Electron–phonon coupling and intrinsic bandgap in highly-screened graphene

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Abstract. Photoemission studies of graphene have resulted in a long-standing controversy concerning the strength of the experimental electron–phonon (el–ph) interaction in comparison with theoretical calculations. Using high-resolution angle-resolved photoemission spectroscopy we study graphene grown on a copper substrate, where the metallic screening of the substrate substantially reduces the electron–electron interaction, simplifying the comparison of the el–ph interaction between theory and experiment. By taking the nonlinear bare bandstructure into account, we are able to show that the strength of the el–ph interaction shows better agreement with theoretical calculations. In addition, we observe a significant bandgap at the Dirac point of graphene.

The electron–electron and electron–phonon (el–ph) interactions are two of the fundamental interactions in many-body physics, giving rise to superconductivity, Mott-insulating behavior, and other collective phenomena. These phenomena are often studied in association with graphene not only because graphene is a simple system featuring two carbon atoms per unit cell [1] but also due to the unique potential of this material [2]. However, there have been many difficulties in matching theoretical predictions to experimental studies of el–ph coupling in graphene [3]. The nature of these discrepancies is due to the way the el–ph coupling constant $\lambda$ is extracted from the experimental data. Within the Migdal–Eliashberg regime,
el–ph coupling results in single phonon excitations that can be treated as perturbations to the bare band dispersion and leads to a renormalization of the group velocity with respect to the electronic bare band. The relative change of the renormalized velocity with respect to the bare velocity provides a measure of the el–ph coupling constant \( \lambda \). Angle-resolved photoemission spectroscopy (ARPES) has shown to be an invaluable probe to extract this constant since it can directly measure the single particle spectral function and hence the renormalized velocity. However, the correct determination of \( \lambda \) rests on an accurate determination of the bare velocity, which is often done by assuming a linear band approximation between the Fermi energy and high energy, a procedure that has been found to be grossly inappropriate for graphene [3].

For example, the local density approximation (LDA) band velocity is in fact known to change significantly over the relevant energy scales, which greatly affects the measured values of the el–ph coupling constant \( \lambda \) if a linear band is assumed. Further complicating the analysis, electronic correlations are known to renormalize the bare-band velocity in a nonlinear manner, to a degree determined by the dielectric screening of the substrate [4–8]. It should also be noted that the el–ph coupling strength may be enhanced by interplay between electron–electron and el–ph interactions [9–11]. Since the experimental bare band is so difficult to determine, ARPES studies typically resort to the linear bare band approximation when determining the el–ph coupling strength in graphene, resulting in an over- or under-estimate of the actual el–ph coupling constant when extracted from the real self-energy [12–18].

In light of these difficulties, one way to simplify the study of el–ph coupling in graphene might be to grow graphene on a metallic substrate, a growth technique that has recently become popular due to its relevance for technological applications [19]. On a metallic substrate, the electron–electron interaction in graphene is expected to be highly screened, which would remove velocity renormalizations due to electronic correlations and cause the bare dispersion (experimental minus el–ph interaction) to converge to the LDA result [20–22]. In this highly screened limit, the curvature of the graphene LDA band structure may be taken into account when analyzing el–ph coupling. Therefore the presence of a metallic substrate allows us to examine the el–ph interaction with an accuracy unmatched in other systems, leading to a straightforward analysis of the experimental data.

Here we present a high-resolution ARPES study of graphene grown on a copper substrate. Starting from a basic characterization of this system, which has never been studied before by photoemission spectroscopy, we observe sharp dispersions due to the copper substrate and graphene overlayer, including a large band gap at the Dirac point of graphene. Unlike past findings of smaller bandgaps at the Dirac point of graphene, the 400 meV bandgap that we observe is large enough that semiconducting characteristics can persist at room temperature without degradation due to thermal excitations. Proceeding to examine the many-body physics in highly screened graphene, we find an overall agreement between the experimental bandstructure and the LDA band calculations. Taking the curvature of the LDA band into account, we find close agreement between experimentally extracted el–ph coupling constants and theoretical calculations, providing accurate measurement of the el–ph coupling constant and providing closure to a long-standing debate.

Samples were grown on copper films as previously reported [19]. High-resolution ARPES data were taken at BL10.0.1 and BL12.0.1 of the Advanced Light Source at a temperature of 15 K after annealing samples to 1000 K, using a photon energy of 50 eV. The vacuum was better than \( 3 \times 10^{-11} \) Torr. Potassium was deposited in situ with an SAES Getters potassium vapor source.
Figure 1. (a) Partial map of the graphene/Cu Fermi surface. Arrows and circles correspond to bands from the copper substrate and graphene overlayer, respectively. Dashed black lines correspond to the hexagonal Brillouin zone of graphene. The K point is labelled, while the Γ-point is not shown, located at \((k_x, k_y) = (0, 0)\). The black vertical line through the K point illustrates the orientation of the data taken in panel (b). (b) EDCs taken along the K–K' direction through the Dirac point, showing that the graphene bands are n-doped with a bandgap and intensity minimum at the Dirac point. The presence of a bandgap creates two peaks in the EDCs at the K-point (peak positions marked in red). (c) Top: angle-integrated ARPES spectrum shows features at the Dirac point and phonon energy. Bottom: the derivative of the angle-integrated spectrum clearly specifies the top and bottom of the valence and conduction bands, respectively, confirming the presence of a bandgap.

Figure 1(a) shows a Fermi surface map with bands due to the copper substrate and graphene overlayers. Two sets of copper bands and Dirac cones can be distinguished due to the presence of rotated crystallographic domains of the substrate. The Dirac cones of graphene are visible, and are electron-doped due to their proximity to the copper substrate. Although doping can change from sample to sample, typical values are approximately \(2 \times 10^{13} \text{ cm}^{-2}\). ARPES data through a single Dirac cone is shown along the K–K' direction in figure 1(b), and along the Γ–K direction in figures 2(a)–(c). Photoemission intensity is suppressed along half of the cone due to matrix element effects [23].

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The dispersion in the vicinity of the Dirac point has been the subject of some controversy in the past. The valence and conduction bands are not collinear, possessing a region of vertical intensity between them. Whether this is due to the presence of a bandgap in the bare dispersion or a many-body effect has been hotly debated [24, 25]. In the present case of graphene on a copper substrate, the dielectric screening of the highly conductive substrate rules out the possibility of electron–plasmon coupling [20, 26], and instead implies the presence of a bandgap at the Dirac point [24, 27]. We find the separation between valence and conduction bands to be somewhat sample-dependent, with a typical bandgap of $400 \pm 50$ meV, when determined from: 1. the separation between the peaks of energy distribution curves (EDCs, intensity profiles at constant momentum), as shown in figure 1(b), with two peaks visible at the Dirac point momentum; or 2. the change in slope of the angle-integrated intensity near the Dirac point (figure 1(c)). The angle-integrated intensity (figure 1(c)) shows a V-shaped intensity profile,
with a minimum at the Dirac point energy, and increasing intensity away from the Dirac point. Far from the Dirac point, the valence and conduction bands are not collinear, with an overall offset of $100 \pm 30 \text{ meV}$, suggesting an unusual band gap opening mechanism [28]. This behavior is clearly similar to results reported previously, although the size of the bandgap at the Dirac point in this sample is larger [24, 27, 29, 30]. In figure 1(c), a dip can also be seen at the phonon energy, where the band dispersions are renormalized due to el–ph coupling [31, 32]. In the past, calculations of el–ph coupling have differed from experimental results [12–16]. This disagreement is believed to have three sources: firstly, the bare band is not completely linear and may have a positive or negative second derivative depending on the magnitude of the screening of the electron–electron interaction [3–5] and the direction along the Brillouin zone [3]; secondly, the electron–electron interaction is believed to enhance the el–ph coupling strength [9]; thirdly, the finite resolution of the experiment may lead to some error in the extracted band velocity [33]. The first two effects might be eliminated by the presence of a metallic substrate as this is expected to screen the electron–electron and electron–plasmon interactions, and also to eliminate the enhancement effect. In the limit of infinite screening, metallic substrates are expected to cause the graphene dispersions to converge to LDA calculations. This greatly simplifies the extraction of the el–ph self-energy.

The el–ph interaction is visible in the photoemission spectrum in two ways: the real part of the self-energy $\text{Re} \Sigma$ modifies the band position; while the spectral width of the bands is proportional to the imaginary part of the self-energy $\text{Im} \Sigma$ [34]. Peak positions and peak widths can be obtained by fitting Lorentzian peaks to the momentum distribution curves (MDCs), the intensity at constant energy as a function of momentum. The strength of the interaction, given by the coupling constant $\lambda$, can be extracted from either part of the self-energy, although in practice the real part of the self-energy is often more reliable, since the imaginary part is more sensitive to noise and the influence of impurity broadening. We have therefore focused on the real self-energy in our analysis.

Knowing the bare graphene band, $\text{Re} \Sigma$ is given by the difference between the experimental and bare band positions. From knowledge of $\text{Re} \Sigma$, the el–ph coupling constant $\lambda$ can be expressed as

$$\lambda_k = -\frac{\partial \text{Re} \Sigma_k(E)}{\partial E} \bigg|_{E=E_F},$$

or equivalently,

$$\lambda_k = \frac{v_k^0(E_F)}{v_k(E_F)} - 1,$$

where $v_k^0(E_F)$ and $v_k(E_F)$ are the bare and renormalized velocities at the Fermi level, respectively. However, the bare band of graphene is not linear, so the method of extracting $\lambda$ according to the formula

$$\lambda_k = \frac{v_1}{v_2} - 1,$$

(where $v_1$ and $v_2$ are the band velocities at higher and lower binding energy than the phonon, respectively) does not work, nor will any other method that assumes a linear bare band [3].

The extracted coupling constants are compared with el–ph coupling calculations [33] in figure 3. The agreement between experiment and theory is striking, providing the first experimental support of theoretical el–ph calculations. Having said this, our analysis may
Figure 3. (a) Experimental coupling constants are given as a function of electronic charge density in red, as extracted from figure 2. The data agrees with theoretical calculations [33], shown in black. The error generated when the linear band approximation is applied to the curved (bare) LDA band is given in blue, for comparison. (b) A zoomed-out version of panel (a), also showing results from the cited references in green (different references have different symbols depending on substrate).

require a small correction. Ab initio calculations expect an increasing el–ph self-energy even at high binding energies [35]. This differs from our results, where the LDA band gives good agreement with experiment at high binding energies. This discrepancy could correspond to an underestimate of the Re $\Sigma$-derived coupling constant by approximately $0.015 \pm 0.005$, and may derive from two physical origins: (i) it is likely that the metallic substrate does not perfectly screen the electron–electron interaction in the graphene overlayer. Since the electron–electron interaction increases the band velocity and the el–ph interaction decreases it, it is possible that at high binding energy both renormalizations affect the band velocity by similar amounts and essentially cancel, leaving the experimental velocity to agree with LDA. (ii) It is also possible that the LDA band is not a perfect description of the bare band dispersion, due to the presence of the gap at the Dirac point. We also note that more recent calculations have predicted larger el–ph coupling constants, which are significantly larger than our experimental results [36].

It should also be noted that el–ph coupling has been studied on a metallic substrate in the past. One study of graphene on iridium attempted to extract the el–ph coupling constant in a self-consistent manner with parabolic bands, although in some cases these were very nearly linear; see [14] for details.

To illustrate how much of a difference the linear bare band approximation makes, we have also applied the linear approximation to just the curved LDA band (which does not include el–ph coupling), where we take $v_0^k$ to be the slope of the line that intersects the LDA band at energies $E = E_F$ and $E = E_F - 0.4 \text{ eV}$ using equation (2). The results, shown as the blue ‘LDA’ line in figure 3, correspond to the linear bare band approximation when no el–ph coupling is taking place. Data from previous works are given in panel (b). The error from the bare band approximation is more than twice as large as the actual el–ph coupling constant [3]. On the other hand, in cases where the bare band curves in the opposite direction (‘concave-up’), such
as in the presence of strong electron–electron interactions [4–8, 37], for the LDA band on the opposite side of the Dirac cone (along the M–K–Γ direction) [3], or for bilayer graphene [18], the linear approximation underestimates the coupling constant.

In conclusion, we have shown for the first time that the magnitude of el–ph coupling in graphene agrees with theoretical calculations. These results settle a long-standing controversy in the field, confirming the validity of theoretical calculations, and casting doubt on the conclusions of many experimental works. This work is also generally applicable to future experiments that require studying el–ph coupling in materials with nonlinear bare bands. We have also shown that there is a significant bandgap in graphene grown epitaxially on a copper substrate, a discovery which may pave the way for future technological applications.

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References

[1] Wallace P R 1946 Phys. Rev. 71 622
[2] Geim A K and Novoselov K S 2007 Nature Mater. 6 183
[3] Park C-H, Giustino F, McChesney J L, Bostwick A, Ohta T, Rotenberg E, Cohen M L and Louie S G 2008 Phys. Rev. B 77 113410
[4] Castro Neto A H, Guinea F, Peres N M R, Novoselov K S and Geim A K 2009 Rev. Mod. Phys. 81 109
[5] González J, Guinea F and Vozmediano M A H 1994 Nucl. Phys. B 424 595
[6] González J, Guinea F and Vozmediano M A H 1996 Phys. Rev. Lett. 77 3589
[7] Das Sarma S, Hwang E H and Tse W-K 2007 Phys. Rev. B 75 121406
[8] Trevisanutto P E, Giorgetti C, Reining L, Ladisa M and Olevano V 2008 Phys. Rev. Lett. 101 226405
[9] Basko D M and Aleiner I L 2008 Phys. Rev. B 77 041409
[10] Basko D M, Piscanec S and Ferrari A C 2009 Phys. Rev. B 80 165413
[11] Lazzari M, Attaccalite C, Wirtz L and Mauri F 2008 Phys. Rev. B 78 081406
[12] Zhou S Y, Siegel D A, Fedorov A V and Lanzara A 2008 Phys. Rev. B 78 193404
[13] McChesney J L, Bostwick A, Ohta T, Emtsev K V, Seyller Th, Horn K and Rotenberg E 2007 arXiv:0705.3264
[14] Bianchi M, Rienks E D L, Lizzit S, Baraldi A, Balog R, Hornekaer L and Hofmann Ph 2010 Phys. Rev. B 81 041403
[15] Valla T, Camacho J, Pan Z-H, Fedorov A V, Walters A C, Howard C A and Ellerby M 2009 Phys. Rev. Lett. 102 107007
[16] Bostwick A, Ohta T, McChesney J L, Seyller T, Horn K and Rotenberg E 2007 Solid State Commun. 143 63
[17] Gruneis A, Attaccalite C, Rubio A, Vyalikh D V, Molodtsov S L, Fink J, Follath R, Eberhardt W, Buchner B and Pichler T 2009 Phys. Rev. B 79 205106
[18] Filliter T, McChesney J L, Bostwick A, Emtsev K V, Seyller Th, Horn K and Bennewitz R 2009 Phys. Rev. Lett. 102 086102
[19] Li X et al 2009 Science 324 1312
[20] Hwang E H and Das Sarma S 2007 Phys. Rev. B 75 205418
[21] Jang C, Adam S, Chen J-H, Williams E D, Das S and Sarma Fuhrer M S 2008 Phys. Rev. Lett. 101 146805
[22] Kotov V N, Uchoa B, Pereira V M, Castro A H and Neto Guinea F 2010 arXiv:1012.3484v1
[23] Shirley E L, Terminello L J, Santoni A and Himpsel F J 1995 Phys. Rev. B 51 13614
[24] Zhou S Y, Gweon G H, Fedorov A V, First P N, de Heer W A, Lee D H, Guinea F, Castro Neto A H and Lanzara A 2007 Nature Mater. 6 770
[25] Bostwick A, Ohta T, Seyller T, Horn K and Rotenberg E 2007 Nature Phys. 3 36
[26] Polini M, Asgari R, Borghi G, Barlas Y, Perez-Barnea T and MacDonald A H 2008 Phys. Rev. B 77 081411
[27] Enderlein C, Kim Y S, Bostwick A, Rotenberg E and Horn K 2010 New J. Phys. 12 033014
[28] Benfatto L and Cappelluti E 2008 Phys. Rev. B 78 115434
[29] Varykhalov A, Scholz M R, Timur Kim K and Rader O 2010 Phys. Rev. B 82 121101
[30] Walter A L, Nie S, Bostwick A, Kim K S, Moreschini L, Chang Y J, Innocenti D, Horn K, McCarty K F and Rotenberg E 2011 Phys. Rev. B 84 195443
[31] Li G, Luican A and Andrei E Y 2009 Phys. Rev. Lett. 102 176804
[32] Brar V W et al 2010 Phys. Rev. Lett. 104 036805
[33] Calandra M and Mauri F 2007 Phys. Rev. B 76 205411
[34] Damascelli A, Hussain Z and Shen Z X 2003 Rev. Mod. Phys. 75 473
[35] Park C-H, Giustino F, Cohen M L and Louie S G 2007 Phys. Rev. Lett. 99 086804
[36] Gusynin V P, Sharapov S G and Carbotte J P 2009 New J. Phys. 11 095103
[37] Siegel D A, Park C-H, Hwang C G, Deslippe J, Fedorov A V, Louie S G and Lanzara A 2011 Proc. Natl Acad. Sci. USA 108 11365