



# Structural characterization of carbon nanotubes via the vibrational density of states



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## ABSTRACT

The electrical and chemical properties of carbon nanotubes vary significantly with different chirality and diameter, making the experimental determination of these structural properties important. Here, we show that the vibrational density of states (VDOS) contains information on the structure of carbon nanotubes, particularly at low frequencies. We show that the diameter and chirality of the nanotubes can be determined from the characteristic low frequency  $L$  and  $L'$  modes in the VDOS. For zigzag nanotubes, the  $L$  peak splits into two peaks giving rise to another low energy  $L''$  peak. The significant changes in the frequencies and relative intensities of these peaks open up a route to distinguish among structurally different nanotubes. A close study of different orientations of Stone–Wales defects with varying defect density reveals that different structural defects also leave distinct fingerprints in the VDOS, particularly in the  $L$  and  $L'$  modes. With our results, more structural information can be obtained from experiments which can directly measure the VDOS, such as inelastic electron and inelastic neutron spectroscopy.

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## 1. Introduction

Carbon nanotubes (CNTs) have emerged as one of the most promising materials because of their peculiar and remarkable electronic, thermal and mechanical properties [1]. Many applications are foreseen for carbon nanotubes in future nanotechnology and semiconductor industry, such as smaller transistors [2,3], and improved batteries [4]; both of which are currently limiting factors in the development of better electronic devices. Recently, the use of carbon nanotubes has been shown in flexible integrated circuits [5,6] and as promising candidates for conductors in nanoelectronics [7]. Another recent discovery is the use of carbon nanotubes as a cavity for ice, to increase its melting point by as much as 100 °C, but this effect critically depends on the diameter of the tube [8]. Distinct carbon nanotubes have shown very different electronic and thermal behavior [9,10], therefore it is fundamentally and experimentally important to distinguish different types of tubes based on their chirality and diameter.

Carbon nanotubes are characterized by two integer numbers  $(n, m)$ , describing the chiral vector between two equivalent points

on a graphene sheet, which coincide when the sheet is rolled into a tube. Two important chiralities are armchair  $(n, n)$ , featuring C–C bonds perpendicular to the tube axis, and zigzag  $(n, 0)$ , featuring C–C bonds parallel to the tube axis. A nanotube with any other  $(n, m)$  chirality is called a chiral tube [11].

It is possible in experiments to identify a single carbon nanotube by its diameter and chiral angle as measured by direct local techniques such as atomic resolution scanning tunneling microscopy (STM) [9], transmission electron microscopy (TEM) [12,13], and electron diffraction [14–16]. Other indirect and rather cheap methods to characterize carbon nanotubes are Raman spectroscopy [17], and photoluminescence excitation spectroscopy [18–20]. Very recently, the determination of chiral indices of two- or three-walled carbon nanotubes by a combination of electron diffraction and Raman spectroscopy has been reported [21].

In experiments, intrinsic defects commonly occur in carbon nanotubes, such as the Stone–Wales (SW) defect which is formed by the rotation of a C–C bond by 90° [22,23]. This rotation results in two pentagons and two heptagons in the otherwise hexagonal lattice. This is a common defect in graphene as well [24] and the formation energy of an SW defect in carbon nanotubes is lower than it is in graphene, and further decreases as a function of decreasing tube diameter [25]. SW defects have direct consequences on the electrical [26], mechanical [27–29], and chemical

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[30,31] properties of carbon nanotubes. The SW defect can be considered to form spontaneously as a result of excess strain [32,33], and is suggested to be responsible for plastic deformation of carbon nanotubes [34]. This defect is considered as a dislocation dipole: rotation of further C–C bonds separates it into two dislocation cores both consisting of a pentagon and a heptagon [35]. Other nanotubes with topological defects, for instance containing octagons, have also been reported [32].

Other types of defects in carbon nanotubes include vacancies, which show a stronger effect on the strength of a carbon nanotube [36]. Vacancy defects are commonly formed by irradiation and can survive for macroscopic times at room temperature; but as a vacancy is metastable, atoms will rearrange to mend the defect [37,38]. Carbon nanotubes can also contain atoms other than carbon; common hetero-atom dopants experimentally integrated into the graphene lattice include nitrogen and boron. Due to the different electrical and chemical properties of doped carbon nanotubes, applications are suggested in chemistry and energy storage devices [39]. It is also possible for foreign atoms or molecules to be adsorbed to the carbon nanotube surface; for many molecules adsorption occurs most strongly at defect sites [31,40]. This effect is studied to use carbon nanotubes as chemical sensors [31,41].

Computer simulation is a powerful tool in carbon nanotube research. By simulations, the properties can be predicted of carbon nanotubes of any chirality or any number of defects: many different nanotubes can be studied without having to synthesize every single one of them. A common and frequently used method to simulate carbon nanotubes is density functional theory (DFT). However, DFT is computationally intensive and therefore limits the size of the system that can be studied [42,43]. A semiempirical potential allows to study much larger systems. Small systems of nanotubes have particularly poorly resolved low frequency vibrational spectra therefore to resolve this regime of VDOS nicely, large system sizes are required. In the case of vibrational spectrum studies; it is particularly important because a system of  $N$  atoms has  $3N$  vibrational degrees of freedom [44,45], therefore the vibrational spectrum of a small system is only a crude approximation of the spectrum of a macroscopically large carbon nanotube. Semiempirical methods have recently been shown to correspond fairly well with experiments [46,47].

The vibrational density of states (VDOS) can well be used to determine many chemical and physical properties of carbon nanotubes. Besides studying chirality and defects, the VDOS can also be used to calculate thermal conductivity [48]. Many properties of carbon nanotubes have been studied using Raman spectroscopy such as chirality and defects [17,22,49–52], but with this technique only certain Raman active phonon modes can be observed [44,49,53]. It is possible to study the full vibrational spectrum in experiments by inelastic neutron scattering [49,54], or inelastic electron tunneling spectroscopy (IETS) [55]. IETS can also be used for localized measurements using the tip of an STM (STM-IETS), which allows the study of local properties such as defects, different tubes joined together, or tube caps [56,57]. The vibrational spectrum of graphene has already been experimentally mapped with IETS [58], and this opens up a possibility to use the same technique to characterize carbon nanotubes.

In this paper, we show that a semiempirical potential developed for graphene [59] can be effectively used for carbon nanotubes. The vibrational spectrum of a carbon nanotube as calculated by the simple elastic potential; approaches that of graphene for large diameters. We show that the armchair and zigzag nanotubes have distinct low frequency vibrational modes and based on these modes one can characterize the chirality of a carbon nanotube. These low frequency phonon modes are very sensitive to the tube diameters and therefore can be used to determine the diameter of a

nanotube. We further show that the density of the point defects such as Stone–Wales defects can be measured by simple study of relative intensities of low energy peaks in vibrational spectrum.

## 2. Method

To calculate the vibrational spectrum of carbon nanotubes, we use a recently developed semiempirical potential for graphene [59] given by

$$E = \frac{3}{16} \frac{\alpha}{d^2} \sum_{ij} (r_{ij}^2 - d^2)^2 + \frac{3}{8} \beta d^2 \sum_{j,i,k} \left( \theta_{jik} - \frac{2\pi}{3} \right)^2 + \gamma \sum_{ijkl} r_{ijkl}^2. \quad (1)$$

Here,  $r_{ij}$  is the length of the bond between two atoms  $i$  and  $j$ ,  $\theta_{jik}$  the angle between the two bonds connecting atom  $i$  to  $j$  and  $k$ , respectively, and  $r_{ijkl}$  the distance between atom  $i$  and the plane formed by its three neighboring atoms  $j$ ,  $k$ , and  $l$ . The parameters  $\alpha = 26.060 \text{ eV/\AA}^2$ ,  $\beta = 5.511 \text{ eV/\AA}^2$ ,  $\gamma = 0.517 \text{ eV/\AA}^2$ , and  $d = 1.420 \text{ \AA}$  are used, which were obtained by density-functional theory (DFT) calculations for graphene [59]. This potential was effectively used to study twisted bilayer graphene [60], vibrational properties of graphene [61], effect of boundary conditions in graphene samples [62], and graphene nanobubbles [63].

Using this potential the Hessian matrix is obtained containing the second derivatives of the energy with respect to the  $x$ -,  $y$ - and  $z$ -coordinates of all atoms. The eigenvalues of this matrix represent the force constants of the vibrational modes in  $\text{eV/\AA}^2$ , and the eigenvectors represent the normal coordinates of the vibrational modes. These force constants  $k$  are converted into frequencies as  $f = \frac{1}{2\pi c} \sqrt{\frac{k}{m}}$ , with  $c$  the speed of light and  $m = 1.99 \times 10^{-26} \text{ kg}$ , the mass of a carbon atom. In our simulations we use force-free periodic boundary conditions [62] in the direction along the tube. There are three translational modes and one rotational mode around the axis, assigned by their force constants which are zero. The area under the VDOS plot is equal to the total number of the vibrational modes.

Using this method, the VDOS is obtained for many carbon nanotubes having 600 atoms with different chiralities and defect densities. The VDOS is convoluted with a Gaussian function with a width  $\sigma = 14 \text{ cm}^{-1}$ , a value chosen for comparison with earlier results for graphene [61].

## 3. Results and discussion

We calculate the VDOS for many carbon nanotubes of different diameters and chiral angles. In particular, we show the dependency of VDOS on the diameter of armchair and zigzag nanotubes. We also show some soft vibrational modes of the tubes which can be used to characterize carbon nanotubes. The vibrational spectrum for different chiral angles has a unique signature in the low frequency vibrational modes. Furthermore, we show that the relative intensities of low frequency vibrational peaks can be used to determine the Stone–Wales defect densities for armchair and zigzag nanotubes.

### 3.1. Armchair nanotubes

We calculate the vibrational spectrum of various armchair nanotubes of different diameters ( $D$ ) and compare them with the VDOS of graphene by Jain et al. [61] as shown in Fig. 1. We show that the small diameter tube (5, 5) has high frequencies for the  $L$  and  $L'$  modes and there is redshift in the peaks as the diameter of the tubes increases and converges to the values of graphene in infinite

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