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The effect of boundary conditions on the vibrations of armchair, zigzag, and chiral single-walled carbon nanotubes

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Single-walled carbon nanotubes (SWCNTs) have three distinct structures: armchair, zigzag, and chiral. It is known that they have different electronic properties, but the situation regarding their vibrational behavior is less clear. Doubly clamped nanotubes of all three types exhibit the same vibrational modes, and their vibrations in the directions perpendicular to the nanotube axis are degenerate. In nanotube applications, such as sensors based on nano-electro-mechanical systems, their ends are not fully clamped, thus their vibrational behavior could differ. Careful molecular dynamics simulations of SWCNTs with boundary conditions, which imitate the partly clamped experimental conditions, show that armchair, zigzag, and chiral nanotubes indeed vibrate differently. The symmetry between the two perpendicular directions is broken, and SWCNT type does influence the vibrational modes. © 2011 American Institute of Physics. [doi:10.1063/1.3667290]

I. INTRODUCTION

Carbon nanotubes (CNTs) possess unique electrical and mechanical properties; they are much stronger than steel, conduct better than copper, and are very elastic materials. These properties make them very attractive for both basic and applied research. One active field is nano-electro-mechanical systems (NEMS) based on CNTs. CNT NEMS are extremely light, usually have very few structural defects, and their fabrication is easier than that of conventional NEMS, which are produced by lithography techniques. CNT can oscillate at high frequencies with high quality factors (Q). Hence, assuming all other properties being equal, CNT resonators are expected to reach the ultimate mass, stress, and pressure sensitivities and are thus suitable for a multitude of technological applications, such as ultra fast sensors, actuators, and signal processing components.1,2

In the last few years, there has been significant progress in experimental measurements of the vibrational modes of single-walled carbon nanotubes (SWCNTs), on achieving extremely high Q values, and on sensing ultra low external masses that stick to the nanotubes.3–6 Since the natural frequency is sensitive to the applied external load, one of the principles of sensing is based on the natural frequency shift of a carbon nanotube resonator under external perturbation.

Let us consider the structure of a nanotube-based NEMS. For high quality CNTs, the growth is performed at the ends of the fabrication process.7 In these situations, the nanotube is suspended between two electrodes, with its lower part attracted to the electrodes by Van der Waal’s forces.5 In such a geometry (see Fig. 1),8 the ends of the vibrating nanotube are partially supported on their lower surfaces. Thus, when modeling this system in order to study its vibrations, one would study a nanotube that is neither doubly clamped at both ends nor has completely free ends. One observes from Fig. 1 that the suspended atoms can be displaced by the AFM tip, but those on the electrode do not move so freely. A partly clamped nanotube would, therefore, provide the situation closest to the experimental one.

There is also a question of which criterion to use to best characterize the vibrational behavior. In our previous studies, where we reported about vibrating SWCNTs which are frozen at both ends, (see details in our previous papers11,12), we selected direct measurement of the first four vibrational modes as the tool for vibrational characterization. This was achieved by directly monitoring the displacement during vibration. Such characterization avoids routes such as deducing Young’s modulus from a single or partial set of modes and then applying a specific analytical model. As we showed in Ref. 11, at least one model, viz., that of Euler-Bernoulli, does not even describe nanotube vibrations correctly.

We have reviewed previous studies of nanotube vibrations with many theoretical/simulative approaches, paying special attention to the nature of the boundary conditions (BCs) at the nanotube ends, and pertinent results are summarized in Table I, with a detailed discussion in Sec. II. Studies with various external parameters and methods, including molecular dynamics (MD) simulations,9–12 continuum mechanics models,13–16 and a structural mechanics approach,17,18 as well as finite element analysis19 have been made. The effect of clamping on the vibrational frequencies has not been systematically investigated, since each study used a single type of BC. Continuum studies use models with doubly clamped ends, where the first and second derivatives of position are zero. Many previous atomistic studies investigated nanotubes, where the ends of the nanotubes can move freely, although we studied doubly clamped tubes. Both extremes differ from the real situation, as introduced above. Study of the clamping effect is also important...
because, in experiment, it is one of the possible origins of dissipation mechanisms and low \( Q \).

In this paper, we explain the effect of changing BCs to partially clamped in order to approach experiment as closely as possible. We will describe our general method, its validation by the Timoshenko beam model, and our previous results in Sec. II. For the doubly clamped case (Fig. 2(a)), we showed clearly\cite{11} that the nanotube structure (armchair, zigzag, or chiral) does not influence the vibrational frequencies. In Sec. III, we introduce the new partially clamped boundary conditions and describe details of the new simulations reported in this paper. We modeled the vibrational behavior of three different types of SWCNTs: armchair (denoted by A), zigzag (ZZ), and chiral (C) under half doubly clamped (HDC) conditions, as depicted in Fig. 2(b), and compare their vibrations to those of the same nanotubes under fully doubly clamped (FDC) conditions (Fig. 2(a)).

We found that the BCs do affect the vibrational modes. Once the full clamping is released, the structure (zigzag, armchair, and chiral) does indeed affect the nature of the vibrations. Moreover, the HDC conditions lift the double degeneracy of the vibrations in the directions perpendicular to the nanotube axis. The nature of this symmetry breaking depends on the nanotube chirality. We conclude with a reconciliation of previous studies, showing that it is indeed the nature of the nanotube chirality. We conclude with a reconciliation of previous studies, showing that it is indeed the nature of the nanotube chirality.

II. REVIEW OF PREVIOUS STUDIES

In previous studies,\cite{11,12} we reported carefully equilibrated molecular dynamics simulations of armchair SWCNTs, including a precise analysis of their vibrations under fully doubly clamped boundary conditions, as depicted in Fig. 2(a). In Ref. 11, we provided clear evidence for the failure of simple analytic models to accurately extract resonance frequencies as the ratio, \( R/L \), between the tube radius \( R \) and the length \( L \) increases. Our results were in excellent agreement with the Timoshenko beam model,\cite{20} which includes the effect of both rotary inertia and of shearing deformation, and we shed light on Yakobson’s paradox,\cite{21} giving an upper cutoff estimate for the effective SWCNT thickness. Unfortunately, analytical models do not take into account structural properties, such as chirality, which may be critical in NEMS applications.

A selection of earlier simulations, which study mechanical properties of different structures of CNTs, are summarized in Table I. The main method for calculation of mechanical properties (Young’s modulus) is monitoring of the dynamics of carbon nanotubes, i.e., their vibrational frequencies, but the interpretation of the dynamics in terms of the Young’s modulus can be problematic. For example, Lu et al.\cite{22} found that, for single and multiwall nanotubes, the elastic moduli are shown to be insensitive to structural details, such as the helicity, the radius, and the number of walls using an empirical force-constant model (EFCM).

Ustinel et al.,\cite{22} based on Ref. 22, but without the distinction of distinct nanotube structure, studied vibrational behavior of such devices with slack, which was caused by hanging the nanotube over the gap during fabrication. On the other hand, a molecular mechanics (MM) study,\cite{23} that reports vibrational frequencies of zigzag and armchair nanotubes as a function of vibrational mode clearly shows that, for nanotubes that are not doubly clamped, radial breathing modes differ for different structures. They also conclude that vibrational modes of the continuum structures deviate noticeably from those of the molecular mechanics method, and this deviation increases with an increase in the vibrational mode.

<table>
<thead>
<tr>
<th>Method</th>
<th>BC</th>
<th>Type</th>
<th>Property</th>
<th>Difference</th>
<th>Agree with Ref. 20</th>
</tr>
</thead>
<tbody>
<tr>
<td>MM (Ref. 23)</td>
<td>Free ends</td>
<td>ZZ, A SWCNTs</td>
<td>Vib. freq.</td>
<td>Yes</td>
<td>No comparison</td>
</tr>
<tr>
<td>EFCM (Ref. 22)</td>
<td>Not reported</td>
<td>ZZ, A, C SWCNTs; A MWCNTs</td>
<td>Young M.</td>
<td>No</td>
<td>No comparison</td>
</tr>
<tr>
<td>MD (Ref. 12)</td>
<td>FDC</td>
<td>ZZ, A, C SWCNTs</td>
<td>Vib. freq.</td>
<td>No</td>
<td>Yes</td>
</tr>
</tbody>
</table>

FIG. 1. (Color online) On the left, we see an AFM image of a vibrating nanotube. The vibration is a consequence of the scanning of the AFM tip. The right panel is an outline cartoon, where the suspended nanotube is shown in the center of the hexagonal envelope (green online), the white regions are flat horizontal surfaces, and the shaded regions are steps between the higher planes at the sides and the lower one in the center. The envelope around the nanotube is a guide to the eye for the maximum left and right nanotube displacements.

FIG. 2. (Color online) (a) Fully doubly clamped and (b) bottom doubly clamped single-walled carbon nanotube. The Y axis is along the length, Z points upwards, and the X axis points out of the page, perpendicular to Z and Y.
The study of Huang et al.\textsuperscript{24} mentioned briefly that chirality may be relevant in calculations of Young’s modulus.

In an attempt to determine which procedure is correct and whether the nanotube type affects vibration, we reported in Ref. 12 on the vibrational behavior of four different types of SWCNTs: armchair, zigzag, and two different chiral ones, which were fully clamped at both ends, as in our previous study.\textsuperscript{11} Comparison between the vibrational behavior of these four types of nanotubes gave the result that the SWCNT structure does not affect the vibrational frequencies under these conditions. How can we reconcile the results of the studies described above and in Table I?

III. DETAILS OF OUR SIMULATIONS

Using the approach that we carefully validated in Refs. 11 and 12, we have generated high quality data with MD simulations on carefully equilibrated clamped tubes (using the Brenner\textsuperscript{25} potential) for the thermal vibrations decomposed into different modes. We obtain the dependence of the four lowest modes on length for each of these three nanotubes. Details about our computational approach, which are made within the canonical ensemble, were presented previously.\textsuperscript{11} We emphasize that we took great care to eliminate intrinsic tension by first equilibrating the tubes with a slow thermalization to 300 K under periodic boundary conditions and waiting until the length of the equilibrated nanotube remained constant up to insignificant fluctuations. We then opened up the tube and introduced the partially or fully clamped boundary conditions. Since a large number of SWCNTs with different chiralities and lengths were studied, the amount of data needed for the vibrational analysis was reduced by selecting some special points where data was recorded (see Ref. 11 for details). To obtain adequate statistics for all vibrational modes, we let every nanotube vibrate 1000 times more than the period of its lowest frequency, using a MD time step of 0.5 fs. We then applied a fast Fourier transform (FFT) analysis to the data from the selected points (including one near the center of mass) to calculate the power density as a function of frequency for each of the nanotubes. Throughout the code development, we generated still and animated atomic images with AViz\textsuperscript{26,27} for verification purposes. AViz has also been used to prepare the figures that illustrate the boundary conditions.

IV. NANOTUBE SELECTION

In order to compare frequencies between different nanotube types, we need to match the radius and length of the different nanotube types as closely as possible.\textsuperscript{12} The large periods of chiral tubes complicate this process. In our previous study,\textsuperscript{12} we selected 3 chiral (9,6), (9,5), and (8,6) nanotubes with the radii of 5.10, 4.81, and 4.76 Å, respectively, for our initial trials. We compared the vibrational behavior of (9,6), (8,6), and (9,5) chiral nanotubes by plotting their vibrational frequencies as a function of length; in spite of the fact that, due to the different lengths of a single period, there are minor discrepancies, the frequencies of these nanotubes are similar when interpolated, and the difference of about 0.29–0.35 Å in radius does not have much affect on the vibrational frequencies. In Fig. 3 from our earlier paper,\textsuperscript{11} it can be seen that frequency as a function of radius is very flat above radii of 4 Å, and the frequencies are almost identical for tubes with radial differences of less than 0.5 Å. For the purposes of that study,\textsuperscript{12} we chose the (8,6) and (9,5) Å tubes for intensive comparison with the ZZ (12,0) and A (7,7) nanotubes selected therein.

Selection of a set of radially matched nanotubes that can be created with a desired range of lengths is difficult enough for FDC tubes, but once we need to partially clamp and require a slightly different length range, it is more complicated. Hence, to achieve the requisite matching between the three nanotube types (A, ZZ, and C) we selected the (9,6) chiral tube this time. We again clamped (froze) the ends
differently for each type. The first (last) three periods were frozen for the A nanotubes, the first (last) two periods for the ZZ nanotubes, and a half of the first (last) period for the chiral nanotubes. Figure 3 demonstrates HDC conditions with frozen atoms in light gray (yellow online) (a) three periods of an A, (b) two periods of a ZZ, and (c) half a period of a C nanotube. The dark (blue online) atoms are free to move.

### Table II. Data sets of length and vibrating length for (7,7) armchair, (12,0) zigzag, and chiral (9,6).

<table>
<thead>
<tr>
<th></th>
<th>L (Å)</th>
<th>L_v (Å)</th>
<th>No. of periods</th>
</tr>
</thead>
<tbody>
<tr>
<td>(7,7) Armchair</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>98.38</td>
<td>83.62</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>108.24</td>
<td>93.48</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>120.52</td>
<td>105.76</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>147.57</td>
<td>132.81</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>196.76</td>
<td>182.0</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>245.95</td>
<td>231.19</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>295.14</td>
<td>280.38</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>(12,0) Zigzag</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>102.24</td>
<td>83.44</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>110.76</td>
<td>91.96</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>123.54</td>
<td>106.50</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>153.36</td>
<td>134.56</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>204.48</td>
<td>185.68</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>255.60</td>
<td>236.80</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>306.72</td>
<td>287.92</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>(9,6) Chiral</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>92.84</td>
<td>74.27</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>129.99</td>
<td>111.42</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>148.56</td>
<td>129.99</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>204.26</td>
<td>185.69</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>259.96</td>
<td>241.39</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>315.67</td>
<td>297.10</td>
<td>17</td>
<td></td>
</tr>
</tbody>
</table>

The radii of the selected nanotubes of types ZZ, A, and C are 4.70 Å, 4.75 Å, and 5.10 Å, respectively (less than 0.5 Å difference), and we give details of the total length and of the length of the vibrating segments (L_v) for all cases in Table II.

### V. RESULTS

We compared the first four vibrational modes of nanotubes with both types of boundary conditions (FDC and HDC) and of different lengths, as listed in Table II. The frequencies as a function of vibrational length are depicted in Figs. 4–6 for each of the A, ZZ, and C nanotubes, respectively. In each case, we compare the degenerate X-Z results of the FDC case with the different X-Z results for the HDC case. There are two clear observations here:

- HDC nanotubes vibrate with lower frequencies in the Z and X directions than FDC nanotubes (see Figs. 4–6)
As a result of the change in boundary conditions, the degeneracy of frequencies in the X and Z directions that was observed for FDC conditions was lifted.

In order to systematically investigate the differences in vibrational behavior between the three nanotube types under the HDC boundary conditions, we plotted the vibrational frequencies as a function of the nanotube length for A, ZZ, and C nanotubes in the X (see Fig. 7) and in the Z directions (see Fig. 8) in separate plots. Figures 7–8 show some differences between the three nanotube types, but it is hard to determine a specific pattern.

Alternatively, one can study the dependence of the symmetry-breaking parameter $\eta = (f_x - f_z)/f$ on the nanotube type, where $f$ is the average frequency of $f_x$ and $f_z$. The symmetry breaking parameter is plotted in Figs. 9–12 for the first, second, third, and fourth modes, respectively, of the different CNT types. The graphs show clear differences in the vibrational behavior of nanotubes of the A, ZZ, and C types. Differences between frequencies in the X and Z directions can be summarized as follows:

1. $\eta$ values of A, ZZ, and C are different for all investigated modes for the nanotubes that are shorter than 20 nm
2. $\eta$ of short nanotubes is negative for the 3rd and 4th modes.

* As a result of the change in boundary conditions, the degeneracy of frequencies in the X and Z directions that was observed for FDC conditions was lifted.

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1. $\eta$ values of A, ZZ, and C are different for all investigated modes for the nanotubes that are shorter than 20 nm
2. $\eta$ of short nanotubes is negative for the 3rd and 4th modes.
3. only chiral nanotubes have negative \( g \) values already for the 2nd vibrational mode
4. the \( g \) values of chiral nanotubes are much larger than those of armchair and zigzag nanotubes.

VI. DISCUSSION AND CONCLUSIONS

The above results demonstrate that boundary conditions are extremely important in the field of SWCNT NEMS design and optimization. Firstly, we see from Figs. 4–6 that the vibrational frequencies of FDC CNTs are higher than those of HDC. This result can be understood on the basis of the actual length of the vibrating segment. For HDC CNTs, the actual vibrating length is a little bit larger and, hence, the vibrational modes are lower. Secondly, we observe that a change from FDC to HDC conditions breaks the symmetry of carbon nanotubes, which splits the degeneracy of vibration in the X and Z directions. It can be seen from this picture that a different number of atoms are frozen in different geometries according to the nanotube symmetry, allowing vibrations of C–C bonds in different directions. The symmetry is broken differently for armchair, zigzag, and chiral nanotubes, and this is expressed in different vibrational behaviors of the three nanotube types. This could not be observed under symmetric doubly clamped boundary conditions. These observations are consistent with Refs. 12 and 23, where, in the former case, the full double clamping led to identical behavior and, in the latter, incomplete clamping led to different behaviors for different chiralities (see Table I).

From the experimental AFM image in Fig. 1, it is clear that HDC is closer to the laboratory situation. Since only in MD or MM such HDC conditions are likely, this confirms the need for a direct atomistic simulation to understand CNT NEMS.

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