Optical phonons of graphene and nanotubes

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Abstract. We review the optical phonon dispersions of graphene. In particular, we focus on the presence of two Kohn anomalies in the highest optical phonon branch at the $\Gamma$ and $K$ points of the Brillouin zone. We then show how graphene can be used as a model for the calculation of phonons in carbon nanotubes. Finally, we present the beyond Born-Oppenheimer corrections to their phonon dispersions. These are experimentally revealed in the Raman spectra of doped samples.

1 Introduction

Graphene is a bi-dimensional crystal of carbon atoms arranged into a honeycomb lattice. Even before its recent discovery in the free state \cite{1,2}, graphene was widely employed as a toy model for the description of the electronic and vibrational properties of other form of $sp^2$ bonded carbons, like graphite and carbon nanotubes \cite{3–5}.

Here we review the vibrational properties of graphene, showing how its phonon dispersion is shaped by the effects of electron–phonon interaction, which results in the presence of two Kohn anomalies in the highest optical branch.

We then show how graphene can be used to accurately compute the phonon frequencies of single wall carbon nanotubes (SWNTs). In particular, we emphasize the description of the Kohn anomalies in the phonon dispersion of metallic SWNTs, underlying how their correct description can be achieved only by considering the time-dependent nature of phonons. Finally we discuss the Raman signatures of adiabatic and non-adiabatic Kohn anomalies in the Raman spectra of graphene and metallic nanotubes.

2 Optical phonons of graphene

Figure 1 presents the high frequency region of the phonon dispersion of graphene, as obtained by density functional theory calculations in \cite{6}. Calculations are performed within the generalized gradient approximation (GGA) \cite{7}, using the density functional perturbation theory (DFPT) scheme \cite{8}, which allows the exact (within DFT) computation of phonon frequencies at any Brillouin Zone (BZ) point. We use plane-waves (90 Ry cut-off) and pseudopotential \cite{9} approaches. We treat the semi-metallic character of the system by performing the electronic integration with a smearing technique \cite{10}, i.e. occupying the electronic levels according to a distribution with a finite fictitious electronic temperature $\sigma$. This smears out the discontinuities present in the Fermi distribution for $\sigma=0$. Calculations are performed at the experimental lattice spacing ($a_0 = 2.46 \text{\AA}$). Graphene layers are separated by 7.4\,Å of vacuum.

The most striking feature of the dispersion in figure 1 is the discontinuity in the frequency derivative of the highest optical branches (HOB) at $\Gamma$ and at $K$ ($E_{2g}$ and $A_1'$ modes). This

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discontinuity, emphasized by the red lines in figure 1, is strongly related to the metallic nature of graphene. Indeed, the two cusps can be observed only if the calculations are strictly converged with respect to the electronic smearing. Within DFPT, the smearing $\sigma$ affects virtual transitions between occupied and empty states, differing in energy by $\sim \sigma$. This proves that the discontinuity are related to an anomalous screening of the electrons around the Fermi energy, and are thus Kohn anomalies [11].

In general, atomic vibrations are partially screened by electronic states. In a metal this screening can change rapidly for vibrations associated to certain $q$ points, entirely determined by the shape of the Fermi surface. The consequent anomalous behavior of the phonon dispersion is called Kohn anomaly [11]. Kohn anomalies may occur only for wavevectors $q$ such that there are two electronic states $k_1$ and $k_2 = k_1 + q$ both on the Fermi surface [11]. In graphene, the gap between occupied and empty electronic states is zero at $K$ and $K'$. Since $K' = 2K$, these are connected by the vector $K$. Thus, Kohn anomalies can occur for $q = \Gamma$ or $q = K$, as shown in figure 1.

The $q = \Gamma$ or $q = K$ cusps cannot be described by a finite set of interatomic force constants or by a set decaying exponentially with the real-space distance. Indeed, if they decayed exponentially, the dependence of the dynamical matrix on the reciprocal space vectors would be analytic, and, because of symmetry, the highest optical branch near $\Gamma$ and $K$ would have a flat slope. Thus, the two discontinuities indicate a non-analytic behavior of the phonon dispersion, due to a polynomial decay of the force constants in real space. This explains why it is impossible for any of the often used few-nearest-neighbors force constants approaches to properly describe the HOB phonons near $K$ and $\Gamma$ [6].

Interestingly for a given value of $q$, the Kohn anomalies are present only in the highest optical branches. This can be understood by noting that the non-analyticities of the dynamical matrix are due to terms proportional to the electron–phonon coupling. Thus, only phonons with a non-zero electron–phonon coupling matrix element (EPC) for transitions close to the Fermi energy can be affected by the Kohn anomalies. An explicit calculation of the EPC for the modes of graphene at $\Gamma$ and $K$ clearly shows that this condition is satisfied by the highest optical branches only [6,12,13,15].

Starting from the adiabatic expression of the dynamical matrix, and describing the electron–phonon coupling with a first neighbor tight binding model, it is possible to derive an entirely analytical description of the Kohn anomalies in graphene [6]. Defining $\langle D_{\pi}^{2} \rangle_{F} = \sum_{i,j} |D_{K_i,K_j}|^2/4$, where the sum is on the two degenerate $\pi$ bands at the Fermi level $\epsilon_{F}$ and $D_{K+q,K'} = (k + q, i)\Delta V_e(k,j)$ is the electron–phonon coupling (EPC) matrix element, with $|k,i\rangle$ the electronic Bloch eigenstate of wavevector $k$, band $i$, energy $\epsilon_{k,i}$, and occupation $f_{k,i}$ given by the Fermi–Dirac distribution function; $\Delta V_e$ is the derivative of the electronic potential with respect to a displacement along the phonon normal coordinate. In particular, we have shown that the slope of the phonon dispersion at $\Gamma$ and $K$ is proportional to the square of the electron–phonon