Nanomanufacturing
University of Michigan
ME599-002 | Winter 2010

06: **Thermal properties of nanostructures**

February 1, 2010

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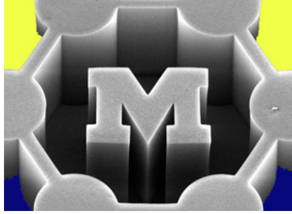
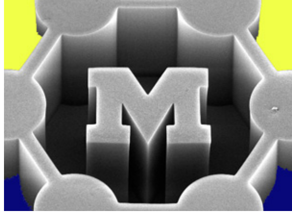
Announcements



- PS1 due **Wed at the beginning of lecture (10.40)**

Recap: mechanical properties of nanostructures



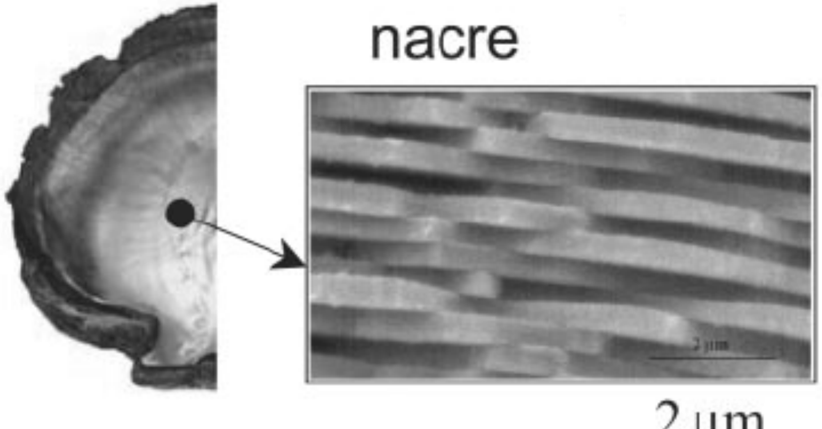
- Bonding determines mechanical properties
  - Simple spring model (potential well) predicts ultimate stiffness and strength
  - Ultimate stiffness is close to real stiffness of materials
  - Ultimate strength realized only in nanoscale volumes which can be defect free; due to discrete numbers of defects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

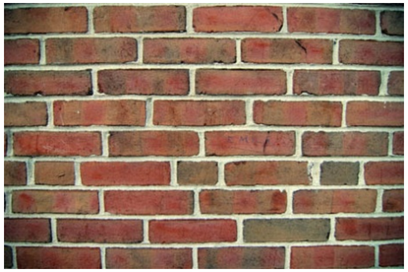
- "Top-down" engineering of material structure, e.g., grain size reduction can affect strength

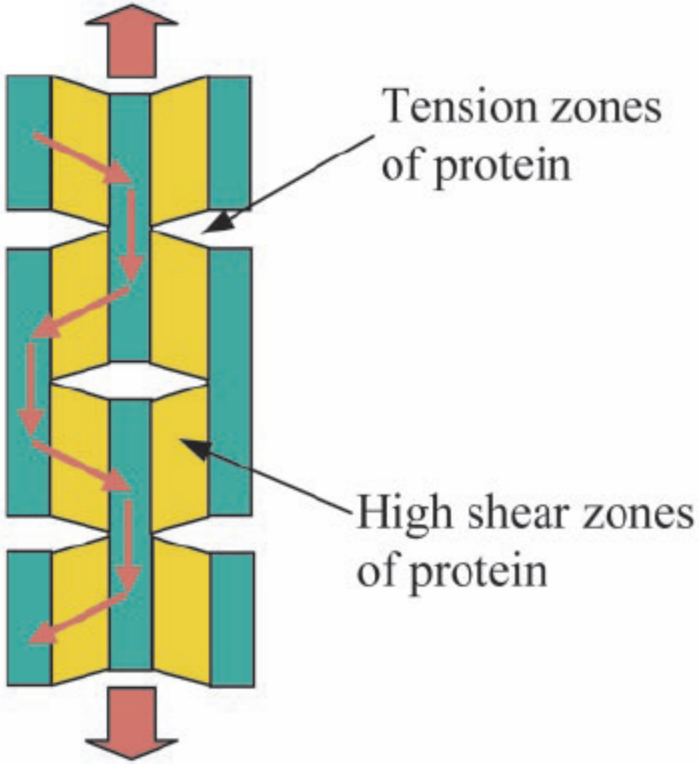
- CNTs (and other wires/tubes) can be modeled as continuous beams
  - Must carefully assign property and geometric parameter values
  - Must consider "real" load-bearing area

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)





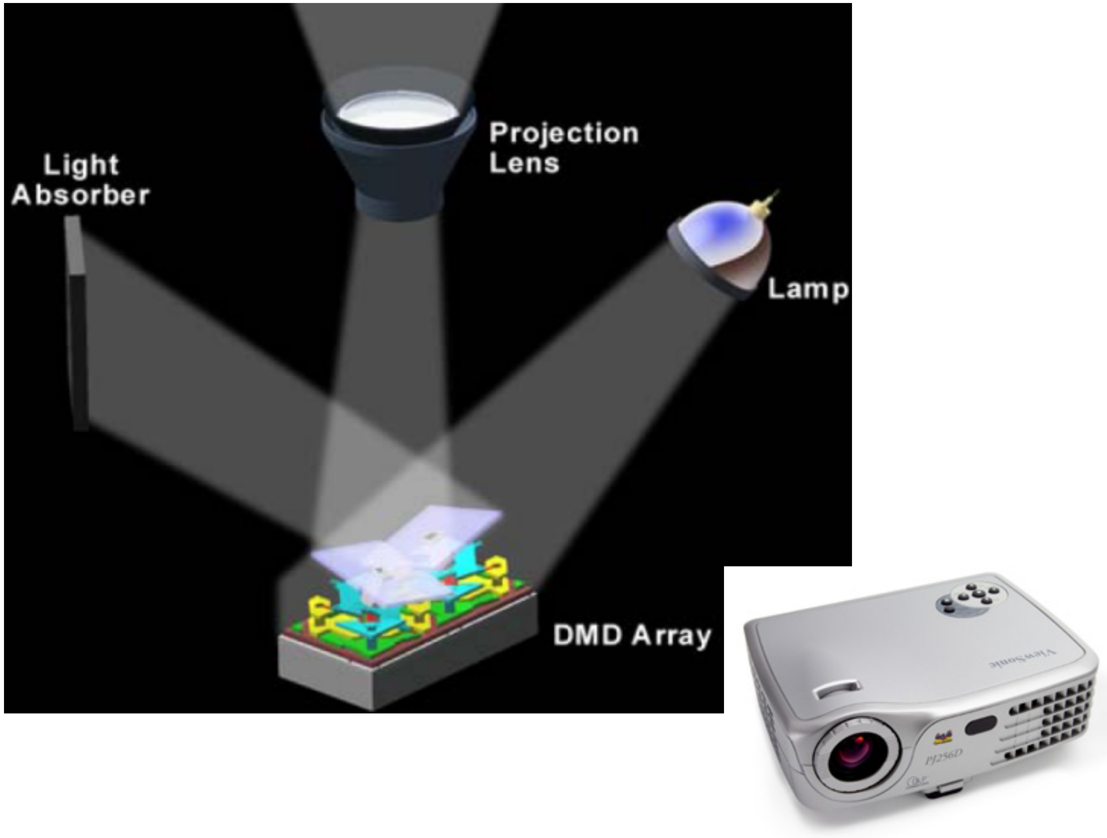


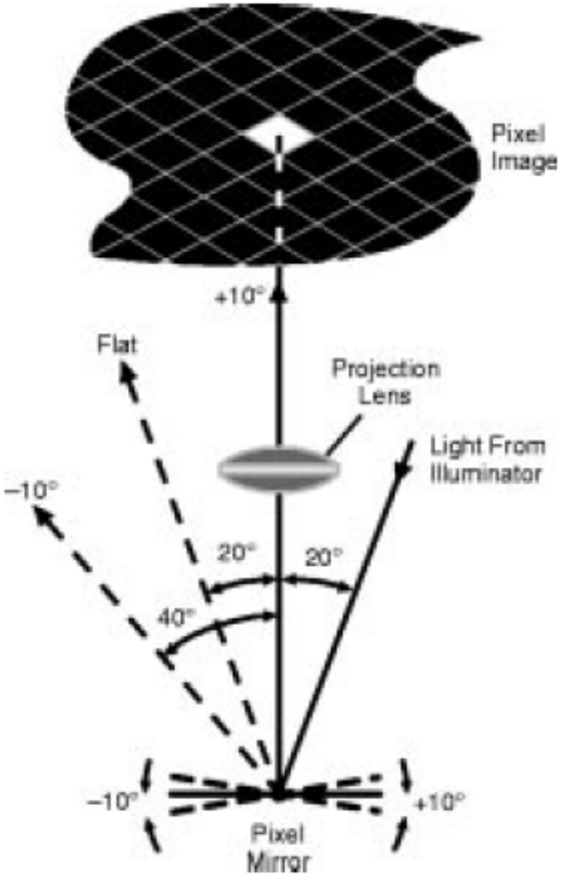
- Many other examples in nature (e.g., skeletons, snail shells)

Gao et al., PNAS 100(10):5597, 2003.

DMD projector

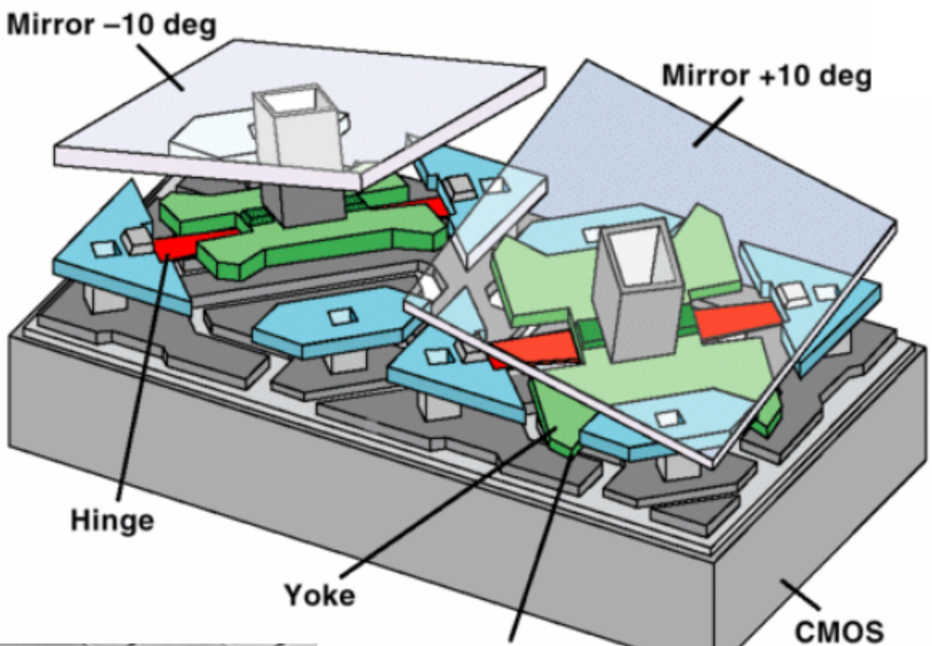
- Projection display based on changing the angle of micromirrors (electrostatic actuation)
- Invented 1987; shipped 1996.
- Support cantilevers are single-crystal Ni

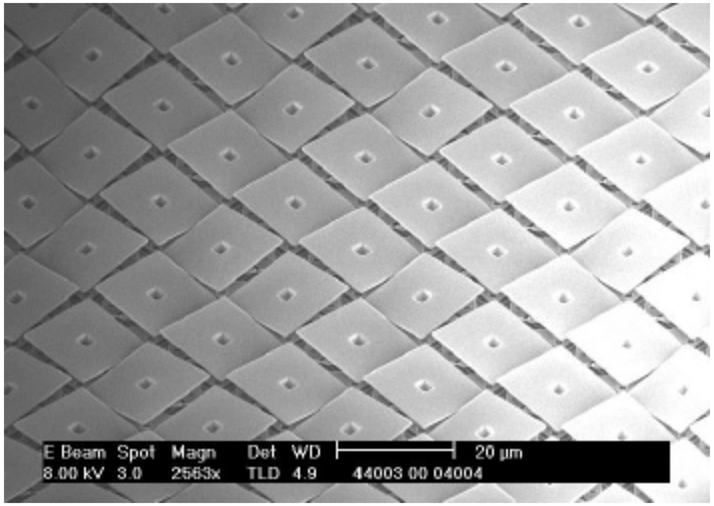


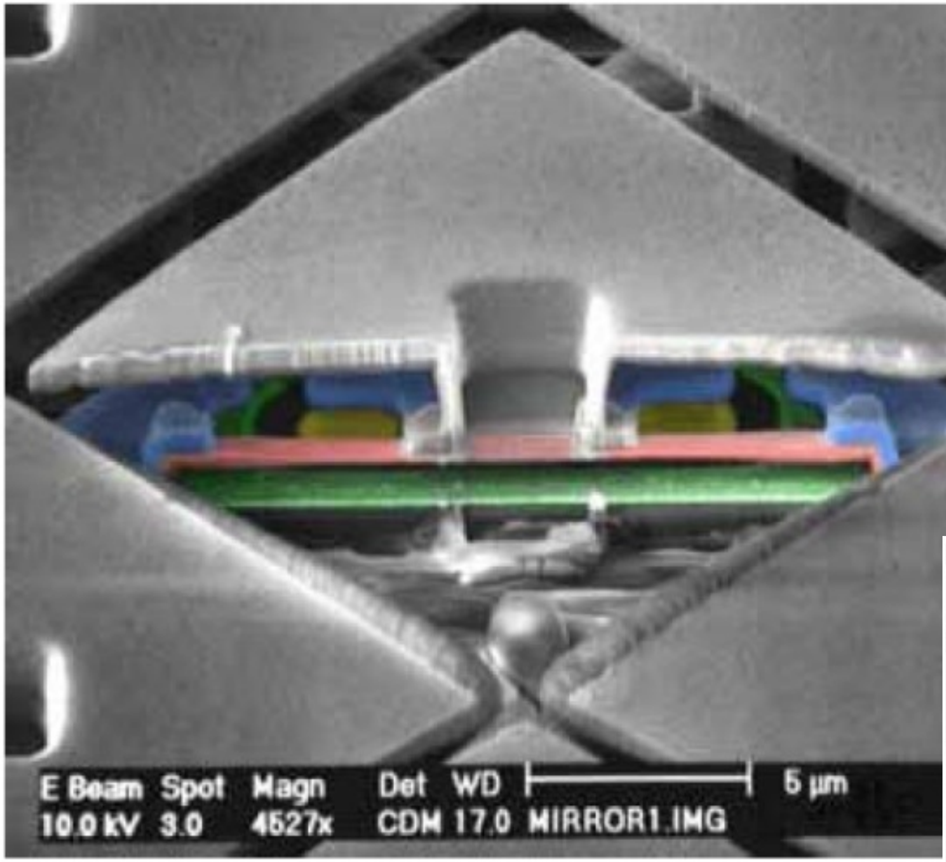


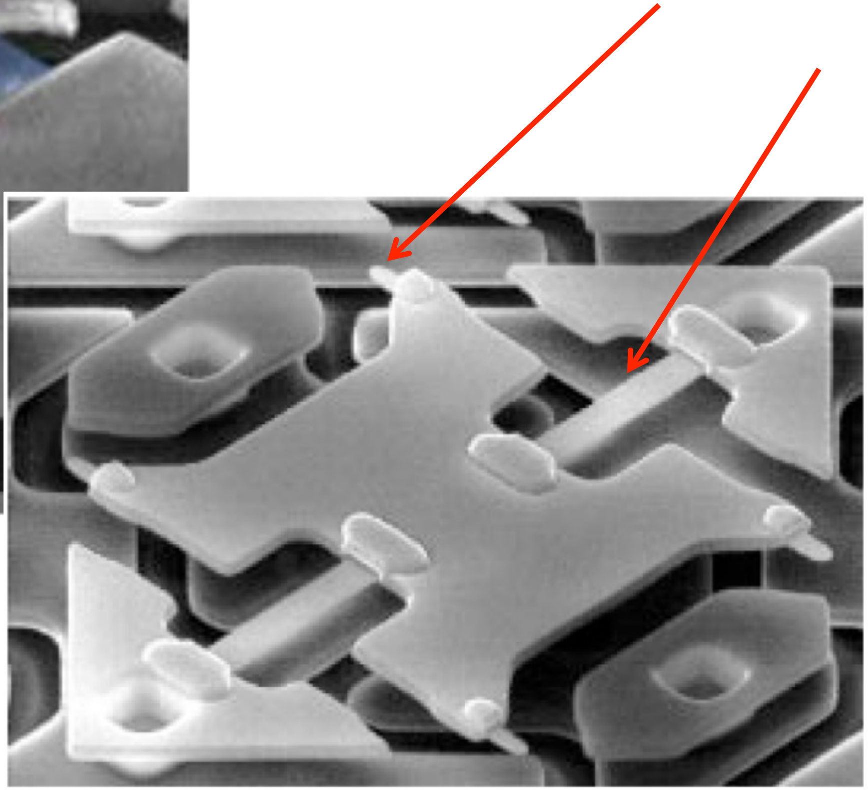
DMD structure

- 4 x 4 micron mirror
- Hinge (flexure)
- Yoke
- Connecting posts
- Electrostatic actuator
- CMOS control / addressing circuit (memory array)
- Moving parts are aluminum





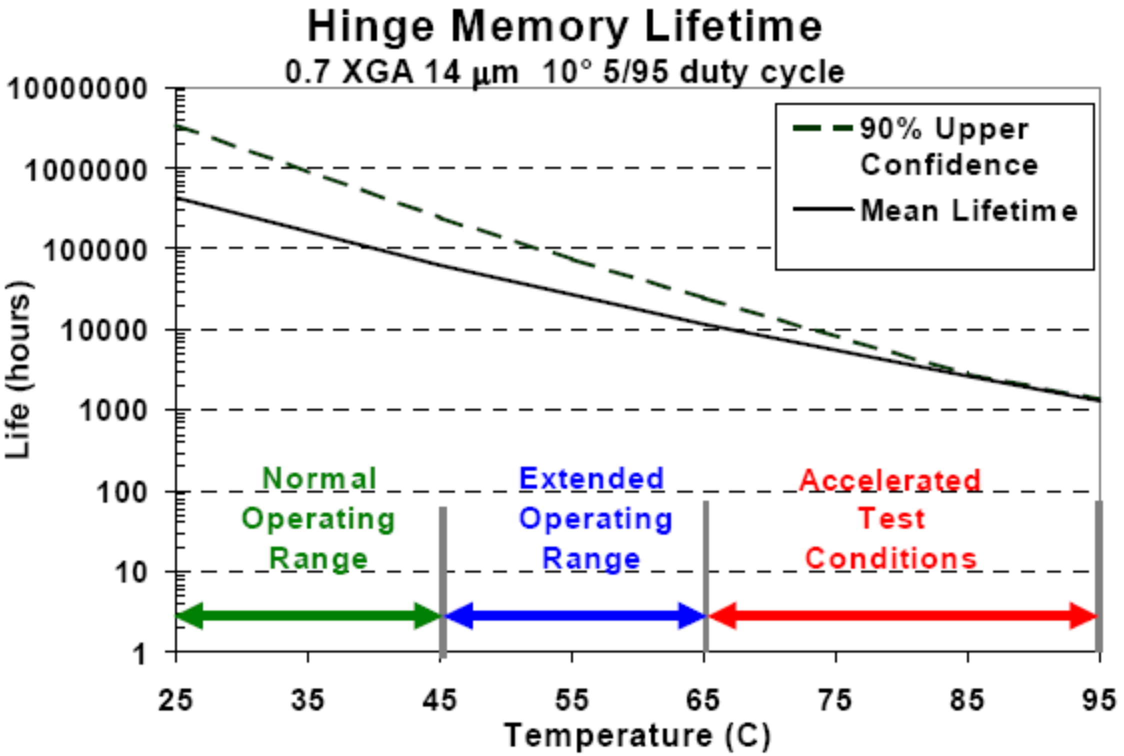




- The hinges are 60 nm thick by 600 nm wide
- The hinges are flexed ±10°
- For a bulk hinge, torsion will result in plastic deformation after only a few cycles

Hinge fatigue and “memory”

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



Douglas, Proceedings of the SPIE, 4980:1-11, 2003.

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)

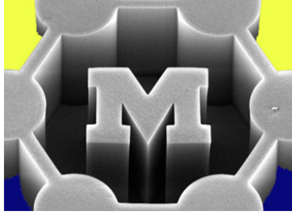
Nominal: (on ctools)

- Rogers, Pennathur, Adams, excerpt on Nanoscale Heat Transfer from <u>Nanotechnology: Understanding Small Systems</u>
- 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 themoelectric 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 = $\frac{1}{2}k_B T$

→ *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

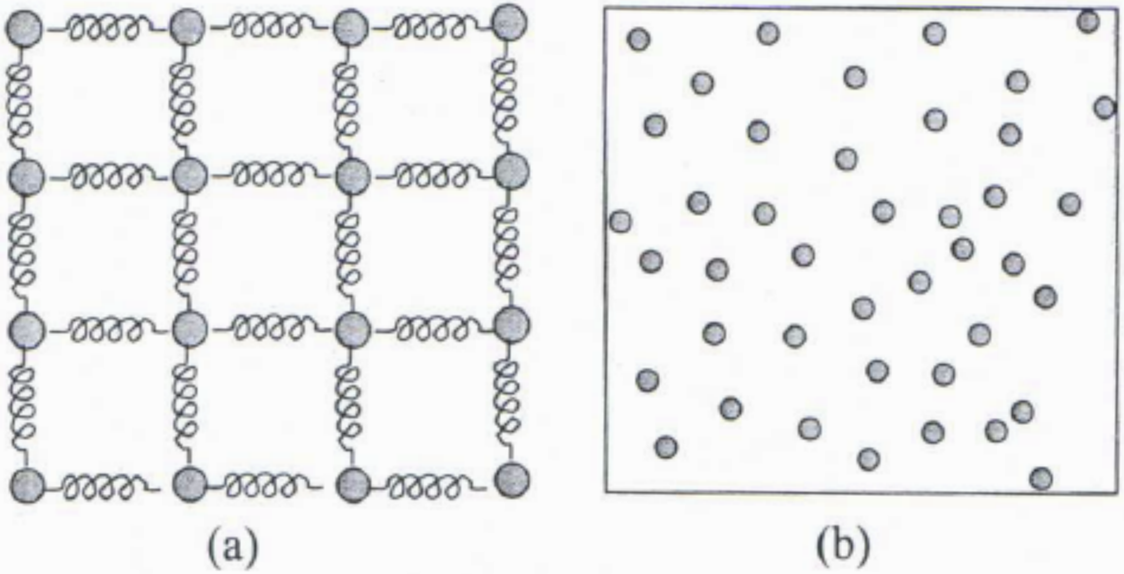


Figure 1.11 (a) A mass-spring system representing interconnected atoms in a crystal, and (b) phonon gas model replaces the solid atoms in a crystal.

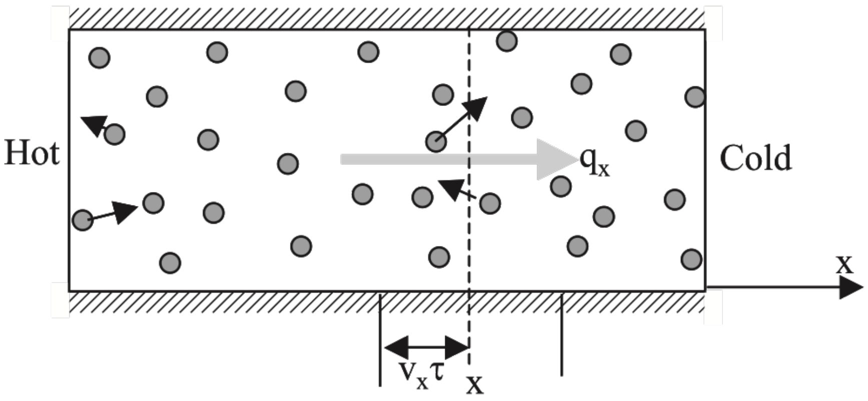
- With enough collisions, "random walk" produces a diffusion process

$$q = -k\nabla T$$

Fourier's Law

Chen.

Diffusive thermal transport



$$q_x = \frac{1}{2}(nEv_x)|_{x-v_x\tau} - \frac{1}{2}(nEv_x)|_{x+v_x\tau}$$

$$q_x = -v_x\tau\frac{d(Env_x)}{dx}$$

$$U = nE \qquad \frac{dU}{dT} = C$$

$$q_x = -\frac{v^2\tau}{3}\frac{dU}{dT}\frac{dT}{dx}$$

$$\boxed{q_x = -Cv^2\tau/3 * dT/dx = -kdT/dx \longrightarrow k = Cv^2\tau/3 = Cv\Lambda/3 = \rho cv\Lambda/3}$$

Chen.

Thermal conductivity of materials

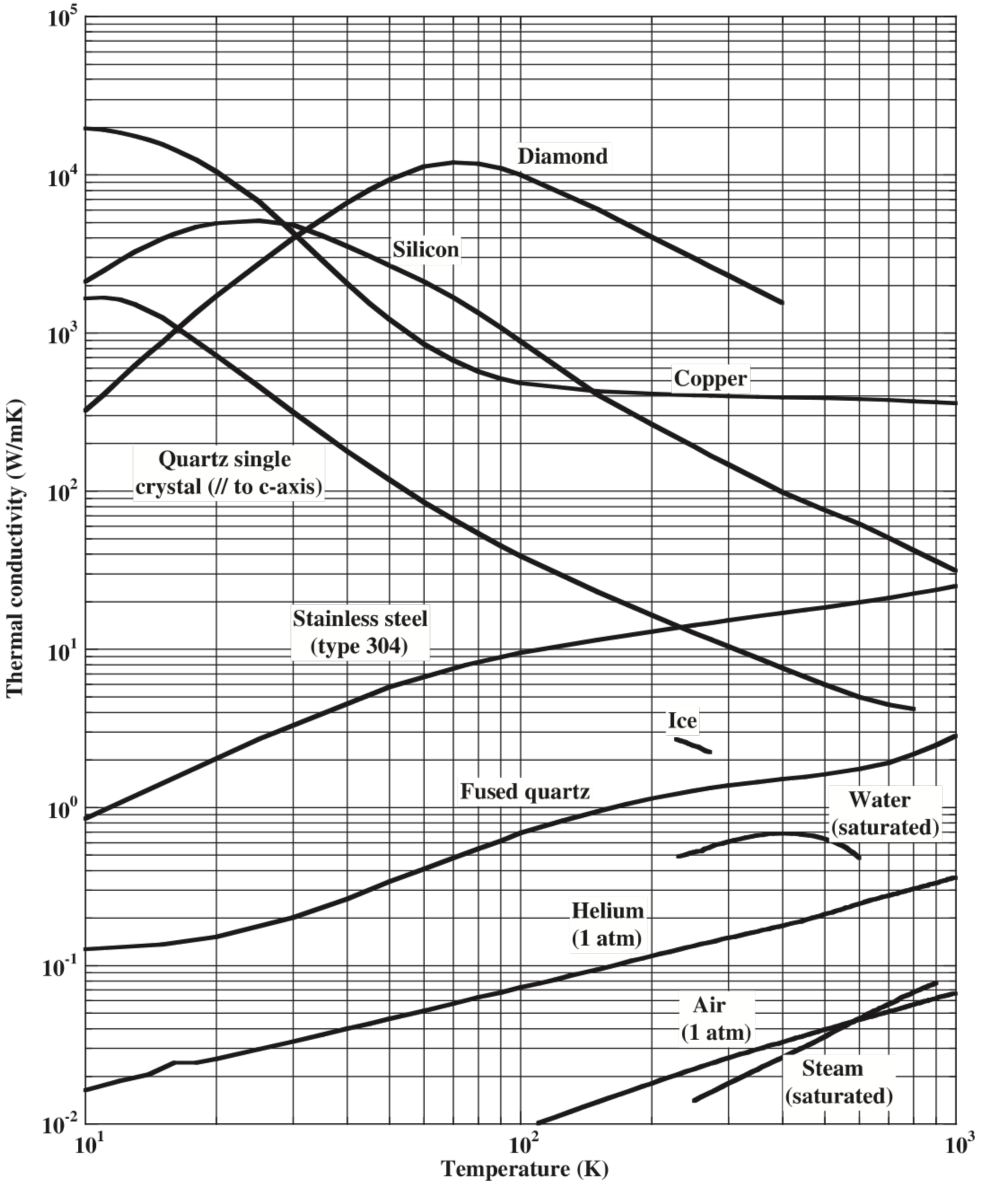


Figure 1.5 Thermal conductivity as a function of temperature for representative materials (data from Touloukian et al., 1970, and http://www.chrismanual.com/Default.htm).

Carrier contributions (at 300K)

	Phonons [W/mK]	Total [W/mK]
Diamond	2000	2000
Silicon	148	148
Copper	10	400
Platinum	4	71

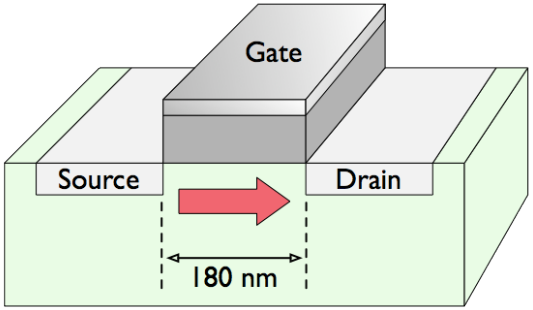
When does Fourier's law fail?

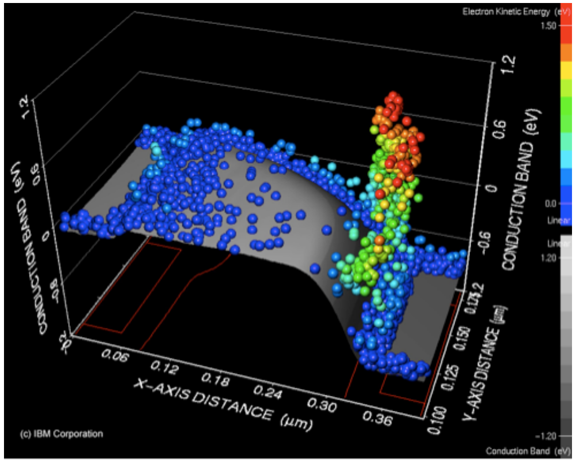
- When the carrier mean free path is comparable to the system size (i.e., < 1 µm)

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

Some examples

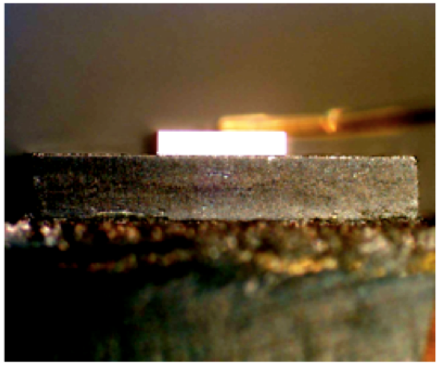
Transistors



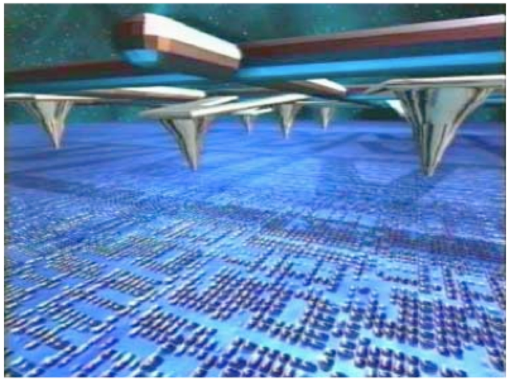


http://www.research.ibm.com/DAMOCLES/html_files/soi.html

Semiconductor lasers

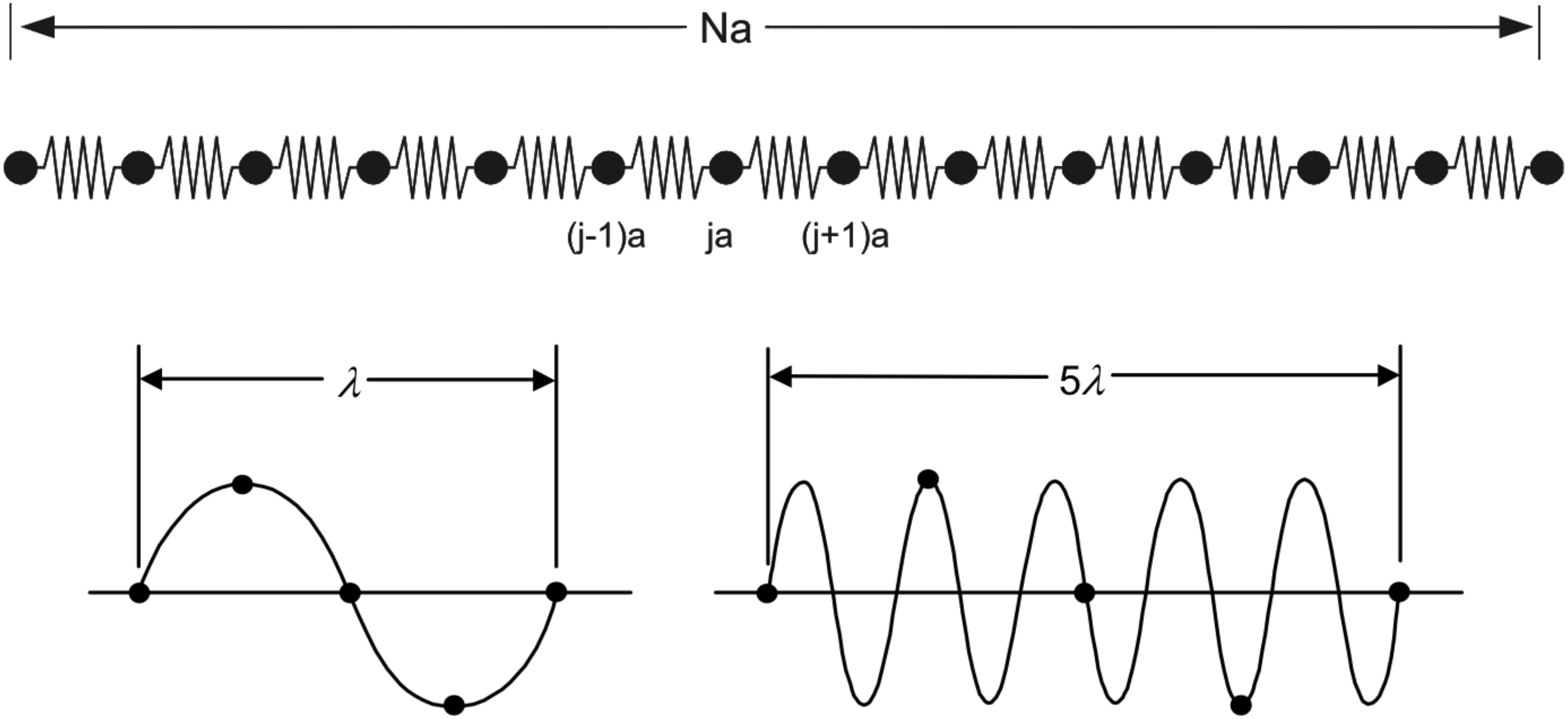


Data storage



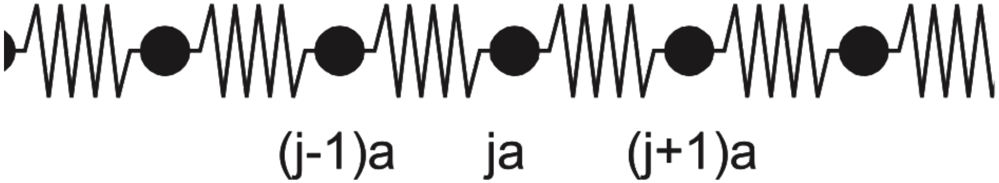
IBM Research Journal, DOI: 10.1147/rd.443.0323

Phonons: atomic vibrations



Chen.

Phonon dispersion I

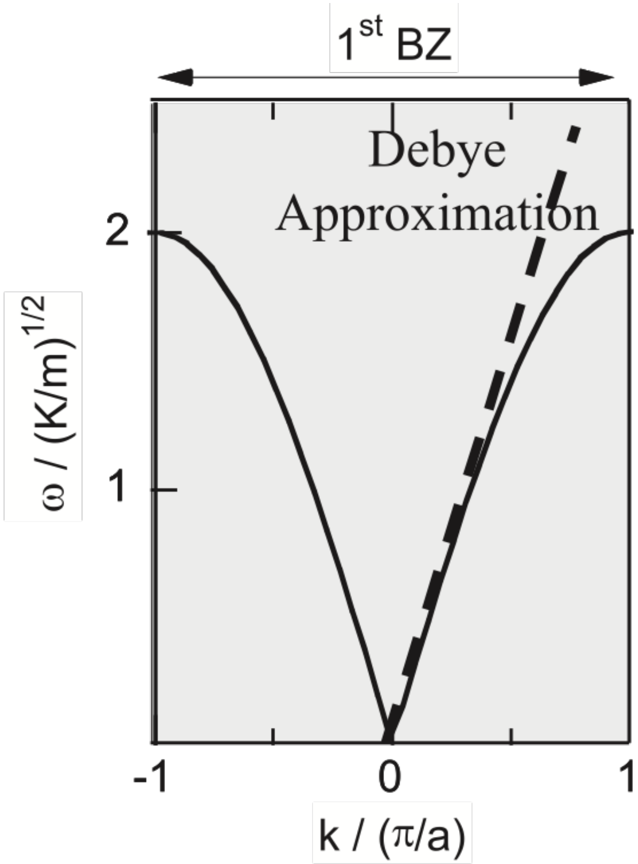


$$m\frac{d^2u_j}{dt^2} = K(u_{j+1} - u_j) - K(u_j - u_{j-1})$$

$$m\frac{\partial^2 u}{\partial t^2} = Ka^2\frac{\partial^2 u}{\partial x^2}$$

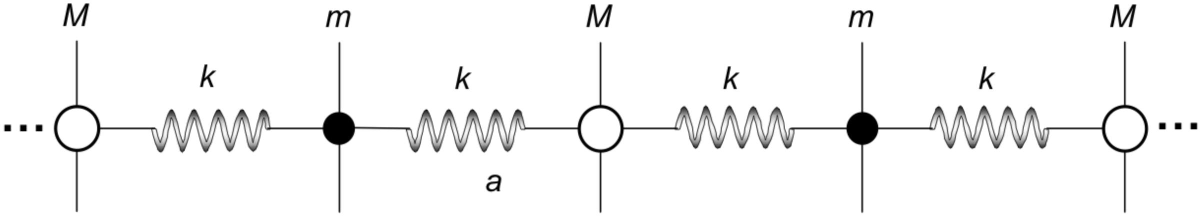
$$u_j = A\exp[-i(\omega t - kja)]$$

$$\boxed{\omega = 2\sqrt{\frac{K}{m}}\left|\sin\frac{ka}{2}\right|}$$

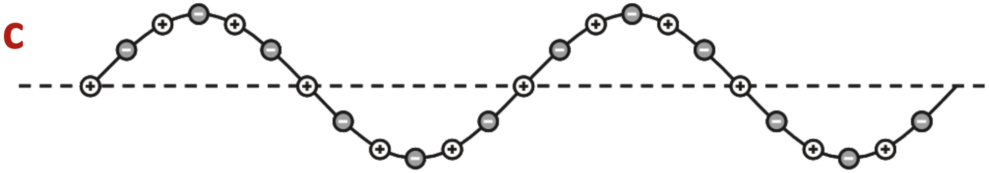


Chen.

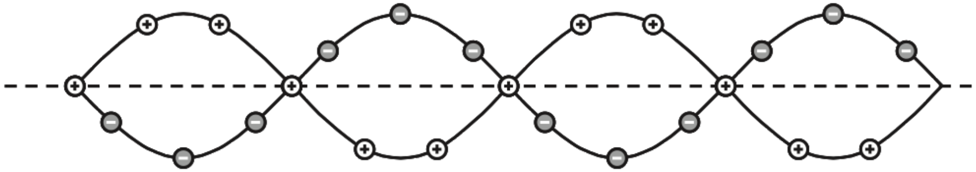
Phonon dispersion II

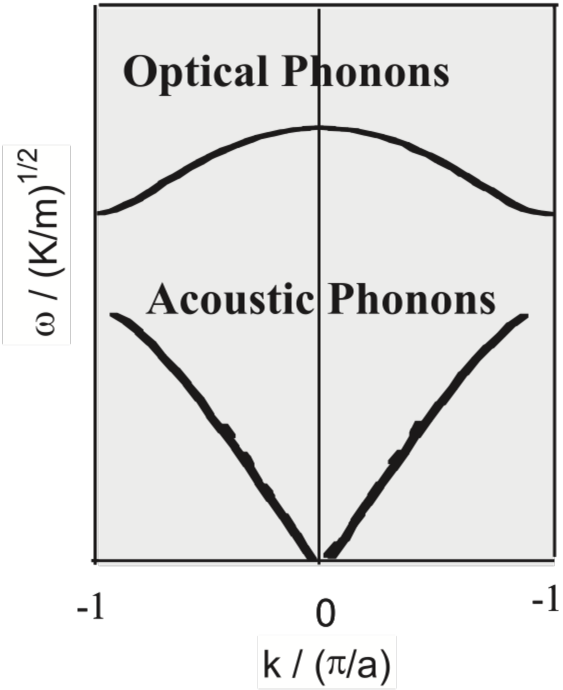


Acoustic



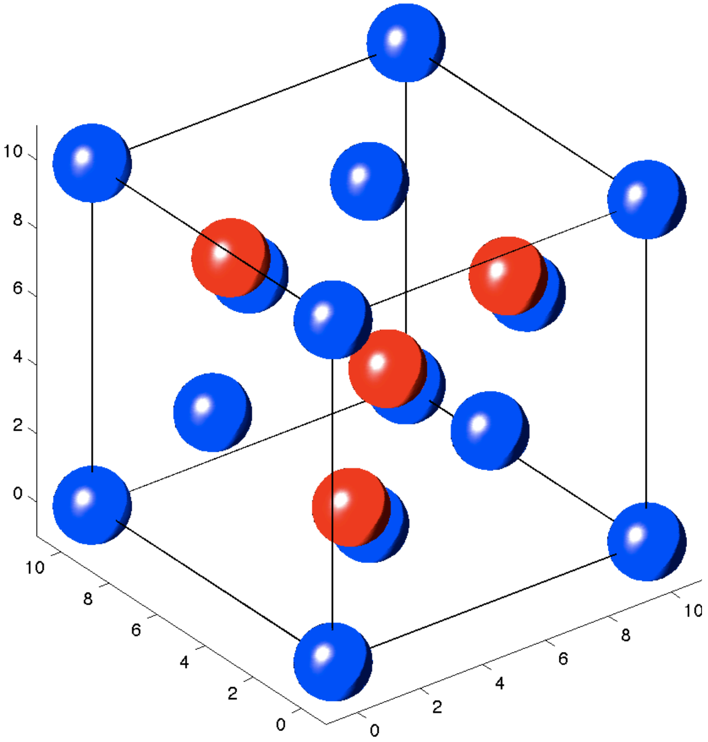
Optical



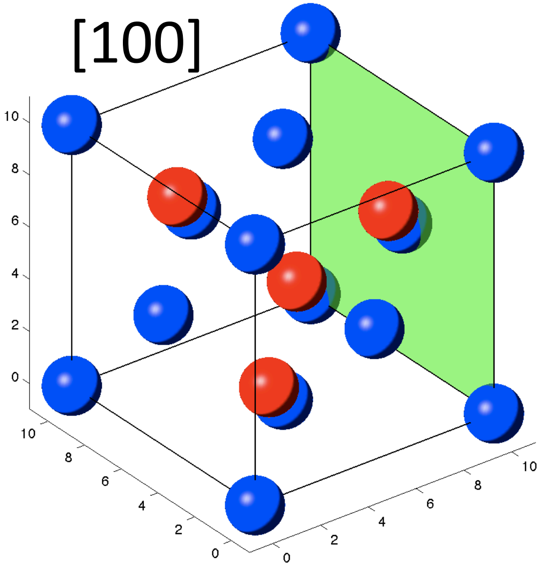


A real crystal: InSb

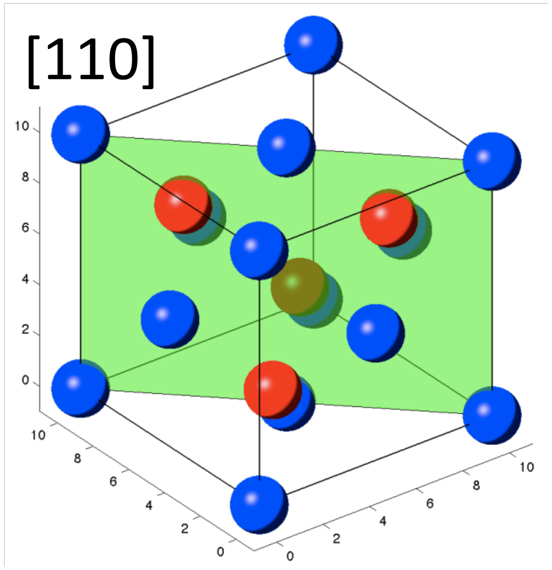
- "Zincblend" structure: FCC with diatomic basis
- Each atom feels stretch and bending force from neighbors



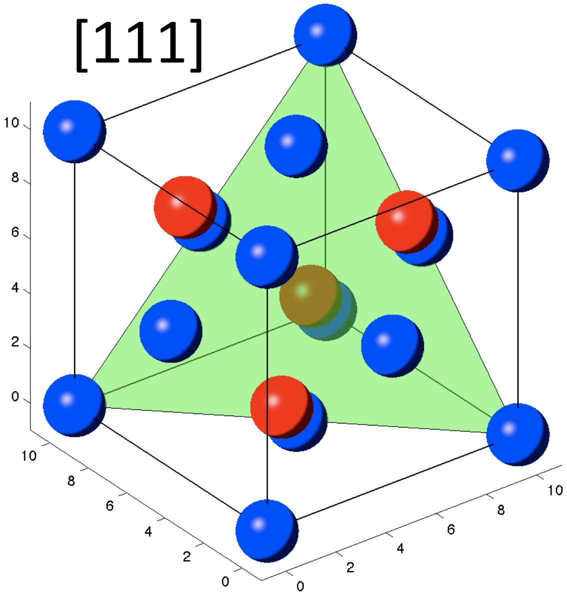
[100]



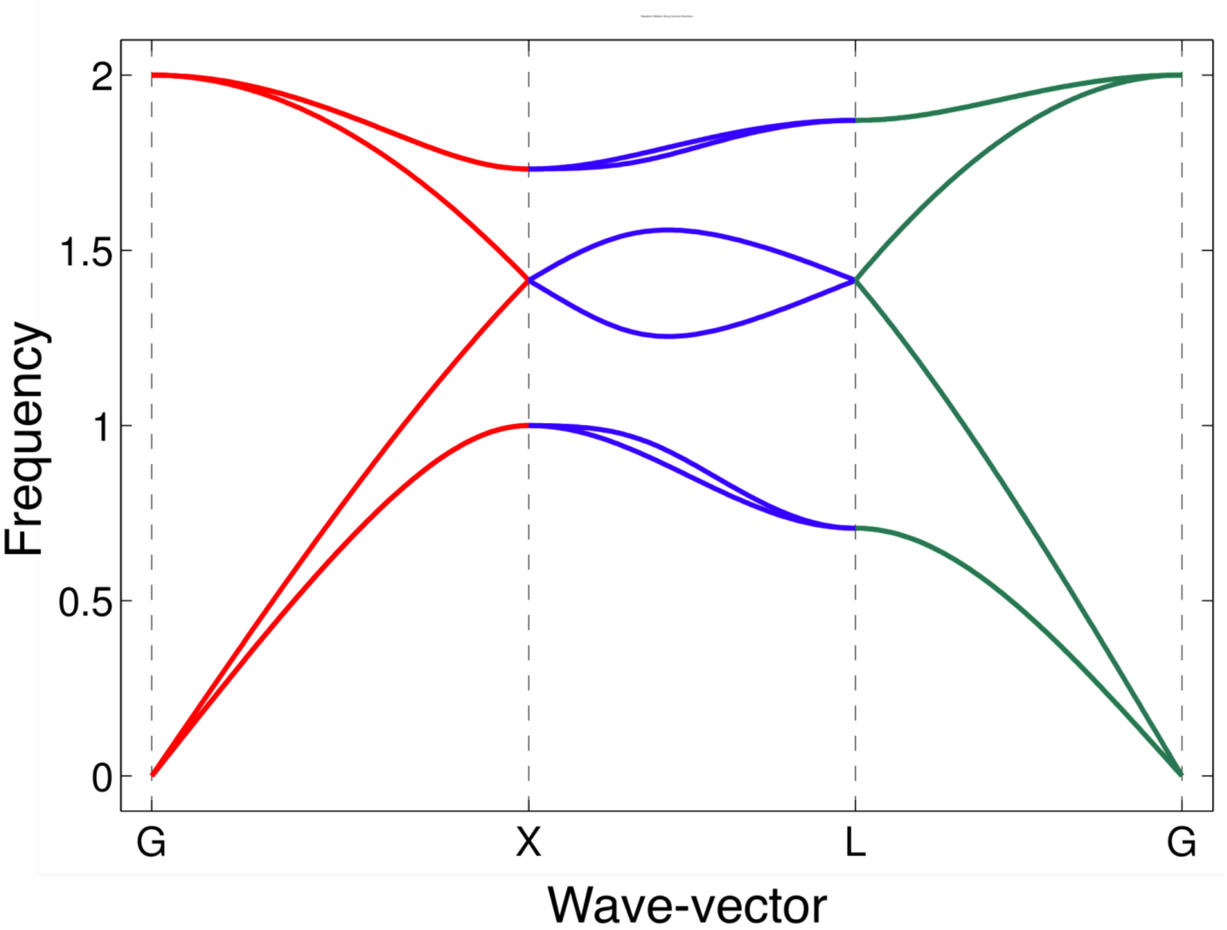
[110]

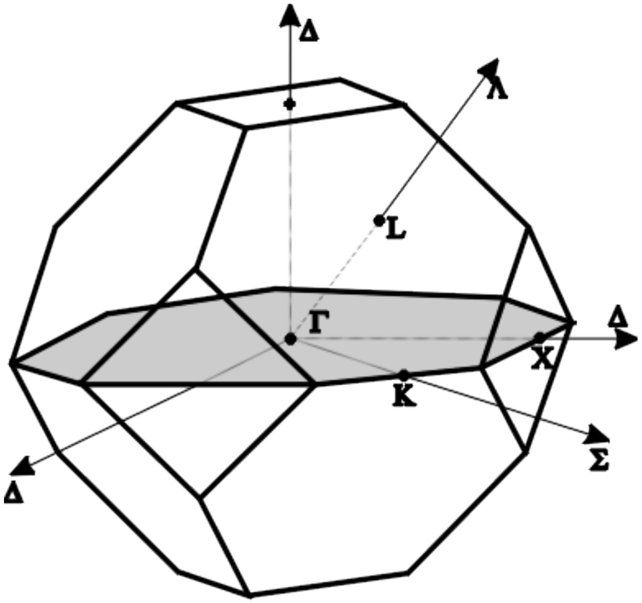


[111]

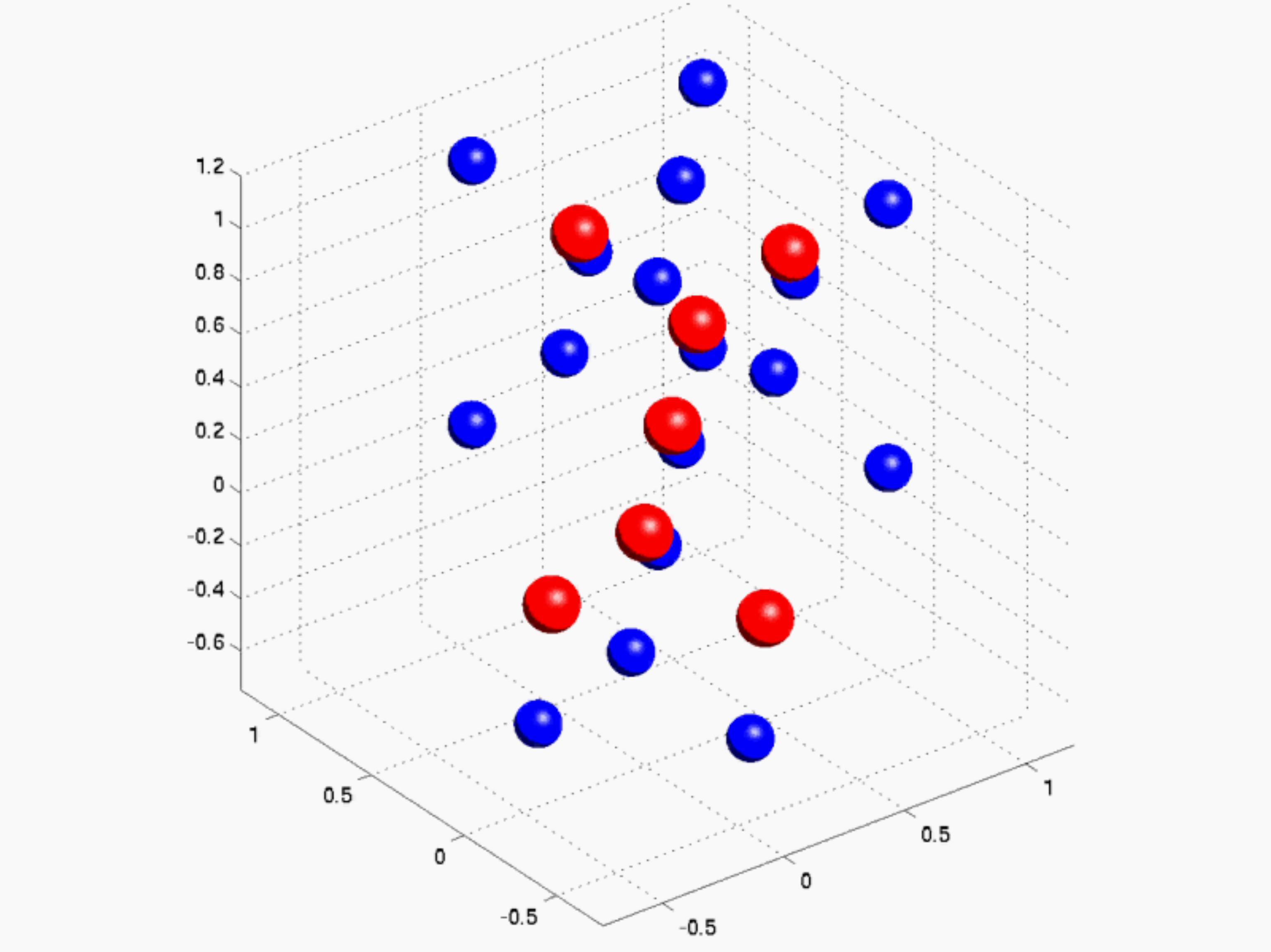


Dispersion curves for InSb

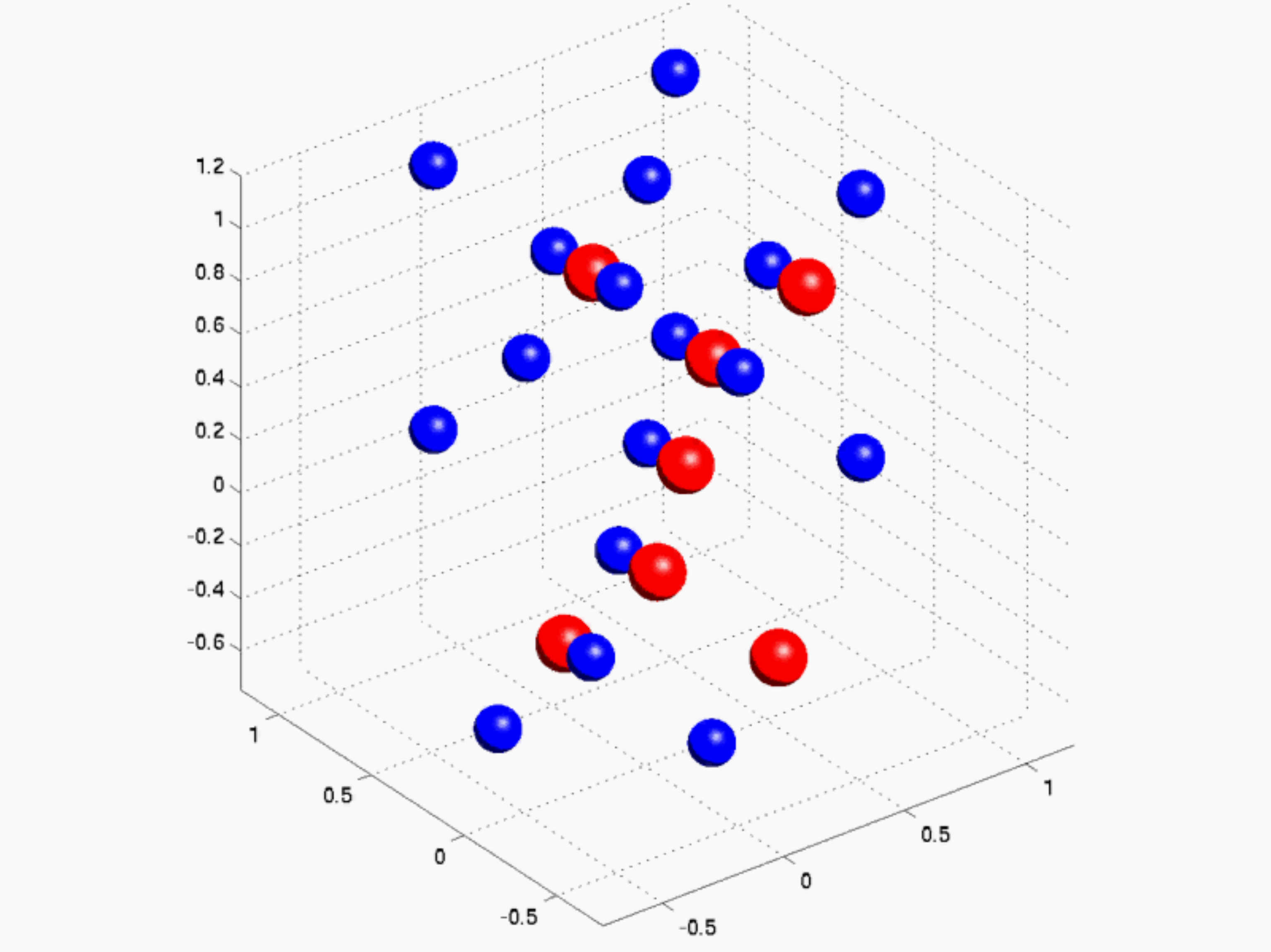




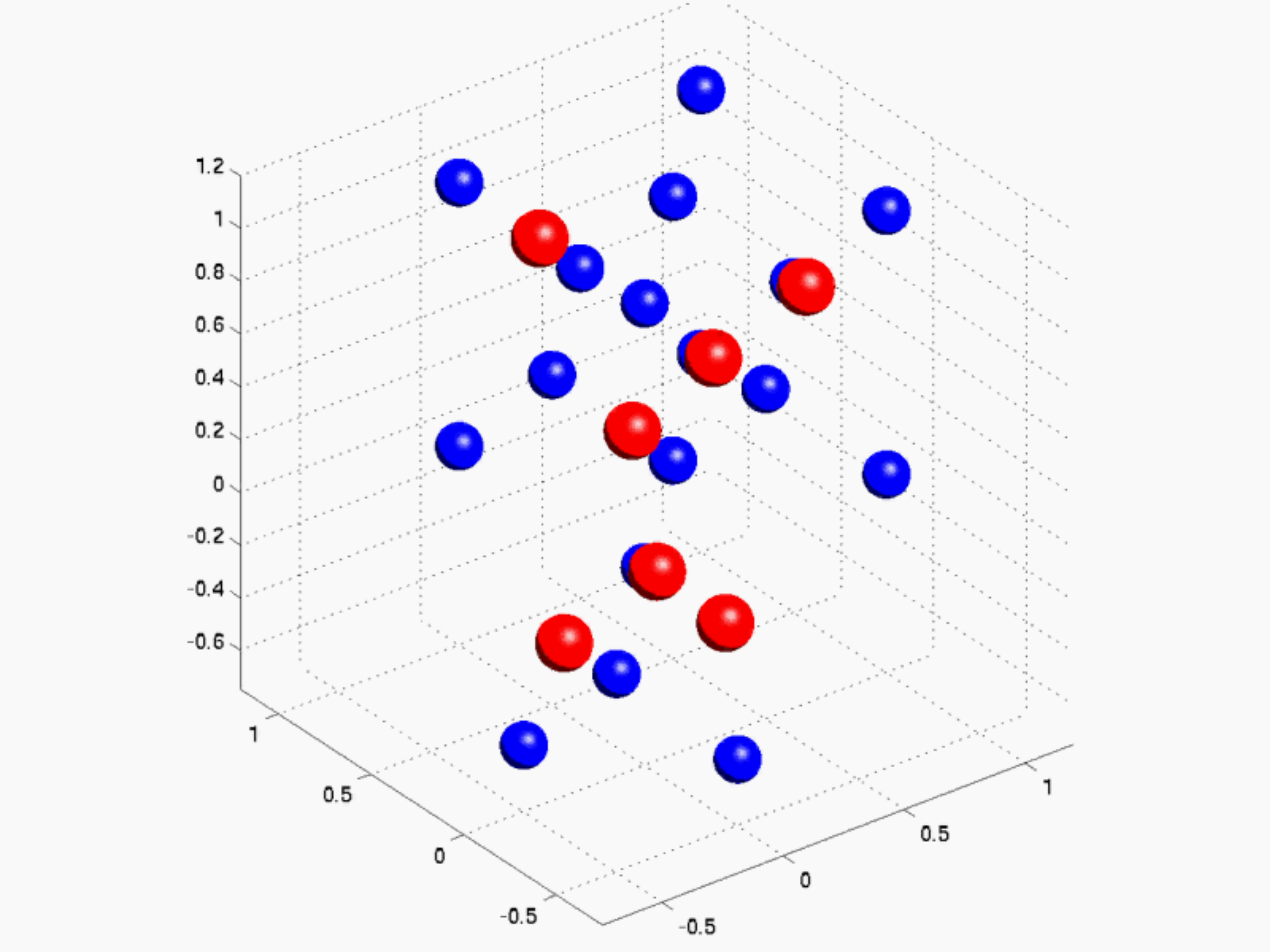
[111] mode 1 (acoustic or optical?)



G point, mode 4 (acoustic or optical?)



X point, mode 6



Phonons: quantized vibrations

- Energy (amplitude) of each mode comes in discrete units:

$$E_n = h\nu\left(n + \frac{1}{2}\right) \qquad (n = 0, 1, 2, 3, \ldots)$$

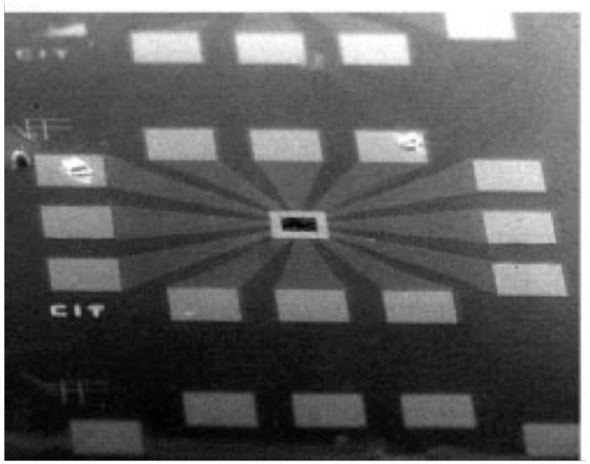
- The modes obey Bose-Einstein statistics (like photons)

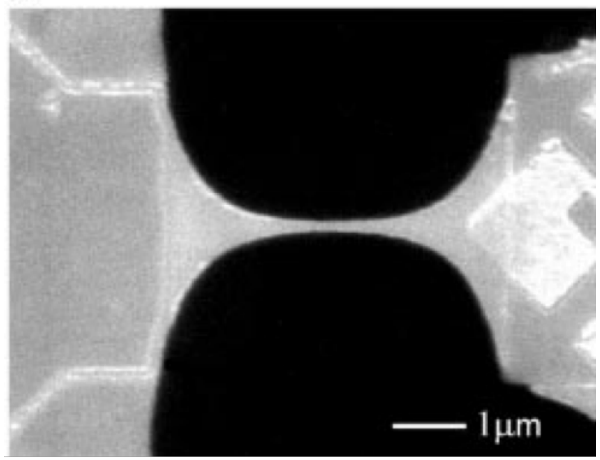
- Quantum of thermal conductance:

$$G_{\mathrm{th}} = g_0 = \pi^2 k_{\mathrm{B}}^2 T/(3h)$$

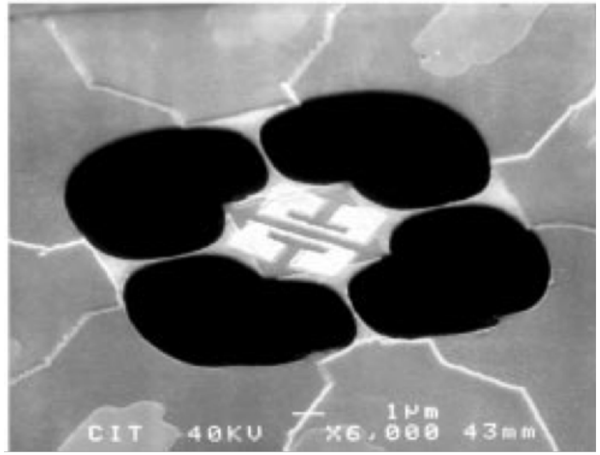
$$g_0 = (9.456 \times 10^{-13}\ \mathrm{W/K^2})T$$

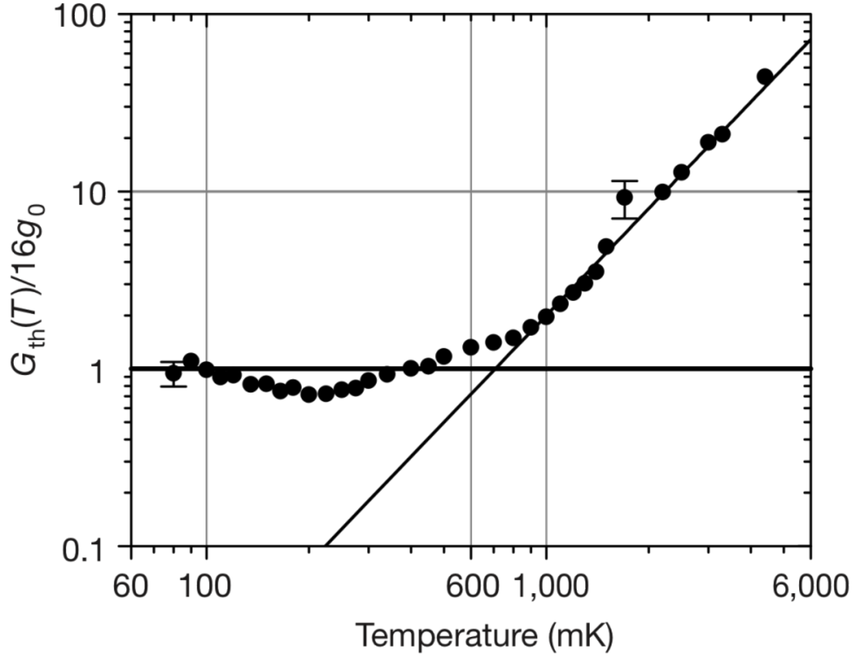
Measuring the quantum of thermal conductance





Mean free path ≈1 μm

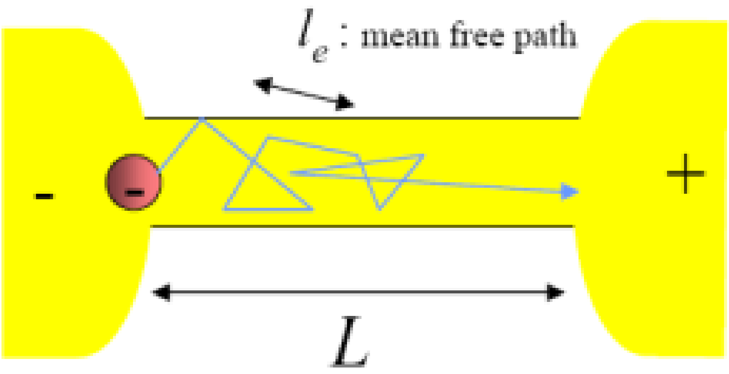




Schwab et al., Nature 404:974, 2000.

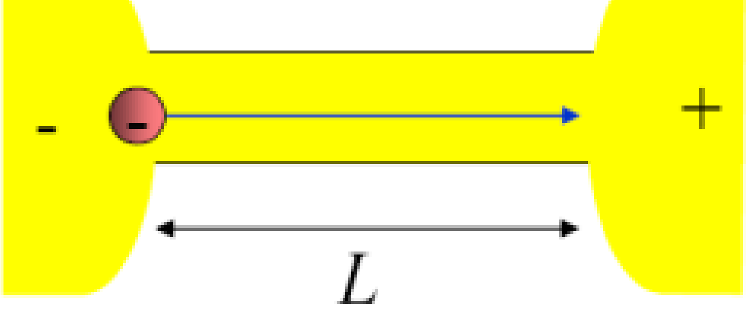
Diffusive vs. ballistic transport

Diffusive transport



$l_e << L$ $R(L) = rL$

Ballistic transport

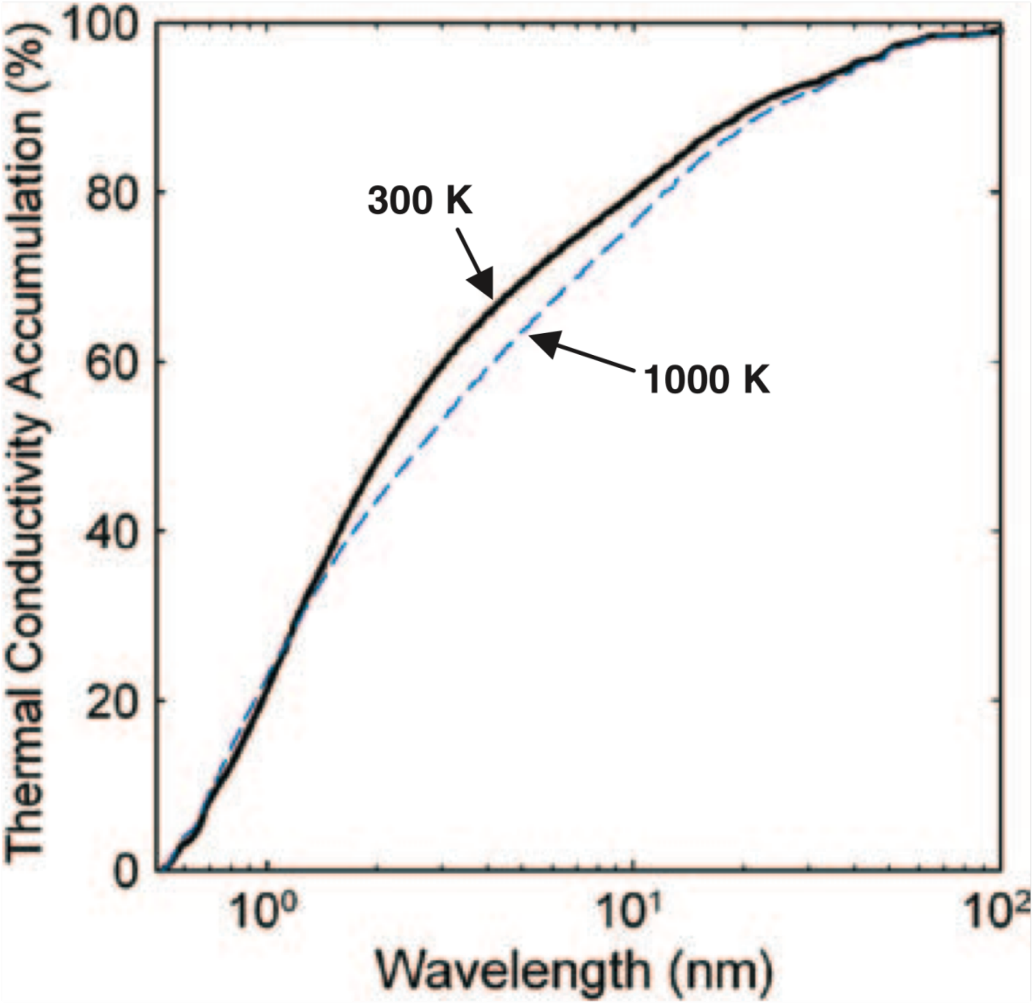


$L < l_e$ $R(L) = R_Q$

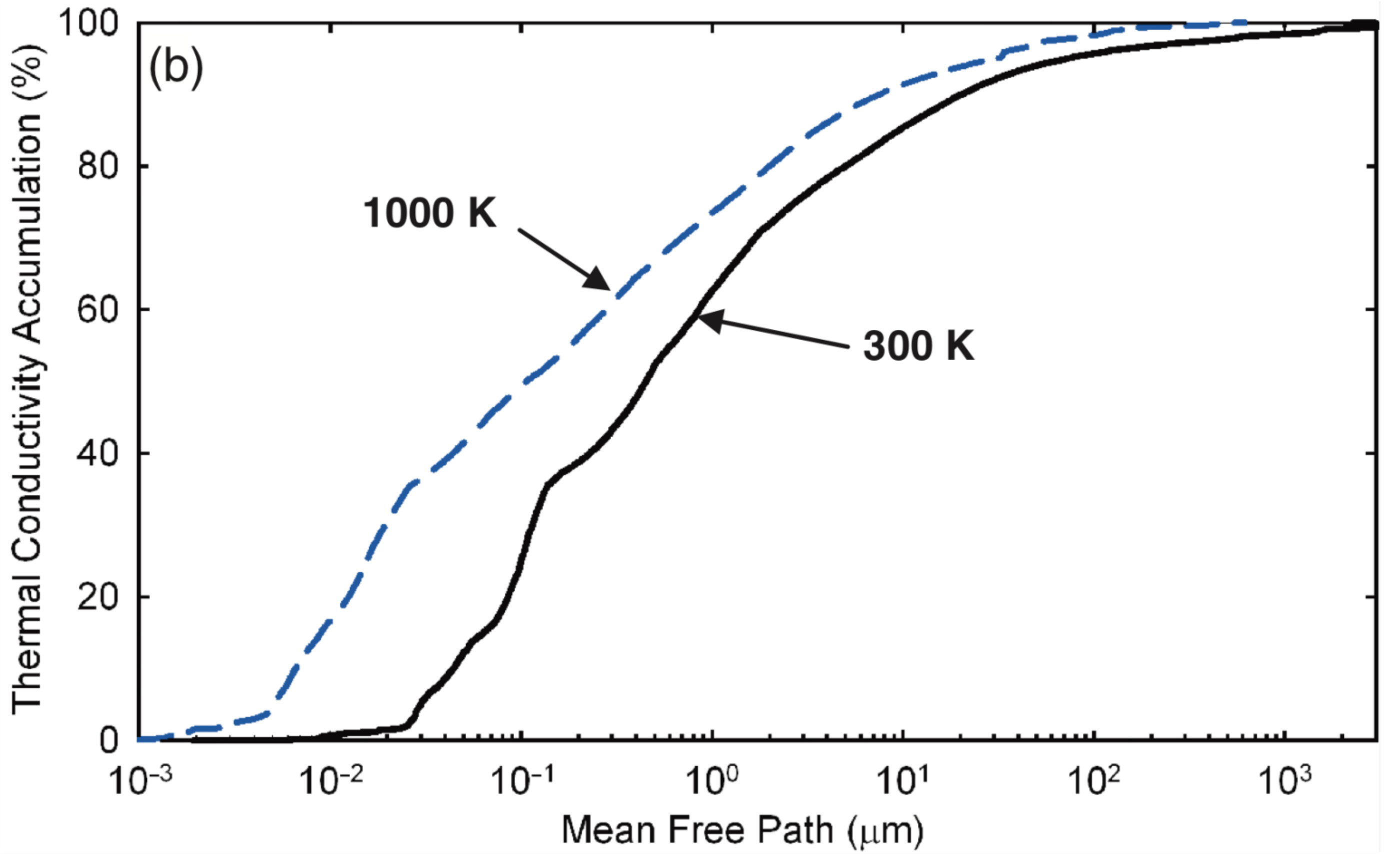
(P. Kim, @NT'06)

(J. Chen, IBM)

Silicon: thermal conductivity vs. phonon wavelength



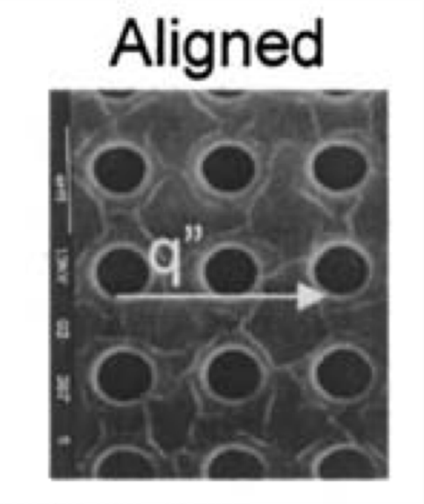
Silicon: thermal conductivity vs. MFP

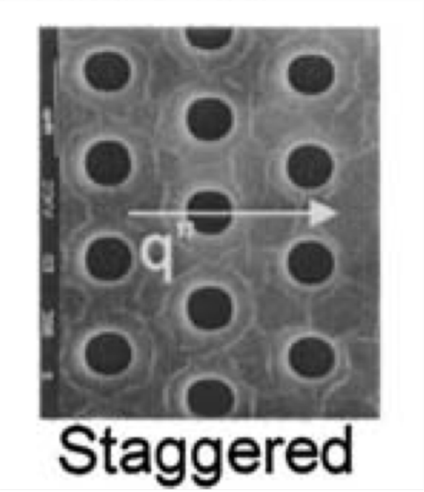


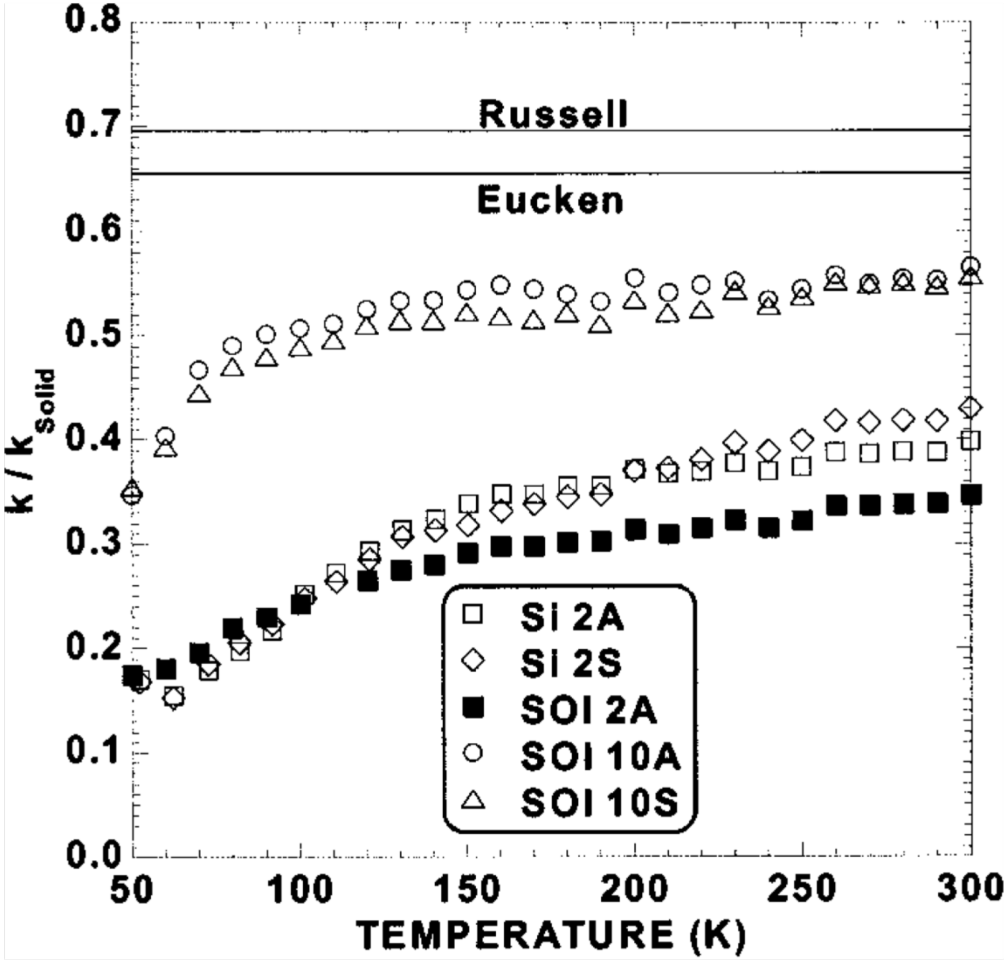
At room temperature, phonons with MFP > 1 μm contribute 30% to thermal conductivity!

J. Comput. Theor. Nanosci. 5, 1–12, 2008

Effect of micro-holes in Si membranes







Appl. Phys. Lett. 84, 687 (2004)

Thin films: phonon scattering at boundaries reduces thermal conductivity

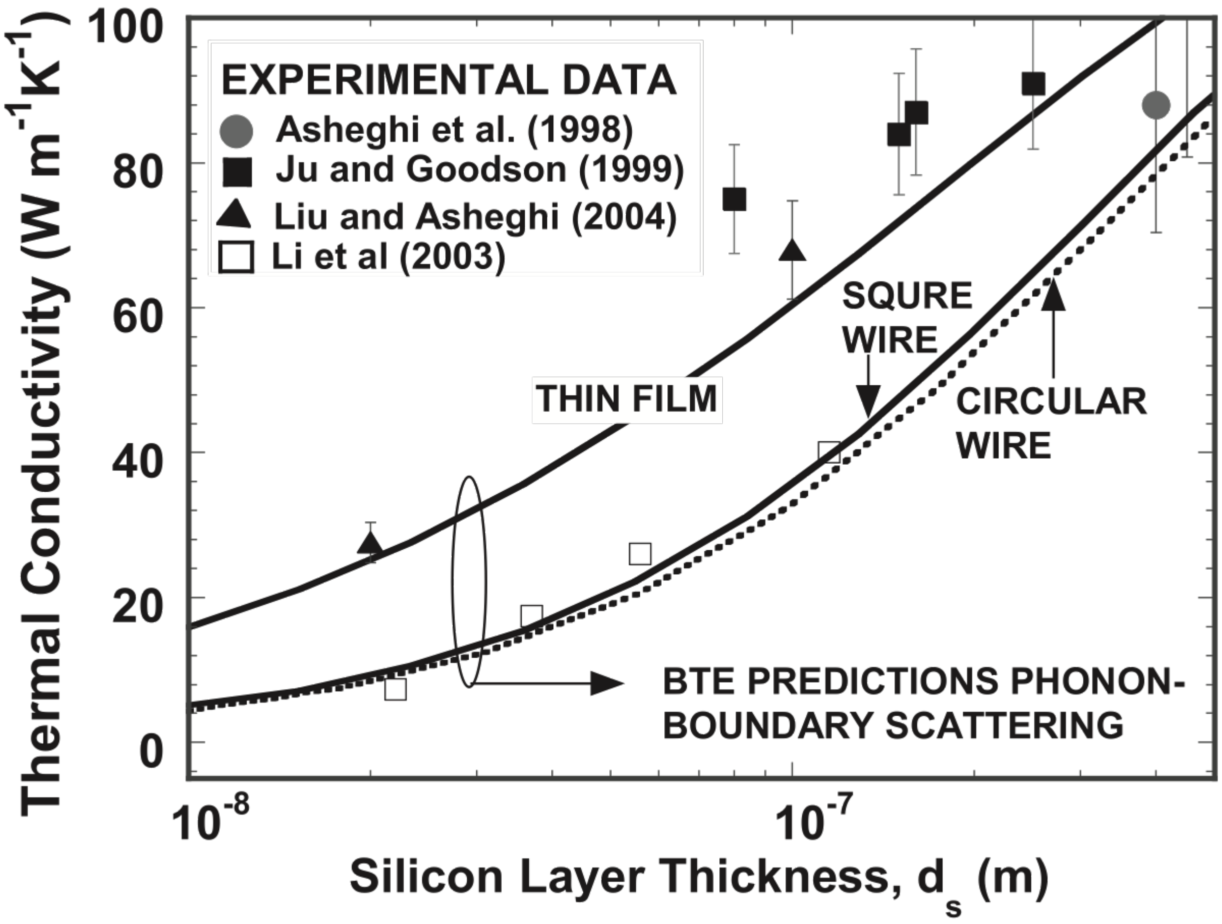
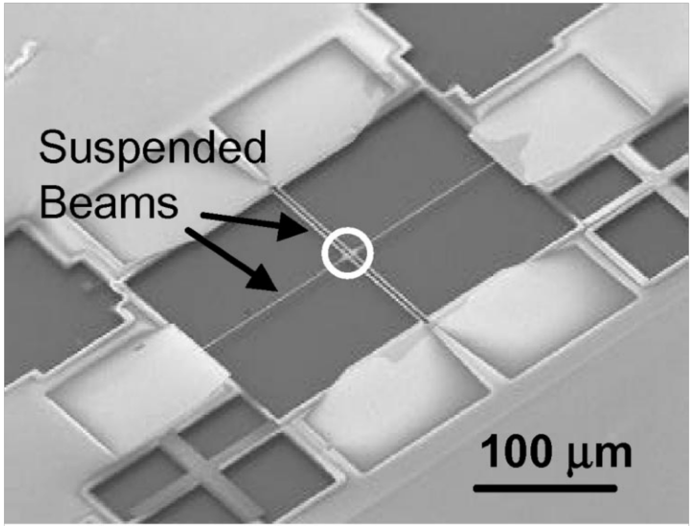
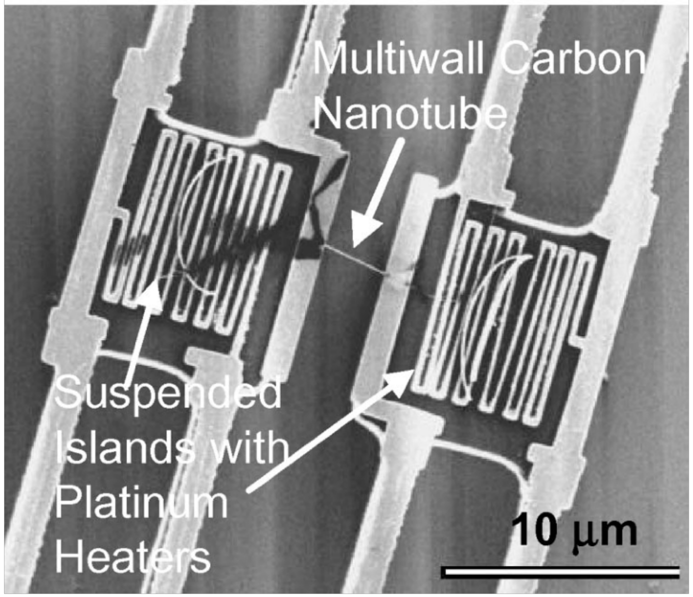


Figure 1.15 Thermal conductivity of silicon films as a function of the film thickness or write diameter. (Courtesy of M. Ashegli).

Chen.

Individual suspended tubes and wires





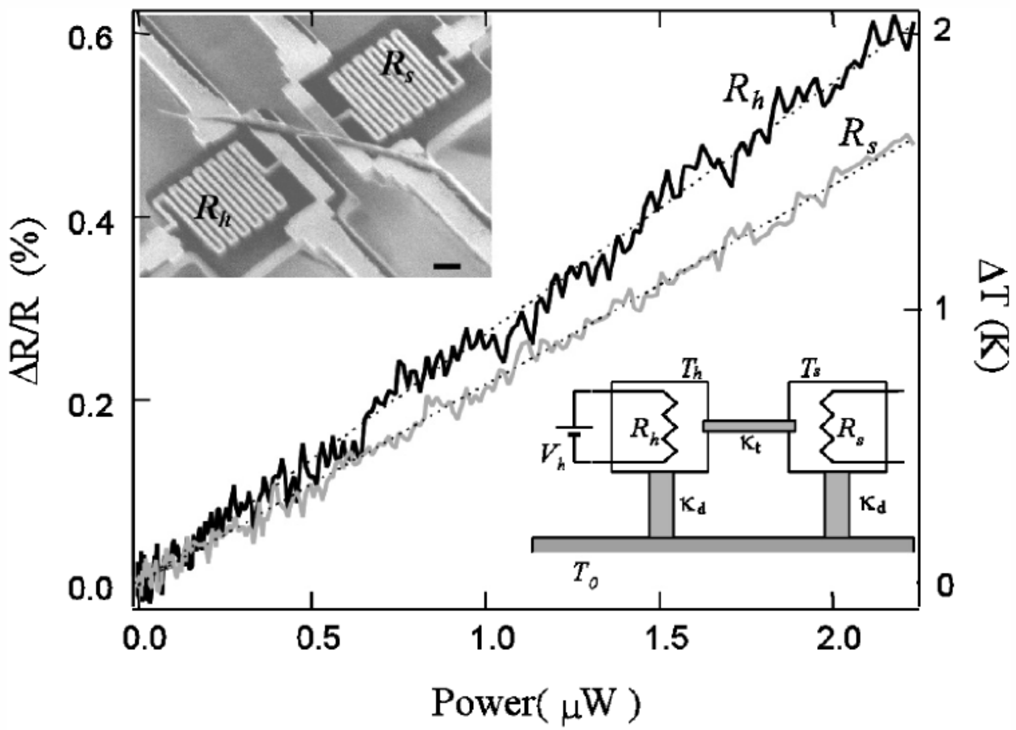


FIG. 2. The change of resistance of the heater resistor (R_h) and sensor resistor (R_s) as a function of the applied power to the heater resistor. Upper inset: SEM image of the suspended islands with a MWNT bundle across the device. The scale bar represents 1 μm. Lower inset: A schematic heat flow model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

Kim et al., Physical Review Letters 87(21):215502, 2001.

Individual suspended MWNTs

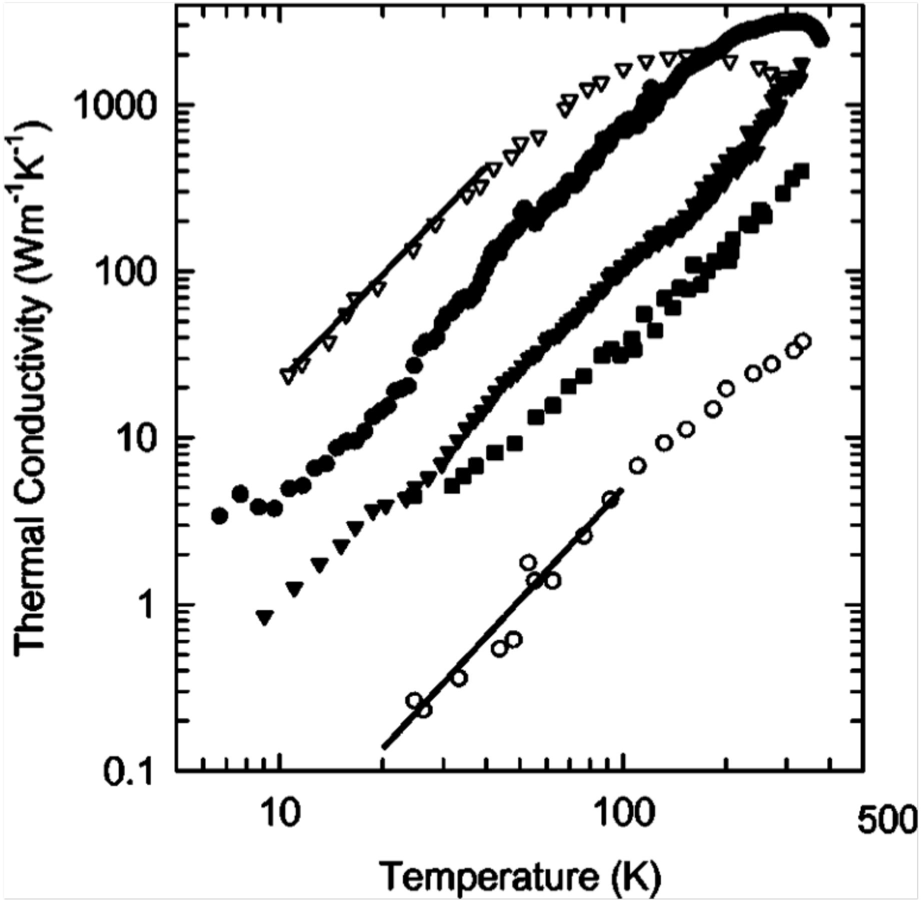


FIG. 9. Measured thermal conductivity of a 14 nm diameter multiwall carbon nanotube (MWCN) (solid circle), an 80 nm diameter MWCN bundle (solid triangle), and a 200 nm diameter MWCN bundle (solid square) (Ref. 94). Data for two vapor-grown graphite fibers (Ref. 95), one heat treated to 3000 °C (open 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).

Kim et al., Physical Review Letters 87(21):215502, 2001.

Individual suspended SWNT

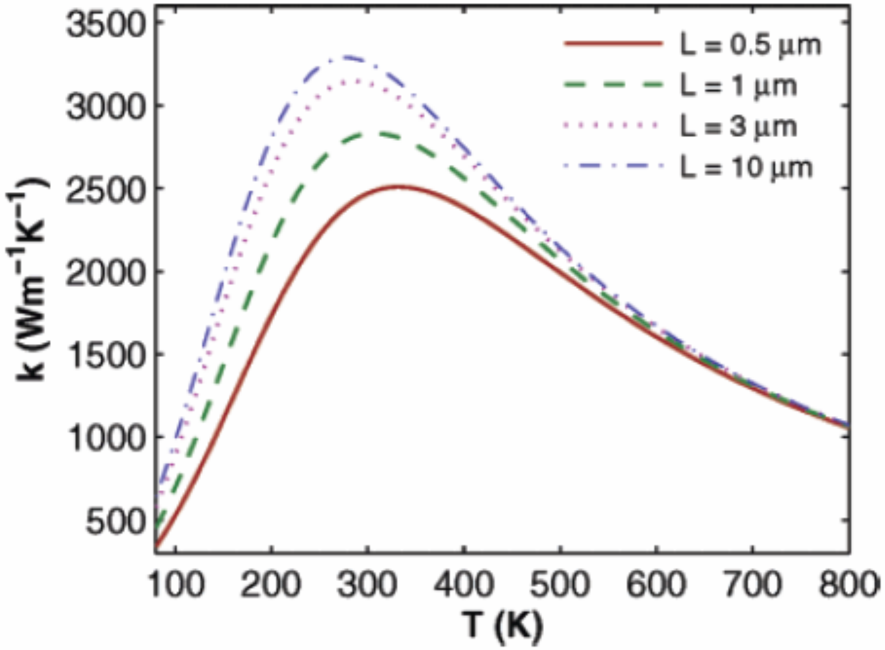


Figure 6. Analytic plot of the intrinsic SWNT thermal conductivity over the 100−800 K temperature range as computed with eq 3. The length dependence is included heuristically with a simple scaling argument, but differences in chirality may lead to variations up to 20% between different tubes.[11]

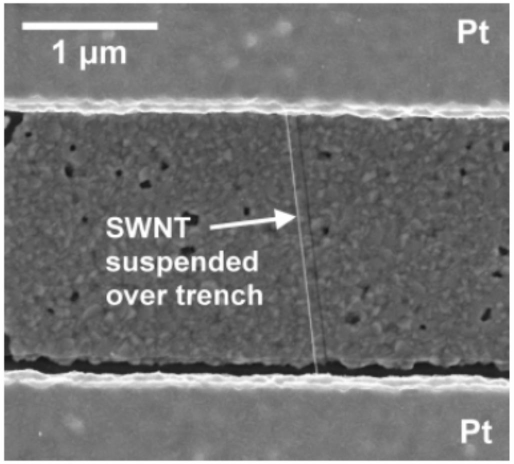


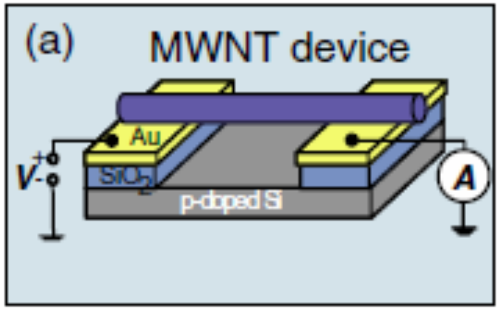
Figure 1. Scanning electron microscope (SEM) image of a typical SWNT freely suspended across a 2-μm trench and lying on top of the Pt contacts. This sample was coated with 1.5 nm Ti/2.5 nm Au to facilitate SEM imaging.

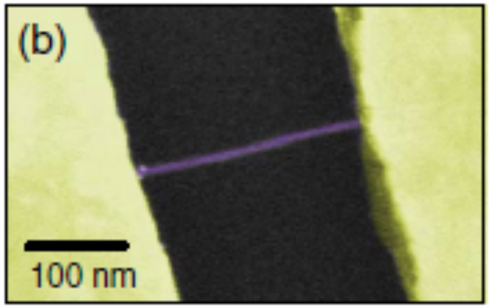
Phonon mean-free path at 300 K

$$k(L, T) = [3.7 \times 10^{-7}T + 9.7 \times 10^{-10}T^2 + 9.3(1 + 0.5/L)T^{-2}]^{-1} \qquad (3)$$

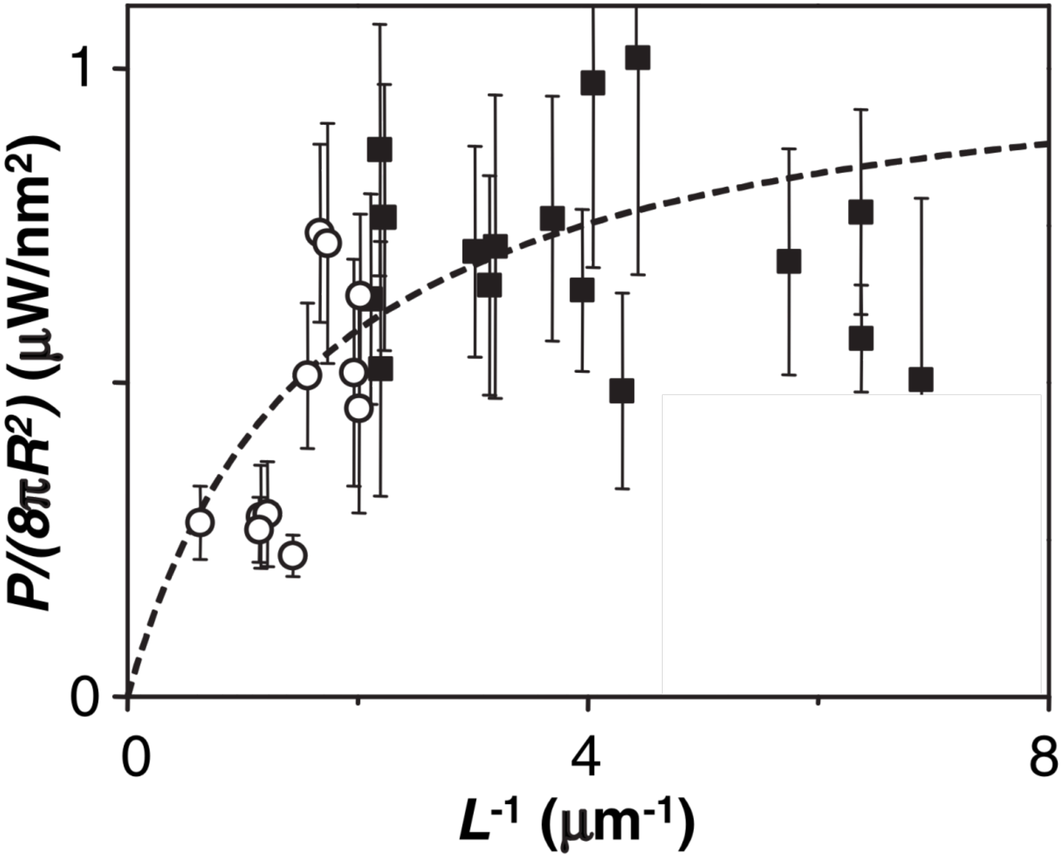
Pop et al., Nano Letters 6(1):96, 2006

Ballistic phonon transport in MWNTs



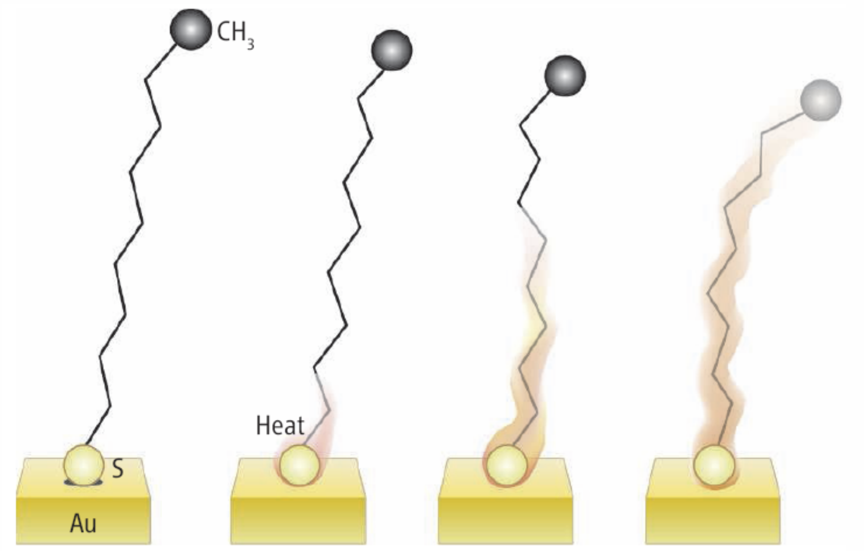


Power independent of length below 500nm



Chiu et al., Physical Review Letters 95:226101, 2005.

Heat conduction in molecular chains



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

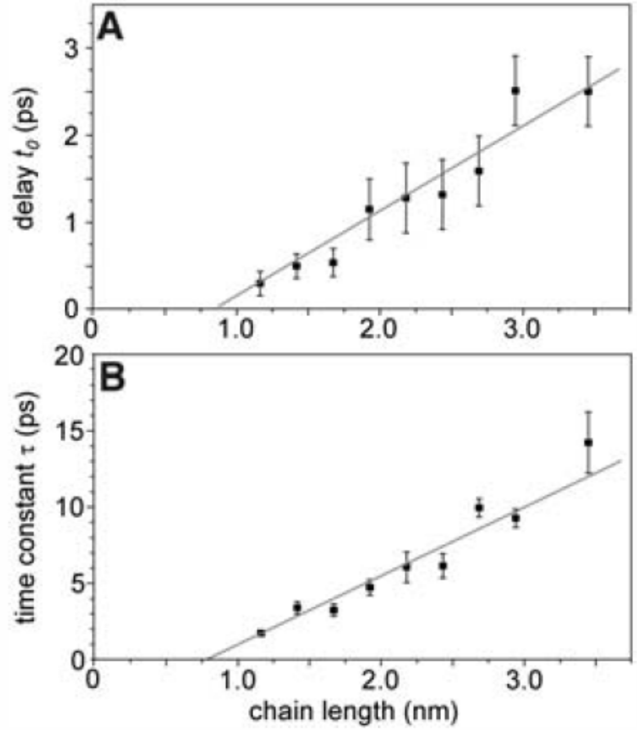
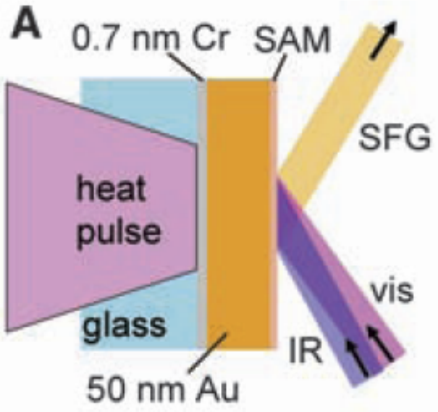


Fig. 4. (**A**) Dependence on chain length of the delay time t_0 between the flash-heating pulse and the arrival of the initial burst of heat at the methyl head groups. (**B**) Dependence on chain length of the time constant τ for thermal equilibration between flash-heated Au and alkane chains.

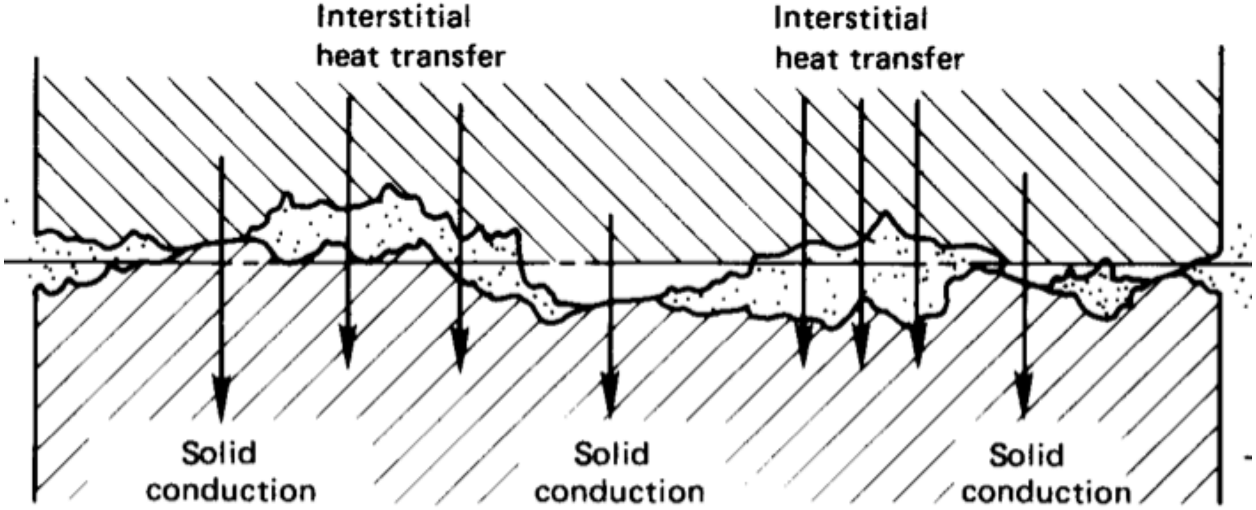


→Ballistic transport, velocity ≈1 m/s

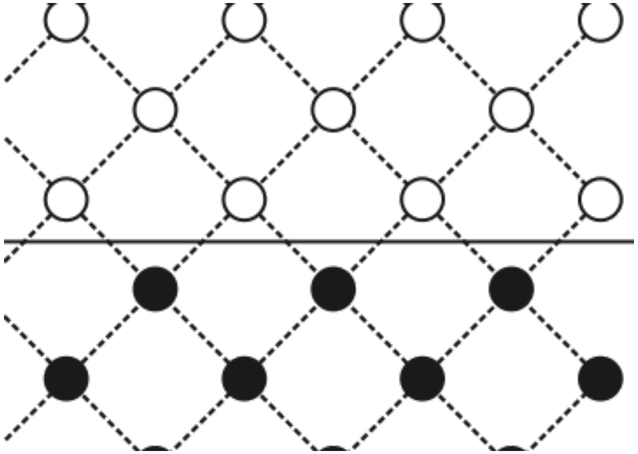
Wang et al., Science 317:787, 2007.

Thermal boundary conductance

$$q = G\Delta T$$



Caused by gaps



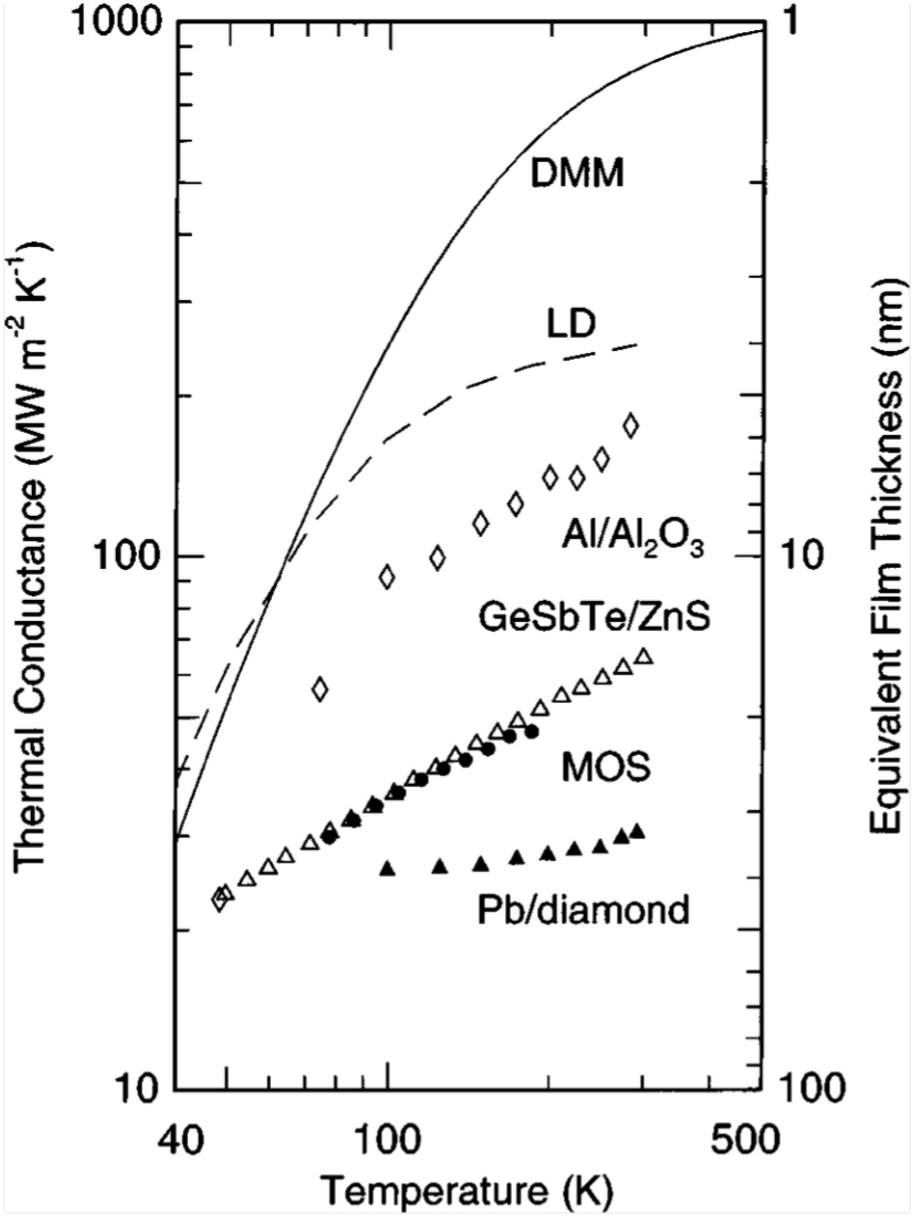
Caused by reflection and transmission of phonons at interfaces

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)

$$G_e = \frac{1}{4}\sum_{j}^{3}\int_0^{\omega_{\mathrm{max,j}}} \underbrace{\boxed{\alpha_{1-2}}}_{\text{transmissivity}}\underbrace{\boxed{\hbar\omega}}_{\text{phonon energy}}\underbrace{\boxed{v_1}}_{\text{phonon speed}}\overbrace{\boxed{D_1}}^{\text{DOS}}\frac{\partial \overbrace{\boxed{f}}^{\text{occupation function}}}{\partial T_e}d\omega$$

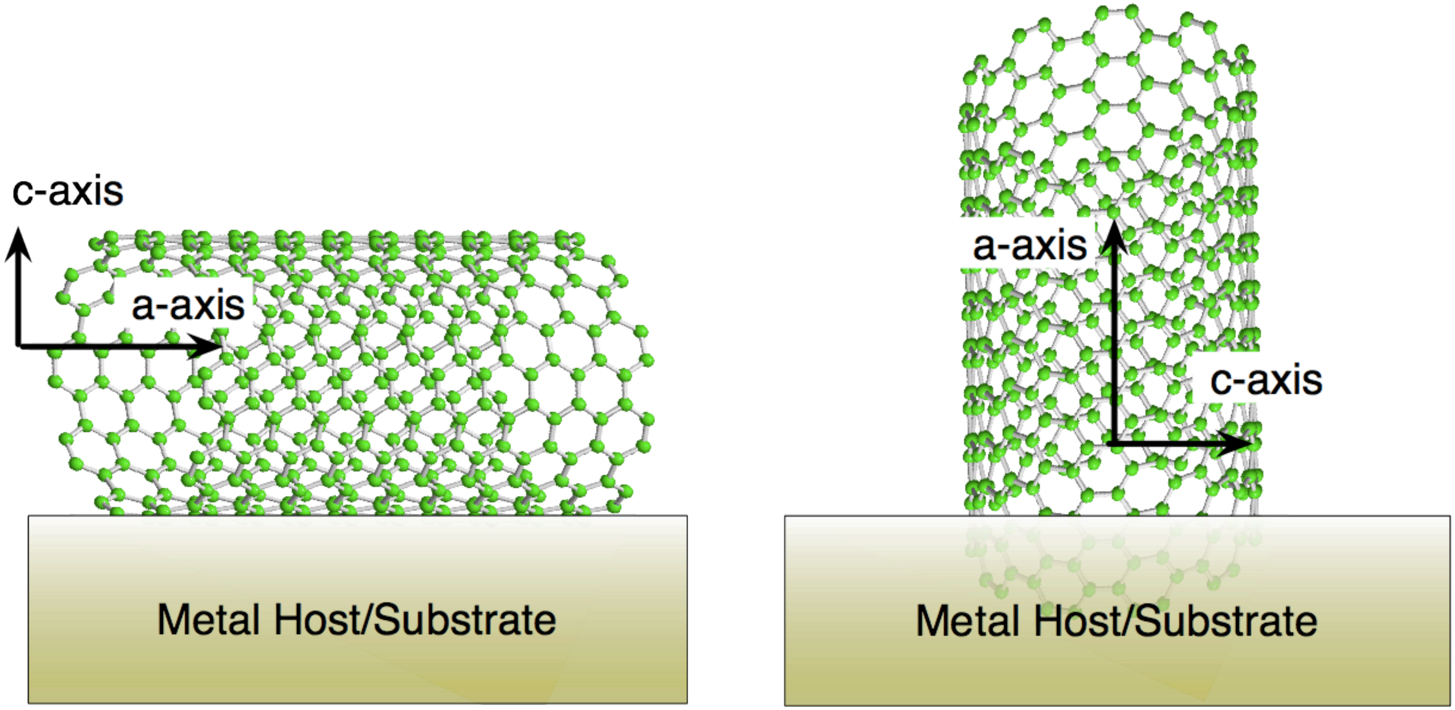
Some values of G



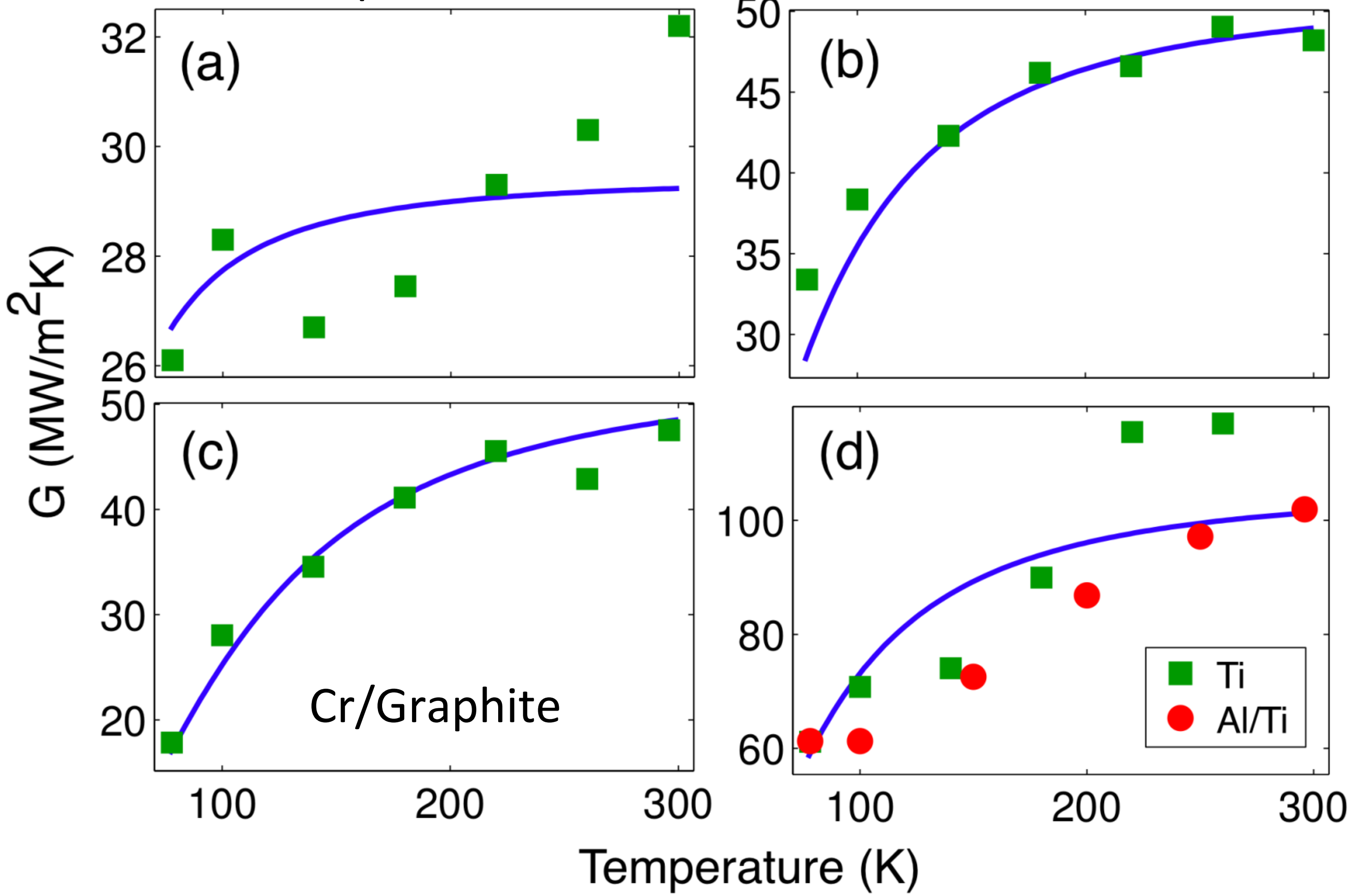
J. Appl. Phys., Vol. 93, No. 2, 15 January

An example: metal-graphite interfaces

- Graphite-based electronics
- Thermal interface materials
- Characterization of carbon nanostructures



Measurements and DMM predictions



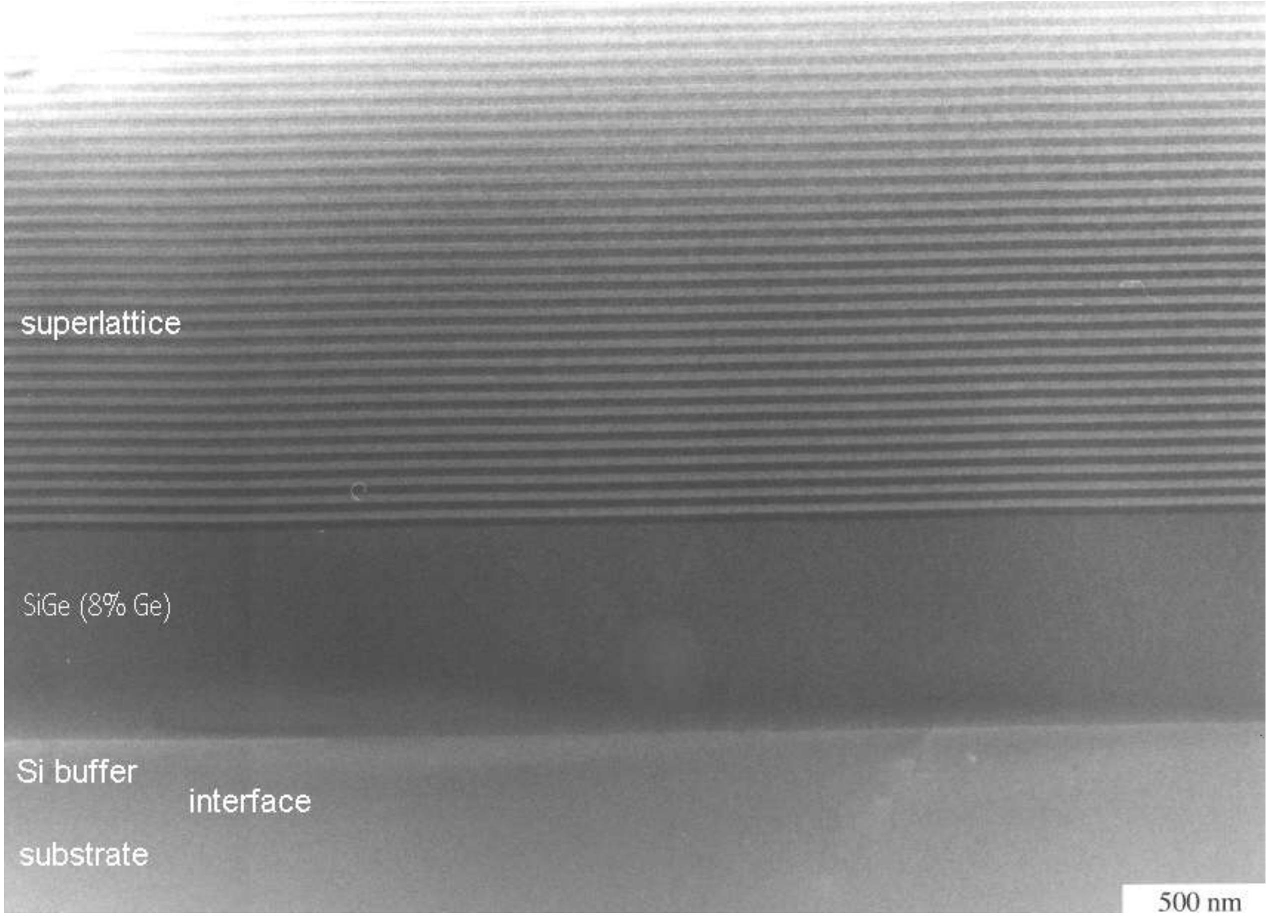
Gold/Graphite

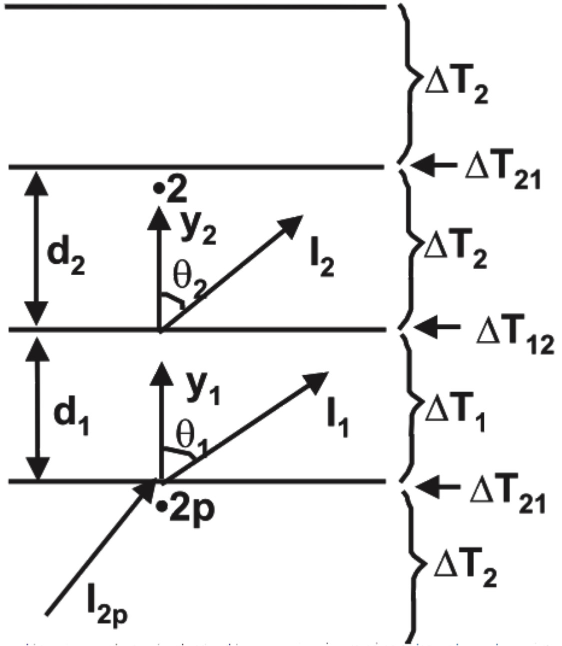
Aluminum/Graphite

Cr/Graphite

Ti/Graphite

Superlattices

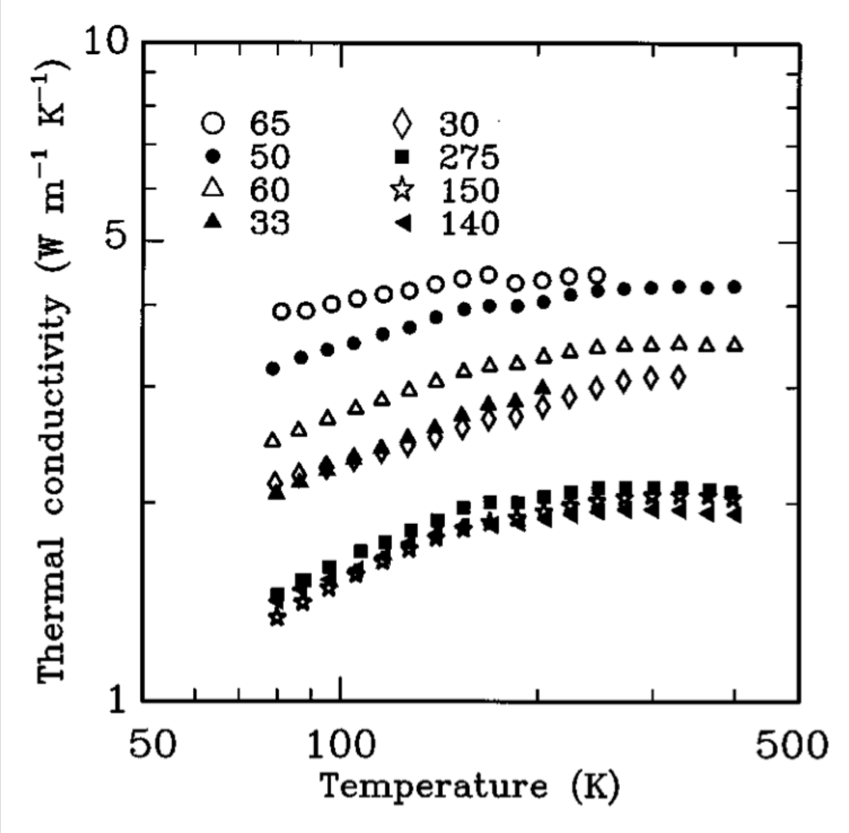




http://lmn.web.psi.ch/shine/sigec.htm

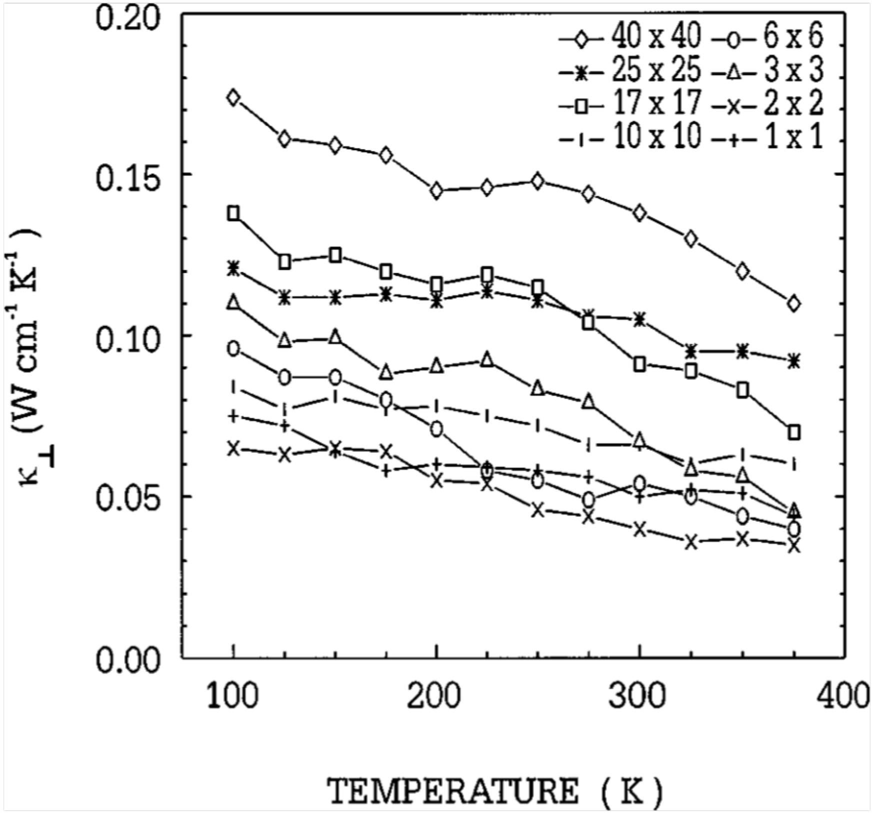
Superlattices

Si/Ge



Appl. Phys. Lett., Vol. 70, No. 22, 2 June 1997

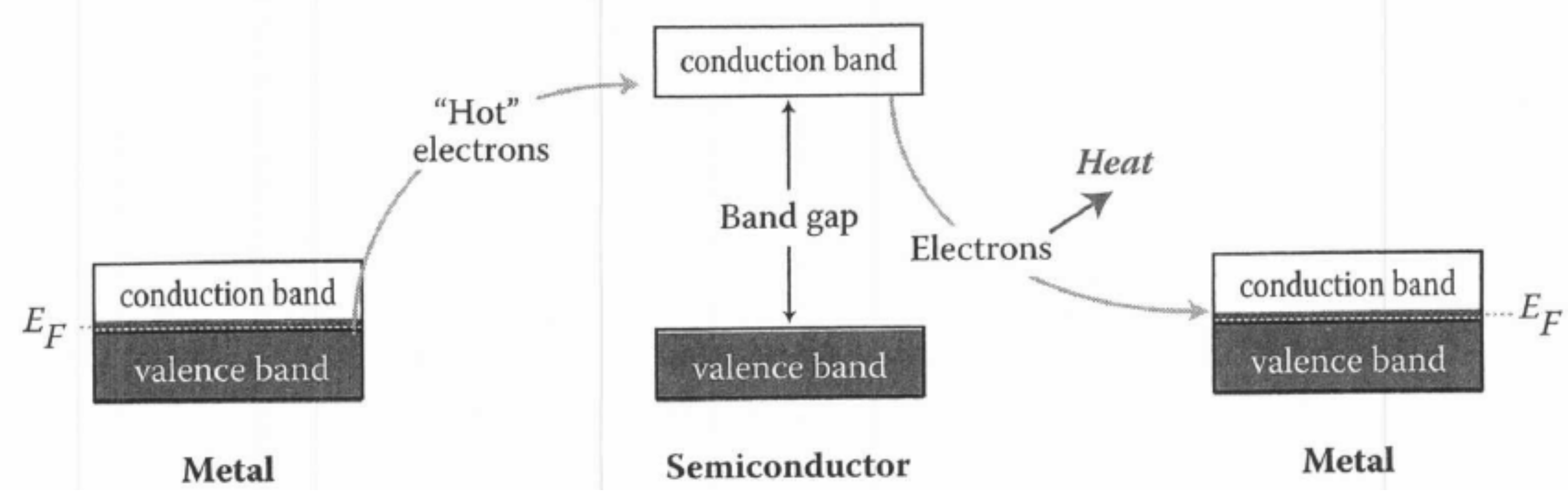
GaAs/AlAs

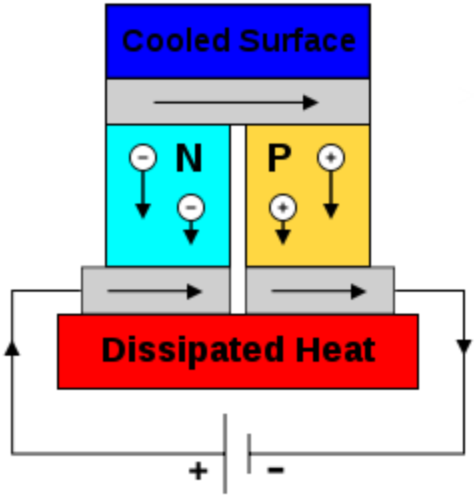


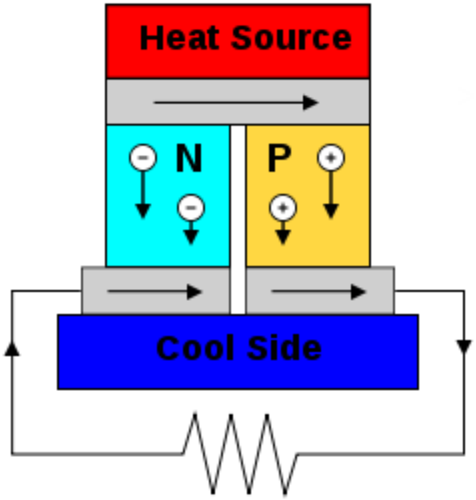
PRB, Vol. 59, No. 12, March 1999

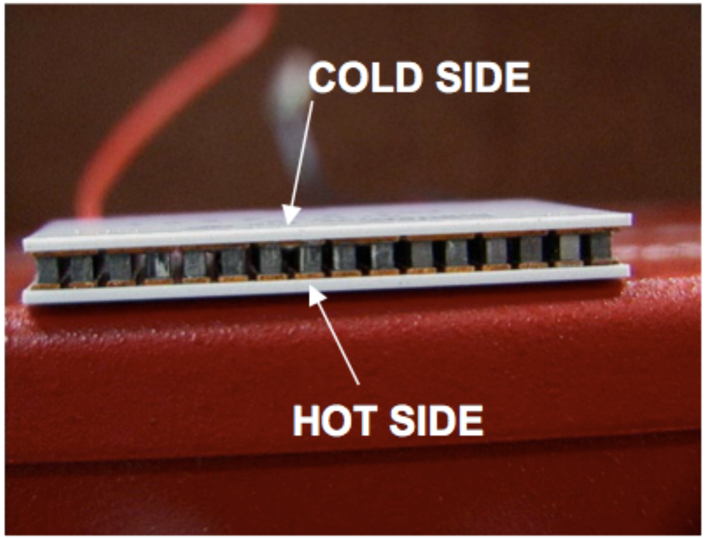
Thermoelectricity - heaters and coolers

- Voltage-induced separation of charge carriers → heat









Rogers, Pennathur, Adams.
Chen, IEEE Transactions on Components and Packaging Technologies 29(2), 2006.

Thermoelectric figure of merit

$$Z = \frac{S^2\sigma}{k} \qquad ZT = \frac{S^2\sigma}{k}T$$

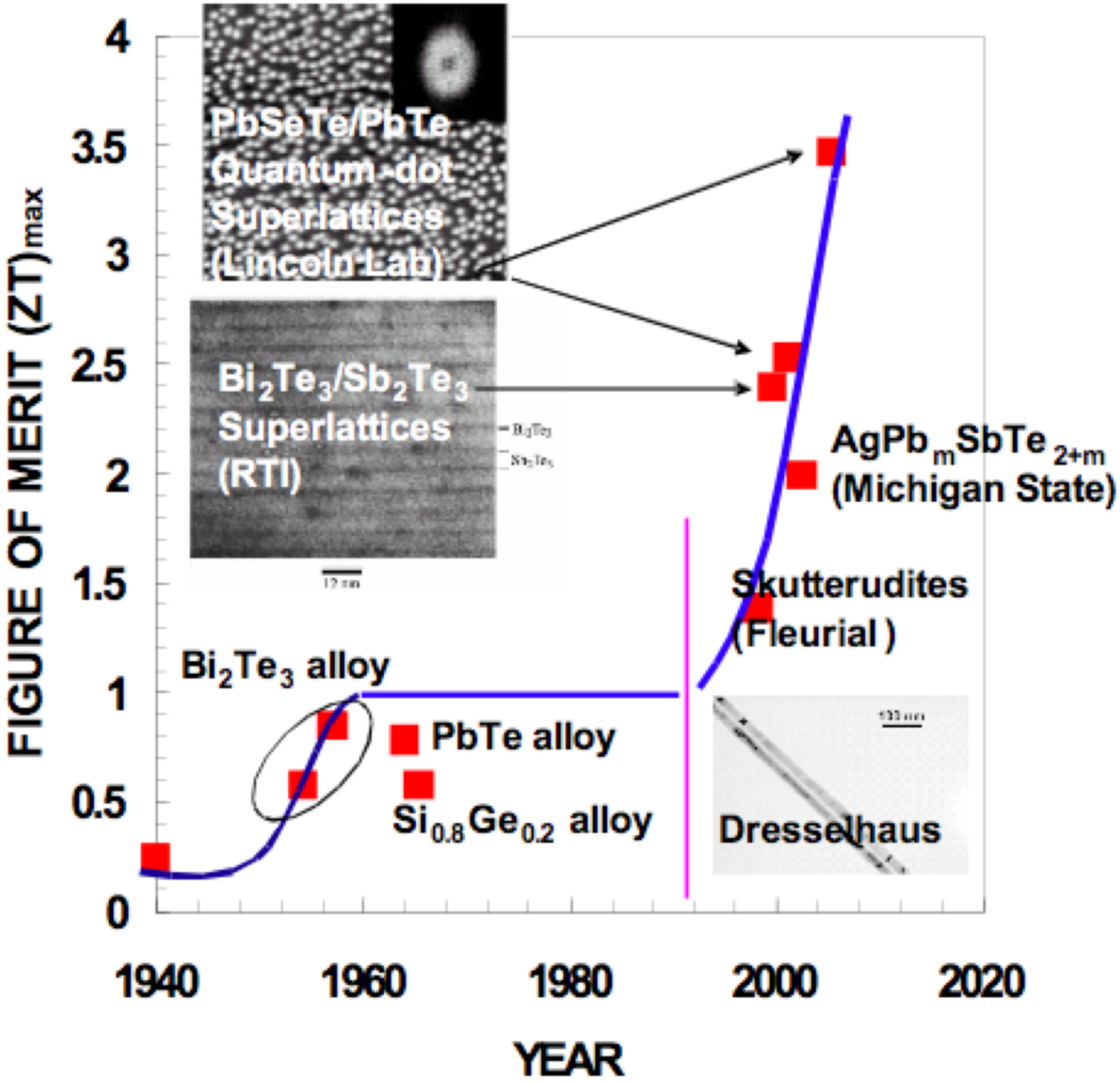
- Need ZT ≈2-3 to compete with conventional technology (e.g., refrigerators)

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

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

- Thermocouples are thermoelectric devices

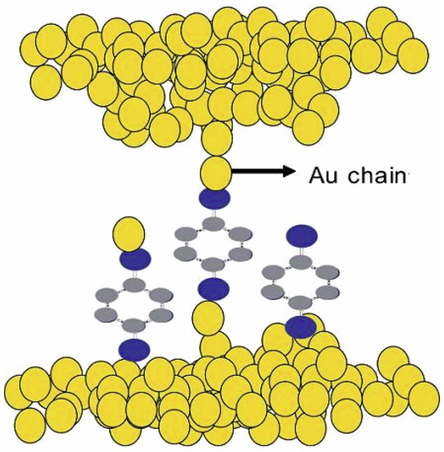
Progress in thermoelectrics: nanoscale heat conduction effects

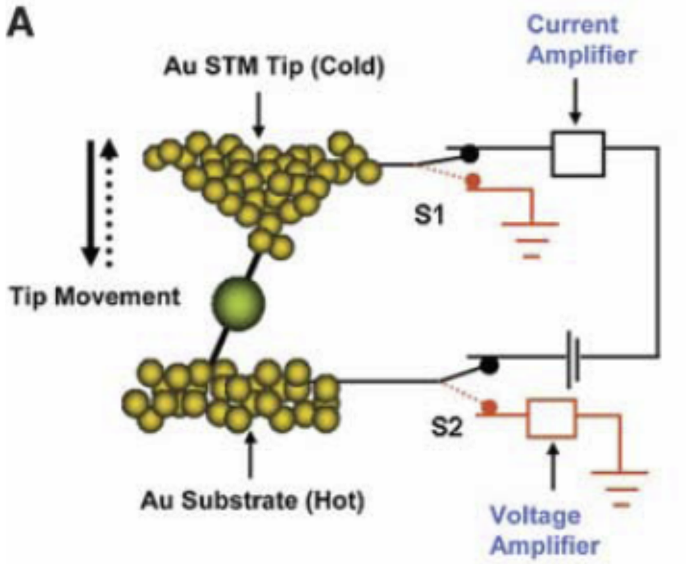


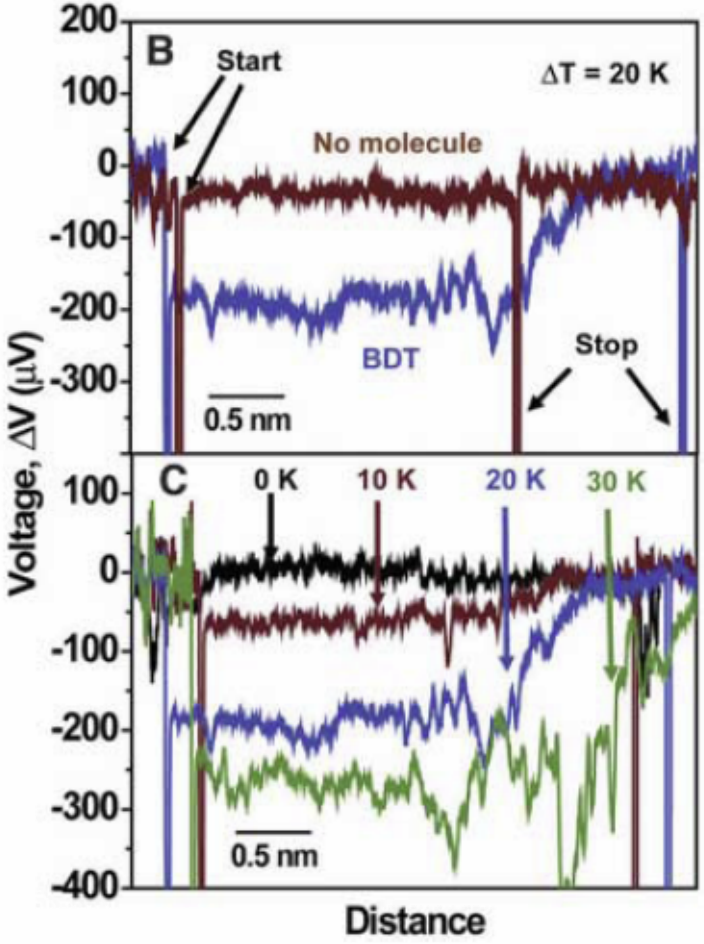
Chen, IEEE Transactions on Components and Packaging Technologies 29(2), 2006.

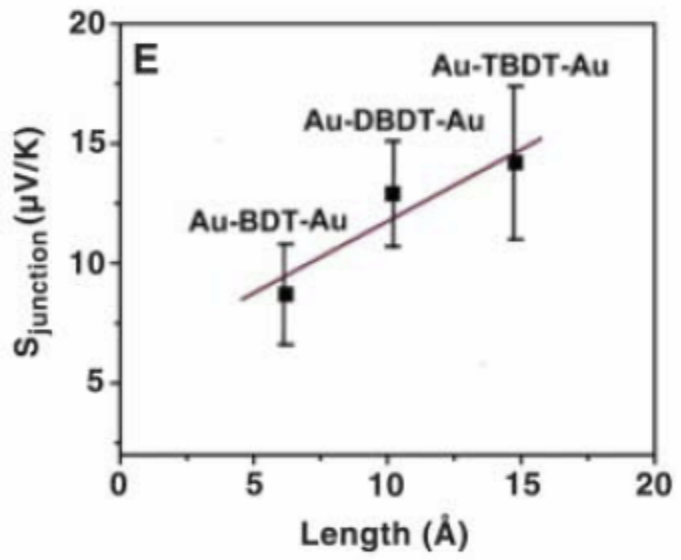
Thermoelectricity in molecular junctions

Single molecule junction, just before the junction breaks



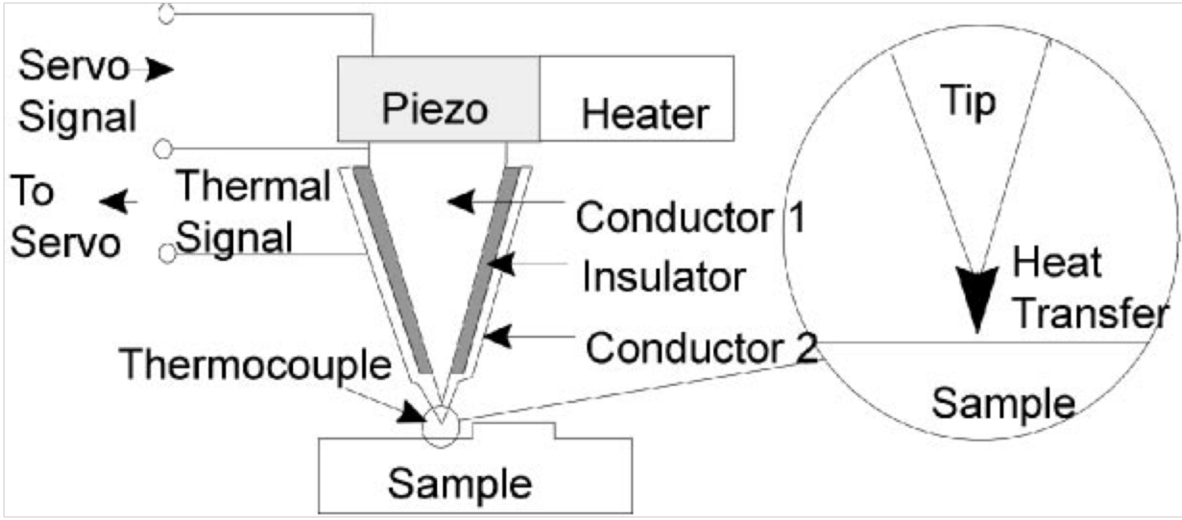






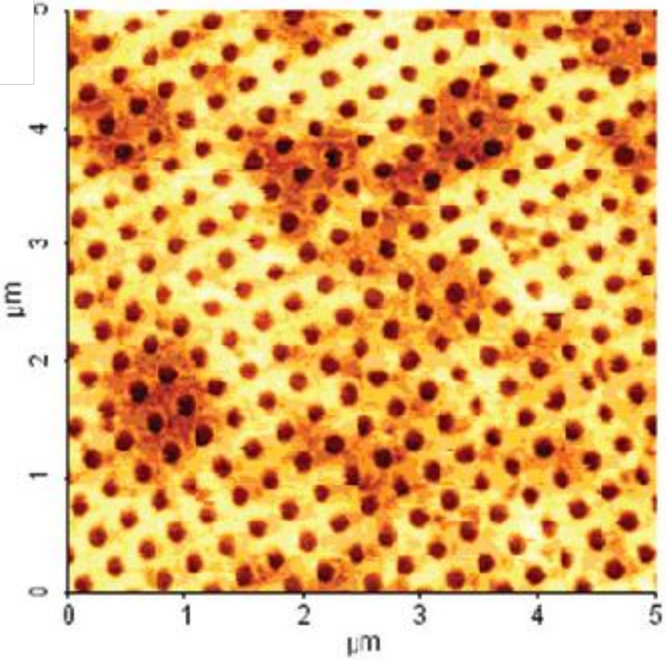
Reddy et al., Science 315:1568-1571, 2007.

Scanning thermal microscopy (SThM)



- Thermometer, ~100nm spatial resolution
- Localized heat source

→ Thermal conductivity map

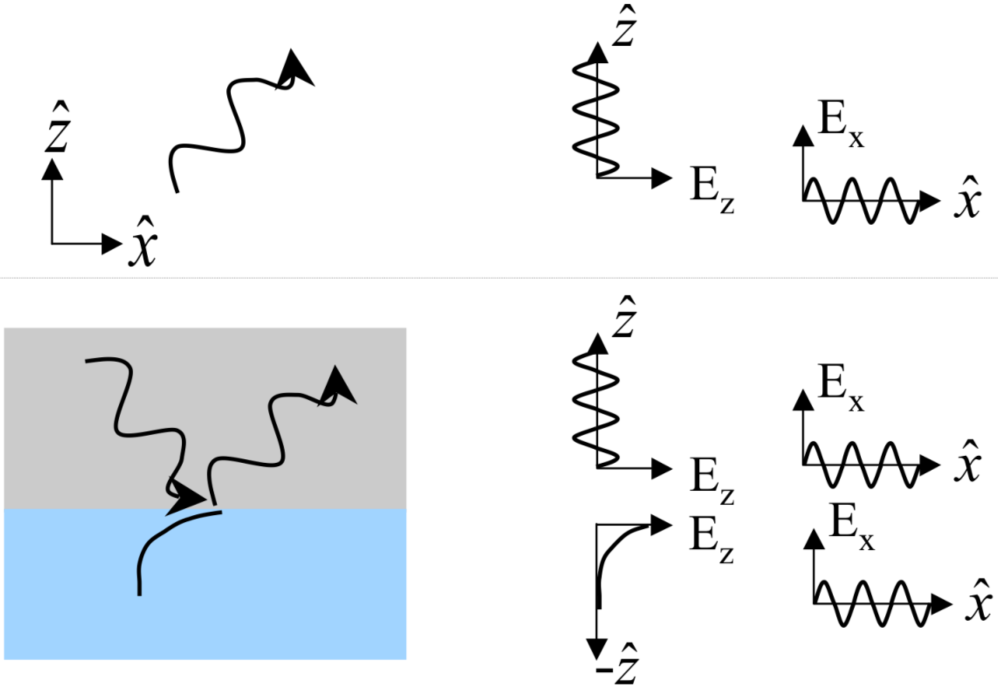


Majumdar, Annual Review of Materials Science 29:505-585, 1999.
http://www.park.com

Near field thermal radiation

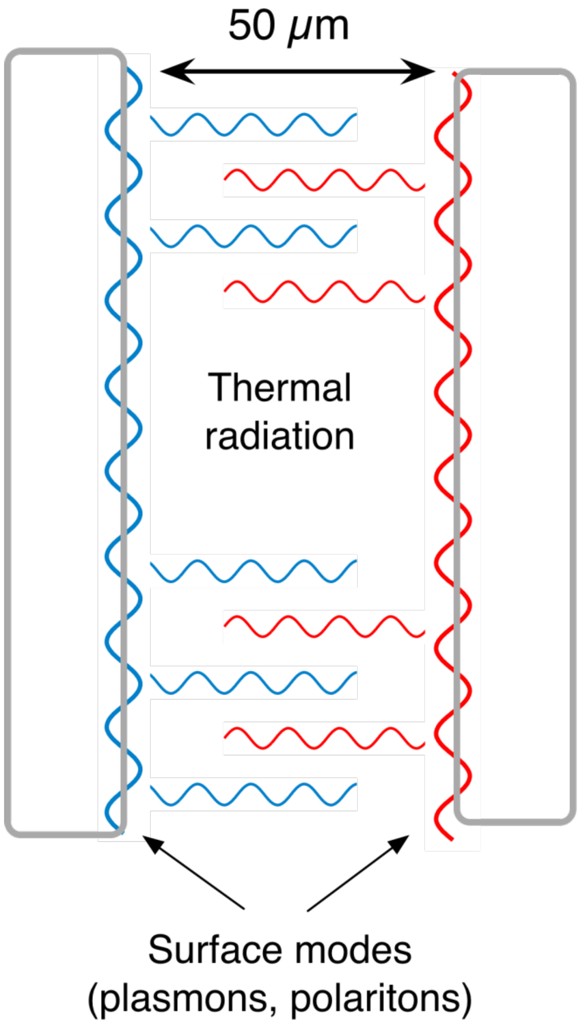
Propagating waves

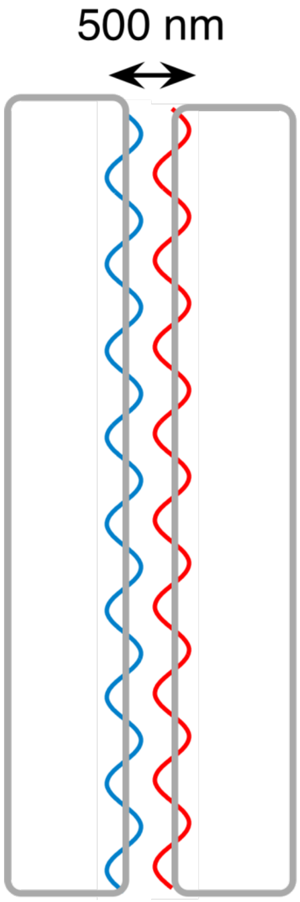
Evanescent waves:
Decay exponentially



Near field thermal radiation II

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

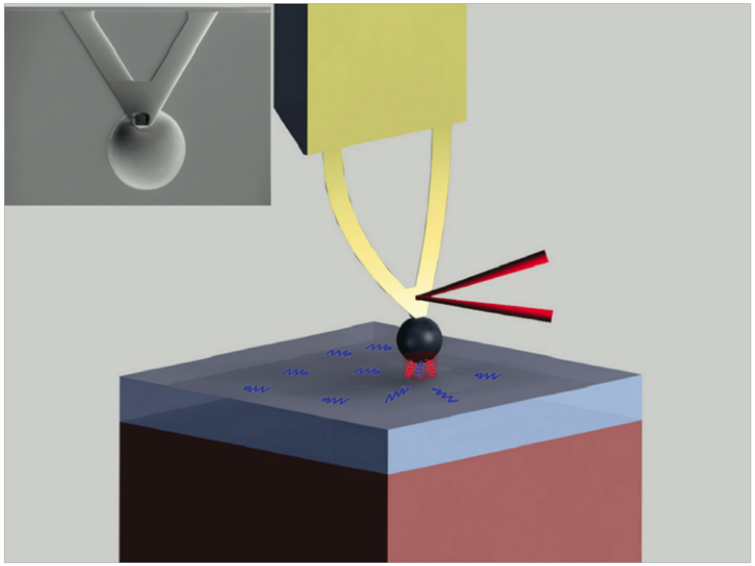


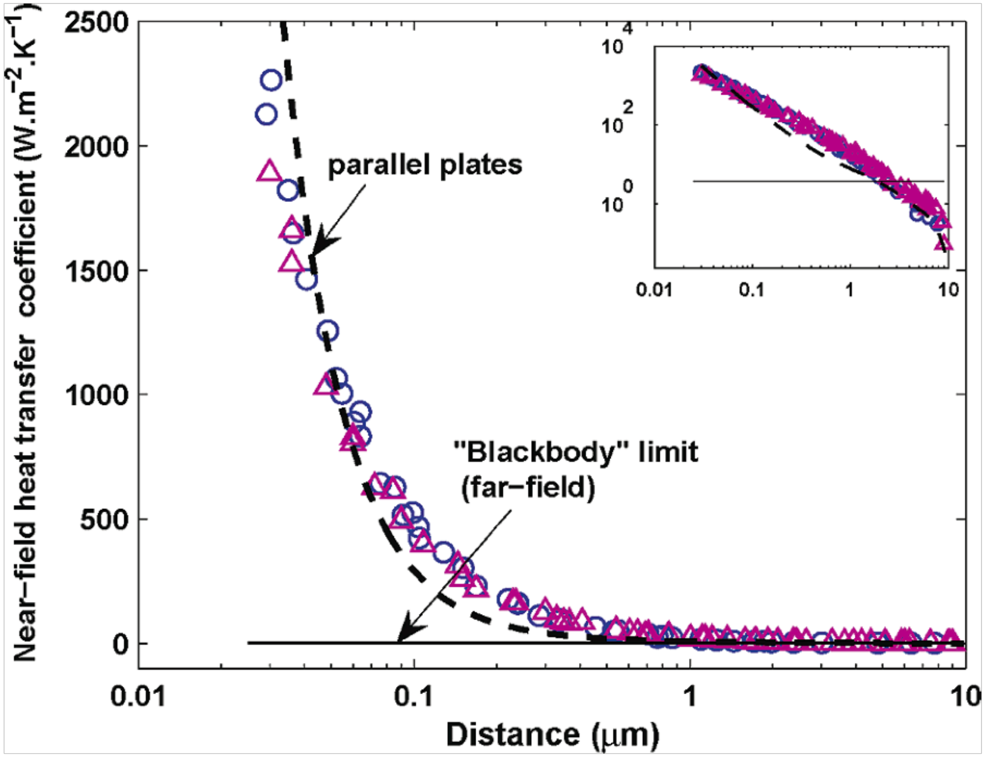


Surface modes are close enough to exchange energy

Example

- Thermal radiation between a microsphere of SiO_2 and a flat surface





Conclusion: recap of energy carriers

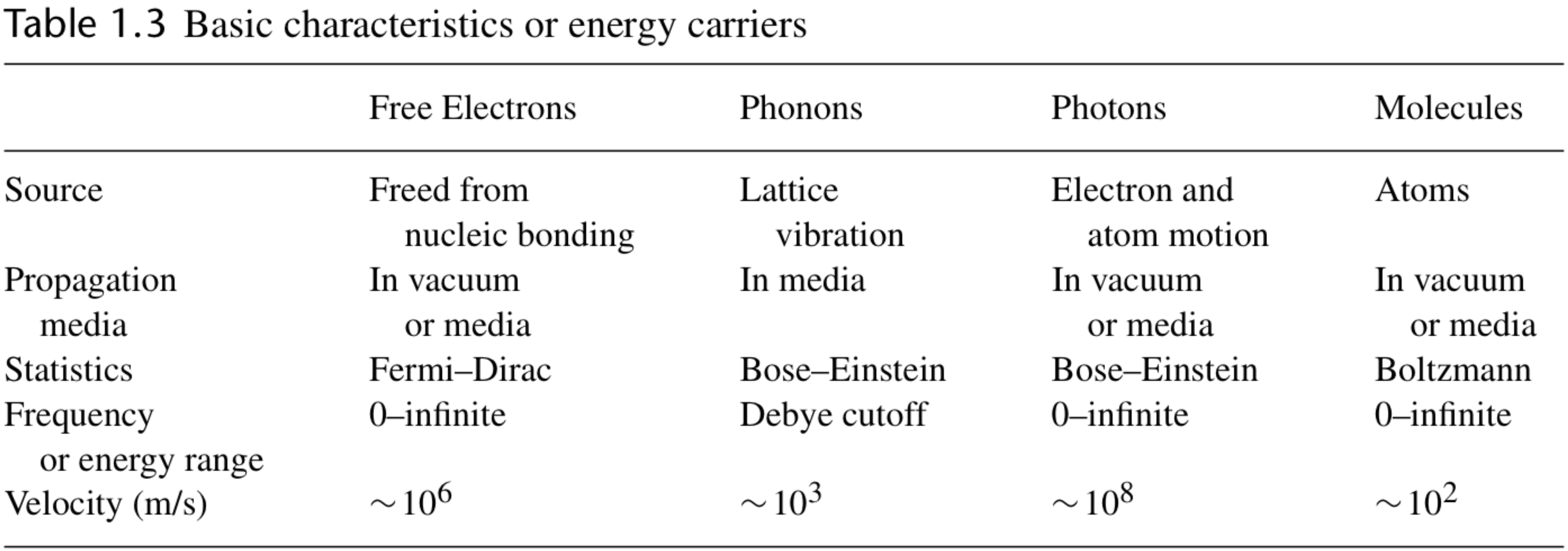


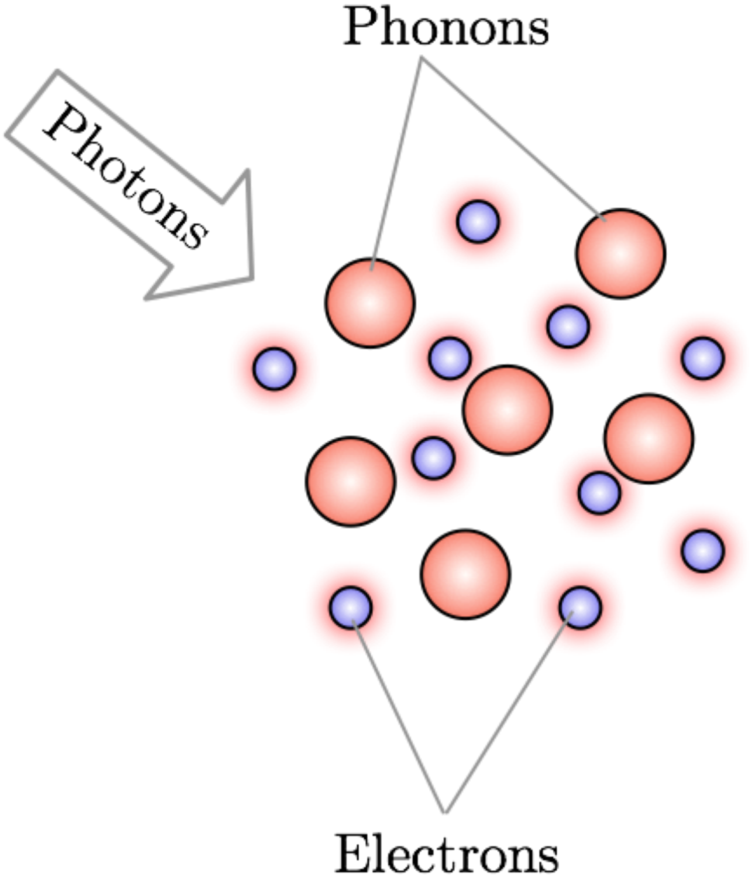
Table 1.3 Basic characteristics or energy carriers

	Free Electrons	Phonons	Photons	Molecules
Source	Freed from nucleic bonding	Lattice vibration	Electron and atom motion	Atoms
Propagation media	In vacuum or media	In media	In vacuum or media	In vacuum or media
Statistics	Fermi–Dirac	Bose–Einstein	Bose–Einstein	Boltzmann
Frequency or energy range	0–infinite	Debye cutoff	0–infinite	0–infinite
Velocity (m/s)	$\sim 10^6$	$\sim 10^3$	$\sim 10^8$	$\sim 10^2$

Chen.

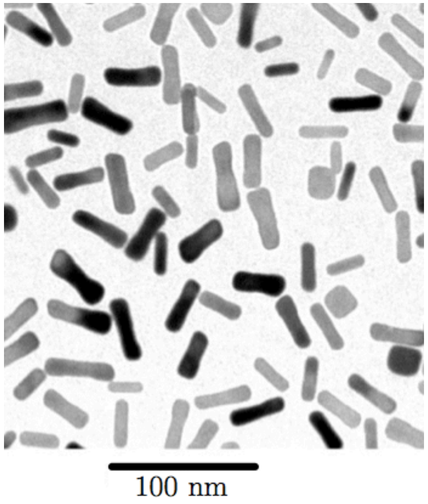
Non-equilibrium (fast) transport example: ultrafast laser interactions

- Photon-electron ~ pulse width
- Electron-electron ~ 100-500 fs
- Electron-phonon ~ 1-10 ps
- Ballistic phonon ~ 10-100 ps
- Diffusion ~ t > 100 ps

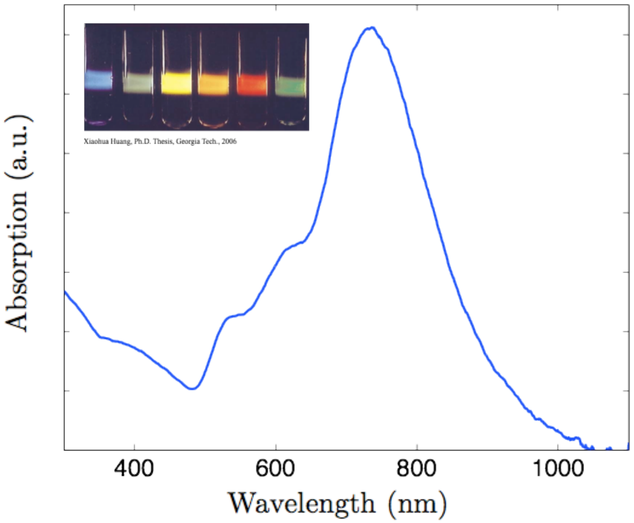


Application: Gold nanorods for tumor hyperthermia with pulsed lasers

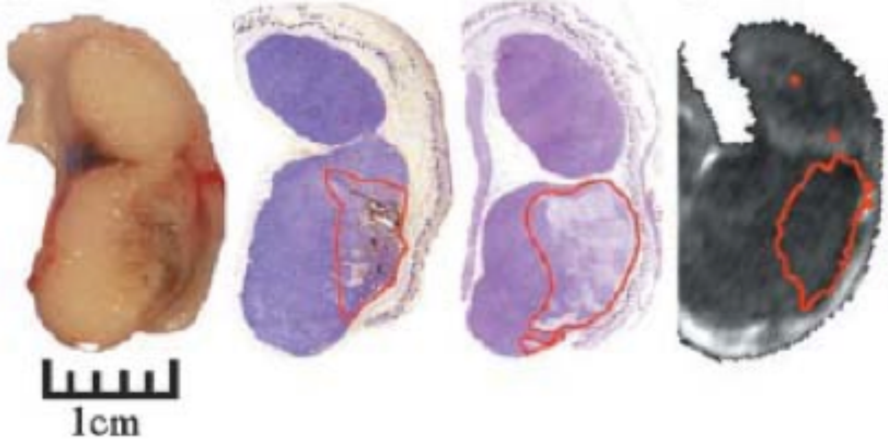
Controlled size



Tunable absorption spectra

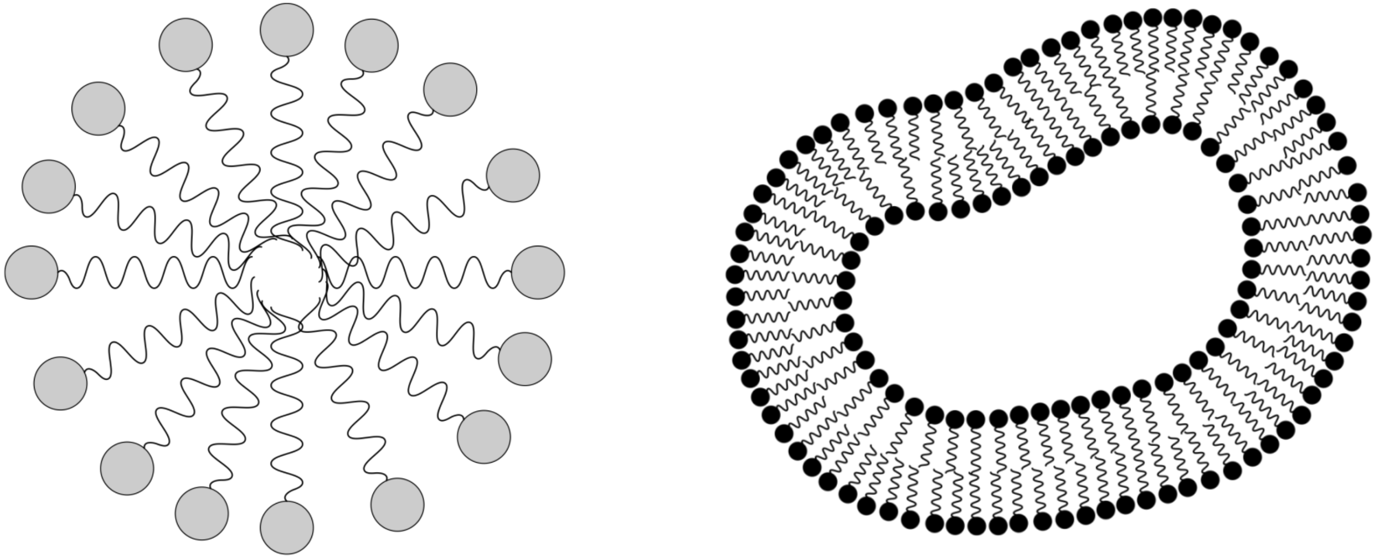


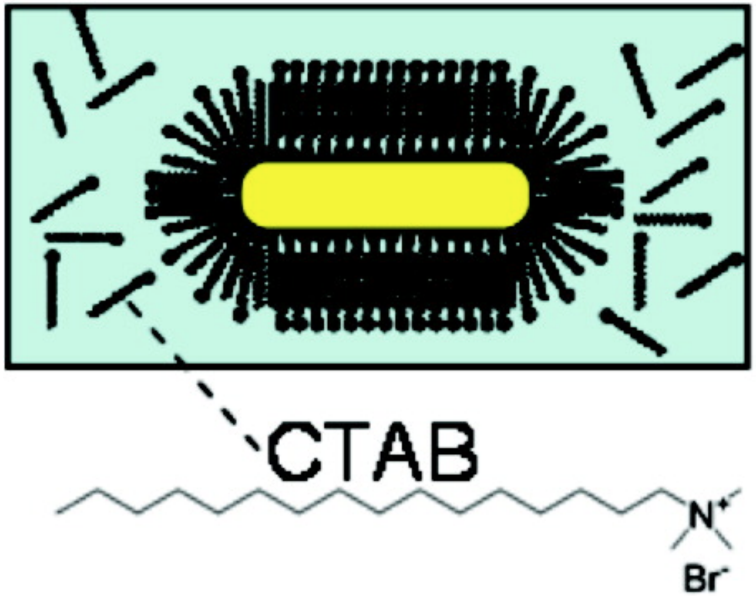
Selective binding



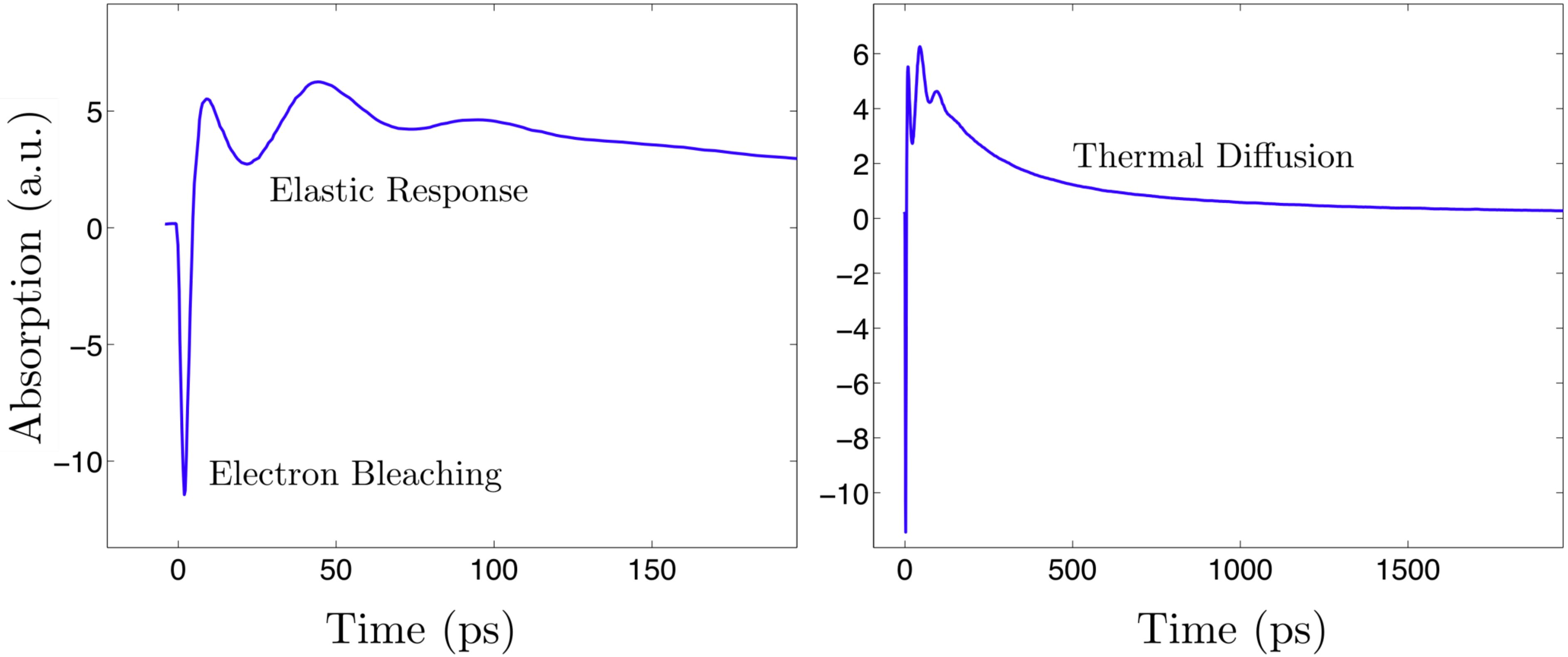
Xiaohua Huang, Ph.D. Thesis, Georgia Tech., 2006

Coating the nanorods



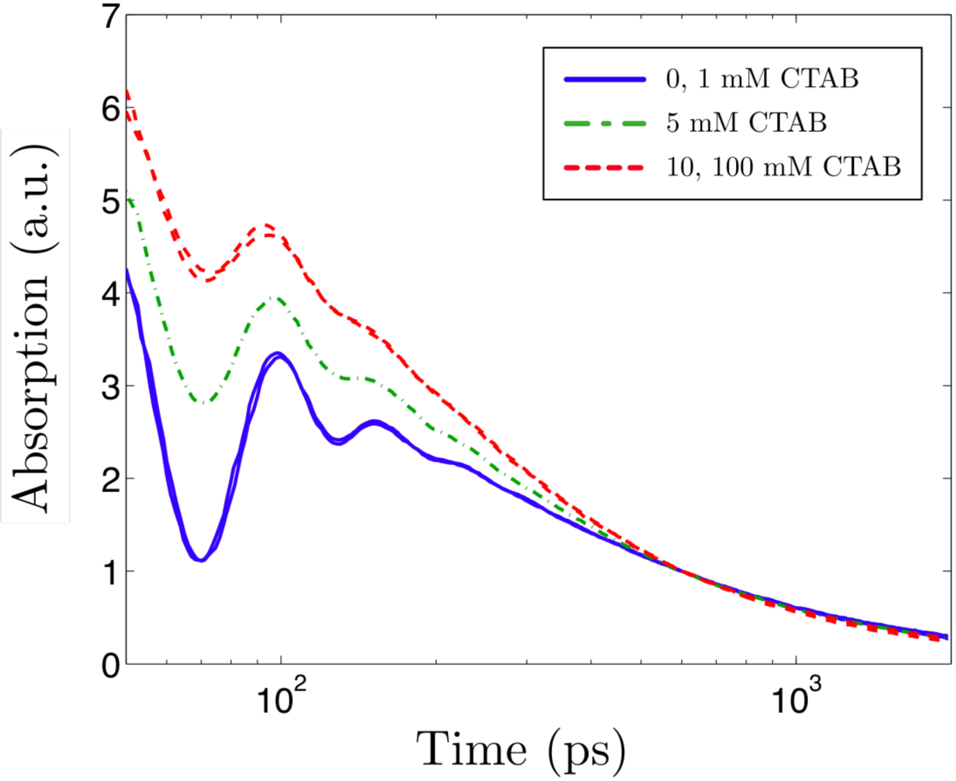


Ultrafast absorption and cooling from laser pulse

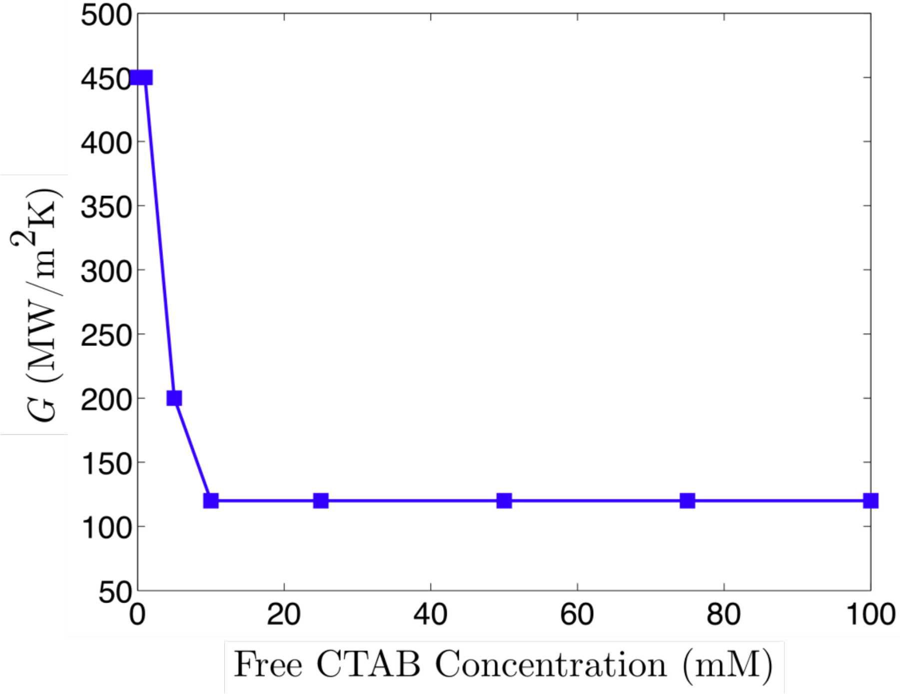


Measuring the effect of the bilayer

Bilayer forms with increased concentration



Bilayer decreases G



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