Multiwalled Carbon Nanotubes as Gigahertz Oscillators

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The retraction energy of a multiwalled carbon nanotube with an extruded core causes the core to oscillate with respect to its fully retracted position where the van der Waals potential energy is minimized. This phenomenon, together with the available nanotechnology, leads to the creation of nanomechanical systems of operating frequency up to several gigahertz.

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Cumings and Zettl [1] recently reported an ideal low-friction and low-wear bearing carved out of a multiwalled carbon nanotube (MWNT) with diameter of a few tens of nanometers. They opened one end of the outer shells and attached a movable nanomanipulator to the core shells in a high-resolution transmission electron microscope, and thus they were able to study the bearing properties of this system by pulling the core out and pushing it into the outer shells. They conclude that the intershell resistance force against sliding of the core is negligibly small from their observation that the extruded core, after released, quickly and fully retracted inside the outer shells due to the restoring force of the van der Waals interaction acting on the extruded core shells. What they have demonstrated in this experiment has profound implications on the path to create various nanomechanical systems operating beyond one gigahertz which has been viewed as one of the milestones in the roadmap of molecular manufacturing [2,3]. There have been continuing efforts in fabricating micromechanical oscillators or resonators using the micromachining techniques, but the gigahertz range is beyond the reach of micromachining. With the nanotechnology capability demonstrated by Cumings and Zettl, one can create a molecular oscillator of frequency up to several gigahertz.

For the setting in the experiment of Cumings and Zettl, the core shells are expected to have a certain amount of kinetic energy at the fully retracted position where the van der Waals energy is minimized, and therefore the core would pass over this position in its retracting motion. The core should be subjected to a repulsive force as soon as it passes the position of minimum potential energy and thus the motion will be reversed, causing the core to extrude again. This leads the core to oscillate with respect to the position of minimum van der Waals energy. For the simplicity of studying the characteristics of such an oscillator, we first consider the setting schematically depicted in Fig. 1 in which both ends of the outer shells are open. The only difference of this setting from that of Cumings and Zettl is that the core would extrude from the opposite end after it passes over the position of minimum potential energy where the restoring force reverses its direction to decelerate the motion and then to reverse the motion after the core reaches the maximum extrusion from the opposite end. Thus, the core oscillates with respect to the fully retracted position where the van der Waals potential energy is minimized and the kinetic energy has its maximum.

To determine the characteristics of this oscillator and their dependence upon the physical and geometrical parameters, we have calculated the excess van der Waals potential energy U between the outer shells and the core shells due to extrusion:

$$U(x) = -\frac{4\pi\sqrt{3}\,D\zeta\Pi}{9a^2}\,x\,,$$

where $a = 0.142$ nm is the carbon-carbon bond length, D is the diameter of the core, and x is the separation of the centers of the core and the outer shells, measuring the effective extrusion. We denote by $-\Pi$ the van der Waals energy between a carbon atom on a single-shell core and all the carbon atoms of the outer shells. Because the energy depends upon the position of this atom relative to the closest hexagonal (lattice) unit of the outer shell [4], we take $-\Pi$ to be the average of the energy among all the possible positions of such an atom relative to the closest hexagonal unit of the outer shell. We further note the dependence of $\Pi = \Pi(n_o)$ upon the number n_o of the outer shells. For instance, $-\Pi(1)$ denotes the average of the van der Waals energy between a carbon atom on a single-shell

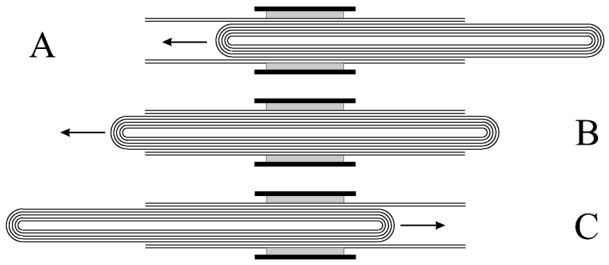

FIG. 1. Schematical illustration of a MWNT as an oscillator. (A) The core section is released with an initial extrusion. (B) The core is fully retracted into the outer shells where the van der Waals potential energy is minimized while the kinetic energy is maximized. (C) The motion of the core is reversed after the maximum extrusion to the opposite end of the outer shells is reached.

core and all the carbon atoms of a single-layered outer shell. The dimensionless numerical factor ζ depends only upon the numbers n_o and n_c of the outer shells and of the core shells [5]. Furthermore, the value of Π depends upon the choice of interatomic interaction potential function and the core diameter D. Taking the Lennard-Jones pair potential [6,7] with the normalized van der Waals distance 2.7 and the intershell spacing $t = 0.34$ nm, we plot in Fig. 2 the calculated value of $\Pi(1)$ versus the core diameter D. It shows that $\Pi(1)$ approaches a constant value 6.42×10^{-21} J (joules) as D increases. This representation of U is valid if the core length L_c and the outer shell length L_o are the same. In the case that $L_c < L_o$, it remains valid only if $x > (L_o - L_c)/2$; otherwise, there is no extrusion and, correspondingly, there is no excess potential energy. For the same reason, this representation is valid only if $x > (L_c - L_o)/2$ in the case that $L_c > L_o$.

With the retraction potential $U(x)$, we obtain the restoring force $F_{vdw} = -dU/dx$. We turn now to Newton's second law to estimate the frequency of the core oscillating with respect to its fully retracted position: $M\ddot{x}(t) = F_{vdw} + F_r$, where M is the total mass of the core, and F_r represents the total intershell sliding resistance force. We note that there generally exist some microscopic mechanisms against sliding the core in the outer shells, including the interatomic locking. Recent investigations [1,8,9] indicate that the intershell sliding resistance force between two neighboring shells of perfect or nearly perfect molecular structure can be substantially smaller than the van der Waals restoring force, as we discuss near the end of this article, and we thus neglect its effect in our estimating the oscillation frequency. We also note that the resistance force due to interatomic locking is a potential force and, hence, is nondissipative. For an n_c-shelled core, its total mass, neglecting the atoms on the shell caps, is $M = (4\pi\sqrt{3}/9)\eta D L_c a^{-2} u$, where u is the mass of a carbon atom, $\eta = n_c[1 - (n_c - 1)t/D]$, and we thus obtain the oscillation frequency:

$$f = \frac{\beta}{4}\sqrt{\frac{\zeta\Pi}{2u\eta L_c\Delta}},$$

with $\beta = \sqrt{1-\delta}/(1-\delta/2)$, where Δ is the initial extrusion and $\delta = |L_o - L_c|/2\Delta$ is the relative length mismatch. We note that β decreases monotonously as δ increases, and is approximately equal to 1 with an error less than 5% if $\delta \leq 0.48$.

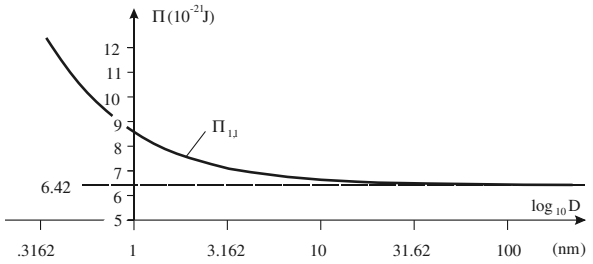

FIG. 2. The van der Waals potential energy versus the core diameter.

For the sample of Cumings and Zettl, the core consists of four shells, and has a diameter 4 nm and an initial extrusion length $\Delta = 330$ nm. For five outer shells as reported by Cumings and Zettl, we have estimated Π to be 9.2×10^{-21} J. Taking the core length L_c, which was not reported, to be twice the extrusion length, we obtain $F_{vdw} = 4.4$ nN, and, correspondingly, $f \approx 0.15$ GHz (gigahertz). We note that the core mass is proportional to the core length while the restoring force is independent of the core length, and, hence, the shorter the core length, the higher the oscillation frequency. For example, if we reduce the core length to 100 nm and take the initial extrusion length to a quarter of the core length, we have $f \approx 1.39$ GHz. If the core consists of a single shell, the frequency would be even higher because of the smaller core mass. We turn now to the setting in Cumings' and Zettl's experiment for which one end of the outer shells is closed. In this case, the core should be subjected to a huge repelling force immediately after it passes over the position of minimum potential energy, and it would extrude again because it should have a velocity towards the open end when it quickly returns, driven by the repelling force, to the position of minimum potential energy. Therefore, the oscillation frequency would be nearly twice the frequency of the nanotube with two open ends of the outer shells.

Recent investigations [1,8,9] indicate that the intershell sliding resistance strength τ_s (the intershell sliding resistance force per unit area) of MWNTs can be substantially lower than the shear strength between two graphite layers which has a mean value 0.48 MPa [6]. We are not surprised by this finding, because the carbon nanotubes in these experiments are of perfect or nearly perfect molecular structure while the graphite samples, especially those tested a few decades ago [6], usually contain a significant amount of defects. To estimate τ_s in sliding the core against the outer shells, we refer to the atomic force microscope (AFM) measurements of Yu *et al.* [9]. In this experiment, they first loaded the outermost shell of a MWNT in tension using two AFM probes until the outermost shell fractured, and they then pulled apart the fractured sections, causing the core to slide out of the outermost shell. Out of 16 tests, 14 resulted in complete separation of the fractured sections just after the outermost shell broke, due to the large snap back of the soft AFM probe, and they therefore completed the sliding test only for the remaining two. The measurements revealed the continuous and smooth pullout of the core for one of the two MWNTs, with an estimated sliding resistance strength $\tau_s = 0.08$ MPa and a zig-zag pullout for the other MWNT, with an estimated sliding resistance strength $\tau_s = 0.30$ MPa. Considering that the second test resulted in a significantly larger τ_s, they have stressed the effect of the interaction of the core with the outermost shell's fractured edge of structural imperfections

in their experiment, although the sliding resistance is expected to be related to the degree of commensurability between two neighboring shells [10]. Hence, the intershell sliding resistance strength between two neighboring shells of perfect molecular structure can be even smaller than 0.08 MPa, for well-graphitized nanotubes, which may exclude the nanotubes produced by catalytic chemical vapor deposition at low temperature. Correspondingly, the maximum intershell sliding resistance force in the setting of Cumings' and Zettl's experiment is smaller than 0.66 nN, again taking the core length L_c to be twice the extrusion length, and we note that this value is nearly 1 order smaller than the van der Waals force F_{vdw} in this setting, which has an estimated value of 4.4 nN. We note that the maximum of F_r would be reduced to 0.10 nN while F_{vdw} remains to be 4.4 nN if the core length is shortened to 100 nm. This suggests that the effect of the intershell sliding resistance force is insignificant for estimating the oscillation frequency, although the importance of accurate estimates of the intershell sliding resistance strength in creating MWNT-based molecular devices calls for further investigation. We recognize that there will be a need to excite the oscillator with an external field in practical applications, and that generating such a field can be extremely challenging. For instance, to generate an electric driving field may require having the core shell charged electrically. A possible approach perhaps would be introducing charges through doping chemically. Being part of a nanoscopic device, such an oscillator would have to be coupled with the rest of the device, and the actual implementation of this coupling represents another challenge in development.

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