

Classical Theory Expectations

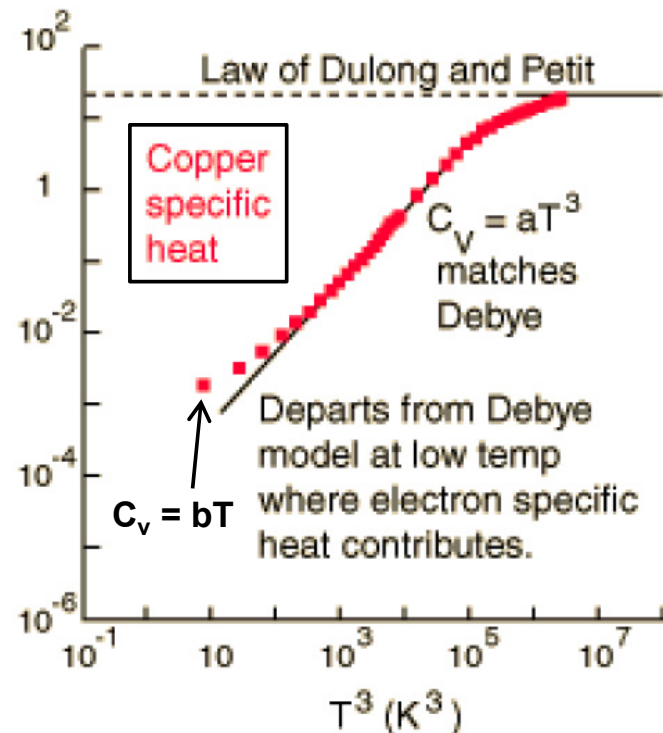
- Equipartition: $1/2k_B T$ per degree of freedom
- In 3-D electron gas this means $3/2k_B T$ per electron
- In 3-D atomic lattice this means $3k_B T$ per atom (why?)
- So one would expect: $C_V = du/dT = 3/2n_e k_B + 3n_a k_B$
- Dulong & Petit (1819!) had found the heat capacity per mole for most solids approaches $3N_A k_B$ at high T

Molar heat capacity @ high T $\rightarrow 25 \text{ J/mol/K}$

Heat Capacity: Real Metals

$$C_V = bT + aT^3$$

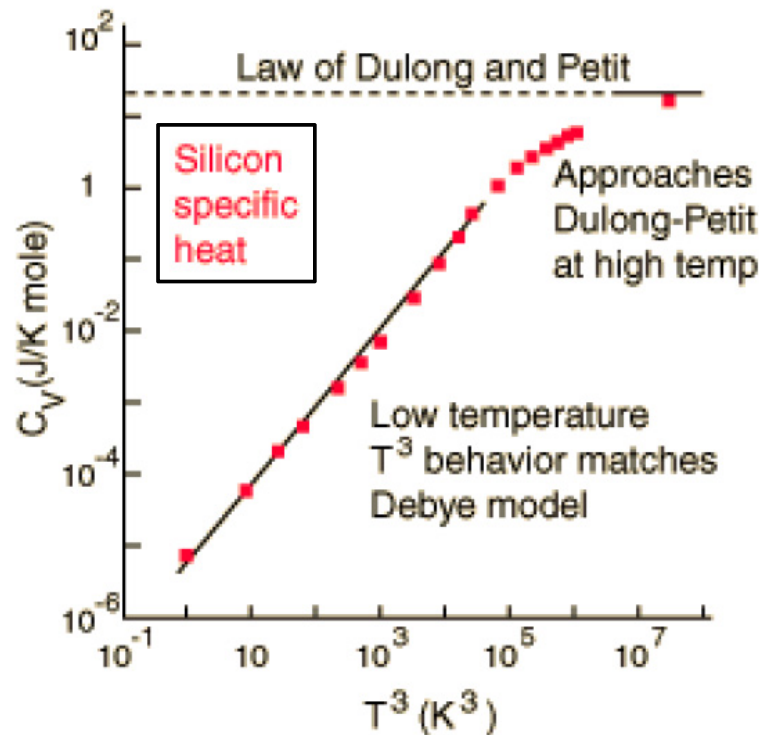
due to bT electron gas due to aT^3 atomic lattice



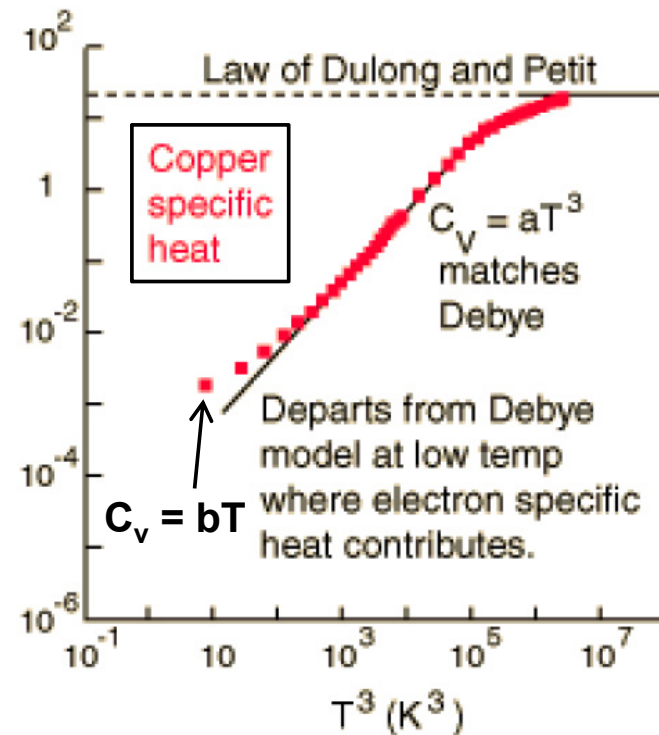
- So far we've learned about heat capacity of electron gas
- But evidence of linear $\sim T$ dependence only at very low T
- Otherwise $C_V \sim \text{constant}$ (very high T), or $\sim T^3$ (intermediate)
- Why?

Heat Capacity: Dielectrics vs. Metals

Dielectrics



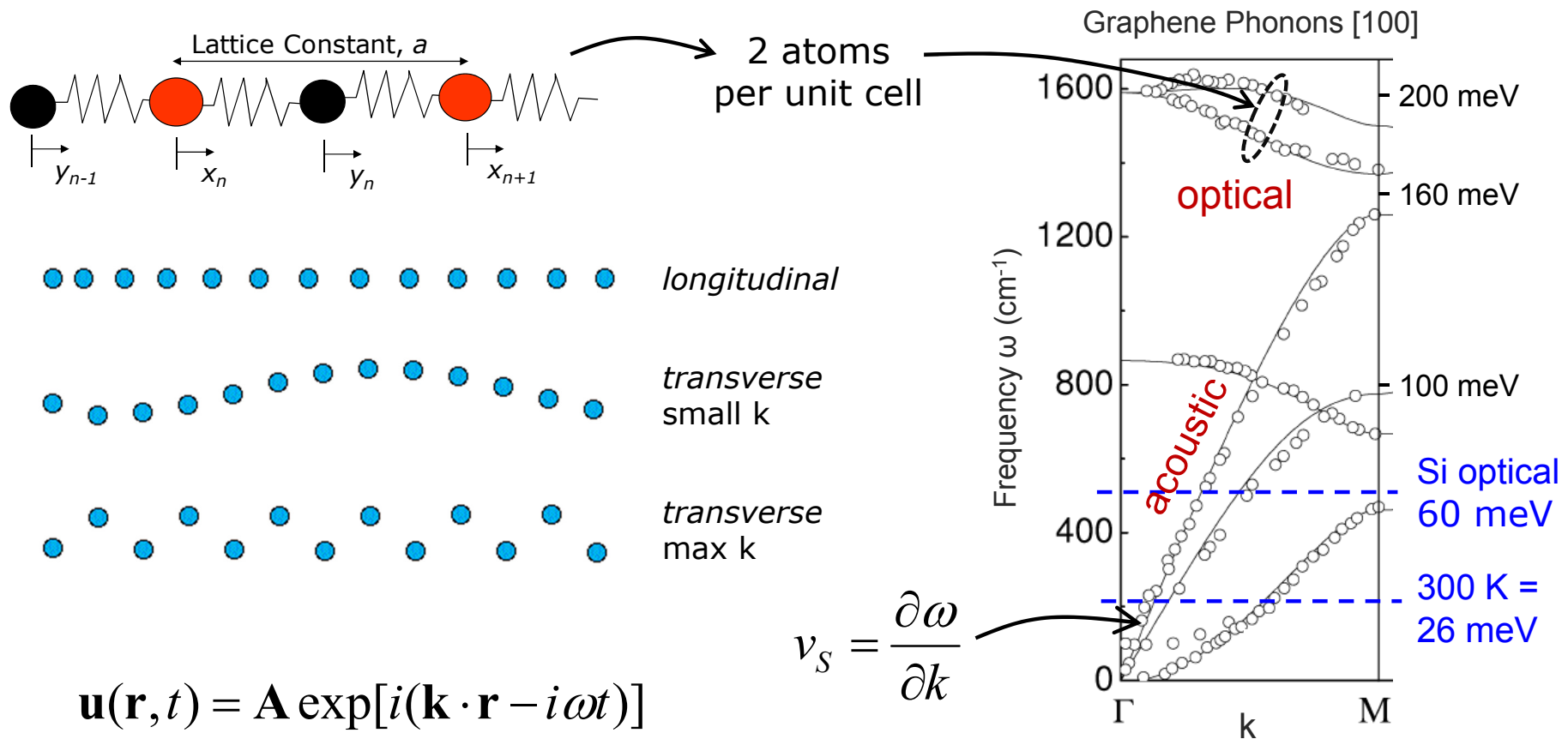
Metals



- Very high T : $C \sim 3nk_B$ (constant) both dielectrics & metals
- Intermediate T : $C \sim aT^{d/n}$ both dielectrics & metals in “ d ” dimensions* } phonon contribution
- Very low T : $C \sim bT$ metals only \rightarrow electron contribution

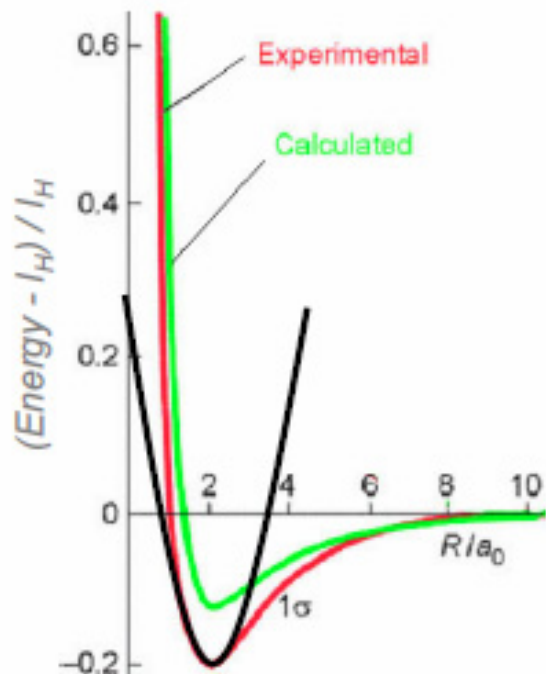
* for $\omega \propto k^n$ phonon dispersion

Phonons: Atomic Lattice Vibrations



- Phonons = quantized atomic lattice vibrations ~ elastic waves
- Transverse ($\mathbf{u} \perp \mathbf{k}$) vs. longitudinal modes ($\mathbf{u} \parallel \mathbf{k}$), acoustic vs. optical
- “Hot phonons” = highly occupied modes above equilibrium temperature

Atomic Potentials and Vibrations

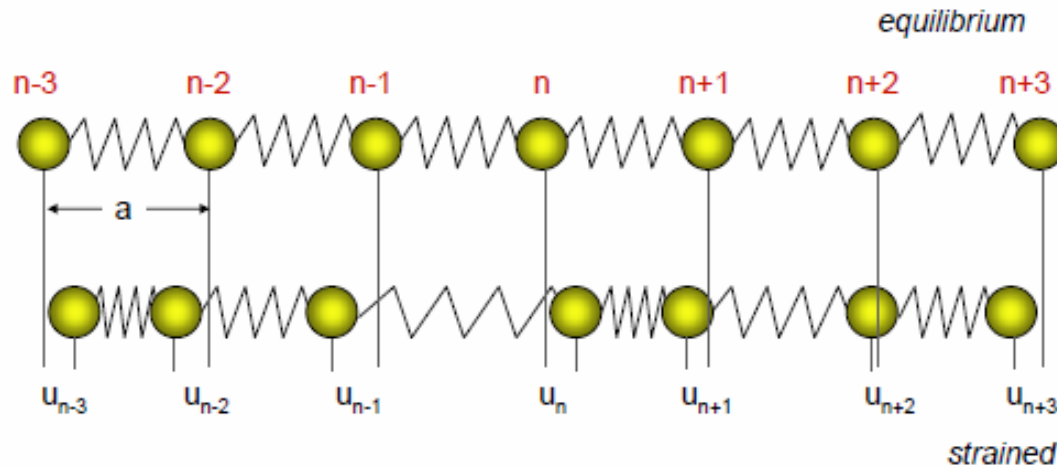


$$V_{\text{eff}}(r) = V_o + \frac{1}{2}(r - R_o)^2 \underbrace{\left(\frac{d^2V}{dr^2} \right)_{R_o}}_{\text{“spring constant”}}$$

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

- 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

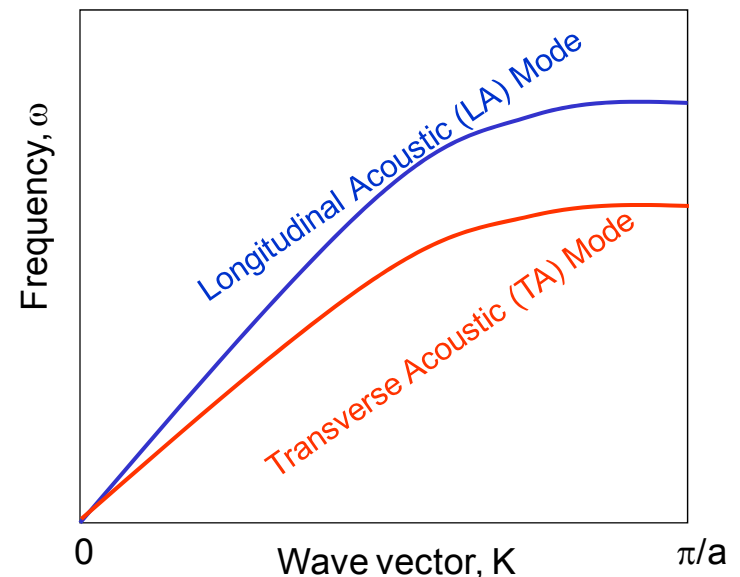


$$\rho \frac{\partial^2 u_x}{\partial t^2} = E_Y \frac{\partial^2 u_x}{\partial x^2}$$



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

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

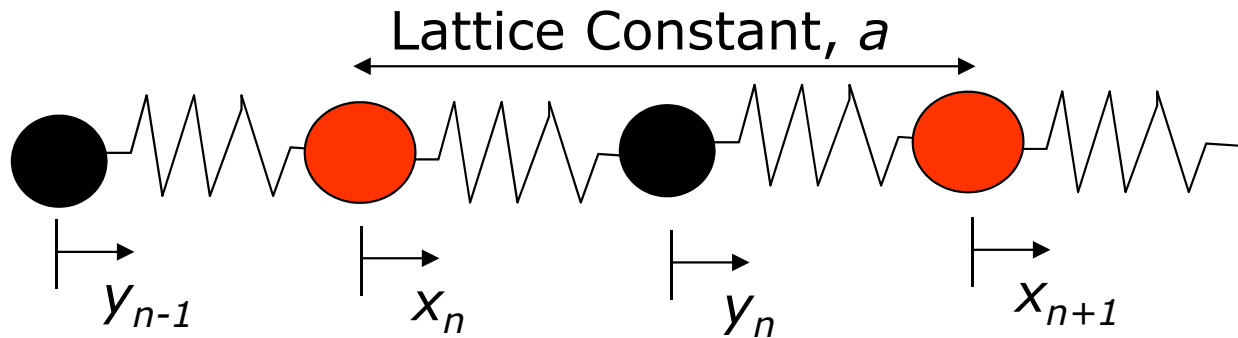


$$u_x(x, t) = A_{\pm} \exp(ikx) \exp(i\omega t)$$

$$\omega = v_s k$$

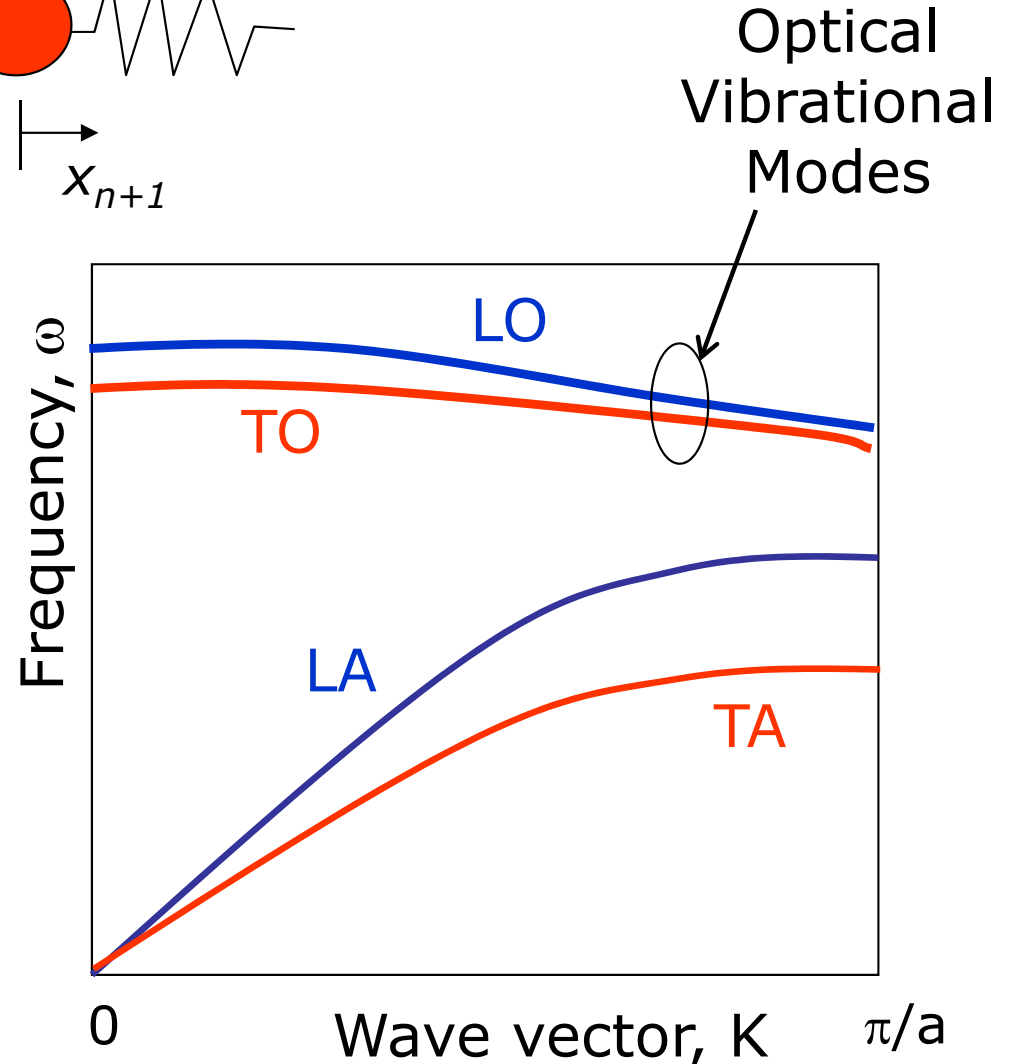
See C. Kittel, Ch. 4
or G. Chen Ch. 3

Two Atoms per Unit Cell



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

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



Energy Stored in These Vibrations

- Heat capacity of an atomic lattice
- $$C_L = \frac{du}{dT} =$$
- High temperature: classically, recall $C = 3N_A k_B$
- Low temperature: experimentally $C \rightarrow 0$
- Einstein model (1907)
 - All oscillators at same, identical frequency ($\omega = \omega_E$)
- Debye model (1912)
 - Oscillators have linear frequency distribution ($\omega = v_s k$)

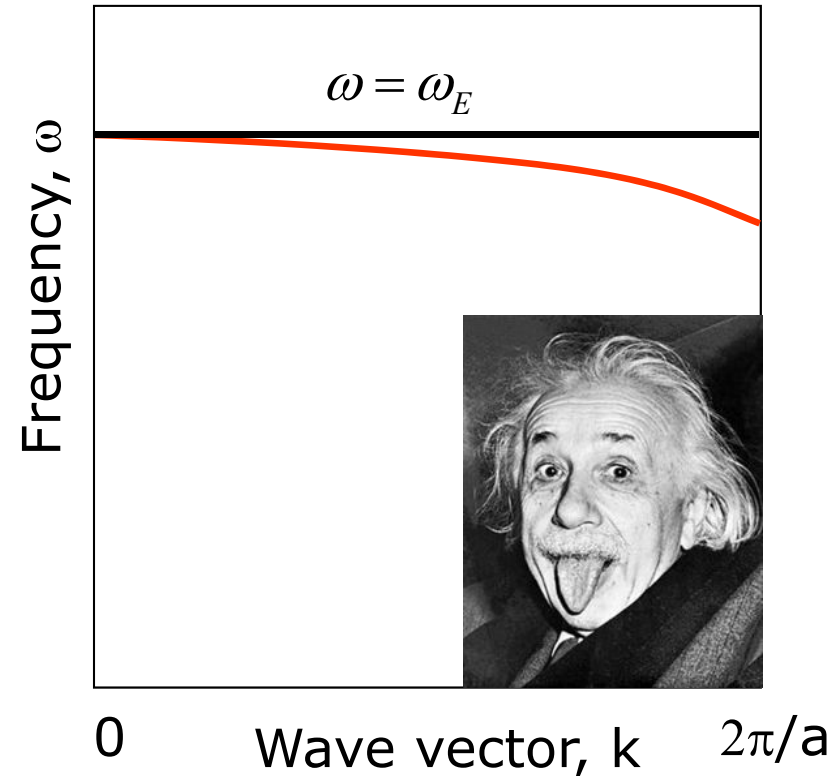
The Einstein Model

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

$$g(\omega) = \underset{\uparrow}{3N} \delta(\omega - \omega_E)$$

- 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)

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

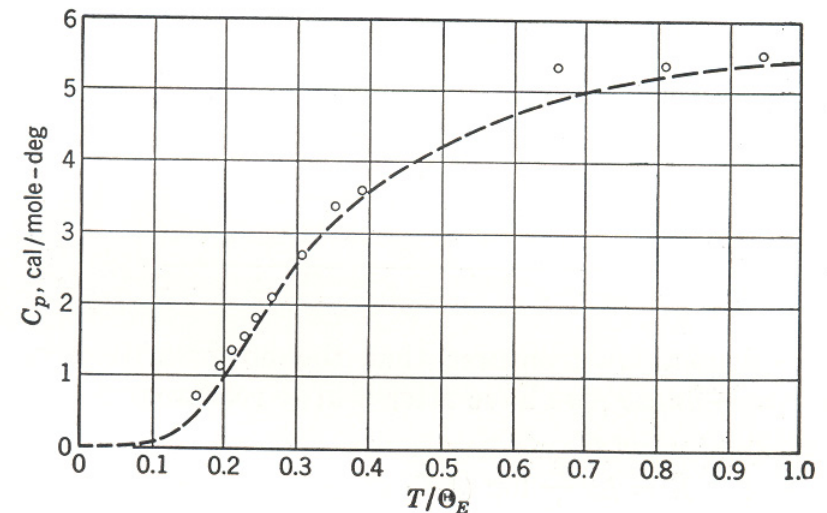


Fig. 6.2. Comparison of experimental values of the heat capacity of diamond and values calculated on the Einstein model, using $\Theta_E = 1320^\circ\text{K}$. [After A. Einstein, Ann. Physik **22**, 180 (1907).]

The Debye Model

- Linear (no) dispersion *with frequency cutoff*

- Density of states in 3D:

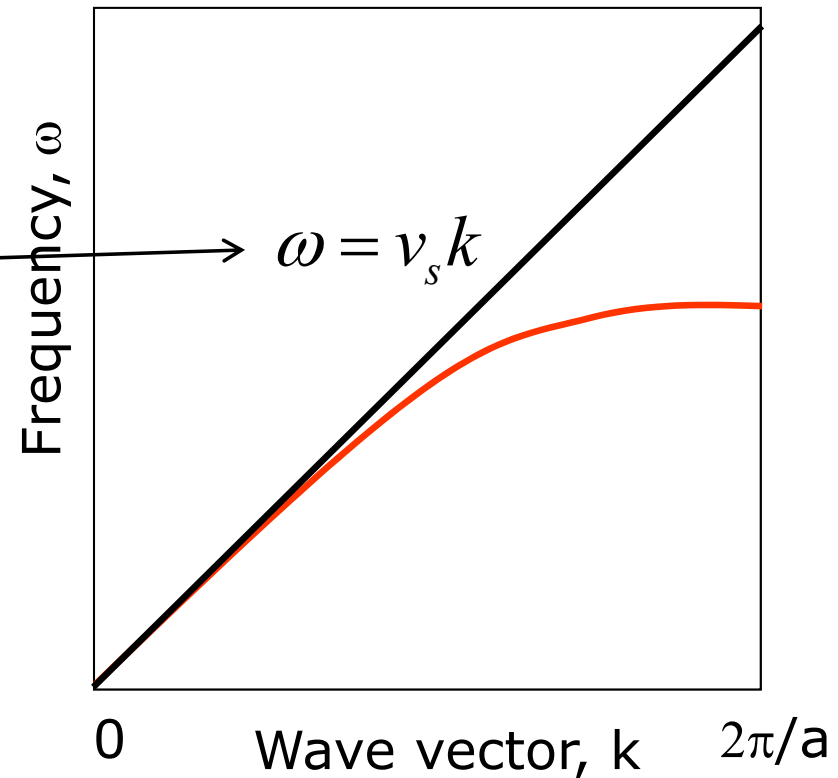
$$g(\omega) = \frac{\omega^2}{2\pi^2 v_s^3}$$

(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

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



k_D roughly corresponds to
max lattice wave vector ($2\pi/a$)

ω_D roughly corresponds to
max acoustic phonon frequency

oder mit Berücksichtigung der Definitionsgleichung (7)

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

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)

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

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

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



Peter Debye (1884-1966)

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

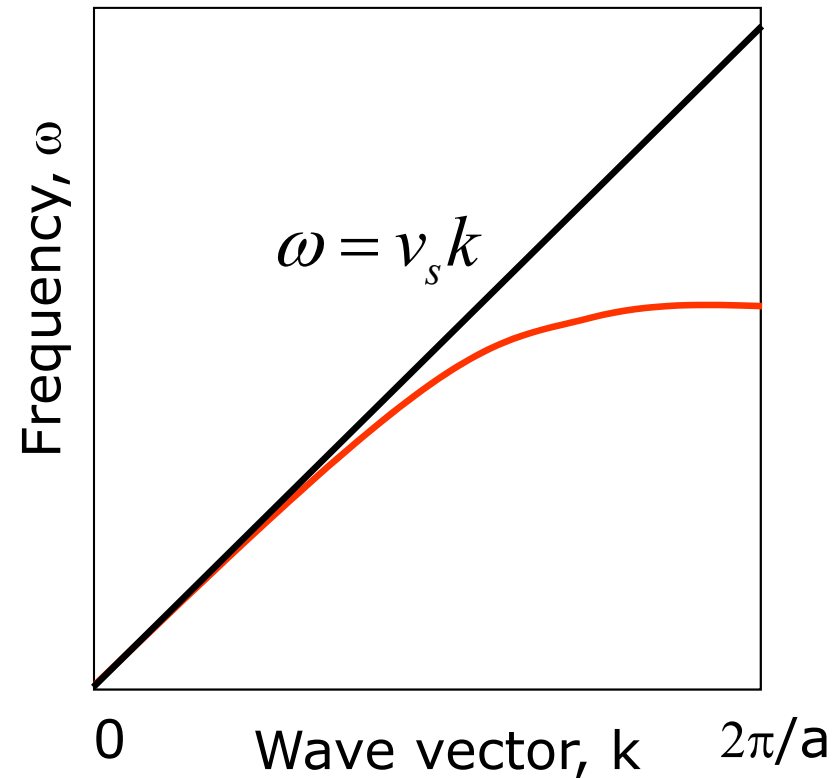
The Debye Integral

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



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 ($< \theta_D/10$): $C_D(T) \approx \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\theta_D}\right)^3$
- At high-T ($> 0.8 \theta_D$): $C_D(T) \approx 3Nk_B$

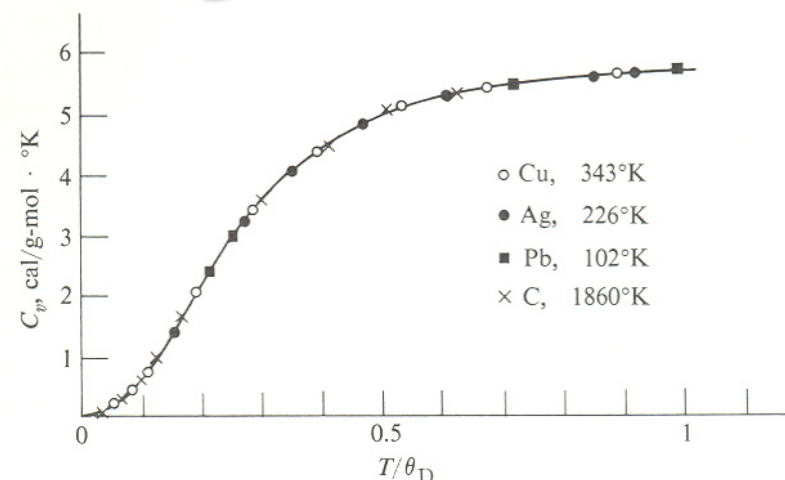


Fig. 3.13 Specific heats versus reduced temperature for four substances. Note the high Debye temperature for diamond.

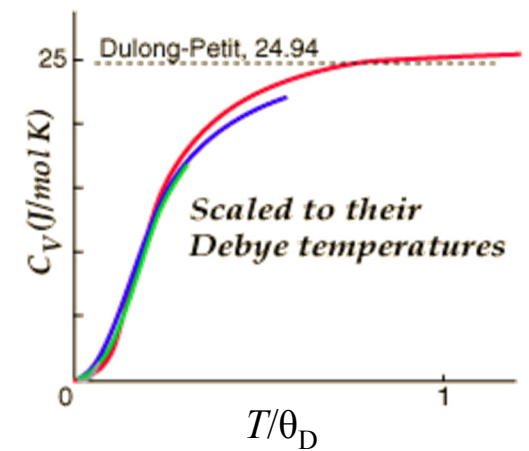
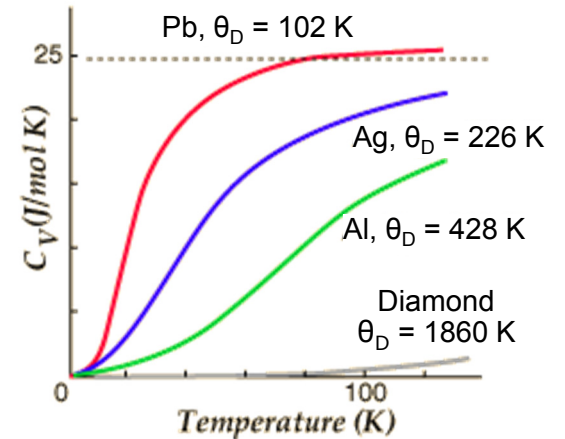
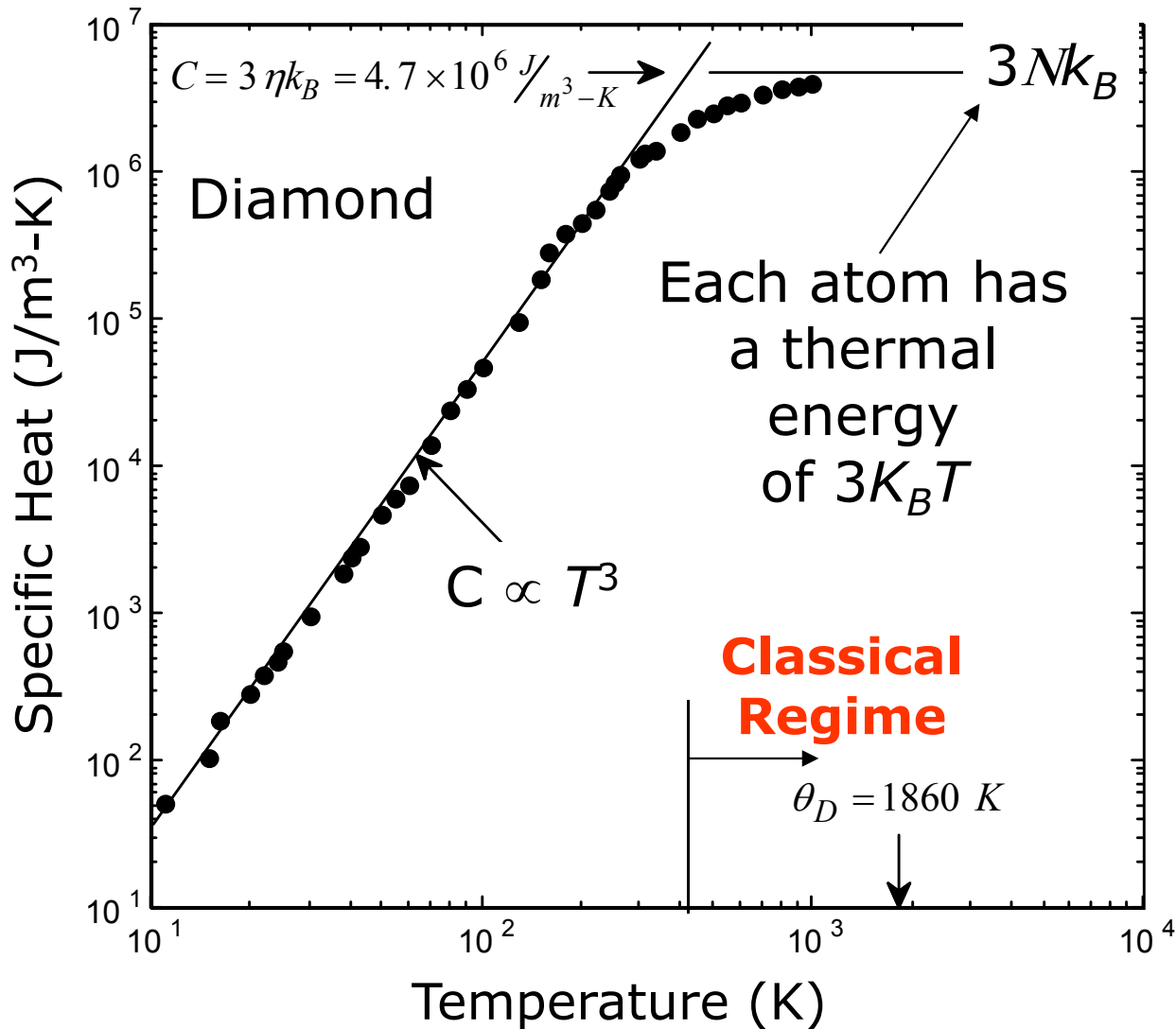
Debye Temperatures

Element	$\theta_D, ^\circ\text{K}$	Compound	$\theta_D, ^\circ\text{K}$
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		
Graphite	{ 2480 → in-plane (sp ²) { 180 → out-of-plane (vdW)		

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

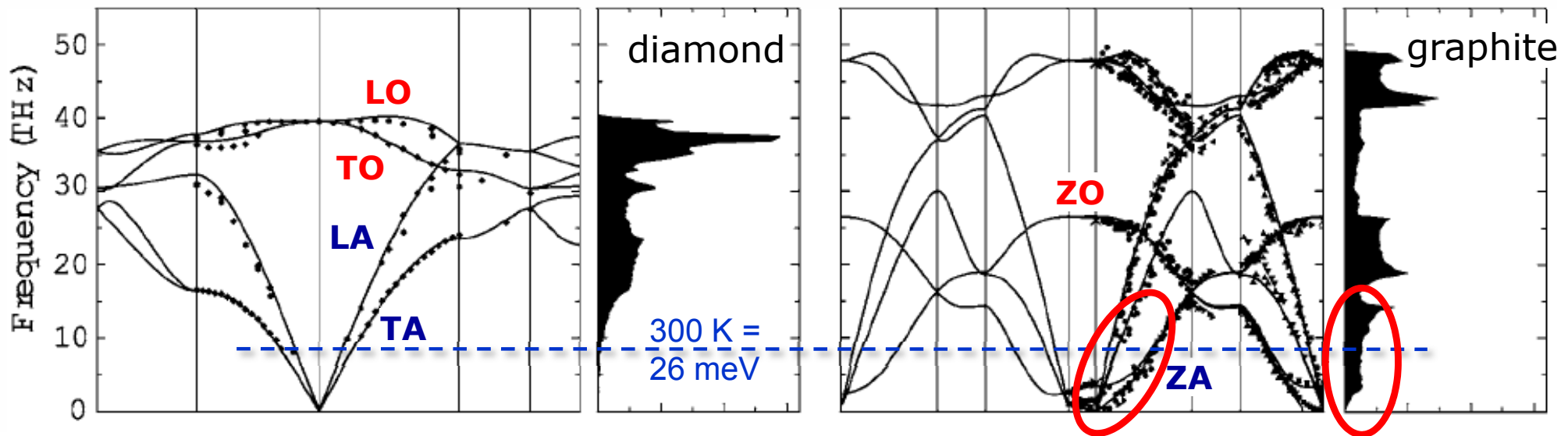
to resolve low-temperature heat capacity “quandary” since graphite data was neither 2-D (T^2) nor 3-D (T^3)

Experimental Specific Heat



In general, when $T \ll \theta_D \longrightarrow u_L \propto T^{d+1}, C_L \propto T^d$

Phonon Dispersion of Diamond & Graphite



- Diamond “like” silicon:

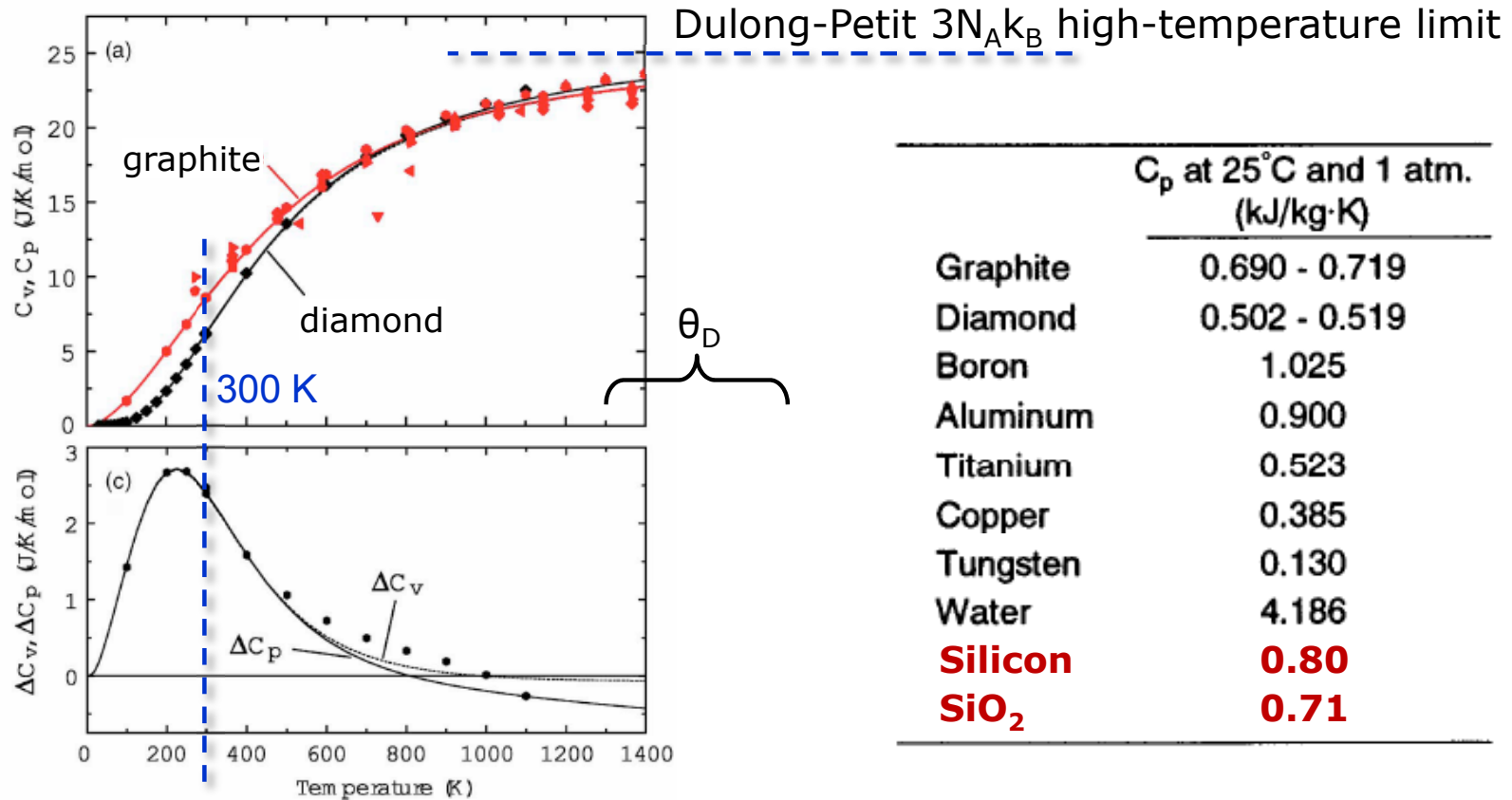
- Longitudinal & transverse (x2) acoustic (LA, TA)
- Longitudinal & transverse (x2) optical (LO, TO)

- 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

Tohei, Phys. Rev. B (2006)

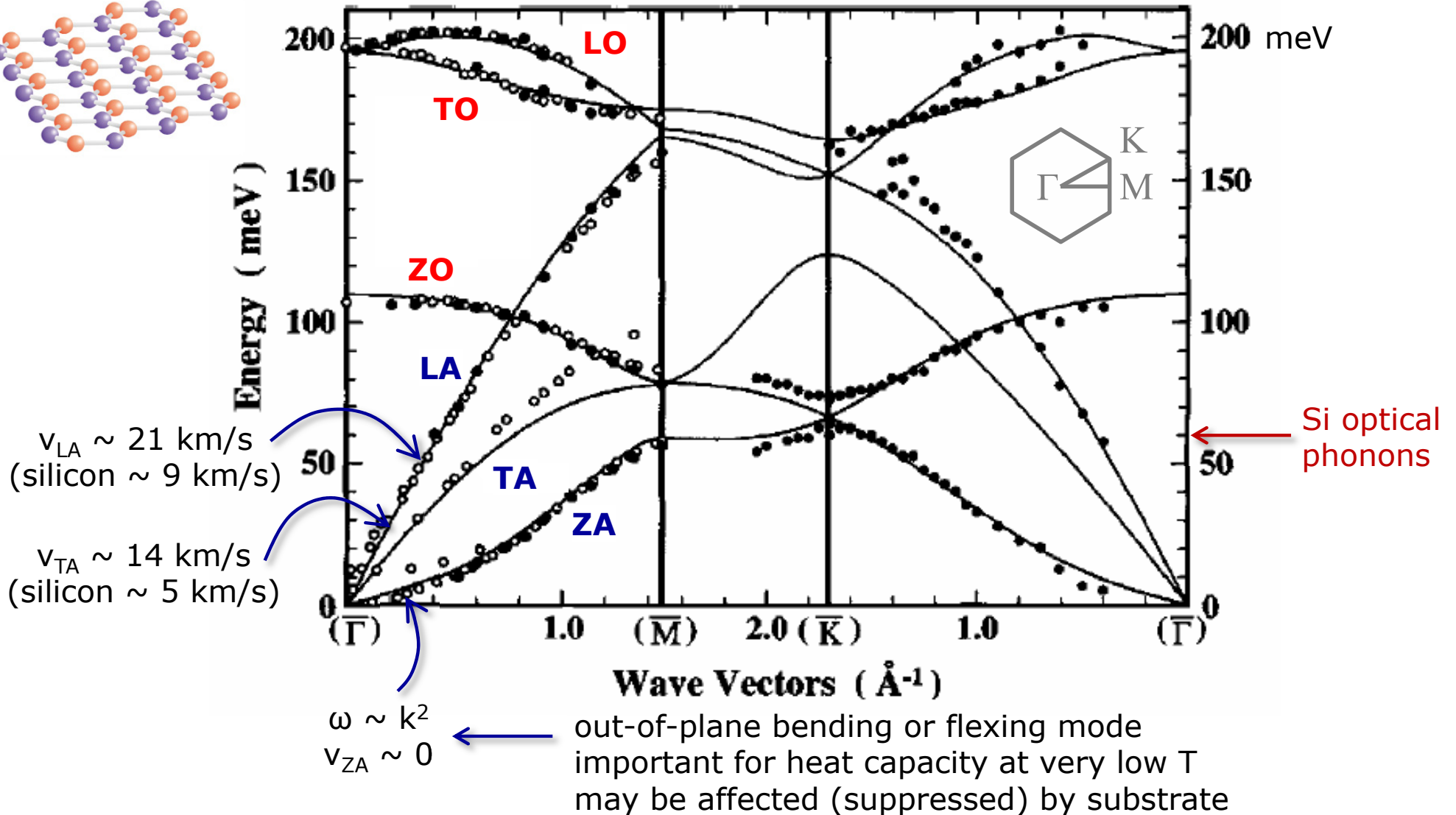
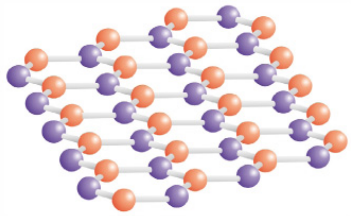
Heat Capacity of Diamond & Graphite



- Graphite has higher phonon DOS at low frequency \rightarrow about 30% higher heat capacity than diamond at room T
- Both increase up to Debye temperature range, then reach “classical” $3N_A k_B$ limit

Pierson (1993)
Tohei, Phys. Rev. B (2006)

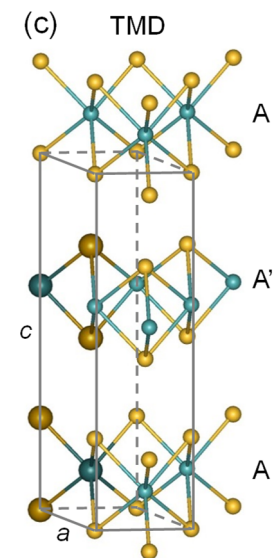
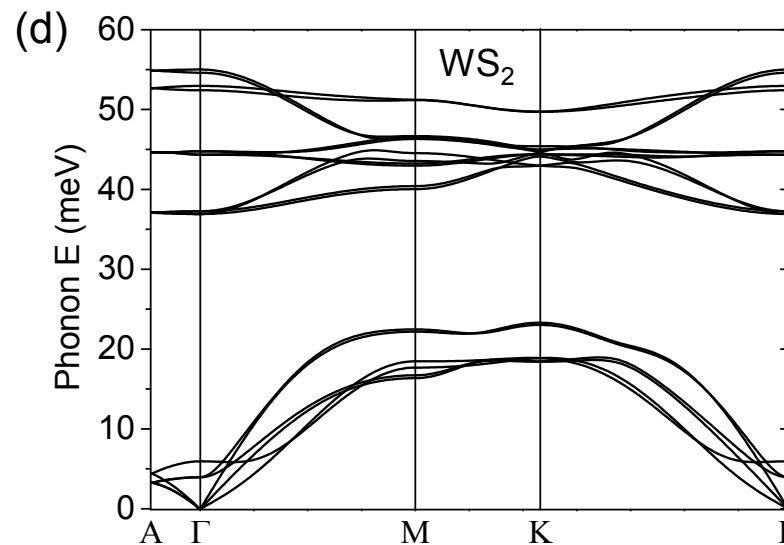
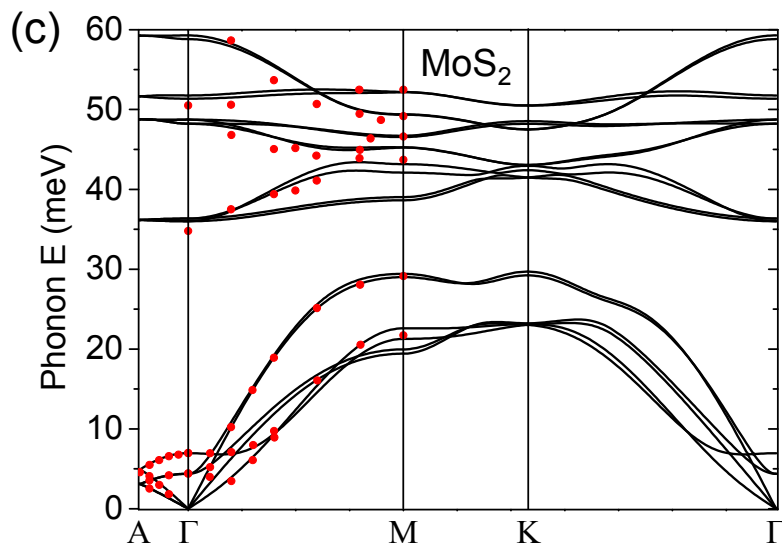
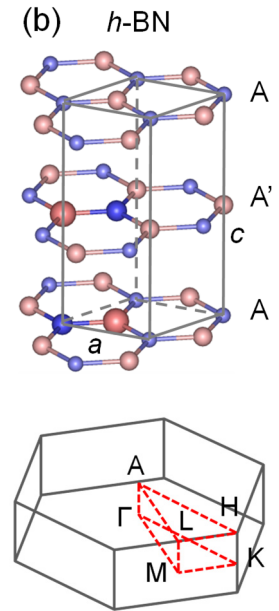
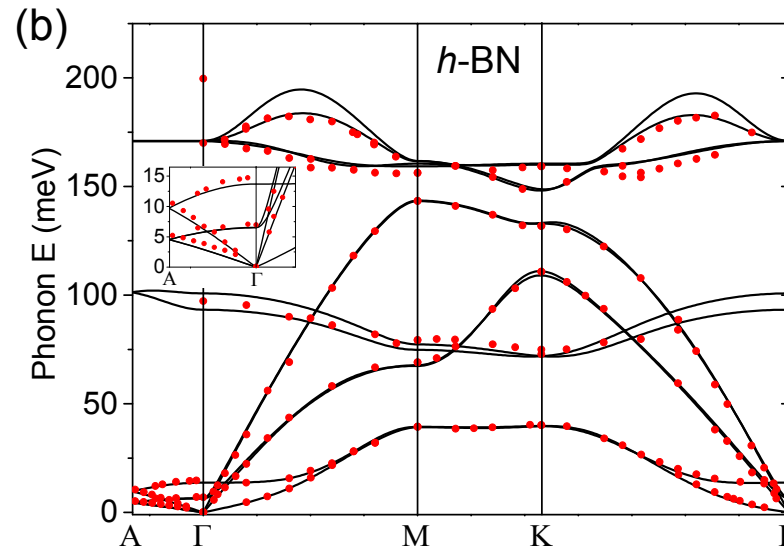
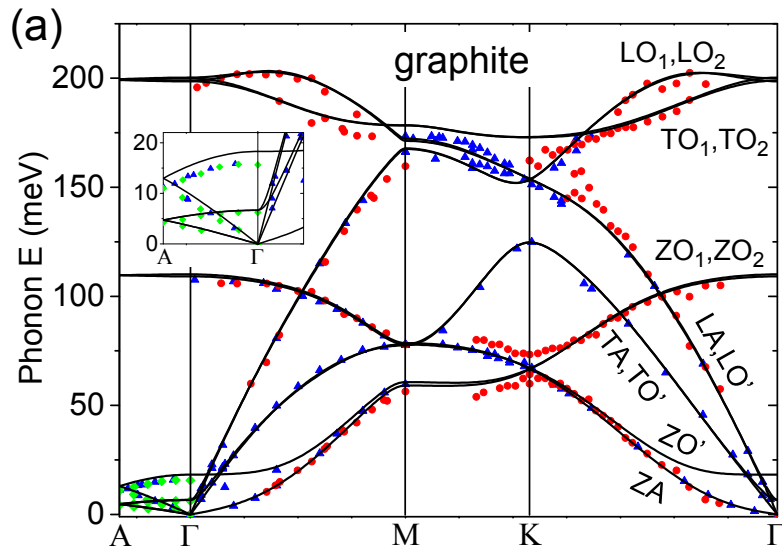
Phonon Dispersion of Graphene



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

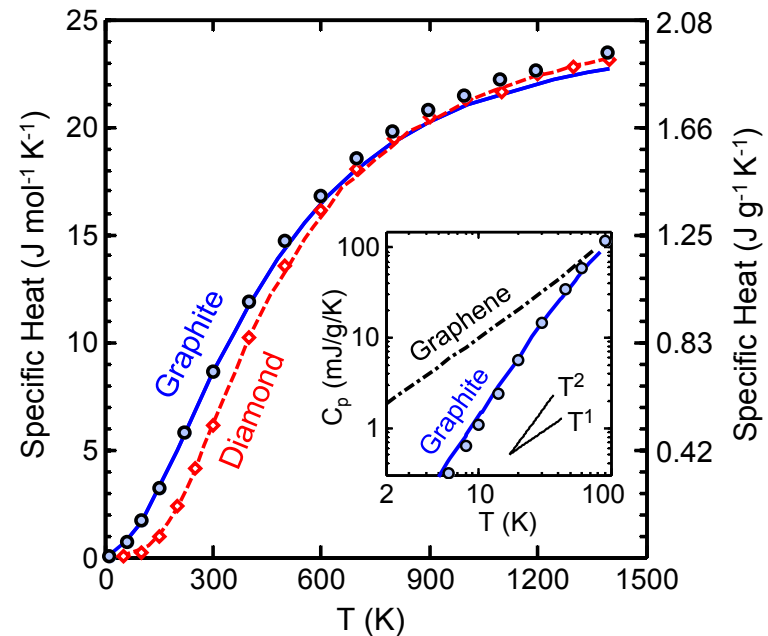
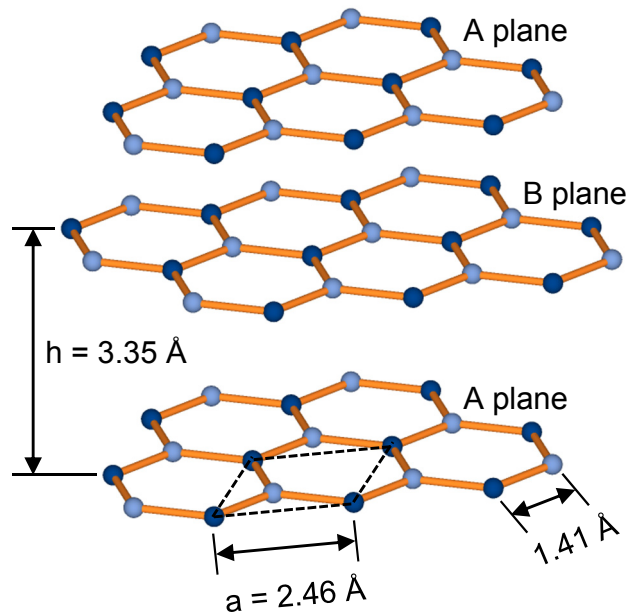
Maultzsch *et al.*, *Phys. Rev. Lett.* 92, 075501 (2004)

Phonon Dispersion of Other 2D Layers



source: Zuanyi Li, Pop Lab (2014)

Heat Capacity of Graphene



- C_p of graphene is same as graphite (and $>$ diamond) above 100 K
- Around room temperature all are about 0.7 J/g/K , about one-third of the classical Dulong-Petit limit
- Below 100 K, C_p scales as $T^{d/n}$ for phonon dispersion $\omega \sim k^n$ in d dimensions \rightarrow graphene C_p as T to T^2 , graphite C_p as T^3 to T^2

see E. Pop et al., *MRS Bulletin* 37, 1273 (2012) and references therein

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 $\omega(k)$, along all crystal directions
- See, e.g. <http://pages.physics.cornell.edu/sss/debye/debye.html>

