Gigahertz breathing oscillators based on carbon nanoscrolls

Xinghua Shi,[1] Nicola M. Pugno,[2,a)] Yuan Cheng,[3] and Huajian Gao[1,a)]
[1]*Division of Engineering, Brown University, 610 Barus & Holley, 182 Hope Street, Providence, Rhode Island 02912, USA*
[2]*Department of Structural Engineering, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy*
[3]*Institute of High Performance Computing, Singapore 138632, Singapore*

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Theoretical study and molecular dynamics simulations are performed to investigate the gigahertz "breathing" oscillatory motion of a carbon nanoscroll (CNS). It is shown that the oscillation frequency depends on surface energy, bending stiffness, interlayer spacing, and length of the basal graphene sheet of the CNS, and that energy dissipation in the system can be controlled by adjusting temperature, graphene length, and surface energy. The analysis indicates potential applications of CNS in nanomechanical devices such as nanooscillators, nanoactuators, as well as drug and gene delivery systems. © *2009 American Institute of Physics*. [doi:10.1063/1.3253423]

Carbon nanoscrolls (CNSs) have attracted significant interests in recent years.[1–4] Unlike the tubular structure of carbon nanotubes, a CNS is made of a continuous basal graphene sheet rolled up in a spiral form. Due to this topology, CNSs have shown unique structural,[5–9] dynamical,[6] and electronic[4,10,11] properties. One of the interesting properties is that the core size of a CNS is not fixed, but can significantly change according to the surface energy and the length of the basal graphene sheet.[12] This flexibility suggests that the inner core of a CNS can be controlled by tuning the effective surface energy via an applied dc/ac electric field.[13] In view of their smooth and ultralow friction spiral layers, it will be interesting to explore potential applications of CNSs as nanoactuators and nanooscillators. Here we perform theoretical study and molecular dynamics (MD) simulations to investigate the "breathing" oscillatory motion of a CNS.

The breathing oscillatory motion of a CNS, as illustrated in Fig. 1, can be initiated by suddenly decreasing the interlayer interaction energy to generate a small perturbation in the system. As a consequence of this perturbation, the CNS starts to oscillate with periodic expansion and contraction phases with circumferential velocity v_C and radial velocity v_R. To quantify this motion, we found it convenient to consider the core radius of a CNS as the controlling degree of freedom. It has been previously shown that a stable equilibrium value of r_0 can be uniquely determined from the basal graphene length B, the interlayer spacing h, the interaction energy γ and the bending stiffness D.[12] The breathing oscillation is defined as the oscillatory motion associated with slight perturbations of r_0 from its equilibrium value. Consider a CNS with inner core radius r_0, outer radius R and interlayer spacing h. The basal graphene sheet has length B and width L. The breathing motion of the CNS can be described using Lagrange's equation $[\partial(K-V)/(\partial r_0)] - [d/(dt)][\partial(K-V)/(\partial \dot{r}_0)] - [(\partial F)/(\partial \dot{r}_0)] = 0$, where K denotes the kinetic energy and V the potential energy, F is Rayleigh's dissipation function, t is time and over-dot represents time derivative. The potential energy of the system has been previously derived.[12] A slightly more general form is $V = [(\pi DL)/h]\ln(R/r_0) + 2\pi\gamma L(r_0+R) - \pi r_0^2 Lp$, where $R = \sqrt{[(Bh)/\pi] + r_0^2}$ is the outer radius, D is the bending modulus and γ is the surface energy per unit area, $p = p_i - p_e$ with p_e and p_i being the external and internal pressures. To evaluate the kinetic energy in the system, we first derive the circumferential velocity $v_C = ds/dt$ of an infinitesimal arc length $ds \approx rd\vartheta$. Noting that the spiral geometry is described by $r = r_0 + [h/(2\pi)]\vartheta$ and $dr = [h/(2\pi)]d\vartheta$, we immediately obtain $v_C = [(ds)/(dt)] = r[(d\vartheta)/(dt)] = [(2\pi r)/h][(dr)/(dt)]$. Since the length of the spiral within radius r is a constant $\ell = (\pi/h)(r^2 - r_0^2)$, simple differentiation shows $r_0[(dr_0)/(dt)] = r[(dr)/(dt)]$ and consequently $v_C = [(2\pi r_0)/h][(dr_0)/(dt)]$. Interestingly, the circumferential velocity is constant along the entire spiral. The radial velocity of the arc length $ds \approx rd\vartheta$ is given by $v_R(r) = dr/dt = (r_0/r)[(dr_0)/(dt)]$. Since $v_C/v_R = 2\pi r/h \gg 1$, we can assume $v = \sqrt{v_C^2 + v_R^2} \approx v_C$. Accordingly, the kinetic energy in the system could be evaluated as $K = (1/2)Mv_C^2 = (2\pi^2 M r_0^2 \dot{r}_0^2)/h^2$, where M is the total mass of the CNS. Previous atomistic simulations suggested there exists a viscous damping force[12] with $(\partial F)/(\partial \dot{r}_0) = C(T)\dot{r}_0$, where $C(T)$ is a damping coefficient which depends on the temperature T of the system. Combining all terms together, the Lagrange equation of motion is derived as

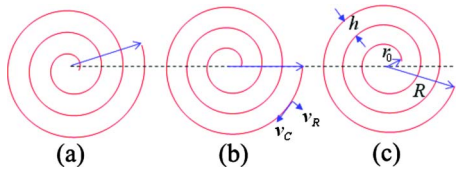

FIG. 1. (Color online) The "breathing" oscillatory motion of a carbon nanoscroll. (a) The initial configuration. The oscillation is initiated by suddenly decreasing the interlayer interaction energy in the system (via, e.g., an applied electric field), at which the CNS starts to expand. (b) The configuration of maximum kinetic energy and minimum potential energy, corresponding to the statically equilibrium state. (c) The end of the expansion phase with zero kinetic energy and maximum potential energy, at which the CNS will soon start contracting. (enhanced online). [URL: http://dx.doi.org/10.1063/1.3253423.1] [URL: http://dx.doi.org/10.1063/1.3253423.2]

a)Authors to whom correspondence should be addressed. Electronic addresses: nicola.pugno@polito.it and huajian_gao@brown.edu.

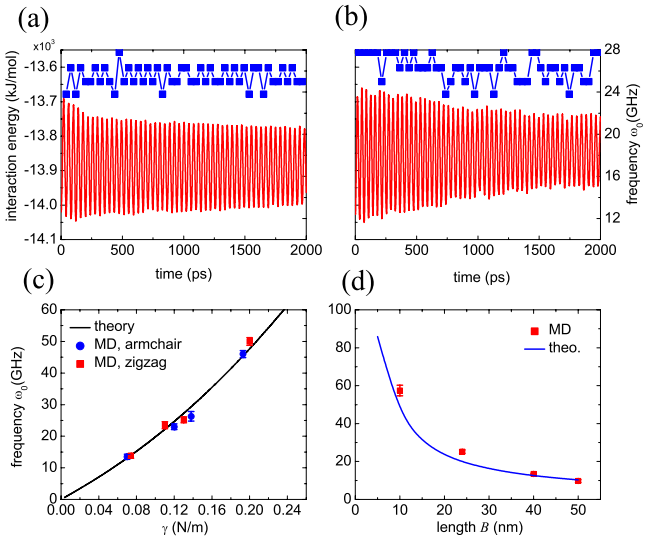

FIG. 2. (Color online) Gigahertz oscillatory motion of CNSs. Molecular dynamics simulation results for the evolution of interlayer interaction energy (red line) and fundamental frequency (blue square) as functions of time for (a) zigzag and (b) armchair CNSs. The length B of the basal graphene sheet is taken to be 24 nm and tuning parameter λ is 0.8. (c) The fundamental frequency as a function of the surface energy of CNSs. Solid line is the theoretical prediction, and red squares and blue circles are the simulation results for zigzag and armchair CNSs, respectively. (d) The fundamental frequency as a function of the grapehene length. Blue line is the theoretical prediction, and red squares are the simulation results for zigzag CNSs.

$$\frac{\pi DL}{h}\left(1-\frac{r_0^2}{Bh/\pi+r_0^2}\right)\frac{1}{r_0}-2\pi\gamma L\left(1+\frac{r_0}{\sqrt{Bh/\pi+r_0^2}}\right)+2\pi r_0 Lp-\frac{4\pi^2 M}{h^2}(r_0\dot{r}_0^2+r_0^2\ddot{r}_0)-C\dot{r}_0=0 \quad (1)$$

which can be used to study any expansion/contraction motion of a CNS. For the breathing oscillatory motion around an equilibrium configuration, we look for a solution in the form $r_0(t)=r_{0e}+\varepsilon(t)$, where $\varepsilon(t)$ is a small perturbation and r_{0e} is a static equilibrium core size satisfying the relation $(2\gamma h)/D=(1/r_{0e})-(1/R)+\{2hp/[D(1/r_{0e}+1/R)]\}$, which can be easily derived from the static energy balance $\partial V/\partial r_0(r_0=r_{0e})=0$. For the small perturbation $\varepsilon(t)$, we retain the first order terms ε, $\dot{\varepsilon}$, and $\ddot{\varepsilon}$ only in the Lagrange equation and obtain a governing equation for the breathing oscillation as $\ddot{\varepsilon}+2\varsigma\omega_0\dot{\varepsilon}+\omega_0^2\varepsilon=0$, where

$$\omega_0=\sqrt{\frac{\pi D}{4\rho B^3h^2}\left[\frac{\alpha^3(\alpha+3)}{(1+\alpha)^2}+2\frac{\gamma}{D}\sqrt{\frac{Bh^3}{\pi}}\frac{\alpha^2\sqrt{\alpha}}{(1+\alpha)^{3/2}}-2\frac{Bh^2p}{\pi D}\alpha\right]} \quad (2)$$

is identified as the oscillation frequency and $\varsigma=(C\alpha)/(8\pi\rho LB^2\omega_0)$ is the effective damping factor. Here, ρ is the material density and $\alpha=(Bh)/(\pi r_{0e}^2)$ is the ratio between the cross-sectional area of CNS and that inside its core. Figure 2(c) plots the relation between the oscillatory frequency and surface energy by taking the rest of the parameters as $p=0$, $B=24$ nm, $D=0.11$ nN nm, $\rho=2267$ kg/m^3, and $h=0.34$ nm. The result indicates that the oscillatory frequency increases with surface energy. On the other hand, if the surface energy is fixed at $\gamma=0.1$ nN/nm, Fig. 2(d) shows the oscillatory frequency as a function of the graphene length B, indicating that the frequency can be increased by shortening the graphene length.

To verify our theoretical model, we have conducted MD simulations with bonded interaction among carbon atoms described by a Morse bond.[14] The resulting bending modulus (0.11 nNnm)[12] agrees well with that calculated using Brenner's potential.[15] The nonbonded vdW interactions are described by the Lennard-Jones potential $U(r_{ij},\lambda)=4\lambda\varepsilon_{CC}[(\sigma_{CC}/r_{ij})^{12}-(\sigma_{CC}/r_{ij})^6]$, where $\varepsilon_{CC}=0.3601$ kJ/mol, $\sigma_{CC}=0.34$ nm, and λ is a tuning parameter ($0<\lambda\leq 1$) that can be used to tune the core size of a CNS. In MD simulations of oscillation around an equilibrium configuration characterized by a specific λ, we first set up an initial equilibrium structure at a slightly perturbed state $\lambda+\delta\lambda$, where $\delta\lambda$ is taken to be 0.2 (experimentally, $\delta\lambda$ can be imposed by applying an electric field[13]). The oscillation of the CNS is initiated by setting the tuning parameter back to the reference value λ. The simulations are conducted using Gromacs4[16] with microcanonical NVE ensemble, initial temperature 10 K and time step 1 fs.

Our simulation results confirm the gigahertz breathing oscillatory motion of CNSs caused by relative sliding of the scroll layers. For a zigzag CNS rolled up from a basal graphene sheet of length $B=24$ nm, the mean oscillatory frequency is about 25.2 GHz when $\lambda=0.8$ [Figs. 2(a) and 2(c)]. Our theoretical result in Eq. (2) shows that the oscillating frequency depends on the surface energy which is controlled by the vdW interaction parameter λ in our simulations. Accordingly, we found that the frequency increases from 25.2 to 50 GHz as λ is raised from 0.8 to 1.0, and decreases from 25.2 to 22.7 GHz as λ is reduced from 0.8 to 0.6. The results of an armchair CNS with the same length $B=24$ nm show similar behaviors as that of the zigzag CNS [Figs. 2(b) and 2(c)], suggesting that the effect of chirality on oscillating frequency is relatively minor. To investigate the effect of the graphene length B on the oscillating frequency, three zigzag CNSs with $B=10$, 40, 50 nm are simulated with $\lambda=0.8$. It is found that the shorter the graphene length, the higher the oscillating frequency [Fig. 2(d)]. Figures 2(c) and 2(d) show that the MD results are in good agreement with the corresponding predictions from our theoretical model.

To investigate energy dissipation associated with the CNS oscillation, we plot the amplitude of vdW interaction energy in Fig. 3(a) as a function of simulation time for a CNS with $B=24$ nm, $\lambda=0.8$ and initial temperature 10 K. It is estimated that energy is dissipated at a rate of 30 kJ/mol ns. Similar energy dissipation has been found in the coaxial oscillation of a carbon bitube[17–20] or oscillation of a graphene-graphene bilayer.[21] Unlike a carbon bitube whose oscillating frequency increase with energy dissipation,[17–20] there is no such correlation for CNS, which is consistent with our theoretical model.

A thorough investigation of energy dissipation in CNS oscillation is beyond the scope of the present paper. Here we focus on a few factors which might be useful in controlling energy dissipation in a given CNS system. First, we explore the effect of the initial temperature by conducting a series of MD simulations with fixed $B=24$ nm and $\lambda=0.8$, while allowing the initial temperatures T_0 to vary from 10 to 160 K. The simulations show similar oscillating frequency ($\sim$26 GHz) but different energy dissipation rates. We estimate the damping ratio ς from our MD simulations according to $\varsigma=1/\sqrt{1+(2\pi/\delta)^2}$, where $\delta=(1/n)\ln(x_0/x_n)$ is the logarithmic decrement, x_0 and x_n being two amplitude peaks separated by n periods. According to our theoretical prediction $\varsigma=(C\alpha)/(8\pi\rho LB^2\omega_0)$, the estimated damping coeffi-

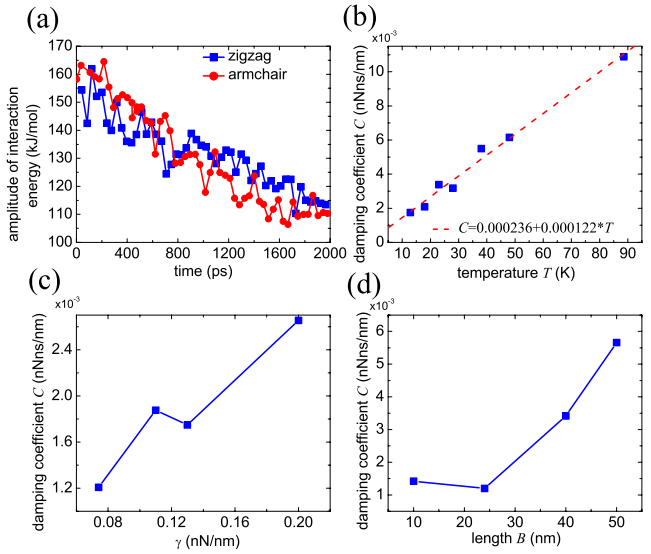

FIG. 3. (Color online) Energy dissipation during gigahertz CNS oscillation. (a) Simulated evolution of oscillating amplitude of interlayer interaction energy as a function of time for a zigzag (blue squares) and an armchair (red circles) CNSs with $B=24$ nm and tuning parameter $\lambda=0.8$. (b) Damping coefficient as a function of simulation temperature. A linear correlation (red dash line) between damping coefficient and temperature is identified as $C=0.000\,236+0.000\,122T$. In all simulations, the length of CNSs B is taken to be 24 nm and tuning parameter λ is 0.8. (c) The damping coefficient as a function of surface energy γ. (d) The damping coefficient as a function of graphene length B.

cients C at different temperatures are listed in Fig. 3(b). Interestingly, we find that the damping coefficient increases linearly with the temperature as $C=0.000\,236+0.000\,122T$. To investigate other factors that may influence the damping coefficient, we have further investigated two simulation systems: One with the basal graphene length fixed at $B=24$ nm while the surface energy is taken to be $\lambda=1.0$, 0.8, 0.6, and 0.4; another with the surface energy fixed at $\lambda=0.8$ while the basal graphene length is taken to be $B=10$, 24, 40, and 50 nm. All simulations are conducted at an initial temperature of 10 K. The results indicate that the damping coefficient increases with the surface energy γ Fig. 3(c)) as well as the graphene length B Fig. 3(d)). The plateau in Fig. 3(d) for $B<20$ nm can be attributed to the failure of our theoretical model in this regime, where $v_C/v_R=2\pi r/h$ is not much greater than one and the radial velocity v_R is no longer negligible. These findings suggest that lower temperature, shorter graphene length and smaller surface energy lead to lower dissipation rates.

An interesting question is how a CNS responds to an oscillating field near the resonant frequency of the system. To mimic an applied ac electric field, we let the energy tuning parameter vary according to $\lambda(t)=[(1-\beta)/2][1+\cos(\omega t)]+\beta$, where ω is the frequency of the applied field and β is a parameter depending on the field strength.[13] We consider a simulation system with $B=24$ nm and set $\beta=0.6$ so that λ varies from 0.6 to 1 with a mean value of 0.8 (see the inset of Fig. 4). Figure 4 shows that the maximum inner core radius varies with the applied frequency ω, with a peak value at $\omega\sim30$ GHz, which is quite close to the fundamental frequency about 25 GHz at $\lambda=0.8$ for the selected CNS. The discrepancy between the observed resonance frequency and the fundamental frequency may be partly attributed to damping ($\varsigma\sim10^{-3}$) in our simulation system. Note

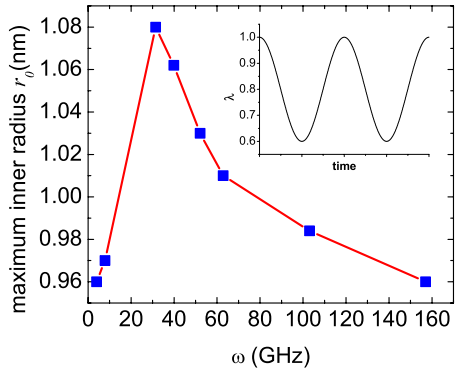

FIG. 4. (Color online) The maximum core radius of a CNS subjected to an oscillating interlayer interaction energy with frequency ω (inset), simulating resonance under an applied ac electric field.

that the core of the CNS is significantly widened at the resonant frequency. This phenomenon may be particularly useful in designing controllable CNS-based drug and gene loading/release systems.

In summary, we have developed a theoretical model to describe the "breathing" oscillatory motion of a CNS, and have validated the theory with molecular dynamics simulations. It is found that the gigahertz oscillation of CNSs can be controlled by tuning the effective surface energy of the system via an applied dc/ac electric field. The energy dissipation rates in the system can be tuned by temperature, basal graphene length and surface energy. These results suggest possible applications of CNSs as nanooscillators and nanoactuators. The resonant oscillation of a CNS near its fundamental frequency might be useful for molecular loading/release in gene and drug delivery systems.

[1]H. Shioyama and T. Akita, Carbon **41**, 179 (2003).
[2]L. M. Viculis, J. J. Mack, and R. B. Kaner, Science **299**, 1361 (2003).
[3]M. V. Savoskin, V. N. Mochalin, A. P. Yaroshenko, N. I. Lazareva, T. E. Konstantinova, I. V. Barsukov, and I. G. Prokofiev, Carbon **45**, 2797 (2007).
[4]X. Xie, L. Ju, X. F. Feng, Y. H. Sun, R. F. Zhou, K. Liu, S. S. Fan, Q. Q. Li, and K. L. Jiang, Nano Lett. **9**, 2565 (2009).
[5]Y. Chen, J. Lu, and Z. Gao, J. Phys. Chem. C **111**, 1625 (2007).
[6]S. F. Braga, V. R. Coluci, S. B. Legoas, G. Giro, D. S. Galvão, and R. H. Baughman, Nano Lett. **4**, 881 (2004).
[7]S. F. Braga, V. R. Coluci, R. H. Baughman, and D. S. Galvão, Chem. Phys. Lett. **441**, 78 (2007).
[8]V. R. Coluci, S. F. Braga, R. H. Baughman, and D. S. Galvão, Phys. Rev. B **75**, 125404 (2007).
[9]G, Mpourmpakis, E. Tylianakis, and G. E. Froudakis. Nano Lett. **7**, 1893 (2007).
[10]H. Pan, Y. Feng, and J. Lin, Phys. Rev. B **72**, 085415 (2005).
[11]R. Rurali, V. R. Coluci, and D. S. Galvão, Phys. Rev. B **74**, 085414 (2006).
[12]X. H. Shi, N. M. Pugno, and H. J. Gao, "Tunable core size of carbon nanoscrolls," J. Comput. Theor. Nanosci. (to be published).
[13]X. H. Shi, Y. Cheng, N. M. Pugno, and H. J. Gao, "Tunable water channels with carbon nanoscrolls" (unpublished).
[14]J. H. Walther, R. Jaffe, T. Halicioglu, and P. Koumoutsakos, J. Phys. Chem. B **105**, 9980 (2001).
[15]D. W. Brenner, O. A. Shenderova, J. A. Harrison, S. J. Stuart, B. Ni, S. B. Sinnott, and J. Phys, Condens. Mat. **14**, 783 (2002).
[16]B. Hess, C. Kutzner, D. van der Spoel, and E. Lindahl, J. Chem. Theory Comput. **4**, 435 (2008).
[17]W. L. Guo, Y. F. Guo, H. J. Gao, Q. Zheng, and W. Zhong, Phys. Rev. Lett. **91**, 125501 (2003).
[18]J. L. Rivera, C. McCabe, and P. T. Cummings, Nanotechnology **16**, 186 (2005).
[19]P. Liu, H. J. Gao, and Y. W. Zhang, Appl. Phys. Lett. **93**, 083107 (2008).
[20]Z. P. Xu, J. Comput. Theor. Nanosci. **5**, 655 (2008).
[21]S. Y. Kim and H. S. Park, Appl. Phys. Lett. **94**, 101918 (2009).