Defect-Induced Mechanical Mode Splitting in Carbon Nanotube Resonators

Ajit K. Vallabhaneni
School of Mechanical Engineering,
Purdue University,
West Lafayette, IN 47907

Jeffrey F. Rhoads[1]
School of Mechanical Engineering,
Birck Nanotechnology Center,
Ray W. Herrick Laboratories,
Purdue University,
West Lafayette, IN 47907
e-mail: jfrhoads@purdue.edu

Jayathi Y. Murthy
Department of Mechanical Engineering,
University of Texas at Austin
Austin, TX 78712

Xiulin Ruan
School of Mechanical Engineering,
Birck Nanotechnology Center,
Purdue University,
West Lafayette, IN 47907

This work examines the impact of defects on the resonant response of single-wall carbon nanotube (CNT) resonators using classical molecular dynamics (MD) simulations. The work demonstrates that the presence of defects in CNTs leads to appreciable resonant mode splitting. A dimensionless parameter has been introduced to quantify this phenomenon. It is observed that increasing the degree of asymmetry in the system generally increases the magnitude of splitting. Given the centrality of single-peak Lorentzian frequency responses in the current device design paradigm, which is utilized in applications such as resonant mass sensing, the non-Lorentzian response characteristics of imperfect devices could present both opportunities and challenges in the future design and development of resonant nanosystems. [DOI: 10.1115/1.4023057]

1 Introduction

Since their discovery in 1991 [1], the distinct thermal, mechanical, and electrical properties of carbon nanotubes (CNTs) have motivated researchers to employ them in a wide variety of applications [2,3]. One such application is in resonant nanoelectromechanical systems (NEMS) [4–6], where single-wall CNTs are ideal to use because of their high elastic modulus [7,8], low mass density, and high natural frequencies (typically in the GHz–THz range) [9]. These benefits have been exploited to date in various applications, including mass and force sensing and signal processing [10–15].

The frequency response of an ideal, single-degree-of-freedom resonator typically exhibits a Lorentzian structure and the associated quality factor (Q) can be calculated using a standard

---

3 dB offset method. However, this structure can begin to break down in the presence of imperfections, such as point defects or isotopes, which are inevitably present in nanosystems, irrespective of the fabrication process. For example, it is well known that processes like irradiation can introduce vacancies in CNTs and these defects can alter the CNTs' thermal, mechanical, electronic, and optical properties. Recent experiments conducted on silicon [16,17] and silver–gallium [11] nanowires demonstrate that the single Lorentzian peak splits into two peaks in the presence of an irregular cross section (due to the moments of inertia along the two orthogonal axes of vibration being distinct in the presence of geometric asymmetry). This mimics previous observations of asymmetry-induced mode splitting in bells and rings, among other macroscale systems (see, for example, Refs. [18–22]). Although the mode shapes and quality factors of pristine CNTs have been investigated using MD simulations [23,24], to the best of the authors' knowledge, no theoretical work has been performed to investigate how the presence of defects can alter CNT resonator performance. Accordingly, in this work, we consider the impact of structural defects on a representative CNT's frequency response structure and discuss possible practical implications.

2 Methodology

CNTs are generally characterized by their chirality (represented by the chiral vector (n,m)), which specifies how the graphene sheet has been rolled to form a particular architecture [3]. Here, we consider a cantilevered, single-wall carbon nanotube (SWCNT) of chirality (10,10), which is 8 nm long, fixed at one end, and contains defects, as shown in Fig. 1. The adaptive intermolecular reactive empirical bond order (AIREBO) potential [25] is used to model the covalent bond interactions between carbon atoms. In this model, the potential energy of the covalent bonds is given by

$$\mathrm{E}_{ij}^{\mathrm{REBO}} = V_{ij}^{\mathrm{R}}(r_{ij}) + b_{ij}V_{ij}^{\mathrm{A}}(r_{ij}) \qquad (1)$$

where V_{ij}^{R} and V_{ij}^{A} are the repulsive and attractive pairwise potentials between atoms i and j, whose magnitude varies with the separation distance r_{ij}, and b_{ij} represents the bond order term that accounts for the strength of a particular bond (see Ref. [25] for additional details). The dynamics of the CNT in this work are simulated through MD simulations using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package [26], which is a classical MD simulation tool developed by Sandia National Laboratories. Initially, the CNT is equilibrated to a desired temperature in an NVT ensemble, wherein the number of
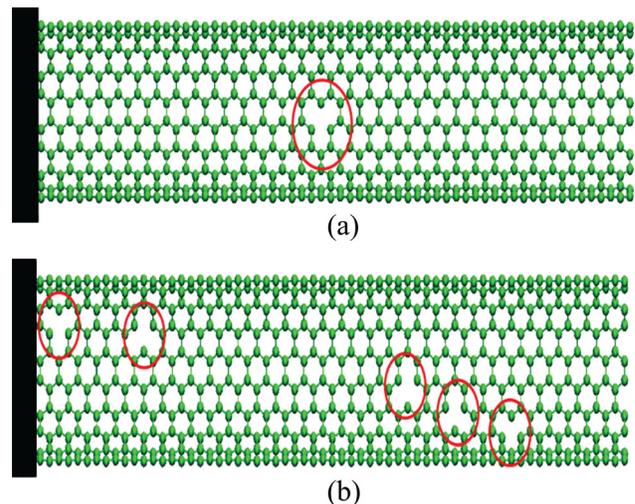

(a)

(b)

Fig. 1 A representative (10,10) 8 nm long, single-wall carbon nanotube with (a) a single defect and (b) multiple defects highlighted

---

atoms (N), the volume (V), and the temperature (T) are maintained constant, using a Nose–Hoover thermostat [27] with a time step of 0.5 fs (1/40th of the lowest time period in the phonon spectra of carbon atoms). A force is subsequently applied on all of the atoms at the tip of the CNT in the transverse direction for half of one period of oscillation. This acts in addition to the interatomic forces that exist within the system. After the removal of force, the CNT is allowed to freely oscillate in a microcanonical ensemble (NVE) where the total energy of the system is conserved. Note that to ensure linearity, the applied force is constrained such that the maximum elongation in the transverse direction is restricted to 5% of the length of the CNT—a constraint commensurate with previous small force experiments [28].

3 Results and Discussion

The resonant frequency associated with the dominant mode of vibration is obtained from a Fourier transform of the time variation of the kinetic (or potential) energy. Figure 2 shows the frequency response obtained from a Fourier transform of kinetic energy of the transversely excited CNT with and without defects. It can be observed that introducing a single defect in the system as shown in Fig. 1(*a*) breaks the previously observed symmetry and leads to the splitting of the resonant modes; ultimately yielding a non-Lorentzian frequency response. It is known that for a pristine system, the stiffness and mass matrices are symmetric. However, introducing a point defect (removing an atom) in a pristine CNT results in imbalance of the stiffness and mass matrices, which in turn leads to the excitation of two modes with frequencies very close, but not identical, to one another. Carbon nanotubes with chiral vectors n ≠ m also exhibit mode splitting behavior under a transverse excitation because of the asymmetric orientation of atoms with respect to the axis of vibration. Likewise, a similar effect can be observed in the presence of isotopes where a C^{12} atom has been replaced with a C^{24} atom or another heavier atom. The effect in this latter scenario may not be as prominent as in the case of vacancies (absence of atoms) because the overall stiffness is not altered.

It should be noted that the aforementioned scenarios are intrinsic phenomenon, independent of temperature and the applied boundary conditions of the system. Also, note that in the case of a non-Lorentzian frequency response (as shown in Fig. 2), defining Q in the conventional way (using a 3 dB offset) can be problematic because of the presence of two local peaks in the frequency domain and corresponding beating phenomenon in the time response.

To quantify the magnitude of this resonant mode splitting, a dimensionless parameter Δ is introduced that is defined as

$$\Delta = \frac{|f_1 - f_2|}{f_1 + f_2} \qquad (2)$$

where f_1 and f_2 are the frequencies corresponding to the two peaks shown in Fig. 2. Not surprisingly, the magnitude of Δ varies significantly with the number of defects (vacancies) present in the system. Figure 3(*a*) shows the variation of the dimensionless parameter Δ as a function of the percentage of atoms randomly removed from the CNT. Ten different initial configurations are generated using a random seed at each percentage of defects shown in Fig. 3(*a*). The magnitude of Δ is then calculated in each case using the previously described method and the recovered variation is plotted. It can be observed that as the number of defects in the CNT increases, the magnitude of splitting generally increases. Interestingly, as the percentage of defects increases to 7%, Δ appears to reach a maximum and further removal of atoms does not increase Δ. This seems to imply that the asymmetry of the distribution of defects affects the magnitude of Δ more than
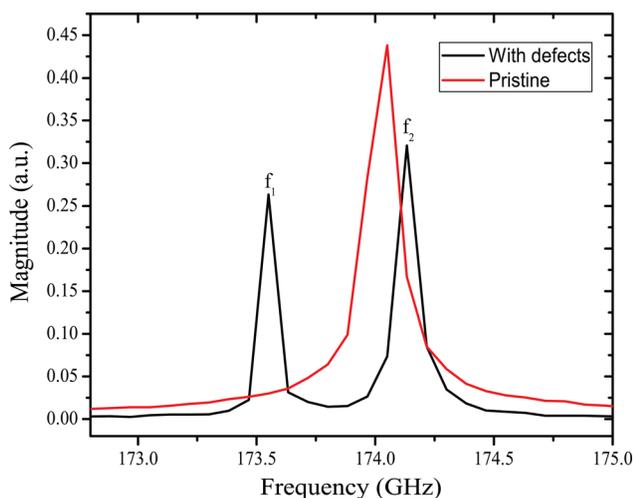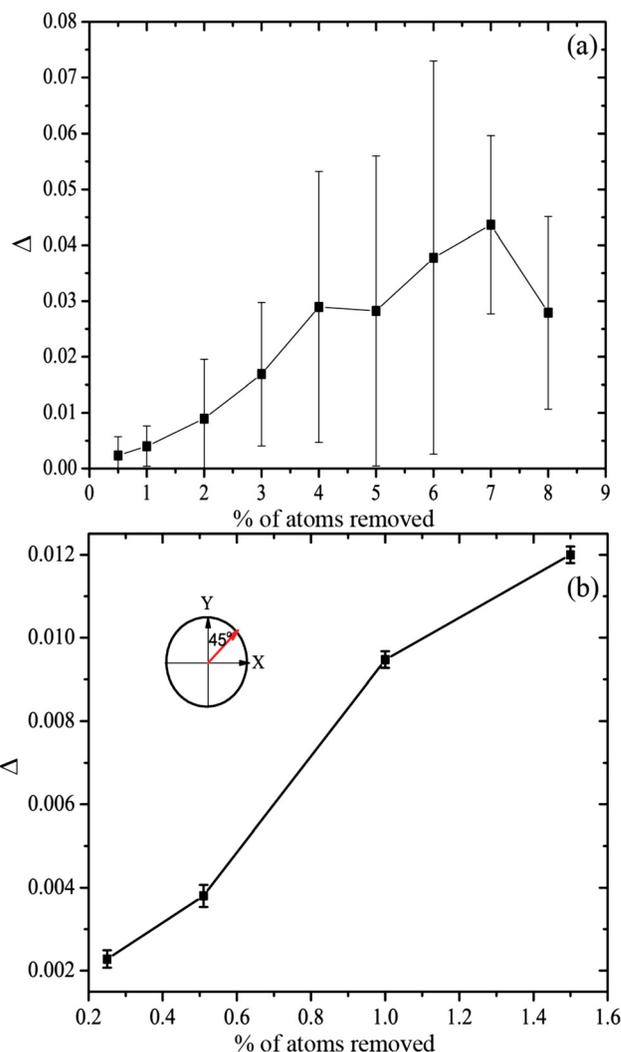

Fig. 2 A comparison of the frequency response of kinetic energy of a (10,10) 8 nm long CNT under transverse excitation with a single defect (black) and without defects (red). Note that the fast Fourier transform algorithm used in this work has a resolution of 62.5 MHz.

Fig. 3 Variation of the nondimensional mode splitting parameter Δ as a function of the percentage of atoms removed from the CNT. In subfigure (*a*) the atoms are removed randomly; in subfigure (*b*) the atoms are removed along a line given by the orientation angle $\theta = 45$ deg.

the absolute number of defects. Hence, it is possible that for the same percentage of defects, a CNT with all the defects located on one side of the axis of vibration has larger Δ than the one with defects distributed symmetrically on either side of the axis. This hypothesis is supported by the fact that minimum values of Δ are low even with high defect concentrations. For large enough concentrations of defects, the degree of asymmetry may actually decrease, due in part to the potential for more than two dominant modes, decreasing Δ. A scenario wherein all of the defects are confined to a particular angle ($\theta = 45$ deg) along the circumference of the CNT is also of interest. The Δ in this case increases from 0.002 to 0.012 as the percentage of atoms removed increases from 0.25% to 1.5% as shown in Fig. 3(b). The spread in the magnitude of Δ in this case is less than the results in Fig. 3(a) due to the high degree of asymmetry, a result of the value of θ chosen.

In addition to concentration, the location and orientation of defects can also affect the near-resonant response of a CNT. Figure 4(a) shows the frequency response structure associated with a CNT resonator with a single defect located at different angles as measured with respect to the direction of force (Y) along the circumference. As can be observed from Fig. 4(b), varying the angle θ results in a variation of the amplitudes of the two peaks. At $\theta = 0$ deg, only one peak is evident (at f_2), as the location of

defect is aligned with the primary axis of vibration (Y-axis). As θ increases from 0 deg to 45 deg, the ratio of amplitudes of the peaks decreases and approaches almost 1. Then as θ increases further from 45 deg to 90 deg, the opposite trend is observed, eventually leading to a single peak at f_1 for $\theta = 90$ deg. A similar effect was also reported in recent experimental works [16,17]. Note that the value of Δ in this particular study lies in the range of 0.0082–0.0091, which is an order of magnitude smaller than the values of Δ shown in Fig. 3. This implies that the magnitude of splitting is relatively independent of the orientation of defects.

One application where CNT resonators have shown particular promise is resonant mass sensing. Here, the amount of adsorbed mass is typically estimated from the shift in the peak frequency of a Lorentzian response structure [10,15], which is implicitly founded upon the single-degree-of-freedom dominant response of the system. If the device exhibits a Lorentzian response behavior, with a sharp peak at resonance (high quality factor), then one can accurately detect these shifts in frequency and, thus, very small amounts of added mass. While pristine CNTs exhibit a perfect Lorentzian frequency response, as shown herein, in the presence of defects (or a heavier isotope), there will be multiple peaks in the frequency response and estimating the added-mass induced frequency shift is no longer straightforward. Recently, Gil Santos et al. [16] derived a more rigorous method to estimate the changes in mass and mechanical properties of the adsorbate in the presence of multiple peaks. However, considerable work remains to extrapolate these results to other systems and application areas.

4 Conclusions

In conclusion, to obtain a Lorentzian frequency response, a structure must maintain symmetry in terms of geometry, mass, and stiffness. Here, we have shown that even a single point defect (vacancy) can appreciably break this symmetry and induce resonant mode splitting in CNTs. This phenomenon is independent of external factors, such as temperature and boundary conditions. Note that the magnitude of splitting generally increases with degree of asymmetry in the system. Though this phenomenon complicates the paradigm currently employed in the design of resonant nanosystems, efforts can, and are, being made to exploit this non-Lorentzian behavior.
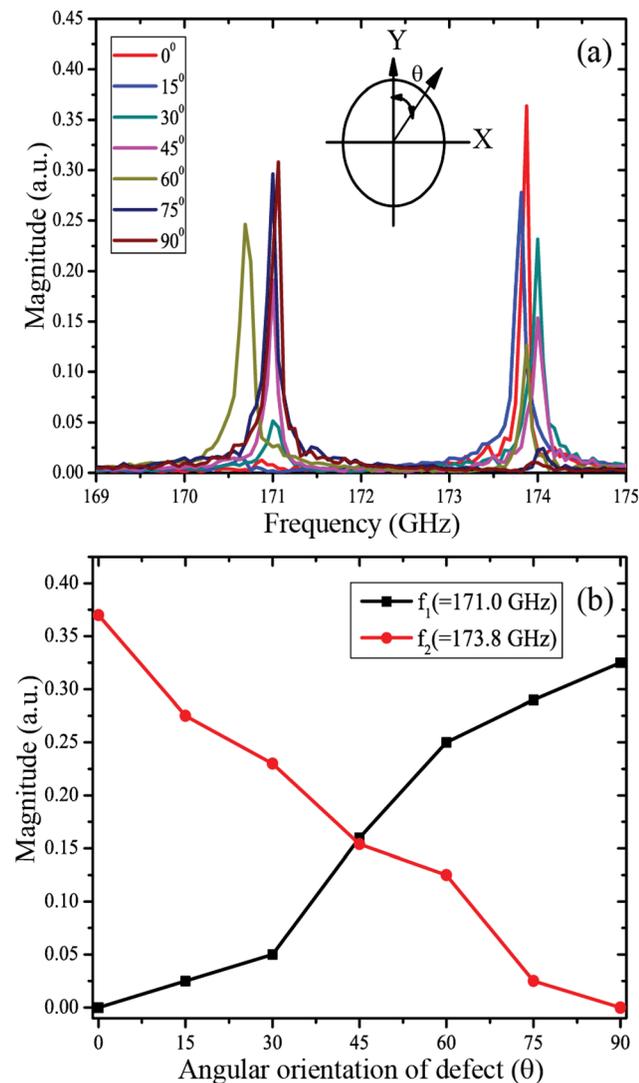
Fig. 4 (*a*) Frequency response of the kinetic energy of the CNT for various angular orientations (θ) of the defects. (*b*) The amplitudes of the two resonance peaks at frequencies f₁ and f₂, respectively.

References

[1] Iijima, S., 1991, "Helical Microtubules of Graphitic Carbon," Nature, **354**, pp. 56–58.
[2] Baughman, R. H., Zakhidov, A. A., and de Heer, W. A., 2002, "Carbon Nanotubes—The Route Toward Applications," Science, **297**, pp. 787–792.
[3] Dresselhaus, M. S., Dresselhaus, G., and Avouris, P., 2001, *Carbon Nanotubes: Synthesis, Structure, Properties, and Applications*, Springer-Verlag, Berlin.
[4] Roukes, M. L., 2000, "Nanoelectromechanical Systems," The 2000 Solid-State Sensor and Actuator Workshop, Hilton Head Island, SC, June 4-8, pp. 1–10.
[5] Ekinci, K. L., and Roukes, M. L., 2005, "Nanoelectromechanical Systems," Rev. Sci. Instr., **76**, p. 061101.
[6] Roukes, M., 2001, "Nanoelectromechanical Systems Face the Future," Physics World, **14**, pp. 25–31.
[7] Treacy, M. M. J., Ebbesen, T. W., and Gibson, J. M. 1996, "Exceptionally High Young's Modulus Observed for Individual Carbon Nanotubes," Nature, **381**, pp. 678–680.
[8] Lu, J. P., 1997, "Elastic Properties of Carbon Nanotubes and Nanoropes," Phys. Rev. Lett., **79**, pp. 1297–1300.
[9] Li, C., and Chou, T.-W., 2003, "Single-Walled Carbon Nanotubes as Ultrahigh Frequency Nanomechanical Resonators," Phys. Rev. B, **68**, p. 073405.
[10] Chiu, H. Y., Hung, P., Postma, H. W. C., and Bockrath, M., 2008, "Atomic-Scale Mass Sensing Using Carbon Nanotube Resonators," Nano Lett., **8**, pp. 4342–4346.
[11] Biedermann, L. B., Tung, R. C., Raman, A., Reifenberger, R. G., Yazdanpanah, M. M., and Cohn, R. W., 2010, "Characterization of Silver–Gallium Nanowires for Force and Mass Sensing Applications," Nanotech., **21**, p. 305701.

[12] Li, M., Tang, H. X., and Roukes, M. L., 2007, "Ultra-Sensitive NEMS-Based Cantilevers for Sensing, Scanned Probe and Very High-Frequency Applications," Nature Nanotech., **2**, pp. 114–120.

[13] Yang, Y. T., Callegari, C., Feng, X. L., Ekinci, K. L., and Roukes, M. L., 2006, "Zeptogram-Scale Nanomechanical Mass Sensing," Nano Lett., **6**, pp. 583–586.

[14] Ekinci, K. L., Huang, X. M. H., and Roukes, M. L., 2004, "Ultrasensitive Nanoelectromechanical Mass Detection," Appl. Phys. Lett., **84**, pp. 4469–4471.

[15] Ekinci, K. L., Yang, Y. T., and Roukes, M. L., 2004, "Ultimate Limits to Inertial Mass Sensing Based Upon Nanoelectromechanical Systems," J. Appl. Phys., **95**, pp. 2682–2689.

[16] Gil-Santos, E., Ramos, D., Martínez, J., Fernández-Regúlez, M., García, R., San Paulo, Á., Calleja, M., and Tamayo, J., 2010, "Nanomechanical Mass Sensing and Stiffness Spectrometry Based on Two-Dimensional Vibrations of Resonant Nanowires," Nature Nanotech., **5**, pp. 641–645.

[17] Nelis, M. R., Yu, L., Zhang, W., Zhao, Y., Yang, C., Raman, A., Mohammadi, S., and Rhoads, J. F., 2011, "Sources and Implications of Resonant Mode Splitting in Silicon Nanowire Devices," Nanotech., **22**, p. 455502.

[18] Garrett, S. L., 1990, "Resonant Acoustic Determination of Elastic Moduli," J. Acoustical Soc. Am., **88**, pp. 210–221.

[19] Allaei, D., Soedel, W., and Yang, T. Y., 1986, "Natural Frequencies and Modes of Rings That Deviate From Perfect Axisymmetry," J. Sound and Vib., **111**, pp. 9–27.

[20] Charnley, T., and Perrin, R., 1978, "Studies With an Eccentric Bell," J. Sound and Vib., **58**, pp. 517–525.

[21] Fox, C. H. J., 1990, "A Simple Theory for the Analysis and Correction of Frequency Splitting in Slightly Imperfect Rings," J. Sound and Vib., **142**, pp. 227–243.

[22] Eley, R., Fox, C. H. J., and McWilliam, S., 1999, "Anisotropy Effects on the Vibration of Circular Rings Made From Crystalline Silicon," J. Sound and Vib., **228**, pp. 11–35.

[23] Jiang, H., Yu, M.-F., Liu, B., and Huang, Y., 2004, "Intrinsic Energy Loss Mechanisms in a Cantilevered Carbon Nanotube Beam Oscillator," Phys. Rev. Lett., **93**, p. 185501.

[24] Vallabhaneni, A. K., Rhoads, J. F., Murthy, J. Y., and Ruan, X., 2011, "Observations of Nonclassical Scaling Laws in the Quality Factors of Cantilevered Carbon Nanotube Resonators," J. Appl. Phys., **110**, p. 034312.

[25] Brenner, D. W., Shenderova, O. A., Harrison, J. A., Stuart, S. J., Ni, B., and Sinnott, S. B., 2002, "A Second-Generation Reactive Empirical Bond Order (REBO) Potential Energy Expression for Hydrocarbons," J. Phys.: Cond. Matt., **14**, pp. 783–802.

[26] Plimpton, S., 1995, "Fast Parallel Algorithms for Short-Range Molecular Dynamics," J. Comp. Phys., **117**, pp. 1–19.

[27] Hoover, W. G., 1985, "Canonical Dynamics: Equilibrium Phase-Space Distributions," Phys. Rev. A, **31**, pp. 1695–1697.

[28] Salvetat, J.-P., Bonard, J.-M., Thomson, N. H., Kulik, A. J., Forro, L., Benoit, W., and Zuppiroli, L., 1999, "Mechanical Properties of Carbon Nanotubes," Appl. Phys. A: Mat. Sci. Proc., **69**, pp. 255–260.