Graphite, graphene and relativistic electrons

- Introduction
- Physics of graphene
- Experiments
  - Transport – electric field effect
  - Quantum Hall Effect – chiral fermions
  - STM – Landau levels of Dirac fermions
  - Induced superconductivity
Chemical Bonding:

- sp²
- sp³
## Carbon allotropes

<table>
<thead>
<tr>
<th>3D</th>
<th>2D</th>
<th>1D</th>
<th>0D</th>
</tr>
</thead>
<tbody>
<tr>
<td>sp³</td>
<td>graphite</td>
<td>diamond</td>
<td>C₆₀</td>
</tr>
</tbody>
</table>

### Carbon Allotropes Overview:
- **3D**
  - sp²: Graphite
  - sp³: Diamond

- **2D**
  - Graphene 2005

- **1D**
  - Carbon nanotube Multi-wall 1991 Single wall 1993

- **0D**
  - Buckyball 1985
Sample Fabrication

- Micromechanical cleavage by “drawing”

- Properties:
  - Large contiguous samples (10 µm)
  - Stable, Inert
  - Strong
  - High conductivity
  - Large field effect

Novoselev et al (2005)

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Sample Processing

- Optical microscope
- AFM
- Electron diffraction
- Electron beam lithography
- Graphene device

Novoselov et al
Why graphene

- **New Physics:**
  - Electrons behave as massless Dirac Fermions (neutrinos with zero mass)

- **Novel devices**
  - Strong Field effect (metallic FET)
  - Intrinsically long mean-free-path - high conductivity
  - Unusual transport (negative dielectric constant - lensing)
  - Naturally inert
  - High-strength composites
  - Nanometer-sized molecular electronic devices
Electron energy depends on momentum (wavelength). In normal metal dispersion is parabolic.

How is graphene different?

... the electrons are strongly diffracted by the graphene lattice--the $E(p)$ relation is unconventional.

Hebrew University Jan 9, 2007
The Honeycomb Lattice

- 2 different types of atomic sites (chemically identical)

Direct lattice

Wigner-Seitz unit cell

"conventional" unit cell

Reciprocal lattice

1st Brillouin zone

triangular reciprocal lattice – hexagonal Brillouin zone

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Electronic Wavefunctions

- 2 different types of atomic sites
- 2 Bravais sub-lattices
- 2 sets of Bloch functions

\[ \Phi_A(\vec{k}, \vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}_A} e^{i\vec{k}.\vec{R}_A} \phi_A(\vec{r} - \vec{R}_A) \]

\[ \Phi_B(\vec{k}, \vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}_B} e^{i\vec{k}.\vec{R}_B} \phi_B(\vec{r} - \vec{R}_B) \]
Electronic Wavefunctions

\[ \Psi(\mathbf{k}, \mathbf{r}) = C_A \Phi_A(\mathbf{k}, \mathbf{r}) + C_B \Phi_B(\mathbf{k}, \mathbf{r}) \]

Linear combination of two sets of Bloch functions

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Tight binding model

Wallace, 1947

Energy:

\[ E_k = \pm \gamma_0 \sqrt{1 \pm 4 \cos \frac{k_y a}{2} \cos \frac{\sqrt{3} k_x a}{2} + 4 \cos^2 \frac{k_y a}{2}} \]

\[ \gamma_0 \approx 3.033 eV \]

\( \pi \) bond overlap, (Saito et al.)
Tight binding model

For neutral sample:
- particle-hole symmetry
- valence and conduction bands touch at $E=0$
- No Fermi surface: six "Dirac" points, only two inequivalent
Electrons in graphene: Dirac fermions

- **Near K point:**
  - **Effective Hamiltonian**
  
  \[ H = v_F \vec{\sigma} \cdot \vec{p} \]

  - **linear dispersion**
  
  \[ E(\vec{q}) = \pm v_F \hbar |\vec{q}|, \]
  \[ \vec{q} = \vec{k} - \vec{K}_F, \quad v_F \approx 10^6 \text{ m/s} \sim c/300 \]

- **Zero band mass**

- **Wavefunction**

\[ \psi = \begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix} = \frac{1}{\sqrt{2}} e^{i\vec{k}\cdot\vec{r}} \begin{pmatrix} e^{-i\varphi/2} \\ e^{i\varphi/2} \end{pmatrix} \]

\[ \varphi = \tan^{-1}(k_x / k_y) \]

- **Bloch function amplitudes on the AB sites ('pseudospin') mimic spin components of a relativistic Dirac fermion.**

**Dirac-Weyl equation:** relativistic massless particle - Dirac fermions ("old" neutrino)

**Semenoff, 1984**

**Haldane, 1988**
Electrons in graphene: Dirac fermions

- Near K point:
  - Effective Hamiltonian
  - Helical particles: pseudospin projection on momentum axis conserved.
  - Berry phase = $\pi$

\[ H = v \cdot \vec{\sigma} \cdot \vec{p} \]

Dirac-Weyl equation: relativistic massless particle - Dirac fermions ("old" neutrino)

\[ E = v|p| \]

\[ \Psi = \frac{1}{\sqrt{2}} \left( e^{-i\varphi/2} e^{i\varphi \cdot \vec{r}} \right) \]

\[ \varphi \rightarrow \varphi + 2\pi \]

\[ \Psi \rightarrow e^{i\pi \Psi} \]
Graphene and conventional electron systems

Low energy excitations

Conventional semiconductor

\[ E = \frac{p^2}{2m_e^*} \]

\[ E = \frac{p^2}{2m_h^*} \]

Graphene

- Zero band mass
- Gapless
- Electron-hole symmetry
- Pair creation
- Chiral (Pseudospin ½)
- Berry phase \( \pi \)

Density of states

\[ N_2D(E) \]

\[ \frac{m_h^*}{\pi \hbar^2} \]

\[ \frac{m_e^*}{\pi \hbar^2} \]
Relativistic electrons in graphene — experimental implications

- Vanishing DOS at Dirac point \( q \)  \( \text{Electric field effect} \)
- Berry phase \( \pi \) (no backscatering) \( q \)  \( \text{Large conductivity} \)
- \( \text{Chiral particles} \) \( q \)  \( \text{Landau level at } E=0 \)
- \( \text{Chiral particles} \) \( q \)  \( \text{Anomalous QHE} \)
- \( \text{pair creation} \) \( q \)  \( \text{Penetration through electrostatic barriers (Klein paradox)} \)
Electric field effect in graphene

conductivity

Novoselov et al, Nature 2005

peak around zero can be shifted by chemical doping (exposure to NO₂, NH₃, CO, etc)
Electric field effect in graphene

conductivity

\[ \sigma = ne\mu = \frac{\varepsilon \varepsilon_0 \mu V_g}{d} \]

Hall effect

\[ \frac{1}{\rho_{xy}} = \frac{ne}{B} \]

Novoselov et al, Nature 2005

Mobilities up to 6,000 cm\(^2\)/V\cdot s at 300K

ballistic transport already on submicron scale!

\~50,000 cm\(^2\)/V\cdot s (below 30K)
DOS – in magnetic field

\[ \omega_c = \frac{eB}{mc} = \frac{\hbar}{ml_B^2} \]

\[ E_n = \hbar \omega_c (j + 1/2) \]
Each filled Landau level contributes an additional quantum of conductance $ge^2/h$ to the Hall conductivity (degeneracy $= g$).

Quantum Hall plateaux when $nh/geB = n/n_0$ = integer -- QHE
- measures commensurability of electrons with flux lattice
- Quantum Hall plateaux - independent of LL energy!!

$$\varepsilon_j = \hbar \omega_c (j + 1/2), \quad j = 0, \pm 1, ...$$
IQHE in graphene

- LL energy – not seen in QHE
- Need direct probe

Landau level at E=0 – no QHE plateau at 0.

Novoselev et al. Nature 2005
Zhang et al. Nature 2005
ARPES on graphite

- Momentum resolution
- No empty states
- No magnetic field

STM

\[ I \propto V \rho_s(0, E_F) \exp(-2k\rho d); \quad \kappa = \frac{\sqrt{2m\Phi}}{\hbar} \]
STM

Topography (STM)

Tip z position

Tip x position

I Constant

Spectroscopy (STS)

d Constant

\[
\frac{dl}{dv} [G_{\Omega}]
\]

\[
V [mV]
\]

\[
E_F
\]

\[
1
\]

\[
Y [nm]
\]

\[
0
\]

\[
1
\]

\[
X [nm]
\]

\[
0
\]

\[
1
\]

\[
150
\]

\[
-150
\]

Trace of 10 nm
STM

Occupied states

Empty states

sample  tip  sample  tip
STM – direct observation of Landau levels

- Low temperatures -2K
- Magnetic field 15T
Low Temperature High Field Scanning Tunneling Microscope

Charge Density Wave

Vortex Lattice

Graphite – Carbon atoms

NbSe$_2$

Superconducting Gap

Relativistic Electrons – Quantum Hall Effect
STM on graphite

Landau level spectroscopy - HOPG

- Direct measure of energy levels
- Both electron and hole states
Landau level spectroscopy

Same offset $E_D \approx 20\text{mV}$

$E = \pm v_p$

Same offset $E_F = -18\text{meV}$
Landau levels of Dirac fermions

\[ E_n = \text{sgn}(j) \sqrt{2e\hbar v_F^2 |j| B} \], \quad j = 0, \pm 1, ...

\[ v_F = 1.07 \times 10^6 \text{ m/s} \]
The linear sequence

Two choices:

- **Standard 2d Electrons**
  - Linear in $B, j$
  - No state at $E=0$
  
  $$E_n = \hbar \omega_c (j + 1/2), \quad j = 0, \pm 1, ...$$

- **2 layer graphene - massive chiral particles**
  - Coupling between layers $\gamma$  
    $$m^* = \frac{\gamma}{v_F^2}$$
  - Cyclotron frequency
    $$\omega_c = eB / m^* c$$
  - Linear in $B$
  - State at $E=0$
  
  $$E_n = \text{sgn}(n) \hbar \omega_c \sqrt{\left| j \right| \left( \left| j \right| + 1 \right)}, \quad j = 0, \pm 1, ...$$
Massive chiral particles

\[ E_n = sgn(j) \hbar \omega_c \sqrt{(|j|(|j|+1))}, \quad j = 0, \pm 1, \ldots \]

\[ m^* = 0.03 m_e \]
Classification of spectra

Massless Dirac fermions

Massive chiral fermions

Bulk electrons

Massive chiral fermions

Bulk electrons
Graphite – band structure

Band structure of graphite (by Bross and Alsheimer)
Graphite – band structure

- **H** – Dirac cone \((E_F \text{ below } DP)\)
- **K** – quadratic \((\text{minimum at } DP)\)
- **L-M** small gap
- **K-H** – continuous band
  - interlayer coupling dominates all non-\(k\) selective measurements:
    - Transport, STM ..

Band structure of graphite (by Bross and Alsheimer)
**Graphite – Landau levels**

- Spectrum dominated by K-H states
- LL due to H and K points are “buried”

STM on Kish graphite - Matsui et al PRL 05
ARPES on graphite


H point

Dirac point at H: 50mV above $E_f$
ARPES on graphite


K point

Parabolic dispersion – maximum at K.
Compare to ARPES

- **ARPES**
  - H point:
    - $E_F - E_D = -50 \text{ mV}$
  - K point $E_F = E_D$

- **STM**
  - $E_F - E_D = -20 \text{ mV}$
  - No energy offset between spectra.
  - No contribution from states with finite $k_z$

STM Spectra inconsistent with bulk

Surface layers of graphene
Summary

Electrons on the surface of graphite
- Massless Dirac fermions
  - Linear energy dispersion
  - Zero band mass
  - Landau level sequence follows $E_j \propto (B_j)^{1/2}$
  - Zero energy Landau level
- Massive chiral fermions
  - Quadratic dispersion
  - Finite band mass
  - Landau level sequence follows $E_j \propto B(j(j+1))^{1/2}$
  - Zero energy Landau level

SNS junction
- Multiple Andreev Reflections observed.
- Thin graphite - evidence of cooper pair current.
- Graphene - proximity effect and MAR are suppressed near the Dirac point.

What next
- STM near Impurities, defects
- Many-body effects – FQHE, WC
- Confinement: electrical, magnetic?
- ...

Beer-Sheba Jan 25, 2007