Colloquium: Graphene spectroscopy

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Spectroscopic studies of electronic phenomena in graphene are reviewed. A variety of methods and techniques are surveyed, from quasiparticle spectroscopies (tunneling, photoemission) to methods probing density and current response (infrared optics, Raman) to scanning probe nanoscopy and ultrafast pump-probe experiments. Vast complimentary information derived from these investigations is shown to highlight unusual properties of Dirac quasiparticles and many-body interaction effects in the physics of graphene.

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CONTENTS

I. INTRODUCTION

A. Scope of this review

Graphene is a single atomic layer of \( sp^2 \)-hybridized carbon atoms arranged in a honeycomb lattice. This two-dimensional (2D) allotrope of carbon is characterized by a number of superlative virtues (Geim, 2009), e.g., a record-high electronic mobility at ambient conditions (Morozov et al., 2008), exceptional mechanical strength (Lee et al., 2008a), and thermal conductivity (Balandin et al., 2008; Ghosh et al., 2008) Remarkable properties of graphene have ignited tremendous interest that resulted in approximately 50,000 publications at the time of writing. A number of authoritative reviews\(^1\) have been written to survey this body of literature but no single review can any longer cover the entire topic. The purpose of this Colloquium is to overview specifically the spectroscopic experiments that have helped to shape the modern understanding of the physical properties of graphene. While selected topics in graphene spectroscopy have been discussed,\(^2\) here we aim to present a panoramic view of physical phenomena in graphene emerging from both spectroscopy and imaging (Fig. 1C).

Spectroscopic observables can be formally categorized as either quasiparticle or current/density response functions. The former are fermionic, the latter are bosonic. The former is traditionally measured by photoemission and tunneling spectroscopy, while the latter can be investigated by, e.g., optical spectroscopy. Yet it may be possible to infer both quasiparticle and collective properties from the same type of measurements. For example, fine anomalies of the quasiparticle spectra seen in photoemission can give information about interactions between quasiparticles and collective modes (Sec. III.D)

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\(^1\)See Castro Neto et al. (2009); Das Sarma et al. (2011); Katsnelson (2012); Kotov et al. (2012); McCann and Koshino (2013); and Peres (2010).

Conversely, optical conductivity, which is a collective response, enables one to infer, with some approximation, the parameters of a quasiparticle band-structure (Secs. III.A, II.B, II.C, and V).

Finding such connections is facilitated by spectacular tunability of graphene. For example, with photoemission or tunneling techniques one can monitor the chemical potential $\mu$ of graphene as a function of the electron concentration $N$ and thereby extract the thermodynamic density of states. The same physical quantity can be measured by a very different technique, the scanning single-electron transistor microscopy. In our analysis of such complementary data we focus on what we believe are the most pressing topics in the physics of graphene, e.g., many-body effects. Additionally, our review covers information obtained by scanned probes and out-of-equilibrium methods that greatly expand available means to study graphene in space and time domains. Finally, we briefly address phenomena that arise when physical properties of graphene are altered via its environment and nanostructuring.

B. Graphene morphology

Graphene can be isolated or fabricated in a number of different forms, which is an important consideration in spectroscopy. Effectiveness of a given spectroscopic tool depends on the accessibility of the sample surface to the incident radiation. The size of the accessible area must normally be larger than the wavelength of the incident beam unless near-field probes are employed (Sec. III.B) Mosaic structure and defects may affect momentum and energy resolution of the measurement. Graphene differs widely in terms of these parameters depending on preparation method. Mechanical exfoliation of graphite typically produces single, bi-, and multilayer graphene (SLG, BLG, and MLG, respectively) of a few $\mu$m in size, although occasionally samples of dimensions of hundreds of $\mu$m can be obtained. Exfoliated samples can be transferred onto insulating substrates, after which they can be gated and subject to transport measurements. The sign and the magnitude of carrier concentration $N$ in gated samples can be precisely controlled over a wide range. The lower bound on $|N| \sim 10^{10}$ cm$^{-2}$ is set by inhomogeneities (Sec. IV.A). The upper bound $|N| \sim 10^{13}$ cm$^{-2}$ is limited by the dielectric breakdown strength of the substrate, although still higher $|N|$ are achievable by electrolytic gating.\footnote{See Efetov and Kim (2010); Ju et al. (2011); Mak et al. (2009); Newaz et al. (2012); and Xia et al. (2009b).} The carrier concentration can also be controlled by doping (Chen et al., 2008).

Morphologically, exfoliated samples are single crystals. They hold the record for transport mobility $\mu_{tr}$ although it varies much with the type of the substrate. Currently, high-quality hexagonal boron nitride (hBN) substrates enable one to achieve $\mu_{tr} \sim 10^5$ cm$^2$/Vs, which is about an order of magnitude higher than what is typical for graphene on SiO$_2$ and corresponds to $\mu$m-scale mean-free path (Dean et al., 2010; Mayorov et al., 2011b). The highest mobility
Large-area graphene can be made by another method: epitaxial growth on SiC by thermal desorption of Si (van Bommel et al., 1975). Epitaxial graphene may contain a single or many dozens of layers. The initial layer (layer number $L = 0$) has strong covalent bonds to the SiC substrate and is electronically different from the ideal SLG (de Heer et al., 2007). The morphology and electronic properties of the subsequent layers, $L > 0$, depend on which SiC crystal face it is grown: the Si-terminated $(0001)$ face or the C-terminated $(0001)$ face.\(^4\) According to de Heer et al. (2011), the Si-face grown graphene is orientationally ordered and has the Bernal stacking (as in graphite). The structure of the C-face epitaxial graphene is consistent with a stacking where every other layer is rotated by approximately $\pm 7^\circ$ with respect to a certain average orientation. The rotations inhibit interlayer tunneling so that the band structure of each layer is similar to SLG (see also Sec. IV.B).

The morphology of the epitaxial graphene after annealing resembles a carpet draping over the staircase (Emtsev et al., 2009). It is characterized by domains a few $\mu$m wide and up to $50 \mu$m long that mirror the underlying SiC terraces (Emtsev et al., 2009; de Heer et al., 2011).

The graphene/SiC interface is charged, inducing the $n$-type doping of about $10^{13}$ cm$^{-2}$ in the first ($L = 1$) graphene layer. Other layers have much smaller carrier concentration because of screening. The screening length of about one layer was measured by ultrafast infrared (IR) spectroscopy (Sun et al., 2010a). The doping of the surface layers can be altered by depositing charged impurities (Ohata et al., 2006; Zhou et al., 2008d). Relatively low mobility $\mu_{tr} = 500-10,000$ cm$^2$/Vs, the inhomogeneity of the doping profile, and the lack of its in situ control can be seen as drawbacks of (the first generation of) epitaxial compared to exfoliated graphene. On the other hand, the much larger surface area of the epitaxial graphene is advantageous for spectroscopic studies and applications (de Heer et al., 2007). An important recent breakthrough is epitaxial growth of graphene on high-quality hBN substrates (Yang et al., 2013).

Graphene samples of strikingly large 30-in width (Bae et al., 2010) can be produced by the chemical vapor deposition (CVD) on metallic surfaces, e.g., Ru,Ni or Cu that act as catalysts. CVD graphene can be transferred to insulating substrates making it amenable to gating and transport experiments (Bae et al., 2010; Kim et al., 2009). The microstructure of CVD graphene sensitively depends on the roughness of the metallic substrate and the growth conditions. Typical structural defects of CVD graphene are wrinkles and folds induced by transfer process and also by thermal expansion of graphene upon cooling. Grain boundaries are other common defects that have been directly imaged by micro-Raman (Li et al., 2010), transmission electron microscopy (Huang et al., 2011), scanning tunneling microscopy (Koeppke et al., 2013; Tapasztó et al., 2012), and near-field microscopy (Fei et al., 2013). The corresponding domain sizes range between $1-20 \mu$m. On the other hand, graphene single crystals with dimension $\sim 0.5 \mu$m have been grown on Cu by CVD (Li et al., 2011). Transport mobilities of CVD-grown graphene and epitaxial graphene on SiC are roughly on par.

At the opposite extreme of spatial scales are nanocrystals and nanoribbons. Graphene crystals of nm-size can be synthesized by reduction of graphene oxide\(^5\) or by ultrasonic cleavage of graphite in an organic solvent (Hernandez et al., 2008; Nair et al., 2012). Laminites of such crystals can be of macroscopic size amenable to X-ray and Raman spectroscopy. Nanocrystals can also be grown epitaxially on patterned SiC surface (de Heer et al., 2011). Graphene nanoribbons (GNRs) can be produced by lithography, nanoparticle etching, and unzipping of carbon nanotubes. There have been a number of spectroscopic studies of GNRs by scanned probes (Tao et al., 2011), transport\(^6\), and photoemission (Siegel et al., 2008; Zhou et al., 2008a) but because of space limitations they could not be covered in this review.

\section*{C. Electronic structure of graphene neglecting interactions}

In this section we summarize basic facts about the SLG band-structure within the independent electron approximation (Castro Neto et al., 2009). The nearest-neighbor carbon atoms in SLG form $sp^2$ bonds, which give rise to the $\pi$ and $\sigma$ electron bands. The $\sigma$-bands are relevant mostly for electronic phenomena at energies $\gtrsim 3$ eV. The unique low-energy properties of graphene derive from the $\pi$-bands whose structure can be understood within the tight-binding model (Wallace, 1947). If only the nearest-neighbor transfer integral $\gamma_0 = 3.0 \pm 0.3$ eV (Fig. 1B) is included, the amplitudes $\psi_j$ of the Bloch functions on the two triangular sublattices $j = A$ or B of the full honeycomb lattice can be found by diagonalizing the $2 \times 2$ Hamiltonian

\begin{equation}
H_{SLG} = \begin{pmatrix}
E_D & -\gamma_0 S_k^* \\
-\gamma_0 S_k & E_D
\end{pmatrix},
\end{equation}

where $E_D$ is the constant on-site energy, $k = (k_x, k_y)$ is the in-plane crystal momentum, $S_k = \exp(i k_x a/\sqrt{3}) + 2 \exp(-i k_x a/2\sqrt{3}) \cos(k_y a/2)$ represents the sum of the

\footnotesize
\(^4\)See Berger et al. (2004, 2006); Chartier et al. (2002); Emtsev et al. (2009); Forbeaux et al. (1998); Nagashima et al. (1993); Ohata et al. (2006); and Rollings et al. (2006).

\(^5\)This can be done chemically (Boehm et al., 1962; Dikin et al., 2007) or via IR irradiation (El-Kady et al., 2012).

\(^6\)See Gallagher et al. (2010); Han et al. (2010, 2007); Liu et al. (2009); Oostinga et al. (2010); Stampfer et al. (2009); and Todd et al. (2008).\normalsize
hopping amplitudes between a given site and its nearest neighbors, and $a = 2.461 \text{ Å}$ is the lattice constant. The spectrum of $H_{\text{SLG}}$ has the form $\varepsilon_{\pm}(k) = E_D \pm \gamma_0 |k_\parallel|$ or

$$
\varepsilon_{\pm} = E_D \pm \gamma_0 \sqrt{3 + 2 \cos k_\parallel a + 4 \cos \frac{\sqrt{3} k_\parallel a}{2} \cos \frac{k_\parallel a}{2}}.
$$

(1.2)

At energies $|\varepsilon - E_D| \ll \gamma_0$, this dispersion has an approximately conical shape $\varepsilon_{\pm}(k) = E_D \pm \hbar v_0 |k - \mathbf{K}|$ with velocity $v_0 = \sqrt{\frac{3}{2} \frac{\hbar}{\epsilon_0} a} = 0.9 - 1.0 \times 10^5 \text{ cm/s}$ near the corners of the hexagonal Brillouin zone (BZ), see Fig. 1A. Only two of such corners are inequivalent, e.g., $\mathbf{K}$, $\mathbf{K}' = \left( \frac{2\pi}{\sqrt{3} a}, \frac{\pm 2\pi}{a} \right)$; the other four are obtained via reciprocal lattice translations. Near the $\mathbf{K}$ point, $H_{\text{SLG}}$ can be expanded to the first order in $q_\parallel$ and $q_\perp$ — the components of vector $q = k - \mathbf{K}$ parallel and perpendicular to $\mathbf{K}$, respectively. This expansion yields the 2D Dirac Hamiltonian

$$
H = E_D + \hbar v_0 (q_\parallel \sigma_x + q_\perp \sigma_y),
$$

(1.3)

which prompts analogies between graphene and quantum electrodynamics (Katsnelson and Novoselov, 2007). Here $\sigma_x$, $\sigma_y$ are the Pauli matrices. Expansion near $\mathbf{K}'$ points gives a similar expression except for the sign of the $q_\parallel$-term. The eigenvector $\Psi = (\psi_A, \psi_B)^T$ of $H$ can be thought of as a spinor. The direction of the corresponding pseudospin is parallel (antiparallel) for energy $\varepsilon_+$ ($\varepsilon_-$). The definite relation between the pseudospin and momentum directions is referred to as the chirality.

The conical dispersion yields the single-particle density of states (DOS) $\nu(E)$ linear in $|E - E_D|$. Accounting for the four-fold degeneracy due to spin and valley, one finds

$$
\nu(E) = \frac{2}{\pi \hbar^2 v_0^2} |E - E_D|.
$$

(1.4)

The frequently needed relations between the zero-temperature chemical potential $\mu$ (referenced to the Dirac point energy $E_D$), Fermi momentum $k_F$, and the carrier density $N$ read:

$$
k_F = \sqrt{\pi |N|}, \quad \mu \equiv E_F - E_D = \text{sign}(N) \hbar v_0 k_F.
$$

(1.5)

For $E - E_D$ not small compared to $\gamma_0$, deviations from the simplified Dirac model arise. The spectrum exhibits saddle points at energies $E_D \pm \gamma_0$, which are reached at the three inequivalent points of the BZ: $\mathbf{M} = \left( \frac{2\pi}{\sqrt{3} a}, 0 \right)$ and $\mathbf{M}', \mathbf{M}'' = \left( \frac{-\pi}{\sqrt{3} a}, \pm \frac{\pi}{a} \right)$, see Fig. 1A. The DOS has logarithmic van Hove singularities at these saddle-points. In the noninteracting electron picture, direct ($q = 0$) transitions between the conduction and valence band states of a given saddle-point would yield resonances at the energy $\hbar \omega = 2\gamma_0 \approx 5.4 \text{ eV}$. (Actually observed resonances are red-shifted due to interaction effects, see Sec. III.)

D. Many-body effects and observables

While the single-electron picture is the basis for our understanding of electron properties of graphene, it is certainly incomplete. One of the goals of the present review is to summarize spectroscopic evidence for many-body effects in graphene. In this section we introduce the relevant theoretical concepts. For simplicity, we assume that the temperature is zero and neglect disorder.

The strength of Coulomb interaction $U(r) = e^2/\kappa r$ in graphene is controlled by the ratio

$$
\alpha = \frac{e^2}{\kappa \hbar v_0},
$$

(1.6)

where $\kappa$ is the effective dielectric constant of the environment. Assuming $v_0 \approx 1.0 \times 10^6 \text{ cm/s}$, for suspended graphene ($\kappa = 1$) one finds $\alpha \approx 2.3$, so that the interaction is quite strong. Somewhat weaker interaction $\alpha \approx 0.9$ is realized for graphene on the common SiO$_2$ substrate, $\kappa = (1 + \epsilon_{\text{SiO}_2})/2 = 2.45$. For graphene grown on metals the long-range part of the interaction is absent, with only residual short-range interaction remaining.

In general, spectroscopic techniques measure either quasi-particle or current (density) response functions. Within the framework of the Fermi-liquid theory (Nozieres and Pines, 1999) interactions renormalize the quasiparticle properties, meaning they change them quantitatively. The current/density response is altered qualitatively due to emergence of collective modes.

A striking theoretical prediction made two decades ago, González et al. (1994) is that Coulomb interaction among electrons should cause a logarithmically divergent renormalization of the Fermi velocity in undoped SLG,

$$
\nu_T(q) = 1 + \frac{1}{4} \alpha(k_c) \ln \frac{k_c}{q} \text{ at } k_F = 0,
$$

(1.7)

which implies the negative curvature of the “reshaped” Dirac cones (Elías et al., 2011). Here, $k_c$ is the high momentum cut-off and $q = |k - \mathbf{K}|$ is again the momentum counted from the nearest Dirac point $\mathbf{K}$. The physical reason for the divergence of $\nu_T(q)$ is the lack of metallic screening in undoped SLG because of vanishing thermodynamic density of states (TDOS) $\nu_T = dN/d(\mu + E_D)$.

While Eq. (1.7) can be obtained from the first-order perturbation theory (Barlas et al., 2007; Hwang et al., 2007b; Polini et al., 2007), the renormalization group (RG) approach of González et al. (1994) indicates that validity of this equation extends beyond the weak-coupling case $\alpha \ll 1$. It remains valid even at $\alpha \sim 1$ albeit in the asymptotic low-$q$ limit where the running coupling constant $\alpha(q) \equiv e^2/\kappa \hbar v(q) \ll 1$ is small. The RG flow equation underlying Eq. (1.7),

$$
\beta(\alpha) \equiv \frac{d \ln \alpha}{d \ln q} \approx \frac{\alpha}{4}, \quad \alpha \ll 1,
$$

(1.8)

is free of nonuniversal quantities $\kappa$ and $k_c$, and so in principle it can be used to compare the renormalization effects in different graphene materials. The problem is that the asymptotic low-$q$ regime is hardly accessible in current experiments where one typically deals with the nonperturbative
The corresponding renormalized velocity scales as

\[ v(q) \sim q^{-\beta}. \tag{1.10} \]

Distinguishing this weak power law from the logarithmic one (1.7) would still require a wide range of \( q \).

The gapless Dirac spectrum should become unstable once \( \alpha \) exceeds some critical value (Drit and Lähde, 2009; Khveshchenko, 2001; Sheehy and Schmalian, 2007). It is unclear whether this transition may occur in SLG as no experimental evidence for it has been reported.

In doped SLG the RG flow (1.8) is terminated at the Fermi momentum scale. Therefore, velocity renormalization should be described by the same formulas as in undoped one at \( q > k_F \) but may have extra features at \( q \leq k_F \). This expectation is born out by calculations (Das Sarma et al., 2007). The result for the Fermi velocity, written in our notations, is

\[ \frac{v_F}{v(k_F)} = 1 + \frac{\alpha}{\pi} \left( \ln \frac{1}{\alpha} - \frac{5}{3} \right) + \frac{\alpha}{4} \frac{k_F}{k_F'}, \quad \alpha \ll 1, \tag{1.11} \]

where \( \alpha \) should be understood as \( \alpha(k_F') \). Comparing with Eq. (1.7), we see that \( v_F \) is larger than \( v(q) \) in undoped SLG at the same momentum \( q = k_F \) by an extra logarithmic term \( \sim \alpha/\ln \alpha \). This logarithmic enhancement of the Fermi velocity is generic for an electron gas with long-range Coulomb interactions in any dimension (Giuliani and Vignale, 2005). As a result, the renormalized dispersion has an inflection point near \( k_F \) [see, e.g., (Das Sarma and Hwang, 2013; Principi et al., 2012)] and a positive (negative) curvature at smaller (larger) \( q \).

Renormalization makes the relation between observables and quasiparticle properties such as \( v(q) \) more complicated than in the noninteracting case. For illustration, consider three key spectroscopic observables: the single-particle DOS \( \nu(E) \), the TDOS \( \nu_T \), and the threshold energy \( h \omega_{\text{th}} \) of interband optical absorption. Since for curved spectrum phase and group velocities are not equal, we must first clarify that by \( v(q) \) we mean the latter, i.e., the slope of the dispersion curve \( E(q) \). In theoretical literature, \( E(q) \) is usually defined by the equation

\[ E(q) = \varepsilon(q) + \Sigma_1(q,E(q)), \tag{1.12} \]

where \( \Sigma(q,\omega) = \Sigma_1(q,\omega) + i\Sigma_2(q,\omega) \) is the electron self-energy and the subscripts \( + \) and \( - \) are suppressed to lighten the notations. In experimental practice (Sec. II.A), more directly accessible than \( \Sigma(q,\omega) \) is the spectral function

\[ A(q,\omega) = \frac{-2\Sigma_2(q,\omega)}{[\omega - \varepsilon(q) - \Sigma_1(q,\omega)]^2 + [\Sigma_2(q,\omega)]^2}, \tag{1.13} \]

and the more convenient definition of \( E(q) \) is the energy \( \omega \) at which \( A(q,\omega) \) has a maximum. As long as this maximum is sharp so that the quasiparticles are well-defined, the two definitions are equivalent. For the velocity, they entail

\[ \frac{v(q)}{v_0} \equiv \frac{1}{\hbar v_0} \frac{dE}{dq} = \left(1 + \frac{\partial_\beta \Sigma_1}{\hbar v_0}\right) Z(q). \tag{1.14} \]

The three quantities in question, \( \nu, \nu_T, \) and \( h \omega_{\text{th}} \), are related to \( v(q) \) as follows:

\[ \nu(E) \equiv \frac{2}{\pi} \frac{q}{\hbar v(q)} Z(q), \quad Z(q) \equiv \frac{1}{1 - \frac{E}{E^*},} \tag{1.15} \]

\[ \nu_T(N) \equiv \frac{dN}{d(\mu + E_D)} = \frac{2}{\pi} \frac{k_F}{\hbar F} Z(k_F) \partial_{k_F} \Sigma_1, \tag{1.16} \]

\[ h \omega_{\text{th}} = E_+(k_F) - E_-(k_F) + \Delta_{\text{eh}}. \tag{1.17} \]

These formulas contain many-body corrections to the relations given in Sec. I.C that enter through the derivatives of the self-energy, while Eq. (1.17) also has a vertex correction \( \Delta_{\text{eh}} \). For example, the DOS \( \nu(E) \) [Eq. (1.15)], measurable by, e.g., scanning tunneling spectroscopy (STS), is multiplied by the quasiparticle weight \( Z \). Near the Fermi level one usually finds \( Z < 1 \) (Giuliani and Vignale, 2005), so that the interactions diminish the DOS. Inferring \( v_F \) from \( \nu(E_F) \) using the formula \( v_F \propto \hbar v(q)/v(E_F) \) of the noninteracting theory would cause overestimation of the Fermi velocity, e.g., by the factor of \( Z^{-1} = 1 + (1/2+1/\pi)\alpha \) at \( \alpha \ll 1 \) (Das Sarma et al., 2007). In practice, the low-bias STS data may be influenced by disorder and finite momentum resolution, see Sec. II.A.

Away from the Fermi level the interaction may enhance rather than suppress \( \nu(E) \). An example is the Dirac point region in a doped SLG where the DOS is predicted to be nonzero (U-shaped) (LeBlanc et al., 2011; Principi et al., 2012) rather than vanishing (V-shaped).

Consider next the TDOS \( \nu_T(N) \) given by Eq. (1.16), which follows from Eqs. (1.14)—(1.15). The TDOS can be found by measuring capacitance between graphene and metallic gates, either stationary (Ponomarenko et al., 2010; Yu et al., 2013) or scanned (Martin et al., 2008). In the absence of interactions, the TDOS coincides with the DOS at the Fermi level. However, for repulsive Coulomb interactions the second term in the denominator of Eq. (1.16) is negative (Giuliani and Vignale, 2005). (This term can be written in terms of parameter \( F_s^0 < 0 \) of the Landau Fermi-liquid theory.) Hence, while \( \nu(E_F) \) is suppressed, \( \nu_T \) is enhanced compared to the bare DOS. Extracting \( v_F \) from \( \nu_T(N) \) (Yu et al., 2013) may lead to underestimation.

The third quantity \( h \omega_{\text{th}} \) [Eq. (1.17)] stands for the threshold energy required to excite an electron-hole pair with zero total momentum in the process of optical absorption. Without interactions \( h \omega_{\text{th}} = 2\mu = 2\hbar v_0 k_F \) (see Fig. 2), and so the bare velocity is equal to \( \omega_{\text{th}}/2k_F \). Using the same formula for interacting system (Li et al., 2008) may lead to underestimation of the renormalized \( v_F \), for two reasons. First, \( v_F \) is the group velocity at the Fermi momentum while the ratio \( [E_+(k_F) - E_-(k_F)]/(2\hbar k_F) \) gives the average phase velocity of the electron and hole at \( q = k_F \). If the dispersion has the...
inflation point near \(k_F\), as surmised above, the group velocity must be higher than the phase one. Second, the threshold energy of the electron-hole pair is reduced by the vertex (or excitonic) correction \(\Delta_{eh} < 0\) due to their Coulomb attraction.

Let us now turn to the collective response of SLG at arbitrary \(\omega\) and \(k\). The simplest type of such a process is excitation of a single particle-hole pair by moving a quasiparticle from an occupied state of momentum \(p\) and energy \(E(p) \leq E_F\) to an empty state of momentum \(p + k\) and energy \(E(p + k) \geq E_F\). (The subscripts \(\pm\) of all \(E\)'s are again suppressed.) The particle-hole continuum that consists of all possible \((E(p + k) - E(p), k)\) points is sketched in Fig. 2. If the energy and the in-plane momentum of an electromagnetic excitation falls inside this continuum, it undergoes damping when passing through graphene. The conductivity \(\sigma(k, \omega) = \sigma' + i\sigma''\) has a finite real part \(\sigma'\) in this region.

Collective modes can be viewed as superpositions of many interacting particle-hole excitations. A number of such modes have been predicted for graphene. Weakly damped modes exist outside the particle-hole continuum, in the three unshaded regions of Fig. 2. At low energy the boundaries of these triangular-shaped regions have the slope \(\pm \hbar v_F\). Collective excitations near the \(\Gamma\)-point (the left unshaded triangle in Fig. 2) are Dirac plasmons. These excitations, reviewed in Sec. III.B, can be thought of as coherent superpositions of intraband electron-hole pairs from the same valley. The excitations near the \(K\) point (the right unshaded triangle) involve electrons and holes of different valleys. Such intervalley plasmons (Tudorovskiy and Mikhailov, 2010) are yet to be seen experimentally. Also shown in Fig. 2 are the “M-point exciton” that originates from mixing of electron and hole states near the M-points of the BZ (Sec. I.C) and its finite-momentum extension, which is sometimes called by a potentially confusing term “\(\pi\)-plasmon.”

Two other collective modes have been theoretically predicted but not yet observed and not shown in Fig. 2. One is the excitonic plasmon (Gangadharaiah et al., 2008) — a single interband electron-hole pair marginally bound by Coulomb attraction. Its dispersion curve is supposed to run near the bottom of the electron-hole continuum. The other mode (Mikhailov and Ziegler, 2007) is predicted to appear in the range \(1.66|\mu| < \hbar \omega < 2|\mu|\) where \(\mu'' < 0\). Unlike all the previously mentioned collective modes, which are TM-polarized, this one is TE-polarized. It is confined to graphene only weakly, which makes it hardly distinguishable from an electromagnetic wave traveling along graphene. Besides electron density, collective modes may involve electron spin. Further discussion of these and of many other interaction effects in graphene can be found in a recent topical review (Kotov et al., 2012).

II. QUASIPARTICLE PROPERTIES

A. Dirac spectrum and chirality

The first experimental determination of the SLG quasiparticle spectrum was obtained by analyzing the Shubnikov-de Haas oscillations (SdHO) in magnetoresistance (Novoselov et al., 2005b; Zhang et al., 2005a). This analysis yields the cyclotron mass

\[
m = \hbar k_F/v_F
\]

and therefore the Fermi velocity \(v_F\). The lack of dependence of \(v_F \approx 1.0 \times 10^8 \text{ cm/s}\) on the Fermi momentum \(k_F\) in those early measurements was consistent with the linear Dirac spectrum at energies below 0.2 eV.

Direct mapping of the \(\pi\)-band dispersion over a range of several eV (Bostwick et al., 2007b; Zhou et al., 2006) was achieved soon thereafter by the angle-resolved photoemission (ARPES) experiments. This experimental technique, illustrated by Fig. 3(a), measures the electron spectral function [Eq. (1.13)] weighted by the square of the matrix element \(M(k, \nu)\) of interaction between an incident photon of frequency \(\nu\) and an ejected photoelectron of momentum \(\mathbf{k}\), see Eq. (2.2) below. The representative dispersion curves measured for epitaxial graphene on SiC are shown in Fig. 3(b) and (c), where red (black) color corresponds to high (low) intensity. The “dark corridor” (Gierz et al., 2011) \(\Gamma–K\) along which one of the two dispersion lines is conspicuously missing, Fig. 3(c), occurs due to the selection rules for the matrix element \(M(k, \nu)\) known from prior work on graphite (Daimon et al., 1995; Shirley et al., 1995). The full angular dependence of the ARPES intensity is depicted in Fig. 3(d).

The ARPES measurements have been carried out on epitaxial graphene grown on a variety of substrates, on free-standing samples (Knox et al., 2011), and on multilayered samples with weak interlayer interactions (Sprinkle et al., 2009). The tight-binding model (Sec. I.C) accounts for the main features of all these spectra. However, there are also subtle deviations. For example, the slope of the dispersion near the Dirac point

\[
\begin{align*}
\text{Energy} & \quad \text{Momentum} \\
0 & \quad 2k_F \\
2\mu & \quad K/2 \\
2\gamma & \quad K-2k_F \\
4\gamma & \quad K \\
\end{align*}
\]

FIG. 2 Schematic dispersion of electron density excitations in SLG (lines). The horizontal axis corresponds to the \(\Gamma–K\) cut through the Brillouin zone. All excitations experience Landau damping inside the electron-hole pair continuum (shaded).
varies systematically with the background dielectric constant $\kappa$ [Fig. 3(d)], which is consistent with the theoretically predicted velocity renormalization, see Secs. I.D and II.B. Certain additional features near the Dirac point (see Fig. 12) have been interpreted\(^7\) as evidence for substrate-induced energy gaps, Sec. IV.B. For graphene on SiC, an alternative explanation invokes electron-plasmon coupling Bostwick et al. (2007b), see Fig. 11 in Sec. III.D.

Complimentary evidence for the Dirac dispersion of quasiparticles comes the tunneling and thermodynamic DOS measurements by means of scanned probes. The Dirac point manifests itself as a local minimum marked by the arrows in the STS tunneling spectra of Fig. 4a. The $U$- rather than the $V$-shaped form of this minimum (Sec. I.C) is due to disorder smearing. The STS data obtained by Zhang et al. (2008b) (Fig. 4a) also exhibit a prominent suppression at zero bias for all gate voltages. To explain it (Zhang et al., 2008b) proposed that this feature arises because of a limitation on the possible momentum transfer in tunneling. This limitation is lifted via inelastic tunneling accompanied by the emission of a BZ-boundary acoustic phonon of energy $\hbar \omega_0 = 63$ meV. This energy must be subtracted from the tip-sample bias $eV$ to obtain the tunneling electron energy inside the sample. By tuning the electron density $N$ with a backgate (Brar et al., 2010; Deshpande et al., 2009; Zhang et al., 2008b), one can change the Fermi energy $E_F$ with respect to the Dirac point $E_D$. Taking the former as the reference point (i.e., assuming $E_F \equiv 0$ for now) one obtains the relation $|E_D| = |eV_D| - \hbar \omega_0$. As shown in Fig. 4c, thus defined $|E_D|$ is proportional to $|N|^{1/2}$, as expected for the linear dispersion, Eq. (1.5). The same zero-bias gap feature is observed in other graphene samples studied by the Berkeley group, e.g., SLG on hBN(Decker et al., 2011a). Yet it is not seen in STS experiments of other groups, see, e.g., Fig. 10(c), Sec. II.B, and Sec. II.C below.\(^8\)

The $\mu(N)$ dependence can be more directly inferred from the TDOS $\nu_T(N)$ measured by the scanning single-electron transistor microscopy (SSETM) (Martin et al., 2008). Unlike the STS spectra in Fig. 4a, the SSETM data are not obscured once again the presence of disorder in graphene on SiO$_2$ substrate, see also Sec. IV.A. The most definitive observation of the Dirac TDOS has been made using exfoliated graphene on hBN (Yankowitz et al., 2012; Yu et al., 2013). Similar to SSETM, the TDOS was extracted from the capacitance measurements; however, it was the capacitance between the sample and the global backgate rather than between the sample and the local probe.

Let us now turn to the chirality of graphene quasiparticles. Recall that chirality refers to the phase relation between the sublattice amplitudes $\psi_j = \psi_j(k)$, $j = A, B$, of the quasiparticle wavefunctions (Sec. I.C). The chirality has been independently verified by several techniques. First, it naturally explains the presence of the special half-filled Landau level at the Dirac point seen in magnetotransport (Novoselov et al., 2005b; Zhang et al., 2005a). Next, in the STS experiments the quasiparticle chirality is revealed by the LDOS features observed near impurities and step edges, see Deshpande et al. (2009); Mallet et al. (2007); Rutter et al. (2007); and Zhang et al. (2009a) and Sec. IV.A. The chirality influences the angular distribution of the quasiparticle scattering by these defects, suppressing the backscattering (Brihuega et al., 2008;)

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\(^7\)See Dedkov et al. (2008); Enderlein et al. (2010); Gao et al. (2010); Himpsel et al. (1982); Nagashima et al. (1994); Papagno et al. (2012); Radet et al. (2009); Siegel et al. (2012); Sutter et al. (2009); Varykhalov et al. (2008); Walter et al. (2011c); and Zhou et al. (2007).

\(^8\)See also (Chae et al., 2012; Deshpande et al., 2009; Li and Andrei, 2012; Song et al., 2010; Xue et al., 2011; Yankowitz et al., 2012).
If spin-orbit (SO) interaction effects can be ignored. Here
est Dirac point. The coefficients
\( j \) in Eq. (2.3) vanishes and so does \( M(\mathbf{k}, \nu) \). This explains the low-intensity “dark corridor” in the observed ARPES signal, Fig. 3(c) and (d).

The ARPES selection rules are also relevant for BLG. Experimentally, the orientation of the low intensity directions rotates by \( \pm 180^\circ \) (\( \pm 90^\circ \)) in SLG (BLG) when the photon polarization vector \( \mathbf{A} \) is switched between two orientations, parallel and perpendicular to \( \mathbf{K} \) (Gierz et al., 2011; Hwang et al., 2011; Liu et al., 2011). Hwang et al. (2011) discussed how these rotation angles can be linked to the Berry phase — a quantity closely related to chirality — in SLG and BLG. However, their theoretical model for the matrix element \( M(\mathbf{k}, \nu) \) has been a subject of controversy, which appears to be rooted in different assumption about the final state wavefunction \( \Psi_f(\mathbf{r}) \) in Eq. (2.2).

At very high energies \( h\nu \), the conventional approximation of \( \Psi_f(\mathbf{r}) \) by a plane wave should be adequate (Mucha-Kruczyński et al., 2008; Shirley et al., 1995). In this case one can replace the velocity operator \( \hat{\mathbf{v}} \) by \( \hbar \mathbf{k}/m \) leading to \( c_1 = c_2 \) in Eq. (2.3). On the other hand, Hwang et al. (2011) replaced \( \mathbf{v} \) by the band velocity \( v_F |\mathbf{q}|/|\mathbf{q}| \). This is perhaps appropriate at low energies \( h\nu \) at which \( \Psi_f \approx \Psi_i \) near the graphene plane. The corresponding \( c_1 \) is equal to zero, which is admissible. However, \( c_2 \propto 1/|\mathbf{q}| \) diverges at \( |\mathbf{q}| \to 0 \), in contradiction to the \( \mathbf{k} \cdot \mathbf{p} \) perturbation theory (Yu and Cardona, 1999). In view of this problem and because other ARPES experiments and calculations Gierz et al. (2011) indicate a nontrivial \( \nu \)-dependence of \( M(\mathbf{k}, \nu) \), further study of this question is desirable.

**B. Renormalization of Dirac spectrum**

Experimental verification of the many-body renormalization of the Dirac spectrum in graphene and its Fermi velocity \( v_F \) in particular has been sought after in many spectroscopic studies. Some of these studies may be subject to interpretation because \( v_F \) usually enters the observables in combination with other quantities, see Sec. I.D. In addition, when the change in \( v_F \) is small, one cannot completely exclude single-particle effects.

Probably the first experimental indication for \( v_F \) renormalization in graphene came from infrared absorption/transmission spectroscopy (Li et al., 2008) of exfoliated SLG on amorphous SiO\(_2\) (a-SiO\(_2\)). This study found that \( v_F \) increases from \( 1.0 \times 10^8 \) cm/s to a 15\% higher value as the carrier density \( N \) decreases from 3.0 to 0.7 \times 10^{12} \) cm\(^{-2}\), see Fig. 5d. Next came an STS study of Landau level spectra (Luican et al., 2011b), which found a 25\% enhancement of \( v_F \) (fifth row Table I) in the same range of \( N \).

A much broader range of \( N \) has been explored in suspended graphene where \( N \) as small as a few times \( 10^6 \) cm\(^{-2}\) can be accessed. Working with such ultra-clean suspended samples, Elias et al. (2011) were able to carry out the analysis of the SdHO of the magnetoresistance over a two-decade-wide span.
of the carrier densities. This analysis yields the cyclotron mass [Eq. (2.1)] and thence $v_F$. The Fermi velocity was shown to reach $v_F \approx 3.0 \times 10^8$ cm/s, the largest value reported to date, cf. Table I. Elias et al. (2011) fitted their data (Fig. 5A) to Eq. (1.7) for undoped graphene by treating $\alpha$ as an adjustable parameter. Figure 3 of Elias et al. (2011) suggests another possible fit, to Eq. (1.10) with the exponent $\beta \approx 0.25$, which is close to Eq. (1.9). It would be better to compare the measured $v_F$ with the theoretical predictions for doped graphene, i.e., with the extension (or extrapolation) of Eq. (1.11) to the case in hand, $\alpha \approx 1$.

From the measurements of quantum capacitance (the quantity proportional to the TDOS) of SLG on hBN, Yu et al. (2013) found that $v_F$ increases by $\sim 15\%$ as $N$ varies from $5 \times 10^{12}$ down to a few times $10^{10}$ cm$^{-2}$, see Fig. 5B. The vertex corrections were not included when the conversion of the quantum capacitance to $v_F$ was done. Therefore, this number represents the lower bound on $v_F$, see Sec. I.D.

Using substrates of different dielectric constant $\epsilon_{sub}$ is another approach to study $v_F$ renormalization. An advantage of this approach is that a broad range of $N$ is not necessary in this case. Instead, the renormalization of velocity is driven by the change in the interaction strength $\alpha \propto 1/\kappa$ where $\kappa = (1 + \epsilon_{sub})/2$, see Eq. (1.7). A crude estimate of this effect is as follows. The dielectric screening by the substrate is effective at distances larger than the separation $d$ between graphene and the substrate. Hence, the momentum cutoff in Eqs. (1.7) and (1.11) should be chosen $k_c \sim 1/d$. If $d \lesssim 1$ nm and $k_F^{-1} \sim 6$ nm, then $\ln(k_c/k_F) \lesssim 2$ and Eq. (1.7) entails

$$\delta v_F \lesssim (1.0 \times 10^8 \text{ cm/s}) \times \delta \left(\frac{2}{\epsilon_{sub}+1}\right).$$

where we use “$\delta$” to denote a change in a quantity. In a recent ARPES study (Hwang et al., 2012a) the smallest $v_F = (0.85 \pm 0.05) \times 10^8$ cm/s was observed on metallic substrates. This number represents presumably the bare quasiparticle velocity in the absence of long-range Coulomb interactions. Note that it is close to the Fermi velocity $v_F = 0.81 \times 10^8$ cm/s measured in carbon nanotubes (Liang et al., 2001). The ARPES results for three other substrates are reproduced in Fig. 5D. They clearly demonstrate a prominent velocity enhancement near the Fermi level. Thus, graphene on (the carbon face of) SiC has $v_F$ that is only slightly larger than what is observed for metallic substrates (Hwang et al., 2012a; Siegel et al., 2011), which can be explained by the high $\kappa$. Graphene on hBN has $v_F$ close to that for SLG on a-SiO$_2$, which is consistent with the effective dielectric constants of hBN and a-SiO$_2$ being roughly equal (Wang et al., 2012; Yu et al., 2013). A surprisingly large $v_F$ is found for graphene on crystalline SiO$_2$ (quartz), see Table I and Fig. 5D.

As mentioned above, renormalization of the quasiparticle velocity in SLG can also arise from single-particle physics. One example is the modification of the electron band-structure by external periodic potentials (Brey and Fertig, 2009; Guinea and Low, 2010; Park et al., 2008c,d; Wallbank et al., 2013). Such potentials are realized in moiré superlattices that form when graphene is deposited on lattice-matched substrates, which we will discuss in Sec. IV.C. Similar effects appear in misoriented graphene bilayers and multilayers that grow on the carbon face of SiC (Hass et al., 2008) (Sec. I.B) and

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$\kappa$</th>
<th>$v$ (10^8 cm/s)</th>
<th>Method</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC (0001)</td>
<td>7.26</td>
<td>1.15(2)</td>
<td>ARPES</td>
<td>Hwang</td>
</tr>
<tr>
<td>hBN</td>
<td>4.22</td>
<td>2.0</td>
<td>ARPES</td>
<td>Siegel</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>1.80</td>
<td>2.5(3)</td>
<td>Capacitance</td>
<td>Yu</td>
</tr>
<tr>
<td>a-SiO$_2$</td>
<td>2.45</td>
<td>1.47(5)</td>
<td>ARPES</td>
<td>Hwang</td>
</tr>
<tr>
<td>Vacuum</td>
<td>1.00</td>
<td>3.0(1)</td>
<td>SdH</td>
<td>Elias</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.6(2)</td>
<td>Transport</td>
<td>Oksanen</td>
</tr>
</tbody>
</table>

Table I. The Fermi velocity of SLG in excess of nominal bare value of $0.85 \times 10^8$ cm/s. In the last column, Hwang, Siegel, Yu, Luican, Elias, and Oksanen stand for (Hwang et al., 2012a), (Siegel et al., 2013), (Yu et al., 2013), (Luican et al., 2011b), (Elias et al., 2011), and (Oksanen et al., 2014), respectively.
are also common in CVD graphene grown on Ni (Luican et al., 2011a). Calculations predict a strong dependence of the velocity on the twist angle (Bistritzer and MacDonald, 2011; Trambly de Laissardière et al., 2010; Lopes dos Santos et al., 2007, 2012; Shallcross et al., 2010). The experimental value of \( v_F \) reported for twisted graphene layers on the carbon face of SiC is about \( 1.10 \times 10^8 \text{ cm/s} \) (Crassee et al., 2011a; Miller et al., 2009; Siegel et al., 2011; Sprinkle et al., 2009).

Changes of \( v_F \) up to 10% among different layers for graphene on the carbon-face of SiC have been deduced from SdH oscillations (de Heer et al., 2007) and magneto-optical measurements (Crassee et al., 2011a,b). In the latter case these changes have been attributed to electron-hole asymmetry and also to variation of the carrier density and dielectric screening among the graphene layers. No variation of \( v_F \) as a function of twist angle was observed by ARPES and STS (Miller et al., 2009; Sadowski et al., 2006; Siegel et al., 2011; Sprinkle et al., 2009). However, a 14% decrease of \( v_F \) at small twist angles was found in the STS study of CVD graphene transferred to the grid of a transmission electron microscope (Luican et al., 2011a).

C. Landau quantization

Spectroscopy of Landau level (LL) quantization in a magnetic field is yet another way to probe quasiparticle properties of graphene. The linear dispersion of SLG leads to unequally spaced LLs: \[ E_n = E_D + \text{sgn}(n)\sqrt{2e\hbar B|n|} \] (Fig. 6a), where \( n > 0 \) or \( n < 0 \) represents electrons or holes, respectively (Gusynin and Sharapov, 2006; Jiang et al., 2007; McClure, 1957). Each of the LLs has four-fold degeneracy due to the spin and valley degrees of freedom. Additionally, the electron-hole symmetric \( n = 0 \) LL gives rise to the extraordinary “half-integer” quantum Hall effect (Novoselov et al., 2005a; Zhang et al., 2005b), the observation of which back in 2005 was the watershed event that ignited the widespread interest in graphene.

The LL spectrum of graphene has been probed using scanning tunneling spectroscopy (STS), IR spectroscopy, and Raman scattering. The STS of graphene LLs was first carried out in graphene on graphite samples, where suspended graphene is isolated from the substrate at macroscopic ridge-like defect (Li et al., 2009a). Figure 6b displays the differential conductance of graphene versus tip-sample bias at different magnetic fields \( B \) normal to the graphene surface. Well defined LDOS peaks corresponding to discrete LL states appear in the tunneling spectra. These LL peaks become more prominent and shift to higher energies in higher magnetic fields consistent with the expected \( \sqrt{B|n|} \) law. Similar LL spectrum was also observed in epitaxial grown graphene layers on SiC (Miller et al., 2009).

To examine the fine structure within a LL, Song et al. (2010) performed high-resolution STS studies at temperatures as low as 10 mK on epitaxial graphene. Figure 6c shows their
data for the \( n = 1 \) LL at the magnetic field range where the LL1 starts to cross the Fermi energy (yellow line). The LL1 level is composed of four separate peaks, indicating that the valley and spin degeneracy is lifted. The larger energy splitting \((\Delta E_v)\) is attributed to the lifting of valley degeneracy. It increases monotonically with the applied magnetic field with the effective \( g \)-factor of 18.4. The smaller splitting \((\Delta E_s)\) has an average \( g \)-factor close to 2, presumably due to the electron spin. Quantitatively, this spin splitting shows a highly unusual dependence on the filling factor. Comparing the spectra at filling factors of 4, 5, and 6, a clear enhancement of the spin splitting is observed at \( \nu = 5 \), which can be attributed to many-body effects (exchange enhancement). In addition, new stable half-filled Landau levels appear at half fillings such as 9/2 and 11/2. Their origin is not yet clear. Landau level spectroscopy of graphene on SiO\(_2\) was presented in Luican et al. (2011) and a similar study for graphene on hBN was reported in Chae et al. (2012). In the latter system, which has lower disorder, observation of many LLs was possible over a wide energy range. Deviations of the LL energies by about \( \sim 10\% \) from the predictions of the single-particle theory were interpreted in terms of the Fermi velocity renormalization, see Fig. 5C. This is in line with the results of other measurements discussed above (Table 1).

The infrared (IR) spectroscopy provides another way to study the LL spectra (Henriksen et al., 2010; Jiang et al., 2007; Sadowski et al., 2006). The IR transitions between LLs have to satisfy the selection rule \( \Delta |n| = \pm 1 \), due to angular momentum conservation. Selection rules also apply to the circular polarization of light. As a result, graphene exhibits strong circular dichroism and Faraday effect (Crassee et al., 2011). Figure 6d displays the experimental data of normalized IR transmission spectra through SLG at several magnetic fields Jiang et al. (2007). The electron density is controlled so that Fermi energy lies between the \( n = -1 \) and 0 LL (inset in Fig. 6d). Two transmission minima \( T_1 \) and \( T_2 \) are readily observable. The \( T_1 \) resonance corresponds to the \( n = -1 \) to \( n = 0 \) intraband LL transition, and the \( T_2 \) resonance arises from the degenerate interband \( n = -1 \) to \( n = 2 \) and \( n = -2 \) to \( n = 1 \) transitions. The LL transition energies scales linearly with \( \sqrt{B} \), as expected from the LL structure described above. A careful examination of the IR transitions as a function of electron filling factor further reveals that at zero filling factor, the \( n = -1 \) to \( n = 0 \) (or \( n = 0 \) to \( n = 1 \)) transition is shifted to a higher energy compared to that at the filling factor of 2 and \(-2\) (Henriksen et al., 2010). This shift was again tentatively attributed to interaction effects.

### III. CURRENT/DENSITY RESPONSE AND COLLECTIVE MODES

#### A. Optical conductivity

Traditionally measured by optical spectroscopy, the “optical” conductivity \( \sigma(\omega) = \sigma'(\omega) + i\sigma''(\omega) \equiv \sigma(q = 0, \omega) \) quantifies the response of current to an external electric field in the low momenta \( q \ll \omega/v_F \) region of the \( q-\omega \) parameter space, see Fig. 2. Both intraband and interband transitions contribute to the optical conductivity; we will start with the interband ones.

In a charge-neutral SLG, which is a zero-gap semiconductor with the Fermi energy at the Dirac point, the interband transitions have no threshold. Particularly interesting is the range of (IR) frequencies \( h\omega \ll \gamma_0 \), where quasiparticles behave as massless Dirac fermions. Since the Dirac spectrum has no characteristic frequency scale and neither does the Coulomb interaction, at zero temperature and in the absence of disorder the conductivity must be of the form \( \sigma(\omega) = (e^2/\hbar) f(\alpha) \), where \( \alpha \) is defined by Eq. (1.6). \[ \text{[How-ever, } \omega = 0 \text{ is, strictly speaking, a singular point (Ziegler, 2007).] \] For the noninteracting case, \( \alpha = 0 \), the theory predicts \( f(0) = \pi/2 \), so that \( \sigma(\omega) \) is real and has the universal value of \( \sigma_0 = \pi e^2/2 \hbar \). (3.1)

The corresponding transmission coefficient \( T = 1 - 4\pi\sigma(\omega)/c \) for suspended graphene is expressed solely in terms of the fine structure constant: \( T = 1 - \pi(e^2/\hbar c) \approx 0.977 \). This prediction matches experimental data surprisingly well, with possible deviations not exceeding 15\% throughout the IR and visible spectral region (Li et al., 2008; Mak et al., 2008; Nair et al., 2008). This implies that the interaction correction \( f(\alpha) - f(0) \) is numerically small even at \( \alpha = 2.3 \). At the level of the first-order perturbation theory this remarkable fact is explained by a nearly complete cancellations between self-energy and vertex contributions (Mishchenko, 2008; Sheehy and Schmalian, 2009; Sodemann and Fogler, 2012).

Doping of graphene creates an effective threshold \( h\omega_{th} \) for interband absorption by the same mechanism as in the Burstein–Moss effect: the blue shift of the lowest energy of interband transitions in a doped semiconductor (Yu and Cardona, 1999). Due to Pauli blocking, no direct interband transitions exist at \( h\omega < 2|\mu| \) in the noninteracting electron picture, see Fig. 2. Experimentally, the existence of such a threshold has been confirmed by IR spectroscopy of gated SLG (Horng et al., 2011; Li et al., 2008; Wang et al., 2008b). As shown in Fig. 4, the frequency position of the broadened step in \( \sigma'(\omega) \) scales as the square-root of the gate voltage \( V_g \), and so is proportional to \( k_F \). This is consistent with the linear dispersion \( 2|\mu| = 2h\omega_F k_F \) of the Dirac quasiparticles. This behavior is seen in both exfoliated (Li et al., 2008) and CVD-grown graphene (Horng et al., 2011). At the smallest gate voltages, deviations from the square-root law are seen Li et al. 2008.
of a conductor is a simple fraction: 

\[ \sigma_{\text{intra}}(\omega) = \frac{i}{\pi} \frac{D}{\omega + i\gamma}, \]

For noninteracting electrons with an isotropic Fermi surface one generally finds (Ashcroft and Mermin, 1976)

\[ D = \pi e^2 |N|/m, \]

where \( m \) is defined by Eq. (2.1). For Dirac electrons with \( v_F = \text{const} \) and \( k_F = \sqrt{\pi |N|} \) both \( m \) and \( D \) scale as \( |N|^{1/2} \). Parameter \( D \) is known as the Drude weight. In the Drude model, the relaxation rate \( \gamma \) is frequency-independent and can be related to the transport mobility \( \mu_t \) by \( h\gamma = e v_F / (k_F \mu_t) \). In exfoliated samples of typical mobility \( \mu_{tr} \sim 10,000 \text{ cm}^2/\text{Vs} \) and carrier density \( N \sim 3 \times 10^{11} \text{ cm}^{-2} \) one estimates \( \gamma \sim 10 \text{ meV} \). This is below the low-frequency cutoff of the IR microscopy (Li et al., 2008). One can extend measurements to lower frequency provided larger area samples are used, such as epitaxial (Choi et al., 2009; Hofmann et al., 2011) and CVD-grown graphene (Horng et al., 2011; Ren et al., 2012; Rouhi et al., 2012). In both cases the gross features of the measured frequency dependence of IR conductivity comply with the Drude model. Note that such samples have relatively low mobility (Sec. 1B) and so show wider Drude peaks in \( \sigma' (\omega) \).

The intraband response as a function of the carrier density has been studied using a gated CVD-grown graphene (Horng et al., 2011). The experimentally observed Drude weight was found to be 20–50% smaller than predicted by Eq. (3.3), see Secs. 1D and II.B.

Vertex corrections (which are also referred to as the excitonic effects) play a prominent role also in the optical energy range 4–6 eV. The dominant spectroscopic feature in this region is the interband transition that connects electron and hole states near the M-point of the Brillouin zone, where the DOS has van Hove singularities (Sec. 1C). This resonance is seen both in SLG and MLG samples.\(^{11}\) This resonance has been detected by EELS and dubbed “\( \pi \)-plasmon” [see, e.g., Eberlein et al. (2008)]. We prefer the term “M-point exciton” to avoid confusion with the Dirac plasmon. Electron-electron interactions significantly renormalize the properties of this resonance. The position of the M-point exciton is red shifted from the noninteracting value of \( 2t_0 \) by as much as 600 meV in SLG samples (Chae et al., 2011; Mak et al., 2011; Yang et al., 2009). The absorption peak has a Fano lineshape indicative of interaction effects.

Let us now discuss the intraband transitions. The commonly used Drude model assumes that the intraband response of a conductor is a simple fraction:

\[ \sigma_{\text{intra}}(\omega) = \frac{i}{\pi} \frac{D}{\omega + i\gamma}, \]

where \( m \) is defined by Eq. (2.1). For Dirac electrons with \( v_F = \text{const} \) and \( k_F = \sqrt{\pi |N|} \) both \( m \) and \( D \) scale as \( |N|^{1/2} \). Parameter \( D \) is known as the Drude weight. In the Drude model, the relaxation rate \( \gamma \) is frequency-independent and can be related to the transport mobility \( \mu_t \) by \( h\gamma = e v_F / (k_F \mu_t) \). In exfoliated samples of typical mobility \( \mu_{tr} \sim 10,000 \text{ cm}^2/\text{Vs} \) and carrier density \( N \sim 3 \times 10^{11} \text{ cm}^{-2} \) one estimates \( \gamma \sim 10 \text{ meV} \). This is below the low-frequency cutoff of the IR microscopy (Li et al., 2008). One can extend measurements to lower frequency provided larger area samples are used, such as epitaxial (Choi et al., 2009; Hofmann et al., 2011) and CVD-grown graphene (Horng et al., 2011; Ren et al., 2012; Rouhi et al., 2012). In both cases the gross features of the measured frequency dependence of IR conductivity comply with the Drude model. Note that such samples have relatively low mobility (Sec. 1B) and so show wider Drude peaks in \( \sigma' (\omega) \).

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\(^{11}\)See Chae et al. (2011); Fei et al. (2008); Kravets et al. (2010); Mak et al. (2011); and Santoso et al. (2011).
plasmas. The dispersion relation of plasmons in a 2D conductor is given by the equation

\[ q_p(\omega) = \frac{i}{2\pi} \frac{\kappa(\omega)}{\sigma(q_p, \omega)}, \tag{3.4} \]

where \( \kappa(\omega) \) is the average of the dielectric functions of the media on the two sides, see, e.g., (Fei et al., 2012; Grigorenko et al., 2012). At \( q \ll k_F \) the \( q \)-dependence of \( \sigma(q, \omega) \) can be neglected, and so the plasmon dispersion is determined by the optical conductivity \( \sigma(\omega) \) discussed above. This implies that \( \sigma(\omega) \), which is usually measured by optical spectroscopy, can also be inferred by studying plasmons (Chen et al., 2012; Fei et al., 2012). (Actually, optics probes transverse rather than longitudinal response but at \( q \ll \omega/v_F \) the two coincide.)

Note that \( q_p = q_p' + iq_p'' \) is a complex number. Its real part determines the plasmon wavelength \( \lambda_p = 2\pi/q_p' \) and the imaginary part characterizes dissipation. The condition for the propagating plasmon mode to exist is \( q_p'' < q_p' \) or \( \sigma' < \sigma'' \), assuming \( \kappa \) is real. In SLG this condition is satisfied (both in theory and in experiment) at frequencies that are smaller or comparable to \( |\mu|/\hbar \). In particular, at \( \hbar \omega \ll |\mu| \), one can use Eqs. (3.2) and (3.4) to express the plasmon dispersion in terms of the Drude weight \( D \):

\[ \omega_p(q) = \sqrt{\frac{2}{\kappa}} D q. \tag{3.5} \]

This \( \sqrt{q} \)-behavior is a well-known property of 2D plasmons. Using (3.3) for \( D \) with Eq. (2.1) for \( m \), one finds

\[ \omega_p(q) = \sqrt{\frac{2\sqrt{\pi} e^2}{\kappa \hbar v_F}} |N|^{1/4} q^{3/2}, \quad q \ll k_F. \tag{3.6} \]

The \( |N|^{1/4} \)-scaling of the plasmon frequency at fixed \( q \) should be contrasted with \( \omega_p \propto |N|^{1/2} \) scaling well known for the 2D electron gas with a parabolic energy spectrum (2DEG). The difference is due to the \( D \propto N \) dependence in the latter system. Another qualitative difference is the effect of electron interactions on \( D \). In 2DEG, interactions do not change \( D \), which is the statement of Kohn’s theorem (Giuliani and Vignale, 2005). In graphene, interactions renormalize the Drude weight (Abedpour et al., 2007; Levitov et al., 2013), which causes quantitative deviations from Eq. (3.6). Qualitative deviations from this equation occur however only at \( q \sim k_F \) where the plasmon dispersion curve enters the particle-hole continuum, see Fig. 2. At such momenta the Drude
model (3.2) breaks down and a microscopic approach such as the random-phase approximation (RPA) becomes necessary (Hwang and Das Sarma, 2007; Jablan et al., 2009; Wunsch et al., 2006). The RPA predicts that inside the particle-hole continuum the plasmon survives as a broad resonance that disperses with velocity that approaches a constant value \( v_F \) at large \( q \).

Experimental measurements of the plasmon dispersion over a broad range of \( q \) have been obtained by means of electron energy loss spectroscopy (EELS). Such experiments\(^{14} \) have confirmed the \( \omega _p \propto \sqrt {q} \) scaling at small momenta and a kink in the dispersion in the vicinity of the particle-hole continuum. EELS study carried out by Pfnür et al. (2011) reported two distinct plasmon modes, a result yet to be verified through other observations.

The IR spectroscopy of graphene ribbons (Ju et al., 2011; Yan et al., 2013) and disks (Fang et al., 2013; Yan et al., 2012a,b) offered a complementary method to probe the plasmon dispersion. The experimental signature of the plasmon mode is the absorption resonance whose frequency \( \omega _{\text{res}} \) is observed to scale as the inverse square root of the ribbon width \( W \) (or disk radius \( R \)). This scaling agrees with the theoretical results relating \( \omega _{\text{res}} \) to the plasmon dispersion in an unbounded graphene sheet [Eq. (3.5)]. For the ribbon, it reads \( \omega _{\text{res}} \approx \omega _p (2.3/W) \) (Nikitin et al., 2011). The same relation can be deduced from the previous work (Eliasson et al., 1986) on plasmons in 2DEG stripes. In fact, most of the results obtained in the context of plasmons in 2DEG in semiconductors (Demel et al., 1990, 1991; Kukushkin et al., 2003) and electrons on the surface of a liquid \(^4\)He (Glattli et al., 1985; Mast et al., 1985) directly apply to graphene whenever the Drude model holds.

As shown theoretically and experimentally in that earlier work, the spectrum of plasmons in ribbons/stripes is split into a set of discrete modes dispersing as \( \omega _l(q_\parallel ) \approx \omega _p \left( \sqrt {q_\parallel ^2 + q_\parallel ^2} \right) \), as a function of the longitudinal momentum \( q_\parallel \) and the mode number \( l = 1, 2, \ldots \), with \( q_\parallel = (\pi l - \delta _l)/W \) having the meaning of the transverse momentum. Numerical results (Eliasson et al., 1986; Nikitin et al., 2011) suggest that the phase shift parameter is equal to \( \delta _l \approx \pi /4 \) at \( q_\parallel = 0 \). The resonance mode detected in graphene ribbons (Ju et al., 2011; Yan et al., 2013) is evidently the \( l = 1 \) mode. Probing \( q_\parallel \neq 0 \) modes with conventional optics is challenging and has not been done in graphene [it may be possible with a gating coupler (Demel et al., 1991).] On the other hand, working with graphene disks, one can effectively access the quantized values \( q_\parallel = m/R \), where \( m \) is the azimuthal quantum number. The observed mode (Fang et al., 2013; Yan et al., 2012a,b) is evidently the dipolar one, \( m = l = 1 \), which has the highest optical weight. An additional mode that appears in both in ribbons and disks is the edge plasmon. We will talk about it at the end of this section where we discuss the effects of magnetic field.

The correspondence between the ribbon and bulk plasmon dispersions enables one to also verify the \( |N|^{1/4} \) scaling predicted by Eq. (3.6). This has been accomplished by electrostatic gating of graphene micro-ribbons immersed in ionic gel (Ju et al., 2011) and monitoring their resonance frequency.

Plasmons in graphene are believed to strongly interact with electrons. Using the ARPES Bostwick et al. (2007a,b, 2010) observed characteristic departure of the quasiparticle dispersion from linearity near the Dirac point energy accompanied by an additional dispersion branch. These features, discussed in more detail in Sec. III.D, were interpreted in terms of plasmarons: bound states of electrons and plasmons (Lundqvist, 1967). Walter et al. (2011a,c) demonstrated that the details of the plasmaron spectrum are sensitive to dielectric environment of graphene. Carbotte et al. (2012) proposed that plasmaron features can be detected in near-field optical measurements, which allow one to probe the IR response at momenta \( q \gg \omega /c. \)

Complementary insights on the interaction between plasmons and quasiparticles have been provided by the STS. Based on the gate dependence of the tunneling spectra, Brar et al. (2010) distinguished phonon and plasmon effects on the quasiparticle self-energy.

Plasmons in graphene strongly interact with surface phonons of polar substrates such as SiC, SiO\(_2\), and BN. Dispersion of mixed plasmon-phonon modes in graphene on SiC was investigated experimentally using high-resolution EELS (Koch et al., 2010; Liu and Willis, 2010; Liu et al., 2008) and modeled theoretically by Hwang et al. (2010). Theoretical dispersion curves (Fei et al., 2011) for graphene on SiO\(_2\) are shown in the inset of Fig. 8b. The dispersion characteristic of mixed plasmon-phonon modes in nanoribbons measured via far-field IR spectroscopy was reported in (Yan et al., 2013, 2012b).

In the near-field IR nanoscopy study of graphene microcrystals on SiO\(_2\) (Fei et al., 2011) the oscillator strength of the plasmon-phonon surface modes was shown to be significantly enhanced by the presence of graphene, Fig. 8a. The strength of this effect can be controlled by electrostatic doping, in agreement with theoretical calculations Fei et al. (2011).

Imaging of plasmon propagation in real-space (Chen et al., 2012; Fei et al., 2012) [Fig. 8(left)] have led to the first direct determination of both real and imaginary parts of the plasmon momentum \( q_p = q_p' + iq_p'' \) as a function of doping. In terms of potential applications of these modes, an important characteristic is the confinement factor \( \lambda _p /\lambda _0 \), where \( \lambda _p = 2\pi /q_p' \) is the plasmon wavelength and \( \lambda _0 = 2\pi c/\omega \) to the wavelength of light in vacuum. Experimentally determined confinement factor in exfoliated graphene Fei et al. (2012) was \( \sim 65 \) in the mid-IR spectral range \( \omega \approx 800 \text{ cm}^{-1} \). According to Eqs (3.6), the scale for the confinement is set by the inverse fine-structure constant, \( \lambda _0 /\lambda _p = (\kappa /2)(\hbar c/\epsilon )^{3/2} (\hbar \omega /|\mu |) \), with stronger confinement achieved at higher frequencies. The propagation length of the plasmons \( \sim 0.5 \lambda _p = 100–150 \text{ nm} \).

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\(^{14}\)See Koch et al. (2010); Liu and Willis (2010); Liu et al. (2008); Shin et al. (2011); and Tegenkamp et al. (2011).
is consistent with the residual conductivity $\sigma' \approx 0.5e^2/h$ measured by the conventional IR spectroscopy (Li et al., 2008). Possible origins of this residual conductivity have already been discussed above, Sec. III.A. In confined structures one additional mechanism of plasmon damping is scattering by the edges (Yan et al., 2013). Despite the observed losses, the plasmonic figures of merits demonstrated by Chen et al. (2012) and Fei et al. (2012) compare well against the benchmarks set by noble metals. Even though surface plasmons in metals can be confined to scales of the order of tens of nm, their propagation length in this regime is plagued by giant losses and does not exceed 0.1$\lambda_p \sim 5$ nm for Ag/Si interface (Jablani et al., 2009). This consideration has not been taken into account in a recent critique of graphene plasmonics (Tassin et al., 2012). Further improvements in the figures of merits are anticipated for graphene with higher electronic mobility. The key forte of graphene in the context of plasmonics is the control over the plasmon frequency and propagation direction (Mishchenko et al., 2010; Vakil and Engheta, 2011) by gating.

The properties of graphene plasmons get modified in the presence of a transverse magnetic field $B$. The magnetoplasmon dispersion is obtained from Eq. (3.4) by replacing $\sigma$ with the longitudinal conductivity $\sigma_{xx}$. For instance, instead of the Drude model (3.2), one would use its finite-$B$ analog, the Drude-Lorentz model (Ashcroft and Mermin, 1976), which yields another well-known dispersion relation (Chiu and Quinn, 1974)

$$\omega_{mp}(q) = \sqrt{\omega_c^2(q) + \frac{\omega_e^2}{2}}. \quad (3.7)$$

This magnetoplasmon spectrum is gapped at the cyclotron frequency $\omega_c = eB/m^*$ defined through the effective mass $m^*$ [Eq. (2.1)]. Equation (3.7) is valid at small enough $B$ where Landau quantization can be ignored. At large $B$, quantum treatment is necessary. In the absence of interactions, the magnetoplasmon gap at $q = 0$ is given by $E_{n+1} - E_n$, the energy difference between the lowest unoccupied $n + 1$ and the highest occupied $n$ Landau levels. Unlike the case of a 2DEG, where the Kohn’s theorem holds, renormalization of the Fermi velocity by interactions directly affects the cyclotron gap. This many-body effect has been observed by magneto-optical spectroscopy, Sec. II.C.

Probing finite-$q$ magnetoplasmons optically is possible via the fine-size effects, such as the mode quantization in graphene disks. As known from previous experimental (Demel et al., 1990, 1991; Glattli et al., 1985; Kukushkin et al., 2003; Mast et al., 1985), numerical (Eliasson et al., 1986), and analytical (Volkov and Mikhailov, 1988) studies of other 2D systems, the single plasmon resonance at $B = 0$ splits into two. The upper mode whose frequency increases with $B$ can be regarded the bulk magnetoplasmon with $q \approx 1/R$, where $R$ is the disk radius. The lower mode whose frequency drops with $B$ can be interpreted as the edge magnetoplasmon, which propagates around the disk in the anti-cyclotron direction. Both the bulk-like and the edge-like modes have been detected by the IR spectroscopy of graphene disk arrays (Yan et al., 2012a,b). Additionally, in epitaxial graphene with a random ribbon-like microstructure, the $B$-field induced splitting of the Drude peak into a high- and a low-frequency branch was observed and interpreted in similar terms (Crassee et al., 2012). The distinguishing property of the edge magnetoplasmon is chirality: its the propagation direction is linked to that of the magnetic field. This property has been verified in graphene systems by time-domain spectroscopy (Kumada et al., 2013; Petković et al., 2013), which also allowed extraction of the edge magnetoplasmon velocity.

Other interesting properties of magnetoplasmons, such as splitting of the classical magnetoplasmon dispersion (3.7) into multiple branches have been predicted theoretically (Goerbig, 2011; R. Roldán et al., 2009) and their similarities and differences with the 2DEG case have been discussed. These effects still await their experimental confirmation.

C. Phonons

Raman spectroscopy is the most widely used tool for probing optical phonons in graphene and related materials (Dreselhaus et al., 2010, 2012; Ferrari et al., 2006; Ferrari, 2007). Quantitative studies of the Raman modes can provide rich information on graphene electron-phonon interaction, electronic structure, as well as on graphene layer thickness, edges, doping, and strain. Because graphene has the same $sp^2$ bonding and hexagonal carbon lattice, its phonon band-structure is almost identical to that in graphite. Figure 9a shows calculated dispersion of the optical phonon branches in graphene (lines) (Piscanec et al., 2004) as well as the experimental data of graphite (symbols) (Maultzsch et al., 2004). One feature of these dispersions is the discontinuity in the frequency derivative at the $\Gamma$ and K points in the highest optical branches. This discontinuity known as the Kohn anomaly arises from the unusual electron-phonon coupling in graphitic materials (Piscanec et al., 2004).

Figure 9b displays typical Raman spectra of SLG and graphite. They show the same qualitative Raman modes, with the two most prominent features being the $G$-mode ($\approx 1580$ cm$^{-1}$) and the $2D$-mode ($\approx 2700$ cm$^{-1}$, also known as $G'$ mode). The other weak but very informative Raman feature is the D-mode ($\approx 1350$ cm$^{-1}$). The lineshape of $2D$ mode is very different in SLG, MLG, and graphite (Fig. 9c) (Ferrari et al., 2006). As illustrated in Fig. 9d, the G-peak arises from Raman scattering of the $\Gamma$-point phonon. The $2D$-peak, on the other hand, is a two-phonon process involving emission of two K-point optical phonons. The $D$-peak is a double resonance process like the $2D$-peak. It requires structural defects to relax the momentum conservation constraint.

A detailed theory of the $G$-mode Raman signal was presented in Basko (2008, 2009); Basko and Aleiner (2008); and Basko et al. (2009). The capability of controlling the electron Fermi energy through electrical gating helped to elucidate electron-phonon interactions (Das et al., 2008; Malard...
and graphite measured at 514 nm laser excitation showing the $G$ and the 2D Raman peaks (Ferrari et al., 2006). (c) The evolution of the 2D Raman peak with the number of graphene layers (Ferrari et al., 2006). (d) Schematics of the $G$-mode and the 2D-mode Raman scattering processes.

FIG. 9 (Color online) Phonon dispersion and Raman spectroscopy of graphene. (a) Calculated phonon dispersion of SLG (Piscanec et al., 2004) (symbols) compared with the experimental data for graphite (Mohr et al., 2007) (lines). (b) Raman spectra of graphite and graphite measured at 514 nm laser excitation showing the $G$ and the 2D Raman peaks (Ferrari et al., 2006). (c) The evolution of the 2D Raman peak with the number of graphene layers (Ferrari et al., 2006). (d) Schematics of the $G$-mode and the 2D-mode Raman scattering processes.

et al., 2008; Pisana et al., 2007; Yan et al., 2007) and the quantum interference between different intermediate excitation pathways (Chen et al., 2011; Kalbac et al., 2010). The frequency and linewidth of the Raman $G$-mode reflect the energy and lifetime of the optical phonon at the $\Gamma$ point. The $\Gamma$-point phonon experiences Landau damping by particle-hole excitations if its energy exceeds $2|\mu|$ (see Fig. 2). As a result, the parameters of the Raman $G$-mode depend on the carrier concentration, as demonstrated experimentally (Pisana et al., 2007; Yan et al., 2007). The $G$-mode Raman shows a reduced damping and a blue shift when the Fermi energy is larger than one half of the phonon energy, so that the phonon decay pathway into electron-hole pairs gets blocked. When the Fermi energy in graphene is increased further, some of the intermediate electronic transitions necessary for Raman scattering become blocked. This reduces destructive interference among different pathways and increases the $G$-mode signal (Chen et al., 2011).

The Raman scattering that gives rise to the 2D mode involves emission of two BZ-boundary phonons close to the $K$-point. Being a two-phonon process, it still has large intensity, which is explained by the triple-resonance mechanism (Fig. 9d), where every intermediate step involves a resonant electronic excitation (Basko, 2008; Basko et al., 2009). Due to smallness of the phonon energy compared with the incident photon energy $h\omega$, the momenta $k$ of the intermediate electron states are restricted to $h\omega \approx E(k)$, where $E(k)$ is the electron dispersion (Sec. I.C). The phonon momentum (relative to a $K$-point phonon) then equals $2(k - K)$. Consequently, phonons and intermediate electronic transitions with specific momentum can be excited by varying incident photon energy for 2D Raman modes. This allows one to map the dispersion of both the phonon and the electrons.

Once the phonon dispersion is known, Raman scattering can be used to probe electronic band-structure changes with a fixed laser excitation. For example, it can distinguish SLG, BLG, and MLG due to their different electronic dispersions (Ferrari et al., 2006). In BLG and MLG there are several conduction and valence bands (Sec. V). Hence, valence electrons at more than one momentum $k$ can satisfy the $h\omega = E(k)$ relation. This leads to an apparent broadening and asymmetry of the 2D Raman peaks for BLG and MLG, compared to those for SLG (Ferrari et al., 2006).

The Raman $D$-mode (short for the defect-mode) requires the existence of atomically sharp defects to provide the required momentum matching to scatter a zone boundary phonon close to $K$-point. The intensity of the $D$-peak is used to characterize the sample quality of graphene (Dresselhaus et al., 2010; Ferrari, 2007; Malard et al., 2009). The $D$-mode is also useful for probing graphene edges, which can be considered as line defects. Experiments show that the $D$-peak is indeed the strongest at graphene edges (Casiraghi et al., 2009; Graf et al., 2007; Gupta et al., 2009), and that the $D$-mode intensity is at maximum for light polarization parallel to the edge and minimum for the perpendicular polarization (Casiraghi et al., 2009). For ideal edges, theory predicts that the $D$-mode Raman peak intensity is zero for zigzag edges but large for armchair ones (Casiraghi et al., 2009). In addition to the effects discussed above, the intensity and frequency of Raman peaks also depend on the substrate (Berciaud et al., 2008; Lee et al., 2008b; Ni et al., 2008a, 2009a; Wang et al., 2008c), temperature (Calizo et al., 2007), and strain (Huang et al., 2009; Mohiuddin et al., 2009; Proctor et al., 2009; Yu et al., 2008) through their effects on the phonon dispersion and electron Fermi energy.

**D. Electron-phonon and electron-plasmon interaction**

The energies and lifetimes of charge carriers in graphene are significantly affected by interactions with plasmons and
phonons. The electron-phonon (el-ph) interaction results in a variety of novel phenomena discussed in Sec. III.C. The ARPES has been used to probe the signature of the el-ph interaction in the electronic spectra of graphene (Bostwick et al., 2007b; McChesney et al., 2007, 2010; Zhou et al., 2008a) via the measurement of the quasiparticle velocity v. The el-ph coupling constant is usually defined by \( \lambda = v_0/v - 1 \) (Ashcroft and Mermin, 1976). However, electron-electron (el-el) interaction also contributes to velocity renormalization (Secs. I.D and II.B). Hence, thus defined \( \lambda \) gives a good estimate of el-ph coupling only if el-el interaction is screened, which is the case for graphene on a metallic substrate Siegel et al. (2011).

The el-ph interaction in graphene strongly depends on the carrier concentration, as shown in Fig. 10a,b. Siegel et al. (2011) have reported a large reduction of \( \lambda \) for quasi-free-standing graphene with \( E_F \) close to the Dirac point \( E_D \). The overall reduction of the el-ph interaction can be reproduced by theoretical calculations (Park et al., 2007). However, to account for the fine features of the quasiparticle dispersion, the el-el interaction has to be included (Lazzeri et al., 2008; Siegel et al., 2011; Zhou et al., 2008b). At high doping \( \lambda \) appears to be enhanced, reaching values \( \lambda \sim 2 \), and strongly anisotropic, similar to what is observed in graphite (Leem et al., 2008; Park et al., 2008a; Zhou et al., 2006) and in the intercalated compound CaC\(_6\) (Valla et al., 1999). Calandra and Mauri (2007b) argued these effects result from distortion of the graphene bands that hybridize with a new Ca-related band. On the other hand, Park et al. (2008b) suggested that the anisotropy of \( \lambda \) comes from the nonlinear band dispersion of the graphene bands at high doping.

From a high resolution ARPES study Zhou et al. (2008c) concluded that the electron-phonon coupling is dominated by the following phonon modes: \( A_{1g} \) phonon at approximately 150 ± 15 meV near the BZ corner, \( E_{2g} \) phonon (\( \sim \) 200 meV) at the zone center, and the out-of-plane phonon at 60 meV. Among these, the \( A_{1g} \) phonon is the one that mostly contributes to \( \lambda \) and mainly responsible for the kinks in the ARPES spectra of a "freestanding" graphene sample in which hydrogen has been intercalated between graphene and SiC to make negligible the interaction between the two. The plasmon of momentum \( k \) is a bound state of a hole with momentum \( k + q \) and a plasmons of momentum \(-q\) (Lundqvist, 1967).

15See Bianchi et al. (2010); Bostwick et al. (2007a); Calandra and Mauri (2007a); Filletet et al. (2009); Grünéis et al. (2009); McChesney et al. (2008, 2007, 2010); Park et al. (2007, 2008b); and Zhou et al. (2008c).
The dopants introduce not only a change in the average carrier concentration but also charge inhomogeneities and scattering. Near the graphene neutrality point inhomogeneities of either sign can arise, which are often referred to as the electron-hole puddles (Geim and Novoselov, 2007). Thus, even at the neutrality point the graphene is always locally doped. This is a qualitative explanation for nonvanishing conductivity (Chen et al., 2008; Geim and Novoselov, 2007; Tan et al., 2007) and TDOS (Martin et al., 2008). A more detailed model (Adam et al., 2007; Hwang et al., 2007a; Rossi and Das Sarma, 2008; Shklovskii, 2007) invokes a system of conducting electron-rich and hole-rich regions separated by p-n junctions (Cheianov et al., 2007b; Zhang and Fogler, 2008). The transport involves percolation through the p and n regions aided by tunneling across the junctions (Cheianov et al., 2007a; Das Sarma et al., 2011). Many elements of this semiclassical model hark back to the earlier studies of two-dimensional (Efros et al., 1993; Fogler, 2004) and three-dimensional (Efros and Shklovskii, 1984) electron systems in semiconductors. However, the puddle model may not be quantitatively reliable for graphene. The correlation length of the density inhomogeneities is typically very short. For SLG on SiO$_2$ it was consistently estimated to be of the order of 20 nm using several complementary scanned probes microscopy techniques (Berezovsky et al., 2010; Deshpande et al., 2011; Luijten et al., 2011b; Martin et al., 2008). A typical electron-hole “puddle” is also too small to contain even a single charge (Martin et al., 2008). Therefore, the inhomogeneities in question may be better described as quantum interference patterns of disorder-scattered electron waves rather than large semiclassical puddles. The situation may change if Coulomb interactions among electrons and impurities is screened. The crossover to the semiclassical regime is predicted to occur (Fogler, 2009) for graphene on a substrate of high dielectric constant $\kappa \gg 1$. Suppression of density inhomogeneities in one graphene layer due to screening by a nearby second layer has been invoked to explain the observed localization transition in graphene-hBN-graphene structures (Ponomarenko et al., 2011).

The inhomogeneities may also be induced by elastic strain and ripples (Brey and Palacios, 2008; Gibertini et al., 2010; Guinea et al., 2008b). Electron density inside the highly strained graphene bubbles (Bunch et al., 2008; Georgiou et al., 2011; Levy et al., 2010) is undoubtedly inhomogeneous. However, the relation between strain and electron density is nonlocal. Indeed, no local correlations between the carrier density in graphene and the roughness of SiO$_2$ substrate is evident in scanned probe images (Deshpande et al., 2011; Martin et al., 2008; Zhang et al., 2009a).

The hypothesis that unintentional doping is caused by impurities trapped under graphene is supported by some micro-Raman experiments showing that proximity to the SiO$_2$ substrate results in increase of carrier density (Berciaud et al., 2008; Bukowska et al., 2011; Ni et al., 2009b). Yet other micro-Raman measurements (Casiraghi et al., 2009) have not observed such correlations.

FIG. 11 (Color online) The ARPES dispersion of doped (N = 8 $\times$ 10$^{15}$ cm$^{-2}$) graphene perpendicular (a) and parallel (b) to the Γ-K direction (Bostwick et al., 2010). The dashed black lines are guides to the eye for the dispersion of the hole and plasmaron bands; the solid red line goes through the Dirac point. The inset shows a schematic of the renormalized spectrum in the presence of plasmarons.

Theoretical calculations (Polini et al., 2008) within the GW approximation predict that the plasmaron band appears at finite charge densities. Its energy separation from the primary quasiparticle band is proportional to $\mu$ with a coefficient that depends on the Coulomb interaction strength $\alpha$, which in turn depends on the dielectric environment of graphene. Quantitative aspects of these calculations were disputed by Lischner et al. (2013) who included vertex corrections neglected in the GW scheme. Compared to Polini et al. (2008), for the same $\alpha$ Lischner et al. (2013) find a broader plasmaron peak at a smaller separation from the primary band, which appears to be in a better agreement with the experiments of Bostwick et al. (2010).

No evidence of the plasmaron band has been reported in samples where decoupling of graphene from the buffer layer was achieved by either gold or fluorine intercalation (Starodub et al., 2011; Walter et al., 2011b). This has been attributed to a stronger dielectric screening by the buffer layer. An alternative interpretation of the apparent nonlinearity of the Dirac spectrum of graphene on SiC invokes a substrate-induced band gap (Benfatto and Cappelluti, 2008; Kim et al., 2008; Zhou et al., 2007, 2008a,c), see Sec. IV.B below.

IV. INDUCED EFFECTS

A. Inhomogeneities and disorder

Intentional and unintentional doping by charged impurities plays a very important role in the electronic phenomena of graphene. It is unclear if there is a single dominant source of unintentional doping even for most studied type of samples: exfoliated graphene on SiO$_2$. In addition to adsorbates from the ambient atmosphere, doping could also result from charged defects in SiO$_2$ (Adam et al., 2007; Coletti et al., 2010; Schedin et al., 2007; Wehling et al., 2007; Zhou et al., 2008d) lithographic residues (Dan et al., 2009), and metal contacts (Connolly et al., 2010).
Charge inhomogeneities can be reduced by either removing the substrate (Du et al., 2008; Knox et al., 2011) or using a high-quality hBN substrate (Dean et al., 2010). The random charge fluctuations of exfoliated graphene on hBN are at least two orders of magnitude smaller than those on SiO$_2$ according to the STM studies (Decker et al., 2011b; Xue et al., 2011). (However, in such structures periodic charge oscillations may appear instead of random ones, see Sec. IV.C.) These random fluctuations are at par with the values estimated from transport data for free-standing graphene (Du et al., 2008). The electronic mobility of graphene on hBN approaches $\sim 10^5$ cm$^2$/Vs implying the mean-free path of several hundreds nm (Dean et al., 2010; Du et al., 2008).

Although detrimental for transport properties, impurities can play a role of elementary perturbations that help reveal useful physical information. We can give two examples. First, disorder-induced LDOS fluctuations seen in STS (Rutter et al., 2007; Zhang et al., 2009a) reveal the dominant momenta for inter- and intra-valley scattering and therefore shed light on chirality and energy spectrum of the quasiparticles. Second, by utilizing ionized Co adatoms one can study screening properties of graphene. The screening cloud surrounding the adatoms was shown to have a qualitatively different profile depending on the total charge of the adatom cluster. In the sub-critical case this profile is governed essentially by the linear response dielectric constant of graphene. Theoretical modeling of the STS spectra (Brar et al., 2011; Wang et al., 2012) suggests the enhanced value $\epsilon \approx 3.0$ of this constant, which is indicative of many-body interactions (Sodemann and Fogler, 2012). In the super-critical case (Wang et al., 2013) sharp resonances in the local DOS appear, which is the hallmark of a nonlinear screening with intriguing analogy to “atomic collapse” of super-heavy elements.

B. Substrate-induced doping

Metallic substrates induce a strong doping of graphene, which is readily seen by the ARPES (Fig. 12a). The chemical potential $\mu = E_F - E_D$ measured with respect to the Dirac point ranges from approximately 0.5 eV for Cu (111) (Gao et al., 2010) and Cu films (Siegel et al., 2012; Walter et al., 2011c) to 2 eV for other transition metals, such as Ni (111) (Dedkov et al., 2008; Nagashima et al., 1994; Varykhalov et al., 2008), Ru (0001) (Enderlein et al., 2010; Himpsel et al., 1982; Sutter et al., 2009), and Co (0001) (Rader et al., 2009). An exception to this is graphene on Ir (111) (N’Diaye et al., 2006; Pletikosić et al., 2009), where the surface states of the substrate cause pinning of $\mu$ near zero.

Naively, graphene is $n$-doped if $W_G > W_M$ and $p$-doped otherwise, where $W_G = 4.5$ eV is the work function of pristine graphene and $W_M$ is that of the metal. In fact, the charge transfer is affected by chemical interaction between graphene and the metal and by their equilibrium separation (Giovanetti et al., 2008). The amount of charge transfer can be modified by intercalation. Fluorine intercalation yields a large $p$-type doping of graphene (Walter et al., 2011b). Hydrogen intercalation leads to decoupling of graphene from the substrate (Riedl et al., 2009), as evidenced by the ARPES dispersions, Fig. 12(b) and (c), typical of suspended graphene, cf. Fig. 12(d). Similar effects can be obtained by Au intercalation (Gierz et al., 2008). When gold atoms are intercalated between graphene and a Ni (111) substrate (Varykhalov et al., 2008), $\mu$ drops down to 25 meV, corresponding to the two orders of magnitude decrease in the carrier concentration.

C. Moiré patterns and energy gaps

When the lattice constants of the graphene layer and the substrate differ by a small relative amount $\delta$ and/or misoriented by an angle $\phi$ a moiré superlattice arises (Marchini et al., 2007; N’Diaye et al., 2006; Wang et al., 2008a; Winterlin and Bocquet, 2009). The electron dispersion in the presence of the moiré superlattice gets modified as a result of hybridization of the original Dirac cones with their replicas folded into a superlattice Brillouin zone (bBZ). Such replicas have been seen in the ARPES spectra of graphene on Ir (111) (Pletikosić et al., 2009) although they may also be due to the final-state diffraction (Sutter et al., 2009).

The most striking experimental manifestations of the moiré superlattice effects have recently been observed in SGL on
hBN. This system has $\delta = 1.8\%$, so that the moiré period can be as long as 14 nm, which can be easily imaged by scanned probes (Fig. 13, insets). Dependence of the moiré period on the misorientation angle $\phi$ is very sharp, Fig. 13A, so achieving large period requires precise alignment.

It has been predicted theoretically that at the intersections of the replica and the main bands new Dirac points appear, Fig. 13C. For the practical case of a weak superlattice potential, these points have energy

$$E_D^0 \simeq E_D \pm \frac{2\pi}{\sqrt{3}} \frac{h\nu}{\Lambda},$$

(4.1)

where $\Lambda$ is the moiré period. [For the opposite limit of strong modulation, see (Brey and Fertig, 2009).] The extra Dirac points are characterized by a modified and generally, anisotropic quasiparticle velocity (Guinea and Low, 2010; Park et al., 2008d; Wallbank et al., 2013). The original Dirac point at the center of the $\mathrm{bZ}$ remains gapless, at least, within the scope of generic theoretical models of the moiré superlattice which preserve sublattice symmetry.

First attempts to identify extra Dirac points in SLG/hBN structures were unsuccessful because these points were outside the experimental energy window (Xue et al., 2011). In more recent experiments, which utilized precisely aligned ($\phi < 0.5^\circ$) structures, the new Dirac points are clearly evidenced by additional minima of the DOS measured by STS (Yankowitz et al., 2012), Fig. 13B. The unmistakable signatures of the second-generation Dirac points in transport include peaks in longitudinal resistance and the sign change of the Hall resistance (Dean et al., 2013; Ponomarenko et al., 2013; Yang et al., 2013; Yankowitz et al., 2012), Fig. 13C and D. Additional Landau level (LL) fans emerging from these extra Dirac points are seen in magnetotransport (Dean et al., 2013; Hunt et al., 2013; Ponomarenko et al., 2013) and the gate capacitance measurements. The detailed structure of such LLs is predicted to be fractal, as spectacularly illustrated by the iconic image of the “Hofstadter butterfly” (Hofstadter, 1976). Experiments (Hunt et al., 2013) in strong fields $B > 20 \, \text{T}$ demonstrate additional quantum Hall plateaus and a large gap (tens of meV) at the neutrality point, the physical origin of which remains to be understood.

Opening a band gap at the Dirac point is indeed the most often cited effect that can enable wider applications of graphene. Inducing gap by confinement in various graphene superstructures such as quantum dots, ribbons, etc., has proved to be problematic due to disorder effects. Inducing a gap through graphene/substrate interaction seems an attractive alternative. The most straightforward mechanism of the gap generation is breaking the sublattice symmetry of graphene (Brey and Fertig, 2006; Giovannetti et al., 2007; Nakada et al., 1996; Nilsson et al., 2007; Trauzettel et al., 2007) For a hypothetical commensurate SLG/hBN structure, a band gap $\sim 50 \, \text{meV}$ was predicted (Giovannetti et al., 2007; Sławińska et al., 2010). Theoretically, the gap can also be induced by hybridization of the two valleys (Mañes et al., 2007). A small band gap in graphene can also be induced by a spin-orbit coupling of Rashba type (Kane and Mele, 2005). The curvature of the graphene sheet is predicted to enhance the Rashba splitting (Huertas-Hernando et al., 2006; Kuemmeth et al., 2008).

Existence of substrate-induced gaps have been indicated by many ARPES experiments. A very wide spread of gap values has been reported, which remains unexplained. One of the earliest ARPES studies (Oshima and Nagashima, 1997) claimed the largest gap so far, 1.3 eV, for a “soft” SLG on TaC (111). Large gaps have also been reported for graphene on certain metallic substrates. Brugger et al. (2009) found $\sim 1 \, \text{eV}$ gap for SLG on Ru (0001). Nagashima et al. (1994) observed 0.7–1.3 eV gaps in SLG on Ni (111) intercalated with alkaline metals. For Ru (0001) covered a with monolayer of gold (Enderlein et al., 2010) and for Ir (111) substrates (Starodub et al., 2011) the gap is 0.2 eV. The effect of intercalants is counterintuitive because these are metals to which graphene interacts weakly. The gap for SLG on Cu is 0.3–0.4 eV. Zhou et al. (2007) made a case for the 0.26 eV gap in epitaxial graphene on SiC. As discussed in Sec. III.D, a competing interpretation of these data is in terms of plasmarons (Bostwick et al., 2007a,b, 2010). Comparable gaps were found for other semiconducting substrates (Siegel et al., 2011; Walter et al., 2011c). For graphene on graphite the gap of 20 meV (Li et al., 2009a; Siegel et al., 2011) was reported. The STS Kawasaki et al. (2002) observed a 0.5 eV for SLG/single-layer hBN/Ni (111) structure.

The largest Rashba splitting $13 \pm 3 \, \text{meV}$ has been reported for graphene on magnetic substrate Ni (111) intercalated by Au (Varykhalov et al., 2008). The mechanism behind this enhancement is still unknown. No Rashba splitting has been observed on another magnetic substrate, Co (0001) intercalated by Au (Rader et al., 2009). Although intrinsic spin-orbit (SO) coupling is also responsible for the opening a band gap, $\Delta_{\text{SO}}$, in pure SLG it is predicted to be extremely small, e.g., $10^{-3}–10^{-2} \, \text{meV}$ (Kane and Mele, 2005). A broken symmetry at the interface of two SLG can somewhat amplify this gap (Schmidt and Loss, 2010). Impurities in graphene resulting in $sp^3$ type deformation of the flat graphene are also predicted to enhance $\Delta_{\text{SO}}$ up to 7 meV (Castro Neto and Guinea, 2009). In fact, a recent experimental study on hydrogenated graphene revealed a drastically enhanced $\Delta_{\text{SO}}$ of 2.5 meV (Balakrishnan et al., 2013). Alternatively, the interactions of charge carriers in graphene with heavy atoms such as In and Tl adsorbed on graphene are predicted to enhance $\Delta_{\text{SO}}$ up to 7 meV and 21 meV, respectively (Weeks et al., 2011).

D. Elastic strain

A controlled uniaxial strain can be readily introduced into graphene by stretching the flexible substrate. The strain modifies graphene phonon energy spectrum, which is effectively probed by Raman spectroscopy. Under uniaxial strain the $G$ and $2D$ phonon bands display significant red shift proportional to the applied strain: a result of the anharmonicity of the interatomic potentials in graphene (Huang et al.,
FIG. 13 (Color online) A. Moiré superlattice wavelength (black) and rotation (red) as a function of the angle between the SLG and hBN lattices. Inset: STM topography images showing (top to bottom) 2.4, 6.0, and 11.5 nm moiré patterns. The scale bars in all the images are 5nm tall. B. The tunneling $dI/dV$ curves for samples with moiré wavelengths 9.0 nm (black) and 13.4 nm (red). The dips in the $dI/dV$ curves marked by arrows occur at secondary Dirac points. C. Longitudinal resistivity $\rho_{xx}$ of SLG on hBN as a function of carrier density. Inset: one possible reconstruction of SLG spectrum. D. The Hall resistivity $\rho_{xy}$ changes sign at high electron and hole doping, revealing well-isolated secondary Dirac points. Inset: conductive atomic force microscope image of the moiré pattern. The separation between the white spots is 11 nm. Panels A-B and C-D are adapted from (Yankowitz et al., 2012) and (Ponomarenko et al., 2013), respectively.

Strain also introduces profound modifications to graphene electronic structure. The defining topology feature of graphene electronic band, namely the degeneracy of conical electron and hole bands at Dirac points, is protected by the inversion symmetry of graphene lattice (Hasegawa et al., 2006; Kishigi et al., 2008; Wunsch et al., 2008). A small perturbation in form of mechanical strain does not lift the degeneracy, but deforms the energy bands and shifts the Dirac points in both the energy and the momentum space. The former is equivalent to a scalar potential also known as the deformation potential. A general nonuniform strain generates a spatially varying dilation of the graphene lattice and therefore local ion density. The deformation potential arises because the corresponding Coulomb potential is only partially screened by electrons (Guinea et al., 2008a; Kim and Castro Neto, 2008; Suzuura and Ando, 2002). Next, shifting the Dirac point in the $k$-space away from the K (K') points (Dietl et al., 2008; Farjad and Rafii-Tabar, 2009; Ni et al., 2008a, 2009a; Pereira and Castro Neto, 2009). is analogous to the effect induced by an external magnetic field applied perpendicular to the graphene plane. One can parametrize the mechanical strain by a gauge field $A$ (Fogler et al., 2008; Iordanskii and Koshelev, 1985; Kane and Mele, 1997; Katsnelson and Novoselov, 2007; Mor-
purgo and Guinea, 2006; Sasaki et al., 2005) and define the pseudomagnetic field \( B_s = \nabla \times A \). The strain-induced \( A \) and \( B_s \) have opposite signs at two valleys K and K’, so that the time-reversal symmetry is preserved.

It is possible to engineer a special nonuniform strain for which \( B_s \) is approximately constant in a finite-size region. If such pseudomagnetic field is strong enough, it can lead to Landau quantization and quantum Hall-like states (Guinea et al., 2010a,b). In a recent experiment (Levy et al., 2010), such an unusual Landau quantization has been observed in highly strained graphene nanobubbles. The strain arises upon cooling because of a mismatch in the thermal expansion coefficients of graphene and the Pt substrate (Fig. 14A). The pseudo-Landau levels, manifested as local density of states peaks, are probed by STS (Figs. 14B and C). Their energies follow the theoretically predicted \( \text{sgn}(n)\sqrt{|n|} \) behavior with a gigantic \( B_s \sim 300 \text{T} \), see Fig. 14C.

E. Photo-induced effects

Optical spectroscopy with ultrafast laser excitation pulses provides a unique tool to probe the dynamic evolution of electrons and phonons in graphene, including the cooling of the non-equilibrium quasiparticle plasma through electron-electron and electron-phonon interactions and the relaxation of hot optical phonons. These processes are not only of fundamental interest due to the unusual electronic structure in graphene, but also important for technological applications of high-field electronics and nonlinear photonic devices (Bao et al., 2009; Bonaccorso et al., 2010; Sun et al., 2010b; Xia et al., 2009a; Zhang et al., 2010).

Response of graphene to a pulsed laser excitation has been studied by several complementary ultrafast spectroscopy techniques. For example, pump-probe IR/visible spectroscopy (Dawlaty et al., 2008; Huang et al., 2010; Newson et al., 2009; Sun et al., 2008) and pump-probe THz spectroscopy (George et al., 2008) has been employed to track the time evolution of optical absorption and transmission by graphene. Ultrafast photoluminescence (Liu et al., 2010; Lui et al., 2010; Stöhr et al., 2010) has been used to monitor light emission by non-equilibrium electron gas. Time-resolved Raman spectroscopy (Chatzakis et al., 2011; Yan et al., 2009) has explored generation and decay of hot optical phonons. Breusing et al. (2009) studied graphite using 7 fs 1.55 eV pump pulses and a broadband probe pulses with energy spectrum from 1.2 to 2 eV. Figure 15a shows the observed increase of transmission during the first 150 eV with sub-10 fs time resolution. This phenomenon is attributed to partial Pauli blocking of the optical transition by photo-excited electron-hole pairs. The change in transmission scales linearly with the pump influence and decays with two time constants of 13 fs and 100 fs. The former characterizes electron-electron interactions, which cause energy redistribution within the conduction and valence band, as well as relaxation of occupation factors by Auger processes. The second time constant describes interaction of quasiparticles with optical phonons. The emission of optical phonons with energy \( \sim 0.2 \text{ eV} \) cools down electron-hole plasma. Once its temperature drops below this number, emission of optical phonons becomes ineffective. Eventual equilibration of the electron and lattice temperatures is achieved by emission of acoustic phonons on a time scale of \( \sim 2 \text{ ps} \).

The decay dynamics of graphene in the 8 ps temporal range is shown in Fig. 15b with three different probe photon energies. In addition to the fast decay processes described above, it shows a slower relaxation process with a time constant of 1.4 ps. This picosecond time scale reflects partial thermalization between the hot electron/holes and optical phonons with...
the acoustic phonons in graphene. We note that the photo-induced transmission change can become negative at certain probe photon energies at longer delay. This is because optical excitation not only leads to Pauli blocking of interband transitions, but also increased high frequency absorption from intraband transitions. At longer pump-probe delay, the intraband absorption may dominate over the Pauli blocking effects at some probe photon energies. Similar photo-induced transmission changes have also been observed in optical pump-THz probe measurements, where photo-induced intraband transitions always dominate (George et al., 2008; Strait et al., 2011; Wright et al., 2009).

Ultrafast photoluminescence monitors the light emission from the highly non-equilibrium electrons after femtosecond pump excitations (Liu et al., 2010; Liu et al., 2010; Stöhr et al., 2010). Broad light emission across the visible spectral range (1.7–3.5 eV) was observed with femtosecond near-IR laser excitation, where the incident photon has an energy of 1.5 eV. This unusual blue-shifted photoluminescence exhibits a nonlinear dependence on the laser fluence, and it has a dominant relaxation time within 100 fs. This nonlinear blue-shifted luminescence was attributed to recombination of hot electron-hole plasma generated right after the femtosecond excitation.

In addition to the electron dynamics, researchers were able to probe the phonon dynamics specifically using time-resolved Raman spectroscopy (Chatzakis et al., 2011; Yan et al., 2009). Such studies show a decay lifetime of 2.5 ps for the BZ-center \( G \)-mode phonons. This time scale corresponds to the cooling of the optical phonons through anharmonic coupling to acoustic phonons, and the 2.5 ps time constant is similar to that obtained in pump-probe transmission spectroscopy.

V. BILAYER AND MULTILAYER GRAPHENE

There has been a rapidly increasing interest in graphene systems with more than one layer (for an early review, see Nilsson et al. (2008)). The electronic structure of BLG and MLG is distinctly different from that of SLG. These differences give rise to many new phenomena, ranging from a tunable bandgap (Castro et al., 2007; McCann, 2006; McCann and Fal’ko, 2006; Oostinga et al., 2008; Zhang et al., 2009b) to strongly correlated ground states (Bao et al., 2010; Feldman et al., 2009; Mayorov et al., 2011a; Velasco et al., 2012; Weitz et al., 2010). Unfortunately, space limitations and the open debate on the nature of these low-energy states (Barlas et al., 2010; Min et al., 2008; Nandkishore and Levitov, 2010a,b, 2011; Nilsson et al., 2006; Vafek and Yang, 2010) do not permit us to describe them in any detail. In this short section we confine ourselves to discussing “higher” energy properties of these materials that have been measured by ARPES and by optical spectroscopy.

We begin with discussing the quasiparticle dispersion of BLG. For the Bernal stacked BLG, which is the most energetically favorable structure, it is conventionally described by means of five parameters. They include four hopping integrals \( \gamma_0 = 3.0 \text{ eV}, \gamma_1 = 0.41 \text{ eV}, \gamma_3 = 0.3 \text{ eV}, \gamma_4 = 0.15 \text{ eV} \), and also the on-site energy shift \( \Delta' = 0.018 \text{ eV} \) (Fig. 1B).16 When BLG is subject to an electric field due to external gates or charged impurities, the sixth parameter, a scalar potential \( \pm \Delta/2 \) on the two layers must be included. The interlayer bias \( \Delta = \epsilon Ed \) is given by the product of the layer separation \( d = 0.335 \text{ nm} \) and the electric field \( E \) between the layers.

The BLG has four atoms in the unit cell, and so the electron spectrum consists of four bands. The two outer (lowest and highest energy) bands are hyperbolic, with the extremal values at approximately \( \pm \gamma_1 \) reached at the BZ corners. The shape of the two inner bands is more intricate. At high energies they are nested with the outer bands. At low energies their dispersion depends on the relation between the gap \( \Delta \) and the hopping integral \( \gamma_3 \), which causes the trigonal warping. At \( \Delta \gg \gamma_3/|\gamma_1| \), the trigonal warping is a small effect. The bands are shaped as sombreros, e.g., the conduction band has a local maximum at energy \( \Delta/2 \) at \( q = 0 \) and a local minimum — the bottom of the sombrero — at the ring \( |q| \approx \Delta/\sqrt{2} \hbar \omega_0 \), see Fig. 16d (right) (McCann and Fal’ko, 2006). As \( \Delta \) is decreased, the trigonal warping of the bottom of the sombrero becomes more and more pronounced. In the absence of the interlayer bias, \( \Delta = 0 \), the parabolic extrema split into the four conical Dirac points. This reconstruction is an example of the Lifshitz transition. The linear rather than parabolic shape of the bands in the symmetric BLG is supported by the linear-\( T \) dependence of low-temperature electric conductivity in extremely clean suspended BLG (Mayorov et al., 2011a).

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16For a discussion of these numerical values and comparison with graphite, see Kazmenko et al. (2009a,c); Li et al. (2009b); and Zhang et al. (2008a).
FIG. 16  (Color online) (a) IR conductivity spectra of MLG with layer number \( L = 1, 2, \ldots, 8 \). The dots identify the position of the peaks in experimental IR conductivity. These transition energies follow well-defined energy-scaling relations predicted by the zone-folding model (solid curves) (Mak et al., 2010). (c) An illustration of the Bernal stacked BLG with electrical field above and below it. (d) Electronic structure of a pristine and a gated BLG. Arrows indicate allowed optical transitions. (e)-(g) ARPES data showing the evolution of an induced bandgap in electronic structure of epitaxial BLG on SiC with chemical adsorbed Ca atoms (Ohta et al., 2006). (h) Electrical field dependence of the induced bandgap in BLG measured through IR absorption spectroscopy (symbols) (Zhang et al., 2009b).

However, in less perfect samples, the quadruple Dirac cones structure is smeared by disorder. It is therefore common to approximate the inner bands by hyperboloids touching at a point, see Fig. 16d (left).

In order to vary \( \Delta \), one has to apply an external electric field to BLG. This can be achieved experimentally through electrostatic gating or doping. If \( D_t \) and \( D_b \) are electric displacement fields on the two sides of BLG (Fig. 16c), then the interlayer electric field \( E \) is determined by their mean \( \bar{D} = (D_b + D_t)/2 \). Notably, \( E \) is smaller than \( \bar{D} \) due to screening effects. Calculations within the self-consistent Hartree approximation (McCann and Fal’ko, 2006) predict a factor of two or so reduction in typical experimental conditions.

The difference \( D = D_b - D_t \) of the displacement fields produces a net carrier doping, and so the Fermi energy shift (Fig. 16d). Unless \( D_t \) and \( D_b \) are precisely equal or precisely opposite, the modification of the band gap \( \Delta \) and the shift of the Fermi energy \( E_F \) occur simultaneously (Castro et al., 2007; McCann, 2006; McCann and Fal’ko, 2006).

The control of electronic structure of BLG was first revealed in ARPES studies of potassium-doped epitaxial graphene on SiC (Ohta et al., 2006). Figures 16e-g display the evolution of the ARPES spectra with doping. As prepared, BLG is \( n \)-type doped. This corresponds to a finite \( D_b \) and zero \( D_t \), leading to a nonzero bandgap (Fig. 16e). Potassium adsorption generates a finite \( D_t \). When its value is the same as \( D_b \), one obtains an electron doped gapless BLG (Fig. 16f). With further increase in potassium doping, the bandgap reappears (Fig. 16g). Tuning of BLG electron structure can be also achieved via coupling to different substrates (Siegel et al., 2010).

Complimentary insights on the band structure of BLG has been provided through IR spectroscopy. There is a total of six inter-band optical transitions possible in this material. The near-perfect nesting of two conduction bands results in a strong absorption peak at mid-IR energy \( \gamma_1 \), when the transition between them is activated by \( n \)-type doping. A refined estimate of \( \gamma_1 = 0.40 \pm 0.01 \text{ eV} \) has been obtained by monitoring the lineshape and position of this peak in a gated BLG structure as a function of the gate voltage and modeling these spectra theoretically (Zhang et al., 2009b). Similarly, the \( p \)-type doping activates transition between the two valence bands. From slight differences of \( p \)- and \( n \)-type spectra, the electron-hole symmetry breaking parameters \( \gamma_4 \) and \( \Delta' \) have been inferred. The parameters obtained from the IR experiments are corroborated by those derived from the Raman spectroscopy (Malard et al., 2007) and the capacitance
measurements of the TDOS (Henriksen and Eisenstein, 2010).

The bandgap tuning by electrical gating was demonstrated using IR spectroscopy through monitoring the gate-induced change in other three transitions shown in Fig. 16d by arrows (Kuzmenko et al., 2009b; Mak et al., 2009; Zhang et al., 2009b). The dependence on the bandgap on the mean displacement field $\bar{D}$ (Fig. 16h) was found to be in agreement with the theory (McCann and Fal’ko, 2006).

On the other hand, observing the predicted bandgap value from electrical transport measurements has been challenging. Gated BLG typically exhibits an insulating behavior only at $T < 1$ K, suggesting a very narrow gap (Oostinga et al., 2008). This is because electrical transport is extremely sensitive to defects and impurities, and a very high quality graphene is required to reach the intrinsic BLG behavior. Recent transport studies (Xia et al., 2010) however demonstrate transport gaps closer to those obtained through IR spectroscopy.

Electron-phonon coupling in gated BLG shows up in tunable electron-phonon Fano resonances (Cappelluti et al., 2010; Kuzmenko et al., 2009a; Tang et al., 2010). There is a host of other effects that originate from unique gate-tunable electronic structure in BLG that have been predicted theoretically and are amenable to spectroscopic studies, e.g., a rich Landau level spectrum structure (Zhang et al., 2011). However, we must leave this topic now to at least briefly discuss MLG.

The electronic structure of MLG has been investigated experimentally using optical spectroscopy. Figure 16a displays a set of IR absorption spectra from $L = 1$ to 8 layer graphene over the photon-energy range of $0.2-0.9$ eV (Mak et al., 2010). At energies in the range $\gamma_1 \ll \hbar \omega \ll \gamma_0$ the MLG is expected to behave in the first approximation as a stack of uncoupled SLG, each possessing the universal optical conductivity $\sigma_0$, Eq. (3.1). Indeed, at energies above $0.8$ eV, the measured optical absorption scales linearly with $L$. However, at lower energies, the absorption becomes highly structured and distinct for different $L$. The evolution of the absorption spectra as a function of $L$ can be visualized from the false color plot Fig. 16b in which the principle transition energies are marked by the solid curves. The shape of these curves can be understood through zone-folding of the graphite bandstructure. In particular, a gapless band is present if $L$ is odd and absent if it is even (Mak et al., 2010).

VI. OUTLOOK

A wealth of spectroscopic data analyzed in this review has provided a panoramic picture of electronic phenomena in graphene. The concept of 2D Dirac quasiparticles offers a unifying description of the gross features revealed in all spectroscopic and transport probes. At the same time, pronounced and reproducible deviations from the predictions of noninteracting models of graphene have been documented. An outstanding challenge for future research is probing these many-body effects using specimens of record-high electron mobility where the role of disorder is further reduced.

Due to space limitations, we have not been able to cover some topics at all, e.g., nanostructured graphene, spin phenomena, graphene at ultra-high doping, or fractional quantum Hall effect in graphene (Goerbig, 2011). We also covered some others, e.g., BLG and MLG in insufficient detail. These topics are being actively explored, and the consensus is still being reached (for review, see (McCann and Koshino, 2013)). In addition, a particularly interesting class of materials for future research are hybrid multilayer structures and superlattices assembled from graphene and other ultrathin atomic crystals, such as hBN, MoS$_2$, etc. (Geim and Grigorieva, 2013).

Besides fundamental research, graphene and its spectroscopy have inspired a number of applications. For example, the spectroscopic studies motivated the development of novel experimental tools and methods compatible with the architecture of gatable devices. Novel scanning spectroscopies have advanced by exploiting the unique aspect of graphene that it is unobstructed by other interfaces. Controlled modification of graphene properties has been demonstrated through using elastic strain, interactions with the substrate, adatoms, and/or other graphene layers. These new experimental approaches are expected to find applications in other areas of condensed matter physics. Examples of viable device concepts spawned by photon-based spectroscopies include compact (passive) optical components, photodetectors and bolometers, and saturable absorbers. In addition, standard plasmonics figures of merit show competitiveness or even superiority of graphene as a plasmonic medium compared to more seasoned metal-based technologies. An unresolved question is whether graphene is suitable for achieving population inversion and lasing.

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17See Castro et al. (2007); Oostinga et al. (2008); Szafranek et al. (2010); and Xia et al. (2010).
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