

# Anisotropic polarization due to electron–phonon interactions in graphene\*

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**Abstract:** Polarization plays an important role in the Raman spectroscopy. We study, in graphene, anisotropic polarization due to electron–phonon coupling (EPC). The numerical results show that the anisotropy is obvious even when the wave vector is in the range of the Raman experiment. The analytical expression is deduced from the structure factor, which indicates the crucial origin of the anisotropy. We also find that, as the phonon energy increases the polarization is clearly weakened due to the screen effect of EPC, but the anisotropy totally remains.

**Key words:** graphene; electron–phonon interaction; anisotropy; polarization

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## 1. Introduction

Graphene, the two dimension (2D) building block for carbon allotropes, has stirred a great deal of recent interest in the scientific community<sup>[1–3]</sup>. It is made out of carbon atoms arranged on a hexagon structure and can be stacked into 3D graphite, rolled into 1D nanotubes, or wrapped into 0D fullerenes. Although it is the mother for all these different allotropes, it was only discovered a few years ago.

The hexagon structure leads to many interesting properties of graphene. It has been inferred that graphene is a perfect hybrid between a metal and a semiconductor and exhibits anomalous integer quantum Hall effect, weak temperature dependence and magnetic field independence in its electronic transport<sup>[4,5]</sup>. The dispersion of electron and hole bands are crossed at the  $K$ ,  $K'$  points of the Brillouin zone. The anisotropic properties near the  $K$  point can be obtained by expanding the full band structure close to the  $K$  vector. The expansion of the spectrum up to second order in  $q/K$  is given by

$$E_{\pm}(q) \approx \pm v_F |q| - \left( \frac{9t'a^2}{4} \pm \frac{3ta^2}{8} \cos(3\theta_q) \right) |q|^2, \quad (1)$$

where

$$\theta_q = \arctan \frac{q_y}{q_x} \quad (2)$$

is the angle in momentum space, and  $q$  is the momentum measured relatively to the  $K$  point, as  $k = K + q$  and  $v_F \approx 1 \times 10^6$  m/s. Up to order  $(q/K)^2$  the dispersion depends on the direction in momentum space and has a three-fold symmetry. This is the so-called trigonal warping of the electronic spectrum<sup>[6,7]</sup>. Hence the high energy excitations could exhibit many anisotropic electronic and optical properties<sup>[8,9]</sup>. Furthermore, the anisotropy would come from the electron–

phonon coupling (EPC). Piscanec and Maultzsch demonstrated that graphene phonon dispersions have two remarkable Kohn anomalies points at  $\Gamma$  and  $K$  and EPC could be directly measured from the experimental dispersions<sup>[10,11]</sup> by the generalized gradient approximation (GGA)<sup>[12]</sup>. The key feature of phonons in graphene is the hybrid character of the electronic structure. In general, the atomic vibrations are partially screened by electrons. In a metal this screening can change rapidly for vibrations determined by the shape of the Fermi surface.

EPC is a key physical parameter in graphene. Ballistic transport, superconductivity, excited state dynamics, Raman spectra and phonon dispersions all fundamentally depend on it<sup>[13–17]</sup>. Many tight-binding calculations of optical phonons EPC in graphene and nanotubes are reported in the literature, with contrasting results<sup>[14,15,18–22]</sup>. In the tight-binding approximation (TBA) and the modulated hopping approximation (MHA), EPC comes from the modulation of the static deformations of the graphene sheet due to bending and strain couple to the Dirac fermions via vector potentials. Therefore, the tight-binding matrix for the EPC depends on the anisotropic honeycomb structure of graphene.

Polarization plays an important role in Raman spectroscopy since it determines the phonon frequency shift<sup>[23–25]</sup>. Moreover, Raman spectroscopy is nondestructive, fast, with high resolution experimental methods used to study the electronic structure and electron–phonon (e–p) interactions<sup>[23,26,27]</sup>.

In this paper, we calculate the polarization due to EPC and show that the anisotropy has the origin from the hexagon structure of graphene. Even when the wave vector is in the range of Raman experiment, the phonon frequency shifts are

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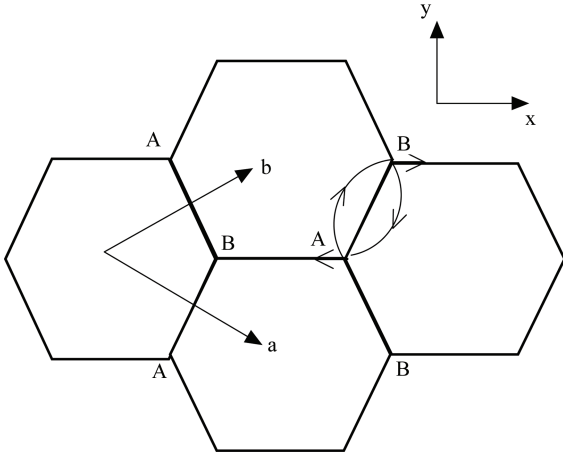


Fig. 1. Hexagon structure of graphene.

obvious and show a twofold warping of the direction in momentum space.

## 2. Theory and calculation

The geometrical structure of the carbon atoms in graphene are arranged as in Fig. 1, where  $\mathbf{a}$  and  $\mathbf{b}$  are the unit vectors of the honeycomb lattice, and A and B the nonequivalent positions of two carbon atoms in the unit cell. Let a 4-dimensional normalized vector  $\mathbf{Q}(\mathbf{q})$ , denote the polarization of the optical phonon modes with wave vector  $\mathbf{q}$ . In the TBA and MHA, the e-p interaction Hamiltonian can be written as<sup>[24]</sup> (we use units such that  $\hbar = 1 = k_B$ ):

$$H_{e-p} = \sum_{\mathbf{k}, \mathbf{q}} \frac{\alpha}{\sqrt{2\rho\omega_q}} M(\mathbf{k}, \mathbf{q}) c_{A\mathbf{k}}^+ c_{B\mathbf{k}+\mathbf{q}} (b_{\mathbf{q}}^+ + b_{-\mathbf{q}}) + H.C., \quad (3)$$

$$M(\mathbf{k}, \mathbf{q}) = \gamma \cdot \mathbf{Q}(\mathbf{q}), \quad (4)$$

$$\gamma = \left( 1 - \frac{e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{a}}}{2} - \frac{e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{b}}}{2}, \frac{\sqrt{3}}{2} [e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{a}} - e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{b}}] \right), \\ - \left[ 1 - \frac{e^{i\mathbf{k}\cdot\mathbf{a}}}{2} - \frac{e^{i\mathbf{k}\cdot\mathbf{b}}}{2} \right], -\frac{\sqrt{3}}{2} [e^{i\mathbf{k}\cdot\mathbf{a}} - e^{i\mathbf{k}\cdot\mathbf{b}}] \right), \quad (5)$$

where  $\alpha$  is the nearest neighbor hopping energy,  $\rho$  is the surface density of graphene,  $\omega_q$  is the phonon frequency,  $c_{i,\mathbf{q}}$  ( $c_{i,\mathbf{q}}^+$ ) annihilates (creates) an electron on the equivalent position  $i = A, B$  in the honeycomb lattice (spin indices are omitted throughout the paper) and  $M(\mathbf{k}, \mathbf{q})$  is the matrix element. Here, it is necessary to emphasize that  $\gamma$  in Eq. (4) is the most significant variable we will discuss in the next section. We call  $\gamma$  the structure fact of the EPC because it includes all the structure information of graphene in the hopping processes.

We are interested in the frequency shifts of optical phonons with wave vector  $\mathbf{q}$ . The corresponding Feynman diagrams which describe the renormalization of the phonon propagator in second order perturbation theory is given by Fig. 2, where the energy is in the Matsubara notation. The convolution of electronic Green's functions shown in the diagram is formally identical to the charge susceptibility of graphene,

$$\Pi(\mathbf{q}, i\omega_m) = \frac{1}{\beta} \sum_{\mathbf{k}, n} M(\mathbf{k}, \mathbf{q}) [\Pi_1 + \Pi_2 + \Pi_3 + \Pi_4], \quad (6)$$

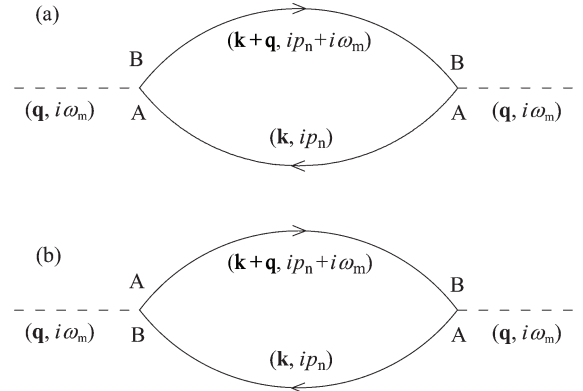


Fig. 2. Renormalization of the phonon propagator in second order perturbation theory.

$$\Pi_1 = \frac{1}{4} G_{AA}(\mathbf{k}, ip_n) G_{BB}(\mathbf{k} + \mathbf{q}, ip_n + i\omega_m), \quad (7)$$

$$\Pi_2 = \frac{1}{4} G_{BB}(\mathbf{k}, ip_n) G_{AA}(\mathbf{k} + \mathbf{q}, ip_n + i\omega_m), \quad (8)$$

$$\Pi_3 = \frac{1}{4} G_{AB}(\mathbf{k}, ip_n) G_{AB}(\mathbf{k} + \mathbf{q}, ip_n + i\omega_m), \quad (9)$$

$$\Pi_4 = \frac{1}{4} G_{BA}(\mathbf{k}, ip_n) G_{BA}(\mathbf{k} + \mathbf{q}, ip_n + i\omega_m), \quad (10)$$

where  $G_{l,l'}(\mathbf{k}, ip_n)$  ( $l = A, B; l' = A, B$ ) is the free electronic Green's function for the transitions from  $l$  to  $l'$ ,  $\beta = 1/T$  can be considered to be a complex time and the factor  $1/4$  in the  $\Pi_i$  ( $i = 1, 2, 3, 4$ ) is the weight describing the contribution to the total susceptibility. We give Figs. 2(a) and 2(b) for Eqs. (7, 9), representing the electronic transitions of equivalent and nonequivalent positions, respectively.

In order to obtain  $\mathbf{Q}(\mathbf{q})$ , we use the force constant model<sup>[28]</sup> (FCM) for calculating the phonon dispersion. And then, we only consider the interaction between two nearest-neighbor carbon atoms. Although this calculation cannot describe the twisted motion effect of carbon atoms and it is not sufficient to reproduce the experimental results, it leads to a phonon dispersion which can be calculated analytically and the anisotropic effect we focus on could be obtained in the range of  $q$  in Raman experiment within this simple model. For this reason, we deal with the EPC within the TBA and the FCM.

A commonly used approximation on the electron gas and ordinary metals problems is to replace the dynamical response  $\Pi(\mathbf{q}, i\omega_m)$  by the static one:  $\Pi(\mathbf{q}, 0)$  while the plasmon frequency  $\omega_p$  is much larger than the phonon frequency so that the phonons respond to a time averaged electron distribution. In 2D graphene, for typical values of  $\omega_p \approx 10$  meV, phonon frequency is much more than  $\omega_p$ . However, our numerical study indicates that there is no remarkable frequency dependence in the range of  $q \sim 10^5 \text{ cm}^{-1}$ . In what follows we will study, in graphene, the effect of a static response. The main result of this paper could be immediately obtained given by

$$\delta\omega_q = \frac{\alpha^2}{2\rho\omega_q} \Pi(\mathbf{q}, 0),$$

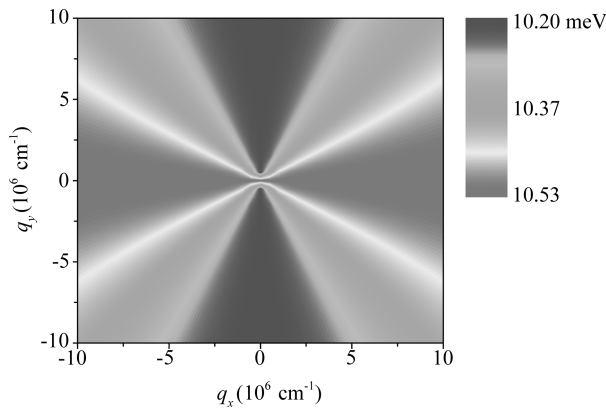


Fig. 3. Anisotropic frequency shift due to the EPC.

where  $\delta\omega_q$  is the  $q$  dependent frequency shift.

### 3. Results and discussions

The remaining problem for the phonon frequency shifts is to calculate the static response  $\Pi(\mathbf{q}, 0)$ . Using frequency sum rules, the summation in Eq. (6) for  $n$  can be eliminated trivially, and the other summation for  $\mathbf{k}$  could be numerically figured out. We calculate frequency shifts of the optical phonon modes at  $|\mathbf{q}| < 10^6 \text{ cm}^{-1}$ . The material parameters used in the evaluation are  $\alpha = 6.4 \text{ eV} \cdot \text{\AA}^{[29,30]}$  and  $\rho = 2.09 \times 10^{-8} \text{ g/cm}^2$ .

Figure 3 shows the anisotropic frequency shifts of the LO phonons. The anisotropy is mainly due to two reasons: (1) the anisotropic dispersion of electrons or phonons and (2) the anisotropic coupling of the electrons and phonons. we will indicate that the second reason (the structure fact  $\gamma$ ) is crucial at long wave in the next paragraph. The blue area and the red in Fig. 3 indicate the strength of the EPC. We can also understand such a result from the structure of graphene and the direction of phonon oscillation. In Fig. 1, we show the direction of LO phonon oscillation and the hopping processes of electronic polarization form  $A$  to  $B$  and then back to  $A$ . It is obvious that  $x$ -direction wave vectors are more favorable than  $y$ -direction's for the electron hopping.

Figure 4 shows the frequency shift of LO phonon versus the direction of wave vector at a typical value  $q = 5 \times 10^5 \text{ cm}^{-1}$ . The curves fit in with the triangle function,  $\delta\omega_q \propto \cos 2\theta_q$  or  $\delta\omega_q \propto \sin 2\theta_q$ , where the shift has a twofold symmetry on the direction in momentum space. As the expression can be obtained by reducing the structure fact  $\gamma$  in the long wave approximation, we could confirm that  $\gamma$  determines the anisotropy at long wave.

We also calculate the effect of dynamical respond  $\Pi(\mathbf{q}, \omega)$  as shown in Fig. 4. As the phonon energy  $\omega$  increases the electronic polarization is clearly weakened due to the screen effect of EPC, but the anisotropy totally remains. This is another evidence that the anisotropy is determined by the structure factor  $\gamma$ . Finally, we point out that the effects of temperature and chemical potential  $\mu$  are left out of our account, because the characteristic energy ( $\sim 10^4 \text{ K}$ ) of electronic dispersion in graphene is much higher than the room temperature

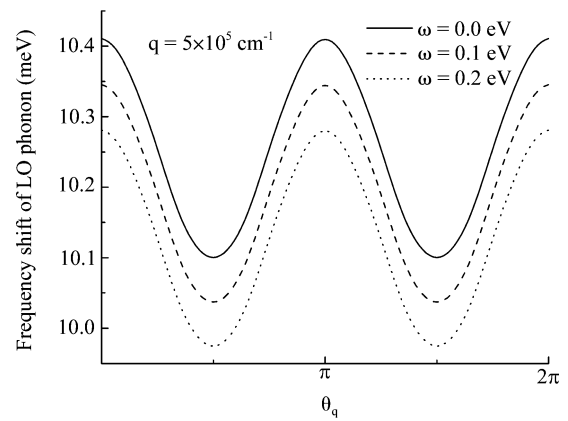


Fig. 4. Frequency shift versus the direction of wave vector.

( $\sim 300 \text{ K}$ ) and the effective Fermi temperature ( $\sim 1300 \text{ K}$  for the electronic surface density  $n \approx 10^{12} \text{ cm}^{-2}$ ). The above discussion could be valid all the way to room temperature.

### 4. Conclusions

Numerical results show that phonon frequency shifts show anisotropy on the direction in momentum space, which would have the most important origin in the anisotropic coupling of electrons and phonons. We also indicate that the anisotropy is insensitive to the temperature and the chemical potential and our theory for  $T = 0$  and  $\mu = 0$  should apply all the way to room temperature.

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