

3.3 Quantization of crystal normal modes

The deformation of the atom in eq. position $\vec{R}_\alpha + \vec{\tau}$ associated to the normal mode \vec{q}, j reads:

$$\vec{u}_{\alpha\tau}(t; \vec{q}, j) = \frac{1}{\sqrt{M_\tau N_{\text{cell}}}} \vec{e}_\tau(\vec{q}, j) e^{i(\vec{q} \cdot \vec{R}_\alpha - \omega_j |\vec{q}| t)} \quad (3.27)$$

The motion of the atom α, τ is a linear combination of the normal modes, whose coefficients are given by the initial conditions. Generally we can thus write:

$$\vec{u}_{\alpha\tau} = \frac{1}{\sqrt{N_{\text{cell}} M_\tau}} \sum_{\vec{q}, j} u_{\vec{q}, j} \vec{e}_\tau(\vec{q}, j) e^{i\vec{q} \cdot \vec{R}_\alpha} \quad (3.31)$$

where $u_{\vec{q}, j} = a_{\vec{q}, j}^0 e^{-i\omega_j |\vec{q}| t}$ and $a_{\vec{q}, j}^0$ are the coefficients mentioned above. Eq. (3.31) can be complemented by the corresponding equation for the momenta which reads:

$$\vec{p}_{\alpha\tau} = \sqrt{\frac{M_\tau}{N_{\text{cell}}}} \sum_{\vec{q}, j} p_{\vec{q}, j} \vec{e}_\tau^*(\vec{q}, j) e^{-i\vec{q} \cdot \vec{R}_\alpha} \quad (3.32)$$

where $p_{\vec{q}, j} = b_{\vec{q}, j}^0 e^{-i\omega_j |\vec{q}| t}$ depends from the initial condition for the momenta, $b_{\vec{q}, j}^0$. Eq. (3.31) and (3.32) can be inverted to give:

$$\begin{cases} u_{\vec{q}, j} = \sum_{\alpha\tau} \sqrt{M_\tau} \vec{u}_{\alpha\tau} \cdot \vec{e}_\tau^*(\vec{q}, j) e^{-i\vec{q} \cdot \vec{R}_\alpha} \\ p_{\vec{q}, j} = \sum_{\alpha\tau} \frac{1}{\sqrt{M_\tau}} \vec{p}_{\alpha\tau} \cdot \vec{e}_\tau(\vec{q}, j) e^{+i\vec{q} \cdot \vec{R}_\alpha} \end{cases} \quad (3.33)$$

where we have used the property that $\sum_{\tau} |\vec{e}_\tau|^2 = 1$ and $\sum_{\alpha} \frac{1}{N_{\text{cell}}} e^{i\vec{q} \cdot \vec{R}_\alpha} = \delta_{\vec{q}, 0}$. The quantization of $u_{\alpha\tau}$ and $p_{\alpha\tau}$ reads

$$[\hat{u}_{\alpha\tau}, \hat{p}_{\alpha'\tau'}] = i\hbar \delta_{\alpha\alpha'} \delta_{\tau\tau'} \delta_{\tau\tau'}$$

now implies immediately

$$[\hat{u}_{\vec{q},j}, \hat{p}_{\vec{q}',j'}] = i\hbar \delta_{\vec{q},\vec{q}'} \delta_{jj'} \quad (3.34)$$

where we have used the relation $\sum_{\vec{r}} \vec{e}(\vec{q},j) \cdot \vec{e}^*(\vec{q}',j') = \delta_{\vec{q},\vec{q}'} \delta_{jj'}$ which follows from:

$$\begin{aligned} [\tilde{D}_{n\vec{r},n'\vec{r}'}(\vec{q})]^* &= \frac{1}{\sqrt{N_{\text{cell}}}} \sum_{\vec{R}} D_{n\vec{r},n'\vec{r}'}(\vec{R}) e^{+i\vec{q}\cdot\vec{R}} = \frac{1}{\sqrt{N_{\text{cell}}}} \sum_{\vec{R}} D_{n\vec{r},n'\vec{r}'}(-\vec{R}) e^{-i\vec{q}\cdot\vec{R}} \\ &= \frac{1}{\sqrt{N_{\text{cell}}}} \sum_{\vec{R}} D_{n'\vec{r}',n\vec{r}}(\vec{R}) e^{-i\vec{q}\cdot\vec{R}} = \tilde{D}_{n'\vec{r}',n\vec{r}}(\vec{q}) \end{aligned}$$

$\Rightarrow \forall \vec{q} \underline{D}$ is hermitian \Rightarrow admits a set of orthonormal eigenstates.

Other properties of the dynamical matrix are:

$$[\tilde{D}_{n\vec{r},n'\vec{r}'}(\vec{q})]^* = \tilde{D}_{n'\vec{r}',n\vec{r}}(-\vec{q}) \Rightarrow \underline{D}(\vec{q})^* = \underline{D}(-\vec{q}) = [\underline{D}^T(-\vec{q})]^*$$

from which we obtain that $\omega_j(\vec{q}) = \omega_j(-\vec{q})$ and $e^*(\vec{q},j) = e(-\vec{q},j)$

We can assume $\hat{u}_{\alpha\tau}$ and $\hat{p}_{\alpha\tau}$ to be hermitian. From (3.33) it follows that

$$\hat{u}_{\vec{q},j}^+ = \hat{u}_{-\vec{q},j} \quad \hat{p}_{\vec{q},j}^+ = \hat{p}_{-\vec{q},j} \quad (3.35)$$

It is convenient now to introduce the operators:

$$\begin{cases} \hat{b}_{\vec{q},j} = \sqrt{\frac{\omega_j(\vec{q})}{2\hbar}} \hat{u}_{\vec{q},j} + i \sqrt{\frac{1}{2\hbar\omega_j(\vec{q})}} \hat{p}_{-\vec{q},j} \\ \hat{b}_{\vec{q},j}^+ = \sqrt{\frac{\omega_j(\vec{q})}{2\hbar}} \hat{u}_{-\vec{q},j} - i \sqrt{\frac{1}{2\hbar\omega_j(\vec{q})}} \hat{p}_{+\vec{q},j} \end{cases} \quad (3.36)$$

which fulfill bosonic commutator relations

$$[\hat{b}_{\vec{q},j}, \hat{b}_{\vec{q}',j'}^+] = \delta_{\vec{q},\vec{q}'} \delta_{jj'} \quad [\hat{b}_{\vec{q},j}, \hat{b}_{\vec{q}',j'}] = 0 \quad (3.37)$$

From (3.35) one obtains the position and momentum operators in terms of the (ladder) operators:

$$\left\{ \begin{aligned} \hat{u}_{\vec{q},j} &= \sqrt{\frac{\hbar}{2\omega_j(\vec{q})}} \left(\hat{b}_{\vec{q},j} + \hat{b}_{-\vec{q},j}^+ \right) \\ \hat{p}_{\vec{q},j} &= i \sqrt{\frac{\hbar\omega_j(\vec{q})}{2}} \left(\hat{b}_{\vec{q},j}^+ - \hat{b}_{-\vec{q},j} \right) \end{aligned} \right. \quad (3.38)$$

Finally, the Hamiltonian for the crystal in the harmonic approx. reads:

$$\begin{aligned} \hat{H}_{\text{harm.}} &= \sum_{\alpha T n} \frac{\hat{p}_{\alpha T n}^2}{2M\tau} + \frac{1}{2} \sum_{\alpha T n} \sum_{\alpha' T' n'} \hat{u}_{\alpha T n} \Phi_{T n T' n'}(\vec{R}_\alpha - \vec{R}_{\alpha'}) \hat{u}_{\alpha' T' n'} \\ &= \frac{1}{2} \sum_{\substack{\vec{q},j \\ \vec{q}',j'}} \sum_{\alpha T n} \frac{1}{N_{\text{cell}}} \hat{p}_{\vec{q},j} e_{T n}^*(\vec{q},j) e_{T' n'}^*(\vec{q}',j') e^{-i(\vec{q} + \vec{q}') \cdot \vec{R}_\alpha} \hat{p}_{\vec{q}',j'} \\ &\quad + \frac{1}{2} \sum_{\substack{\vec{q},j \\ \vec{q}',j'}} \sum_{\alpha T n} \sum_{\alpha' T' n'} \frac{1}{N_{\text{cell}}} \hat{u}_{\vec{q},j} e_{T n}(\vec{q},j) \Delta_{T n T' n'}(\vec{R}_\alpha - \vec{R}_{\alpha'}) e^{i(\vec{q} \cdot \vec{R}_\alpha + \vec{q}' \cdot \vec{R}_{\alpha'})} \\ &\quad \hat{u}_{\vec{q}',j'} e_{T' n'}(\vec{q}',j') = e^{i\vec{q}' \cdot (\vec{R}_\alpha - \vec{R}_{\alpha'})} \quad \uparrow \text{insert} \\ &= \frac{1}{2} \sum_{T n \vec{q},j} e_{T n}^*(\vec{q},j) e_{T n}(\vec{q},j) \hat{p}_{\vec{q},j} \hat{p}_{-\vec{q},j} + \frac{1}{2} \sum_{\substack{T n \\ \vec{q},j}} \hat{u}_{\vec{q},j} e_{T n}(\vec{q},j) \Delta_{T n T, (-\vec{q})} \\ &\quad \hat{u}_{-\vec{q},j} e_{T n}(-\vec{q},j) \\ &= \frac{1}{2} \sum_{\vec{q},j} \left[\hat{p}_{\vec{q},j} \hat{p}_{-\vec{q},j} + \omega_j(\vec{q})^2 \hat{u}_{\vec{q},j} \hat{u}_{-\vec{q},j} \right] = \\ &= \frac{1}{2} \sum_{\vec{q},j} \left[-\frac{\hbar\omega_j(\vec{q})}{2} (\hat{b}_{\vec{q},j}^+ - \hat{b}_{-\vec{q},j}) (\hat{b}_{-\vec{q},j}^+ - \hat{b}_{\vec{q},j}) + \frac{\hbar\omega_j(\vec{q})}{2} (\hat{b}_{\vec{q},j} + \hat{b}_{-\vec{q},j}^+) (\hat{b}_{-\vec{q},j} + \hat{b}_{\vec{q},j}^+) \right] \end{aligned}$$

$$\begin{aligned}
&= \frac{1}{2} \sum_{\vec{q}_j} \frac{\hbar \omega_j(\vec{q}_j)}{2} \left(\cancel{-b_{\vec{q}_j}^+ b_{-\vec{q}_j}^+} + b_{\vec{q}_j}^+ b_{\vec{q}_j} + b_{-\vec{q}_j} b_{-\vec{q}_j}^+ - \cancel{b_{-\vec{q}_j} b_{\vec{q}_j}^+}} \right. \\
&\quad \left. + \cancel{b_{\vec{q}_j} b_{\vec{q}_j}^+} + b_{\vec{q}_j} b_{\vec{q}_j}^+ + b_{-\vec{q}_j} b_{-\vec{q}_j}^+ + \cancel{b_{-\vec{q}_j} b_{\vec{q}_j}^+} \right) \\
&= \sum_{\vec{q}_j} \frac{\hbar \omega_j(\vec{q}_j)}{2} \left(b_{\vec{q}_j}^+ b_{\vec{q}_j} + b_{\vec{q}_j} b_{\vec{q}_j}^+ \right) = \sum_{\vec{q}_j} \hbar \omega_j(\vec{q}_j) \left(b_{\vec{q}_j}^+ b_{\vec{q}_j} + \frac{1}{2} \right)
\end{aligned}$$

The eigenvalue and eigenstates of the H_{phon} read:

$$\begin{cases} E_{\{n_{\vec{q}_j}\}} = \sum_{\vec{q} \in 1st} \sum_{j=1}^{rd} \hbar \omega_j(\vec{q}_j) \left(n_{\vec{q}_j} + \frac{1}{2} \right) \\ |\{n_{\vec{q}_j}\}\rangle = \prod_{\vec{q}_j} \frac{(\hat{b}_{\vec{q}_j}^+)^{n_j}}{\sqrt{n_{\vec{q}_j}!}} |0\rangle \end{cases} \quad (3.39)$$

where $|0\rangle$ is defined by $b_{\vec{q}_j}|0\rangle = 0$ and the normalization $\langle 0|0\rangle = 1$.

3.4 Specific heat of solids

One interesting question that can be answered with the knowledge acquired in the previous sections is the one on the specific heat of a solid. The first step is the evaluation of the internal energy of the phonon.

$$E = \langle H_{\text{phon}} \rangle = \sum_{\vec{q}_j} \hbar \omega_j(\vec{q}_j) \left(\langle b_{\vec{q}_j}^+ b_{\vec{q}_j} \rangle + \frac{1}{2} \right) \quad (3.40)$$

where $\langle \cdot \rangle$ is the thermal average i.e

$$\langle \hat{O} \rangle = \frac{1}{Z} \text{Tr} \left\{ \hat{O} e^{-\beta \hat{H}_{\text{phon}}} \right\} \quad \beta = k_B T \quad (3.41)$$

where $Z = \text{Tr} \left\{ e^{-\beta \hat{H}_{\text{phon}}} \right\}$. Given (3.39) and that $n_{\vec{q}_j} = 0, 1, 2, \dots$, after some algebra one obtains for $\langle b_{\vec{q}_j}^+ b_{\vec{q}_j} \rangle$ the

Bose-Einstein distribution:

$$\langle \hat{n}_{\vec{q},j} \rangle = \langle b_{\vec{q},j}^\dagger b_{\vec{q},j} \rangle = \frac{1}{e^{\frac{\hbar \omega_j(\vec{q})}{k_B T}} - 1} \quad (3.42)$$

The explicit form of the internal energy reads thus:

$$E = E_0 + \sum_{\vec{q},j} \frac{\hbar \omega_j(\vec{q})}{e^{\frac{\hbar \omega_j(\vec{q})}{k_B T}} - 1} \quad (3.43)$$

where $E_0 = \sum_{\vec{q},j} \frac{1}{2} \hbar \omega_j(\vec{q})$ is the zero point energy of the crystal.

The sum in (3.43) can be calculated analytically in 2 limits:

• High temperature limit

$$k_B T \gg \hbar \omega_j(\vec{q}) \quad \forall \vec{q}, j \quad (3.44)$$

Expanding the exponential function in (3.43) one obtains:

$$E = \sum_{\vec{q},j} \hbar \omega_j(\vec{q}) \left(\frac{1}{1 + \frac{\hbar \omega_j(\vec{q})}{k_B T} + o\left(\frac{\hbar \omega}{k_B T}\right)} + \frac{1}{2} \right) = \sum_{\vec{q},j} k_B T \left(1 + \frac{1}{2} \frac{\hbar \omega_j(\vec{q})}{k_B T} + o\left(\frac{\hbar \omega}{k_B T}\right) \right)$$

To leading order we can simply write

$$E(T) = d N r k_B T \quad (3.45)$$

which goes under the name of law of Dulong-Petit. This is actually a classical result of equipartition of thermal energy $k_B T/2$ for every kinetic and potential degree of freedom.

• Low temperature limit For every temperature T there are oscillating eigenfrequencies such that $\hbar \omega_j(\vec{q}) < k_B T$. One can

assume, though that the temperature is so low that only acoustic modes are thermally excited. The internal energy reads, in this limit:

$$E - E_0 = \sum_{\vec{q}, s} \frac{\hbar c_s q}{e^{\hbar c_s q / k_B T} - 1} \quad (3.46)$$

where s labels the acoustic mode of sound velocity c_s . If we replace the \vec{q} sum with the integral:

$$E - E_0 = \frac{V}{(2\pi)^d} \sum_s \int d^d q \frac{\hbar c_s q}{e^{\hbar c_s q / k_B T} - 1} = \frac{V}{(2\pi)^d} \sum_s \left(\frac{k_B T}{\hbar c_s} \right)^d k_B T \int d^d x \frac{x}{e^x - 1} \quad (3.47)$$

where we have introduced the substitution $x = \frac{\hbar c_s q}{k_B T}$. The integration limits do not represent a real problem. The dispersion relation of the acoustic phonons is not any more linear at the $\mathbb{B}\mathbb{Z}$ boundaries, but the exponential in (3.46) makes these contributions anyway irrelevant at low enough temperatures

$$k_B T \ll \frac{\hbar c_s \pi}{a} \quad (3.48)$$

The integration limits in (3.47) can thus be safely extended to ∞ and obtain for $d=3$

$$E - E_0 = \frac{V}{(2\pi)^3} \frac{(k_B T)^4}{(\hbar \bar{c}_s)^3} 4\pi \int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{\pi^2}{10} \frac{V}{(\hbar \bar{c}_s)^3} (k_B T)^4 \quad (3.49)$$

where we have introduced an average sound velocity \bar{c}_s and used the exact relation $\int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{\pi^4}{15}$.

For what concern the specific heat one obtains thus, in 3D:

$$\left\{ \begin{array}{l} C_V = \frac{1}{V} \frac{\partial E}{\partial T} \approx \frac{2}{5} \pi^2 k_B \left(\frac{k_B T}{\hbar c_s} \right)^3 \quad k_B T \ll \frac{\pi \hbar c_s}{a} \\ C_V = 3 \frac{N}{V} r k_B \quad k_B T \gg \omega_j(\vec{q}) \quad \forall j, \vec{q} \end{array} \right. \quad (3.50)$$

A simplified model that can interpolate the two limits is the Debye model. It consists of the following assumptions:

1. Linear dispersion relation in $\omega(\vec{q}) = c_s q$ in the relevant \vec{q} range
2. The 1BZ is replaced by a sphere of radius q_D
 q_D is calculated in such a way to ensure that all states are inside the Debye sphere

$$\sum_{\vec{q}, |\vec{q}| < q_D} 1 = N = \frac{V}{(2\pi)^3} \int_{|\vec{q}| < q_D} d^3 q = \frac{V}{2\pi^2} \frac{q_D^3}{3}$$

$$q_D = \sqrt[3]{6\pi^2 \frac{N}{V}} = \sqrt[3]{6\pi^2 \frac{rd}{V_{cell}}} \quad (3.51)$$

The internal energy in the Debye model thus reads

$$E - E_0 = 3 \frac{V}{(2\pi)^3} \int_{|\vec{q}| < q_D} d^3 q \frac{\hbar c_s q}{e^{\hbar c_s q / k_B T} - 1} = \frac{3V}{2\pi^2} \left(\frac{k_B T}{\hbar c_s} \right)^3 k_B T \int_0^{x_D} dx \frac{x^3}{e^x - 1} \quad (3.52)$$

where $x = \frac{\hbar c_s q}{k_B T}$ and $x_D = \frac{\hbar c_s q_D}{k_B T}$. If one introduces now the Debye temperature and frequency via the relations

$$k_B \Theta_D = \hbar c_s q_D = \hbar \omega_D \quad (3.53)$$

and remembers from (3.51) that $V = \frac{6\pi^2 N}{q_D^3}$.

$$E - E_0 = 9N \left(\frac{T}{\Theta_D} \right)^3 k_B T \int_0^{\Theta_D/T} dx \frac{x^3}{e^x - 1}$$

For the specific heat

$$C_V = \frac{1}{V} \frac{\partial}{\partial T} (E - E_0) = \frac{3}{2\pi^2} \int_0^{q_D} dq \hbar c_s q^3 \frac{\partial}{\partial T} \frac{1}{e^{\hbar c_s q / k_B T} - 1}$$

$$= \frac{3}{2\pi^2} \int_0^{q_D} dq \hbar c_s q^3 \frac{\hbar c_s q}{k_B T^2} \frac{e^{\hbar c_s q / k_B T}}{(e^{\hbar c_s q / k_B T} - 1)^2} =$$

$$= \frac{3}{2\pi^2} \left(\frac{k_B T}{\hbar c_s} \right)^3 k_B \int_0^{\Theta_D/T} dx \frac{x^4 e^x}{(e^x - 1)^2} = 9 \frac{N}{V} \left(\frac{T}{\Theta_D} \right)^3 k_B \int_0^{\Theta_D/T} dx \frac{x^4 e^x}{(e^x - 1)^2}$$

(3.54)

In the high and low temperature limits one recovers the known results

$$\left. \begin{aligned} C_V &= \frac{12}{5} \pi^4 \cdot \frac{N}{V} \left(\frac{T}{\Theta_D} \right)^3 k_B \\ C_V &= 3 \frac{N}{V} k_B \end{aligned} \right\}$$

In general one defines $f_D(x) = \int_0^x dy \frac{y^3}{e^y - 1}$.

$$E(T) = 9N k_B T \left(\frac{T}{\Theta_D} \right)^3 f_D \left(\frac{\Theta_D}{T} \right)$$

The Debye temperature Θ_D represents the scaling factor for a universal specific heat curve. The Debye temperature for different materials:

$\Theta_D = 394 \text{ K}$	Al	Aluminum
1860 K	C (diamond)	
100 K	K	Potassium

These numbers agree with the estimate $c_s \sim 40^2 - 10^3 \frac{\text{m}}{\text{s}}$ $q_D \sim \frac{\pi}{a} \sim 10^{10} \text{ m}^{-1}$.