Classical Theory Expectations

- Equipartition: $1/2k_BT$ per degree of freedom
- In 3-D electron gas this means $3/2k_BT$ per electron
- In 3-D atomic lattice this means $3k_BT$ per atom (why?)
- So one would expect: $C_V = du/dT = 3/2n_ek_B + 3n_ak_B$

- Dulong & Petit (1819!) had found the molar heat capacity of most solids approaches $3N_Ak_B$ at high T

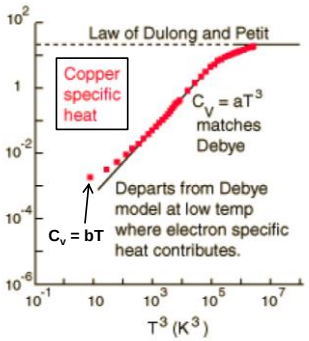
Molar heat capacity @ high T → 25 J/mol/K

Heat Capacity: Real Metals

$$C_V = bT + aT^3$$

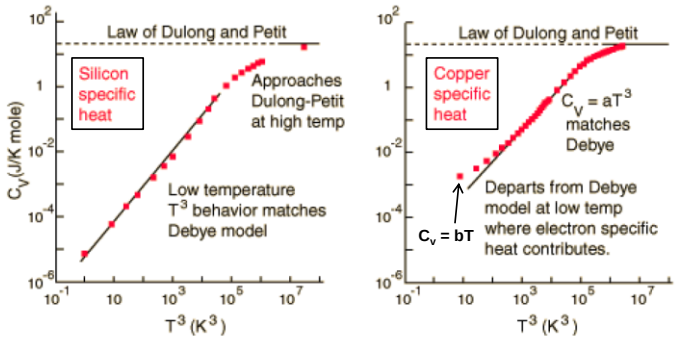
due to electron gas

due to atomic lattice



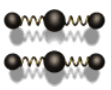
- So far we've learned about heat capacity of electron gas
- But evidence of linear ~T dependence only at very low T
- Otherwise C_V = constant (very high T), or ~T^3 (intermediate)
- Why?

Heat Capacity: Dielectrics vs. Metals

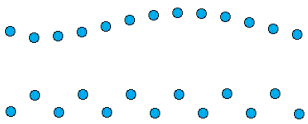


- Very high T: $C_V = 3nk_B$ (constant) both dielectrics & metals
- Intermediate T: $C_V \sim aT^3$ both dielectrics & metals
- Very low T: $C_V \sim bT$ metals only (electron contribution)

Phonons: Atomic Lattice Vibrations



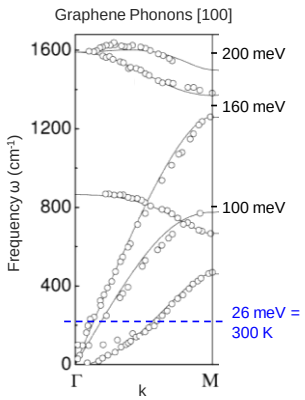
CO_2 molecule vibrations



transverse small k

transverse max k=2π/a

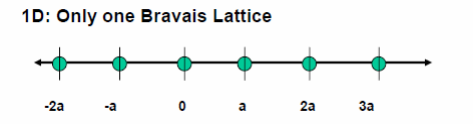
$$\mathbf{u}(\mathbf{r},t) = \mathbf{A}\exp[i(\mathbf{k}\cdot\mathbf{r} - i\omega t)]$$



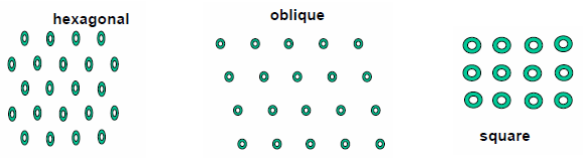
- Phonons = quantized atomic lattice vibrations
- Transverse ($u \perp k$) vs. longitudinal modes ($u \parallel k$), acoustic vs. optical
- "Hot phonons" = highly occupied modes above room temperature

A Few Lattice Types

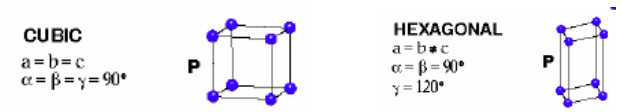
- Point lattice (Bravais)
  - 1D



  - 2D

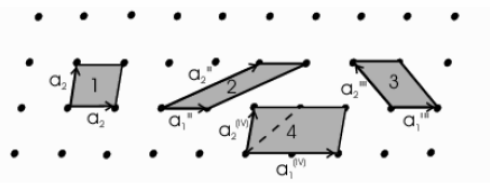


  - 3D

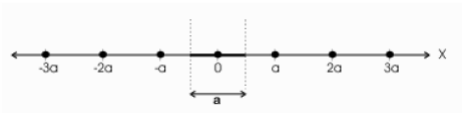


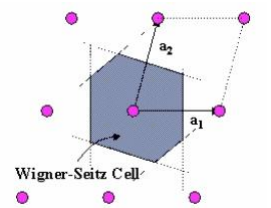
Primitive Cell and Lattice Vectors

$$\mathbf{R}_\ell = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

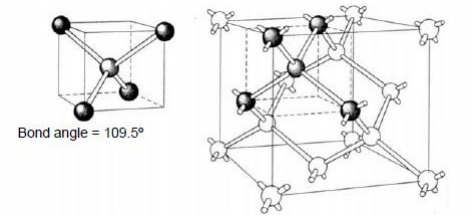


- Lattice = regular array of points $\{R_l\}$ in space repeatable by *translation* through primitive lattice vectors
- The vectors a_i are all primitive lattice vectors
- Primitive cell: Wigner-Seitz



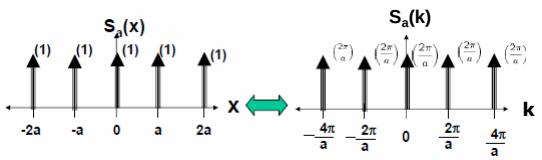


Silicon (Diamond) Lattice

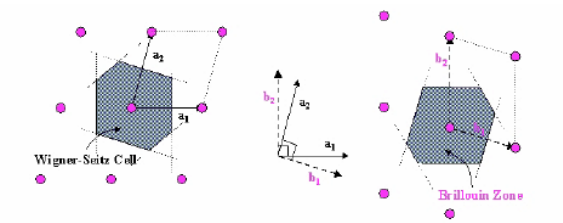


- Tetrahedral bond arrangement
- 2-atom basis
- Each atom has 4 nearest neighbors and 12 next-nearest neighbors
- What about in (Fourier-transformed) k-space?

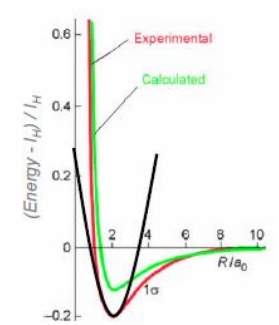
Position → Momentum (k-) Space



- The Fourier transform in k-space is also a lattice
- This *reciprocal lattice* has a lattice constant 2π/a



Atomic Potentials and Vibrations

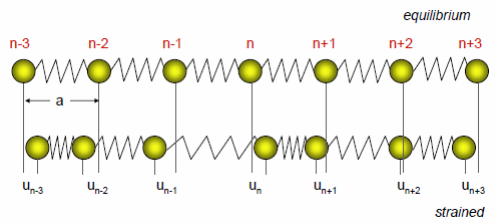


$$V_{\text{eff}}(r) = V_o + \frac{1}{2}(r - R_o)^2 \underbrace{\left(\frac{d^2V}{dr^2}\right)_{R_o}}_{\text{“spring constant”}}$$

$$\boxed{E_r^{n0} = V_o + \hbar\omega_o(n + \frac{1}{2})}$$

- Within small perturbations from their equilibrium positions, atomic potentials are nearly quadratic
- Can think of them (simplistically) as masses connected by springs!

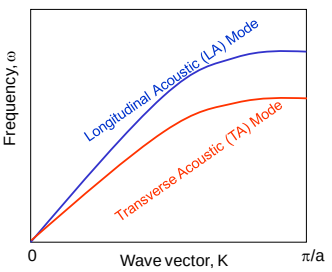
Vibrations in a Discrete 1D Lattice



$$\rho\frac{\partial^2 u_x}{\partial t^2} = E_Y\frac{\partial^2 u_x}{\partial x^2}$$

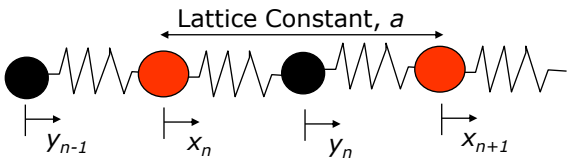
$$\frac{\partial^2 u_x}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 u_x}{\partial t^2} \qquad c = \sqrt{\frac{E_Y}{\rho}}$$

- Can write down wave equation
- Velocity of sound (vibration propagation) is proportional to stiffness and inversely to mass (inertia)



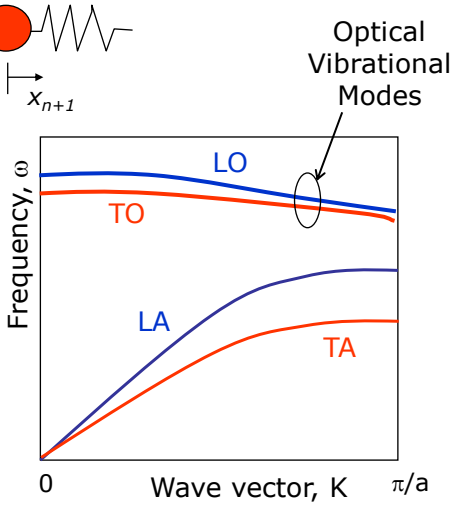
$$u_x(x,t) = A_{\pm}\exp(ikx)\exp(i\omega t) \qquad \omega = ck$$

Two Atoms per Unit Cell



$$m_1 \frac{d^2 x_n}{dt^2} = k\left(y_n + y_{n-1} - 2x_n\right)$$

$$m_2 \frac{d^2 y_n}{dt^2} = k\left(x_{n+1} + x_n - 2y_n\right)$$



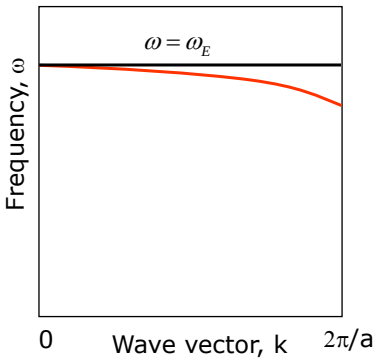
Energy Stored in These Vibrations

- Heat capacity of an atomic lattice
- C = du/dT =

- Classically, recall C = 3Nk, but only at high temperature
- At low temperature, experimentally C → 0
- Einstein model (1907)
  - All oscillators at same, identical frequency ($\omega = \omega_E$)

- Debye model (1912)
  - Oscillators have linear frequency distribution ($\omega = v_s k$)

The Einstein Model



- All *N* oscillators same frequency
- Density of states in ω (energy/freq) is a delta function

$$g(\omega) = 3N\delta(\omega - \omega_E)$$

- Einstein specific heat

$$C_E = \frac{du}{dT} = \int \hbar\omega \frac{df(\omega)}{dT} g(\omega) d\omega =$$

Einstein Low-T and High-T Behavior

- High-T (correct, recover Dulong-Petit):

$$C_E(T) \approx 3Nk_B \left(\frac{\hbar\omega_E}{T}\right)^2 \frac{\left(1+\frac{\hbar\omega_E}{T}\right)}{\left(1+\frac{\hbar\omega_E}{T}-1\right)^2} \approx 3Nk_B$$

Einstein model OK for optical phonon heat capacity

- Low-T (incorrect, drops too fast)

$$C_E(T) \approx 3Nk_B \left(\frac{\hbar\omega_E}{k_BT}\right)^2 \frac{e^{\hbar\omega_E/k_BT}}{\left(e^{\hbar\omega_E/k_BT}\right)^2}$$

$$\approx 3Nk_B \left(\frac{\hbar\omega_E}{k_BT}\right)^2 e^{-\hbar\omega_E/k_BT}$$

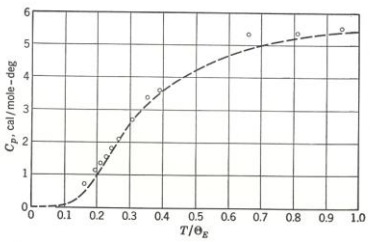


Fig. 6.2. Comparison of experimental values of the heat capacity of diamond and values calculated on the Einstein model, using $\Theta_E = 1320°K$. [After A. Einstein, Ann. Physik **22**, 180 (1907).]

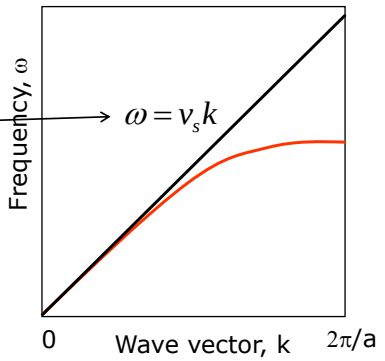
The Debye Model

- Linear (no) dispersion *with frequency cutoff*
- Density of states in 3D:

$$g(\omega) = \frac{\omega^2}{2\pi^2 v_s^3}$$

(for one polarization, e.g. LA)

(also assumed isotropic solid, same v_s in 3D)



- N acoustic phonon modes up to ω_D
- Or, in terms of Debye temperature

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

k_D roughly corresponds to max lattice wave vector (2π/a)

ω_D roughly corresponds to max acoustic phonon frequency

Annalen der Physik 39(4) p. 789 (1912)

oder mit Berücksichtigung der Definitionsgleichung (7)

$$U = 9\,N k\,T\left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} \frac{\xi^3\,d\xi}{e^\xi - 1}. \tag{9}$$

Bekanntlich (wie übrigens natürlich auch aus (9) folgt) würde dem Dulong-Petitschen Gesetz der Wert

$$U = 3\,N k\,T$$

entsprechen. Die in (9) ausgesprochene Beziehung können wir also folgendermaßen in Worte fassen:

Die Energie eines Körpers bekommt man, indem man den Dulong-Petitschen Wert multipliziert mit einem Faktor, welcher eine universelle Funktion ist von dem Verhältnis T/Θ, d. h. Temperatur T dividiert durch charakteristische Temperatur Θ.

Setzen wir abkürzend

$$\frac{\Theta}{T} = x,$$

so hat jener Faktor nach (9) den Wert:

$$\frac{3}{x^3}\int_0^x \frac{\xi^3\,d\xi}{e^\xi - 1}.$$

Verstehen wir unter N die Anzahl Atome pro Atomgewicht, so stellt (9) die entsprechende Energie dar und wir bekommen dann durch Differentiation nach T die Atomwärme bei konstantem Volumen C_v, wofür wir, solange keine Verwechslung zu befürchten ist, einfach C ohne Index schreiben wollen. So ergibt sich aus (9)

$$C = 3\,N k\left[\frac{12}{x^3}\int_0^x \frac{\xi^3\,d\xi}{e^\xi - 1} - \frac{3\,x}{e^x - 1}\right], \tag{10}$$

wenn wir wieder mit x das Verhältnis Θ/T bezeichnen.

Die Größe $3\,N k$ hat bekanntlich den Wert 5,955 cal.; bezeichnen wir denselben mit C_∞, weil er in der Grenze für $T = \infty$ erreicht wird, so können wir statt (10) auch schreiben

$$\frac{C}{C_\infty} = \frac{12}{x^3}\int_0^x \frac{\xi^3\,d\xi}{e^\xi - 1} - \frac{3\,x}{e^x - 1}. \tag{10'}$$

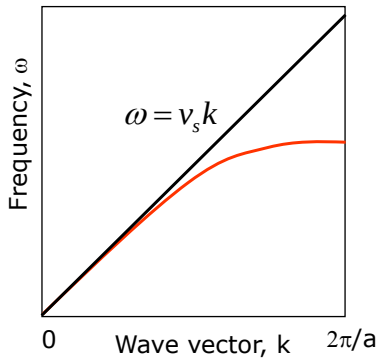
Peter Debye (1884-1966)

The Debye Integral

- Total energy

$$u(T) = \int_0^{\omega_D} \hbar\omega f(\omega) g(\omega) d\omega$$

$$=$$



- Multiply by 3 if assuming all polarizations identical (one LA, and 2 TA)
- Or treat each one separately with its own (v_S,ω_D) and add them all up
- C = du/dT ⟶

people like to write:
(note, includes 3x)

$$C_D(T) = 9Nk_B \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x dx}{(e^x - 1)^2}$$

Debye Model at Low- and High-T

- At low-T (< θ_D/10):

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

- At high-T: (> 0.8 θ_D)

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

- "Universal" behavior for all solids
- In practice: θ_D ~ fitting parameter to heat capacity data
- θ_D is related to "stiffness" of solid as expected

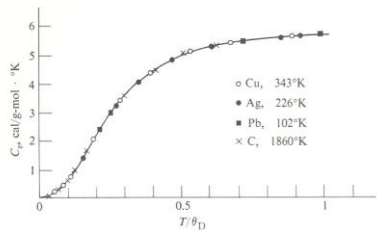
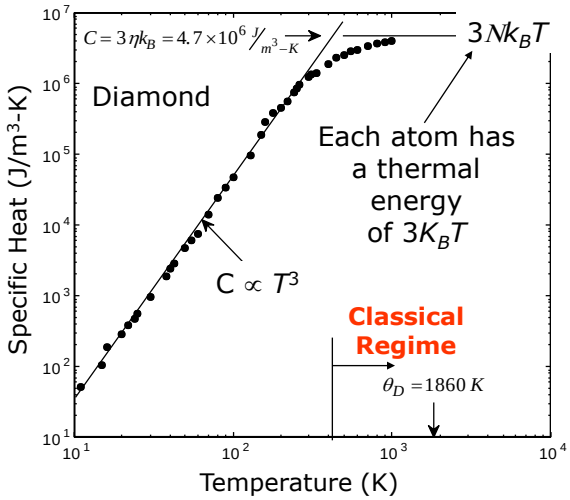


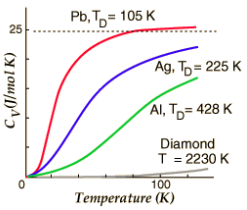
Fig. 3.13 Specific heats versus reduced temperature for four substances. to Debye temperatures. Note the high Debye temperature for diamond.

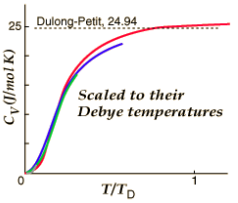
Debye Temperatures

Element	θ_D, °K	Compound	θ_D, °K
Li	335	NaCl	280
Na	156	KCl	230
K	91.1	CaF_2	470
Cu	343	LiF	680
Ag	226	SiO_2 (quartz)	255
Au	162		
Al	428		
Ga	325		
Pb	102		
Ge	378		
Si	647		
C	1860		

Experimental Specific Heat





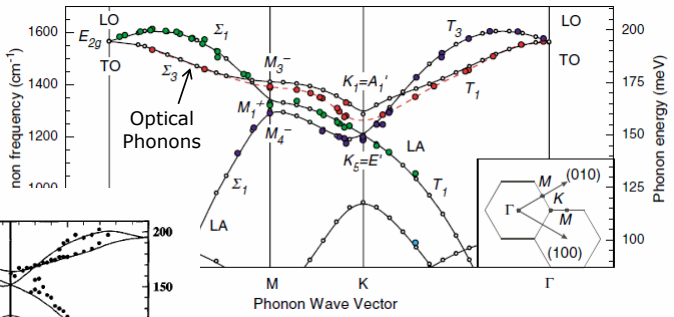


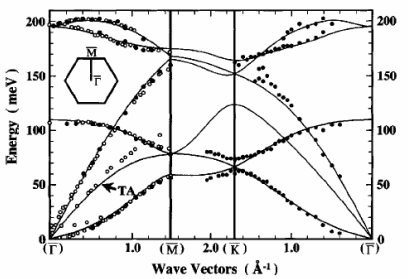
In general, when T << θ_D

$$u_L \propto T^{d+1}, \quad C_L \propto T^d$$

Phonon Dispersion in Graphene

Maultzsch *et al.*, *Phys. Rev. Lett.* 92, 075501 (2004)



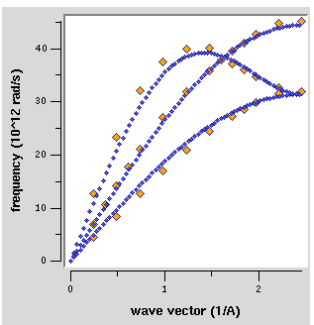


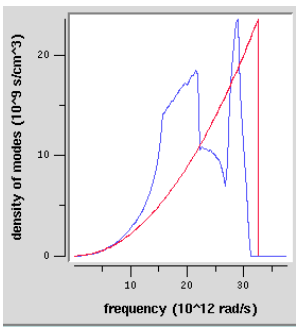
Yanagisawa *et al.*, *Surf. Interf. Analysis* 37, 133 (2005)

Figure 4. Phonon energy dispersion curves of the graphene sheets determined experimentally (solid circles) and theoretically (solid curves). Phonons in the bulk graphite surfaces are also shown for comparison (open circles).

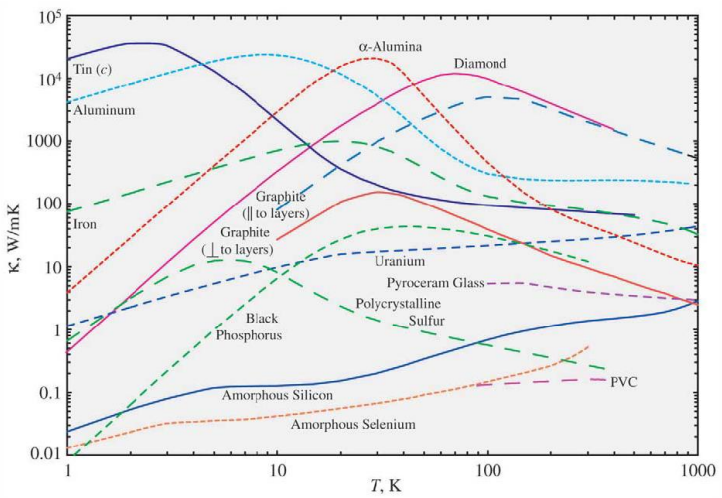
Heat Capacity and Phonon Dispersion

- Debye model is just a simple, elastic, isotropic approximation; be careful when you apply it
- To be "right" one has to integrate over phonon dispersion ω(k), along all crystal directions
- See, e.g. http://www.physics.cornell.edu/sss/debye/debye.html



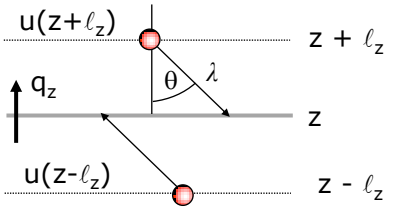


Thermal Conductivity of Solids



how do we explain this mess?

Kinetic Theory of Energy Transport



Net Energy Flux / # of Molecules

$$q'_z = \frac{1}{2} v_z \left[u(z - \ell_z) - u(z + \ell_z) \right]$$

through Taylor expansion of *u*

$$q'_z = -v_z \ell_z \frac{du}{dz} = -\left(\cos^2 \theta\right) v\lambda \frac{du}{dz}$$

Integration over all the solid angles → total energy flux

$$q_z = -\frac{1}{3} v\lambda \frac{du}{dT} \frac{dT}{dz} \equiv -k \frac{dT}{dz}$$

Thermal conductivity: $k = \frac{1}{3} C v \lambda$

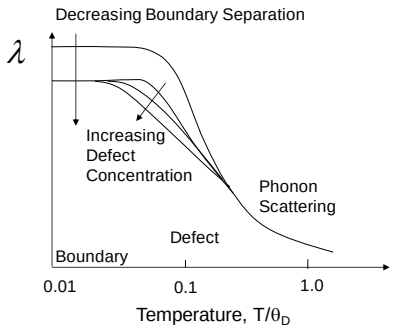
Simple Kinetic Theory Assumptions

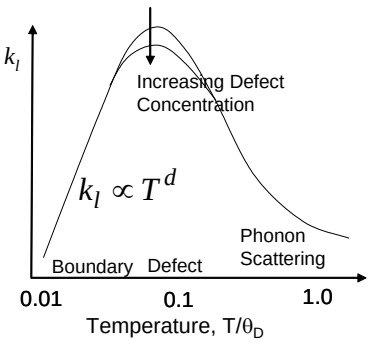
- Valid for particles ("beans" or "mosquitoes")
  - Cannot handle wave effects (interference, diffraction, tunneling)
- Based on BTE and RTA
- Assumes local thermodynamic equilibrium: u = u(T)
- Breaks down when L ~ _____ and t ~ _____
- Assumes single particle velocity and mean free path
  - But we can write it a bit more carefully:

Phonon MFP and Scattering Time

- Group velocity only depends on dispersion ω(k)
- Phonon scattering mechanisms
  - Boundary scattering
  - Defect and dislocation scattering
  - Phonon-phonon scattering

$$k \approx \frac{1}{3} C v \lambda \approx \frac{1}{3} C v^2 \tau$$





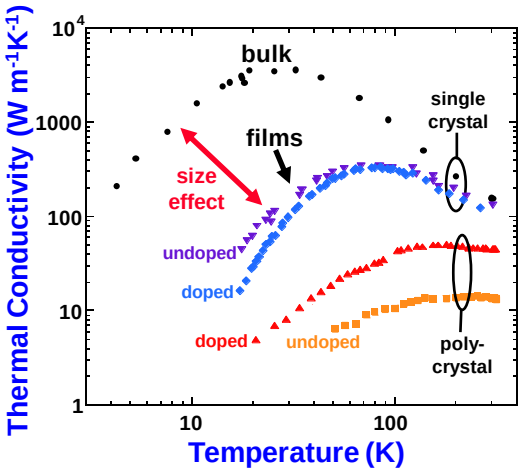
Temperature Dependence of Phonon K_{TH}

$$C \begin{cases} \propto T^d & low\ T \\ 3Nk_B & high\ T \end{cases} \qquad \lambda_{ph-ph} \propto \frac{1}{n_{ph}} = e^{\hbar\omega/kT} - 1 \begin{cases} \to \infty & low\ T \\ \dfrac{\hbar\omega}{kT} & high\ T \end{cases}$$

	C	λ ⟶ κ
low T	∝ T^d	$n_{ph} \to 0$, so $\lambda \to \infty$, but then $\lambda \to$ D (size)
high T	$3Nk_B$	∝ 1/T

Ex: Silicon Film Thermal Conductivity

McConnell, Srinivasan, and Goodson, *JMEMS* 10, 360-369 (2001)



$$k(d_G, n) = \frac{1}{3} Cv \left(\frac{A_1}{d_G} + A_2 n_i \right)^{-1}$$

Bulk single-crystal silicon:
Touloukian et al. (1970)
d = 0.44 cm

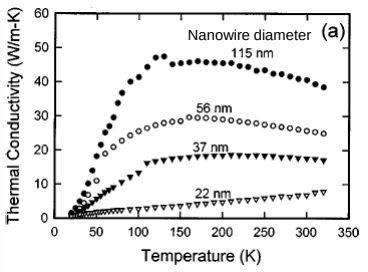
Undoped single-crystal film:
Asheghi et al. (1998)
d = 3 μm

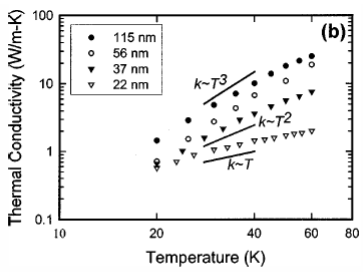
Doped single-crystal film:
Asheghi et al. (1999)
d = 3 μm
n = 1·10^{19} cm^{-3} boron

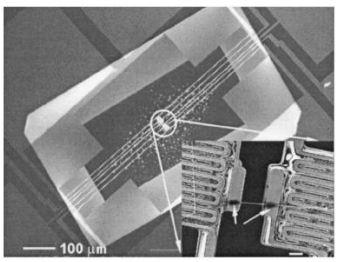
Doped polysilicon film:
McConnell et al. (2001)
d = 1 μm
d_g = 350 nm
n = 1.6·10^{19} cm^{-3} boron

Undoped polysilicon film:
Srinivasan et al. (2001)
d = 1 μm
d_g = 200 nm

Ex: Silicon Nanowire Thermal Conductivity





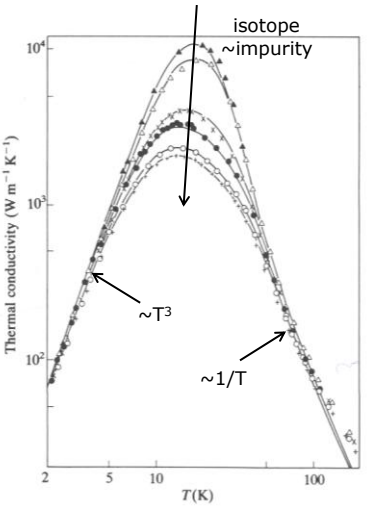


Li, Appl. Phys. Lett. 83, 2934 (2003)

FIG. 3. (a) Measured thermal conductivity of different diameter Si nanowires. The number beside each curve denotes the corresponding wire diameter. (b) Low temperature experimental data on a logarithmic scale. Also shown are T^3, T^2, and T^1 curves for comparison.

- Recall, undoped bulk crystalline silicon k ~ 150 W/m/K (previous slide)

Ex: Isotope Scattering



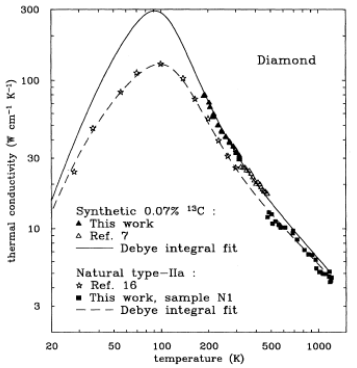


FIG. 5. Thermal conductivity of natural type-IIa diamond and synthetic diamond with 0.07% ^{13}C isotope concentration. The dashed line is the fit calculated from the Debye model as described in the text. The solid line is the fit for the nearly isotopically pure diamond, where the point defect scattering (Rayleigh term) was the only parameter changed.

Figure 5.27 (a) The principal form for the variation of thermal conductivity. (b) Experimental data for LiF crystals containing different amounts of the isotope ^6Li: ▲, 0.02% ^6Li; △, 0.01%; ×, 4.6%; ●, 9.4%; ○, 25.4%; +, 50.1%. (After Berman and Brock 1965.)

Why the Variation in K_{th}?

- A: Phonon λ(ω) and dimensionality (D.O.S.)
- Do C and v change in nanostructures? (1D or 2D)
- Several mechanisms contribute to scattering
  - Impurity mass-difference scattering

$$\frac{1}{\tau_{ph-i}} \approx \frac{n_i V^2}{4\pi v_s^2}\left(\frac{\Delta M}{M}\right)^2 \omega^4$$

  - Boundary & grain boundary scattering

$$\frac{1}{\tau_{ph-b}} \approx \frac{v_s}{D}$$

  - Phonon-phonon scattering

$$\frac{1}{\tau_{ph-ph}} \approx A\omega^{\alpha} T^{\beta} \exp\left(-B\frac{\hbar\omega}{k_B T}\right)$$

What About Electron Thermal Conductivity?

- Recall electron heat capacity

$$C_e = \frac{du}{dT} = \int_0^\infty E \frac{df}{dT} g(E)\, dE \qquad \boxed{C_e = \frac{\pi^2}{2}\left(\frac{k_B T}{E_F}\right) n_e k_B}$$

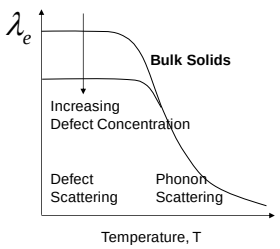
at most T in 3D

- Electron thermal conductivity

$k_e =$

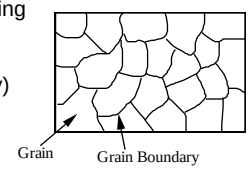
Mean scattering time:

$\tau_e =$



Electron Scattering Mechanisms

- Defect or impurity scattering
- Phonon scattering
- Boundary scattering (film thickness, grain boundary)



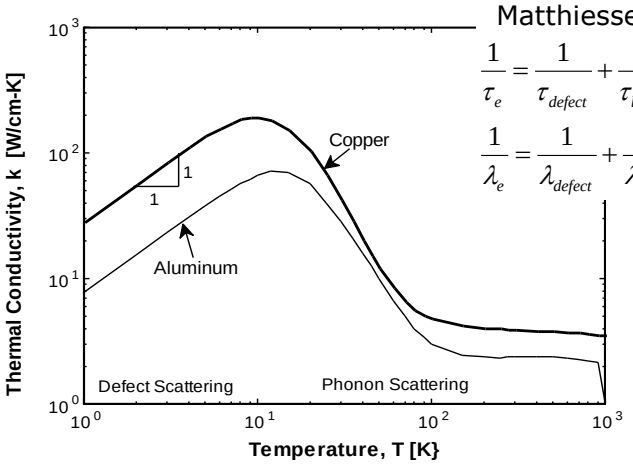
Ex: Thermal Conductivity of Cu and Al

- Electrons dominate k in metals

Matthiessen Rule:

$$\frac{1}{\tau_e} = \frac{1}{\tau_{defect}} + \frac{1}{\tau_{boundary}} + \frac{1}{\tau_{phonon}}$$

$$\frac{1}{\lambda_e} = \frac{1}{\lambda_{defect}} + \frac{1}{\lambda_{boundary}} + \frac{1}{\lambda_{phonon}}$$



Wiedemann-Franz Law

$$\kappa_e = \frac{1}{3}\left(\frac{\pi^2}{2}k_B^2 n\frac{T}{E_F}\right)v_F^2\tau \qquad \text{where} \qquad E_F =$$

recall electrical conductivity $\sigma = q\mu n = \frac{q^2\tau}{m}n$

taking the ratio $\frac{k_e}{\sigma} =$

- Wiedemann & Franz (1853) empirically saw k_e/σ = const(T)
- Lorenz (1872) noted k_e/σ proportional to T

Lorenz Number

$$L = \frac{\kappa_e}{\sigma T} = \frac{\pi^2 k_B^2}{3q^2}$$

$$L = 2.45\times10^{-8}\ \text{W}\Omega/\text{K}^2$$

This is remarkable!
It is independent of n, m, and even τ !

Experimentally

	L = κ/σT 10^{-8} WΩ/K²	
Metal	0 ° C	100 °C
Cu	2.23	2.33
Ag	2.31	2.37
Au	2.35	2.40
Zn	2.31	2.33
Cd	2.42	2.43
Mo	2.61	2.79
Pb	2.47	2.56

Agreement with experiment is quite good, although L ~ 10x lower when T ~ 10 K… why?!

Amorphous Material Thermal Conductivity

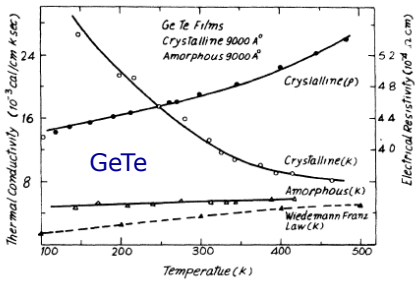
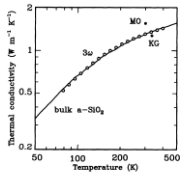


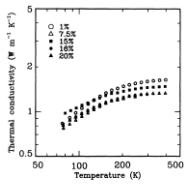
FIG. 3. Thermal conductivity vs temperature for amorphous and crystalline GeTe films. Also shown is the variation of the electrical resistivity with temperature and the variation of the electronic part of the thermal conductivity with temperature for a crystalline GeTe film (9000 Å), deposited at 420 °K.

Amorphous (semi)metals: both electrons & phonons contribute



a-SiO_2

FIG. 4. Data (open circles) for a 0.99-μm-thick a-SiO_2 layer thermally grown on Si(001). Data for bulk a-SiO_2 are shown as the solid line, see Ref. 24. Two data points at room temperature marked "MO" and "KG" are also for thermally grown oxide films, see Refs. 33 and 23.



a-Si

FIG. 5. Thermal conductivity of a-Si:H. The key to each symbol gives the hydrogen content in atomic percent. Substrate temperature and film thickness are listed in Table I.

Amorphous dielectrics: K saturates at high T (why?)

Summary

- Phonons dominate heat conduction in dielectrics
- Electrons dominate heat conduction in metals
  (but not always! when not?!)

- Generally, $C = C_e + C_p$ and $k = k_e + k_p$
- For C: remember T dependence in "d" dimensions
- For k: remember system size, carrier λ's (Matthiessen)

- In metals, use WFL as rule of thumb