Fourth Stig Lundqvist Conference on
Advancing Frontiers of Condensed Matter Physics

3 - 7 July 2006

Electron transport in molecules, nanotubes and graphene

Philip KIM
Columbia University
Department of Physics
538 West 120th Street
New York, NY 10027
U.S.A.

These are preliminary lecture notes, intended only for distribution to participants
Electron Transport in Molecules, Nanotubes and Graphene

Philip Kim

Department of Physics
Columbia University
Rolling Up Graphene: Periodic Boundary Condition

Periodic Boundary Condition

\[ C_h \cdot \vec{k}_\perp = 2\pi q \]

Allowed states

Metallc nanotube

Semiconducting nanotube
Tuning Carrier Density by Electric Field Effect

Induced charge: $C_g V_g = e n = e \text{(D.O.S)} \Delta E_F$

Metallic nanotube

Semiconducting nanotube
Electrical Transport in Nanotube Devices

**Metallic nanotube**

\[ I (nA) \]

\[ V_{sd} = 10 \text{ mV} \]

\[ V_g (V) \]

**Semiconducting nanotube**

\[ I (nA) \]

\[ V_{sd} = 10 \text{ mV} \]

\[ V_g (V) \]

**ON**

**OFF**
Controlled Growth of Ultralong Nanotubes

**Figure 3.** SEM and TEM images of ultralong MWNTs. (a) Schematic representation for the diameter-dependent stabilization of reaction gas flows. By inserting the smaller tube inside the outer chamber, microscopic turbulent flows can be stabilized into laminar flows with lower Reynolds numbers. (b) SEM image of MWNTs, which are several centimeters long. Scale bar, 2 mm. (c) A SEM image of MWNTs grown across a 100 μm slit. Scale bar, 20 μm. (d) HRTEM images showing single, double, triple, and multi-walled CNTs. Scale bars, 5 nm.
Extremely Long SWNT Field Effect Transistor

FET characteristics

\[ V_{sd} = 20 \text{ V} \]

\[ \rho \sim 10^{-7} \, \Omega \text{ m} \]
Electron Transport in Long Single Walled Nanotubes

Multi-terminal Device with Pd contact

* Scaling behavior of resistance: $R(L)$

Ballistic Transport and Mean Free Path

Electron Transport in 1D Channel

Diffusive transport: $l_e \ll L$

$$R(L) = \rho L$$

Ballistic transport: $L < l_e$

$$R(L) = \frac{h}{Ne^2} + \frac{h}{Ne^2} \frac{L}{l_e}$$

Resistance of $N$-1D Channel:

For a nanotube, $N = 4$ (2 from spin and 2 from $K$ and $K'$)
Electron Mean Free Path of Nanotube

Lines are fit to

\[ R(L) = R_c + \frac{h}{4e^2} + \frac{h}{4e^2} \frac{L}{l_e} \]

\[ \frac{h}{4e^2} = 6.45 \text{ k}\Omega \]

Non-ideal contact resistance \( R_c < 2 \text{ k}\Omega \)

\[ l_e \sim 0.5 \mu\text{m} @ \text{RT}!! \]
Extremely Long Mean Free Path: Hidden Symmetry?

Carbon nanotube:

\[ l_e \sim 10 \, \mu m \quad @ \quad 1.6 \, K \]
\[ l_e \sim 0.5 \, \mu m \quad @ \quad 300 \, K \]

Ga[Al]As HEMT:

\[ l_e \sim 100 \, \mu m \quad @ \quad 1.6 \, K \]
\[ l_e \sim 0.06 \, \mu m \quad @ \quad 300 \, K \]

- Small momentum transfer backward scattering must be inefficient.

Selection rules by hidden symmetry in graphene?

Electric Field Effect in Mesoscopic Graphite

Fabrication and electric-field-dependent transport measurements of mesoscopic graphite devices

Yuanbo Zhang, Joshua P. Small, William V. Ponsius, and Philip Kim
Department of Physics and the Columbia Nanoscale Science and Engineering Center, Columbia University, New York, New York 10027
(Received 31 August 2004; accepted 11 December 2004; published online 7 February 2005)

FIG. 1. (a) Scanning electron microscope image of an HOPG crystalite mounted on a microcantilever. Inset: bulk HOPG surface patterned by masked anisotropic Ar ion etching. (b) Schematic drawing of the microfabrication process. (c) Thin graphite samples cleaved onto the Si/SiO₂ substrate. (d) A typical mesoscopic device fabricated from a cleaved graphite sample.

Electric Field Modulation of Galvanomagnetic Properties of Mesoscopic Graphite

Yuanbo Zhang, Joshua P. Small, Michael E. S. Amori, and Philip Kim
Department of Physics and the Columbia Nanoscale Science and Engineering Center, Columbia University, New York, New York 10027, USA
(Received 31 August 2004; published 3 May 2005)
Using Scotch Tape is Essential!!
A Few Layer Graphene on SiO₂/Si Substrate

Optical microscope images

AFM Image

1.2 nm

0.4 nm

0.8 nm

20 μm
Transport Single Layer Graphene

Single layer graphene device

Field Effect Resistance

\[ R_{xx} \approx \frac{\hbar}{4e^2} \]

Zhang, Tan, Stormer & Kim (2005), see also Novoselov et al (2005).
Graphene: Dirac Particles in 2D Box

Band structure of graphene

Massless Dirac Particles with effective speed of light $v_F$. $E \approx \hbar v_F |\vec{k}_\perp'|$
Graphene v.s. Conventional 2D Electron System

Conventional 2D Electron System

$$E = \frac{\hbar^2 k^2}{2m_e}$$

Graphene

- Zero band mass
- Strict electron hole symmetry
- Electron hole degeneracy

$$E = \hbar v_F |k'_{\perp}|$$

Band structures

Density of States

$$N_{2D}(E) \sim \frac{m^*_e}{\pi \hbar^2}$$

$$N_{2D}(E) \sim \frac{m^*_h}{\pi \hbar^2}$$

$$\sim \frac{\hbar}{4e^2}$$
2D Gas in Quantum Limit: Conventional Case

Density of States

Landau Levels in Magnetic Field

\[ \hbar \omega_c = \hbar eB / m^* \]

Integer Quantization:

\[ R_{xy}^{-1} = \pm v \cdot g_s \cdot \frac{e^2}{h} \]

- \( \nu = 1, 2, 3 \ldots \)
- \( g_s = 2 \ (\text{spin}) \)

Graphene

- Vanishing carrier mass near Dirac point
- Strict electron hole symmetry
- Electron hole degeneracy \( \omega_c = \frac{eB}{m^*} \)
Quantum Hall Effect in Graphene

Quantization:

\[ R_{xy}^{-1} = 4 \left( n + \frac{1}{2} \right) \frac{e^2}{h} \]
Relativistic Landau Level and Half Integer QHE

Landau Level

\[ E_n = \pm \sqrt{2e\hbar v_F^2 |n| B} \]

Landau Level Degeneracy
\[ g_s = 4 \]
2 for spin and 2 for sublattice

Quantized Condition
\[ \frac{1}{R_{xy}} = \pm g_s (n + \frac{1}{2}) \frac{e^2}{\hbar} \]
\[ \nu = \pm g_s (n + 1/2) \]

Haldane, PRL (1988)

Quantum Hall Effect in Graphene

Mobility
\( \sim 60,000 \text{ cm}^2/\text{V s} \)

\( T = 1.7 \text{ K} \)
\( B = 9 \text{ T} \)
Quantum Hall Effect in Graphene at High Magnetic Field

\[ B = 45 \text{ T} \]
\[ T = 1.4 \text{ K} \]

Splitting of Landau Levels in High Magnetic Fields

\[ \sigma_{xy} = \frac{-R_{xy}}{R_{xy}^2 + R_{xx}^2} \]

- **Low fields (B < 10 T)**
  \[ \nu = \pm 2, \pm 6, \pm 10, \ldots \]

- **High fields (B > 20 T)**
  \[ \nu = 0, \pm 1, \pm 2, \pm 4, \pm 6, \ldots \]

\[ E_n = \text{sgn}(n) \sqrt{2e\hbar v_f^2 |nB|} \]
Fig 6. Examples of all graphene device with their band diagram.
Graphene Ribbon Devices (Preliminary)

Before Etching

Conductance (mS)

After Etching

Gap Opening
~ 10 meV
For ~ 80 nm
Graphene ribbon

M. Han, Y. Zhang and P. Kim (2006)
Nanotube Electrodes for Molecular Electronics

- Nanotubes are inherently small, yet compatible to microfabrication processes
- Covalent chemistry between electrode and molecules
- Potentially good conduction via $\pi$-bonding network
Nanotube Nanogaps

Nanotube device

Narrow (<10nm) trench via e-beam lithography

Thin PMMA coating

Oxygen Plasma etching creates gaps (0-10 nm) in tubes.

Cut ends likely to be carboxyl-terminated

Hone, Wind, Nuckolls, Brewslow and Kim Collaboration
Nanotube Nanogaps

Process are optimized to Yield of cut tubes: 25% of ~2600 devices

Columbia NSEC (Hone, Wind, Brewslow, Nuckolls, and Kim) Collaboration
Molecular Bridges

- Self-assembled
- Covalently bonded
- Conduction through \( \pi \)-back bone

Does It Work?

~ 10-15% of reconnection out of ~ 100 fully cut tubes

Semiconducting Nanotube + Molecular Bridge

Metallic Nanotube + Molecular Bridge

Vsd = 50 mV
Control Experiments

- Pyridine + EDCI without molecules: No connection
- Bis-oxazole without amines: No connection
- Bis-oxazole with Monoamine: No connection
- 1,12 dodecane diamine (insulator): No connection
Oligoaniline: PH sensing
Transport Measurement

Bis-oxazole + metallic SWNT
Temperature Dependence Transport Spectroscopy

![Graphs showing temperature dependence of transport spectroscopy.](image)
Gate Voltage Dependence

<table>
<thead>
<tr>
<th>Vg (V)</th>
<th>Vsd (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-9.25</td>
<td>-150</td>
</tr>
<tr>
<td>-9.23</td>
<td>-175</td>
</tr>
<tr>
<td>-9.21</td>
<td>-200</td>
</tr>
<tr>
<td>-9.19</td>
<td>-225</td>
</tr>
<tr>
<td>-9.17</td>
<td>-250</td>
</tr>
</tbody>
</table>

\[
dI/dV_{sd} (\mu S)
\]

\[
V_{sd} (mV)
\]

\[
V_g (V)
\]
Summary

• Transport in long nanotubes:
  Extremely long mean-free path in SWNTs

• Transport in graphene:
  Unusual quantum Hall effect
  Graphene nano ribbon devices

• Nanotube electrode for
  single molecular electronics
Acknowledgement

Special Thanks to:
Yuanbo Zhang
Meninder Purewal
Byung Hee Hong
Josh Small
Melinda Han
Barbaros Oezyilmaz

Collaboration:
Stormer, Pinczuk, Heinz,
Nuckolls, Brus, Flynne, Hone,

Funding: NSF, NYSTAR, DARPA, Office of Naval Research, Samsung