

PHONON HEAT CAPACITY

Lecture 10

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Specific Heats

To recapitulate:

- Lattice vibrations, in the harmonic approximation, described as normal modes of the crystal;
- Each normal mode has the same Hamiltonian as a harmonic oscillator;
- The energy in each normal mode k is $(n_k + \frac{1}{2})\hbar\omega_k$;

Calculate the specific heat, by adding the contributions of all the modes.

- Assume a continuous spread of frequencies/energies
- Find how many normal modes there are in a given range of frequency
- Remember specific heat of harmonic oscillator of frequency ω
- Integrate over ω

4.3 Phonon Density of States

4.3.1 One Dimension - $g(k)$

Take crystal of length L , and impose *periodic boundary conditions*, so that for a wave

$$\exp(ikx) = \exp(ik(x + L)),$$

so

$$\exp(ikL) = 1,$$

or

$$k = n\frac{2\pi}{L},$$

where n is an integer. The allowed states are uniformly distributed in reciprocal space (k -space) with spacing $2\pi/L$.

The density of states is the inverse of the spacing,

$$g(k) = \frac{L}{2\pi}.$$

The number of allowed states with wavevectors between k and $k + dk$ is $g(k) dk$. Note that if there are N unit cells so that $L = Na$ the total number of allowed states in the Brillouin zone is

$$\int_{-\pi/a}^{\pi/a} g(k) dk = \frac{L}{2\pi} \times 2\frac{\pi}{a} = \frac{L}{a} = N.$$

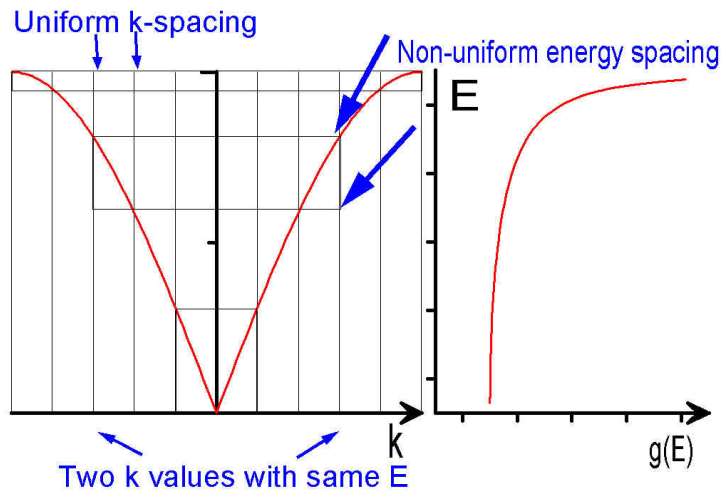
The number of allowed states in the Brillouin zone is equal to the number of *unit cells* in the system. N.B. unit cells, not atoms. More atoms \rightarrow more degrees of freedom \rightarrow more branches of the spectrum.

4.3.2 Assumption of Continuous Energy

How closely spaced are the energy levels? Suppose the crystal is 0.01 m long. Then the spacing between k values is $\Delta k = 2\pi/L = 200\pi \text{ m}^{-1}$. If the sound wave speed is $v = 5000 \text{ m s}^{-1}$ then on the acoustic branch the minimum angular frequency is 0 and the next is $\Delta\omega = v\Delta k = 5000 \times 200\pi = 10^6\pi \text{ rad s}^{-1}$. This is small enough compared with the maximum frequency (about $10^{13} \text{ rad s}^{-1}$) that replacing a sum over discrete frequencies with an integral is a good approximation.

The energy spacing is $\Delta E = \hbar\Delta\omega \approx 3 \times 10^{-28} \text{ J} = 2 \times 10^{-9} \text{ eV}$.

4.3.3 One Dimension: $g(E)$



Go from evenly spaced allowed values of k to, in general, unevenly spaced values of energy. Note that positive and negative k have same E .

Define the density of states in frequency: number of allowed states between ω and $\omega + d\omega$ is $g(\omega) d\omega$. This must be the same as the number in the region of k -space containing states in that frequency interval, so in $0 < k < \pi/a$

$$g(\omega) d\omega = g(k) dk,$$

or

$$g(\omega) = g(k) \frac{dk}{d\omega} = g(k) / \frac{d\omega}{dk}.$$

Allowing also for the states with negative k we get in one dimension

$$g(\omega) = 2 \frac{L}{2\pi} \frac{dk}{d\omega}.$$

$$\frac{d\omega}{dk} = v_g,$$

the group velocity of the wave. *Non-dispersive system* v_g is constant, so

$$g(\omega) = \frac{L}{\pi v_g} = \text{constant}.$$

Monatomic chain

$$\omega = \omega_0 \sin(ka/2),$$

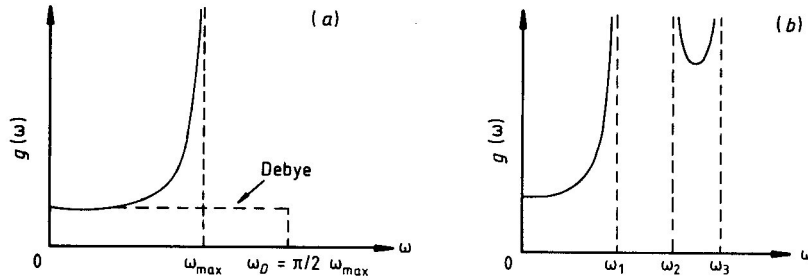
so

$$\begin{aligned} v_g &= \frac{a\omega_0}{2} \cos(ka/2) \\ &= \frac{a\omega_0}{2} \sqrt{1 - \sin^2(ka/2)} \\ &= \frac{a\omega_0}{2} \sqrt{1 - \omega^2/\omega_0^2} \\ &= \frac{a}{2} \sqrt{\omega_0^2 - \omega^2}. \end{aligned}$$

and then

$$g(\omega) = \frac{2L}{\pi a \sqrt{\omega_0^2 - \omega^2}}.$$

One-dimensional density of states for real monatomic structure, non-dispersive system (Debye model), and real diatomic structure.



Note that in one dimension we have singularities whenever the $\omega(k)$ curve is flat.

4.4 Three dimensions – $g(E)$

Apply periodic boundary conditions along x , y and z . The number of states in the reciprocal space volume $dk_x dk_y dk_z$ is then

$$\frac{L_x L_y L_z}{(2\pi)^3} dk_x dk_y dk_z = \frac{V}{8\pi^3} dk_x dk_y dk_z,$$

for crystal volume V . Now assume that the crystal is *isotropic* – ω depends only on magnitude of k , not its direction. Then

$$dk_x dk_y dk_z = 4\pi k^2 dk$$

and the number of states with modulus of wavevector between k and $k + dk$ is

$$g(k)dk = \frac{V}{8\pi^3} 4\pi k^2 dk = \frac{V}{2\pi^2} k^2 dk$$

Here we've accounted for all directions, so no extra factor of 2 as in one dimension when going to $g(\omega)$.

But we do have to include all the modes (acoustic, optic, longitudinal, transverse), each with its own dispersion relation, so

$$g(\omega) = \frac{V}{2\pi^2} \sum_s k(\omega_s)^2 \frac{d\omega_s}{dk},$$

where s denotes the mode. *Non-dispersive system* If we assume that

$$\omega_s(k) = v_s k,$$

i.e. the sound speed does not depend on frequency, we have

$$k(\omega_s) = \frac{\omega}{v_s},$$

and

$$\frac{dk}{d\omega_s} = \frac{1}{v_s},$$

so

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

If we define an average sound speed v by

$$\frac{1}{v^3} = \left\langle \frac{1}{v_s^3} \right\rangle,$$

where $\langle \dots \rangle$ denotes an average. e.g.

$$\frac{1}{v^3} = \frac{1}{3} \left[\frac{1}{v_L^3} + \frac{2}{v_T^3} \right],$$

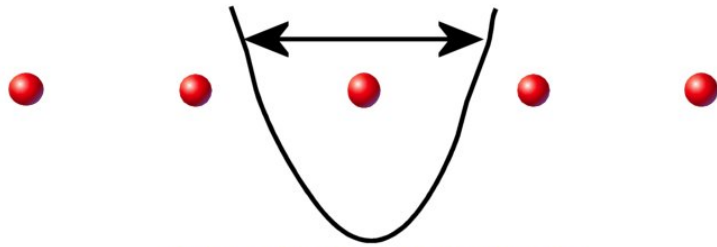
then

$$g(\omega) = \frac{V}{2\pi^2} \frac{S\omega^2}{v^3}.$$

Here S is the number of branches in the phonon spectrum – 3 for a monatomic 3-D solid.

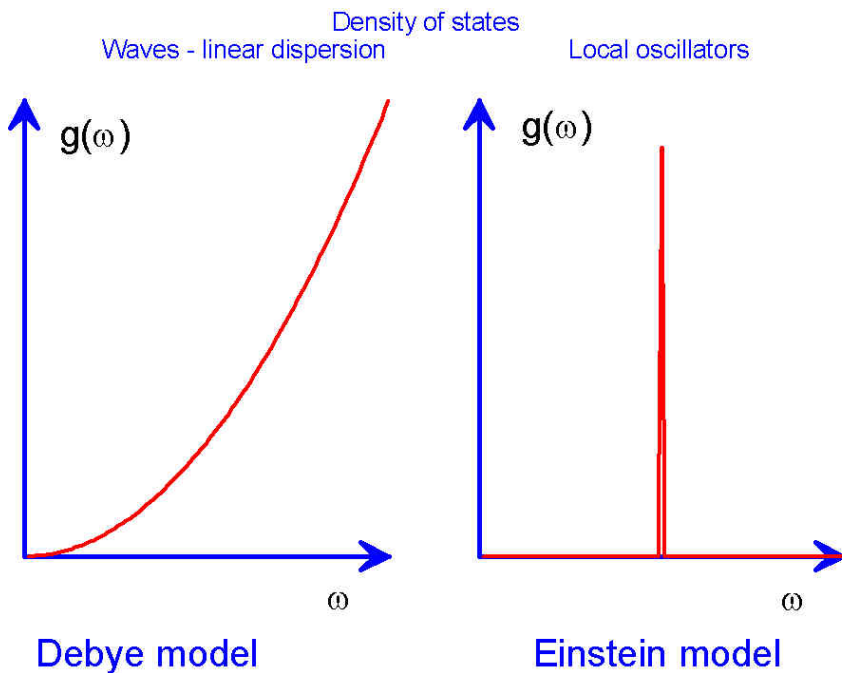
4.4.1 Special case - single frequency

If we assume (the Einstein model)



All atoms except one fixed - Einstein model

we get a delta-function density of states.



N.B. Einstein model can be used as model of narrow optical branch of phonon spectrum.

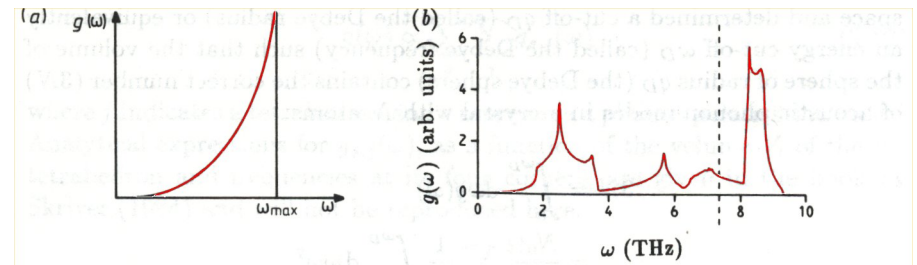


Figure The density of normal modes in a three-dimensional crystal. (a) The Debye model, (b) The density of states for Ge, as calculated with the adiabatic bond charge model (Weber 1977).

Real density of states: complicated structure – no singularities (contrast 1-D), but discontinuities in slope.

4.4.2 Quantised Simple Harmonic Oscillator

(Revision of 2B28) For an oscillator of frequency ω in its n th energy level the partition function is

$$\begin{aligned}
 Z &= \sum_{n=0}^{\infty} \exp\left(-\frac{E_n}{k_B T}\right) \\
 &= \sum_{n=0}^{\infty} \exp\left(-\frac{(n + 1/2)\hbar\omega}{k_B T}\right) \\
 &= \frac{1}{2 \sinh\left(\frac{\hbar\omega}{2k_B T}\right)} \\
 &= \frac{1}{2 \sinh\left(\frac{\beta\hbar\omega}{2}\right)}
 \end{aligned}$$

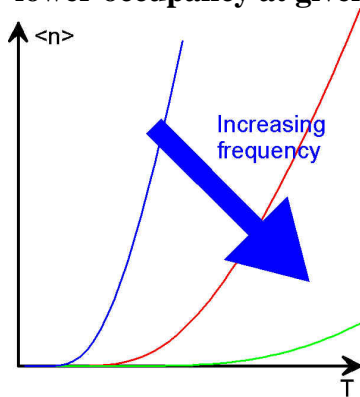
$$\begin{aligned}\langle E \rangle &= -\frac{\partial \ln Z}{\partial \beta} \\ &= (\langle n \rangle + \frac{1}{2})\hbar\omega,\end{aligned}$$

The crucial result is the mean occupation number of the n th level:

$$\langle n \rangle = \frac{1}{\exp(\hbar\omega/k_B T) - 1},$$

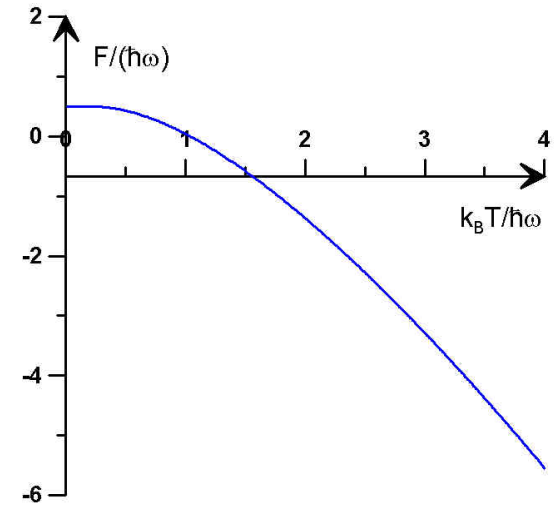
for Bose-Einstein statistics.

Higher frequency \rightarrow lower occupancy at given temperature.



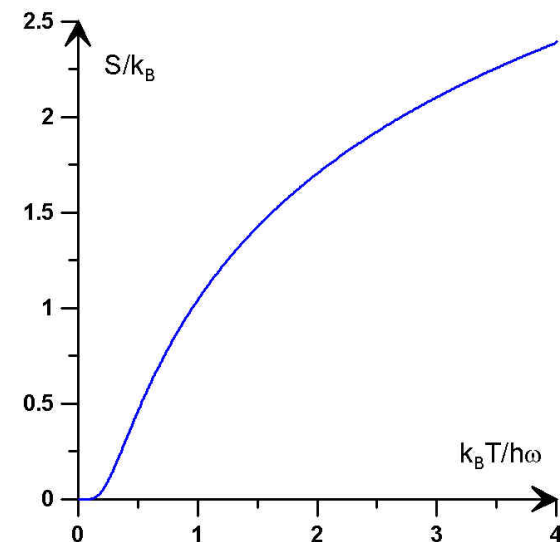
Free energy

$$\begin{aligned}F &= -k_B \ln(Z) \\ &= k_B T \ln \left(\sinh \left(\frac{\hbar\omega}{2k_B T} \right) \right)\end{aligned}$$



Entropy The decrease in free energy with T is due to an increase in entropy. at $p = 0$

$$S = \frac{E - F}{T}.$$



Increase T , increase S : more displacement from equilibrium position

means more *disorder*.

- low T : exponential dependence $C \propto T^{-2} \exp(-\hbar\omega/k_B T)$
- intermediate $T \approx \hbar\omega/3k_B$: steep rise in C
- high $T > \hbar\omega/k_B$: C saturates to classical result, $C = k_B$ per oscillator.
- C universal function of T/Θ , where $\Theta = \hbar\omega/k_B$

Specific heat:

