

5.1 Thermal excitation of phonons.

Phonons are created and destroyed by thermal excitation and make a significant contribution to specific heat:

$$C = C_{\text{phonon}} + C_{\text{electrons}} + C_{\text{magnetic}}$$

all solids
metals only
magnets only.

Thus a ^{non-magnetic} insulator has only the phonons acting.

Definition $C_V = \left(\frac{\partial U}{\partial T}\right)_{Vol}$ almost the same as C_p for a solid

$$U = U_{\text{lattice}} = \sum_K \sum_P \langle n_{Kp} \rangle \hbar \omega_p(K) \quad \left[\begin{array}{l} \text{independent} \\ \text{modes } K, p. \end{array} \right]$$

n_{Kp} is the number of phonons on branch p with wave vector K .

$\omega_p(K)$ is the frequency from dispersion relation

In thermal equilibrium, $\langle n \rangle$ is given by the

Planck distribution, as for black-body radiation

$$\langle n \rangle = \frac{1}{\exp(\hbar \omega / k_B T) - 1} \quad \left[\begin{array}{l} \text{Follows from Boltzmann} \\ \frac{N_{n+1}}{N_n} = e^{-\hbar \omega / k_B T} \end{array} \right]$$

All that remains is to count up the phonons:

A large crystal has many modes, so we can replace the sum by an integral:

$$U = \sum_P \int_{\text{all bands}} D_P(\omega) \frac{\hbar \omega}{\exp(\hbar \omega / k_B T) - 1} d\omega$$

weighting factor is "density of (frequency) states" that is derived from the dispersion relation.

(40a)

Origin of Planck distribution

Collection of oscillators, each containing a variable number of phonons, n .

$$\frac{\text{No. containing } n+1}{\text{No. containing } n} = e^{-h\omega/k_B T}, \text{ Boltzmann.}$$

$$\frac{N_{n+1}}{N_n} = e^{-h\omega/k_B T}$$

$$\text{Total no. of oscillators} = \sum_{s=0}^{\infty} N_s = N_0 + N_0 e^{-\frac{h\omega}{k_B T}} + \dots + N_0 (e^{-\frac{h\omega}{k_B T}})^2 + \dots$$

$$\text{Fraction containing } n \text{ phonons} = \frac{N_n}{\sum_{s=0}^{\infty} N_s} = f_n.$$

So average no. of phonons is

$$\langle n \rangle = \sum_{s=0}^{\infty} s f_s = \frac{\sum s N_s}{\sum N_s}$$

Evaluate sums: $e^{-h\omega/k_B T} = x$.

$$\sum_s N_s = N_0 (1 + x + x^2 + \dots) = N_0 \frac{1}{1-x} \quad \text{geom. prog.}$$

$$\sum_s s N_s = x \frac{d}{dx} \sum N_s = N_0 \frac{x}{(1-x)^2}$$

$$\Rightarrow \langle n \rangle = \frac{N_0 x / (1-x)^2}{N_0 1 / (1-x)} = \frac{x}{1-x} = \frac{1}{\frac{1}{x} - 1} = \frac{1}{e^{+h\omega/k_B T} - 1}$$

(41)

Since $D(\omega)$ does not depend on T , we can perform the T -differentiation immediately

$$C_V = \frac{\partial U}{\partial T} = \sum_P \int_{\text{bands}} D(\omega) \frac{\hbar\omega \exp(\hbar\omega/k_B T)}{(\exp(\hbar\omega/k_B T) - 1)^2} \frac{\hbar\omega d\omega}{k_B T^2}$$

$$= k_B \sum_P \int D(\omega) \frac{x^2 e^x}{(e^x - 1)^2} d\omega \quad \text{where } x = \frac{\hbar\omega}{k_B T}$$

5.2 Einstein Model (1907)

This is the earliest model of the lattice specific heat. It short-cuts all the details of the density of states.

Not a bad approximation for a molecular crystal with lots of optical modes.

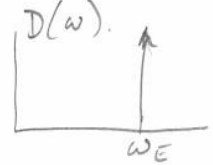
N atoms in crystal \leftrightarrow

$3N$ degrees of freedom in 3D.

all assumed to have the same frequency ω_E

$\omega_E \sim$ typical optical frequency $\sim 10^{12}$ Hz

$D(\omega) = \delta$ -function, zero everywhere except $\omega = \omega_E$



$$C_V = k_B \left(\frac{\hbar\omega_E}{k_B T} \right)^2 \frac{\exp(\hbar\omega_E/k_B T)}{(\exp(\hbar\omega_E/k_B T) - 1)^2} \cdot 3N$$

from sum + integral

High- T limit:

$$T \rightarrow \infty \quad x \rightarrow 0 \quad e^x \rightarrow 1 + x$$

$$(e^x - 1)^2 \rightarrow x^2$$

$$C_V \rightarrow 3N k_B$$

This agrees with expt. law of Dulong & Petit. that all substances have same sp. ht. per mole.

5 Phonons II. Thermal Properties

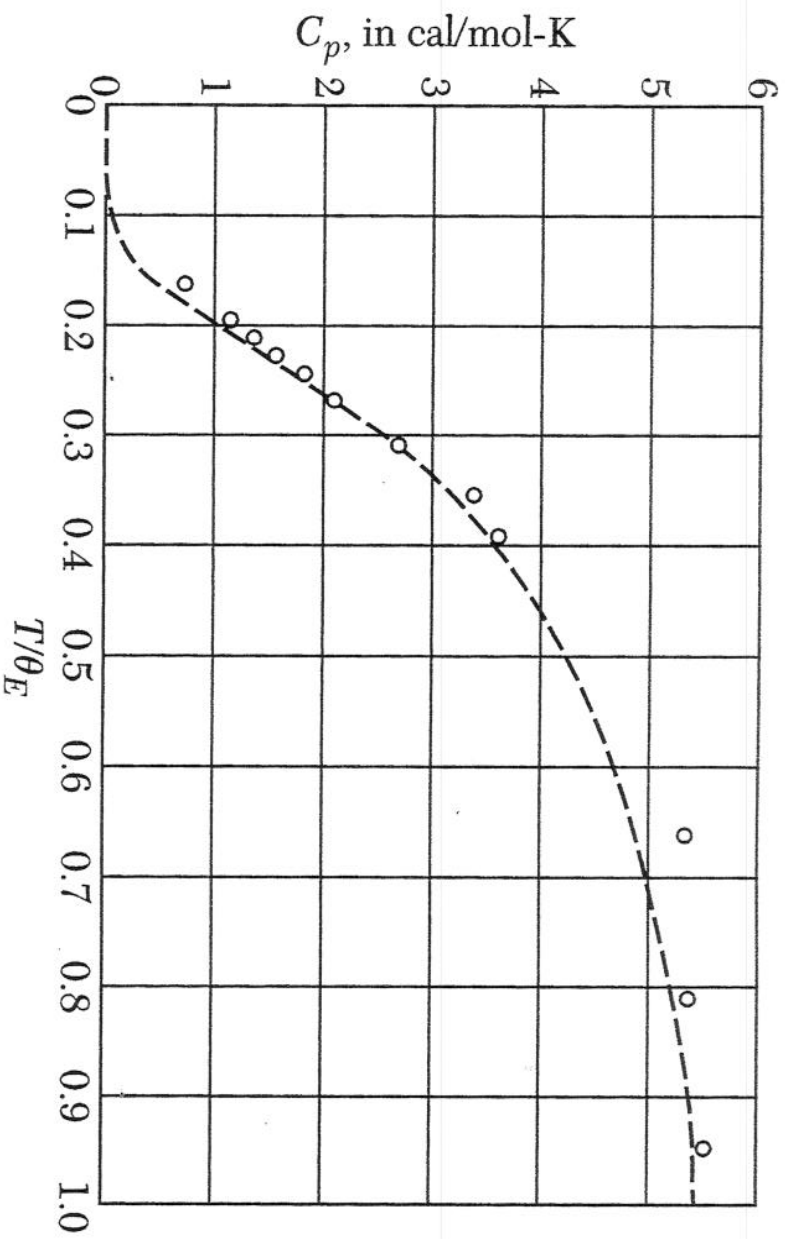
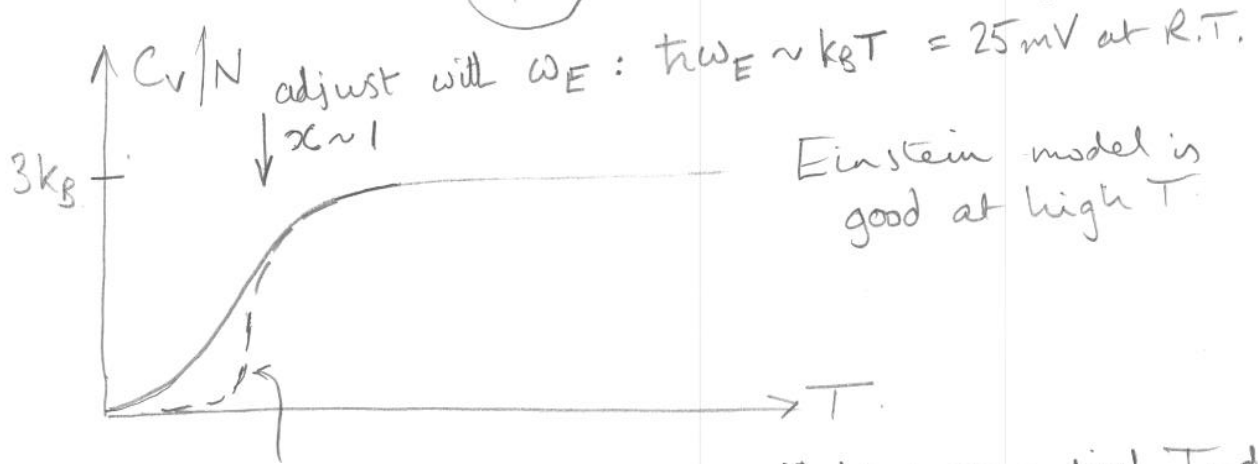


Figure 11 Comparison of experimental values of the heat capacity of diamond with values calculated on the earliest quantum (Einstein) model, using the characteristic temperature $\theta_E = \hbar\omega/k_B = 1320$ K. To convert to J/mol-deg, multiply by 4.186.

(42) $1/h = 2.4 \times 10^{14} \text{ Hz}$ $1/k_B = 1.16 \times 10^4 \text{ K}$



fails here, where it predicts exponential T-dep. "freeze out" of vibrations.

5.3 Density of states in 1D.

Need a better model for counting the 3N vibration modes and finding their frequencies.

Recipe:

i) Find the allowed K -values

ii) Look up their frequencies on $\omega_p(k)$

It is mainly the acoustic modes that will explain the failure of Einstein's model.

Boundary-value problem:

Finite crystal on a line with fixed ends (C_v)

[or use open-ended string, or periodic boundary condition. All give same result.]

Wave solution $u_s = u e^{i(Ksa - \omega t)}$

To satisfy B.C., superpose K and $-K$ states or write solution of wave eqn. this way:

$$u'_s = \frac{1}{2i} (u_s(K) - u_s(-K)) = u e^{-i\omega t} \sin Ksa$$

= 0 at $s=0$ by construction

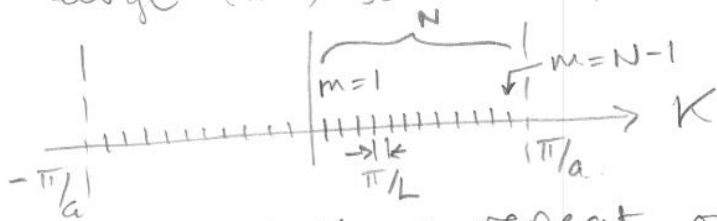
= 0 at $s=N$ now required.

B.C. $\sin KNa = 0 \Rightarrow KNa = m\pi$
 \uparrow integer.

So $K = \frac{m}{N} \frac{\pi}{a}$ allowed values. = $\frac{m\pi}{L}$
 = (fraction) (FBZ boundary)

N is large (10^8) so these points are closely spaced

6.02.2006.



Recall that solutions repeat outside $-\pi/a < K < \pi/a$ and are indistinguishable from FBZ.

- The solutions are all orthogonal to each other, so are independent modes of excitation.
- $\pm K$ solutions are also the same this time, so the total number of solutions is N.
- If the atoms move in 3D (off the line) there will be 3 modes for each atom $\rightarrow 3N$ solutions.
- If we had used periodic boundary condition

HW? $u_s = u_{s+N}$, allowed K's are $\pm \frac{2m\pi}{L}$

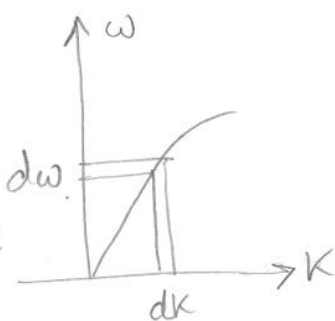
spacing is double, but $\pm K$ now different, total = N.

Counting up (periodic BC case).

Density of K states = no. states from K to K+dk.

One state occupies $\Delta K = \frac{2\pi}{L}$

$D(K) \Delta K = 1 \Rightarrow D(K) = 1/\Delta K = L/2\pi.$



$D(\omega) d\omega = D(K) dk.$

$D(\omega) = \frac{dk}{d\omega} D(K) = \frac{L}{2\pi} \frac{1}{(d\omega/dk)} \times 2$
 \uparrow group velocity \uparrow for $\pm K$ direction

9.02.09 I
 4.02.2008 II
 5.02.2007

5.4 Density of States in 2D and 3D.

Easiest to think of a square/cube array of atoms on a square/cubic lattice. The result can be shown to generalise for all cases.

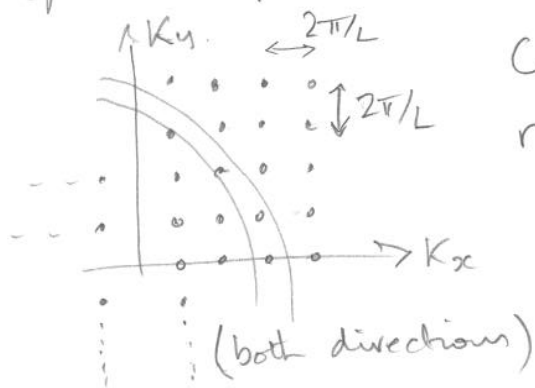
Crystal has size $L = Na$ in each direction. Vibrations have discrete K_x , K_y and K_z components.

$$u_{s_1, s_2, s_3} = u e^{-i\omega t} e^{iK_x s_1 a} e^{iK_y s_2 a} e^{iK_z s_3 a}$$

B.C. requires $u_{s_1+N, s_2, s_3} = u_{s_1, s_2, s_3}$ etc [periodic]

so $K_x = \frac{m}{N} \frac{2\pi}{a} = \frac{2m\pi}{L}$ ← [m+ or -] same for K_y , K_z .

3D reciprocal lattice is covered with points spaced apart by $2\pi/L$ in K_x , K_y and K_z .



Count one state per reciprocal space volume $\left(\frac{2\pi}{L}\right)^3$

[3 states with polarization]

For the thermal models we consider, we only need the isotropic case where $\omega(k)$ is the same in all directions.

Then $D(k)dk = \text{no. of states in shell } k \rightarrow k+dk$

Sphere of radius k contains $N = \frac{4}{3}\pi k^3 \left(\frac{L}{2\pi}\right)^3$ states

Shell of thickness dk contains $\frac{dN}{dk} dk$ states.

$$D(k) = \frac{dN}{dk} = 4\pi k^2 \left(\frac{L}{2\pi}\right)^3 = \frac{VK^2}{2\pi^2} \quad [\text{for each polarization}]$$

$$D(\omega) = \frac{dN}{d\omega} = \frac{VK^2}{2\pi^2} \left(\frac{dk}{d\omega}\right) \leftarrow 1/\text{group velocity}$$

5.5 Density of States in real life.

$D(\omega)$ is something we can relate to. It is the spectrum of vibration frequencies of a solid.

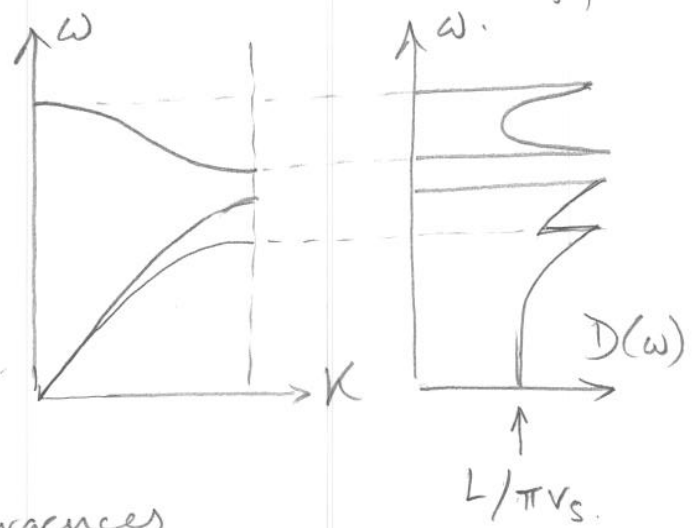
Just as an engineer asks about the vibration modes of a bridge, we ask about a crystal.

i) If we know $\omega(K)$ from neutron scattering, we can convert it:

eg diatomic chain.

- frequency 'gaps' appear as gaps in spectrum

- turning points are divergences (in 1D)



In 2D and 3D the divergences are more spread out and show up as kinks and plateaus in the spectrum.

ii) Measurements are possible by optical spectroscopy & neutron scattering.

$\nu = 10^{12} \text{ Hz}$ $h\nu = 0.01 \text{ eV} \ll 2 \text{ eV}$ photon. visible

Brillouin scattering \rightsquigarrow \square \rightsquigarrow DOS- \uparrow DOS+ ω

\rightarrow strong peaks at optical zone centre ω_0

Neutron scattering, Powder sample to average all directions \rightarrow similar result.

Inelastic X-ray scattering. Lower resolution, but possible on small volumes eg under pressure.

Powder \rightarrow average over all $K \rightarrow$ resolve in ω .
[don't need K -resolution, just E/ω]

the megabar diamond cell (Fig. 1). Isotopically enriched ^{57}Fe samples were loaded in a Be gasket (19). No pressure medium was used. NRIXS was performed at the undulator beamline (31D) of the Advanced Photon Source (APS) with a high-resolution (2 meV) monochromator scanning the range of ± 100 meV in steps of 0.4 meV (20). Pressures were calibrated by the ruby scale (21) and confirmed by the

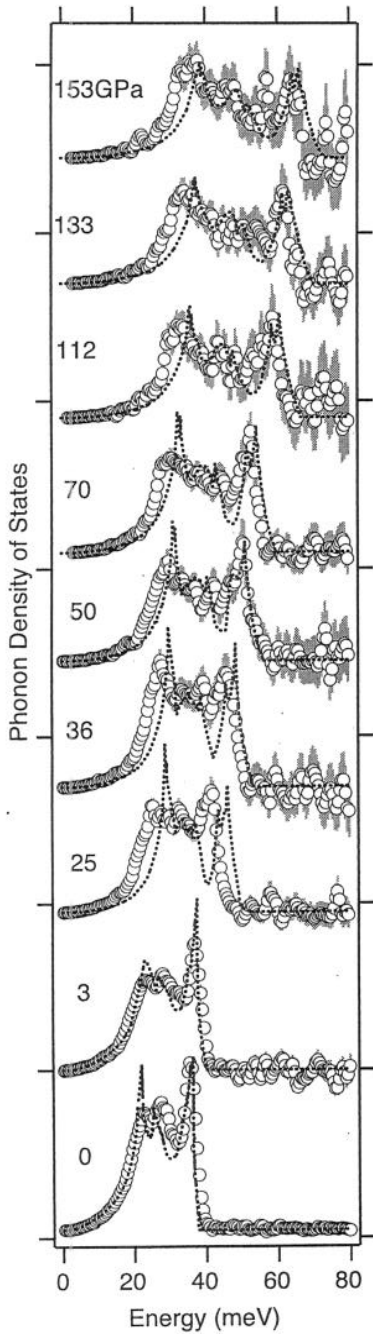


Fig. 2. Phonon DOS of Fe. Thin dotted curves, ab initio theory; circles with error bars, NRIXS data.

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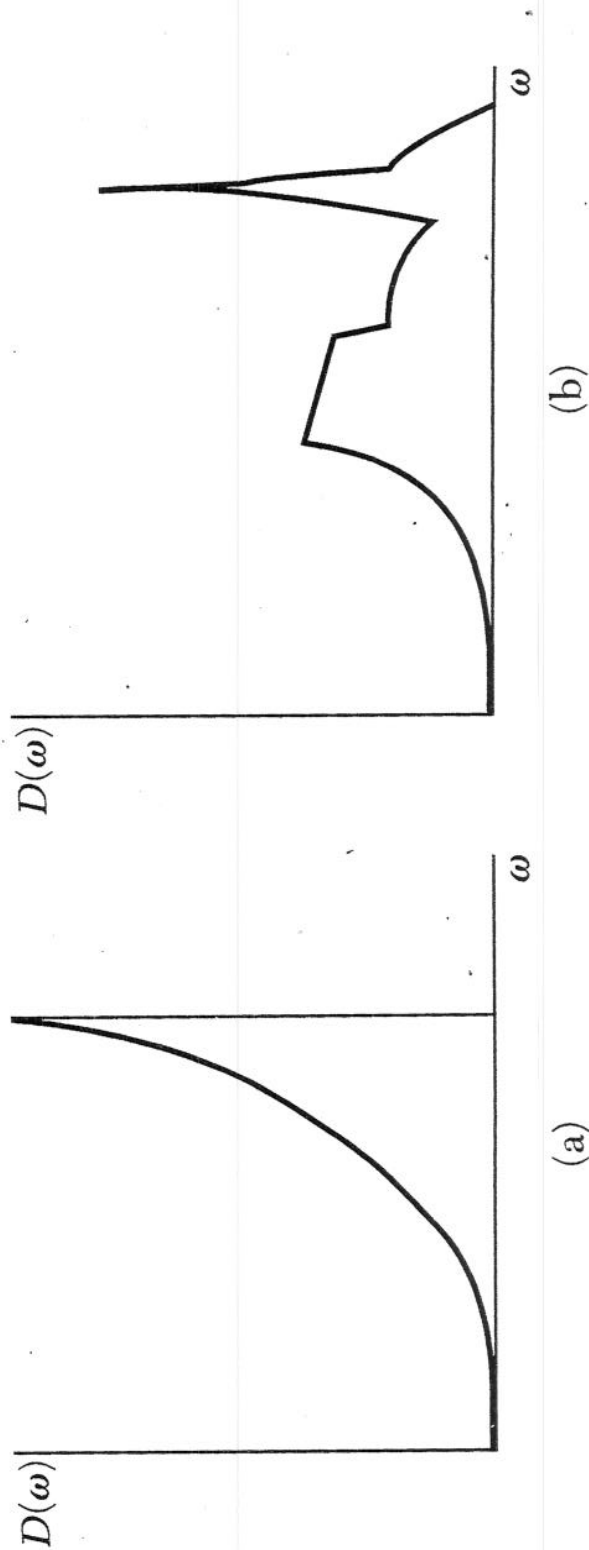
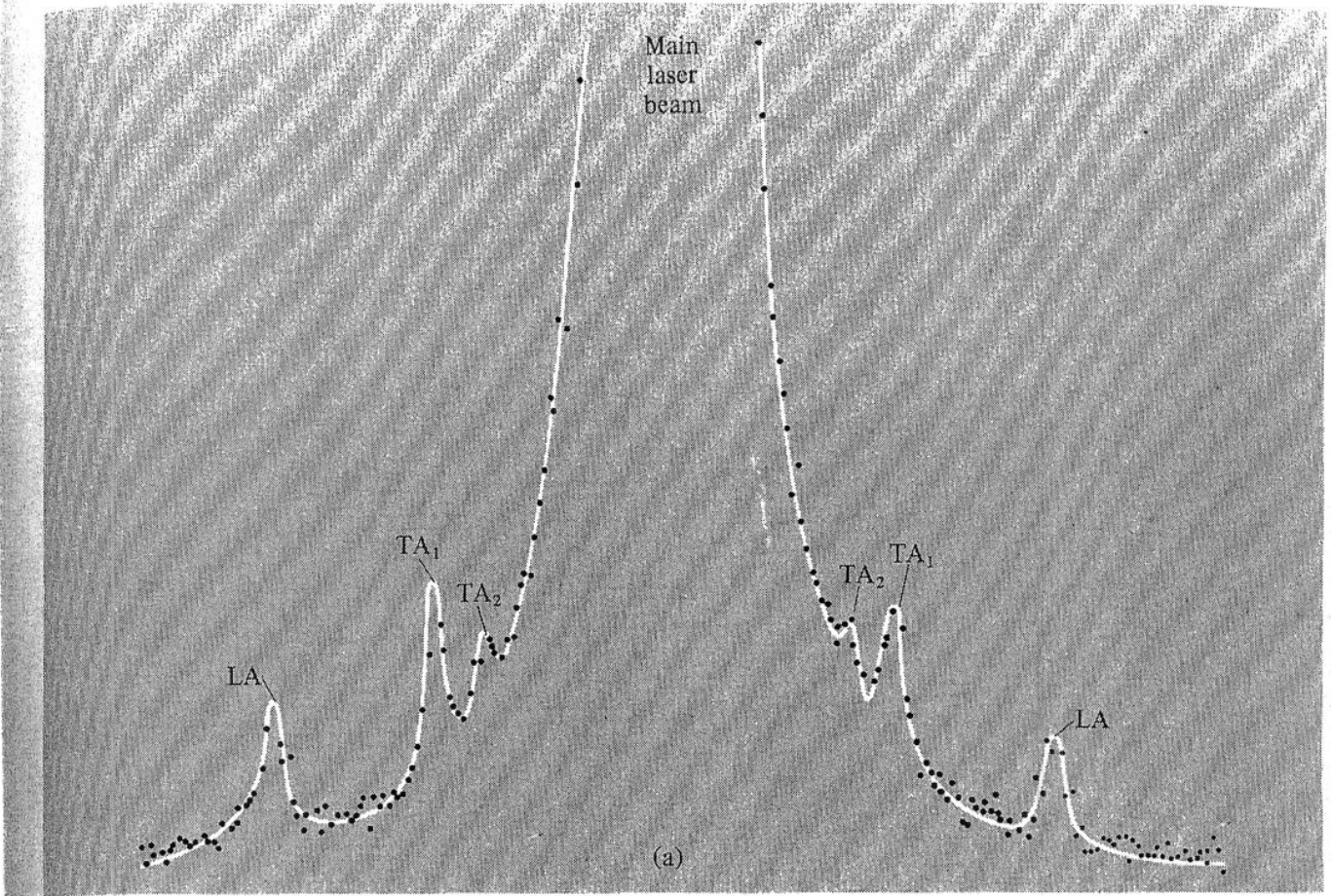
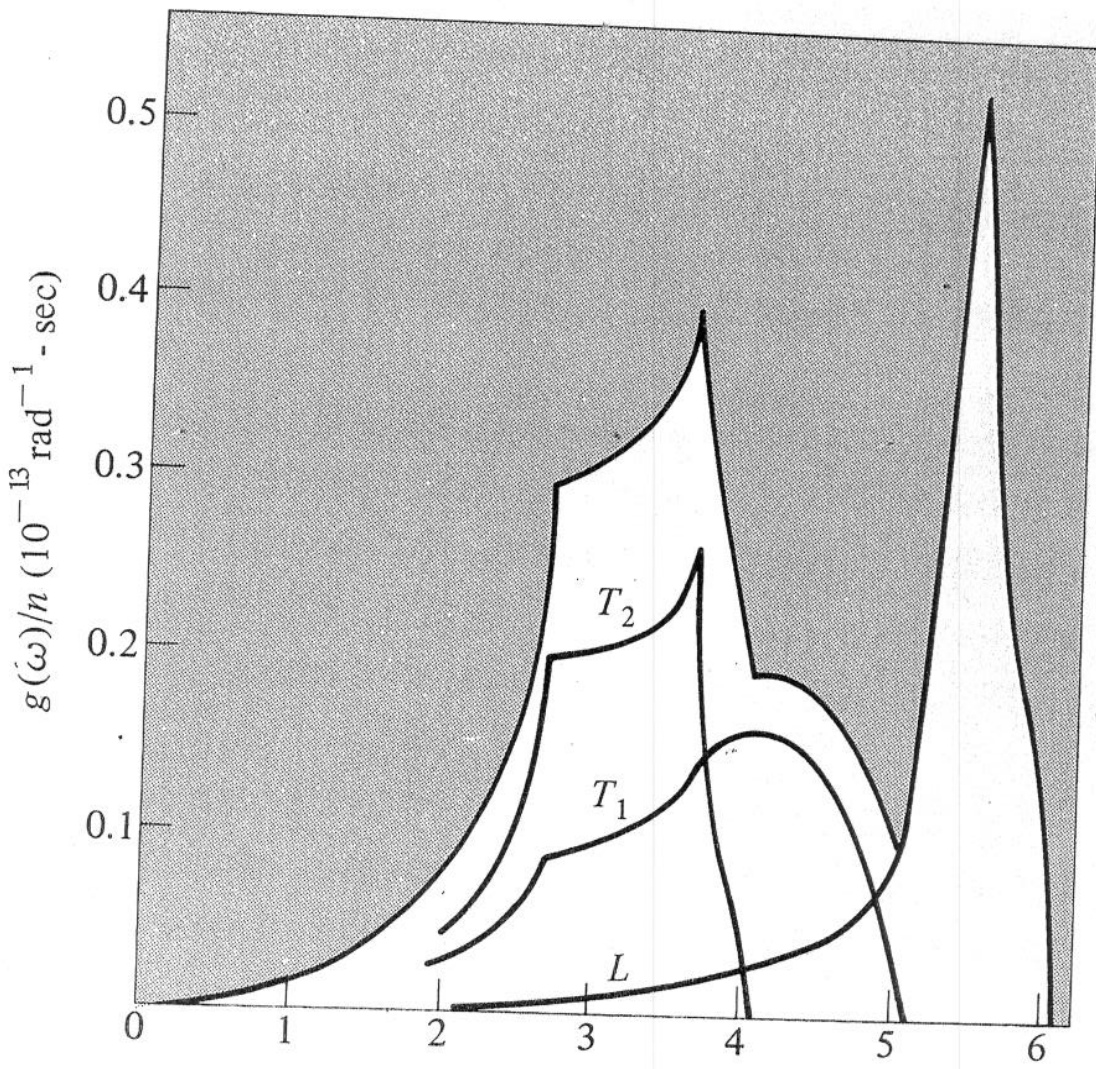


Figure 14 Density of states as a function of frequency for (a) the Debye solid and (b) an actual crystal structure. The spectrum for the crystal starts as ω^2 for small ω , but discontinuities develop at singular points.



5.6 Heat capacity in Debye model.

We can now improve on the Einstein model by including the long-wavelength acoustic phonons, ignoring all ZB effects.

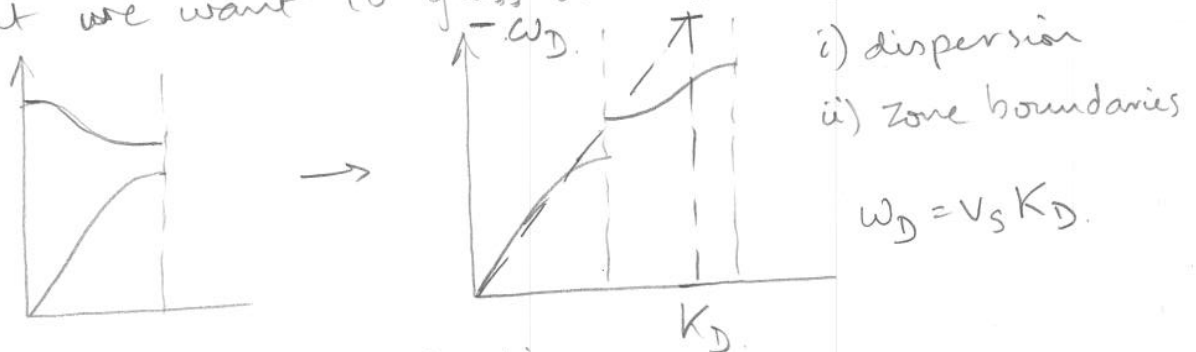
$\omega = v_s K$, $v_s = \text{sound velocity}$. $D(K) = \frac{VK^2}{2\pi^2}$ before [sphere].

$$D(\omega) = \frac{VK^2}{2\pi^2 v_s} = \frac{V\omega^2}{2\pi^2 v_s^3}$$

This is the first assumption of Debye.

Second assumption is that there is no dispersion out to a cut-off frequency set by the total number of allowed modes. = N_{atoms}

- Real crystal has exactly the correct number, but we want to gloss over details of



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- Quite good approximation because thermal props are dominated by the low frequencies. [x3 comes later for 3D]

Cut off: $\frac{4}{3} \pi K_D^3 \left(\frac{L}{2\pi}\right)^3 = N_{\text{atoms}} = N \text{ deg. freedom.}$

Volume of K-sphere (Volume of 1 state)⁻¹

Putting $L^3 = V = \text{volume of sample}$,

$$K_D^3 = 3 \frac{(2\pi)^3}{4\pi} \frac{N}{V} = 6\pi^2 \frac{N}{V}$$

$$\omega_D^3 = 6\pi^2 v_s^3 \frac{N}{V}$$

We now have all the pieces ready:

$$U = 3 \int D(\omega) \langle n(\omega) \rangle \hbar \omega d\omega$$

$$= 3 \int_0^{\omega_D} \frac{V \omega^2}{2\pi^2 v_s^3} \frac{\hbar \omega}{e^{\hbar \omega / k_B T} - 1} d\omega.$$

Multiply by 3 for the 3 polarizations, but we can easily improve this by noting that transverse waves are slower than longitudinal

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$$U = 3 \frac{V \hbar}{2\pi^2 v_s^3} \int_0^{\omega_D} \frac{\omega^3 d\omega}{e^{\hbar \omega / k_B T} - 1} \quad \frac{\hbar \omega}{k_B T} = x$$

$$= 3 \frac{V \hbar}{2\pi^2 v_s^3} \left(\frac{k_B T}{\hbar} \right)^4 \int_0^{x_D} \frac{x^3 dx}{e^x - 1} \quad x_D = \frac{\hbar \omega_D}{k_B T} = \frac{\Theta_D}{T}$$

$$\Theta_D = \frac{\hbar \omega_D}{k_B} = \frac{\hbar v_s}{k_B} \left(6\pi^2 \frac{N}{V} \right)^{1/3} = \text{Debye characteristic temperature}$$

This can be used to tidy up the prefactors in U considerably. Note that Θ_D is an intrinsic property of the solid material; N/V is the density.

$$U = 9 N k_B T \left(\frac{T}{\Theta_D} \right)^3 \int_0^{x_D} \frac{x^3 dx}{e^x - 1}$$

$$C_V = \frac{\partial U}{\partial T} = 9 N k_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^{x_D} \frac{x^4 e^{2x} dx}{(e^x - 1)^2}$$

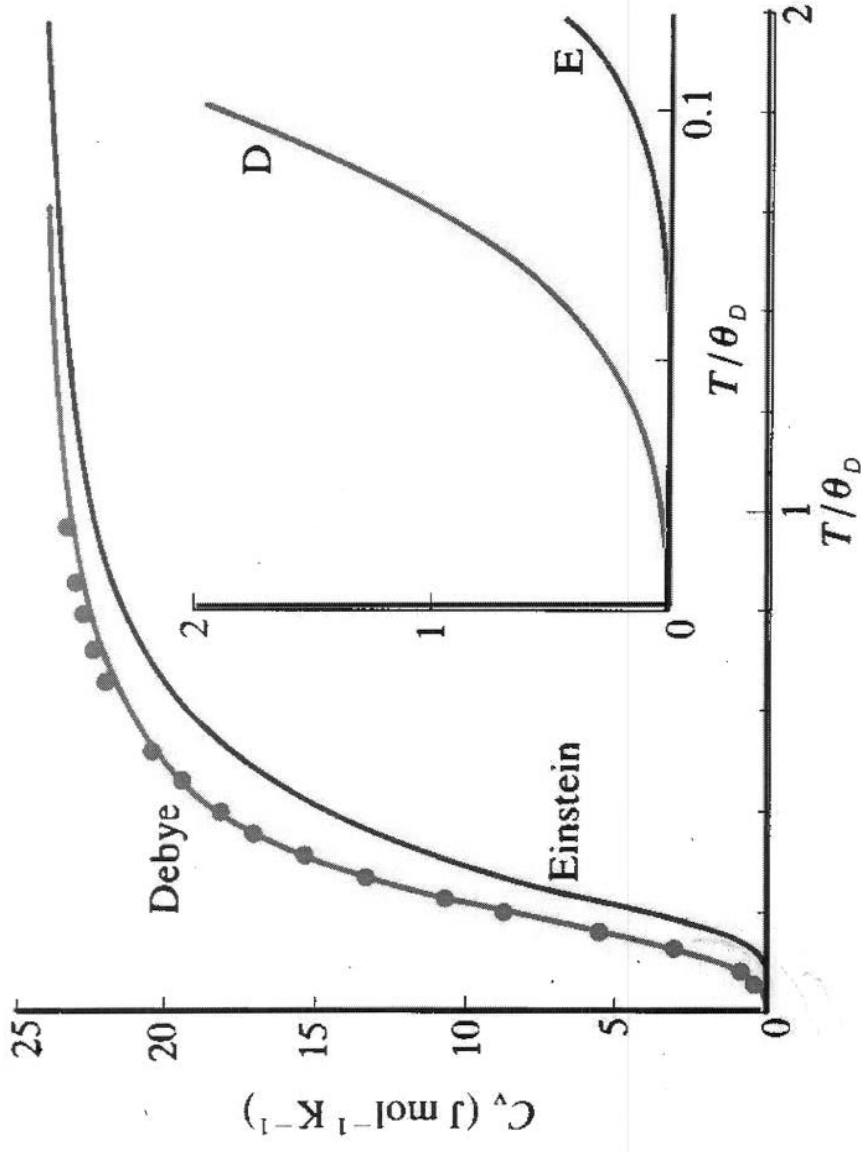
We already did this differentiation and you can check it on next week's homework!

This is the sought-after improvement over the Einstein model. Dulong-Petit value

High-T limit (as before), $C_V \rightarrow 3 N k_B$

$$x \rightarrow 0 \quad e^x \rightarrow 1 + x \quad \int_0^{x_D} x^2 dx^2 = \frac{x_D^3}{3} \quad \begin{matrix} \uparrow \text{both} \\ \text{integrals} \\ \text{same.} \end{matrix}$$

Improvement over Einstein model.



Debye and Einstein models compared with experimental data for Silver. Inset shows details of behaviour at low temperature.

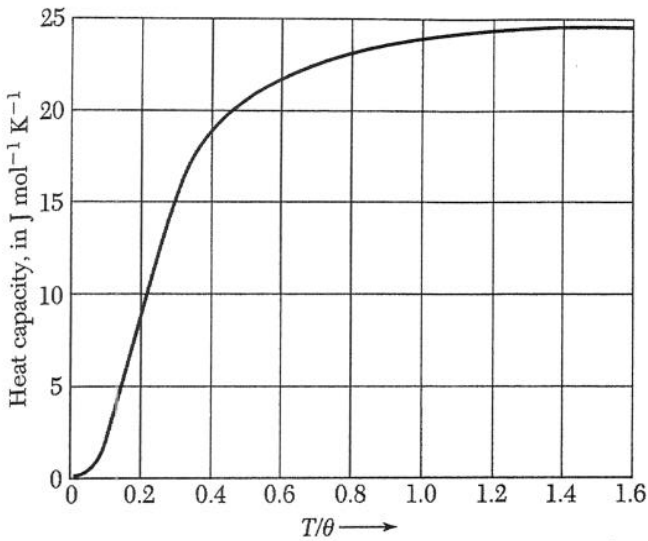


Figure 7 Heat capacity C_V of a solid, according to the Debye approximation. The vertical scale is in $\text{J mol}^{-1} \text{K}^{-1}$. The horizontal scale is the temperature normalized to the Debye temperature θ . The region of the T^3 law is below 0.1θ . The asymptotic value at high values of T/θ is $24.943 \text{ J mol}^{-1} \text{ deg}^{-1}$.

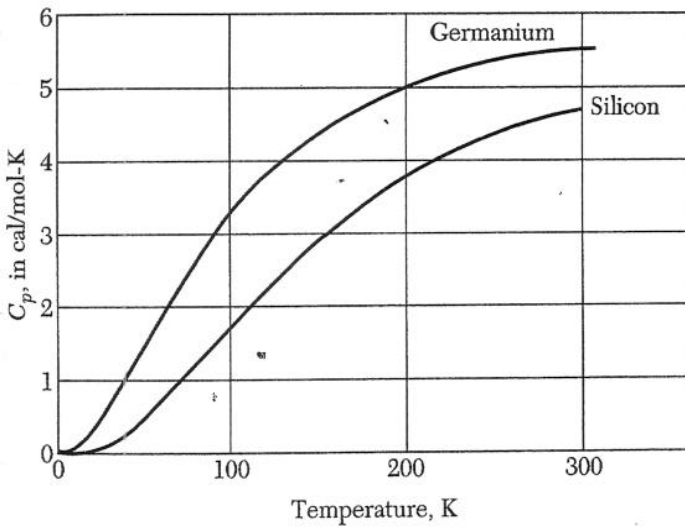


Figure 8 Heat capacity of silicon and germanium. Note the decrease at low temperatures. To convert a value in cal/mol-K to J/mol-K , multiply by 4.186.

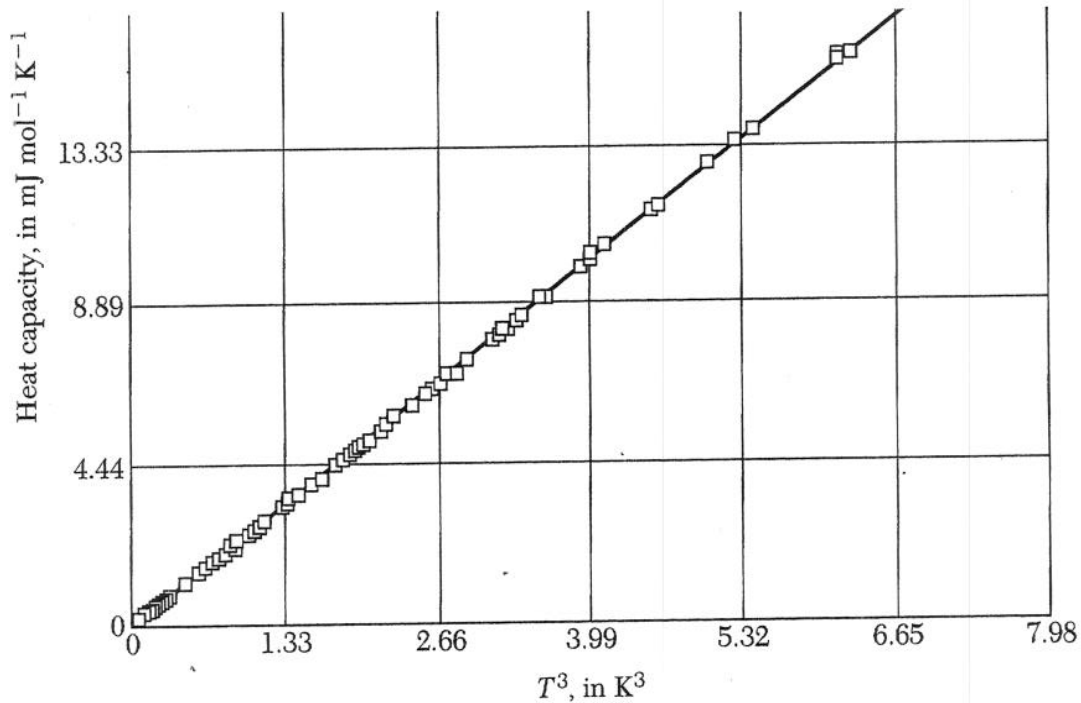


Figure 9 Low temperature heat capacity of solid argon, plotted against T^3 . In this temperature region the experimental results are in excellent agreement with the Debye T^3 law with $\theta = 92.0 \text{ K}$. (Courtesy of L. Finegold and N. E. Phillips.)

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5.7 Low-T limit.

Important practical note: take the limit for U before evaluating C_V . The integrals are easier!

$$T \rightarrow 0 \quad x_D = \Theta_D / T \rightarrow \infty$$

$$\int_0^{x_D} \frac{x^3 dx}{e^x - 1} \rightarrow \int_0^{\infty} \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15} \text{ standard integral.}$$

$$U = 9Nk_B T \left(\frac{T}{\Theta_D} \right)^3 \frac{\pi^4}{15}$$

[you will be given this on exams!]

$$C_V = \frac{\partial U}{\partial T} = 4T^3 \frac{9Nk_B}{\Theta_D^3} \frac{\pi^4}{15} = \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\Theta_D} \right)^3$$

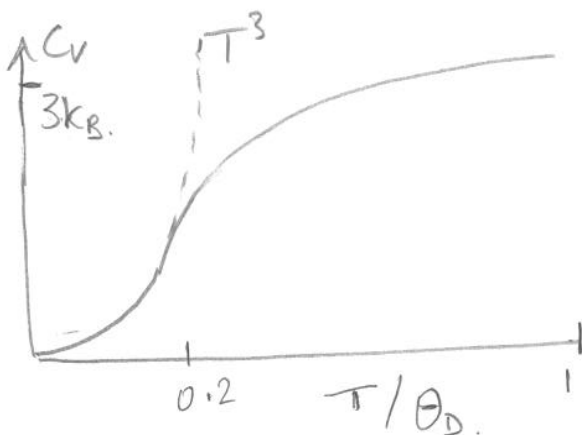
This is the important Debye T^3 law. [pic].

5.8 Debye Theory.

The basic idea of ignoring the dispersion effects has other applications:

Debye-Waller factor, accounting for the effective reduction of the form-factor for scattering of atoms in a vibrating crystal.

Expt: temperature dependence of diffraction intensity \rightarrow change of vibration amplitude
temperature variation $\rightarrow \Theta_D$ as "fitting" param.



Values of Θ_D :

K 56K.

Cu 332K [315 from v_s]

Ag 214K [215].

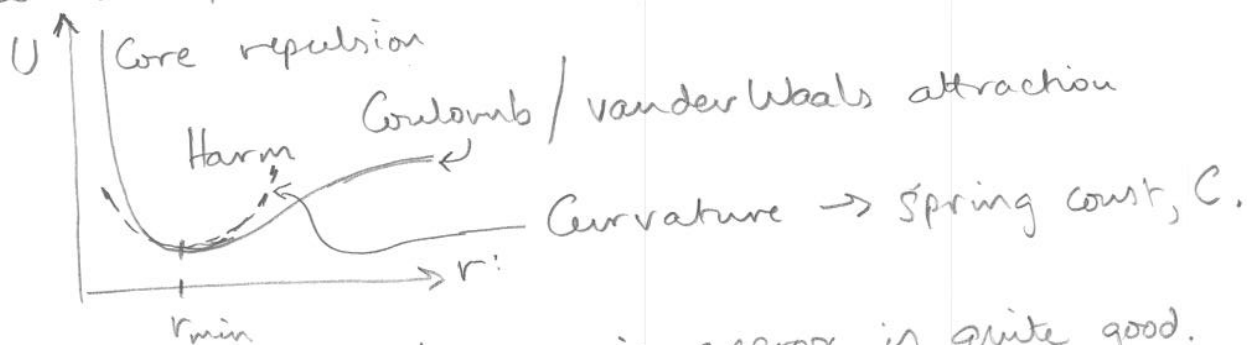
C 1860K

Correct high- and low-T limits.

5.9 Anharmonicity

Model of balls and springs is "harmonic".
Spring compressed by x exerts the same force as one expanded by x .

Cohesive forces are inherently "anharmonic"



Small deviations: harmonic approx is quite good.
Large deviations (at high T) becomes bad.

Consequences:

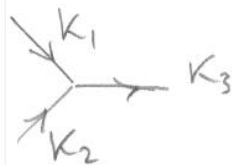
- i) thermal expansion. Average position $\neq r_{min}$ when neighbours travel far from $\equiv r_{min}$ separation.
- ii) phonons interact with each other.
Phonon scattering would not happen in a purely harmonic crystal. Modes are independent.
Instead, one phonon causes $r \neq r_{min}$ on one side or the other (momentarily). Second phonon sees a different spring constant (higher on left). So they are not independent.

7.02.06.

Rules for phonon-phonon interactions:

Conserve momentum $K_1 + K_2 = K_3$

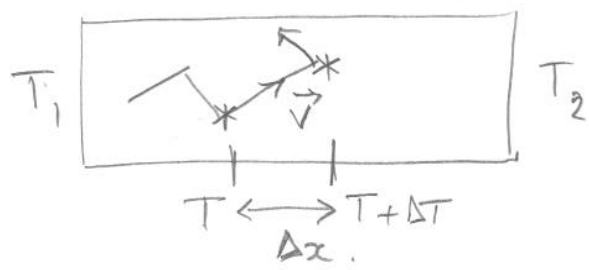
Conserve energy $\omega_1 + \omega_2 = \omega_3$



Rate of anharmonicity, γ (Gruneisen)

Can measure by ballistic experiments

Review of Kinetic theory of gases.



* is a collision (equilibration event)

Particle transmits an energy $c \Delta T$ $c = \frac{C_v [\text{vol}]}{\bar{n} [\text{vol}]}$

$$\Delta T = \frac{dT}{dx} \Delta x = \frac{dT}{dx} v_x \tau$$

v_x - component of \vec{v} τ - time between collisions

Heat flow per unit area:

$$j_V = n \quad c \Delta T \quad \langle v_x \rangle = n c \langle v_x \rangle^2 \tau \frac{dT}{dx}$$

(density) (heat) (velocity)

definition of κ

Thermal conductivity:

$$\kappa = n c \langle v_x \rangle^2 \tau = C_v \frac{1}{3} v^2 \tau = \frac{1}{3} C_v v l$$

where $l = v \tau = \text{mean free path}$.

In a gas, $C_v = \text{kinetic energy of molecules}$.

In a solid, $C_v = \text{energy contained in phonons}$

5.10 Thermal Conductivity.

Analogous argument to kinetic theory of gases.

$$\kappa = \frac{1}{3} C_V v_s l \quad [\text{Derivation on next page}]$$

C_V = specific heat, explained by Debye.

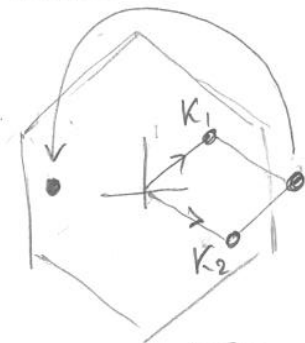
v_s = sound velocity

l = "mean free path" between collisions.

But even the anharmonic collisions are not enough because they conserve momentum.

We need a new process "Umklapp collision"

↳ "folding" (Peierls)



$k_3 = k_1 + k_2$ outside Brillouin Zone.
no longer conserves real momentum, only crystal momentum.

l is the MFP between Umklapps/impurities/boundaries.

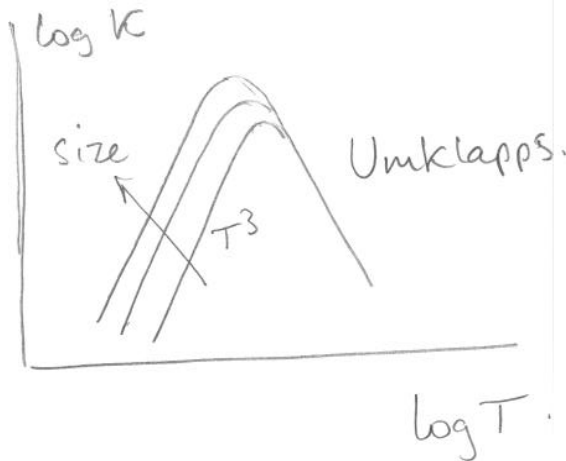
Temperature dependence:

$C_V \propto T^3$, then constant

v_s : none, property of crystal

l : strong activation at high T , becoming shorter.

Typical insulator, LiF



Variation with size of sample, is not an intrinsic property.

Phonons traverse entire sample.

Thermal Conductivity of Isotopically Modified Single Crystal Diamond

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(Received 16 February 1993)

We present new experimental results on the thermal conductivity of isotopically enriched ^{12}C diamond crystals at low temperatures. To our knowledge, the measured value for a 99.9% ^{12}C crystal at 104 K, 410 W/cm K, is the highest measured thermal conductivity for a solid above liquid nitrogen temperature. Our measured temperature dependent conductivities for the isotopically enriched diamond and natural abundance diamond specimens are well described by Callaway's theoretical model. We predict that the thermal conductivity of a 99.999% ^{12}C diamond crystal should exceed 2000 W/cm K at ~ 80 K.

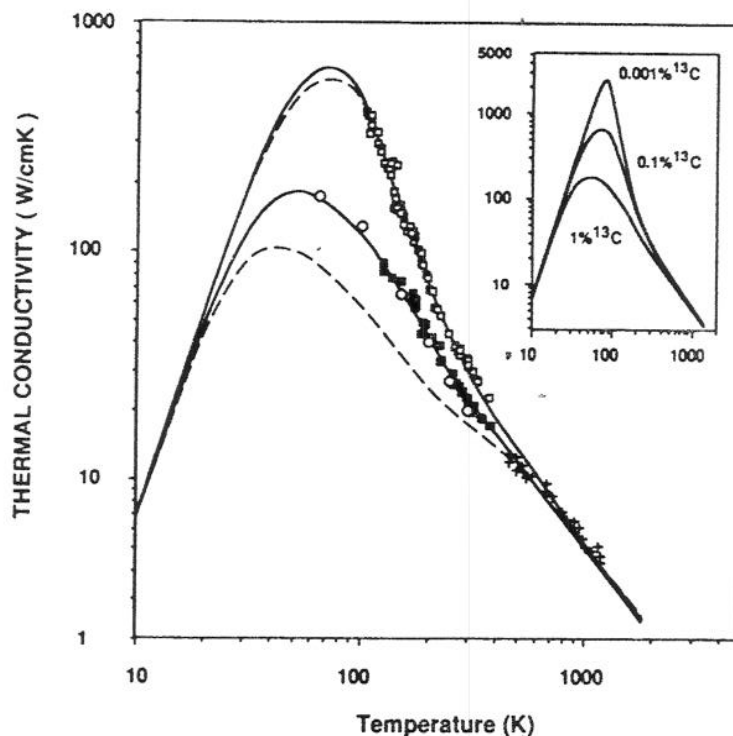
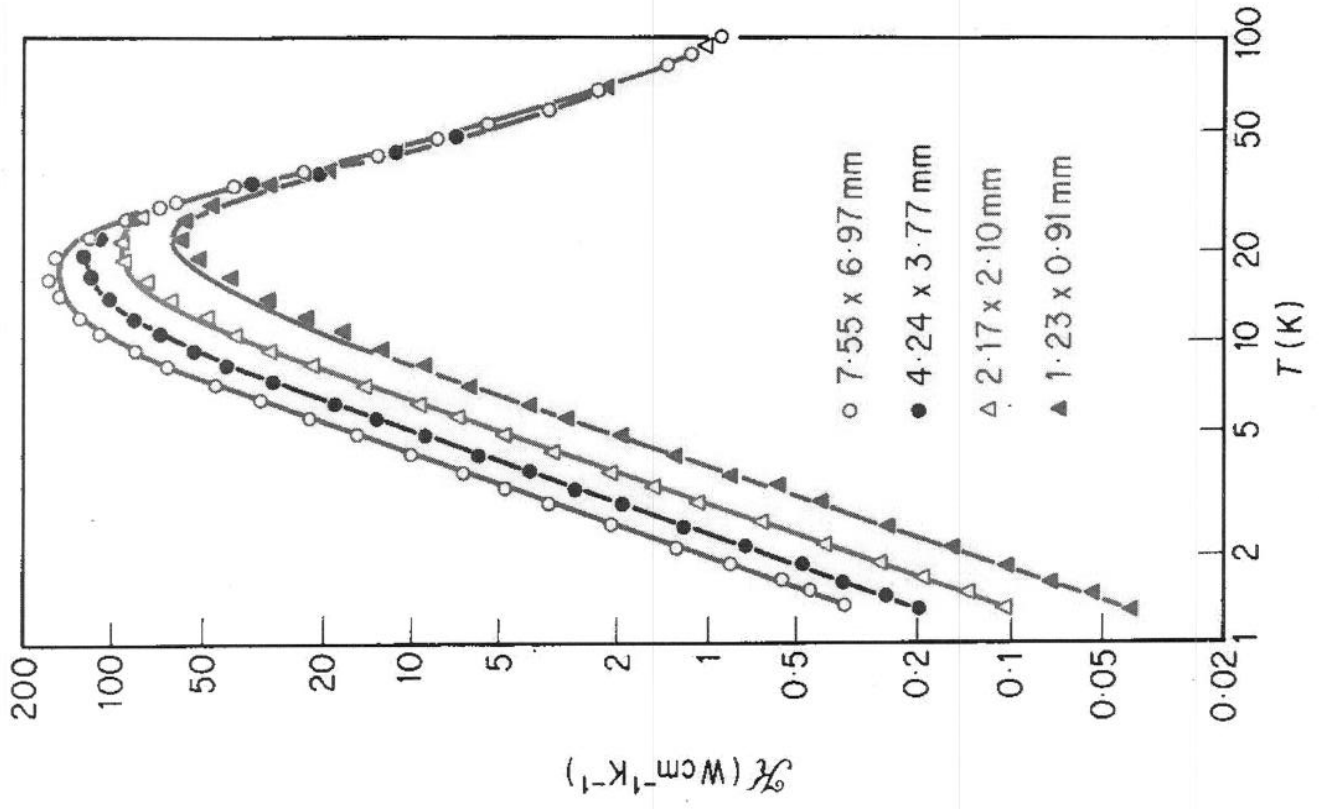


FIG. 2. Thermal conductivity of natural abundance (1.1% ^{13}C) diamond (lower squares), isotopically enriched (0.1% ^{13}C) diamond (upper squares), together with the low temperature data of Slack [17] (circles) and the high temperature data of Vandersande *et al.* [18] (plusses). The solid curves are the results of fitting the Callaway theory to the data, using a single set of fitting parameters. The dashed curves are the results of fitting with the assumption that N processes dominate, as in Ref. [4]. The inset shows the calculated thermal conductivity corresponding to 1%, 0.1%, and 0.001% ^{13}C concentrations corresponding to the Callaway theory with the same set of parameters used to generate the solid curves.

Thermal conductivity of LiF as function of specimen size at low temperature, showing effect of boundary scattering.



10. The energy of a collection of oscillators of frequencies ω_K in thermal equilibrium is

$$U = \sum_K \underbrace{\frac{1}{\exp(\hbar\omega_K/k_B T) - 1}}_I \underbrace{\hbar\omega_K}_{II},$$

where K is the wavenumber. For convenience, we have omitted the polarisation here.

(a) Describe the physical meaning of the terms I and II. [4]

(b) Assume periodic boundary conditions and derive an integral expression for the energy U of a one-dimensional crystal of length L , consisting of N equidistant identical atoms. Show that this involves a density of states given by

$$D(K) = \frac{L}{\pi}.$$

[6]

(c) Which two main assumptions are made in the Debye theory about the distribution of frequency modes as a function of wavenumber K ? [6]

(d) Show that these assumptions lead to the following expression for U :

$$U = \frac{Lk_B^2 T^2}{\pi v_s \hbar} \int_0^{x_D} \frac{x}{e^x - 1} dx.$$

The calculation of x_D is not requested here. [9]

(e) Some materials consist of weakly coupled, nearly one-dimensional structures, leading to material properties that strongly deviate from three-dimensional materials. Based on the result in (d) and on the low-temperature limit of the standard (three-dimensional) Debye model, suggest an experiment to determine whether a material is one- or three-dimensional. [5]

$$D(k) = \frac{VK^2}{2\pi^2} \text{ in 3D. } \quad \frac{L}{2\pi} \text{ in 2D. } \quad -\frac{\pi}{a} < k < \frac{\pi}{a}$$

(d) Internal energy of phonon population.

$$U = \int_0^{\omega_D} D(\omega) \frac{1}{e^{\hbar\omega/k_B T} - 1} \hbar\omega d\omega.$$

$$D(\omega) = D(k) \left/ \frac{d\omega}{dk} \right\} = v_s = \frac{L}{2\pi v_s} \left[\times 2 \leftarrow \begin{array}{l} \pm k \\ \text{directions} \\ \omega! \end{array} \right]$$

usual substitution $x = \frac{\hbar\omega}{kT}$ $\omega = \left(\frac{kT}{\hbar}\right)x$

$$U = \frac{L\hbar}{2\pi v_s} \left(\frac{kT}{\hbar}\right)^2 \int_0^{x_D} \frac{x dx}{e^x - 1} = \frac{Lk_B^2 T^2}{2\pi v_s \hbar} \int_0^{x_D} \frac{x dx}{e^x - 1}$$

(e) Low T limit.

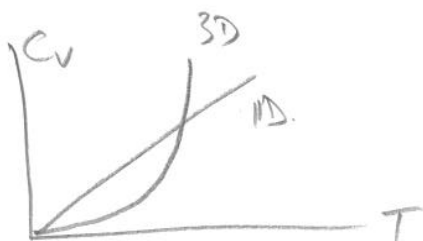
$$x_D = \frac{\hbar\omega_D}{k_B T} \rightarrow \infty \quad \int_0^{x_D} \frac{x}{e^x - 1} dx \rightarrow \frac{\pi^2}{6}$$

$$U \rightarrow \frac{Lk_B^2 T^2}{2\pi v_s \hbar} \frac{\pi^2}{6} = \frac{Lk_B^2 T^2}{12 v_s \hbar}$$

$$\frac{dU}{dT} \rightarrow \frac{Lk_B^2 T}{6 v_s \hbar} = C_V \propto T \quad \text{1D result.}$$

$$C_V \propto T^3 \quad \text{3D result}$$

Experiment is to measure C_V vs T .



8. The internal energy of a harmonic crystal can be written as

$$U = \underbrace{U_0}_1 + \int_0^\infty \underbrace{\sum_p D_p(\omega)}_2 \underbrace{\hbar\omega}_3 \underbrace{\frac{1}{e^{\hbar\omega/k_B T} - 1}}_4 d\omega$$

Explain the meanings of the numbered terms in this expression. [8]

Consider a single two-dimensional sheet of graphite (usually called graphene). In its unit cell there are two carbon atoms. How many branches in the phonon spectrum are there? What kind of phonons do they correspond to? [4]

Part of the phonon spectrum of graphene can be described by the Debye model, and part by the Einstein model. The total spectrum can then be described by the sum of the two parts. What type of phonons does the Debye model describe? What type of phonons does the Einstein model describe? [2]

For the Debye model, the relation between the phonon frequency ω and wavevector k is $\omega = ck$. What is c ? [1]

For one branch, the k -space density of states is

$$\tilde{D}_p(k) dk = \frac{Na}{2\pi} k dk$$

where a is the area of the graphene unit cell. Determine the corresponding $D_p(\omega)$ for the Debye model. [3]

For the Einstein model the phonon frequency ω is independent of k and $D_p(\omega) = N\delta(\omega - \omega_{Einstein})$ for N unit cells. Using this result, and the results obtained earlier for the Debye model, construct $D(\omega) = \sum_p D_p(\omega)$ for graphene. [2]

Show that

$$U = U_0 + 3N \left\{ \frac{\hbar\omega_{Einstein}}{e^{\hbar\omega_{Einstein}/k_B T} - 1} + k_B T \left(\frac{T}{\theta}\right)^2 \int_0^{x_D} \frac{x^2}{e^x - 1} dx \right\}$$

where $k_B\theta = \hbar c\sqrt{2\pi/a}$ and $x_D = \hbar\omega_D/k_B T$. What is ω_D ? [5]

At low temperature $U \approx U_0 + 6\zeta N k_B T (T/\theta)^2$ where $\zeta = \int_0^\infty x^2/(e^x - 1) dx$. Which phonons are contributing to the thermal energy at low temperature? [1]

Determine the heat capacity at low temperature, and explain how the dimensionality of the system reveals itself in your expression. [4]

Example: Exam 2007 Q8

If graphene were really 2D, no motions out of plane.

$d = 2$? $p = 2$ atoms per unit cell. but world is 3D.

$\Rightarrow 6$ modes $\begin{cases} 3 \times \text{acoustic (1xL, 2xT)} \\ 3 \times \text{optic modes.} \end{cases}$

Debye \leftrightarrow acoustic phonons

Einstein \leftrightarrow optic phonons

$c =$ speed of sound.

note 2D form
for one branch.

$$D(\omega) = \frac{dK}{d\omega} D(K) = \frac{1}{c} \frac{Na}{2\pi} K = \frac{1}{c^2} \frac{Na}{2\pi} \omega.$$

Combining: $D(\omega) = 3N \left(\frac{a\omega}{2\pi c^2} + \delta(\omega - \omega_E) \right)$
3 polarisations $\sum_P D_P$ \nearrow acoustic \quad optic modes

Inserting into given integral: \swarrow NB cut off.

$$U = U_0 + 3N \left\{ \frac{\hbar\omega_E}{e^{\hbar\omega_E/kT} - 1} + \int_0^{\omega_D} \frac{a\omega}{2\pi c^2} \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} d\omega \right\}$$

remove temperature from integral: $x = \hbar\omega/kT$
 $x_D = \hbar\omega_D/kT$

$$\int = \int_0^{x_D} \frac{a\hbar}{2\pi c^2} \frac{1}{e^x - 1} x^2 dx \left(\frac{k_B T}{\hbar} \right)^3 \quad \text{for one branch}$$

ω_D is frequency cutoff: total no. modes = N .

Low-T limit: $x_D \rightarrow \infty$; Einstein mode vanishes.

not asked
 $U = U_0 + 3N \frac{a\hbar}{2\pi c^2} \left(\frac{k_B T}{\hbar} \right)^3 \zeta_3 = U_0 + 3N k_B T \left(\frac{T}{\Theta} \right)^2$

where $\Theta = \sqrt{\frac{2\pi}{a}} \frac{\hbar c}{k_B}$ only acoustic modes contribute
[don't know why $3 \rightarrow 6$ here]

$$C_V = \frac{dU}{dT} = 6 \zeta_3 \frac{N k_B}{\Theta^2} 3T^2 = 18 \zeta_3 N k_B \left(\frac{T}{\Theta} \right)^2$$

quadratic variation, different from 3D case,
tells us it is a 2D system.