From Graphene to Graphite to Nanotubes to Graphene

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Outline

• Historical Graphene to Graphene path
• Carbon Nanotubes as Prototype Materials
• Disordered Graphite
• Graphene and Graphene Ribbons
• Looking to the Future of Carbon Nanostructures
Graphene is the Mother of all nano-Graphitic forms

- A graphene sheet is one million times thinner \((10^{-6})\) than a sheet of paper.
- Graphene is a 2D building block material for other \(sp^2\) bonded carbon materials. It can be wrapped up into 0D fullerenes, rolled into 1D nanotubes, cut into 1D graphene ribbons or stacked into 3D graphite.
From graphene to graphite to fullerenes to nanotubes to graphene

In the opening overview, we follow a path:
- from the early work on graphene
- to the developments in graphite
- to graphite intercalation compounds
- to fullerenes
- to nanotubes
- and then back to graphene
The Electronic Structure of Graphene is the starting point for the electronic structure of graphite

P.R. Wallace, Phys. Rev. 71, 622 (1947)

Near the K point

linear $\kappa$ relation

where

and

and is the overlap integral between nearest neighbor $\pi$-orbitals

($\gamma_0$ values are from 2.9 to 3.1 eV)
2D Graphite (Graphene) unit cells

Direct lattice

First Brillouin zone (BZ)

\[
\vec{a}_1 = \frac{a}{2} \left( \sqrt{3} \hat{x} + \hat{y} \right)
\]

\[
\vec{a}_2 = \frac{a}{2} \left( -\sqrt{3} \hat{x} + \hat{y} \right)
\]

\[
a = 2.456 \text{ Å}
\]

\[
\vec{b}_1 = \frac{2\pi}{a} \left( \frac{\sqrt{3}}{3} \hat{k}_x + \hat{k}_y \right)
\]

\[
\vec{b}_2 = \frac{2\pi}{a} \left( -\frac{\sqrt{3}}{3} \hat{k}_x + \hat{k}_y \right)
\]
Energy bands of 2D Graphite (graphene)


- $\pi$ bands of graphene
  - Unit Cell, B. Z.

- Graphene is a zero gap semiconductor

\[
\begin{align*}
\mathbf{a}_1 &= \left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right)a, \quad \mathbf{a}_2 = \left(\frac{\sqrt{3}}{2}, -\frac{1}{2}\right)a \\
\mathbf{b}_1 &= \left(\frac{1}{2}, \frac{\sqrt{3}}{2}\right)\frac{4\pi}{\sqrt{3}a}, \quad \mathbf{b}_2 = \left(\frac{1}{2}, -\frac{\sqrt{3}}{2}\right)\frac{4\pi}{\sqrt{3}a} \\
E_k &= \pm t \sqrt{1 \pm 4 \cos \frac{k_y a}{2} \cos \frac{\sqrt{3} k_x a}{2} + 4 \cos^2 \frac{k_y a}{2}}
\end{align*}
\]
3D Graphite

4 atoms/unit cell

Direct lattice

AB layer stacking

\[ \vec{a}_1 = \frac{a}{2} \left( \sqrt{3} \hat{x} + \hat{y} \right) \]

\[ \vec{a}_2 = \frac{a}{2} \left( -\sqrt{3} \hat{x} + \hat{y} \right) \]

\[ \vec{a}_3 = c \hat{z} \]

\[ a = 2.456 \text{ Å} \]

\[ c = 6.6708 \text{ Å} \]

First Brillouin zone

\[ \vec{b}_1 = \frac{2\pi}{a} \left( \frac{\sqrt{3}}{3} \hat{k}_x + \hat{k}_y \right) \]

\[ \vec{b}_2 = \frac{2\pi}{a} \left( -\frac{\sqrt{3}}{3} \hat{k}_x + \hat{k}_y \right) \]

\[ \vec{b}_3 = \frac{2\pi}{c} \hat{k}_z \]
Extension of Graphene to Graphite

- McClure extended 2D graphene electronic structure calculation to 3D graphite.
- Magneto-optical experiment measured energy bands of graphite at several regions of the Brillouin zone (near K and H)

M.S. Dresselhaus and J.G. Mavroides. IBM Journal of Research and Development 8, 262 (1964)

- Experiment (1961) was enabled by the availability of a new material, highly oriented pyrolytic graphite (HOPG) Ubbelohde (1960)
- Used symmetry-based E(k) model of McClure to yield band parameters for the electronic structure of graphite.

Identification of Electrons and Holes in Graphite

Using circular polarized radiation in the first magneto-optical experiment to use a laser, the locations of electrons and holes in the Brillouin zone were identified.

Experiment showed that electrons were located near K (K’)


The locations of electrons and holes are incorrectly given in the literature, prior to 1968. The effective masses for electrons and holes in graphite are often used in the current graphene literature.
Spintronics in Graphene

• An early paper by Gene Dresselhaus defined what is now known as the “Dresselhaus spin-orbit term” in III-V semiconductors {G. Dresselhaus, Phys. Rev. 71, 220 (1955)} with $E(k)$ having a linear $k$-dependence. A model for the spin-orbit interaction in graphite as imposed by symmetry was developed {G. Dresselhaus & M.S. Dresselhaus, Phys. Rev. 140, A401 (1965)}.

• Since the spin-orbit interaction in graphite is very small, the spin lifetime in graphene can be very long. Therefore graphene has become an interesting material for studying spin transport.
Entry into the Nanoworld

• Through the unexpected observation by Hannay et al. at AT&T Bell Labs of superconductivity in stage 1 graphite intercalation compounds (C₈K) (Hannay et al, Phys.Rev.Lett. 14, 225 (1965) much interest was aroused since neither potassium nor carbon is superconducting.

• Intercalation compounds allowed early studies to be made of individual or few graphene layers in the environment of the intercalant species.
Low Dimensional Science Studies in Graphite Intercalation Compounds (1973-1993)

Magnetoreflection
Transport
Raman
Optical
Structural
Magnetic
Superconductivity

Studies on single or few layer Graphene were carried out in the environment of the intercalant species were carried out by many researchers.
Concurrent Studies on Forerunners to Fullerenes

Intercalation led to ion implantation and laser irradiation of graphite

- Liquid carbon studies (1983)

  *Liquid carbon was found to be metallic*


- The Laser ablation process used to make liquid carbon produced large clusters (like $C_{100}$) rather than $C_2$ or $C_3$

- Trip to Exxon Research Lab to discuss results.

- Soon Exxon published famous result showing mass spectroscopy intensity vs numbers of C atoms in clusters with peaks at $C_{60}$ and $C_{70}$

- The Exxon result led to the discovery of fullerenes by Kroto, Smalley and Curl (1985)

Forerunners of Carbon Nanotubes

• Vapor grown carbon fibers
• At center of these carbon fibers is a multiwall carbon nanotube
• A connection between fullerenes and nanotubes was made by going from $C_{60} \rightarrow C_{70} \rightarrow C_{80} \rightarrow$ nanotubes
• This idea suggested that a single wall Carbon nanotube would be interesting (August 1991) and led to calculating the electronic structure of SWNTs before they were ever seen

M.S. Dresselhaus et al., Graphite Fibers and Filaments, Springer (1988)
Saito, Fujita, Dresselhaus$^2$, Electronic structure of carbon fibers based on $C_{60}$.
Unique One Dimensional (1D) Properties

Carbon nanotubes and nanoribbons have:

- High aspect ratio
- Enhanced density of states in 1D
- Molecular behavior (spikes in DOS)
- Solid state behavior (tails in DOS)
General Relations between 1D and 2D Systems shown in terms of carbon nanotubes

Rolling up a 2D sheet

Confinement of 1D electronic states on cutting lines

1D van Hove singularities give high density of electronic states (DOS) at well defined energies

- Carbon nanotubes are metallic if cutting line passes through the K point
- Otherwise they are semiconducting
Unique Properties of Carbon Nanotubes within the Nanoworld

- **Small size:** \( \sim 1 \text{ nm diameter (down to } \sim 10 \text{ atoms around the circumference) } \)

- **Electronic Properties:** can be either metallic or semiconducting depending on diameter and orientation of the hexagons

- **Mechanical:** Very high strength, modulus, and resiliency.

- **Physics:** model system for 1D density of electronic states.

- **Single molecule Raman spectroscopy, luminescence and transport properties.**
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Nanotube Structure in a Nutshell

Graphene Sheet  SWNT

Rolled-up graphene layer with a large unit cell.

(4,2)

Each \((n,m)\) nanotube is a unique molecule

R.Saito et al, Imperial College Press, 1998
Carbon Nanotubes

- (5,5) Armchair Nanotube
- (9,0) Zigzag Nanotube
- (6,5) Chiral Nanotube

Hemispherical fullerene caps are shown for armchair and zigzag nanotubes.
Energy Bands of Nanotubes


- $N$ one-dimensional electronic energy bands

\( (5,5) \) \hspace{1cm} \( (9,0) \) \hspace{1cm} \( (10,0) \)
Metallic Carbon Nanotubes


• 1D Energy Dispersion of SWNT
  – K point is always on a cutting line
  – Two inequivalent neighboring cutting lines --- cause splitting in the density of states

\[ |K_1| = \frac{2}{d_i} \]
Semiconducting Carbon Nanotubes


- K points are always at 1/3 (or 2/3) position
  - Two neighboring lines contribute to different energies
  - No DOS splitting for any chirality

DOS(10,0)
STM/STS Experiments

Identified metallic and semiconducting nanotubes


Each \((n,m)\) SWNT has a unique electronic structure.
Resonance Raman Spectroscopy (RRS)


- Enhanced Signal

✓ Optical Absorption
✓ e-DOS peaks

Raman spectra from SWNT bundles

Trigonal warping effect

\[ E = 0.94\text{eV} \]
\[ = 1.17\text{eV} \]
\[ = 1.58\text{eV} \]
\[ = 1.92\text{eV} \]
\[ = 2.41\text{eV} \]

Diameter-selective resonance process

\[ \omega_{RBM} = \frac{\alpha}{d_t} \]

Confirms:

- Resonant DOS
- Each \((n,m)\) tube has different spectrum
Resonant Raman Spectra of Carbon Nanotube Bundles


Metallic and semiconducting tubes have different lineshapes

G-band resonant Raman spectra

\[ d_t = 1.37 \pm 0.18 \text{ nm} \]
Single Nanotube Spectroscopy yields $E_{ii} \ (n,m)$

Therefore the geometrical structure of an individual carbon nanotube can be found by Raman spectroscopy.


Raman signal from *one* SWNT indicates a strong resonance process

\[ (\omega_{RBM}, E_{ii}) \rightarrow (n,m) \]

Each nanotube has a unique DOS because of trigonal warping effects.

Raman Spectra of SWNT Bundles

- RBM gives tube diameter and diameter distribution
- Raman D-band characterizes structural disorder
- G\textsuperscript{-} band distinguished M, S tubes and G\textsuperscript{+} relates to charge transfer
- G\textsuperscript{'} band (2nd order of D-band) provides connection of phonon to its wave vector
- Each feature in the Raman spectra provides complementary information about nanotubes
Band Gap Fluorescence


Good method to determine the (n,m) of semiconducting nanotubes in a given sample

e-DOS of (n, m) = (10,5)
Excitons in Carbon Nanotubes

Experimental Justification for excitons

2-photon excitation to a $2A^+$ symmetry exciton (2p) and 1-photon emission from a $1A^-$ exciton (1s) cannot be explained by the free electron model

The observation that excitation and emission are at different frequencies supports exciton model rather than free electron model

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Raman spectra of graphitic materials: defect detection.


G band: Second harmonic of D band. (also called 2D band)

Nanostructured graphite with defects

G band: Defect-induced D band: (iTO mode at the K point)
Intravalley double-resonance process explains the D’ band process.

\[ k_0 = \hbar \omega_I / 2v_F \]
\[ k_1 = k_0 - \hbar \omega_q / v_F \]

Intervalley double-resonance process
Explains the origin of the D-band
Scattering by defect in an energy conserving process

Intravalley vs. intervalley double-resonance processes


- **G band**: first order allowed (closed to the Γ point).
- **D' band**: double resonance intravalley process.
- **D and G' bands**: double resonance intervalley process.
Determination of the average crystallite size $L_a$ of nanographite films by STM and X-ray diffraction using synchrotron radiation

The values of $L_a$ obtained by STM and X-ray diffraction are in good agreement:

<table>
<thead>
<tr>
<th>HTT (°C)</th>
<th>$L_a$ (nm) (X ray)</th>
<th>$L_a$ (nm) (STM)</th>
</tr>
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<tbody>
<tr>
<td>2700</td>
<td>490</td>
<td>550</td>
</tr>
<tr>
<td>2600</td>
<td>340</td>
<td>300</td>
</tr>
<tr>
<td>2400</td>
<td>190</td>
<td>220</td>
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<tr>
<td>2300</td>
<td>150</td>
<td>120</td>
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<td>2200</td>
<td>65</td>
<td>60</td>
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<tr>
<td>2000</td>
<td>35</td>
<td>40</td>
</tr>
<tr>
<td>1800</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>

Dependence of the ratio $I_D / I_G$ on the crystallite size $L_a$ in the Raman spectra of disordered graphite

\[ L_a = \kappa \left[ \frac{I_D}{I_G} \right]^{-1} \]


\[ \kappa = 4.4\text{nm for} \lambda = 514.5 \text{ nm (2.41eV)} \]

Dependence of the ratio $I_D / I_G$ on the excitation laser energy $E_l$ in the Raman spectra of disordered graphite.

General equation for the determination of the crystallite size $L_a$ of nanographite by Raman spectroscopy

$$L_a (\text{nm}) = \frac{560}{E_l^4} \left( \frac{I_D}{I_G} \right)^{-1}$$

$$L_a (\text{nm}) = (2.4 \times 10^{-10}) \lambda_l^4 \left( \frac{I_D}{I_G} \right)^{-1}$$

Measuring the dependence of the differential cross section of the Raman bands in graphite on the excitation laser energy $E_l$

Measuring the dependence of the differential cross section of the Raman bands in graphite on the excitation laser energy $E_l$

- G band is proportional to $E_l^4$.
- D, D' and G' bands do not depend on $E_l$.

Quantifying the stacking order in nanographites by Raman spectroscopy

\[ V = V_{3D} + V_{2D} \]

\[ \nu_{3D} = \frac{V_{3D}}{V} \quad \text{and} \quad \nu_{2D} = \frac{V_{2D}}{V} \]

\[
\begin{align*}
  c \text{ (nm)} &= 0.682 - 0.11R \\
  L_c \text{ (nm)} &= 10 + \frac{10}{1.05 - R}
\end{align*}
\]

\[
R = \frac{I_{G'_{3DB}}}{I_{G'_{3DB}} + I_{G'_{2D}}} \\
v_{3D} = R, \quad \text{and} \quad v_{2D} = 1 - R
\]

Cançado et al., Carbon 46, 272 (2008).
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Electronic structures of graphene and bilayer graphene

Raman G' band identifies the number of layers

Distinguishes graphite from graphene

- \( G' \) (3D graphite) – two peaks
- \( G' \) (2D graphite) – one peak

Identifies the number of graphene layers

- Gupta et al., Nanoletters 6, 2667 (2006).
Raman confocal image of single graphene layer

The D band is detected only at the edges in contrast to the G-band and G′-band.
Near-field optics

Conventional microscope

Near-field microscope

Conventional microscopy limited by diffraction effects.

Near-field microscopy permits independent interaction between tip and sample.

*Abbé, Arch. Mikrosk., Anat., (1873).*

*Wessel, JOSA B, (1985).*

*Novotny et al., Ultramicroscopy, (1998).*
STRUCTURAL DEFECTS IN BURIED NANOTUBES

Topography:

Confocal Raman:

Near-field Raman:

Structural variations (defects, branching, .. ) hidden in confocal imaging!

Nano Lett. 6, 744 (2006).
Out-of-plane modes show larger enhancement than in-plane modes:

In near field optics

L.G.Cancado, unpublished work
Graphene Ribbons

Zigzag

Armchair

Direction of cutting lines

- Special feature of graphene ribbons is that they have edges and few columns of carbon atoms along the width.
Electronic structure of graphene ribbons

Armchair

- Metallic for $N=3M-1$ (M integer)
- Semiconducting for $N=3M$ & $3M-2$

Examples:
- Metallic for $N=5$
- and Semiconducting for $N=4$, 6

Zigzag

- Always metallic
- Presence of localized edge states at the Fermi level

Van Hove singularities in the DOS

Unique Properties of Graphene Nanoribbons

- A special feature of graphene ribbons is their long edges with narrow widths.
- The crystallographic orientation of the edges strongly influences their electronic and other properties.
- Zigzag ribbons show a high density of states at $E_F$ and are zero gap semiconductors.
- Armchair edge ribbons (like single wall carbon nanotubes) can be either metallic ($N=3M-1$) or semiconducting ($N=3M$, $N=3M+1$), where $N,M$ are integers.

$N=$number of hexagon columns along the ribbon width.
Raman structure used to Identify graphene nanoribbons

AFM image of many graphene nanoribbons parallel to each other:

AFM image of a graphene nanoribbon:

STM image of a zigzag ribbon:


Synthesis:
• Electrophoretic deposition of nano-diamond particles on a HOPG substrate.
• At a HTT of 1600°C, the nano-diamond particles are graphitized, forming nanographite sheets and ribbons.

Raman spectra of graphene nanoribbons


\[ W(\vec{k}) \propto |\vec{P} \times \vec{k}|^2 \]
Influence of the atomic structure in the Raman spectra of graphite edges


$I_{D1} > I_{D2}$

$I_{D'1} \sim I_{D'2}$
Influence of the atomic structure in the Raman spectra of graphite edges

Edge 1: Armchair

Edge 2: Zigzag

The $D$ band Raman spectra are used to distinguish between armchair and zigzag edges

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Outlook

- 1D carbon nanotubes continue to be an expanding field, now focusing more heavily on applications.
- 1D carbon nanoribbons is a newly emerging field that is expected to grow rapidly in the near future, particularly if higher quality ribbons can be made.
- The synergy between nanotubes, graphene and nanoribbons will surely enrich one another strongly in advancing both their nanoscience and applications.
More emphasis now is on applications

Potential Applications of Carbon Nanotubes

Chapter by M. Endo, M. S. Strano, P. M. Ajayan @ Springer

TAP111

<table>
<thead>
<tr>
<th>Large Volume Applications</th>
<th>Limited Volume Applications (Mostly based on Engineered Nanotube Structures)</th>
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<tbody>
<tr>
<td>Present</td>
<td></td>
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<tr>
<td>- Battery Electrode Additives (MWNT)</td>
<td>- Scanning Probe Tips (MWNT)</td>
</tr>
<tr>
<td>- Composites (sporting goods; MWNT)</td>
<td>- Specialized Medical Appliances (catheters) (MWNT)</td>
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<tr>
<td>- Composites (ESD* applications; MWNT)</td>
<td></td>
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<tr>
<td>- (*ESD – Electrical Shielding Device)</td>
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<tr>
<td>Near Term (less than ten years)</td>
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<tr>
<td>- Battery and Super-capacitor Electrodes</td>
<td>- Single Tip Electron Guns</td>
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<tr>
<td>- Multifunctional Composites</td>
<td>- Multi-Tip Array X-ray Sources</td>
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<tr>
<td>- Fuel Cell Electrodes (catalyst support)</td>
<td>- Probe Array Test Systems</td>
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<tr>
<td>- Transparent Conducting Films</td>
<td>- CNT Brush Contacts</td>
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<tr>
<td>- Field Emission Displays / Lighting</td>
<td>- CNT Sensor Devices</td>
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<tr>
<td>- CNT based Inks for Printing</td>
<td>- Electro-mechanical Memory Device</td>
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<tr>
<td>- CNT based Inks for Printing</td>
<td>- Thermal Management Systems</td>
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<tr>
<td>Long Term (beyond ten years)</td>
<td></td>
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<tr>
<td>- Power Transmission Cables</td>
<td>- Nano-electronics (FET,Interconnects)</td>
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<tr>
<td>- Structural Composites (aerospace and automobile etc.)</td>
<td>- Flexible Electronics</td>
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<tr>
<td>- CNTs in Photovoltaic Devices</td>
<td>- CNT based bio-sensors</td>
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<td>- CNT Filtration/Separation Membranes</td>
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<td>- Drug-delivery Systems</td>
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The End