Phonon spectroscopy through the electronic density of states in graphene

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We study how phonon structure manifests itself in the electronic density of states of graphene.
A procedure for extracting the value of the electron-phonon renormalization \( \lambda \) is developed. In addition, we identify direct phonon structures. With increasing doping, these structures, along with \( \lambda \), grow in amplitude and no longer display particle-hole symmetry.

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It is a remarkable result of many body physics that in electronic systems in which the density of states (DOS) is constant on the scale of a phonon energy, electron-phonon renormalizations entirely drop out\(^1, 2\) and no phonon signatures are expected or seen. This has now changed with the advent of graphene. Graphene was isolated only in 2004\(^3, 4\) but has since been extensively studied and found to exhibit many unusual properties. These include a novel quantum Hall effect, a minimum conductivity, a Berry phase of \( \pi \) and other effects related to the chirality of its charge carriers.\(^5, 6, 7\)

In this letter, we show how measurements of the DOS in graphene offer a new opportunity to obtain detailed information on electron-phonon coupling in sharp contrast to the case of ordinary metals. This is important as it illustrates a strong violation of a well-established result of many body physics and provides unusual doping-dependent predictions for the manifestation of the electron-phonon interaction in experiments on graphene. This result arises for two reasons. First, the charge carriers exhibit relativistic dispersions with quasiparticle energy \( (\epsilon_k) \) linear, rather than quadratic, in momentum \( (k) \), \( \epsilon_k = \pm \hbar v_0 |k| \). Here, \( v_0 \) plays the role of the velocity of light and the \( \pm \) gives the upper and lower Dirac cones, respectively. At neutrality, the lower cone is fully occupied and the upper one, empty. This dispersion gives rise to an energy dependence of the DOS which is linear in high energies. Second, both theory and experiment indicate that the major coupling is to high energy phonons of order 200 meV.\(^8, 9, 10\) Thus, an electron scattering from an initial state to a final state through the assistance of a phonon will sample changes in the DOS on the scale of the phonon energy, which is significant in graphene. Another special feature of graphene is that the number of charge carriers can be changed through charging in a field effect device where the chemical potential \( (\mu_0) \), measured with respect to the Dirac point (neutrality point), is proportional to the square root of the gate voltage. These characteristics offer a rich new spectroscopy for the study of phonon effects including their variation with \( \mu_0 \).

In graphene, the bare band DOS varies linearly with energy and hence the renormalized density of states \( N(\omega) \) is given by\(^11, 12, 13, 14\)

\[
N(\omega) = \frac{\int_{-W_C}^{W_C} \frac{dc}{c}}{\pi} \left( \frac{\omega - \text{Re}\Sigma(\omega) + \mu - \epsilon^2 + |\text{Im}\Sigma(\omega)|^2}{\omega - \mu} \right)\]

(1)

with \( N_0 = 2/\pi \hbar^2 v_0^2 \). In Eq. (1), \( W_C \) is an upper cutoff on the Dirac cones given by \( \sqrt{\pi \sqrt{\omega}} \), with \( t \) the nearest neighbor hopping parameter, and \( \Sigma(\omega) \) is the electronic self-energy given by\(^12\)

\[
\Sigma(\omega) = \int_0^{+\infty} d\nu \xi^2 F(\nu) \int_{-\infty}^{+\infty} d\omega' \frac{N(\omega')}{N_0 W_C} \left\{ n(\nu) + f(-\omega') + \frac{n(\nu) + f(\omega')}{\omega - \omega' + \nu + i0^+} \right\}
\]

(2)

where \( \alpha^2 F(\nu) \) is the electron-phonon spectral density and \( n(\nu) \) and \( f(\omega') \) are, respectively, the Bose-Einstein and Fermi-Dirac distribution functions at temperature \( T \). For the bare band case \( (\Sigma(\omega) \to 0) \), the chemical potential \( \mu \) reduces to its noninteracting value \( \mu_0 \) and sets the doping level. Also, the Lorentzian form in Eq. (1) reduces to \( \delta(\omega + \mu_0 - \epsilon) \) and the DOS becomes \( |\omega + \mu_0| \).

Park et al.\(^8\) performed a full first-principles study of the electron-phonon interaction in graphene and found that the result could be approximated by an Einstein mode at 200 meV. For coupling to an Einstein mode, the electronic self-energy in a system with a linear DOS can be evaluated in the usual manner to give, at zero temperature, an analytic form with\(^12\)

\[
\text{Re}\Sigma(\omega) = \frac{A}{W_C} \left\{ \frac{\omega E}{\ln \left( \frac{\mu_0 + \omega + \omega E}{\omega^2 - \omega E^2} \right)} - (\mu_0 + \omega) \ln \left( \frac{W_C^2 (\omega + \omega E)}{(\omega - \omega E)(\omega + \mu_0 + \omega E)} \right) \right\}
\]

(3)

where \( A \) is the area under the Einstein mode and \( \omega_E \) is the Einstein frequency. For simplicity, we have assumed in writing Eq. (3) that \( W_C \) is larger than any other energy of interest, but in all numerical results presented here, this approximation was not made. The corresponding
imaginary part is $-\text{Im}\Sigma(\omega) = \frac{4\pi}{\hbar^2} |\omega - \omega_E + \mu_0|$, for $\omega_E < \omega < W_C - \mu_0 + \omega_E$ and $\frac{4\pi}{\hbar^2} |\omega + \omega_E + \mu_0|$ for $-\omega_E > \omega > -W_C - \mu_0 - \omega_E$. In terms of this self-energy, the renormalized density of states is given by

$$
\frac{N(\omega)}{N_0} = \frac{\bar{\omega}}{\pi} \left[ 2 \tan^{-1} \left( \frac{\bar{\omega}}{\omega_C} \right) - \tan^{-1} \left( \frac{\bar{\omega} - \omega_C}{\Gamma} \right) - \tan^{-1} \left( \frac{\bar{\omega} + \omega_C}{\Gamma} \right) \right] + \frac{\Gamma}{2\pi} \ln \left( \frac{\left( \bar{\omega} - \omega_C \right)^2 + \Gamma^2 \left( \bar{\omega} + \omega_C \right)^2 + \Gamma^2}{\left( \omega^2 + \Gamma^2 \right)^2} \right). \tag{4}
$$

where $\Gamma = -\text{Im}\Sigma(\omega)$ and $\bar{\omega} = \omega - \text{Re}\Sigma(\omega) + \mu$. For finite $\mu$, the problem no longer has particle-hole symmetry and $\text{Re}\Sigma(\omega = 0)$ is not zero and provides a shift in chemical potential from bare to dressed value with $\mu = \mu_0 + \text{Re}\Sigma(\omega = 0)$.\cite{12,16} For a clean system $\Gamma$ will vanish for $-\omega_E < \omega < \omega_E$, and Eq. (4) reduces to

$$
\frac{N(\omega)}{N_0} = \bar{\omega} \text{sgn}\bar{\omega}, \quad \text{for } -\omega_E < \omega < \omega_E. \tag{5}
$$

In this special range, the DOS is very closely related to the $\text{Re}\Sigma(\omega)$. Returning to Eq. (1), it is important to realize that, for infinite bands with constant DOS, the $|c|$ factor would not appear and the integral over $\epsilon$ would give a constant independent of $\omega$ so that phonon renormalizations simply drop out. Graphene is very different.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{(Color online) $-d\text{Re}\Sigma(\omega)/d\omega$ vs $\omega$ for a truncated Lorentzian electron-phonon spectral density peaked around $\omega_E = 200$ meV. Shown are curves for $\mu_0 = 0, 150, 500,$ and 700 meV.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{(Color online) (a) $N(\omega)/N_0$ (in eV) vs $\omega$ for the bare chemical potential $\mu_0 = 150$ meV. The solid blue curve gives the phonon renormalized case and the black dotted, the bare band case. The arrows show the bare (long black) and renormalized (short blue) value of $\mu$. (b) Same as for (a) but with $\mu_0 = 500$ meV.}
\end{figure}

While Eq. (3) has been written for a single Einstein oscillator, it nevertheless provides us with valuable insight into the relationship between phonon structure and the real part of the self-energy. $\text{Re}\Sigma(\omega)$ has singularities of the form $\ln |\omega \pm \omega_E|$ at $\omega = \pm \omega_E$ and a third weaker logarithmic singularity of the type $(\omega + \omega_E + \mu_0) \ln |\mu_0 + \omega + \omega_E|$ at $\omega = -(\mu_0 + \omega_E)$. The neutrality point is special, however. For $\mu_0 = 0$, only two singularities remain and they are both of the weaker kind $(\omega \pm \omega_E) \ln |\omega \pm \omega_E|$. In a real system there will of course be a distribution of phonons and the self-energy of Eq. (3) needs to be averaged over such a distribution. This will reduce the prominence of the expected singularities in this quantity. In such a case it becomes useful to consider a first derivative $-d\text{Re}\Sigma(\omega)/d\omega$. This is shown in Fig. 1 for four values of the chemical potential, $\mu_0 = 0, 150, 500$, and 700 meV. The phonon distribution used in these numerical calculations was a truncated Lorentzian centered around $\omega_E = 200$ meV with width $\delta = 15$ meV.\cite{12,17} As expected the top left frame exhibits only two phonon anomalies while the three other frames have three. Also in these three cases the anomalies at $\omega = \pm \omega_E$ are much more pronounced than the ones at $\omega = -(\omega_E + \mu_0)$, and also than those in the top left frame. In all four frames, the black dotted horizontal line was drawn through the local minimum at $\omega = 0$ and identifies the value of the electron-phonon mass renormalization parameter $\lambda$ as we will now describe. For $\omega$ small near the Fermi energy $(\omega = 0)$, $\text{Re}\Sigma(\omega)$ in Eq. (3) can be shown to vary as $\text{Re}\Sigma(\omega) \simeq -\lambda \omega + \text{Re}\Sigma(\omega = 0)$ and the dressed quasiparticle energy $E_k$ is given by the equation $E_k - \text{Re}\Sigma(E_k) + \mu = \pm \hbar v_0 |k| = E_k(1 + \lambda) + \mu_0$. Or $E_k = [\pm \hbar v_0 |k| - \mu_0] / (1 + \lambda) = \pm \hbar v_0 (k - k_F) / (1 + \lambda)$, which means that $\lambda$ simply renormalizes the bare Fermi velocity from $v_0$ to $v_0^* = v_0 / (1 + \lambda)$. As Fig. 1 shows, $\lambda$ grows with increasing $\mu_0$ as Eq. (3) implies. The red arrow indicates the Dirac point defined by $|k| = 0$. The relationship between boson structure in the self-energy and its manifestation in the DOS is given by
Eq. (1). Results for $N(\omega)$ are shown in Fig. 2. The frame (a) is for $\mu_0 = 150$ meV, which is smaller than $\omega_E$ and (b) is for $\mu_0 = 500$ meV $> \omega_E$. The shaded yellow region is the occupied part of the bare band which is shown as the black dotted curve. Phonon renormalizations change the shape of the DOS and hence the value of the chemical potential must be altered to keep the correct number of particles. The long black and short blue arrows point to the value of the bare and dressed chemical potential with $\mu - \mu_0 = \text{Re} \Sigma(\omega = 0)$. Phonon anomalies are clearly seen in the dressed curves. To emphasize this structure an Einstein spectrum was used with $\omega_E = 200$ meV so that the phonon structures fall at $\omega = \pm \omega_E$, one on either side of the Fermi energy. The expected singularity at $\omega = - (\omega_E + \mu_0)$ is by comparison very weak and appears as a slight change in slope in Fig. 2. Two additional features of these curves are to be noted. At the Fermi energy ($\omega = 0$), the dressed and bare DOS have exactly the same value. In the region of the Fermi energy Eq. (5) applies and $N(\omega)/N_0 = |\omega(1 + \lambda) + \mu_0|$, which differs from its bare value only by the additional factor of $(1 + \lambda)$. At $\omega = 0$, this difference disappears and dressed and bare DOS are the same. Phonons do not change the value of the DOS at the Fermi level. The slope out of $\omega = 0$, however, is changed by a factor of $(1 + \lambda)$ as can be seen in both frames of Fig. 2 and we also note that this linear behavior persists over a considerable energy range set by the value of the Einstein oscillator. Recognizing that the normalization for the DOS is $N_0 \approx 1/\sqrt{\omega}$, one might naively think that the $(1 + \lambda)$ renormalization can be included in $N(\omega)$ simply by changing $v_0$ to $v_0^\lambda$ in $N_0$, but we see here that this is not correct. Only one $(1 + \lambda)$ factor enters and not its square. The basic reason underlying this fact is that the coherent part of the electronic Green’s function, which defines the quasiparticles in the interacting system, contains only $1/(1 + \lambda)$ of the spectral weight. The remainder $\lambda/(1 + \lambda)$ is found in the incoherent piece describing phonon-assisted processes.

Phonon structure in $N(\omega)$ can be brought out through differentiation. Results for $dN(\omega)/d\omega$ vs $\omega$ are given in Fig. 3 as the solid blue curves, where $N(\omega)$ is normalized by $N_0$. Frame (a) is for $\mu_0 = 150$ meV and (b) is for $500$ meV. The vertical drop where $dN(\omega)/d\omega$ goes from positive to negative is at the Dirac point of the interacting system. Comparison with the bare band case, the dotted black line, shows a small shift of the position of the Dirac point between bare and dressed case. The bare case provides a useful reference line about which the effects of the electron-phonon interaction are easily seen. Besides the phonon structures at $\omega = \pm \omega_E$, $-(\omega_E + \mu_0)$, we note that the height of the curve above one at $\omega = 0$ gives the value of $\lambda$ directly which increases significantly with increasing value of chemical potential [as shown by the red solid curve in (c)]. The red dashed line is included for comparison and gives $-d\text{Re} \Sigma(\omega)/d\omega$. There are some differences between these two sets of results but we can conclude that all qualitative features seen in the DOS curves can be seen in the $\text{Re} \Sigma(\omega)$. This is not to say that the imaginary part of $\Sigma(\omega)$ plays no significant role. In frame (b), we see clearly that the jump at the Dirac point energy is no longer vertical but exhibits some smearing. This can be traced to the behavior about the Dirac point in the DOS shown in Fig. 2(b). The DOS no longer goes to zero at this point ($\omega_d$) but rather has a minimum about which it rises as a quadratic $(\omega - \omega_d)^2$, seen in experiment. We can show that for $|\omega - \omega_d| Z \ll \Gamma$, 

$$
\frac{N(\omega)}{N_0} = 2\Gamma \ln \left| \frac{W_C}{\Gamma} \right| + \frac{(\omega - \omega_d)^2 Z^2}{\pi \Gamma^2},
$$

with $Z \equiv 1 - |d\text{Re} \Sigma(\omega)/d\omega|_{\omega = \omega_d}$ and $\Gamma \equiv -|\text{Im} \Sigma(\omega)|_{\omega = \omega_d}$, which shows the lifting of the Dirac point and its conversion from linear to quadratic in $(\omega - \omega_d)$. This immediately leads to the smearing at Dirac point noted in the blue curve of Fig. 3(b). In Fig. 3(c), we plot the absolute value of the height of the phonon structures as a function of $\mu_0$ for the $\alpha^2 F(\nu)$ spectrum used here, a truncated Lorentzian (see in the inset in Fig. 3 long-dashed red curve). While the height of the phonon peak at $\omega = -(\omega_E + \mu_0)$ hardly changes with doping ($\mu_0$) the other two peaks do, note the curve for $\omega = \omega_E$. We have not plotted the peak height for $\omega = -\omega_E$ as for $\mu_0 < \omega_E$ it is similar to the result for $\omega = \omega_E$ and for $\mu_0 > \omega_E$ it becomes ambiguous. These predictions provide verifiable tests that observed structures are
deed due to phonons. They also show how the increase in the DOS at the Fermi surface with increasing doping is reflected in larger coupling to the phonons.

**FIG. 4:** (Color online) (a) $1 - |dN(\omega)/d\omega|$ vs $\omega$ for $\mu_0 = 0$ and $\omega_E = 155$ meV (solid blue curve). The inset on the lower right compares the phonon region with the input electron-phonon spectral density (red-dashed curve). (b) $1 - \sqrt{N(\omega)/N_0(\omega)}$ vs $\omega$ (solid blue curve) compared with the result using the procedure of Li et al. (long-dashed red curve).

In contrast to the standard expectation in wide band metals with nearly constant DOS on the phonon energy scale, phonon structure does appear prominently. These increases reflect the increase in the underlying $\alpha^2 F(\nu)$ spectrum used. It is shown in the inset as the long dashed red curve where it is scaled down and compared with the absolute value of the blue curve about $\omega = 155$ meV. While there is some agreement, the two curves have different profiles with the blue solid one much broader than the red long-dashed one. It is clear that such a plot is very useful in identifying phonon structure, i.e., not just the value of the mass enhancement factor $\lambda$ involved but also the position of the peaks in $\alpha^2 F(\nu)$ and their strength. In experiments, it may be more desirable not to differentiate. In Fig. 4(b), we show as the solid blue curve a different quantity $1 - \sqrt{N(\omega)/N_0(\omega)}$, where $N_0(\omega)$ is the bare band density of states. In this quantity, the value of the local maximum at $\omega = 0$ gives $1 - \sqrt{1 + \lambda} = -0.095$ rather than the $-\lambda$ of frame (a). We also note that the phonon structures at $\omega = \pm \omega_E$ are not as sharp, however, some signature of a sharp peak in the $\alpha^2 F(\nu)$ used remains. The long-dashed red curve is for comparison and represents the quantity that was used by Li et al. in their analysis of their STM data. The new laboratory in which to study variations in electron-phonon coupling with changing carrier concentration.

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