Graphene Thermal Physics

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- Heat capacity of graphene
- Thermal conductivity of graphene
- Graphene devices
- “Other” physics
  (thermoelectrics, asymmetry, quantum thermal conductance...)

+ Background
• Graphite is highly asymmetric
• **Strong** in-plane covalent sp\(^2\) sigma bonds (524 kJ/mol)
• **Weak** out-of-plane van der Waals pi bonds (7 kJ/mol)

### Heat Capacity: Energy Stored \(\Delta U = C\Delta T\)

- **Heat capacity of a solid:** \(C = C_{\text{electrons}} + C_{\text{lattice}}\)

\[
C_L = \frac{du}{dT} = \int h\omega \frac{df(\omega)}{dT} g(\omega) d\omega
\]

- **High temperature:** classically recall \(C = 3N_A k_B\)
  Dulong-Petit Law (1819) → most solids → 25 J/mol/K at high T
- **Low temperature:** experimentally \(C \rightarrow 0\)
• Transverse ($u \perp k$) vs. longitudinal modes ($u \parallel k$)
• Acoustic (transport sound & heat) vs. optical (scatter light & electrons)
• “Hot phonons” = highly occupied modes above room temperature

\[ u(r, t) = A \exp[i(k \cdot r - i\omega t)] \]

\[ \nu_2 = \frac{d\omega}{dk} \]

- Lattice Constant, $a$
- 2 atoms per unit cell

Graphene Phonons [100]

- Acoustic
- Optical

<table>
<thead>
<tr>
<th>Frequency (cm$^{-1}$)</th>
<th>Energy (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>30 meV</td>
</tr>
<tr>
<td>800</td>
<td>60 meV</td>
</tr>
<tr>
<td>1200</td>
<td>90 meV</td>
</tr>
<tr>
<td>1600</td>
<td>120 meV</td>
</tr>
</tbody>
</table>

- $\omega = \sqrt{\frac{\pi}{\hbar}}$ for Si optical
- $\omega = \frac{\hbar k}{m^*}$ for 300 K = 26 meV

- Graphene Phonons [100]
- 200 meV
- 160 meV
- 100 meV

\[ \exp\left(\frac{E}{k_B T}\right) \]

\[ \exp\left(\frac{-E}{k_B T}\right) \]

- Fermi-Dirac vs. Bose-Einstein Statistics

\[ f_{FD}(E) = \frac{1}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1} \]

\[ f_{BE}(E) = \frac{1}{\exp\left(\frac{E}{k_B T}\right) - 1} \]

- Fermions = half-integer spin (e.g. electrons, protons)
- Bosons = integer spin (e.g. phonons, photons)

- In the limit of high energy, both reduce to the classical Maxwell-Boltzmann statistics:
  \[ f_{MB}(E) \approx \exp\left(-\frac{E}{k_B T}\right) \]
Heat Capacity: Dielectrics vs. Metals

- Very high T: \( C = 3nk_B \) (constant) both dielectrics & metals
- Intermediate T: \( C \sim aT^D \) both dielectrics & metals in D dimensions*
- Very low T: \( C \sim bT \) metals (electron contribution only)

* assuming linear \( \omega = \nu k \) phonon dispersion

Heat Capacity: Einstein Model (1907)

- Key assumption: all oscillators have same frequency
- High-T (correct, recover Dulong-Petit Law):
  \[ C_E(T) \approx 3Nk_B \]
- Low-T (incorrect, drops too fast)
  \[ C_E(T) \approx 3Nk_B \left( \frac{\hbar \omega_0}{k_BT} \right)^2 e^{-\frac{\hbar \omega_0}{k_BT}} \]

But... Einstein model OK for optical phonon heat capacity

Fig. 6.2 Comparison of experimental values of the heat capacity of Si and the Einstein model, using \( \omega_0 = 1200\text{cm}^{-1} \). After A. Einstein, Ann. Phys. 23, 188 (1907).
Heat Capacity: Debye Model (1912)

- Key assumption: oscillators have linear $\omega - k$ with cutoff $\omega_D$
- Often in terms of Debye temperature

$$\theta_D = \frac{\hbar v_s}{k_B} \left( \frac{6\pi^2 N}{3} \right)^{\frac{1}{3}}$$

- ... roughly corresponds to max acoustic phonon frequency cutoff $k_B \theta_D = \hbar \omega_D$
- Low-$T$ ($< \theta_D/10$):

$$C_D(T) \approx \frac{12\pi^4}{5} N k_B \left( \frac{T}{\theta_D} \right)^3$$

- High-$T$: ($> 0.8 \theta_D$)

$$C_D(T) \approx 3Nk_B$$

In D-dimensions when $T << \theta_D$:

$$C_D \propto T^D$$
Debye Model at Low- and High-T

- In practice: $\theta_D \sim$ fitting parameter to heat capacity data
- $\theta_D$ is related to “stiffness” of solid and melting temperature

### Debye Temperatures

<table>
<thead>
<tr>
<th>Element</th>
<th>$\theta_D$ (°K)</th>
<th>Compound</th>
<th>$\theta_D$ (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>335</td>
<td>NaCl</td>
<td>280</td>
</tr>
<tr>
<td>Na</td>
<td>156</td>
<td>KCl</td>
<td>230</td>
</tr>
<tr>
<td>K</td>
<td>91.1</td>
<td>CaF$_2$</td>
<td>470</td>
</tr>
<tr>
<td>Cu</td>
<td>343</td>
<td>LiF</td>
<td>680</td>
</tr>
<tr>
<td>Ag</td>
<td>226</td>
<td>SiO$_2$ (quartz)</td>
<td>255</td>
</tr>
<tr>
<td>Au</td>
<td>162</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>428</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ga</td>
<td>325</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>102</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>378</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Si $\theta_D$ = 647
- Graphite
  - in-plane (sp2) $\theta_D$ = 2480
  - out-of-plane (vdW) $\theta_D$ = 180

*To resolve low-temperature heat capacity “quandary” since graphene data was neither 2-D ($T^2$) nor 3-D ($T^3$)*

### Diamond “like” silicon:
- Longitudinal & transverse (x2) acoustic (LA, TA)
- Longitudinal & transverse (x2) optical (LO, TO)

### Graphite is unusual:
- Layer-shearing, -breathing, and -bending modes (ZA, ZO)
- Higher optical freq. than diamond, strong sp$^2$ bond stretching modes
- Graphite has more low-frequency modes

Graphite has higher phonon DOS at low frequency $\rightarrow$ higher heat capacity than diamond at room $T$

Both increase up to Debye temperature range, then reach “classical” $3N_Ak_B$ limit

Pierson (1993)

Phonon Dispersion in Graphene

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  (thermoelectrics, asymmetry, quantum thermal conductance...)

Thermal Conductivity of Solids

Unlike electrical conductivity, thermal spans “only” 4 orders of magnitude
**Thermal Conductivity: Kinetic Theory**

Integrate energy flux over all angles:

\[ J_q = -\frac{1}{3} v \lambda \frac{du}{dt} \frac{dz}{dz} = -k \frac{dT}{dz} \]

Thermal conductivity:

\[ k = \frac{1}{3} C_v \lambda \]

**Heat diffusion eq:**

\[ \nabla \cdot (k \nabla T) - q'' = 0 \]

**Poisson eq:**

\[ \nabla \cdot (e \nabla V) - \rho = 0 \]

**Thermal Conductivity and Phonon MFP**

- Heat capacity depends on \( \omega(k) \) and \( T \)
- Phonon group velocity depends only on \( \omega(k) \)
- Mean free path \( \lambda \) to phonon scattering mechanisms:
  - Boundary & edge scattering
  - Defect & impurity scattering
  - Phonon-phonon scattering \( \sim \frac{1}{T} \)

<table>
<thead>
<tr>
<th></th>
<th>( C )</th>
<th>( \lambda )</th>
<th>( k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>low ( T )</td>
<td>( \propto T^d )</td>
<td>( \lambda \rightarrow L \text{ (size)} )</td>
<td>( \propto T^d )</td>
</tr>
<tr>
<td>high ( T )</td>
<td>( 3Nk_B )</td>
<td>( \propto \frac{1}{T} )</td>
<td>( \propto \frac{1}{T} )</td>
</tr>
</tbody>
</table>

\[ k \approx \frac{1}{3} C_v \lambda \approx \frac{1}{3} C v^2 \tau \]
Thermal Conductivity of Graphite*

* typical commercial pyrolytic graphite

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal Conductivity (W/m·K) at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolytic graphite:</td>
<td></td>
</tr>
<tr>
<td>ab directions</td>
<td>390</td>
</tr>
<tr>
<td>c direction</td>
<td>2</td>
</tr>
<tr>
<td>Graphite fiber (pitch-based)</td>
<td>1160</td>
</tr>
<tr>
<td>Diamond (Type II)</td>
<td>2000 - 2100</td>
</tr>
<tr>
<td>Silver</td>
<td>420</td>
</tr>
<tr>
<td>Copper</td>
<td>385</td>
</tr>
<tr>
<td>Beryllium oxide</td>
<td>260</td>
</tr>
<tr>
<td>Aluminum nitride</td>
<td>200</td>
</tr>
<tr>
<td>Alumina</td>
<td>25</td>
</tr>
<tr>
<td>Silicon</td>
<td>140</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.4</td>
</tr>
</tbody>
</table>

High (100-1000x) thermal anisotropy in all graphite

Pierson (1993)

Graphene Thermal Conductivity (Theoretical)

- **Graphite** ab- thermal conductivity generally lower because of interlayer interactions (could be same for graphene on substrate)
- **Graphite** \( \sim T^{2.5} \) at very low T due to bending modes \( \omega \sim k^2 \)
- **Graphene** \( \sim T^{1.5} \) at very low T due to \( \omega \sim k^2 \)

The Imprint of Dimensionality

Phonon dispersion $\rightarrow$ phonon DOS $\rightarrow$ heat capacity $\rightarrow k \sim C v \lambda$

Information about dimensionality of system can be obtained from low-temperature k-T (or C-T) measurements

Ex: Si nanowires ~ from 1-D to 3-D features!

Graphene Thermal Conductivity (Experimental)

- Graphene flakes suspended over SiO$_2$ trenches ($\sim$3 um wide)
- Thermometry using Raman G-band (1583 cm$^{-1}$) shift
- Room temperature results in-line with existing CNT data

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>$k$ (W/mK)</th>
<th>Method</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC</td>
<td>~3000-5150</td>
<td>optical</td>
<td>individual; suspended</td>
</tr>
<tr>
<td>MW-CNT</td>
<td>~3000</td>
<td>electrical</td>
<td>individual; suspended</td>
</tr>
<tr>
<td>SW-CNT</td>
<td>~3500</td>
<td>electrical</td>
<td>individual; suspended</td>
</tr>
<tr>
<td>SW-CNT</td>
<td>~3500</td>
<td>electrical</td>
<td>suspended</td>
</tr>
<tr>
<td>Bulk graphite</td>
<td>500-2000 max &gt;2000</td>
<td>thermocouples</td>
<td>Variety</td>
</tr>
</tbody>
</table>

Wiedemann-Franz Law

- Q: what is the electronic contribution to thermal transport?
- Wiedemann & Franz (1853) empirically saw $\frac{k_e}{\sigma} = \text{const}(T)$
- Lorenz (1872) noted $\frac{k_e}{\sigma}$ proportional to $T$

\[
\begin{align*}
\kappa_e &= \frac{1}{3} \left( \frac{\pi^2}{2} \frac{k_B^2 n}{E_F} \right) v_F^2 \tau \\
\sigma &= q \mu m = \frac{q^2 \tau}{m} n
\end{align*}
\]

Taking the ratio:

\[
L_0 = \frac{\kappa_e}{\sigma T} = \frac{\pi^2 k_B^2}{3 q^2}
\]

Remarkable: independent of $n$, $m$, and even $\tau$!

- Graphene electronic contribution appears <10% throughout $T$ range

<table>
<thead>
<tr>
<th>Experimentally</th>
<th>$L = \kappa / \sigma T$</th>
<th>$10^8 \text{ W} \Omega / \text{K}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal</td>
<td>$0 \degree \text{C}$</td>
<td>$100 \degree \text{C}$</td>
</tr>
<tr>
<td>Cu</td>
<td>2.23</td>
<td>2.33</td>
</tr>
<tr>
<td>Ag</td>
<td>2.31</td>
<td>2.37</td>
</tr>
<tr>
<td>Au</td>
<td>2.35</td>
<td>2.40</td>
</tr>
<tr>
<td>Zn</td>
<td>2.31</td>
<td>2.33</td>
</tr>
<tr>
<td>Cd</td>
<td>2.42</td>
<td>2.43</td>
</tr>
<tr>
<td>Mo</td>
<td>2.61</td>
<td>2.79</td>
</tr>
<tr>
<td>Pb</td>
<td>2.47</td>
<td>2.56</td>
</tr>
</tbody>
</table>

$L_0 = 2.45 \times 10^{-8} \text{ W} \Omega / \text{K}^2$

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E. Pop / DRC 2009
Background on Thermal Resistance

Ohm’s Law (1827)

\[ P = I^2 \times R \]

\[ \Delta T = P \times R_{th} \]

\[ \Delta V = I \times R_{el} \]

\[ R_{th} = \frac{L}{kA} \]

\[ R = f(\Delta T) \]

\[ R_{el} = \frac{\rho L}{A} \]

Fourier’s Law (1822)

Thermal-Electrical Cheat Sheet

\[ J_q = -k \nabla T \]

\[ \nabla \cdot (k \nabla T) - q''' = 0 \]

\[ R_{th} = \frac{L}{kA} \]

\[ J_{diff} = -qD\nabla H \]

\[ \nabla \cdot (\epsilon \nabla V) - \rho = 0 \]

\[ R_{el} = \frac{\rho L}{A} \]
Thermal Resistance of Devices

High thermal resistances:
- SWNT due to small thermal conductance (very small d ~ 2 nm)
- Others due to low thermal conductivity, decreasing dimensions, increased role of interfaces

Power input also matters:
- SWNT ~ 0.01-0.1 mW
- Others ~ 0.1-1 mW


Modeling Device Thermal Response

- Steady-state models
  - Finite-Element models
- Transient models

\[ R_{TH} \approx \frac{1}{2k_{Si}D} \approx \frac{1}{2k_{Si}\sqrt{LW}} \]

\[ R_{TH} \approx \frac{1}{2W} \left( \frac{t_{BOX}}{k_{BOX}k_{Si}t_{Si}} \right)^{1/2} \]
Graphene FET

Assumptions:
\[ t_{ox} = 300 \text{ nm} \]
\[ L = 25 \text{ um} \]
\[ W = 6 \text{ um} \]
\[ k_{ox} = 1.3 \text{ Wm}^{-1}\text{K}^{-1} \]
\[ k_{si} = 80 \text{ Wm}^{-1}\text{K}^{-1} \]

\[ \frac{T_W}{T_G} \approx 0.29 \]
\[ R_{in} \approx \frac{t_{ox}}{k_{ox}LW} \approx 1538 \frac{K}{W} \]
\[ R_{si} \approx \frac{1}{2k_{si}\sqrt{LW}} \approx 510 \frac{K}{W} \]
\[ \frac{T_W}{T_G} \approx \frac{R_{in}}{R_{si} + R_{in}} \approx 0.25 \]

Bae, Ong, Estrada, Pop (2009)

Raman Thermal Imaging of Graphene FET

- Spatially resolved (~0.5 um) Raman (2D ~ 2700 cm\(^{-1}\)) thermal imaging
- Suggests power dissipation directly with SO phonons (60 meV) in SiO\(_2\)
- Suggests thermal boundary \( R_b \) (graphene-SiO\(_2\)) \( \approx 4 \times 10^{-6} \text{ m}^2\text{K}/\text{W} \)

Thermal Expansion of Graphite

- Thermal expansion coefficient (TEC) is
  - Positive and large in c- direction
  - Negative (at room temperature) in ab- plane
- Graphite thermal expansion anisotropy can result in large internal stresses

Pierson (1993)
**Thermal Expansion of Graphene**

- Recent estimate of thermal contraction in single-layer suspended graphene*
- TEC ~ $-7 \times 10^{-6}$ K$^{-1}$, 5-6x greater than in graphite ab-plane

* Bao et al, arxiv/cond-mat (2009)

**Thermoelectric Properties of Graphene**

- Measured graphene thermopower $S \leq 100$ $\mu$V/K
  - note: $|S_{\text{graphene}}| >> |S_{\text{Pd}}, S_{\text{Au}}|$ at $T > 300$ K
- Peltier coefficient at metal junction: $\Pi = (S_1 - S_2)T$
- Peltier heating/cooling $Q = \Pi I \approx \Pi_{\text{graphene}} I$
Thermal Anisotropy in Graphene

- Thermal conductivity variation with angle:
  - ~1% variation in graphene ($\pi/3$ angle period)
  - ~10% variation in dimerite
  - ~25% variation in nanoribbon by Molecular Dynamics*

- Triangular graphene nanoribbon with 30° vertex $\rightarrow$ up to 2x thermal anisotropy (rectification)*

*Hu, arxiv/cond-mat (2009)

Graphene nanoribbons: does the WFL hold in 1D? $\rightarrow$ YES

1D ballistic electrons carry energy too, what is their equivalent thermal conductance?

$$G_{th} = L\sigma_e T = \left(\frac{\pi^2 k_B^2}{3e^2}\right)\left(\frac{e^2}{h}\right) T = \frac{\pi^2 k_B^2 T}{3h}$$

(x2 if electron spin included)

$$G_{th} \approx 0.28 \text{ nW/K at 300 K}$$

Phonon Quantum Thermal Conductance

- **Same** thermal conductance quantum, irrespective of the carrier statistics (Fermi-Dirac vs. Bose-Einstein)

![Phonon measurement graph]

Phonon $G_\text{th}$ measurement in GaAs bridge at $T < 1$ K

$$G_\text{th} = \frac{\pi^2 k_B^2 T}{3h} \approx 0.28 \text{ nW/K at 300 K}$$

![Single nanotube $G_\text{th}=2.4$ nW/K at T=300K]


Graphene Thermal Properties Summary

**What we think we know...**
- Thermal conductivity 3000-5000 Wm$^{-1}$K$^{-1}$ at 300 K ($k\downarrow T$)
  - Phonon-dominated, electron contribution < 10%
  - Phonon mean free path ~0.7 μm
- Heat capacity (graphite) ~0.7 kJ/kg at room temperature ($C\uparrow T$)
- Thermal boundary resistance with SiO$_2$ ~4x10$^{-8}$ m$^2$K/W (SO phonon)
- Role of dimensionality:
  - Neither "2-D" nor "3-D"
  - Flexing mode ($\omega\sim k^2$) dominates heat capacity at $T<50$ K

**Much we don’t know...**
- Temperature dependence of $k$, $C$, TBR
- Role of substrate interaction on all of the above
- Role of edges, defects, doping, isotopes…
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