Electronic Properties of Graphene and Carbon Nanotube

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A brief review is given on characteristic features of electronic states and transport in graphene consisting of a single sheet of graphite and its cylinder called carbon nanotube from a theoretical point of view.

1. Introduction

The best known carbon crystal is diamond, whose hardness and high dispersion of light make it useful for industrial applications and jewelry. Under ambient pressures and at room temperatures, however, the most stable form is graphite, used as an industrial lubricant and for ‘lead’ in pencils. Graphite is a layered material, each layer consisting of a sheet of carbon atoms forming hexagons like benzene rings. A monolayer of graphite is called graphene and a carbon nanotube is a cylinder made of graphene.

Carbon nanotubes were discovered by Sumio Iijima during synthesis of fullerene C$_{60}$ in 1991. A nanotube exhibits extraordinary mechanical properties, ideal for reinforced composites: It has huge Young’s modulus and is stiff as diamond, and the estimated tensile strength is more than 10 times stronger than steel wire with the same weight. It has even been suggested that nanotubes could be used in the “space elevator,” an earth-to-space cable. It can be metallic or semiconducting and offers possibilities to create future nanoelectronics devices, circuits, and computers.

There have been various efforts world over to make thin layers of graphite and quite recently the group of Andre Geim and Kostia Novoselov of Manchester University succeeded in fabricating a field-effect transistor made of graphene on Si/SiO$_2$ substrate.$^{1,2}$ They simply stuck a flake of graphite debris onto plastic adhesive tape, folded the sticky side of the tape over the flake, and then pulled the tape apart, cleaving the flake into two. After repetition of the process, the resulting fragments grew thinner and some of them turned out to be monolayer graphene. The electron ($n_s>0$) and hole concentration ($n_s<0$) can be controlled by the gate voltage between the graphene layer and the heavily doped silicon through insulating SiO$_2$ in the wide range $-5\times10^{13} < n_s < 5\times10^{13}$ cm$^{-2}$.

It is quite amazing that carriers in a thin atomic layer can be controlled almost freely by a gate and that the maximum carrier concentration is comparable to that in
silicon MOSFETs. Graphene can also be synthesized epitaxially on silicon carbide, in which the silicon leaves the surface and remaining carbon reconstructs into graphene layers when being heated.\textsuperscript{3,4} Such epitaxial graphene is much more suitable for actual device applications. A monolayer graphene was known to be formed on metal surfaces such as Ni and its phonon properties were measured.\textsuperscript{5}

Two reports were published in Nature on the observation of the integer quantum Hall effect by the group of Manchester University and Columbia University in October, 2005.\textsuperscript{6,7} It is sometimes called the half-integer quantum Hall effect because the Hall conductivity is quantized into $(4e^2/h)(j+1/2)$ with $j$ being an integer.\textsuperscript{8} Since then, the graphene became the subject of extensive and very competitive theoretical and experimental study. Some examples include reports on interband magnet-optical absorption,\textsuperscript{9} cyclotron resonance absorption,\textsuperscript{10,11} the observation of local density of states using a scanning single-electron transistor,\textsuperscript{12} the measurement of weak-field magnetoresistance,\textsuperscript{13,14,15,16} the observation of optical phonons by Raman experiments,\textsuperscript{17,18} the observation of spin transport,\textsuperscript{19,20} angle resolved photoemission spectroscopy,\textsuperscript{21,22} the observation of lattice image using scanning tunneling microscopy,\textsuperscript{23} etc.

There have been piles of theoretical works, including the proposal of the electron lens using negative refractive index at a $p$-$n$ junction formed by attaching an extra top-gate.\textsuperscript{24} More references on graphene research can be found in review papers published recently.\textsuperscript{25,26,27} It should be noted that graphene has been a subject of theoretical study prior to the experimental realization because of the peculiar electronic structure also responsible for intriguing properties of carbon nanotubes.\textsuperscript{28}

2. Two-Dimensional Neutrino

As shown in Fig. 1, graphene has a honeycomb lattice and a unit cell contains two carbon atoms denoted by A and B. An electron in a solid sometimes behaves as a particle quite different from that in vacuum because of the presence of a periodic atomic potential. Graphene is an extremely interesting example of such cases, where the electron motion becomes equivalent to that of a massless neutrino.

Figure 2 shows the band structure of graphene near the Fermi level. In the vicinity of the K and K’ points located at corners of the hexagonal first Brillouin zone, it has a cone-like dispersion and the Fermi level lies at the crossing point. When wave vector $k$ is measured from the K point, the energy is given by $\varepsilon(k) = \pm \hbar v|k| = \pm v|p|$ for small $k = |k|$, where $p = \hbar k$ is the momentum and $v$ is the velocity of the order $c/300$ with $c$ being the light velocity. According to the special theory of relativity, the energy of a relativistic particle is given by $\varepsilon = \sqrt{m^2c^4 + p^2c^2}$ with $m$ being a rest mass. When we set $m = 0$, this gives dispersion $\varepsilon = c|p|$ equivalent to that of light. This particle is a massless neutrino and the negative energy corresponds to an antineutrino. The dispersion of an electron in graphene is obtained by replacing $c$ with $v$ in this equation.
**Fig. 1** The honeycomb lattice of graphene. A unit cell given by a hexagon denoted by a dashed line contains two carbon atoms A and B. The chiral vector determining the structure of a carbon nanotube is given by $\mathbf{L}$ and its length gives the circumference. $\eta$ denotes the chiral angle with zigzag $\eta = 0$ and armchair $\eta = \pi/6$ nanotubes.

**Fig. 2** (a) The energy bands near the Fermi level in graphene. The conduction and valence bands cross each other at the K and K’ points. (b) The conic energy bands in the vicinity of the K and K’ point. (c) The density of states near the Fermi level with Fermi energy $E_F$.

The corresponding Schrödinger equation is given by a set of first order differential equations:

$$\hbar v \begin{pmatrix} 0 & \hat{k}_x - i \hat{k}_y \\ \hat{k}_x + i \hat{k}_y & 0 \end{pmatrix} \begin{pmatrix} F_A(r) \\ F_B(r) \end{pmatrix} = \varepsilon \begin{pmatrix} F_A(r) \\ F_B(r) \end{pmatrix},$$

with $\hat{k} = -i(\partial/\partial x, \partial/\partial y)$, where $F_A(r)$ and $F_B(r)$ represent the amplitude at A and B sublattice points, respectively. The similar discussion is possible for the K’ point. Thus, the two-dimensional electron system in graphene makes it possible to study properties of highly relativistic particles.
One intriguing feature of the neutrino wave function is the appearance of Berry’s phase. In fact, when the direction of the motion is rotated by $2\pi$, the phase of the wave function changes by $\pm \pi$, changing its sign. This leads to the absence of backscattering when a particle is scattered by impurities, because the backscattering corresponds to the rotation of the direction by $\pm \pi$ and the amplitudes for $\pm \pi$ rotations cancel each other due to the sign difference.\textsuperscript{29,30} In carbon nanotubes, the electron motion along the circumference is quantized and the electron motion effectively becomes one-dimensional, where the resistance is determined solely by backscattering. Therefore, the absence of backscattering means that metallic carbon nanotubes become an ideal conductor with perfect conduction even in the presence of scatterers.

3. Carbon nanotube is either a metal or semiconductor

Let us introduce lattice translation vector $L$. A nanotube can be constructed in such a way that the hexagon at position $L$ is rolled onto the hexagon at the origin. This $L$ is called the chiral vector and becomes a circumference of the nanotube. The direction angle $\eta$ of $L$ is called the chiral angle. Because each translation vector is written as $L=n_a a + n_b b$ with $a$ and $b$ being the primitive translation vectors, the structure of a nanotube is specified by a set of two integers $n_a$ and $n_b$. The axis is perpendicular to $L$ and therefore a nanotube usually has helical structure. There are some exceptions of nonhelical nanotubes, zigzag nanotubes with $\eta=0$ and armchair tubes with $\eta=\pi/6$. Other helical tubes are called chiral nanotubes. Because the stability is mainly determined by their thickness or circumference,
the direction of $L$ of grown nanotubes is distributed almost uniformly.

The wave function satisfies periodic boundary condition $\psi(r+L) = \psi(r)$ in a carbon nanotube. This shows that wave vector $k$ satisfying condition $\exp[ik \cdot (r+L)] = \exp(ik \cdot r)$ is allowed in the first Brillouin zone of graphene. The condition is rewritten as $\exp(ik \cdot L) = 1$, which gives straight lines perpendicular to $L$ with neighboring distance $2\pi/L$ as shown in Fig. 3. When these lines pass through the K and K' points, i.e., $\exp(iK \cdot L) = 1$ or $\exp(iK' \cdot L) = 1$ with $K$ and $K'$ being the wave vector of the K and K' point, respectively, there is no gap at the Fermi level and the nanotube becomes metallic. In other cases, the nanotube becomes a semiconductor with a gap near the Fermi level.

Explicit calculations show that $\exp(iK \cdot L) = \exp(2\pi i \nu/3)$ and $\exp(iK' \cdot L) = \exp(-2\pi i \nu/3)$ with $\nu$ being an integer, which is 0 or $\pm 1$ depending on $n_a$ and $n_b$. As a result metallic ($\nu = 0$) and semiconducting ($\nu = \pm 1$) nanotubes appear with the ratio of one to two, when $L$ is varied. In a semiconducting nanotube, the straight line closest to the K or K' point gives the conduction and valence bands. Because the spacing between neighboring lines is $2\pi/L$ and the energy is a linear function of the wave vector near the K and K' points, the energy gap is proportional to the inverse of the diameter $d = L/\pi$. The important feature is that there can be both metallic and semiconducting nanotubes with similar diameter and therefore one tough challenge lies in selective growth of semiconducting and metallic nanotubes or their separation after growth.

4. Graphene is a metal

Graphene has often been called a zero-gap semiconductor because the density of states is given by $D(E) = |E|/2\pi \hbar^2 v^2$ which vanishes at $E = 0$ as shown in Fig. 2. This naming is quite inappropriate, however. The more appropriate naming becomes clear when we consider the conductivity of graphene.

The conductivity is usually given by the Einstein relation, $\sigma_0 = g_v g_s e^2 D^* D(E_F)$, in terms of diffusion coefficient $D^*$, where $g_v = 2$ is the valley degeneracy corresponding to the presence of the K and K' points and $g_s = 2$ is the spin degeneracy. Let $\tau$ be the relaxation time due to impurity scattering. Then, the diffusion coefficient is given by $D^* \sim v^2 \tau$. We have $\tau^{-1} \sim (2\pi/\hbar)n_i \langle u_i^2 \rangle_{E_F} D(E_F)$, where $n_i$ is the impurity density, $u_i$ is the matrix element of the impurity potential between initial and final states, and $\langle \cdots \rangle_{E_F}$ denotes the average at the Fermi level. As a result the conductivity becomes $\sigma_0 = g_v g_s e^2/2\pi^2 \hbar W$ independent of the density of states, where $W = n_i \langle u_i^2 \rangle_{E_F}/4\pi \hbar^2 v^2$ is a dimensionless parameter characterizing the strength of the impurity scattering. Strictly speaking, the relaxation time determining the conductivity is different from the simple scattering time, but the difference is not so important here.

The above shows that the conductivity is independent of the Fermi energy or the carrier concentration as long as possible dependence of scattering strength $W$ on $E_F$ or $n_s$ is neglected. Therefore, graphene should be regarded as a metal rather than a semiconductor.
Fig. 4 Some examples of the density of states (a) and the conductivity (b) of a monolayer graphene calculated in a self-consistent Born approximation. Here, $\varepsilon_0$ 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 $E_F \neq 0$ down to $\sigma = e^2/\pi^2\hbar$ at $E_F = 0$. After Ref. 31.

At $E_F = 0$ where $D(E_F) = 0$, however, this description can become inappropriate. In fact, potential fluctuations due to impurities make the density of states at $E_F = 0$ nonzero. Theoretical calculations including this level broadening effect were performed prior to experiments and showed that the conductivity takes a universal value $\sigma_{\text{min}} = g_v g_e e^2 / 2\pi^2\hbar$ at $E_F = 0$. Figure 4 shows examples of calculated density of states and conductivity. In graphene with weak disorder, i.e., $W \ll 1$, the conductivity drops down to $\sigma_{\text{min}}$ from $\sigma_0$ in a very narrow energy range close to $E = 0$. Similar calculations were performed for the conductivity in magnetic fields and the Hall conductivity, in particular, was predicted to be quantized into $(4e^2/\hbar)(j + 1/2)$ with integer $j$, i.e., the half-integer quantum Hall effect.\(^8\)

Experimentally, the minimum conductivity was shown to be nearly independent of samples.\(^6\) Its absolute value seems to be $3 \sim 4$ times as large as the theoretical prediction, however. In the vicinity of zero energy, because of the weak screening effect due to small density of states and small kinetic energy of electrons, effective scattering strength can be substantial and the system inhomogeneity can also be significant. Some reports show that the minimum conductivity varies from sample to sample.\(^{32}\) This problem on the minimum conductivity remains as an important subject to be understood in future.

Another important difference lies in the dependence of the conductivity on the electron
concentration. The theory predicts that the conductivity in clean graphene should be independent of the electron concentration and drops down to $\sigma_{\text{min}}$ in the extreme vicinity of zero energy and the width of this region is singularly narrow. Experimentally, however, the conductivity is nearly proportional to the electron concentration as if there is an effective mobility independent of the electron concentration. A part of the reason lies in the fact that scattering strength $W$ is large at $E_F \sim 0$ (typically $W \sim 0.1$) as mentioned above. Another reason is that the effective strength of dominant scatterers depends on the electron concentration as $W \propto |n_s|^{-1}$ and the Boltzmann conductivity becomes proportional to the electron concentration.

Typical examples of such scatterers causing this $n_s$ dependence are charged impurities. In fact, charged centers localized in SiO$_2$ are known to play important roles in silicon MOSFETs (metal-oxide-semiconductor-field-effect-transistors). Explicit calculations for charged-impurity scattering with screening effect properly included gave $W \propto |n_s|^{-1}$, i.e., $\sigma \approx e|n_s| \mu$ with mobility $\mu \propto n_i^{-1}$ independent of $n_s$. The typical mobility in graphene on a SiO$_2$ substrate is $\mu \sim 10^4$ cm$^2$/Vs. The required impurity concentration is $n_i \sim 5 \times 10^{11}$ cm$^{-2}$, comparable to that in a MOSFET.

A singular behavior appears also in the dynamical conductivity. The dynamical conductivity consists of two terms, the Drude conductivity determined by states in the vicinity of the Fermi level and the interband conductivity dominant for $\hbar \omega > 2|E_F|$. The latter conductivity corresponding to optical transitions from valence- to conduction-band states is
Fig. 6 Schematic illustration of the enhancement of effective gap caused by confinement of conduction electrons and valence holes in a semiconductor quantum well.

given by universal value $g_v g_s e^2/16\hbar$. Explicit calculations show that the frequency dependence is completely scaled by the Fermi energy if level-broadening effects are completely neglected, i.e., $\sigma(\omega, E_F) = \sigma(h\omega/|E_F|)$, as shown in Fig. 5 (a). This shows that at $E_F = 0$, $\sigma(\omega) = \sigma_0$ for $\omega = 0$ and $\sigma(\omega) = g_v g_s e^2/16\hbar$ for $\omega \neq 0$. It was shown that this singularity present at $E_F = 0$ can be removed by level-broadening effects as shown in Fig. 5 (b).\textsuperscript{36)Quite recently, the dynamical conductivity was observed, demonstrating the universality of the interband conductivity.\textsuperscript{37,38)\]

5. Opening band gap in graphene

One most important challenge toward the transistor application arises from the fact that graphene is not a semiconductor but a metal. Because of the dependence of $W$ on $n_s$, the conductivity changes as a function of the electron concentration proportional to the gate voltage. In fact, the conductivity in graphene fabricated on a SiO$_2$ substrate changes from $\sigma_{\text{min}}$ at $E_F = 0$ to 20∼30 times larger values by the gate. This amount of the change is certainly not sufficient for transistors and further the gate-voltage range corresponding to $\sigma_{\text{min}}$ is too narrow. There have been various attempts to introduce a band gap for the purpose of converting graphene into a semiconductor.

Let us consider a fictitious case that the A and B sublattice atoms have different energies, $+\delta$ for A atoms and $-\delta$ for B atoms. In this case, the energy bands become $\varepsilon_{\pm}(k) = \pm \sqrt{(\hbar v |k|)^2 + \delta^2}$ instead of $\varepsilon_{\pm}(k) = \pm \hbar v |k|$. This shows that gap $2|\delta|$ opens up at $k = 0$. Such a difference in the energy of the A and B atoms can be realized by growing graphene on an appropriately chosen substrate giving rise to asymmetry between two sublattices.

In usual semiconductors, a band gap is enhanced by the increase of kinetic energy of
conduction electrons and valence holes when they are spatially confined into quantum wells or quantum wires. Let the effective mass of electrons and holes be $m_e$ and $m_h$, respectively, and the well width be $d$. Then the effective gap increases by $(\hbar^2 \pi^2 / 2d^2)(m_e^{-1} + m_h^{-1})$. Figure 6 shows a schematic illustration of this enhancement. In graphene also a gap can be formed when electrons and holes are confined into a narrow region.

First, we should note that the spatial confinement is not possible by an external potential. In fact, an electron incident perpendicularly on a barrier potential transmits through the barrier with probability unity because of the absence of backscattering mentioned above. The confinement is achieved only by cutting graphene into a ribbon with narrow width.

In usual semiconductors, the electron motion is described by an effective-mass approximation characterized by a second-order differential equation. In this case, the wave function has vanishingly small amplitude at the boundary as illustrated in Fig. 6 and therefore electrons are only weakly affected by disorder present at the boundary, such as weak boundary roughness scattering. In graphene, however, the Schrödinger equation is given by a set of first-order differential equations and therefore we cannot impose the condition that the wave functions vanish there. As a result the amplitude of the wave functions is almost same at edges and inside of a graphene ribbon, showing that electronic states in graphene ribbon are quite sensitive to the edge structure.

The sensitivity to edges was previously demonstrated by explicit calculations of electronic states in ribbons.\textsuperscript{39,40} In fact, there exist edge states without dispersion, localized in the vicinity of edges, in zigzag ribbons having an edge with a zigzag form. Armchair ribbons having an edge with an armchair form, on the other hand, change between metallic and semiconducting behaviors periodically with their width, quite analogous to the behavior in carbon nanotubes. In ribbons fabricated by conventional lithography technique their edges are suffered from substantial damages and therefore far from being ideal. The conductance of narrow ribbons was measured at various temperatures and a gap was estimated to be roughly proportional to the inverse of the width.\textsuperscript{41,42} The obtained gap has turned out to be independent of the ribbon direction and the conductance considerably decreases with the decrease of the ribbon width, suggesting that it is likely to be a mobility gap due to edge disorder rather than a band gap. The presence of a band gap was suggested in chemically derived ribbons.\textsuperscript{43}

Multi-layer graphenes such as bilayer and trilayer have also been fabricated. In bilayer graphene, in particular, electronic states become quite different from those in monolayer graphene due to strong interlayer interactions. The dispersion in the vicinity of the Fermi level changes from $\varepsilon_{\pm}(k) = \pm \hbar v |k|$ in monolayer into $\varepsilon_{\pm}(k) = \pm \hbar^2 k^2 / 2m^*$, where $m^*$ is the effective mass.\textsuperscript{44} In multi-layer graphenes, in general, the Hamiltonian has been shown to be decomposed into that of monolayer graphene and those of bilayer graphenes when only dominant terms in interlayer interactions are considered.\textsuperscript{45,46}
When a strong electric field is applied perpendicular to bilayer graphene as illustrated in Fig. 7 (a), the induced potential difference between the two layers gives rise to a band gap of the order of the potential difference. The actual difference is determined in a self-consistent manner because it also leads to asymmetry in the electron density distribution. This corresponds to screening of external potential and tends to decrease the gap roughly into half. Some examples of calculated potential difference are shown in Fig. 7 (b). Several experiments have been reported, including those giving a small band gap and those suggesting opening of a huge gap.

6. Outlook

Characteristic features of electronic and transport properties of graphene and carbon nanotube have been discussed from a theoretical point of view. An electron in graphene is equivalent to a massless neutrino in two dimension and therefore a system of relativistic particles moving with light velocity is effectively realized in graphene. The actual velocity is about 1/300 of the light velocity. This leads to unique electronic and transport properties in graphene and carbon nanotubes. A typical example is the absence of backscattering making a metallic carbon nanotube a perfect conductor even in the presence of scatterers.
Graphene and nanotube will continue to attract attention because of their high potential toward device applications as well as purely scientific interests.

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