06: Thermal properties of nanostructures

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Announcements

- PS1 due *Wed* at the beginning of lecture (10.40)
Recap: mechanical properties of nanostructures

- Bonding determines mechanical properties
  - Simple spring model (potential well) predicts ultimate stiffness and strength
  - Ultimate stiffness is close to real stiffness of materials
  - Ultimate strength realized only in nanoscale volumes which can be defect free; due to discrete numbers of defects we see distributions of strengths in nanostructures

- “Top-down” engineering of material structure, e.g., grain size reduction can affect strength

- CNTs (and other wires/tubes) can be modeled as continuous beams
  - Must carefully assign property and geometric parameter values
  - Must consider “real” load-bearing area
Nacre (mother of pearl): distributed flaw tolerance

- Hexagonal platelets of aragonite (a form of calcium carbonate) 10-20 µm wide and 0.5 µm thick, arranged in a continuous parallel lamina, separated by sheets of elastic biopolymers (such as chitin, lustrin and silk-like proteins)

- Many other examples in nature (e.g., skeletons, snail shells)

DMD projector

- Projection display based on changing the angle of micromirrors (electrostatic actuation)
- Invented 1987; shipped 1996.
- Support cantilevers are single-crystal Ni
DMD structure

- 4 x 4 micron mirror
- Hinge (flexure)
- Yoke
- Connecting posts
- Electrostatic actuator
- CMOS control / addressing circuit (memory array)
- Moving parts are aluminum
• The hinges are 60 nm thick by 600 nm wide
• The hinges are flexed ±10°
• For a bulk hinge, torsion will result in plastic deformation after only a few cycles
Hinge fatigue and “memory”

- NO fatigue failures
  - $3 \times 10^{12}$ device cycles = 120 years life at 1000 hours per year
  - 500,000 mirrors per device → $14 \times 10^{18}$ individual mirror cycles without a single hinge fatigue failure!

Today’s agenda

- Diffusive and ballistic thermal transport; quantum limit
- Measurements of nanoscale thermal properties: wires, nanotubes, and molecules
- Thermal interfaces
- Thermoelectric materials
- Near-field thermal radiation
Today’s readings (ctools)

Nominal: (on ctools)
- Rogers, Pennathur, Adams, excerpt on Nanoscale Heat Transfer from Nanotechnology: Understanding Small Systems
- Kim et al., “Thermal transport measurements of individual multiwalled nanotubes”

Extras: (on ctools)
- Cahill et al., “Thermometry and thermal transport in micro/nanoscale solid-state devices and structures”
- Shi et al., “Measuring thermal and thermoelectric properties of one-dimensional nanostructures using a microfabricated device”
- Schwab et al., “Measurement of the quantum of thermal conductance” (with news/views by Kouwenhoven)
Heat and temperature

- **Heat** = random (thermal) energy. Electrons, phonons, photons and atoms can all carry heat.

- **Temperature** = a measure of average energy in each degree of freedom in a system.

- Example: ideal gas, $<E>$ of each degree of freedom $= \frac{1}{2} k_B T$

$\rightarrow$ *Need many particles near equilibrium for temperature to have meaning*
Modes of heat transfer

**Conduction**
- By motion of phonons within a solid (metals, semiconductors, insulators)
- By motion of electrons within a solid (metals, semiconductors)

**Convection**
- By motion of molecules within a fluid

**Radiation**
- By electromagnetic waves traveling through space, from one body to another (atoms not in contact)
Diffusive thermal transport

- With enough collisions, "random walk" produces a diffusion process:
  \[ q = -k \nabla T \]
  Fourier's Law

Figure 1.11 (a) A mass-spring system representing interconnected atoms in a crystal, and (b) phonon gas model replaces the solid atoms in a crystal.
Diffusive thermal transport

\[ q_x = \frac{1}{2} (nE v_x) |_{x-v_x \tau} - \frac{1}{2} (nE v_x) |_{x+v_x \tau} \]

\[ q_x = -v_x \tau \frac{d(E n v_x)}{dx} \]

\[ U = nE \quad \frac{dU}{dT} = C \]

\[ q_x = -v^2 v_x \tau \frac{dU}{dT} \frac{dT}{dx} \]

\[ q_x = -C v^2 \tau / 3 * dT/dx = -kdT/dx \quad \rightarrow \quad k = Cv^2 \tau / 3 = Cv\Lambda / 3 = \rho cv\Lambda / 3 \]
Thermal conductivity of materials

Carrier contributions (at 300K)

<table>
<thead>
<tr>
<th>Material</th>
<th>Phonons [W/mK]</th>
<th>Total [W/mK]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>2000</td>
<td>2000</td>
</tr>
<tr>
<td>Silicon</td>
<td>148</td>
<td>148</td>
</tr>
<tr>
<td>Copper</td>
<td>10</td>
<td>400</td>
</tr>
<tr>
<td>Platinum</td>
<td>4</td>
<td>71</td>
</tr>
</tbody>
</table>

Figure 1.5 Thermal conductivity as a function of temperature for representative materials (data from Touloukian et al., 1970, and http://www.chrismanual.com/Default.htm).
When does Fourier's law fail?

- When the carrier mean free path is comparable to the system size (i.e., < 1 μm)

- At times less than carrier collision times (fast processes, i.e., << 1 ns)
Some examples

Transistors

Semiconductor lasers

Data storage

Some examples

Transistors

Semiconductor lasers

Data storage

IBM Research Journal, DOI: 10.1147/rd.443.0323
Phonons: atomic vibrations

Chen.
Phonon dispersion I

\[ m \frac{d^2 u_j}{dt^2} = K (u_{j+1} - u_j) - K (u_j - u_{j-1}) \]

\[ m \frac{\partial^2 u}{\partial t^2} = K a^2 \frac{\partial^2 u}{\partial x^2} \]

\[ u_j = A \exp[-i(\omega t - kja)] \]

\[ \omega = 2 \sqrt{\frac{K}{m}} \left| \sin \frac{ka}{2} \right| \]
Phonon dispersion II

Acoustic

Optical

Optical Phonons

Acoustic Phonons
A real crystal: InSb

- "Zincblend" structure: FCC with diatomic basis
- Each atom feels stretch and bending force from neighbors
Dispersion curves for InSb
[111] mode 1 (acoustic or optical?)
G point, mode 4 (acoustic or optical?)
X point, mode 6
Phonons: quantized vibrations

- Energy (amplitude) of each mode comes in discrete units:
  \[ E_n = h \nu \left( n + \frac{1}{2} \right) \quad (n = 0, 1, 2, 3, \ldots) \]

- The modes obey Bose-Einstein statistics (like photons)

- Quantum of thermal conductance:
  \[ G_{th} = g_0 = \frac{\pi^2 k_B^2 T}{(3h)} \]
  \[ g_0 = (9.456 \times 10^{-13} \text{ W/K}^2) T \]
Measuring the quantum of thermal conductance


Mean free path \( \approx 1 \, \mu m \)
Diffusive vs. ballistic transport

**Diffusive transport**

\[ l_e \ll L \quad R(L) = rL \]

**Ballistic transport**

\[ L < l_e \quad R(L) = R_Q \]

(P. Kim, @NT’06) (J. Chen, IBM)
Silicon: thermal conductivity vs. phonon wavelength
At room temperature, phonons with MFP > 1 µm contribute 30% to thermal conductivity!

Effect of micro-holes in Si membranes

Thin films: phonon scattering at boundaries reduces thermal conductivity

Figure 1.15 Thermal conductivity of silicon films as a function of the film thickness or write diameter. (Courtesy of M. Ashegli).
**Individual suspended tubes and wires**


**FIG. 2.** The change of resistance of the heater resistor \( R_h \) and sensor resistor \( R_s \) as a function of the applied power to the heater resistor. Upper inset: SEM image of the suspended islands with a MWNT bundle across the device. The scale bar represents 1 \( \mu \)m. Lower inset: A schematic heat flow model of the device.
Individual suspended MWNTs

FIG. 9. Measured thermal conductivity of a 14 nm diameter multiwall carbon nanotube (MWCN) (solid circle), an 80 nm diameter MWCN bundle (solid triangle), and a 200 nm diameter MWCN bundle (solid square) (Ref. 94). Data for two vapor-grown graphite fibers (Ref. 95), one heat treated to 3000 °C (open triangle) and one without heat treatment (open circle) are included for comparison. The lines represent the calculated (Ref. 95) basal-plane thermal conductivity of graphite, assuming temperature-independent low-temperature phonon mean free path $\ell = 2.9 \mu$m (upper line) and $\ell = 3.9$ nm (lower line).

Individual suspended SWNT

Figure 6. Analytic plot of the intrinsic SWNT thermal conductivity over the 100–800 K temperature range as computed with eq 3. The length dependence is included heuristically with a simple scaling argument, but differences in chirality may lead to variations up to 20% between different tubes.\textsuperscript{11}

\[ k(L, T) = \frac{3.7 \times 10^{-7}T + 9.7 \times 10^{-10}T^2 + 9.3(1 + 0.5/L)T^{-2}}{[3.7 \times 10^{-7}T + 9.7 \times 10^{-10}T^2 + 9.3(1 + 0.5/L)T^{-2}]^{-1}} \]

Pop et al., Nano Letters 6(1):96, 2006
Ballistic phonon transport in MWNTs

Power independent of length below 500nm

Heat conduction in molecular chains

How molecules heat up. In the experiments reported by Dlott and co-workers, heat is transferred from the heated gold substrate along the molecular chain, causing the chain to become increasingly disordered.

Fig. 4. (A) Dependence on chain length of the delay time $t_0$ between the flash-heating pulse and the arrival of the initial burst of heat at the methyl head groups. (B) Dependence on chain length of the time constant $\tau$ for thermal equilibration between flash-heated Au and alkane chains.

→Ballistic transport, velocity $\approx 1$ m/s

Thermal boundary conductance

\[ q = G \Delta T \]
Simple models for $G$

- Caused by reflection and transmission of phonons at interfaces

- Mismatch of phonons
  - Acoustic mismatch (AMM): all phonons scattered specularly at an interface (Snell's law)
  - Diffuse mismatch (DMM): all phonons scattered diffusely (no "memory" of where they came from)

- Diffuse mismatch is better at room temperature (even 1 atom roughness can scatter thermal phonons)

\[ G_e = \frac{1}{4} \sum_j^3 \int_0^{\omega_{\text{max},j}} \frac{\partial f}{\partial T_e} d\omega \]

- Transmissivity
- Phonon energy
- Phonon speed
- Occupation function
- DOS
Some values of G

![Graph showing thermal conductance vs. temperature for different materials.](image-url)
An example: metal-graphite interfaces

- Graphite-based electronics
- Thermal interface materials
- Characterization of carbon nanostructures
Measurements and DMM predictions

Gold/Graphite

Aluminum/Graphite

Cr/Graphite

Ti/Graphite

G (MW/m²K)

Temperature (K)

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Superlattices

http://lmn.web.psi.ch/shine/sigec.htm
Superlattices

Si/Ge

Temperature (K)

Thermal conductivity (W m⁻¹ K⁻¹)

50 100 500

65 50 30 275 60 150 33 140

GaAs/AlAs

Temperature (K)

kₜ (W cm⁻¹ K⁻¹)

100 200 300 400

40 x 40 6 x 6 25 x 25 3 x 3 17 x 17 2 x 2 10 x 10 1 x 1


PRB, Vol. 59, No. 12, March 1999
Thermoelectricity - heaters and coolers

- Voltage-induced separation of charge carriers $\rightarrow$ heat

Rogers, Pennathur, Adams.
Thermoelectric figure of merit

\[ Z = \frac{S^2 \sigma}{k} \quad ZT = \frac{S^2 \sigma}{k} T \]

- Need \( ZT \approx 2-3 \) to compete with conventional technology (e.g., refrigerators)

- Seebeck coefficient \( (S) \) measures voltage response to applied temperature difference
  - \( S \) depends on crystal structure and temperature
  - Good thermoelectrics: \( S \approx 100's \ \mu V/K \)

- Ideal thermoelectric has maximum electrical conductivity and zero thermal conductivity: electron crystal, phonon glass

- Thermocouples are thermoelectric devices
Progress in thermoelectrics: nanoscale heat conduction effects

Thermoelectricity in molecular junctions

Scanning thermal microscopy (SThM)

- Thermometer, ~100nm spatial resolution
- Localized heat source
- Thermal conductivity map

http://www.park.com
Near field thermal radiation

Propagating waves

Evanescent waves: Decay exponentially
Near field thermal radiation II

- When two objects are closer than photon wavelength, thermal radiation heat transfer can exceed the blackbody limit.

Surface modes (plasmons, polaritons)

50 μm

500 nm

Surface modes are close enough to exchange energy
Example

- Thermal radiation between a microsphere of SiO$_2$ and a flat surface
Conclusion: recap of energy carriers

<table>
<thead>
<tr>
<th></th>
<th>Free Electrons</th>
<th>Phonons</th>
<th>Photons</th>
<th>Molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source</td>
<td>Freed from nucleic bonding</td>
<td>Lattice vibration</td>
<td>Electron and atom motion</td>
<td>Atoms</td>
</tr>
<tr>
<td>Propagation</td>
<td>In vacuum or media</td>
<td>In media</td>
<td>In vacuum or media</td>
<td>In vacuum or media</td>
</tr>
<tr>
<td>media</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Statistics</td>
<td>Fermi–Dirac</td>
<td>Bose–Einstein</td>
<td>Bose–Einstein</td>
<td>Boltzmann</td>
</tr>
<tr>
<td>Frequency</td>
<td>0–infinite</td>
<td>Debye cutoff</td>
<td>0–infinite</td>
<td>0–infinite</td>
</tr>
<tr>
<td>or energy range</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Velocity (m/s)</td>
<td>$\sim 10^6$</td>
<td>$\sim 10^3$</td>
<td>$\sim 10^8$</td>
<td>$\sim 10^2$</td>
</tr>
</tbody>
</table>
Non-equilibrium (fast) transport example: ultrafast laser interactions

- Photon-electron \( \sim \) pulse width
- Electron-electron \( \sim \) 100-500 fs
- Electron-phonon \( \sim \) 1-10 ps
- Ballistic phonon \( \sim \) 10-100 ps
- Diffusion \( \sim t > 100 \) ps
Application: Gold nanorods for tumor hyperthermia with pulsed lasers

- Controlled size
- Tunable absorption spectra
  
  ![Absorption spectrum graph]

- Selective binding

  ![Selective binding images]

Xiaohua Huang, Ph.D. Thesis, Georgia Tech., 2006
Coating the nanorods
Ultrafast absorption and cooling from laser pulse

- Elastic Response
- Electron Bleaching
- Thermal Diffusion
Measuring the effect of the bilayer

Bilayer forms with increased concentration

Schmidt et al., Journal of Physical Chemistry C, 112(35), 13320-13323, 2008