th to the 40th ps, the system undergoes a significant transition, in which the phonons acquire a large portion of the initial energy from the translational degree of
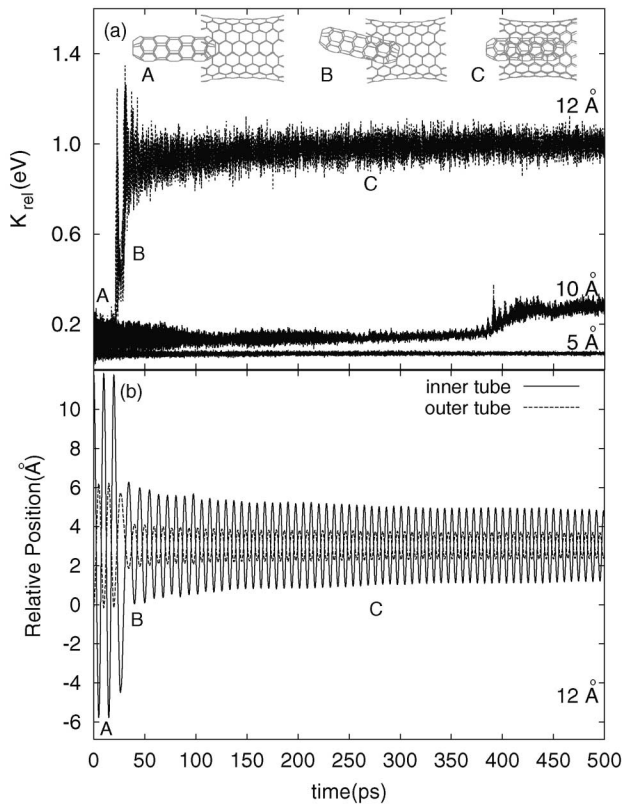
FIG. 1. (a) Calculated $K_{\text{rel}}(t)$ for short-tube oscillators (14.5/14.5 Å): three values of $s = 5$, 10, 12 Å. Configurational graphs are drawn for (A) before the onset of the rocking motion (B) during the rocking motion (C) after the rocking motion. All except for $s = 5$ Å, portions of translational energies are transferred into $K_{\text{rel}}(t)$ within 400 ps from the start of the simulation. (b) The center of mass displacements of two nanotubes for $s = 12$ Å: solid line: inner tube; dashed line: outer tube. The frequency of translational oscillations long after the leap of acquired phonon kinetic energies is about 140 GHz.

freedom, and approximately 1 eV of orderly translational energies are thus transferred into $K_{\text{rel}}(t)$. After the transition, the system settles into another stable dynamic process in which $K_{\text{rel}}(t)$ is approximately constant within a fluctuation amplitude of 0.17 eV. This implies that the oscillator reaches a sustained nearly frictionless translational motion after initial energy dissipation.

For a detailed examination, we now follow the dynamics of the oscillator from the beginning of the simulation. We find the atoms start to vibrate instantaneously after $t = 0$, mostly within the individual walls of the two tubes, because of the limited residue interaction between the two tubes. Since the interaction is rather small, the oscillator settles quickly into a metastable axial motion after an initial $K_{\text{rel}}(t)$ acquisition of ~ 0.17 eV. This metastable dynamics is interrupted by a form of rocking motion of the inner tube [cf. inset (B) of Fig. 1(a)], i.e., off-axial movements which create radial intertube collisions and

hindrance to the translational oscillation. After many simulations, we find that for large initial extrusions, the rocking motion occurs most preferably when the inner tube is at the positions of maximum extrusions. At these positions, the energy surface for the inner tube is rather flat with respect to the small deviations from the axial position $\theta = 0$ with θ being the angle between the axes of the two nanotubes (for $s = 10$ Å, e.g., the range of the energy variation is about 9.3 meV for $|\theta| < 2°$), while the free energy G ($G = E - TS$) at the temperature T peaks at $\theta = 0$ as the overall entropy increases quadratically with the deviation angle θ. It follows that the rocking motion of the inner tube would occur upon slight thermal fluctuations at those positions of maximum extrusions because at finite temperatures the most probable conformation of the oscillator is determined by the free energy G (not the energy E). On the other hand, contrary to the case of large initial extrusions, if the inner-tube extrusion length is short enough, the free energy G has instead a minimum at $\theta = 0$ due to a steep energy surface (e.g., for $s = 5$ Å, an energy variation of 0.23 eV is found for $|\theta| < 2°$). Therefore, in order for the rocking motion to occur, the inner-tube extrusion length has to exceed a threshold which is to be determined. The rocking motion introduces radial movements of the inner tube with respect to the outer tube and, thus, excites a large number of phonons in the system. This rocking motion instability, however, is self-mitigating as it creates phonons and reduces the overall amplitude of the radial movements. The negative feedbacks suppress the rocking motion, and correspondingly, the two-tube oscillator reaches a new quasiequilibrium where orderly radial motion dissipates completely into thermal vibrations [cf. inset (C) of Fig. 1(a)]. It is remarkable that such a quasiequilibrium can be sustained for a long time with relatively little frictional effects between the nanotubes. The above picture is further supported by Fig. 1(b) where we plot the trajectories of the centers of mass for the inner (solid line) and outer (dashed line) tubes. The amplitude of oscillation drops drastically after a few periods due to the rocking motion, and after that, it decreases much more slowly.

For $s = 5$ Å, no rocking motion appears, and the system maintains translational oscillation with little frictional effects, while for $s = 10$ Å, an increase of $K_{\text{rel}}(t)$ preceded by a rocking motion occurs after 380 ps, as shown in Fig. 1(a). An important quantity here is the threshold s_c of the initial extrusion length at which the rocking mode kicks in. Simulations with different values of s have been performed, and s_c is found to be at 30%–40% of the total tube length. Below this threshold s_c, the rocking motion [cf. inset (B) of Fig. 1(a)] is suppressed because it is energetically unfavorable, and above s_c, the initial metastable motion [cf. inset (A) of Fig. 1(a)] is unstable with respect to the rocking motion due to the entropic effect.

The short-tube combination examined above has a relatively small system size, consisting of a few hundreds of atoms. To further explore the configurational cause of frictional effects, we now examine a long-tube combination in which the outer tube has a length of 70 Å, and the inner, 55 Å. There are altogether 1242 carbon atoms in the long-tube combination (about 4 times larger than the short-tube combination), and our simulations indicate that the s_c threshold for the long-tube combination is between 14% to 21% of the inner-tube length. If the initial extrusion exceeds this value, for example, $s = 27.5$ Å, a significant transfer of the translational energy into intra-tube vibrations takes place, as shown in Fig. 2(a). Our simulations reveal that the translational motion is further damped in the case that the length of the inner tube is longer than or comparable to the wavelength of a wavy deformation, which is found to be 30 Å [see the inset of Fig. 2(a) for a demonstration of the outer-tube wavy deformation]. On the contrary, in the case that the inner tube is much shorter (for example, 14.5 Å), and thus it can move freely to adjust to the movements of the much longer outer tube, the translational motion is not damped by the wavy deformation of the outer tube. $K_{rel}(t)$ for a mixed-tube oscillator with a 70 Å outer tube and a 14.5 Å inner tube is shown in Fig. 2(b). The initial extrusion length is set to be $s = 12.25$ Å, and a leap of the phonon kinetic energies preceded by the rocking motion takes place, approximately, after 300 ps. Further evidence of damping caused by the wavy deformation of the outer tube is provided by a simulation using the long-tube combination, in which the atoms of the outer tube are all fixed in space. In this run, a leap of the phonon kinetic energies takes place shortly after the simulation begins with an initial extrusion length $s = 55.5$ Å, and after the leap, the system settles into the metastable translational motion, which appears nearly frictionless, as shown in Fig. 2(b). This phenomenon is, in principle, the same as that of the short-tube combination without fixing any atoms [cf. Fig 1(a)]. In comparison, $K_{rel}(t)$ calculated without freezing the atoms in the outer tube is also displayed in Fig. 2(b). This demonstrates that the dissipative effect of the rocking motion is overshadowed, in the long-tube combination, by that of the wavy deformation, and that the latter can be suppressed by selecting a short inner tube or by freezing the atoms of the outer tube. If the initial extrusion length is smaller than the threshold s_c, or the initial energy is sufficiently low, for example, $s = 7.5$ Å, our simulations show that the rocking motion of the inner tube does not occur and neither does the wavy deformation of the outer tube. As a result, the oscillation encounters virtually no heating and is nearly frictionless, as shown in Fig. 2(a).

The frictional force per carbon atom can be estimated from the energy dissipation rate. From Fig. 1(b), we determine that the average velocity of the inner tube from $t = 150$ to 500 ps is 1.4 Å/ps. Consequently, the
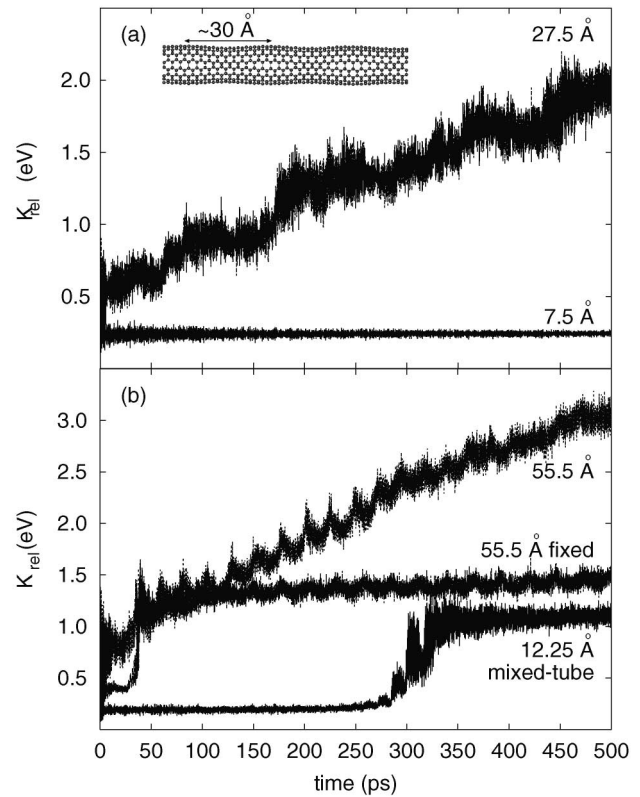

FIG. 2. (a) Calculated $K_{rel}(t)$ for long-tube oscillators (70/55 Å): two values of $s = 7.5, 27.5$ Å. Inset: a demonstration of the wavy deformation in the outer tube. The wavelength is 30 Å. (b) Comparison of $K_{rel}(t)$ with and without freezing the atoms in the outer tube for $s = 55.5$ Å. The frequency of the wavy deformation of the outer tube is found to be about 2 terahertz. The 40 GHz modulation in the $K_{rel}(t)$ corresponds to twice the frequency of the translational oscillation. A third curve near the bottom with a steplike jump near 300 ps is the calculated $K_{rel}(t)$ for a mixed-tube oscillator (70/14.5 Å) with an initial extrusion length $s = 12.25$ Å.

frictional force estimated for the same time period is about 2×10^{-15} N per atom. For the long-tube combination (70/55 Å) and $s = 55.5$ Å, the average velocity between 150 and 500 ps is 4.4 Å/ps, and the average frictional force is 1×10^{-14} N per atom. For long-tube combinations (70/55 Å) and $s = 7.5$ Å, no rocking motion or wavy deformation is present. The decay rate of translational energies is about 400 times smaller than that for $s = 55.5$ Å, and the corresponding velocity is 2.2 Å/ps. The frictional force is then estimated to be about 2×10^{-17} N per atom. The wavy deformation, while boosting frictional effects by 3 orders of magnitude, only slightly alters the intertube normal forces of $\sim 10^{-10}$ N per atom because the intertube distance is beyond the repulsive wall. Cumings and Zettl [2] estimated from their measurements that static (dynamic) frictional force associated with the sliding of the core against the outer shells of an MWNT is less 2.3 (1.5) $\times$ 10^{-14} N per atom. In a study of sliding between nested

shells of MWNTs [9] Yu *et al.* estimated a frictional force of 1.4×10^{-15} N per atom by pulling an inner tube out of an outer nanotube extremely slowly. We note that Cumings and Zettl excluded the oscillatory motion in their estimates, and that the estimate of Yu *et al.* was based upon a quasistatic process. We also note some recent atomic-scale frictional force measurements on conventional materials, which have yielded values 3 orders of magnitude greater [10] than the estimates of Cumings and Zettl.

The Kolmogorov-Arnold-Moser (KAM) theory states that there exists a critical value of a small perturbation which determines the boundary of motion stability [11]. For DWNT oscillators motion stability exists for low system energies, and the onset of instability is found to be initiated by an inner-tube rocking motion or by a wavy deformation underlaid by the radial vibrations of the outer tube. In general, the phase space of a classical system of coupled oscillators can be decomposed into regions of very different dynamical properties separated by boundaries corresponding to various energy thresholds. If the system energy is very close to a local energy minimum, the KAM regime, ordered or quasiperiodic motion should be found. This may be utilized in the design of nearly frictionless nanomechanical devices. On complex energy surfaces as is the case here, stochastic motion appears as the energy is much higher than the minimum.

Similar to the nano-oscillators, low-friction and superdurable nanobearings can also be contemplated. Consider a DWNT, the inner wall of which rotates with respect to the outer wall at a constant rate, driven by an external torque. Simulations on the nanobearings have been carried out by Tuzun *et al.* [1]. Among their findings, drag coefficients, which display size, velocity, and temperature dependencies, are shown to be small only if the atoms in the outer tube are frozen. This is in agreement with our results with frozen outer tubes. Legoas *et al.* have performed MD simulations [12] on DWNT oscillators as proposed by Zheng and Jiang. They reported that for certain values of intertube spacings, such as that between $(9, 0)$ and $(18, 0)$ tubes, there is sustained oscillatory behavior, while for other tube combinations a much higher phonon conversion rate is found. Their claim that no frictional force was present can be attributed to the fact that they fixed atomic positions in the outer tube. Compared with the work of Legoas *et al.* [12], our simulation shows a noncoaxial instability with resonance frequencies in the terahertz range [13]. The motion-induced heating process occurs as inner-tube extrusion lengths exceed s_c, and dissipation via off-axial rocking motion or a wavy deformation in the outer-tube sets in. Similar dissipation mechanisms via off-axial rocking motion are also found in a different oscillator configuration in which the outer tube has one end capped and the other end open, and the inner tube has both ends capped. However, due to the impact incurred when the inner tube reverses directions at the capped sleeve end, the rate of decay of the translational energies is found to be 2 times greater compared with uncapped oscillators under similar conditions.

In the literature, coupled oscillator systems are usually used for investigating energy exchange among various degrees of freedom, ergodicity on energy surfaces, and equipartition as systems relax. Fermi, Pasta, and Ulam reported the first numerical study on a chain of coupled oscillators with quartic anharmonicity [14]. Nano-oscillators discussed here can therefore serve as a test bed for ergodicity and equipartition on complex energy surfaces. Work in this direction is in progress.

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