Phonon dispersion relations and soft modes of 4 Å carbon nanotubes*

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The phonon dispersion relations of three kinds of 4 Å carbon nanotubes are calculated by using the density functional perturbation theory. It is found that the frequencies of some phonon modes are very sensitive to the smearing width used in the calculations, and eventually become negative at low electronic temperature. Moreover, two kinds of soft modes are identified for the (5,0) tube which are quite different from those reported previously. Our results suggest that the (5,0) tube remains metallic at very low temperature, instead of the metallic-semiconducting transition claimed before.

Keywords: phonon dispersion relations, density functional theory, carbon nanotubes
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1. Introduction

Carbon nanotubes have attracted much attention from the science community for more than ten years. Among them, the vibrational properties of carbon nanotubes are intensively investigated since they are very useful for the characterization of different nanotubes in experiments. For example, the diameter of a nanotube can be predicted by examination of the Raman spectra measured experimentally.[1] Recently, much effort[2−5] has been devoted to the study of phonon modes in very small diameter carbon nanotubes. Moreover, superconductivity[6] has been observed in single-wall carbon nanotubes (SWNTs) with diameters of about 4 Å (1 Å=0.1 nm), probably at or close to the theoretical limit. However, due to the strong electron–phonon (e–ph) coupling, a one-dimensional (1D) metallic system should favour the occurrence of the Peierls transition to drive it into an insulating phase. Indeed, it was previously reported[4,5,7] that the Peierls transition temperature in the (3,3) tube is predicted to be comparable to room temperature. Besides, the armchair (3,3), the zigzag (5,0) and the chiral (4,2) also have diameters of 4 Å, and all of them are known to co-exist inside zeolite channels.[8−10] However, the phonon dispersion relations of (5,0) and (4,2) tubes are less well studied. To have a complete understanding of the 4 Å tubes, we present in this paper detailed phonon calculations for these three kinds of tubes. In particular, the phonon softening closely related to the Peierls transition is carefully investigated.

2. Computational method

As a first approximation, the phonon dispersion relation for a carbon nanotube can be obtained by folding that of the 2D graphene sheet. However, such a method does not always yield the correct dispersion relation for a carbon nanotube, especially in the low frequency region. For example, the radial breathing mode (RBM), which is characteristic of a nanotube, cannot be predicted from the simple band-folding picture. Moreover, the accuracy of the phonon dispersion relation may be affected if the force constants are fitted to those from graphite.[11] This is especially the case if one is interested in the phonon softening, which does not appear in classical lattice models even when the curvature effect is explicitly considered.

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Our calculations have been performed by using an alternative approach of density functional perturbation theory (DFPT)[12] which allows for accurate calculations of phonon modes at generic wave vectors. We use the so-called PWSCF simulation code[13] where the interaction between ions and electrons is described by an ultrasoft pseudopotential, and a plane wave basis set is used to expand the electronic eigenstates. We use the local density approximation (LDA)[14] and the exchange–correlation energy is in the form of Ceperley–Alder[15] as parameterized by Perdew and Zunger.[16] The plane wave cutoff is set to 35 Ryd and the $\boldsymbol{k}$ points are sampled on a uniform grid along the tube axis (in what follows $\boldsymbol{k}$ and $\boldsymbol{q}$ are labelled as electron and phonon wave vectors, respectively). The energy levels are populated using either the Gaussian (GS)[17] or Fermi–Dirac (FD)[18] smearing method.

3. Results and discussions

As a test of the reliability of our DFPT approach, we have calculated the phonon dispersion relation of a graphene sheet (Fig. 1). The optimized lattice constant we obtained is 2.44 Å, which corresponds to a carbon–carbon distance of 1.41 Å and is very close to the experimental value of 1.42 Å.[19] As can be seen from Fig. 1, the overall topology of the phonon dispersion relation is very similar to those found experimentally.[20,21] Our calculated frequencies also agree well with the recent theoretical calculations.[3,22,23]

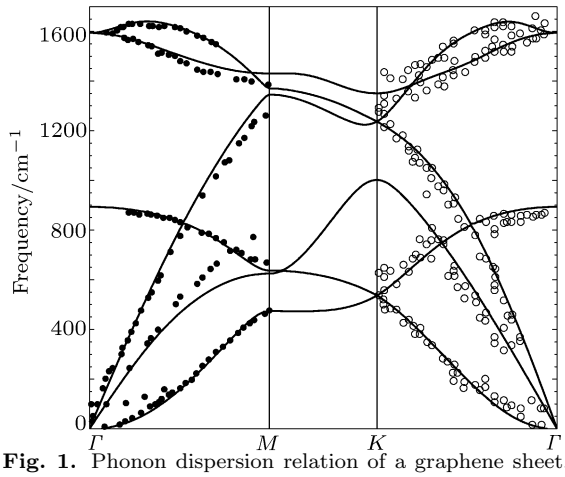


Fig. 1. Phonon dispersion relation of a graphene sheet. The solid lines show the results of the DFPT approach. The solid and open circles represent the experimental data from Refs. [20] and [21], respectively.

Figure 2(a) shows the calculated phonon dispersion relation of a (3,3) tube. The solid curves are obtained with a GS broadening of 0.2 eV. We found that the phonon frequencies are generally softer than the band-folding results, which is due to the curvature effect that weakens the interatomic forces.[3] It should be mentioned that the frequencies of some phonon modes depend strongly on the broadening width used in the calculations. For example, the frequency of mode A at the Γ point decreases monotonically from 745 cm^{-1} to 674 cm^{-1} when the FD broadening width is decreased from 0.2 eV to 0.012 eV. Another mode labelled as B at the Γ point has similar behaviour, as listed in Table 1. Such phonon softening is more interesting at $q = 2k_{\rm F}$, where three modes (C, D, and E) are softened upon the reduction of the broadening. In particular, the frequency of mode C becomes negative (-185 cm^{-1}) at very small broadening of 0.012 eV (or low electronic temperature). The phonon softening is connected with the Kohn anomaly and Peierls distortion caused by strong e–ph coupling in 1D metallic nanotubes.[2–5,24–27] The frequencies of soft modes are summarized in Table 1, and also indicated in Fig. 2(a) by dashed curves and asterisks for 12 meV FD broadening. Note that the characteristic RBM of (3,3) tube has a frequency of 546 cm^{-1}, and is insensitive to the broadening used.

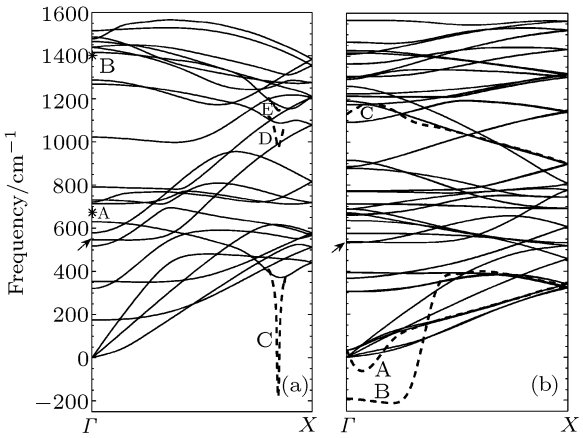


Fig. 2. Phonon dispersion relation of (a) (3,3) tube and (b) (5,0) tube. The solid curves are obtained using a Gaussian broadening of 0.2 eV. The dashed curves and asterisks correspond to a 12 meV (25 meV) Fermi–Dirac broadening for the (3,3) tube (the (5,0) tube). The arrows indicate the RBM.

Table 1. Calculated frequencies (cm^{-1}) of a (3,3) tube for certain phonon modes with different FD broadening width σ (eV). The values at Γ and $q = 2k_{\rm F}$ are both given.

q	mode	ω				
		$\sigma = 0.2$	0.1	0.050	0.025	0.012
Γ	A	745	725	708	691	674
	B	1506	1484	1457	1430	1401
$q = 2k_{\rm F}$	C	423	374	303	181	−185
	D	1120	1088	1049	1011	973
	E	1202	1172	1158	1152	1147

The phonon dispersion relation of a (5,0) tube is shown in Fig. 2(b), where the solid curves are obtained with a GS broadening of 0.2 eV. The dashed curves correspond to additional explicit calculations of the phonon modes with a reduced broadening (25 meV FD distribution). We see that three bands are obviously softened, and two of them have negative frequencies at low electronic temperature. The negative phonon modes at the Γ point are illustrated in Fig. 3, where 3(a) and 3(b) are degenerate in frequency and are labelled as A in Fig. 2(b). The most negative phonon mode B in Fig. 2(b) is also doubly degenerate and corresponds to Fig. 3(c) and 3(d). We see that Fig. 3(a) shows an elliptic deformation as previously reported in Ref. [5]. There is another ellipse-like deformation as shown in Fig. 3(b) which was not mentioned before. Both distortions could drive the metallic (5,0) tube into semiconducting, known as the 'Peierls transition', discussed in Ref. [5]. However, it is surprising that the values of the associated frequency do not change monotonically with the reduction of the broadening. As can be seen from Table 2, the frequency of phonon mode A decreases from positive to negative, and then increases to positive again. The negative frequency exists in a small range of broadening width. We want to emphasize that a similar feature is observed using a supercell approach[28] for the phonon calculations. It is thus reasonable to expect that the Peierls instability only occurs in an intermediate temperature region, which is quite different from those reported before.[4,5] The structure deformations in Fig. 3(c) and 3(d) are square-like, and the corresponding phonon frequencies are significantly softened at reduced electronic temperatures. Such a kind of phonon mode was never reported before. As summarized in Table 2, there is a big drop of the frequency of phonon mode B when the broadening width is decreased from 0.2 eV to 0.012 eV. This is also clearly indicated by the corresponding dashed curve in Fig. 2(b). Unlike that of modes A and B, the softening of mode C is much less, as can be seen from Table 2 and Fig. 2(b). The calculated frequency of RBM is found to be 532 cm^{-1} and remains unchanged with the broadening. It should be noted that the same phonon calculations have been performed for another zigzag (6,0) tube with a larger diameter. Unlike the (5,0) tube, no phonon softening is found at the Γ point for the (6,0) tube. Such a difference is probably due to the much stronger curvature effect in the (5,0) tube. As is known, the softening of phonon frequencies increases with increasing curvature.[29]

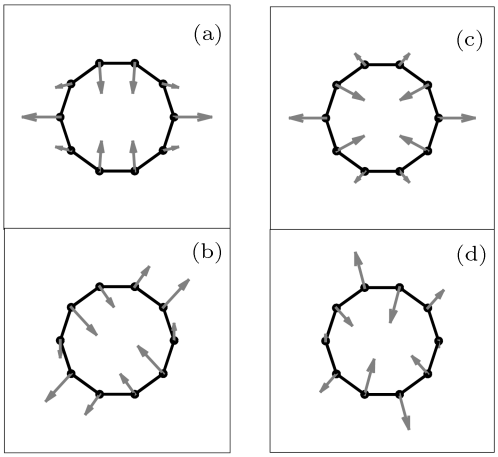


Fig. 3. Displacement patterns of two negative phonon modes at the Γ point in the (5,0) tube: (a) and (b) are degenerate with elliptic deformation; (c) and (d) are also degenerate with square-like deformation.

Table 2. Calculated frequencies (cm^{-1}) of the (5,0) tube for certain phonon modes at Γ with different FD broadening width σ (eV).

mode	ω							
	$\sigma = 0.2$	0.1	0.065	0.050	0.034	0.030	0.025	0.012
A	107	68	22	−42	−14	30	36	59
B	507	420	328	251	50	−125	−193	−257
C	1198	1179	1163	1151	1138	1133	1129	1123

In Fig. 4 we plot the energy band structures for the phonon modes A and B of (5,0) tube at low electronic temperatures. As known, the (5,0) tube is a metal with fairly large density of states (DOS) at the Fermi level.[10] However, we see from Fig. 4(a) that the elliptic deformation of mode A opens a gap of $\sim$ 0.2 eV at the Fermi level, which implies a metallic-semiconducting transition. In this respect, our results are in good agreement with those of Ref. [5]. On the other hand, the square-like deformation of mode B

causes band-splitting around the Fermi level, as indicated in Fig. 4(b). However, there is no gap-opening even at very low temperature and the (5,0) tube remains metallic. In principle, the phonon modes A and B might compete with each other. Considering the more negative value of the frequency (see Table 2), phonon mode B seems more favourable at low temperatures. In this sense, the (5,0) tube is still metallic, instead of semiconducting or the Peierls transition claimed in Ref. [5].

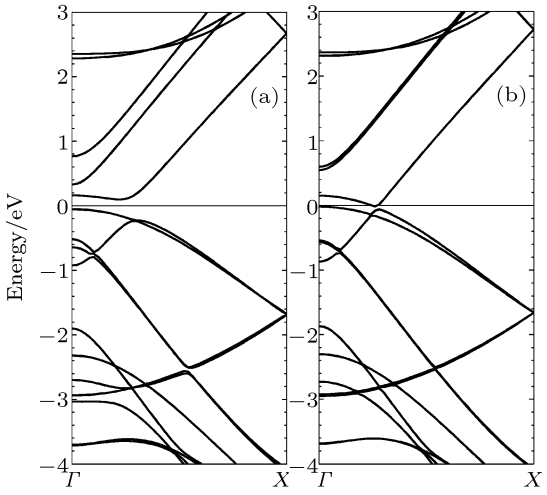


Fig. 4. Energy band structures of the (5,0) tube for (a) phonon mode A with elliptic deformation and (b) phonon mode B with square-like deformation at low electronic temperatures.

As the unit cell of the (4,2) tube is large, we cannot afford full phonon calculations by DFPT with the limited computation resources available to us. We thus use the supercell method to calculate the phonon dispersion relation of the (4,2) tube. In fact, we have done the same supercell calculations for the (3,3) and (5,0) tubes, and the results are close to those obtained by DFPT. Indeed, the explicit calculations of certain phonon modes at the Γ point by DFPT agree well with the supercell results for the (4,2) tube (not shown here). As the (4,2) tube is a semiconductor,[10] we do not observe phonon softening or Peierls instability as occurred in the (3,3) and (5,0) tubes. The calculated RBM frequency of the (4,2) tube is found to be 537 cm^{-1}. If we compare the RBM frequencies of these three kinds of tubes, we see that they do not follow the usual reciprocal relation when the tubes are nearly of the same radius but of quite different chirality. In fact, they exhibit a weak chirality dependence with the order $\omega_{(5,0)} < \omega_{(4,2)} < \omega_{(3,3)}$. Remember that the chiral angles of these 4 Å tubes are 0, 19 and 30 degree, respectively. These calculated RBM frequencies are in reasonably good agreement with the experimentally observed A_{1g} breathing mode in the measured Raman spectra.[30,31]

4. Summary

In summary, we have discussed the phonon dispersion relations of three kinds of 4 Å tubes. Special focus is on the soft modes which are very sensitive to the broadening used in the calculations. The underlying Peierls instability is investigated and two kinds of soft modes are identified for the (5,0) tube. The mode with square-like distortion seems more favourable than the one with elliptic deformation at very low temperature. In contrast to those reported before, our calculated results suggest that the (5,0) tube may be still metallic even at very low temperature.

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