Graphene:
Worlds oldest and newest material
Properties and Current Research

Bennett Goldberg
Physics Department; Biomedical Engineering and Electrical Engineering
Center for Nanoscience and Nanobiotechnology
Graphene

Graphene – very old new material
Panoply of interesting physics
Measuring strain with light scattering
Friction – What happens when you pull it?
Scientists often find ingenious ways to attain their research objectives, even if that objective is a truly two-dimensional material that many physicists felt could not be grown. In 2003, one ingenious physicist took a block of graphite, some Scotch tape and a lot of patience and persistence and produced a magnificent new wonder material that is a million times thinner than paper, stronger than diamond, more conductive than copper. It is called graphene, and it took the physics community by storm when the first paper appeared the following year.

The man who first discovered graphene, along with his colleague, Kostya Novoselov, is Andre Geim. Geim studied at the Moscow Physical-technical University and earned his PhD from the Institute of Solid State Physics in Chernogolovka, Russia. He spent two years at the Institute for Microelectronics Technology before taking a fellowship at nature by first making a three-dimensional material, which is graphite, and then pulling an individual layer out of it,” said Geim.

In October 2004, Geim published a paper announcing the achievement of graphene sheets in Science magazine, entitled “Electric field effect in atomically thin carbon films.” It is now one of the most highly cited papers in materials physics, and by 2005, researchers had succeeded in isolating graphene sheets. Graphene is a mere one atom thick—perhaps the thinnest material in the universe—and forms a high-quality crystal lattice, with no vacancies or dislocations in the structure. This structure gives it intriguing properties, and yielded surprising new physics.

From a fundamental standpoint, graphene’s most exciting capability is the fact that its conducting electrons arrange themselves into quasi-particles...
Graphene: most popular search word in *Nature*
Graphene beats cancer, HIV, and obesity

**Citation Report**  Topic=(graphene)  

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Graphene Research at Boston University

David Campbell (Physics), Bennett Goldberg (Physics), Ramesh Jasti (Chemistry), Harold Park (Mechanical Engineering), Antonio Castro-Neto (Physics), Claudio Chamon (Physics), Chuanhua Duan (ME), Michael El-Batanouny (Physics), Roberto Paiella (ECE), So-Young Pi (Physics), Anna Swan(ECE)
What do you know or think about Graphene?

- Worksheet, 1st page
- Draw lattice structure
- 10 minutes or so
Graphene lattice

- Single layer of graphite; sp2 bonding
  - interlayer spacing $\approx 3.4 \text{ Å}$
- Triangular Bravais lattice with 2 atom basis
  - $a \approx 1.42 \text{ Å}$
- 1 electron per orbital
  - Half filled
- Hexagonal reciprocal lattice
  - High symmetry points: $\Gamma$, $K$, $K'$

Bonding in Carbon

$sp^3$

Diamond

$sp^2$

Graphite
What does it mean when we say something is 0, 1, 2 or 3 Dimensional?

- Worksheet, 2nd page
- Define what you think dimensionality means to a physicist
0D, 1D, and 2D Carbon
Graphene - Mother of all graphitic forms

The rise of graphene
Geim and Novoselov
Nature Mat. 6 2007

2004 – Graphene 2D

1991 - Carbon nanotubes 1D

1985 – Buckyballs - 0D

Nobelprize.org
The Official Web Site of the Nobel Prize
Unusual material

• Strictly 2-dimensional material
• High mobility, $\mu \approx 2 \times 10^5 \text{cm}^2/\text{Vs}$ Bolotin et al, Solid State Comm(2008)
• Thermal conductivity, $\kappa \approx 5 \times 10^3$ W/mK Balandin et al, Nano Lett(2008)
  – Comparison to diamond $\kappa \approx 3 \times 10^3$ W/mK
• Resilience to strain, $\sigma_{\text{intrinsic}} \approx 130$ GPa Changgu et al, Science(2008)
• New physical effects
• Recommended reading:
Wide ranging applications

- Stretchable displays
- High frequency devices
- Sensors (e.g. pressure)
- Energy storage; ultracaps
- CMOS electronics
- Non volatile memory
- Biotechnology
- Coatings
Electronic structure
Electronic structure

- Conduction & valence band touch in $K, K'$, "Dirac-Points", making a semimetal
- $E_k \approx \pm v_F k + \text{higher order terms}$
  - Dispersion of massless particles
  - Analogy to relativistic physics
  - $v_F \approx 10^6 \text{m/s} \approx c/300$

\[
\begin{align*}
E_\pm(p) &= \pm v_F \sqrt{p_x^2 + p_y^2} = \pm v_F p \\
E_\pm(p, m) &= \pm \sqrt{m^2 v_F^4 + v_F^2 p^2} \quad \text{with } m = 0 \\
v_F &= \frac{3ta}{2} \approx c / 300
\end{align*}
\]
Graphene Field Effect Transistor

- Optical or ebeam lithography
- Standard semiconductor processing
- Field effect devices
- Control amount of charge in the system
- For 300nm oxide
  - $n \approx 0.7 \times 10^{11} \text{cm}^{-2} \text{V}^{-1}$
Transport

- $V_{\text{gate}}$ determines Fermi energy $E_F$
- Change type of charge carrier

\[ E_F(V_{\text{Gate}}) \]

Filled electron states

\[ \begin{align*}
| & | \\
| & | \\
| & |
\end{align*} \]

Resistivity (kΩ) vs. Gate Voltage (V)

- Dirac point
- h-conduction
- e-conduction

Conductivity
How we use light to study materials

Raman Scattering in Graphene

- Lattice structure
- Non-invasive, local probe
- Elastic properties
- Electron-phonon coupling
- ...

\[ \lambda_{out} = \lambda_{in} \pm \lambda_{ph} \]

\[ \omega = \sqrt{\frac{k}{m}} = \sqrt{\frac{\text{Stiffness}}{\text{Mass}}} \]
Phonons in Graphene

Phonon band structure of graphene

G Band
1\textsuperscript{st} order process

2D Band
2\textsuperscript{nd} order process, \(E_{2g}\)

0 momentum phonons, G-Band
2D Band
G’ Band
D* Band

BOSTON UNIVERSITY
Place uniaxial strain on graphene: symmetry of lattice broken

Raman is sensitive tool to monitor strain!
Strain Engineering of Graphene – a New Toolset

- Strain! Confinement, 1D channels, collimation,…
- Substrate patterned, not graphene
- Anisotropic in-plane hopping
- But…Challenges…
- Require high strain
- But.. Opportunities… transport

Strain measurements in graphene

- Uniaxial strain in single layer on SU8, PDMS
- G, 2D soften with strain
- Degenerate G phonon splits into polarization dependent lines

Mohiuddin, Ferrari
Graphene as impermeable membrane

- Graphene sealed micro chamber
  - Impermeability to gases
  - Confirmed even for He
- Pressure difference causes graphene membrane to bend
- Measurement of deflection
  - Direct detection (optical)
  - Measure capacitive change in the graphene – Si system

Bunch et al, Nano Lett. 2008
Graphene membranes as micro- and nano-pressure sensors

- Environmental testing of graphene material, membranes and devices
- Graphene membrane fabrication
- Measurement of fundamental mechanical properties of graphene membranes
- Demonstration of capacitance pressure sensing
How graphene slides: Measurement and theory of frictional forces between graphene and SiO$_2$

Alex Kitt, Zenan Qi, Sebastian Remi, Harold Park, Anna Swan, Bennett Goldberg
How graphene slides: Measurement and theory of **frictional forces** between graphene and SiO$_2$

Alex Kitt, Zenan Qi, Sebastian Remi, Harold Park, Anna Swan, Bennett Goldberg
Friction 101

Amontons’ (macroscopic) Laws:
Friction is...
1. Proportional to applied load, $F_N$
2. Independent of contact area

\[ f = \mu F_N \]
Fric4on

Graphene on SiO₂:

$F = \mu F_N$

Macroscopic

$F_N \sim A_c$

Microscopic

$F = \eta \nu A_c$

What happens when load isn’t needed for perfect conformation?

Krim Langmuir 12, 4654 (1996)
Frictions role in graphene devices

Flexible polymer dispersed liquid crystal device:

Graphene mechanical switch:


Strain engineered devices:

Milaninia et al. *APL* 95, 183105 (2009)

Graphene mechanical resonators:
Outline

1. Experiment
2. Qualitative observations
3. Modeling
4. Pressure and strain dependence of friction

Outline:

- Experiment
- Qualitative observations
- Modeling
- Pressure and strain dependence of friction
Experimental Design

0.1-0.8 MPa
15-100 psi
N₂ gas
Dual role or pressure

Pressure acts as a load

Pressure pulls graphene

5 \mu m
Raman G band strain response

Perturbing the inter-ionic forces with strain:

\[ \Delta \omega_G = -\omega_0 \gamma (\epsilon_{xx} + \epsilon_{yy}) \pm \frac{1}{2} \beta \sqrt{(\epsilon_{xx} - \epsilon_{yy})^2 + 4\epsilon_{xy}^2} \]

<table>
<thead>
<tr>
<th></th>
<th>( \gamma )</th>
<th>( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Huang et al. 2009</td>
<td>.69</td>
<td>.38</td>
</tr>
<tr>
<td>Mohiuddin et al. 2009</td>
<td>1.99</td>
<td>.99</td>
</tr>
<tr>
<td>Metzger et al. 2010</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>Frank et al. 2010</td>
<td>2.01</td>
<td>1.01</td>
</tr>
<tr>
<td>Yoon et al. 2011</td>
<td>2.2</td>
<td>.93</td>
</tr>
<tr>
<td>Zabel et al. 2012</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>Cheng et al. 2011</td>
<td>1.86</td>
<td>.96</td>
</tr>
</tbody>
</table>
Qualitative results: Sliding!

1. Supported graphene strained
2. Strain further distributed at higher pressure
3. Reproducible
   - Spatially
   - Temporally
   - 8 devices
     - 1, 2, and 3 layers
     - $R=1.2$ to 5 $\mu$m
Compressive tangential strain

\[ \varepsilon_{tr} = 0.6\% \]
\[ \varepsilon_{tt} = -0.3\% \]

D=10 μm monolayer
P=0.08 MPa=115 psi
Can’t simply invert spectra to get strains

D=10 µm monolayer
P=0.08 MPa=115 psi
Pressure dependence of friction

1. Trilayer graphene
2. Monolayer and bilayer graphene
3. Microscopic explanation
Pressure dependence

![Graph showing pressure dependence of sliding friction. The graph plots pressure (P in MPa) on the x-axis and sliding friction (f in MPa) on the y-axis. There are four different layers: Monolayer, Bilayer, Trilayer, and a line marked R 5.0m. Each layer has a specific radius: R = 1.2 m, R = 2.0 m, R = 3.0 m, and R = 5.0 m. The graph indicates how the sliding friction changes with pressure for each layer.]
Trilayer graphene

Amontons’ law:

\[ F_f = \mu F_N \]
\[ f = \mu P \]

<table>
<thead>
<tr>
<th></th>
<th>( \mu )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teflon on Teflon</td>
<td>0.04</td>
</tr>
<tr>
<td>Trilayer on SiO2</td>
<td>0.1</td>
</tr>
<tr>
<td>Metal on Wood</td>
<td>0.2-0.6</td>
</tr>
</tbody>
</table>

Graph showing sliding friction vs. pressure for different layers:

- Trilayer
- Metal on Wood

\( \mu = 0.099 \pm 0.07 \)

Pressure, \( P \) \( \text{MPa} \)
Monolayer and bilayer?

Sliding friction:

1. Decreases with pressure?
2. Decreases with radius?
Dual role or pressure

Pressure acts as a load

Pressure pulls graphene

5 μm
Friction as a function of strain
Microscopic explanation

Trilayer

Mono and bilayer

Pressure increases conformation

Strain smooths out graphene

Cullen et al. PRL 105, 215504 (2010)