Physics of Graphene

--- Zero-Mode Anomalies and Roles of Symmetry ---

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A brief review is given on electronic and transport properties of monolayer graphene from a theoretical point of view. The topics include the effective-mass description of electronic states, topological anomaly associated with Berry’s phase, singular diamagnetic susceptibility, zero-mode anomalies and their removal due to level broadening effects, the symmetry crossover among symplectic, unitary, and orthogonal due to the presence of special time reversal symmetry, and interaction with acoustic, optical, and zone-boundary phonons.

§1. Introduction

In an effective-mass approximation, an electron in a graphite monolayer or graphene is described by Weyl’s equation for a massless neutrino.\(^1\)–\(^4\) Transport properties in such an exotic electronic structure are quite intriguing, and the conductivity with/without a magnetic field including the Hall effect,\(^5\),\(^6\) quantum corrections to the conductivity,\(^7\) and the dynamical transport\(^8\) were investigated theoretically. The results show that the system exhibits various characteristic behaviors different from conventional two-dimensional systems.\(^9\) Quite recently, this single layer graphene was fabricated using the so-called scotch-tape technique\(^10\) and the magnetotransport was measured including the integer quantum Hall effect, demonstrating the validity of the neutrino description of the electronic states.\(^11\),\(^12\) Since then the graphene became the subject of extensive theoretical and experimental study. The purpose of this paper is to give a brief review on such electronic and transport properties from a theoretical point of view.

Later experiments in higher magnetic fields showed spin splitting for several low-lying Landau levels and additional splitting for level \(n = 0\).\(^13\) Inter-band magneto-absorptions were reported for the first time\(^14\) in graphenes epitaxially grown on SiC substrates.\(^15\),\(^16\) The cyclotron resonance was reported also in scotch-tape graphene.\(^17\),\(^18\) The local density-of-states and carrier concentrations were measured using scanning single-electron-transistor.\(^19\) The negligibly small negative magnetoresistance was observed\(^20\) and a weak positive magnetoresistance was reported.\(^21\) There were reports on optical phonons using the Raman scattering,\(^22\),\(^23\) spin transport,\(^24\),\(^25\) angle-resolved photoemission spectroscopy,\(^26\),\(^27\) and so on. There has also been a rapid development in the theory of graphene.\(^28\)

The effective-mass description of electronic states is discussed in §2. The topological anomaly associated with Berry’s phase and the resulting unique Landau-level structure are discussed in §3. The singular diamagnetic susceptibility is reviewed in §4. In §5, various zero-mode anomalies appearing in transport quantities and
their removal due to level broadening effects are discussed. The presence of special time-reversal symmetry and associated symmetry crossover are discussed in §6. The electron-phonon interactions are discussed in §7.

§2. Neutrino description

The structure of 2D graphite sheet is shown in Fig. 1. A unit cell contains two carbon atoms which are denoted by A and B. We have the primitive translation vectors \( \mathbf{a} = a(1,0) \) and \( \mathbf{b} = a(-1/2, \sqrt{3}/2) \), and the vectors connecting between nearest neighbor carbon atoms \( \mathbf{\tau}_1 = a(0,1/\sqrt{3}) \), \( \mathbf{\tau}_2 = a(-1/2,-1/2\sqrt{3}) \), and \( \mathbf{\tau}_3 = a(1/2,-1/2\sqrt{3}) \), where the lattice constant is given by \( a = 2.46 \, \text{Å} \). The corresponding reciprocal lattice vectors are given by \( \mathbf{a}^* = (2\pi/a)(1,1/\sqrt{3}) \) and \( \mathbf{b}^* = (2\pi/a)(0,2/\sqrt{3}) \). The first Brillouin zone is given by a hexagon with two corner points \( K \) and \( K' \). The corresponding wave vectors are given by \( K = (2\pi/a)(1/3,1/\sqrt{3}) \) and \( K' = (2\pi/a)(2/3,0) \) for \( K \) and \( K' \) points, respectively. Further, we have

\[
\exp(iK \cdot \mathbf{\tau}_1) = \omega, \quad \exp(iK \cdot \mathbf{\tau}_2) = \omega^{-1}, \quad \exp(iK \cdot \mathbf{\tau}_3) = 1,
\]

\[
\exp(iK' \cdot \mathbf{\tau}_1) = 1, \quad \exp(iK' \cdot \mathbf{\tau}_2) = \omega^{-1}, \quad \exp(iK' \cdot \mathbf{\tau}_3) = \omega,
\]

with \( \omega = \exp(2\pi i/3) \), satisfying \( 1 + \omega + \omega^{-1} = 0 \).

Let \( \phi(r) \) be a \( p_z \) orbital localized around the origin. In a nearest-neighbor tight-binding model, the wave function is written as

\[
\psi(r) = \sum_{\mathbf{R}_A} \psi_A(\mathbf{R}_A)\phi(r-\mathbf{R}_A) + \sum_{\mathbf{R}_B} \psi_B(\mathbf{R}_B)\phi(r-\mathbf{R}_B),
\]

(2.2)

where, \( \psi_A(\mathbf{R}_A) \) and \( \psi_B(\mathbf{R}_B) \) are the amplitudes at \( \mathbf{R}_A = n_a\mathbf{a} + n_b\mathbf{b} + \mathbf{\tau}_l \) and \( \mathbf{R}_B = n_a\mathbf{a} + n_b\mathbf{b} \) with integer \( n_a \) and \( n_b \). Taking into account only the hopping integral \(-\gamma_0\) (\( \gamma_0 \sim 3 \, \text{eV} \)) between nearest-neighbor atoms and neglecting overlapping integrals, we have

\[
\varepsilon \psi_A(\mathbf{R}_A) = -\gamma_0 \sum_{l=1}^{3} \psi_B(\mathbf{R}_A - \mathbf{\tau}_l), \quad \varepsilon \psi_B(\mathbf{R}_B) = -\gamma_0 \sum_{l=1}^{3} \psi_A(\mathbf{R}_B + \mathbf{\tau}_l),
\]

(2.3)

Fig. 1. The lattice structure (a) and the first Brillouin zone (b) of graphene. The unit cell contains two carbon atoms denoted by A and B. Two primitive translation vectors are denoted by \( \mathbf{a} \) and \( \mathbf{b} \) and three vectors connecting neighboring A and B atoms are \( \mathbf{\tau}_l \) \((l = 1, 2, 3)\). Reciprocal lattice vectors are given by \( \mathbf{a}^* \) and \( \mathbf{b}^* \).
where we have chosen the energy origin at the level of an isolated \( p_z \) orbital.

Setting \( \psi_A(R_A) = f_A(k) \exp(i k \cdot R_A) \) and \( \psi_B(R_B) = f_B(k) \exp(i k \cdot R_B) \), we have

\[
\begin{pmatrix}
0 & h_{AB}(k) \\
h_{AB}(k)^* & 0
\end{pmatrix}
\begin{pmatrix}
f_A(k) \\
f_B(k)
\end{pmatrix} = \varepsilon \begin{pmatrix} f_A(k) \\ f_B(k) \end{pmatrix}, \quad h_{AB}(k) = -\gamma_0 \sum_{l=1}^{3} \exp(-i k \cdot \tau_l).
\]

Then, the energy bands become

\[
\varepsilon_\pm(k) = \pm \gamma_0 \left| \sum_{l=1}^{3} \exp(-i k \cdot \tau_l) \right|.
\]

According to Eq. (2.2), we have \( \varepsilon_\pm(K) = \varepsilon_\pm(K') = 0 \), showing that there is no gap at \( K \) and \( K' \) points. Figure 2 shows the obtained \( \pi \) bands.

To see the behavior in the vicinity of the \( K \) point, for example, we rewrite \( k \) as \( K + k \) and expand \( \varepsilon_\pm(k) \) in terms of \( |k|a \). To the lowest order, we have

\[
-\gamma_0 \sum_{l=1}^{3} \exp[-i(k+K) \cdot \tau_l] = -\omega^{-1} \gamma(k_x - i k_y),
\]

with \( \gamma = \frac{\sqrt{3}}{2} a \gamma_0 \).

Therefore, when we define \( f_A(K+k) = \tilde{f}_A(k) \) and \( f_B(K+k) = -\omega \tilde{f}_B(k) \), we have

\[
\gamma \begin{pmatrix} 0 & k_x-i k_y \\ k_x+i k_y & 0 \end{pmatrix} \begin{pmatrix} \tilde{f}_A(k) \\ \tilde{f}_B(k) \end{pmatrix} = \varepsilon \begin{pmatrix} \tilde{f}_A(k) \\ \tilde{f}_B(k) \end{pmatrix}.
\]

With the use of the Pauli spin matrices

\[
\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},
\]

we have

\[
\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.
\]
Fig. 3. The energy dispersion and density of states in the vicinity of K and K’ points obtained in a \( \mathbf{k} \cdot \mathbf{p} \) scheme.

the above equation is rewritten as

\[
\gamma (\sigma \cdot \mathbf{k}) \tilde{\mathbf{f}}(\mathbf{k}) = \varepsilon \tilde{\mathbf{f}}(\mathbf{k}), \quad \mathbf{f}(\mathbf{k}) = \left( \begin{array}{c} \tilde{\mathbf{f}}_A(\mathbf{k}) \\ \tilde{\mathbf{f}}_B(\mathbf{k}) \end{array} \right), \tag{2.10}
\]

with \( \sigma = (\sigma_x, \sigma_y) \). In a similar manner, we obtain the equation for the K’ point, for which \( \sigma \) is replaced with \( \sigma^* \).

Thus, in the vicinity of the K and K’ points, the energy dispersion is given by

\[
\varepsilon_s(\mathbf{k}) = s \gamma |\mathbf{k}|, \quad s = \pm 1, \tag{2.11}
\]

and the density of states becomes

\[
D(\varepsilon) = \frac{g_v g_s}{L^2} \sum_{s, \mathbf{k}} \delta(\varepsilon - s \gamma |\mathbf{k}|) = \frac{g_v g_s |\varepsilon|}{2\pi \gamma^2}, \tag{2.12}
\]

where \( L^2 \) is the area of the system, \( g_s = 2 \) is the spin degeneracy, and \( g_v = 2 \) is the valley degeneracy corresponding to the K and K’ points. These results are illustrated in Fig. 3. The density of states vanishes at \( \varepsilon = 0 \) and therefore graphene is often called a zero-gap semiconductor. As will later become clear, the energy-dependence of the conductivity indicates that graphene is a metal rather than a semiconductor.

In an effective-mass approximation or a \( \mathbf{k} \cdot \mathbf{p} \) scheme near the K or K’ point, the electron motion is described by a Schrödinger equation in which \( \mathbf{k} \) is replaced by operator \( \hat{\mathbf{k}} = -i \hat{\nabla} \). We have

\[
\gamma (\sigma \cdot \hat{\mathbf{k}}) \mathbf{F}^K(\mathbf{r}) = \varepsilon \mathbf{F}^K(\mathbf{r}), \quad \gamma (\sigma^* \cdot \hat{\mathbf{k}}) \mathbf{F}^{K'}(\mathbf{r}) = \varepsilon \mathbf{F}^{K'}(\mathbf{r}), \tag{2.13}
\]

where \( \mathbf{F}^K(\mathbf{r}) \) and \( \mathbf{F}^{K'}(\mathbf{r}) \) are a two-component wave function

\[
\begin{align*}
\mathbf{F}^K(\mathbf{r}) &= \left( \begin{array}{c} F^K_A(\mathbf{r}) \\ F^K_B(\mathbf{r}) \end{array} \right), \\
\mathbf{F}^{K'}(\mathbf{r}) &= \left( \begin{array}{c} F^{K'}_A(\mathbf{r}) \\ F^{K'}_B(\mathbf{r}) \end{array} \right). \tag{2.14}
\end{align*}
\]

This is exactly the same as Weyl’s equation for a neutrino, except that the velocity, given by

\[
v = \frac{\gamma}{\hbar}, \tag{2.15}
\]

is much smaller than the light velocity (about 1/300). This equation of motion is quite useful for the description of characteristic features of electronic states in graphene.
§3. Topological anomaly and Berry’s phase

The wave function near the K point is written as

\[ F_{sk}(r) = \frac{1}{L} \exp(i k \cdot r) F_{sk}, \]  

where \( F_{sk} \) is the spin function in which the spin is in the direction of \( k \) or \(-k\).

Here, \( \phi_s(k) \) is an arbitrary phase, \( \theta(k) \) is the angle between \( k \) and the \( k_y \) axis, i.e., \( k_x + i k_y = +i|k|e^{i\theta(k)} \) and \( k_x - i k_y = -i|k|e^{-i\theta(k)} \), \( R(\theta) \) is the spin rotation operator around the \( z \) direction perpendicular to graphene sheet, and \( |s\rangle \) is the spin function when \( k \) is in the \( k_y \) axis,

\[ |s\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} -is \\ 1 \end{pmatrix}. \]  

The spin rotation operator is given by

\[ R(\theta) = \exp \left( i \theta \sigma_z / 2 \right) = \begin{pmatrix} \exp(+i\theta/2) & 0 \\ 0 & \exp(-i\theta/2) \end{pmatrix}. \]  

The rotation operator has the property

\[ R(\theta_1)R(\theta_2) = R(\theta_1+\theta_2), \quad R(-\theta) = R^{-1}(\theta). \]  

Further, we have

\[ R(\theta \pm 2\pi) = -R(\theta), \quad R(-\pi) = -R(+\pi). \]  

Therefore, for a phase \( \phi_s(k) \) independent of the direction of \( k \), wave function \( F_{sk} \) changes its sign under the \( 2\pi \) rotation of \( k \) or it has the opposite sign under \( +\pi \) and \(-\pi \) rotation of \( k \).

The sign of the wave function itself depends on the choice of the phase. We can choose \( \phi_s(k) = -\theta(k)/2 \), for example. Then, we have

\[ F_{sk} = \frac{1}{\sqrt{2}} \begin{pmatrix} -i s e^{-i\theta(k)} \\ 1 \end{pmatrix}, \]  

which does not change the sign under \( \theta(k) \rightarrow \theta(k) \pm 2\pi \). However, this wave function changes its sign if we consider Berry’s phase under the wave-vector rotation.\(^{29},^{30}\)

In fact, Berry’s phase \( e^{-i\eta} \) under the wave-vector rotation is calculated as

\[ \eta = -i \int_{0}^{T} dt \langle sk(t) | \frac{d}{dt} | sk(t) \rangle = -\pi, \]  

where \( k(t) \) moves along a closed contour around \( k = 0 \) between time \( t = 0 \) and \( T \). Therefore, the wave function acquires phase \(-\pi \) when \( k \) is rotated around the origin.\(^{4},^{31},^{32}\) The sign change occurs only when the closed contour encircles the
origin \( k = 0 \) but not when the contour does not contain \( k = 0 \), showing the presence of a topological singularity at \( k = 0 \). This topological singularity at \( k = 0 \) associated Berry’s phase is the origin of the absence of backward scattering in metallic carbon nanotubes.\(^4\),\(^3\),\(^2\)

A singularity at \( \varepsilon = 0 \) manifests itself in magnetic fields even in classical mechanics. The equation of motion in magnetic field \( B \) perpendicular to the system is given by

\[
\hbar \dot{k} = -\frac{e}{c} v \times B.
\]

(3.9)

This gives the cyclotron frequency

\[
\omega_c = \frac{eBv^2}{c\varepsilon}.
\]

(3.10)

The cyclotron frequency \( \omega_c \) diverges and changes its sign at \( \varepsilon = 0 \),\(^6\),\(^3\) showing that \( \varepsilon = 0 \) is singular in a magnetic field.

In quantum mechanics \( \hat{k}_x \) and \( \hat{k}_y \) satisfy the commutation relation \( [\hat{k}_x, \hat{k}_y] = -i/l^2 \), where \( l \) is the magnetic length given by \( l = \sqrt{\hbar/eB} \). Semiclassically, the Landau levels can be obtained by the condition

\[
\oint k_x dk_y = \pm \frac{2\pi}{l^2} \left( |n| + \frac{1}{2} \right),
\]

(3.11)

as \( \varepsilon_n = \text{sgn}(n) \sqrt{|n| + 1/2} \hbar \omega_B \) with integer \( n \), where \( \hbar \omega_B = \sqrt{2\gamma/l} \) and \( \text{sgn}(n) = n/|n| \) for \( n \neq 0 \) and 0 for \( n = 0 \). Because of the uncertainty principle, \( k^2 = 0 \) is not allowed and there is no Landau level at \( \varepsilon = 0 \). However, a full quantum mechanical treatment gives

\[
\varepsilon_n = \text{sgn}(n) \sqrt{|n|} \hbar \omega_B,
\]

(3.12)

leading to the formation of Landau levels at \( \varepsilon = 0 \).\(^1\) This can be understood by the cancellation of factor 1/2 in Eq. (3.11) by Berry’s phase corresponding to the rotation in the \( k \) space.

§4. Singular diamagnetism

The unique Landau-level structure gives rise to a singular diamagnetism,\(^1\) which is the origin of large diamagnetic susceptibility of bulk graphite.\(^3\),\(^4\) The thermodynamic function \( \Omega \) is given by

\[
\Omega = -k_B T \frac{g_s g_n}{2\pi l^2} \sum_n \varphi(\varepsilon_n),
\]

(4.1)

\[
\varphi(\varepsilon) = \ln \left\{ 1 + \exp[\beta(\zeta - \varepsilon)] \right\},
\]

(4.2)

where \( T \) is the temperature, \( k_B \) is the Boltzmann constant, \( \beta = 1/k_B T \), and \( \zeta \) the chemical potential. Let \( n_s \) be the electron concentration. Then, the free energy is written as

\[
F = n_s \zeta + \Omega.
\]

(4.3)
With the use of the relation \( n_s = -\left( \frac{\partial \Omega}{\partial \zeta} \right)_B \), the magnetization is given by

\[
M = -\left( \frac{\partial F}{\partial B} \right)_{n_s} = -\left( \frac{\partial \Omega}{\partial B} \right)_{\zeta}.
\]

(4.4)

Therefore, susceptibility \( \chi \), defined by \( M = \chi B \) for small \( B \), can be obtained by calculating \( \Omega \) up to the order of \( B^2 \).

The thermodynamic function is rewritten as

\[
\Omega = -k_B T \frac{g_v g_s}{2 \pi l^2} \sum_{n=0}^{\infty} g(h \omega_B \sqrt{n}) \left( 1 - \frac{1}{2} \delta_{n0} \right) \ln \left[ 1 + 2e^{\beta \zeta} \cosh(\beta h \omega_B \sqrt{n}) + e^{2\beta \zeta} \right],
\]

(4.5)

where \( 1/2 \pi l^2 \) is the degeneracy of a Landau level and \( g(\varepsilon) \) is a cutoff function which decays smoothly but sufficiently rapidly in such a way that the summation converges. For example, we can choose

\[
g(\varepsilon) = \frac{\varepsilon^{\alpha_c}}{\varepsilon^{\alpha_c} + \varepsilon_c^{\alpha_c}},
\]

(4.6)

with cutoff energy \( \varepsilon_c \) and parameter \( \alpha_c (\alpha_c \geq 2) \).

Consider a smooth function \( F(x) \) and its integral

\[
\int_0^\infty F(x) dx = \int_0^{h/2} F(x) dx + \sum_{j=1}^{\infty} \int_{-h/2}^{h/2} F(x+jh) dx,
\]

(4.7)

where \( h \) is a small positive number. By expanding this with respect to \( h \), we have

\[
h \left[ \frac{1}{2} F(0) + \sum_{j=1}^{\infty} F(x+jh) \right] = \int_0^\infty F(x) dx - \frac{1}{12} h^2 \left[ F'(0) + \frac{1}{2} F'(-\infty) \right],
\]

(4.8)

up to the second order in \( h \). Let \( h = (h \omega_B)^2, x = nh \), and

\[
F(x) = g(\sqrt{x}) \ln \left[ 1 + 2 \exp(\beta \zeta) \cosh(\beta \sqrt{x}) + \exp(2\beta \zeta) \right].
\]

(4.9)

Then, we have

\[
\Omega = \Omega_0 + \Delta \Omega,
\]

(4.10)

where \( \Omega_0 \) is the thermodynamic potential in the absence of a magnetic field and

\[
\Delta \Omega = \frac{1}{12} \frac{g_v g_s (h \omega_B)^2}{2 \pi l^2} \frac{\beta \exp(\beta \zeta)}{[1+\exp(\beta \zeta)]^2} - \frac{g_v g_s \gamma^2}{12 \pi l^4} \int_{-\infty}^{\infty} \left( - \frac{\partial f(\varepsilon)}{\partial \varepsilon} \right) \delta(\varepsilon) d\varepsilon,
\]

(4.11)

where \( f(\varepsilon) \) is the Fermi distribution function. The susceptibility becomes

\[
\chi = -\frac{g_v g_s \gamma^2}{6 \pi} \left( \frac{e}{c h} \right)^2 \int_{-\infty}^{\infty} \left( - \frac{\partial f(\varepsilon)}{\partial \varepsilon} \right) \delta(\varepsilon) d\varepsilon.
\]

(4.12)

This singular susceptibility is characteristic to graphene and obtained first by McClure\(^1\) and later by many others.\(^{36–38}\)
Consider the average contribution of states around $\varepsilon_n$ ($|n| \gg 1$) to the thermodynamic potential in the weak-field limit. We have

$$\int_{-1/2}^{1/2} \text{sgn}(n)\hbar\omega_B \sqrt{|n|+t} \varphi[\text{sgn}(n)\hbar\omega_B \sqrt{|n|+t}] dt = \varphi(\varepsilon_n) + \frac{\beta}{96}(\hbar\omega_B)^4 [\varepsilon_n^{-3} f(\varepsilon_n) - \varepsilon_n^{-2} f'(\varepsilon_n)] + \cdots. \tag{4.13}$$

Therefore, the change in the thermodynamic potential in a magnetic field becomes

$$\Delta \Omega = \frac{g_v g_\sigma (\hbar\omega_B)^2}{2\pi l^2} \frac{1}{48} \int_{-\infty}^{\infty} \text{sgn}(\varepsilon)[\varepsilon^{-2} f(\varepsilon) - \varepsilon^{-1} f'(\varepsilon)] d\varepsilon. \tag{4.14}$$

When the Fermi level lies well away from $\varepsilon = 0$, the integral vanishes identically and therefore the susceptibility vanishes.

At $\varepsilon = 0$, the integrand becomes singular and gives the "paramagnetic" contribution

$$\Delta \Omega = -\frac{g_v g_\sigma}{2\pi l^2} \frac{1}{24} (\hbar\omega_B)^2 \int_{-\infty}^{\infty} \left(-\frac{\partial f(\varepsilon)}{\partial \varepsilon}\right) \delta(\varepsilon) d\varepsilon. \tag{4.15}$$

In fact, we have

$$\int_0^{\infty} \left(\frac{f(\varepsilon)}{\varepsilon^2} - \frac{f'(\varepsilon)}{\varepsilon}\right) d\varepsilon - \int_{-\infty}^{0} \left(\frac{f(\varepsilon)}{\varepsilon^2} - \frac{f'(\varepsilon)}{\varepsilon}\right) d\varepsilon = \lim_{\varepsilon \to +0} \left(\frac{f(\varepsilon)}{\varepsilon} + \frac{f(-\varepsilon)}{-\varepsilon}\right) = 2f'(0). \tag{4.16}$$

For $n = 0$, the average contribution to the thermodynamic potential in the weak-field limit becomes

$$\int_{-1/2}^{1/2} \varphi[\text{sgn}(t)\hbar\omega_B \sqrt{|t|}] dt = \frac{1}{8}(\hbar\omega_B)^2 \varphi''(0) + \cdots = -\frac{\beta}{8}(\hbar\omega_B)^2 f'(0) + \cdots, \tag{4.17}$$

giving

$$\Delta \Omega = \frac{g_v g_\sigma}{2\pi l^2} \frac{1}{8} (\hbar\omega_B)^2 \int_{-\infty}^{\infty} \left(-\frac{\partial f(\varepsilon)}{\partial \varepsilon}\right) \delta(\varepsilon) d\varepsilon. \tag{4.18}$$

By adding the contribution from $n \neq 0$ given by Eq. (4.15), we have the result given by Eq. (4.11). This shows clearly that the presence of the Landau level at $\varepsilon = 0$ is the origin of the singular behavior of the susceptibility.

In a bilayer graphene with the so-called AB stacking as illustrated in Fig. 4, most important inter-layer interaction is given by the nearest-neighbor hopping $\gamma_1$. Within this approximation, the effective Hamiltonian in the vicinity of the Fermi level is written as\(^{(39),(40)}\)

$$H = \frac{\hbar^2}{2m^*} \begin{pmatrix} 0 & (\hat{k}_x + i\hat{k}_y)^2 \\ (\hat{k}_x - i\hat{k}_y)^2 & 0 \end{pmatrix}, \tag{4.19}$$

with $m^* = \hbar^2 \gamma_1/2\gamma^2$. This gives the Landau level $\varepsilon_{\pm n} = \pm \hbar\omega_c \sqrt{n(n+1)}$ with $n = 0, 1, \cdots$ with $\omega_c = eB/m^*c$. In a similar but more complicated manner, the susceptibility can be calculated as

$$\chi = -\frac{(e\hbar)^2}{2m^*c} \frac{g_v g_\sigma m^*}{2\pi \hbar^2} \int_{-\infty}^{\infty} g(\varepsilon) \ln \left|\frac{\varepsilon}{\varepsilon_c}\right| \left(-\frac{\partial f}{\partial \varepsilon}\right) d\varepsilon, \tag{4.20}$$
Fig. 4. The lattice structure of a bilayer graphene with the so-called AB stacking. Some representative hopping integrals are shown.

except for a constant term independent of energy. The above agrees with the result obtained previously for a model of intercalated graphite. The energy-independent term depends on details of the energy cutoff.

It has been shown that in multi-layers the Hamiltonian can be decomposed into that of mono-layer and those of bilayers. In fact, for odd layers $2M + 1$, the system is divided into the monolayer and $M$ bilayers, and for even layers $2M$, the system is decomposed into $M$ bilayers. In each of the bilayer Hamiltonian, the effective interlayer coupling is different from each other. This exact decomposition is quite useful in discussing electronic properties of multi-layer graphenes such as diamagnetic susceptibility and optical properties both in the presence and absence of a magnetic field.

§5. Zero mode anomalies

We consider, for example, a system with scatterers with a potential range much smaller than the typical electron wavelength (which is actually infinite at $\varepsilon = 0$) but larger than the lattice constant of graphene. The relaxation time in the absence of a magnetic field becomes

$$\frac{1}{\tau_0} = \frac{2\pi}{\hbar} \frac{1}{2} \langle n_i | u_i |^2 \rangle \frac{|\varepsilon|}{2\pi \gamma^2} = \frac{2\pi}{\hbar} |\varepsilon| W,$$

(5.1)

with $W$ being a dimensionless parameter characterizing the scattering strength given by

$$W = \frac{\langle n_i u_i^2 \rangle}{\pi \gamma^2},$$

(5.2)

where $u_i$ and $n_i$ are the strength and the concentration of scatterers, respectively, and $\langle \cdots \rangle$ means the average over impurities. We usually have $W \ll 1$. With the use of the Boltzmann transport equation, the transport relaxation time becomes
\( \tau(\varepsilon) = 2\tau_0(\varepsilon) \) and the conductivity

\[
\sigma_0 = g_v g_s \frac{e^2}{4\pi^2\hbar W}, \tag{5.3}
\]

independent of the Fermi level.\(^5\) This can also be derived from the Einstein relation

\[
\sigma_0 = e^2 D^* D(\varepsilon), \tag{5.4}
\]

where the diffusion coefficient is given by \( D^* = v^2 \tau(\varepsilon)/2 = \gamma^2 \tau(\varepsilon)/2\hbar^2 \). This shows that graphene should be regarded as a metal rather than a zero-gap semiconductor. It is interesting to note that the conductivity is nonzero even at \( \varepsilon = 0 \) (when the limit \(|\varepsilon| \to 0 \) is taken). However, there can be singularity at \( \varepsilon = 0 \) because the density of states vanishes at the point \((\varepsilon, \gamma \varepsilon) = 0 \). The correct way may be to let \( \varepsilon \to 0 \) independent of the Fermi level.

In the presence of a magnetic field, the conductivity tensor \( \sigma_{\mu\nu} \) with \( \mu = x, y \) and \( \nu = x, y \) is given by

\[
\sigma_{xx} = \sigma_{yy} = \frac{\sigma_0}{1 + (\omega_c \tau)^2}; \quad \sigma_{xy} = -\sigma_{yx} = \frac{\sigma_0(\omega_c \tau)}{1 + (\omega_c \tau)^2}. \tag{5.5}
\]

Using the explicit expressions for \( \omega_c \) and \( \tau \), we have \( \sigma_{xx} = \sigma_0 \xi^4/(1 + \xi^4) \) and \( \sigma_{xy} = -\sigma_0 \xi^2/(1 + \xi^4) \), with \( \xi = \sqrt{2\pi W(\varepsilon_F/\hbar \omega_B)} \). Because \( \tau(\varepsilon_F)^{-1} \propto |\varepsilon_F| \), the dependence on the Fermi energy \( \varepsilon_F \) is fully scaled by \( \hbar \omega_B \). Therefore, the conductivity is singular at \((\hbar \omega_B, \varepsilon_F) = (0, 0) \). For example, \( \sigma_{xx} \) exhibits a singular jump to zero at \( \varepsilon_F = 0 \) from \( \sigma_0 \) for nonzero \( \varepsilon_F \) in the limit of the vanishing magnetic field \( \hbar \omega_B \to 0 \).

A singular behavior also appears in the dynamical conductivity.\(^8\) In a relaxation-time approximation, the dynamical conductivity is given by

\[
\sigma(\omega) = g_v g_s \frac{e^2}{16\hbar} \left[ \frac{4}{\pi} \frac{i\varepsilon_F}{\hbar \omega + i[\hbar/\tau(\varepsilon_F)]} + 1 + \frac{i}{\pi} \ln \frac{\hbar \omega + i[\hbar/\tau(\hbar \omega/2)] - 2\varepsilon_F}{\hbar \omega + i[\hbar/\tau(\hbar \omega/2)] + 2\varepsilon_F} \right], \tag{5.6}
\]

where the first term in the bracket represents the Drude conductivity determined by states in the vicinity of the Fermi level and the second and third terms represent interband optical transitions. It is interesting to note that the interband conductivity is given by a universal value \( e^2/8\hbar \) for \( \hbar \omega > 2\varepsilon_F \) in the case of weak scattering.

Because \( \hbar/\tau(\varepsilon) \propto |\varepsilon| \), the frequency dependence is completely scaled by the Fermi energy, i.e., \( \sigma(\omega, \varepsilon_F) = \sigma(\hbar \omega/\varepsilon_F) \). This scaling shows that \( \sigma(\omega, \varepsilon_F) \) exhibits a singular behavior at the point \((\omega, \varepsilon_F) = (0, 0) \). The correct way may be to let \( \omega \to 0 \) at each \( \varepsilon_F \), leading to a singular jump of the static conductivity to \( g_v g_s e^2/16\hbar \) at \( \varepsilon_F = 0 \) from \( \sigma_0 \) for nonzero \( \varepsilon_F \). Further, for \( \varepsilon_F = 0 \), \( \sigma(\omega) = g_v g_s e^2/16\hbar \) independent of \( \omega \).

A more refined treatment has been performed for the density of states and the static conductivity in a self-consistent Born approximation,\(^44\)\(-\)\(^46\) in which level-broadening effects are properly taken into account.\(^5\) Figure 5 shows an example. The density of states becomes nonzero at \( \varepsilon = 0 \) because of level broadening and also enhanced due to level repulsion effect near \( \varepsilon = 0 \).

Further, the conductivity at \( \varepsilon_F = 0 \) is given by

\[
\sigma_{\min} = \frac{g_v g_s e^2}{2\pi^2\hbar}; \tag{5.7}
\]
Fig. 5. Some examples of the density of states (a) and the conductivity (b) of a monolayer graphene calculated in the self-consistent Born approximation. $\varepsilon_0$ is an arbitrary energy unit and $\varepsilon_c$ is the cutoff energy corresponding to the half of the $\pi$-band width. The conductivity exhibits a sharp jump in the limit of weak scattering ($W \ll 1$) from the Boltzmann result $\sigma_0$ for $\varepsilon \neq 0$ down to $\sigma = e^2/\pi^2\hbar$ at $\varepsilon_F = 0$.

which is universal and independent of the scattering strength. The resulting conductivity varies smoothly across $\varepsilon_F = 0$ but exhibits a sharp jump in the limit of weak scattering ($W \ll 1$) from the Boltzmann result $\sigma_0$ for $\varepsilon \neq 0$ down to $\sigma_{\text{min}}$ at $\varepsilon_F = 0$. A similar calculation for a bilayer graphene shows much smoother variation with energy with minimum value $\sigma \approx g_v g_s e^2/2\pi^2\hbar$ slightly dependent on the scattering strength.\textsuperscript{40)

The Boltzmann transport equation, as well as the Einstein relation, gives $\sigma \propto e^2\tau(\varepsilon_F)v(\varepsilon_F)^2D(\varepsilon_F)$. In conventional systems, we have the relation $\varepsilon_F = m^* v(\varepsilon_F)^2/2$, where $m^*$ is an effective mass. With the use of the fact $n_s \propto \varepsilon_F D(\varepsilon_F)$, this leads to the usual expression $\sigma = n_s e\mu$ with mobility $\mu = e\tau(\varepsilon_F)/m^*$, where $n_s$ is the electron concentration. In the present system, however, the velocity $v$ is independent of $\varepsilon_F$ or $m^* \propto \varepsilon_F$ if we assume $\varepsilon_F = m^* v^2/2$ as above. Further, the scattering probability $\hbar/\tau(\varepsilon_F)$ is proportional to the final-state density of states with a coefficient independent of $\varepsilon_F$. Because the density of states is proportional to $\varepsilon_F$, the relaxation time is inversely proportional to $\varepsilon_F$. As a result the mobility $\mu$ becomes proportional to $\varepsilon_F^{-2} \propto n_s^{-1}$, leading to the conductivity $\sigma = n_s e\mu$ independent of the Fermi energy and the electron concentration.

In the case of charged-impurity scattering, however, the matrix element itself is proportional to the inverse of the Fermi energy both in the presence and absence of screening.\textsuperscript{33), 47}) Consequently, the low-temperature mobility becomes independent
Fig. 6. Some examples of the dynamical conductivity of a monolayer graphene calculated in the self-consistent Born approximation. (a) $W^{-1} = 50$. (b) $W^{-1} = 20$. The frequency dependence is nearly scaled by $\epsilon_F$ as long as $\epsilon_F \neq 0$. This scaling becomes less valid when $\epsilon_F$ is close to 0 as is more clear in (b).

of the electron concentration and the conductivity increases in proportion to the electron or hole concentration $n_s$. Therefore, the dependence of the conductivity on the electron concentration can be sensitive to the nature of dominant scatterers in the system. Note, however, that this does not change the situation that graphene should be regarded as a metal rather than a semiconductor.

Calculations in the self-consistent Born approximation were performed also for the dynamical conductivity. Figure 6 shows some examples of the results. The frequency dependence is scaled completely by $\epsilon_F$ as long as $\epsilon_F \neq 0$. When $\epsilon_F$ is very close to 0, however, the conductivity at $\omega = 0$ becomes small and the discrete jump present in the Boltzmann conductivity is removed. The energy scale causing this crossover behavior becomes exponentially small for weaker $W$, i.e., $\propto \exp(-W^{-1/2})$, leading to a singular behavior of the dynamical conductivity in the weak scattering limit.

The singular diamagnetic susceptibility discussed in the previous section is also affected by disorder. When a constant broadening $\Gamma$ independent of the energy is assumed, the delta function is broadened into a Lorentzian, i.e., $\delta(\epsilon) \rightarrow \Gamma / \pi(\epsilon^2 + \Gamma^2)$. A more appropriate treatment in the self-consistent Born approximation gives a more singular result with much sharper peak and long tail decaying slowly in proportion to $|\epsilon|^{-1}$. Figure 7 shows an example of the results. In a bilayer graphene disorder effects can simply be included by replacing $|\epsilon|$ with $\sqrt{\epsilon^2 + \Gamma^2}$ with a phenomenological parameter $\Gamma$ because the susceptibility exhibits only a weaker
Fig. 7. Some examples of the diamagnetic susceptibility obtained in the self-consistent Born approximation. The susceptibility has a sharp peak at $\varepsilon = 0$ and a long tail decaying in proportion to $|\varepsilon|^{-1}$.

logarithmic singularity as mentioned above and the density of states is independent of energy near $\varepsilon = 0$.

The calculation within the self-consistent Born approximation can be made for transport quantities in high magnetic fields. In the high-field limit where Landau levels are separated from each other, the density of states and the diagonal conductivity are given by

\begin{equation}
D(\varepsilon) = \frac{g_v g_s}{2\pi l^2} \frac{1}{\pi \Gamma_n} \sqrt{1 - \left(\frac{\varepsilon - \varepsilon_n}{\Gamma_n}\right)^2},
\end{equation}

\begin{equation}
\sigma_{xx}(\varepsilon) = \frac{g_v g_s}{2\pi^2 \hbar} (|n| + \delta_{n0}) \left[1 - \left(\frac{\varepsilon - \varepsilon_n}{\Gamma_n}\right)^2\right],
\end{equation}

\begin{equation}
\Gamma_n = \hbar \omega_B \sqrt{2W(1+\delta_{n0})}.
\end{equation}

The conductivity at $\varepsilon = 0$ is independent of a magnetic field and is given by Eq. (5.7). Further, when the Fermi level lies in the gap between adjacent Landau levels, the Hall conductivity is quantized into $g_v g_s(j + 1/2)(e^2/h)$ with integer $j$. Although the electron localization effects at tail regions of Landau levels were not explicitly included in this quantized conductivity, it is obvious that states are exponentially localized except in the vicinity of the center of each Landau level and the Hall conductivity is quantized into the same value. The recent experiments are in agreement with the theoretical prediction. Figure 8 shows the density of states, the diagonal conductivity, and the Hall conductivity $\sigma_{xy}$ as a function of energy $\varepsilon$.

The observed minimum conductivity at zero energy in the absence of a magnetic field seems to be $3 \sim 4$ times as large as $\sigma_{\text{min}}$ given by Eq. (5.7) predicted in the self-consistent Born approximation. It is difficult to discuss the exact value of the conductivity in the vicinity of zero energy, including $\sigma_{\text{min}}$, because a self-consistent determination of the screening and the density of states is necessary and because
Fig. 8. (a) Some examples of the density of states (a), the diagonal conductivity $\sigma_{xx}$ (b), and the Hall conductivity $\sigma_{xy}$ (c) of a monolayer graphene calculated in the self-consistent Born approximation. The broadening of the Landau level $n$ becomes $\hbar\omega_B \sqrt{2W(1 + \delta_{n0})}$ and the peak value of $\sigma_{xx}$ becomes $(|n| + \delta_{n0})(e^2/\pi^2\hbar)$. The conductivity at $\varepsilon = 0$ remains $e^2/\pi^2\hbar$ independent of the magnetic field. The Hall conductivity in the gap between adjacent Landau levels is quantized into $4(j + 1/2)(e^2/\hbar)$ with integer $j$.

effects of higher-order scattering\textsuperscript{55}) are likely to be important. The behavior near $\varepsilon \approx 0$ in vanishing magnetic field is expected to remain as an interesting and challenging subject both theoretically and experimentally.
§6. Symmetry crossover

The Weyl equation (2.13) is invariant under a special time-reversal operation $S$,

$$F^S = K F^*, \quad (6.1)$$

where $F^*$ represents the complex conjugate of the wave function $F$ and $K$ is an anti-unitary matrix $K = -i \sigma_y$ satisfying $K^2 = -1$. The corresponding operation for an operator $P$ is given by $P^S = K^t P K^{-1}$, where $^t P$ stands for the transpose of $P$. This corresponds to the time reversal in systems with spin-orbit interaction and leads to

$$F^{S^2} \equiv (F^S)^S = -F. \quad (6.2)$$

The system belongs to the symplectic universality class when only $S$ constitutes a relevant symmetry.\(^{56}\)

This symmetry prevails even in the presence of impurities unless their potential range is smaller than the lattice constant $a$. In fact, for such scatterers, the effective potential is the same for the A and B sites and does not cause any mixing between the K and K' points.\(^{31}\) In this case a quantum correction or a weak-localization correction to the Boltzmann conductivity becomes positive and diverges logarithmically.\(^{7}\) This so-called anti-localization behavior is the same as that appears in systems with strong spin-orbit interaction.\(^{57}\)

The operation $S$ is not the real time-reversal in graphene. Actually, the Bloch functions at the K and K' points are mutually complex conjugate and therefore, the K point is converted into the K' point and the K' point into the K point under the real time reversal. In the present $k \cdot p$ scheme, this operation $T$ is expressed as

$$F^T_K = e^{-i \psi} \sigma_z F^*_{K'}, \quad F^T_{K'} = e^{-i \psi} \sigma_z F^*_{K}, \quad (6.3)$$

where $\psi$ is an arbitrary phase factor and $F_K$ and $F_{K'}$ are the wave functions at the K and K' points, respectively.\(^{7},58\) This immediately gives

$$F^{T^2}_K \equiv (F^T_K)^T = F_K, \quad F^{T^2}_{K'} \equiv (F^T_{K'})^T = F_{K'}, \quad (6.4)$$

characteristic of the conventional orthogonal symmetry. When we can neglect mixing between the K and K' points and confine ourselves to states in each valley, however, the $T$ symmetry is irrelevant and the special $S$ symmetry becomes relevant. In the presence of short-range scatterers causing mixing between K and K' points, the $S$ symmetry is violated, but the $T$ symmetry prevails. As a result the system now belongs to the orthogonal class.\(^{7},59\)

The actual equi-energy line deviates from the circle and has trigonal warping when the energy becomes nonzero. This effect can be included by a higher order $k \cdot p$ term. For the K point it is given by

$$H_1 = \gamma \begin{pmatrix} 0 & h_1(\hat{k}_x, \hat{k}_y) \\ h_1^*(\hat{k}_x, \hat{k}_y)^t & 0 \end{pmatrix}, \quad h_1(\hat{k}_x, \hat{k}_y) = \alpha \frac{a}{4\sqrt{3}}(\hat{k}_x + i \hat{k}_y)^2, \quad (6.5)$$

where $\alpha$ is a constant of the order of unity. This higher order term gives rise to a trigonal warping of the dispersion. This expression with $\alpha = 1$ has been derived from
a nearest-neighbor tight-binding model\(^{60}\) but is much more general if we regard \(\alpha\) as an adjustable parameter. In the presence of \(H_1\), the special time reversal symmetry is destroyed because \(H_1^S = -H_1\).\(^{61}\) As a result the system now belongs to the unitary class. For the \(K'\) point, the effective Hamiltonian is obtained by the replacement of \(h_1\) by \(-h_1^\dagger\).

The time reversal symmetry is known to manifest itself as a quantum correction to the conductivity. If the system has the \(S\) symmetry, quantum correction \(\Delta \sigma\) given by so-called maximally crossed diagrams exhibits an anti-localization behavior, i.e., the conductivity increases logarithmically with the decrease of the temperature.\(^{57}\) If the system has the \(T\) symmetry, \(\Delta \sigma\) exhibits a weak-localization behavior and the conductivity decreases logarithmically with the temperature decrease. The crossover between the weak- and anti-localization behavior caused by short-range scatterers was demonstrated.\(^{7}\) Suppression of weak localization observed in graphene\(^{20}\) was analyzed by the crossover among symplectic, orthogonal, and unitary due to various perturbations mentioned above.\(^{62}\) A weak positive magnetoresistance was also experimentally observed in epitaxial graphenes.\(^{21}\)

The symmetry plays important roles in carbon nanotubes.\(^4\) In nanotubes, the wave vector along the circumference direction is quantized into \(\kappa_\nu(n) = (2\pi/L)[n - (\nu/3)]\) by periodic boundary conditions due to their cylindrical form, where \(L\) is the circumference, \(n\) is an integer, and \(\nu = 0\) or \(\pm 1\) determined by the structure.\(^4\) A nanotube becomes a metal when \(\nu = 0\) and a semiconductor when \(\nu = \pm 1\). Figure 9 shows the energy bands in a metallic nanotube. In the presence of the \(S\) symmetry, the reflection coefficients satisfy the symmetry relation \(r_{\bar{\alpha}\beta} = -r_{\bar{\beta}\alpha}\), where \(\alpha\) and \(\beta\) denote in-coming channels and \(\bar{\alpha}\) and \(\bar{\beta}\) their time reversal or out-going channels. Metallic nanotubes satisfy this symmetry and possess an odd number of current carrying channels for each of the \(K\) and \(K'\) points. When only a single conducting channel is present, we have \(r_{\bar{\alpha}\alpha} = 0\) and the conductance is given by an ideal value \(2e^2/\pi\hbar\).\(^{31,32}\)

The determinant of an antisymmetric matrix with odd dimension is known to vanish identically. By definition, \(r_{\bar{\beta}\alpha}\) represents the amplitude of a reflective wave \(\bar{\beta}\) with wave function \(\psi_{\bar{\beta}}(r)\) corresponding to an in-coming wave \(\alpha\) with wave function \(\psi_{\alpha}(r)\). The vanishing determinant of \(r\) shows that there exists at least one nontrivial solution for the equation \(\sum_{\alpha=1}^{n_c} r_{\bar{\beta}\alpha} a_\alpha = 0\). Then, there is no reflected wave for the incident wave \(\sum_{\alpha} a_\alpha \psi_{\alpha}(r)\). Therefore, this becomes a perfectly conducting channel.
which transmits through the system without being scattered back.$^{63}$

An interesting feature of nanotubes is the Aharonov-Bohm (AB) effect on the band structure.$^{64,65}$ Recently, the splitting of optical absorption and emission peaks due to flux was observed.$^{66-68}$ In the presence of a magnetic flux the time-reversal symmetry is absent and therefore the perfectly conducting channel is destroyed. Explicit numerical calculations$^{69}$ showed that the perfect channel is quite fragile and disappears for flux less than 1% of the flux quantum $\phi_0 = eh/e$, while the absence of backscattering in linear bands is quite robust against such perturbations.

When the flux is a half of the flux quantum, the time-reversal symmetry is recovered but the channel number is even. In this case, the determinant of an antisymmetric matrix does not vanish and the perfect channel is destroyed. Therefore, the flux dependence in nanotubes is quite different from a $\phi_0/2$ oscillation in metallic systems on a cylinder surface, predicted theoretically$^{70}$ and observed experimentally.$^{71}$ This AAS oscillation arises due to the symmetry change caused by the flux with period $\phi_0/2$. The symmetry crossover due to magnetic field,$^{60}$ short-range scatterers,$^{59}$ and trigonal warping$^{61}$ manifests itself in the flux dependence of the localization effect in metallic carbon nanotubes.$^{58}$

Quantum correction to the conductivity was also studied in metallic carbon nanotubes,$^{72}$ but turned out to be not so successful in describing the features demonstrated in the numerical results. This absence of backscattering and the presence of a perfect channel lead also to intriguing behavior in the dynamical conductivity.$^{73-76}$ Further, strong short-range scatterers like lattice vacancies$^{77-80}$ and topological defects like five- and seven-membered rings$^{81,82}$ and a Stone-Wales defect$^{83}$ also cause a singular scattering behavior.

§7. Electron-phonon interaction

There are three different in-plane phonon modes having significant contributions to interaction with electrons, long-wavelength acoustic phonons, zone-center optical phonons, and zone-boundary phonons. Out-of-plane modes, strongly affected by substrates and therefore not well understood yet, do not strongly interact with in-plane electron motion and therefore can usually be neglected.

Acoustic phonons are described well by a continuum mode.$^{84}$ The potential energy functional for displacement $u = (u_x, u_y)$ is written as

$$U[u] = \frac{1}{2L^2} \int dxdy \left( B(u_{xx} - u_{yy})^2 + S[(u_{xx} - u_{yy})^2 + 4u_{xy}^2] \right), \quad (7.1)$$

where $B$ is the bulk modulus, $S$ is the shear modulus, and the strain tensor is given by

$$u_{xx} = \frac{\partial u_x}{\partial x}, \quad u_{yy} = \frac{\partial u_y}{\partial y}, \quad u_{xy} = \frac{1}{2} \left( \frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x} \right). \quad (7.2)$$

The kinetic energy is written as

$$K[u] = \frac{M}{2L^2} \int dxdy [(\dot{u}_x)^2 + (\dot{u}_y)^2], \quad (7.3)$$
where $M$ is the carbon mass. This immediately leads to a transverse mode $\omega_T = v_T q$ and longitudinal mode $\omega_L = v_L q$ with velocity $v_T = \sqrt{S/M}$ and $v_L = \sqrt{B/M}$, respectively.

The effective interaction Hamiltonian is given by

$$H_2 = g_1(u_{xx} + u_{yy}) + g_2[(u_{xx} - u_{yy})\sigma_x - 2u_{xy}\sigma_y],$$

(7.4)

for the K point. The interaction strength $g_1$ is called the deformation potential ($\sim 20$ eV in bulk graphite) and $g_2 \approx \beta_\Gamma \gamma_0/4$ appears due to change in the bond length, where the dimensionless parameter $\beta_\Gamma$ is given by

$$\beta_\Gamma = -\frac{d\ln \gamma_0}{d\ln b},$$

(7.5)

where $b$ is the bond length of nearest-neighbor carbon atoms given by $b = a/\sqrt{3}$.

The Hamiltonian for the K' point is obtained by replacing $\sigma$ by $-\sigma^*$. The second term proportional to $g_2$ is usually not important because $g_1 \gg g_2$, except in metallic carbon nanotubes in which the deformation potential cannot give rise to backscattering and therefore does not contribute to the resistance. It is straightforward to calculate the transport relaxation time or the mobility using this Hamiltonian.

The long-wavelength optical phonons in the two-dimensional graphite was discussed previously based on a valence-force-field model, and in the following we shall limit ourselves to the long-wavelength limit. Let $u = (u_x, u_y)$ be the relative displacement of two sub-lattice atoms A and B, i.e.,

$$u(R) = \frac{1}{\sqrt{2}}[u_A(R) - u_B(R)],$$

(7.6)

where $R$ denotes a coordinate specifying a unit cell. In the long-wavelength limit $R$ can be replaced by a continuous coordinate $r$. Then we have

$$u(r) = \sum_{q, \mu} \sqrt{\frac{\hbar}{2NM\omega_\Gamma}} (b_{q\mu} + b_{-q\mu}^\dagger)e_{\mu}(q)e^{iq\cdot r},$$

(7.7)

where $N$ is the number of unit cells, $\omega_\Gamma$ is the phonon frequency at the $\Gamma$ point, $q = (q_x, q_y)$ is the wave vector, $\mu$ denotes the modes ($t$ for transverse and $l$ for longitudinal), and $b_{q\mu}$ and $b_{q\mu}^\dagger$ are the creation and destruction operators, respectively. Define $q_x = q\cos \varphi(q)$ and $q_y = q\sin \varphi(q)$ with $q = |q|$. Then, we have

$$e_1(q) = i(\cos \varphi(q), \sin \varphi(q)), \quad e_t(q) = i(-\sin \varphi(q), \cos \varphi(q)).$$

(7.8)

The optical phonon modifies the distance between neighboring carbon atoms and therefore the band structure through the change in the resonance integral between carbon atoms. The interaction Hamiltonian for the K point is given by

$$H^K_{int} = -\sqrt{2}\frac{\beta_\Gamma \gamma}{b^2} \sigma \times u(r),$$

(7.9)

where the vector product for vectors $a = (a_x, a_y)$ and $b = (b_x, b_y)$ in two dimension is defined by $a \times b = a_x b_y - a_y b_x$. For the K' point, we should replace $\sigma$ by $-\sigma^*$. 

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220

T. Ando
Next, we consider the phonon around the K and K′ point, or the zone-boundary phonon. In a manner similar to the extraction of the envelope functions for electrons, the lattice displacement vector is written as:

\[
\begin{align*}
    u_A(R_A) &= u^K_A(R_A)e^{iK \cdot R_A} + u^{K'}_A(R_A)e^{iK' \cdot R_A}, \\
    u_B(R_B) &= u^K_B(R_B)e^{iK \cdot R_B} + u^{K'}_B(R_B)e^{iK' \cdot R_B}.
\end{align*}
\] (7.10)

We neglect the dispersion also for the zone-boundary phonon. In general, there exist four independent eigenmodes for each wavevector. However, after straightforward calculations, we can see that only one mode with the highest frequency contributes to the electron-phonon interaction. This mode is known as a Kekulé type distortion generating only bond-length changes. The interaction Hamiltonian is given by:

\[
H_{int}^{KK'} = 2\beta_K\gamma \begin{pmatrix}
    0 & \omega^{-1}\Delta_{K'}(r)\sigma_y \\
    \omega\Delta_K(r)\sigma_y & 0
\end{pmatrix},
\] (7.11)

where \(\beta_K\) is another appropriate parameter, which is equal to \(\beta_T\) for the tight-binding model, and \(\Delta_K(r)\) and \(\Delta_{K'}(r)\) are defined by the projection of the displacement to the Kekulé mode,

\[
\begin{align*}
    \Delta_K(r) &= \omega f^\dagger u^K_A(r) + (f^\ast)^\dagger u^K_B(r), \\
    \Delta_{K'}(r) &= (f^\ast)^\dagger u^{K'}_A(r) + f^\dagger u^{K'}_B(r),
\end{align*}
\] (7.12)

and they are complex conjugate to each other, \(\Delta_K(r) = \Delta_{K'}(r)^\ast\). In the second quantized form,

\[
\begin{align*}
    \Delta_K(r) &= \sum_q \sqrt{\frac{\hbar}{2NM\omega_K}}(b_{Kq} + b_{K'-q}^\dagger)e^{i\mathbf{q} \cdot \mathbf{r}}, \\
    \Delta_{K'}(r) &= \sum_q \sqrt{\frac{\hbar}{2NM\omega_K}}(b_{K'q} + b_{K-q}^\dagger)e^{i\mathbf{q} \cdot \mathbf{r}},
\end{align*}
\] (7.13)

where \(\omega_K\) is the frequency of the Kekulé mode. It is worth noting that \(\Delta_K\) cannot be given by a simple summation over the K and K′ modes. We should take a proper linear combination of the K and K′ modes in order to make the lattice displacement a real variable. We can easily understand the operator form of \(\Delta_K\) and \(\Delta_{K'}\) in the interaction Hamiltonian by considering the momentum conservation with the fact that \(2\mathbf{K} - \mathbf{K}'\) and \(\mathbf{K} - 2\mathbf{K}'\) are reciprocal lattice vectors. The Hamiltonian is the same as that obtained previously for a static Kekulé distortion.\(^{87}–^{89}\)

We can calculate the electron lifetime \(\tau\) due to emission and absorption of an optical phonon. The lifetime of an electron with energy \(\varepsilon\) is given by the scattering probability from the initial state to possible final states via emission and absorption of one phonon. For the zone-center phonon, the final states are limited to the same valley to which the initial electron state belongs. Further, we should evenly evaluate contributions from the longitudinal and transverse modes.

In contrast, only inter-valley components exist in the interaction Hamiltonian \(H_{int}^{KK'}\) given by Eq. (7.11) for the zone-boundary phonon. Any scattering processes
are classified into two types: One is the transition between “one K-electron with one K-phonon” and “one K’-electron,” and the other is between “one K-electron” and “one K’-electron with one K’-phonon.” For example, an electron around the K point can be scattered to the K’ point accompanied by absorption of one phonon around the K point, and this belongs to the former process. The electron scattering from the K to K’ point can also be induced by the emission of one phonon around the K’ point, while this is classified into the latter one.

It appears that there is no remarkable similarity between zone-center and zone-boundary phonons, but calculated scattering probabilities for both phonons are given by the same formula,

\[ \frac{\hbar}{\tau} = \pi \lambda_\alpha \left[ n_\alpha |\varepsilon + \hbar \omega_\alpha| + (n_\alpha + 1) |\varepsilon - \hbar \omega_\alpha| \right], \]  

(7.14)

where \( \alpha \) represents \( \Gamma \) or \( K \), \( n_\alpha \) is the Planck distribution function for phonon of the frequency \( \omega_\alpha \), and \( \lambda_\alpha \) denotes the dimensionless coupling constant,

\[ \lambda_\alpha = \frac{36 \sqrt{3}}{\pi} \frac{\hbar^2}{2M a^2 \hbar \omega_\alpha} \left( \frac{\beta_\alpha}{2} \right)^2. \]  

(7.15)

On the assumption that \( \beta_\alpha \) is independent of \( \alpha \) as that in the nearest-neighbor tight-binding model, the phonon frequency is the unique parameter which determines the electron lifetime. For zone-center phonons, \( \hbar \omega_\Gamma = 196 \text{ meV} \) and \( \lambda_\Gamma = 2.9 \times 10^{-3} (\beta_\Gamma/2)^2 \), while \( \hbar \omega_K = 161.2 \text{ meV} \) and \( \lambda_K = 3.5 \times 10^{-3} (\beta_K/2)^2 \) for zone-boundary phonons. As a consequence, the contributions from zone-boundary phonons are larger than those from zone-center phonons. Moreover, it is reasonable to assume \( n_\alpha = 0 \) since optical phonons are hardly excited even at room temperature. Namely, the phonon emission process becomes dominant and we have

\[ \frac{\hbar}{\tau} = \pi \lambda_\alpha |\varepsilon - \hbar \omega_\alpha|. \]  

(7.16)

This simply shows that the electron lifetime is inversely proportional to the coupling parameter \( \lambda_\alpha \) and to the density of states at the energy of the final state. What should be stressed here is that the phonon emission is possible only when the energy of the initial electron is larger than that of the phonon to be emitted. Otherwise, the final states are fully occupied at zero temperature and the phonon emission never takes place. In this sense, the zone-boundary phonon has another advantage over the zone-center phonon. Therefore, the zone-boundary phonon gives dominant scattering for high-field transport in graphenes owing to its smaller frequency and larger coupling constant.

The electron-phonon interaction also modifies phonon spectra. Consider the long-wavelength optical phonon at the \( \Gamma \) point. The phonon spectrum is described by Green’s function, written as

\[ D_\mu(q, \omega) = \frac{2 \hbar \omega_\Gamma}{(\hbar \omega)^2 - (\hbar \omega_\Gamma)^2 - 2 \hbar \omega_\Gamma \Pi_\mu(q, \omega)}. \]  

(7.17)
The phonon frequency is determined by the pole of $D_{\mu}(q, \omega)$. In the present case, the phonon self-energy is sufficiently small, leading to the shift of the phonon frequency $\Delta \omega_{\mu}$ and broadening $\Gamma_{\mu}$,

$$\Delta \omega_{\mu} = \frac{1}{\hbar} \text{Re} \Pi_{\mu}(q, \omega_{F}), \quad \Gamma_{\mu} = -\frac{1}{\hbar} \text{Im} \Pi_{\mu}(q, \omega_{F}).$$

(7.18)

To the lowest order in the interaction, the phonon self-energy is calculated to be

$$\Pi_{\mu}(\omega) = -\lambda_{F} \int_{0}^{\infty} \varepsilon d\varepsilon \left[ f(-\varepsilon) - f(\varepsilon) \right] \left( \frac{1}{\hbar\omega + 2\varepsilon + i0} - \frac{1}{\hbar\omega - 2\varepsilon + i0} \right),$$

(7.19)

independent of the phonon mode. We are calculating the self-energy of optical phonons starting with the known phonon modes in graphene. Therefore, the direct evaluation of the above self-energy causes a problem of double counting. In fact, if we apply the above formula to the case of vanishing Fermi energy, we get the frequency shift due to virtual excitations of all electrons in the $\pi$ bands. However, this contribution is already included in the definition of the frequency $\omega_{F}$. In order to avoid such a problem, we have to subtract the contribution in the undoped graphene for $\omega = 0$ corresponding to the adiabatic approximation.

This contribution can be obtained from the above by putting $\omega = 0$ and $f(\varepsilon) = f_{0}(\varepsilon)$, with $f_{0} = 0$ for $\varepsilon > 0$ and 1 for $\varepsilon < 0$ as

$$\Pi_{\mu}^{2D}(\omega) = -\lambda_{F} \int_{0}^{\varepsilon_{c}} \varepsilon d\varepsilon \left( \frac{1}{2\varepsilon + i0} + \frac{1}{2\varepsilon - i0} \right) = -\lambda_{F} \varepsilon_{c},$$

(7.20)

where we have introduced the cutoff energy $\varepsilon_{c}$ of the order of the half of the $\pi$-band.
width. Thus, the redefined self-energy becomes

$$\Pi_\mu(\omega) = \lambda R \int_0^\infty d\varepsilon \left[ 1 - f(-\varepsilon) + f(\varepsilon) \right] \pm \lambda R \int_0^\infty d\varepsilon \left[ f(-\varepsilon) - f(\varepsilon) \right] \frac{(\hbar \omega + i\delta)^2}{\hbar \omega + 4 \varepsilon}, \quad (7.21)$$

where a phenomenological imaginary part $\delta = \hbar / \tau$ has been introduced as a parameter characterizing scattering of electrons due to disorder. We have the relation $f_\omega(\varepsilon) = 1 - f(-\varepsilon)$, which leads to the conclusion that the self-energy is symmetric between $\varepsilon > 0$ and $\varepsilon < 0$, i.e., the electron-hole symmetry.

At zero temperature, in particular, we have

$$\Pi_\mu(\omega) = \lambda R \varepsilon_F - \frac{1}{4} \lambda R \hbar \omega \left( \ln \frac{\hbar \omega + 2 \varepsilon_F + i\delta}{\hbar \omega - 2 \varepsilon_F + i\delta} + \pi i \right), \quad (7.22)$$

where $\varepsilon_F$ is the Fermi energy. In the clean limit $\tau \rightarrow 0$, we have

$$\Pi_\mu(\omega) = \lambda R \varepsilon_F - \frac{1}{4} \lambda R \hbar \omega \left[ \ln \left| \frac{\hbar \omega + 2 \varepsilon_F}{\hbar \omega - 2 \varepsilon_F} \right| + \pi i \theta(\hbar \omega - 2 \varepsilon_F) \right], \quad (7.23)$$

where $\theta(t) = 1$ for $t > 1$ and 0 for $t < 1$. The frequency shift, i.e., the real part, diverges logarithmically to $-\infty$ at $\varepsilon_F = \hbar \omega / 2$. Apart from this logarithmic singularity, the phonon frequency increases roughly in proportion to $\varepsilon_F$ for $\varepsilon_F > \hbar \omega / 2$. The broadening is nonzero only for $\varepsilon_F < \hbar \omega / 2$.

Figure 10 shows the frequency shift and broadening for various values of $\delta$. For nonzero $\delta$, the logarithmic singularity of the frequency shift and the sharp drop in the broadening disappear, but the corresponding features remain for $\delta \ll 1$. Figure 11 shows the corresponding spectral function $(-1/\pi) \text{Im} D(q, \omega_R)$. Similar results were reported independently$^{91}$ and experiments giving qualitatively similar results were reported recently.$^{22, 23}$

The calculation can easily be extended to the case in the presence of a magnetic field, where discrete Landau levels are formed and oscillations due to resonant interactions appear in the frequency shift and the broadening.$^{92}$ It has also been performed in bilayer graphene.$^{93}$

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