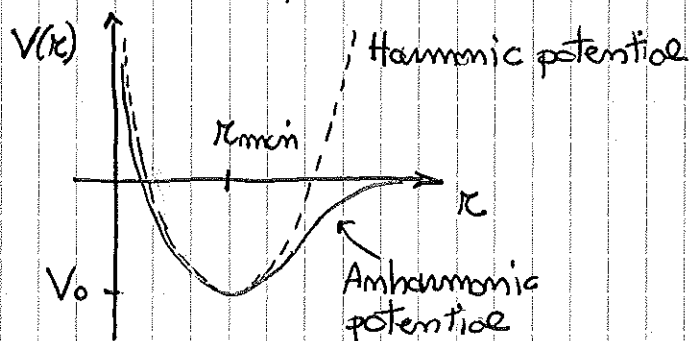


PHONONS IN A CRYSTAL

Let us consider the energy stored in vibrational waves inside a solid at temperature T . This problem has many similarities with the black body distribution for photons in a box.

In our model, atoms are at equilibrium at distance x_{min} from their neighbours and, for small distances, they make small oscillations, under a force with an harmonic potential:



$$V(x) \approx \frac{1}{2} K (x - x_{min})^2 + V_0$$

when $x \sim x_{min}$

Let us now take a cube of N atoms, vibrating around their equilibrium positions. Let us take the cube to have sides L , and the distance x_{min} between atoms to be equal to d . The solid is in equilibrium with a reservoir at temperature T .

The wave equation is familiar:

$$\nabla^2 \vec{u} = \frac{1}{v^2} \frac{\partial^2 \vec{u}}{\partial t^2}$$

where v is the speed of sound propagation, and $\vec{u}(x, y, z, t)$ is the displacement of the atom in (x, y, z) from its equilibrium position, at time t .

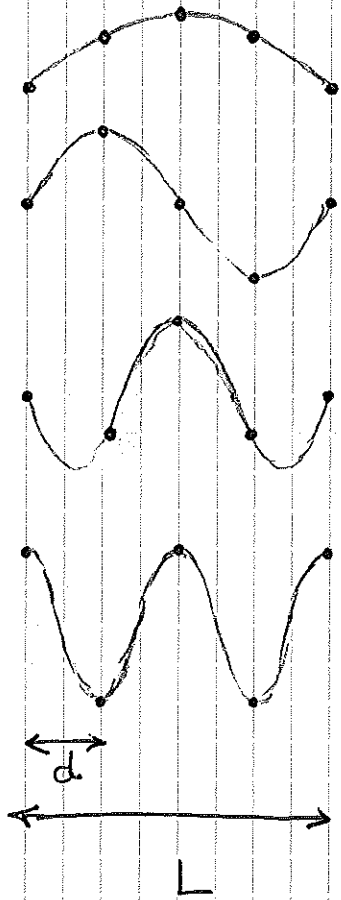
The solution is very similar to the photon-in-a-box case, with the replacement of c with v . The mode frequencies ω_m become:

$$\omega_m = \frac{m \pi v}{L}, \quad m = \sqrt{m_x^2 + m_y^2 + m_z^2}$$

$$\omega_m = v \cdot k_m$$

We do have two important differences between photons and phonons:

- 1) phonons have 3 possible polarization states, two transverse and one longitudinal, while photons have only 2 (no longitudinal polarization)
- 2) the number of modes is finite: in the photon-in-a-box case, I can have photons with as large ω_m as I want (large $\omega_m \rightarrow$ large $m \rightarrow$ large $k_m \rightarrow$ short wavelength $\lambda_m = 2\pi/k_m$), but my vibrating atoms cannot support waves with wavelength shorter than $2d$. Easy to see in 1-D case:



$$m=1 \quad \lambda = 2L$$

$$m=2 \quad \lambda = L$$

$$m=3 \quad \lambda = \frac{2L}{3}$$

$$m=4 \quad \lambda = \frac{L}{2} = 2 \cdot d$$

note: I have $N+1$ atoms in a line, and $L = N \cdot d \Rightarrow N=4$ in this example

How many modes do we have? $3N$: N is the number of unit cells in the crystal (easy to see that, in 1-D, N corresponds to the number of normal modes; let us ^{use} N also in the 3-D case), 3 comes from the three polarizations (in other words: oscillations can go in the \hat{x} , \hat{y} , or \hat{z} direction).

Similarly to the photon case, however, we have the following features:

- 1) the wavenumber of a phonon is $k_m = 2\pi/\lambda_m = \pi m/L$, where $m = \sqrt{m_x^2 + m_y^2 + m_z^2}$, and $m_x, m_y, m_z = 1, 2, 3, \dots$

2) the dispersion relation is the same:

$$\omega = v K \quad \text{phonons} \quad \longleftrightarrow \quad \omega = c K \quad \text{photons}$$

\swarrow speed of sound
 \swarrow speed of light

3) momentum and energy are the same:

$$\vec{p} = \hbar \vec{k}$$

$$E = \hbar \omega$$

4) the number of phonons is not fixed $\implies \mu = 0$

5) the density of states $g(\omega)$ is proportional to ω^2

Let us calculate some properties of a system of phonons in a solid at temperature T .

The total energy of phonons in a solid at temperature T is:

$$U = \frac{gN}{\omega_{\max}^3} \int_0^{\omega_{\max}} \frac{\hbar \omega}{e^{\hbar \omega / k_B T} - 1} \omega^2 d\omega$$

where:

$\frac{1}{e^{\hbar \omega / k_B T} - 1}$: Bose-Einstein distribution for system of phonons at thermal equilibrium

$\hbar \omega$: energy of phonon at frequency ω

$\frac{gN \omega^2}{\omega_{\max}^3}$: density of states (as anticipated, proportional to ω^2)

Let us take a step back, and see if we can derive the density of states. We use the usual trick: we move to k -space, and count the states in a shell of

thickness dk :

$$g(k) dk = \frac{\text{volume of shell, one octant}}{\text{volume occupied by one state}} \cdot \text{number of polarizations}$$

We obtain:

$$g(k) dk = \overset{\text{polarisations}}{\downarrow} \frac{1}{3} \cdot \frac{1}{8} 4\pi k^2 dk / \frac{\pi^3}{V} = \frac{3}{2} \frac{V k^2 dk}{\pi^2}$$

The dispersion relation is $\omega = v k$, hence $d\omega/dk = v$:

$$g(\omega) = \frac{3}{2} \frac{V \omega^2}{\pi^2 v^3} \quad (\text{we ask } g(\omega) d\omega = g(k) dk)$$

How can I get rid of v ? Let us use the constraint that ω is limited, and that the total number of states is $3N$. Hence:

$$3N = \int_0^{\omega_{\max}} g(\omega) d\omega = \int_0^{\omega_{\max}} \frac{3}{2} \frac{V \omega^2}{\pi^2 v^3} d\omega = \frac{V \omega_{\max}^3}{2\pi^2 v^3} \Rightarrow \frac{V}{2\pi^2 v^3} = \frac{3N}{\omega_{\max}^3}$$

Finally:

$$g(\omega) = \frac{9N}{\omega_{\max}^3} \cdot \omega^2$$

ω_{\max} is called $\omega_D = \text{DEBYE FREQUENCY}$.

Let us rewrite the energy of all our phonons:

$$U = \frac{9N}{\omega_{\max}^3} \int_0^{\omega_{\max}} \frac{\hbar \omega^3}{e^{\hbar\omega/k_B T} - 1} d\omega = \frac{9N\hbar}{\omega_{\max}^3} \left(\frac{k_B T}{\hbar} \right)^4 \underbrace{\int_0^{x_{\max}} \frac{x^3}{e^x - 1} dx}_{\text{some number}}$$

where $x_{\max} = \frac{T_{\max}}{T}$ and $T_{\max} = \frac{\hbar \omega_{\max}}{k_B} = \text{DEBYE TEMPERATURE}$

Another way of writing energy:

$$U = 9N k_B T \left(\frac{T}{T_{\max}} \right)^3 \int_0^{T_{\max}/T} \frac{x^3}{e^x - 1} dx \quad (\text{let me now finally use } T_D \text{ and } \omega_D \text{ for Debye temperature and frequency})$$

Let us look at two extreme cases: $T \ll T_D$ and $T \gg T_D$. In the low temperature limit, we can extend the integral to ∞ without making a big change. We get:

$$U = 9N k_B T \left(\frac{T}{T_{\max}} \right)^3 \frac{\pi^4}{15} = \text{constant} \cdot T^4$$

This is very similar to Stefan-Boltzmann law for photons in a box.

For phonons, we get:

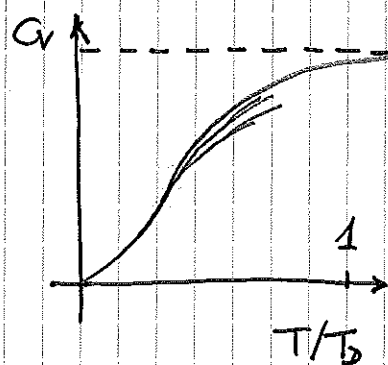
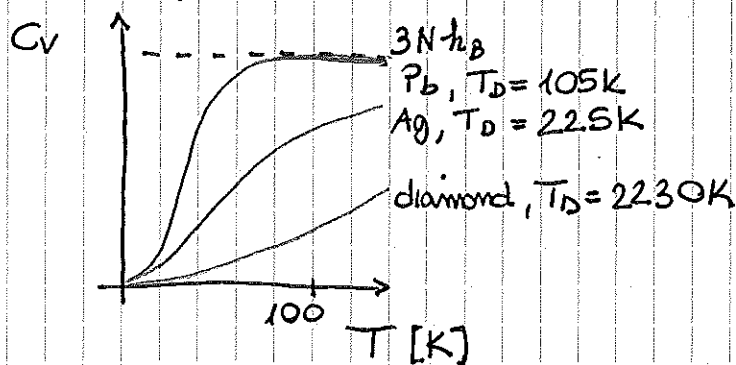
$$U = \frac{3}{5} \frac{N h_B \pi^4}{T_D^3} T^4 \quad (T \ll T_D)$$

The heat capacity results proportional to T^3 :

$$C_v = \left. \frac{dU}{dT} \right|_V = \frac{12 N h_B \pi^4}{5} \left(\frac{T}{T_D} \right)^3 \quad (T \ll T_D)$$

constant volume

Note that C_v depends on T/T_D : this is an example of a scaling law: if I plot C_v vs. T/T_D , instead of T , the curves corresponding to materials with different T_D will overlap (in the limit $T \ll T_D$, of course).



the three curves overlap when $T \ll T_D$, and plotted vs. T/T_D

What about the limit $T \gg T_D$? Then, the heat capacity tends to a constant: $3N h_B$.

$$U = 9N h_B T \left(\frac{T}{T_{max}} \right)^3 \int_0^{T_{max}/T} x^3 \cdot \frac{1}{e^x - 1} dx \approx 9N h_B T \left(\frac{T}{T_{max}} \right)^3 \int_0^{T_{max}/T} \frac{x^3}{1+x-1} dx =$$

$$= 9N h_B T \left(\frac{T}{T_{max}} \right)^3 \int_0^{T_{max}/T} x^3 dx = 9N h_B T \left(\frac{T}{T_{max}} \right)^3 \cdot \frac{x^3}{3} \Big|_0^{T_{max}/T} = \underline{3N h_B T}$$

$$C_v = \left. \frac{dU}{dT} \right|_V = 3N h_B \quad (T \gg T_D)$$

The heat capacity is constant for high temperatures: Dulong-Petit Law