3. Harmonic lattice vibrations : phonons

The effective ion Hamiltonian derived in the adiabatic approximation

$$H_{\text{eff}} = \sum_n \frac{1}{2}\frac{m}{M_n}\left(-\vec{\nabla}_n^2\right) + \sum_{n,m}\frac{1}{2}\,\delta\vec{R}_n^{\,i}\;D_{nm}^{ij}\;\delta\vec{R}_m^{\,j}$$

(i, j: vector component; n, m: label of ion)

where $\delta\vec{R}_n = \vec{R}_n - \vec{R}_n^{(0)}$ is the displacement of the n-th ion from the equilibrium configuration, and

$$D_{nm}^{ij} = \frac{\partial}{\partial \vec{R}_n^{\,i}}\frac{\partial}{\partial \vec{R}_m^{\,j}}\,\mathcal{E}_0(\{\vec{R}\})\Big|_{\{\vec{R}^{(0)}\}}$$

derives from the potential in the harmonic approximation and is called the <u>dynamical matrix</u>.

The Hamiltonian H_{eff} describes a system of coupled harmonic oscillators and can, in principle, be diagonalized by standard (numerical) means. Doing so identifies the <u>normal modes</u> of lattice vibrations, similar as in molecules.
For the characterization of the normal modes in a crystal, however, one exploits the <u>translation symmetry</u> of the crystal.
We can label the ions with the help of a Bravais lattice vector $\vec{\ell}$ that identifies a specific primitive unit cell of the crystal and an index λ that counts the ions within the unit cell ($\lambda = 1, 2, \ldots, r$ for r ions in the unit cell).

$$D_{nm}^{ij} \longrightarrow D^{ij}(\underbrace{\vec{\ell}, \lambda}_{n\text{-th ion}}\,;\,\underbrace{\vec{m}, \mu}_{m\text{-th ion}})$$

where $\vec{\ell}$ and $\vec{m}$ are Bravais lattice vectors, and $\lambda, \mu = 1, 2, \ldots, r$

Due to the translational symmetry of the Bravais lattice we have

$$\begin{aligned} \mathcal{D}^{ij}(\vec{e},\lambda\,;\,\vec{m},\mu) &= \mathcal{D}^{ij}(\vec{e}-\vec{n},\lambda\,;\,\vec{m}-\vec{n},\mu) \\ &= \mathcal{D}^{ij}(\vec{e}-\vec{m},\lambda\,;\,\vec{0},\mu) \end{aligned}$$

for any Bravais lattice vector $\vec{n}$. Choosing $\vec{n}=\vec{m}$ one immediately finds that $\mathcal{D}$ only depends on the difference $\vec{e}-\vec{m}$.

In ordes to proceed furthes, we will make use of Bloch's theorem.

3.1 Bloch's theorem

Cousides a trauslatiou opeator $T_{\vec{R}}$ defined for a Bravais lattice vector $\vec{R}$ that acts ou a wavefuuctiou as

$$T_{\vec{R}}\,\psi(\vec{r}) = \psi(\vec{r}+\vec{R})$$

Trauslatiou opeators commute $[T_{\vec{R}}, T_{\vec{R}'}] = 0$

Siuce we have

$$T_{\vec{R}}\,T_{\vec{R}'}\,\psi(\vec{r}) = \psi(\vec{r}+\vec{R}+\vec{R}') = T_{\vec{R}'}\,T_{\vec{R}}\,\psi(\vec{r}) = T_{\vec{R}+\vec{R}'}\,\psi(\vec{r}) \qquad (*)$$

Furthermore, cousides au opeator $\mathcal{H}$ that commutes with the trauslatiou opeator, i.e. $[\mathcal{H}, T_{\vec{R}}] = 0$

for all $\vec{R}$ of the Bravais lattice.

We cau theu choose <u>simultaneous eigeustates</u> ψ_α of $\mathcal{H}$ and $T_{\vec{R}}$ for all $\vec{R}$:

$$\mathcal{H}\,\psi_\alpha = \mathcal{E}_\alpha\,\psi_\alpha$$

$$T_{\vec{R}}\,\psi_\alpha = c_\alpha(\vec{R})\,\psi_\alpha$$

For the coefficients / eigenvalues $C_\alpha(\vec{R})$ it follows from (*)

$$C_\alpha(\vec{R})\, C_\alpha(\vec{R}') = C_\alpha(\vec{R}+\vec{R}') \quad \text{and} \quad C_\alpha(\vec{R})\, C_\alpha(-\vec{R}) = 1$$

Moreover, from the normalization condition

$$1 = \int d^3\vec{r}\ |\psi_\alpha(\vec{r})|^2 = \int d^3\vec{r}\ |\psi_\alpha(\vec{r}+\vec{R})|^2 = \int d^3\vec{r}\ |C_\alpha(\vec{R})|^2 |\psi_\alpha(\vec{r})|^2$$
$$= |C_\alpha(\vec{R})|^2$$

In total, this implies that

$$C_\alpha(\vec{R}) = e^{i\vec{k}\vec{R}}$$

where the momentum $\vec{k}$ is specific for the ψ_α state.
The eigenvectors therefore obey

$$\boxed{\psi_\alpha(\vec{r}+\vec{R}) = e^{i\vec{k}\vec{R}}\, \psi_\alpha(\vec{r})}$$

Bloch's theorem

Since $e^{i\vec{G}\cdot\vec{R}} = 1$ for all $\vec{G}$ of the reciprocal lattice, the momentum $\vec{k}$ will be restricted to the 1. BZ.

Identifying α with a set of quantum numbers containing $\vec{k} \in$ 1. BZ we can write $\alpha = \{\vec{k}, n\}$ and use the alternative expressions $\psi_\alpha(\vec{r}) = \psi_{n\vec{k}}(\vec{r})$ such that

$$\boxed{\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{r}}\, u_{n\vec{k}}(\vec{r})}$$

where the <u>Bloch function</u> $u_{n\vec{k}}(\vec{r})$ obeys $u_{n\vec{k}}(\vec{r}+\vec{R}) = u_{n\vec{k}}(\vec{r})$ for all $\vec{R}$ of the Bravais lattice.

$$u_{n\vec{k}}(\vec{r}+\vec{R}) = e^{-i\vec{k}(\vec{r}+\vec{R})}\, \psi_{n\vec{k}}(\vec{r}+\vec{R}) = e^{-i\vec{k}\vec{r}}\, e^{-i\vec{k}\vec{R}}\, e^{i\vec{k}\vec{R}}\, \psi_{n\vec{k}}(\vec{r}) = u_{n\vec{k}}(\vec{r}).$$

Note: For systems that are invariant under arbitrary translation the momentum is conserved (Noether's theorem) and as such a good quantum number.
In contrast, for systems that are only invariant under discrete translations, only the quasimomentum $\vec{k}$ is conserved, i.e. the momentum modulo a reciprocal lattice vector, $\vec{k} \in 1.\,BZ$.

3.2 Diagonalization of the phonon Hamiltonian

We can now proceed and use Bloch's theorem to diagonalize the dynamical matrix, i.e. we want to consider the eigenvalue problem

$$\sum_{j,\mu,\vec{m}} \tilde{D}^{ij}(\vec{e},\lambda\,;\,\vec{m},\mu)\,\psi^{j}(\vec{m},\mu) = \omega\cdot\psi^{i}(\vec{e},\lambda)$$

where, for later convenience, we have introduced a rescaling of the form

$$\tilde{D}^{ij}(\vec{e},\lambda\,;\,\vec{m},\mu) = \frac{m}{\sqrt{M_\lambda M_\mu}}\cdot D^{ij}(\vec{e},\lambda\,;\,\vec{m},\mu)$$

Due to the translational symmetry of the Bravais lattice we have

$$T_{\vec{R}}\,\psi^{i}(\vec{m},\mu) = \psi^{i}(\vec{m}+\vec{R},\mu)$$

and $$T_{\vec{R}}\,\tilde{D}^{ij}(\vec{e},\lambda\,;\,\vec{m},\mu) = \tilde{D}^{ij}(\vec{e}+\vec{R},\lambda\,;\,\vec{m}+\vec{R},\mu)\,T_{\vec{R}}$$
$$= \tilde{D}^{ij}(\vec{e},\lambda\,;\,\vec{m},\mu)\,T_{\vec{R}}$$

that is the dynamical matrix $\tilde{D}$ commutes with $T_{\vec{R}}$ for a Bravais vector $\vec{R}$.

It thus follows from Bloch's theorem that the eigenstates take the form

$$\psi^{j}_{n\vec{k}}(\vec{m},\mu) = e^{i\vec{k}\vec{m}}\,u^{j}_{n\vec{k}}(\vec{m},\mu) = e^{i\vec{k}\vec{m}}\,\vec{e}^{\,j}_{n\vec{k}}(\mu)$$

where the polarization vector $\vec{e}_{n\vec{k}}$ with components

$$\vec{e}^{\,j}_{n\vec{k}}(\mu) = u^{j}_{n\vec{k}}(\vec{m},\mu) = u^{j}_{n\vec{k}}(\vec{0},\mu)$$

is the corresponding Bloch function and the set of quantum numbers $\{n,\vec{k}\}$ with $\vec{k}\in 1.BZ$

So we have $$\sum_{j,\mu,\vec{m}} \mathcal{D}^{ij}(\vec{e},\lambda;\vec{m},\mu)\,\psi^{j}_{n\vec{k}}(\vec{m},\mu) = d_{n\vec{k}}\,\psi^{i}_{n\vec{k}}(\vec{e},\lambda)$$

We can solve this eigenvalue problem via a Fourier transformation.
To this end, we need to cousides <u>periodic boundary conditions</u>, which in this context are also referred to as <u>Born-von Kármán boundary conditions</u>, for which we have

$$V_{PUC}\sum_{\vec{R}\in \text{Bravais lattice}} e^{-i\vec{k}\vec{R}} = V\cdot\delta(\vec{k}) \xrightarrow{V\to\infty} (2\pi)^3\,\delta(\vec{k})$$

(V: total volume; reminder: $\frac{(2\pi)^3}{V_{PUC}}$ is volume of 1. BZ)

$$\sum_{k\in 1.BZ} e^{i\vec{k}\vec{R}} = N\cdot\delta(\vec{R}) \quad \text{with } N = \#\text{ of lattice sites} = \frac{V}{V_{PUC}}$$

for $V\to\infty$ the points in the 1. BZ become dense so that

$$\int_{1.BZ}\frac{d\vec{k}}{(2\pi)^3}\,e^{i\vec{k}\vec{R}} = \frac{1}{V_{PUC}}\,\delta(\vec{R})$$

So, we can write the Fourier transformation as

$$\sum_{j,\mu,\vec{m}} V_{PUC}\underbrace{\sum_{\vec{e}} e^{-i\vec{k}\vec{e}}\,\mathcal{D}^{ij}(\vec{e},\lambda;\vec{m},\mu)\,e^{i\vec{k}\vec{m}}}_{=\tilde{\mathcal{D}}^{ij}_{\vec{k}}(\lambda,\mu)}\,\vec{e}^{\,j}_{n\vec{k}}(\mu) = d_{n\vec{k}}\underbrace{V_{PUC}\sum_{\vec{e}} e^{-i\vec{k}(\vec{e}-\vec{e})}}_{=V}\,\vec{e}^{\,i}_{n\vec{k}}(\lambda)$$

Since $\tilde{\mathcal{D}}^{ij}$ only depends on $\vec{e}-\vec{m}$

with $\sum_{\vec{e}} V_{PUC} = V$

$$\rightarrow \boxed{\sum_{j,\mu}\tilde{\mathcal{D}}^{ij}_{\vec{k}}(\lambda,\mu)\,\vec{e}^{\,j}_{n\vec{k}}(\mu) = d_{n\vec{k}}\,\vec{e}^{\,i}_{n\vec{k}}(\lambda)}$$

It is this eigenvalue problem that determines the polarization vectors $\vec{e}_{n\vec{k}}$.
→ corresponds to diagonalizing a $3r\times 3r$ matrix with $\lambda,\mu = 1,2,\dots,r$ where r is the numbes of atoms per unit cell; the eigenvectors are labeled by the quantum numbes $n = 1,2,\dots,3r$
This eigenvalue problem needs to be solved for each vector $\vec{k}$ of the 1. BZ.
→ evolution of eigenvalues $d_{n\vec{k}}$ as a function of $\vec{k}$.

Further properties:

- orthonormality $\sum_{\lambda,i} \vec{e}^{\,i*}_{n\vec{k}}(\lambda)\, \vec{e}^{\,i}_{m\vec{k}}(\lambda) = \delta_{n,m}$

- completeness $\sum_{n} \vec{e}^{\,i*}_{n\vec{k}}(\lambda)\, \vec{e}^{\,j}_{n\vec{k}}(\mu) = \delta_{ij}\,\delta_{\lambda\mu}$

- the dynamical matrix is real and symmetric, $\tilde{D}^{ij}_{nm} = \tilde{D}^{ji}_{mn}$
  → its Fourier transform is thus Hermitian $\tilde{D}^{ij}_{\vec{k}}(\lambda,\mu) = \tilde{D}^{ji}_{\vec{k}}(\mu,\lambda)^*$
  and the eigenvalues $d_{n\vec{k}}$ are real.

In addition, the stability of the crystal requires positive eigenvalues $d_{n\vec{k}} > 0$

Moreover, $\tilde{D}^{ij}_{\vec{k}}(\lambda,\mu)^* = \tilde{D}^{ij}_{-\vec{k}}(\lambda,\mu)$ which allows us to choose the quantum numbers n such that $d_{n\vec{k}} = d_{n-\vec{k}}$ and eigenvectors $\vec{e}^{\,*}_{n\vec{k}} = \vec{e}_{n-\vec{k}}$

Expansion in normal modes

We proceed by expanding position and momentum in normal coordinates $q_{n\vec{k}}$ and $p_{n\vec{k}}$ respectively

$$\delta\vec{R}^i(\vec{m},\mu) = \frac{1}{\sqrt{N}} \sum_{n,\vec{k}} \sqrt{\frac{m}{M_\mu}}\, e^{i\vec{k}\vec{m}}\, \vec{e}^{\,i}_{n\vec{k}}(\mu)\, q_{n\vec{k}}$$

$$\vec{P}^i(\vec{m},\mu) = \frac{1}{\sqrt{N}} \sum_{n,\vec{k}} \sqrt{\frac{M_\mu}{m}}\, e^{-i\vec{k}\vec{m}}\, \vec{e}^{\,i*}_{n\vec{k}}(\mu)\, p_{n\vec{k}} = -i\vec{\nabla}_{\{\vec{m},\mu\}}$$

↑ N = # of Bravais lattice sites

For the normal coordinates we have

$$[q_{n\vec{k}}, q_{n'\vec{k}'}] = [p_{n\vec{k}}, p_{n'\vec{k}'}] = 0 \quad \text{and} \quad [q_{n\vec{k}}, p_{n'\vec{k}'}] = i\,\delta_{nn'}\,\delta_{\vec{k}\vec{k}'}$$

This ensures in particular that the following commutator is obeyed

$$[\delta\vec{R}^i(\vec{m},\mu), \vec{P}^j(\vec{e},\lambda)] = \frac{1}{N} \sum_{\substack{n\vec{k}\\ n'\vec{k}'}} e^{i\vec{k}\vec{m} - i\vec{k}'\vec{e}}\, \vec{e}^{\,i}_{n\vec{k}}(\mu)\, \vec{e}^{\,j*}_{n'\vec{k}'}(\lambda)\, [q_{n\vec{k}}, p_{n'\vec{k}'}]$$

$$= i\,\underbrace{\frac{1}{N}\sum_{\vec{k}} e^{i\vec{k}(\vec{m}-\vec{e})}}_{\delta_{\vec{m},\vec{e}}}\; \underbrace{\sum_{n} \vec{e}^{\,i}_{n\vec{k}}(\mu)\, \vec{e}^{\,j*}_{n\vec{k}}(\lambda)}_{\delta_{\mu\lambda}\,\delta_{ij}\ \text{(completeness)}} = i\,\delta_{\vec{m}\vec{e}}\,\delta_{\mu\lambda}\,\delta_{ij}$$ ✓

This lets us rewrite the effective ionic Hamiltonian

$$\mathcal{H}_{\text{eff}} = \sum_{\vec{m},\mu} \frac{m}{M_\mu} \cdot \frac{1}{2} \vec{P}^2(\vec{m},\mu) + \sum_{\substack{\vec{m},\vec{e} \\ \mu,\lambda}} \frac{1}{2} \delta\vec{R}^i(\vec{e},\lambda)\, \mathcal{D}^{ij}(\vec{e},\lambda;\vec{m},\mu)\, \delta\vec{R}^j(\vec{m},\mu)$$

into the form

$$\mathcal{H}_{\text{eff}} = \frac{1}{2} \sum_{\vec{m},\mu} \frac{1}{N} \sum_{\substack{n,\vec{k} \\ n',\vec{k}'}} \underbrace{e^{-i\vec{k}\vec{m} - i\vec{k}'\vec{m}}}_{\to N\cdot\delta_{\vec{k},-\vec{k}'}} \vec{e}^{\,i*}_{n\vec{k}}(\mu)\, \vec{e}^{\,i*}_{n'\vec{k}'}(\mu)\, P_{n\vec{k}}\, P_{n'\vec{k}'}$$

$$+ \frac{1}{2} \frac{1}{N} \sum_{\substack{n\vec{k} \\ n'\vec{k}'}} \sum_{\substack{\vec{m},\vec{e} \\ \mu,\lambda}} e^{i\vec{k}\vec{e} + i\vec{k}'\vec{m}}\, \vec{e}^{\,i}_{n\vec{k}}(\lambda) \underbrace{\sqrt{\frac{m}{M_\lambda M_\mu}}\, \mathcal{D}^{ij}(\vec{e},\lambda;\vec{m}\mu)}_{\frac{1}{N}\sum_{\vec{q}\in 1.BZ} e^{i\vec{q}(\vec{e}-\vec{m})}\, \tilde{\mathcal{D}}^{ij}_{\vec{q}}(\lambda,\mu)}\, \vec{e}^{\,j}_{n'\vec{k}'}(\mu)\, q_{n\vec{k}}\, q_{n'\vec{k}'}$$

sum over $\vec{e}$ and $\vec{m}$ $\to N^2 \delta_{\vec{k},-\vec{q}}\, \delta_{\vec{k}',\vec{q}}$

$$= \frac{1}{2} \sum_{\mu,n,n'} \vec{e}^{\,i*}_{n\vec{k}}(\mu)\, \vec{e}^{\,i*}_{n'-\vec{k}}(\mu)\, P_{n\vec{k}}\, P_{n'-\vec{k}}$$

$$+ \frac{1}{2} \sum_{\substack{n,n' \\ \mu,\lambda}} \vec{e}^{\,i}_{n\vec{k}}(\lambda)\, \underbrace{\tilde{\mathcal{D}}^{ij}_{-\vec{k}}(\lambda,\mu)\, \vec{e}^{\,j}_{n'-\vec{k}}(\mu)}_{= d_{n'-\vec{k}}\, \vec{e}^{\,j}_{n'-\vec{k}}(\mu)}\, q_{n\vec{k}}\, q_{n'-\vec{k}}$$

Using $\vec{e}^{\,i*}_{n-\vec{k}} = \vec{e}^{\,i}_{n\vec{k}}$ and orthonomality we arrive at

$$\boxed{\mathcal{H}_{\text{eff}} = \frac{1}{2} \sum_{\substack{\vec{k}\in 1.BZ \\ n=1,2,\ldots,3r}} \left[P_{n\vec{k}}\, P_{n-\vec{k}} + d_{n\vec{k}}\, q_{n\vec{k}}\, q_{n-\vec{k}} \right]}$$

Finally, we introduce annihilation and creation operators

$$q_{u\vec{k}} = \frac{1}{\sqrt{2\sqrt{d_{nk}}}} \left(b^+_{u\vec{k}} + b_{u-k} \right) \qquad p_{u\vec{k}} = i \sqrt{\frac{\sqrt{d_{nk}}}{2}} \left(b^+_{u\vec{k}} - b_{u-\vec{k}} \right)$$

which obey bosonic commutation relations

$$\left[b_{u\vec{k}} , b^+_{u'\vec{k}'} \right] = \delta_{n,n'} \delta_{k,k'} \qquad \left[b^+_{u\vec{k}} , b^+_{u'\vec{k}'} \right] = \left[b_{u\vec{k}} , b_{u'\vec{k}'} \right] = 0$$ exercise!

In terms of these operators, the effective ionic Hamiltonian reads

$$H_{eff} = \frac{1}{2} \sum_{n,\vec{k}} \left[-\frac{\sqrt{d_{nk}}}{2} \left(b^+_{uk} - b_{u-k} \right) \left(b^+_{u-k} - b_{uk} \right) + \frac{\sqrt{d_{nk}}}{2} \left(b^+_{uk} + b_{u-k} \right) \left(b^+_{u-k} + b_{uk} \right) \right]$$

$$= \frac{1}{2} \sum_{u,\vec{k}} \sqrt{d_{nk}} \left[b^+_{uk} b_{uk} + b_{u-k} b^+_{u-k} \right]$$

which we can further simplify introducing $\omega_{uk} = \sqrt{d_{uk}}$ and $\omega_{u-k} = \omega_{uk}$ as well as $b_{u-k} b^+_{u-k} = b^+_{u-k} b_{u-k} + 1$ to give

$$\boxed{H_{eff} = \sum_{u\vec{k}} \omega_{u\vec{k}} \left[b^+_{u\vec{k}} b_{u\vec{k}} + \frac{1}{2} \right]}$$

phonon Hamiltonian

Remarks:

- the creation operator b^+_{uk} creates a phonon – an elementary quantum of a lattice vibration
- $\omega_{u\vec{k}} = \omega_u(\vec{k})$ defines a phonon dispersion for $\vec{k} \in$ 1. BZ
- the dispersion relations $\omega_u(\vec{k})$ possess the full symmetry of the point group
- Three of the 3r bands have the property

$$\omega_u(\vec{k}) \to 0 \quad \text{for} \quad \vec{k} \to 0$$

These types of phonons can be excited with very long wavelengths $\lambda \sim \frac{2\pi}{|\vec{k}|}$. As such they are responsible for the propagation of sound in the crystal
→ acoustic phonon branches

(concert pitch A with 440 Hz and sound velocity of gold $v \approx 3200 \frac{m}{s} \to \lambda \approx 7m$
— " — air $v \approx 340 \frac{m}{s} \to \lambda \approx 0.8m$)

The existence of the accoustic phonon branches can be rationalized by symmetry arguments: they are a consequence of the spontaneous breaking of the translation symmetry (of free space) by the formation of a crystal structure.

In general, the breaking of a continuous symmetry implies the presence of gapless, low-energy excitations, so-called Goldstone modes.

The accoustic phonons are the Goldstone modes of the crystal.

Consides a constant translation of the crystal in any of the three directions of space $\delta\vec{R}^i(\vec{e},\mu) \equiv \delta R^i$ with $i = x,y,z$

This should not cost any energy as rigid translation does not generate a restoring force of the crystal $\Rightarrow$ three accoustic phonon branches

Further, for small $\vec{k}$ we have a linear dispersion

$$\boxed{\omega_u(\vec{k}) \cong c_u(\hat{k}) \cdot |\vec{k}|}$$

with the sound velocities $c_u(\hat{k})$ that in general depend on the orientation $\hat{k} = \vec{k}/|\vec{k}|$. They are related to the elastic constants of the crystal like bulk and shear modulus.

Note: A liquid in contrast possesses only a single longitudinal sound mode, since there is no shear modulus!

- The other $3r-3$ phonon branches are known as optical phonon branches because they can often be excited by light.

- Anharmonic corrections of the form

$$\mathcal{E}_0^{(3)}(\{R\}) = \frac{1}{3!} A_{nml}\, \delta R_n \delta R_m \delta R_l$$

result in an interaction between phonons, e.g. $b^\dagger bb$ etc.

→ necessary to explain e.g. thermal expansion.

Experimental / ab initio theory example

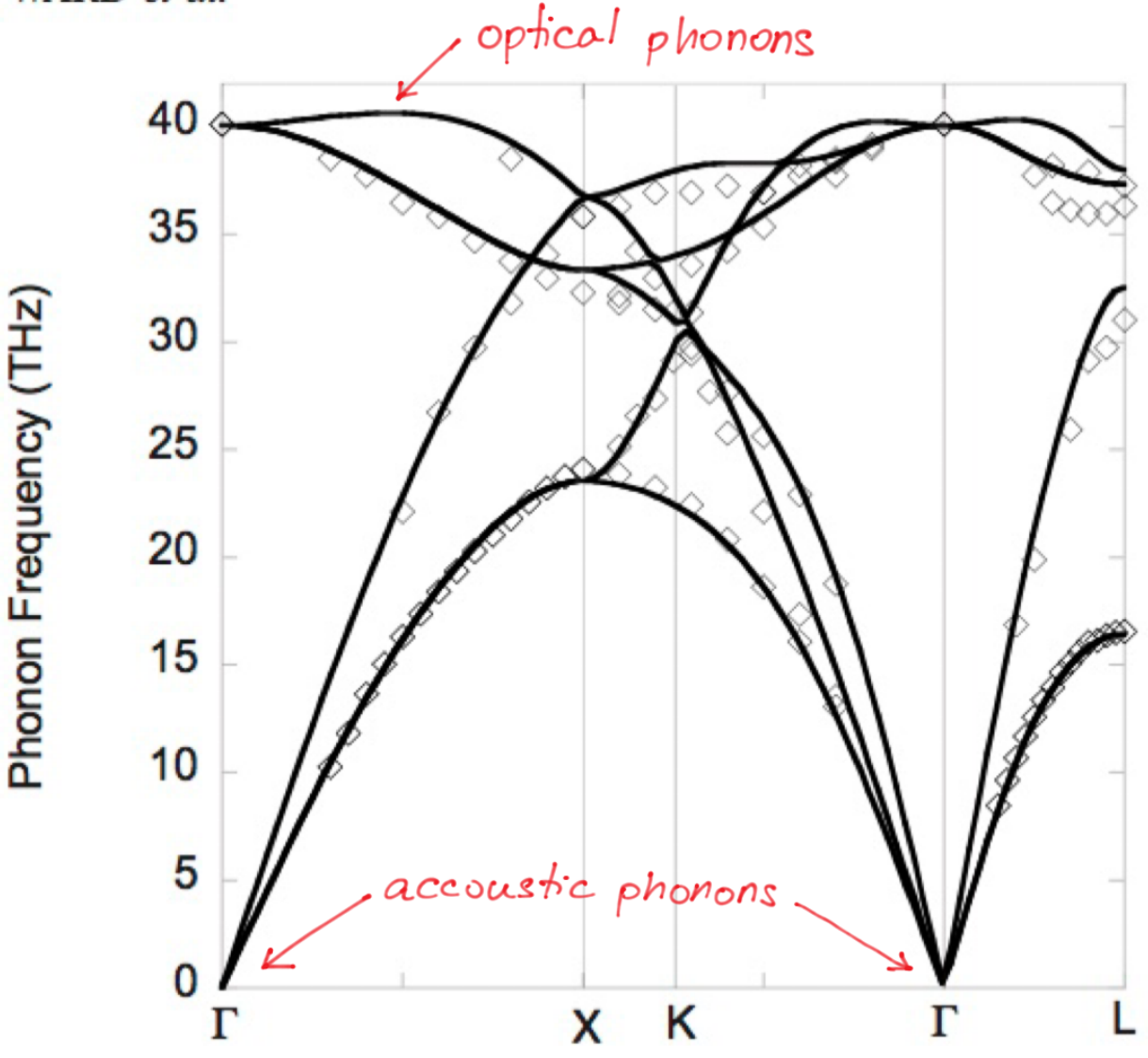
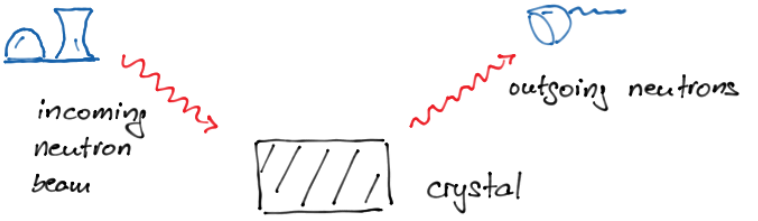


FIG. 1. Phonon dispersions of diamond. *Ab initio* calculations (solid line) and experiment (open diamonds).

from A. Ward et al., Phys. Rev. B 80, 125203 (2009).

3.3 Measuring phonon dispersions: neutron scattering

The phonon dispersions $\omega_n(\vec{k})$ can be measured by neutron scattering.



Neutrons (created in a nuclear reaction / reactor) are neutral particles that mainly interact with the atomic nuclei and thus also with phonons.
(However, neutrons also interact with magnetic moments, which is used for the investigation of quantum magnetism, e.g. determination of magnetic order, measurements of spin waves etc. → Braden group)

We can capture the neutron-ion interaction by

$$V(\vec{r}) = \sum_{\vec{e} \in \text{Bravais lattice}} \sum_{\lambda \in \text{basis}} v_\lambda(\vec{r} - \vec{R}(\vec{e}, \lambda))$$

The interaction potential v_λ is very short-ranged with its range being of the order of the typical nuclear dimensions, i.e. $10^{-15}\,m = 1\,fm$.
Comparing this to the typical length scale of crystal constants $\sim 10^{-10}\,m = 1\,\text{Å}$ the potential can be approximated by δ-functions:

$$V(\vec{r}) \approx \sum_{\vec{e},\lambda} v_\lambda \cdot \delta(\vec{r} - \vec{R}(\vec{e}, \lambda))$$

The probability per unit time for the neutron to scatter from $\vec{k}_{in}$ to $\vec{k}_{out}$ in lowest order perturbation theory is given by Fermi's golden rule

$$P_i = \sum_f \frac{2\pi}{\hbar} \left| \langle f, \vec{k}_{out} | V(\vec{r}) | i, \vec{k}_{in} \rangle \right|^2 \cdot \delta(E_f - E_i + \hbar\omega)$$

↑ sum over all possible final states of crystal

↑ final momentum of neutron detected by detector

with E_f = final energy of the crystal

E_i = initial energy of the crystal

$\hbar\omega = \frac{(\hbar\vec{k}_{out})^2}{2m_n} - \frac{(\hbar\vec{k}_{in})^2}{2m_n}$ = energy gained by the neutron in the scattering process

(m_n → mass of neutron)

$$\rightarrow P_i = \sum_f \frac{2\pi}{\hbar} \left| \frac{1}{vol} \int d^3\vec{r}\; e^{-i\vec{k}_{out}\vec{r}} \langle f | V(\vec{r}) | i \rangle e^{i\vec{k}_{in}\vec{r}} \right|^2 \delta(E_f - E_i + \hbar\omega)$$

($|f\rangle$, $|i\rangle$ → final and initial state of crystal)

with $\vec{q} = \vec{k}_{out} - \vec{k}_{in}$ transfered wavevector and inserting explicit potential

$$P_i = \frac{2\pi}{\hbar} \sum_f \left| \frac{1}{vol} \sum_{\vec{e},\lambda} v_\lambda \langle f | e^{-i\vec{q}\vec{R}(\vec{e},\lambda)} | i \rangle \right|^2 \delta(E_f - E_i + \hbar\omega)$$

Typically, the crystal is <u>not</u> in a definite eigenstate $|i\rangle$, but rather the states are <u>thermally populated</u> → thermally averaged transition rate

$$P = \langle P_i \rangle = \sum_i \frac{1}{Z_i} e^{-\beta E_i} P_i \quad \text{with partition sum} \quad Z_i = \sum_i e^{-\beta E_i}$$

($\langle P_i \rangle$ → thermal expectation value; Z_i → partition sum; β → inverse temperature $\beta = 1/k_B T$)

The thermal transition rate P is related to the scattering cross section

$$\frac{d^2\sigma}{d\Omega\, d\omega}\, d\Omega\, d\omega = \frac{P \times \text{number of final states per neutron}}{\text{incoming flux density of neutrons}}$$

$$= \frac{P \cdot vol \cdot \frac{d^3\vec{k}_{out}}{(2\pi)^3}}{\frac{|\hbar\vec{k}_{in}|}{m_n} \cdot \frac{1}{vol}} = P \cdot vol^2 \cdot \frac{m_n}{\hbar|\vec{k}_{in}|} \cdot \frac{\vec{k}_{out}^2\, dk_{out}\, d\Omega}{(2\pi)^3}$$

($d\Omega$ → solid angle)

with $\frac{d\omega}{d|k_{out}|} = \frac{\hbar|k_{out}|}{m_n}$ (since $\hbar\omega = \frac{(\hbar\vec{k}_{out})^2}{2m_n}$)

$$\rightarrow \frac{d^2\sigma}{d\Omega\, d\omega} = P \cdot \frac{vol^2}{(2\pi)^3} \cdot \frac{|\vec{k}_{out}|}{|\vec{k}_{in}|} \cdot \frac{m_n^2}{\hbar^2}$$

For a monatomic Bravais lattice this simplifies further to

$$\frac{d^2\sigma}{d\Omega\, d\omega} = \frac{|\vec{k}_{out}|}{|\vec{k}_{in}|} \cdot \frac{m_n^2\, v_0^2}{(2\pi)^3 \hbar^4} \cdot N \cdot S(\vec{q},\omega)$$

N = # of lattice sites

with the dynamical structure factor

$$S(\vec{q},\omega) = \sum_{f,i} \frac{e^{-\beta E_i}}{Z_i} \cdot \frac{1}{N} \sum_{\vec{e},\vec{m} \in \text{Bravais lattice}} \langle i | e^{i\vec{q}\vec{R}(\vec{e})} | f \rangle\langle f | e^{-i\vec{q}\vec{R}(\vec{m})} | i \rangle\, 2\pi\hbar\, \delta(E_f - E_i + \hbar\omega)$$

with $\int_{-\infty}^{\infty} dt\, e^{i\omega t} = 2\pi\,\delta(\omega)$ and $e^{-\frac{iE_i t}{\hbar}} |i\rangle = e^{-\frac{i\hat{H}t}{\hbar}} |i\rangle$ etc. ($\hat{H}$ → ionic Hamiltonian)

$$\rightarrow S(\vec{q},\omega) = \sum_{f,i} \frac{e^{-\beta E_i}}{Z_i} \int_{-\infty}^{\infty} dt\, e^{i\omega t} \frac{1}{N} \sum_{\vec{e},\vec{m}} \langle i | e^{i\vec{q}\vec{R}(\vec{e})} | f \rangle\langle f | \underbrace{e^{i\hat{H}t/\hbar}\, e^{-i\vec{q}\vec{R}(\vec{m})}\, e^{-i\hat{H}t/\hbar}}_{= e^{-i\vec{q}\vec{R}(\vec{m},t)}} | i \rangle$$

$e^{-i\vec{q}\vec{R}(\vec{m},t)}$: operator in the Heisenberg picture

using completeness $\sum_f |f\rangle\langle f| = 1$

$$\rightarrow S(\vec{q},\omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega t}\, S(\vec{q},t)$$

where

$$S(\vec{q},t) = \frac{1}{N} \sum_{\vec{e},\vec{m}} \sum_i \frac{1}{Z_i} \langle i | e^{-\beta\hat{H}}\, e^{i\vec{q}\vec{R}(\vec{e},t=0)}\, e^{-i\vec{q}\vec{R}(\vec{m},t)} | i \rangle$$

Now, for a monatomic Bravais lattice: $\vec{R}(\vec{m},t) = \vec{m} + \underbrace{\delta\vec{R}(\vec{m},t)}_{\text{deviation from equilibrium} \rightarrow \text{phonons!}}$

$$S(\vec{q},t) = \frac{1}{N} \cdot \sum_{\vec{e},\vec{m}} e^{i\vec{q}(\vec{e}-\vec{m})} \left\langle e^{i\vec{q}\,\delta\vec{R}(\vec{e},0)}\, e^{-i\vec{q}\,\delta\vec{R}(\vec{m},t)} \right\rangle$$

$\langle\ldots\rangle$: thermal average

If the phonons are treated in the harmonic approximation the thermal average simplifies to

$$S(\vec{q},t) \cong \frac{1}{N}\sum_{\vec{e},\vec{m}} e^{i\vec{q}(\vec{e}-\vec{m})} \exp\left[-\tfrac{1}{2}\langle(\vec{q}\,\delta\vec{R}(\vec{e},0))^2\rangle - \tfrac{1}{2}\langle(\vec{q}\,\delta\vec{R}(m,t))^2\rangle + \langle\vec{q}\,\delta\vec{R}(\vec{e},0)\,\vec{q}\,\delta\vec{R}(\vec{m},t)\rangle\right]$$

Using that $\langle(\vec{q}\,\delta\vec{R}(\vec{e},0))^2\rangle = \langle(\vec{q}\,\delta\vec{R}(\vec{m},t))^2\rangle \equiv 2W$ independent of lattice site and time

and $\langle(\vec{q}\,\delta\vec{R}(\vec{e},0))\cdot(\vec{q}\,\delta\vec{R}(\vec{m},t))\rangle = \langle\vec{q}\,\delta\vec{R}(\vec{0},0)\;\vec{q}\,\delta\vec{R}(\vec{m}-\vec{e},t)\rangle$

due to discrete translation invariance of the Bravais lattice

$$\rightarrow \boxed{S(\vec{q},t) = e^{-2W}\sum_{\substack{\vec{m}\in \\ \text{Bravais} \\ \text{lattice}}} e^{i\vec{q}\vec{m}} \exp\left[\langle(\vec{q}\,\delta\vec{R}(0,0))(\vec{q}\,\delta\vec{R}(\vec{m},t))\rangle\right]}$$

with Debye-Waller factor e^{-2W} (temperature dependent)

The time dependence is determined by the last factor, which we can treat in perturbation theory using $e^x = \sum_{n=0}^{\infty}\frac{x^n}{n!}$

Zero phonon contribution $n=0$

$$S^{(0)}(\vec{q},\omega) = \int_{-\infty}^{\infty} dt\; e^{i\omega t}\, e^{-2W}\sum_{\vec{m}} e^{i\vec{q}\vec{m}}$$

$$= 2\pi\,\delta(\omega)\cdot e^{-2W}\,\frac{(2\pi)^3}{V_{puc}}\sum_{\vec{G}\in \text{ reciprocal lattice}} \delta(\vec{q}-\vec{G})$$

↳ note that $\vec{q}$ not necessary within 1. BZ

δ-functions in frequency and momentum space

→ scattering Bragg peaks remain sharp

only their weight is reduced by the Debye-Waller factor e^{-2W}.

Single-phonon contribution $n = 1$

In first order ($u=1$) we need to calculate the expectation value

$$\langle \delta R^i(0,0)\, \delta R^j(\vec{m},t)\rangle = \frac{1}{N} \sum_{\substack{k,k' \in 1.BZ \\ u,u'}} \frac{m}{M} e^{i\vec{k}'\vec{m}}\, \vec{e}^{\,i}_{u\vec{k}}\, \vec{e}^{\,j}_{u'\vec{k}'}\, \langle q_{u\vec{k}}(t=0)\, q_{u'\vec{k}'}(t)\rangle$$

with $\langle q_{uk}(0)\, q_{u'k'}(t)\rangle = \frac{1}{2} \frac{1}{\sqrt{\omega_{uk}\,\omega_{u'k'}}} \langle (b^+_{uk} + b_{u-k}) \cdot (b^+_{u'k'}(t) + b_{u'-k'}(t))\rangle$

$$= \frac{1}{2} \frac{1}{\sqrt{\omega_{uk}\,\omega_{u'k'}}} \langle b^+_{uk}\, b_{u'-k'}\, e^{-i\omega_{u'k'}t} + \underbrace{b_{u-k}\, b^+_{u'k'}}\, e^{i\omega_{u'k'}t}\rangle$$

$$= b^+_{u'k'}\, b_{u-k} + \delta_{k',-k}\,\delta_{uu'}$$

$$= \frac{1}{2} \cdot \frac{1}{\omega_{uk}} \cdot \delta_{k',-k}\,\delta_{uu'} \left[n_B(\omega_{uk})\, e^{-i\omega_{uk}t} + (1+n_B(\omega_{uk}))\, e^{i\omega_{uk}t}\right]$$

with $\omega_{uk} = \omega_{u-k}$ and $\vec{e}^{\,i}_{u-k} = \vec{e}^{\,i*}_{uk}$

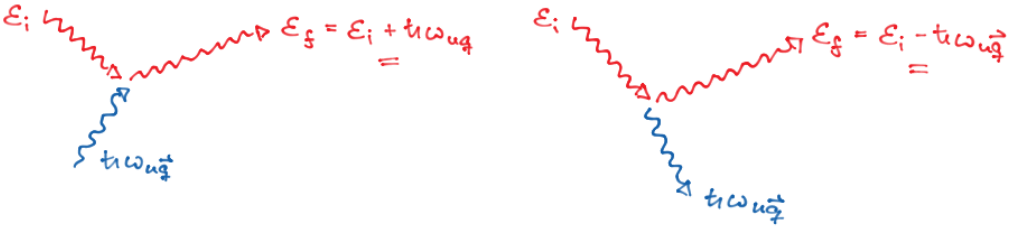
$$\rightarrow S^{(1)}(\vec{q},\omega) = e^{-2W} \sum_{\vec{u}} e^{i\vec{q}\vec{m}}\, \frac{1}{N} \sum_{u\vec{k}} \frac{m}{M}\, e^{i\vec{k}\vec{m}}\, |\vec{q}\cdot\vec{e}_{u\vec{k}}|^2 \cdot \frac{1}{2\omega_{uk}}$$

$$\times \left[n_B(\omega_{uk})\, 2\pi\,\delta(\omega-\omega_{uk}) + (1+n_B(\omega_{uk}))\, 2\pi\,\delta(\omega+\omega_{uk})\right]$$

and finally using $\frac{1}{N}\sum_{\vec{u}} e^{i(\vec{q}+\vec{k})\vec{m}} = \sum_{\vec{G}\in \text{reciprocal lattice}} \delta_{\vec{q}+\vec{k},\vec{G}}$

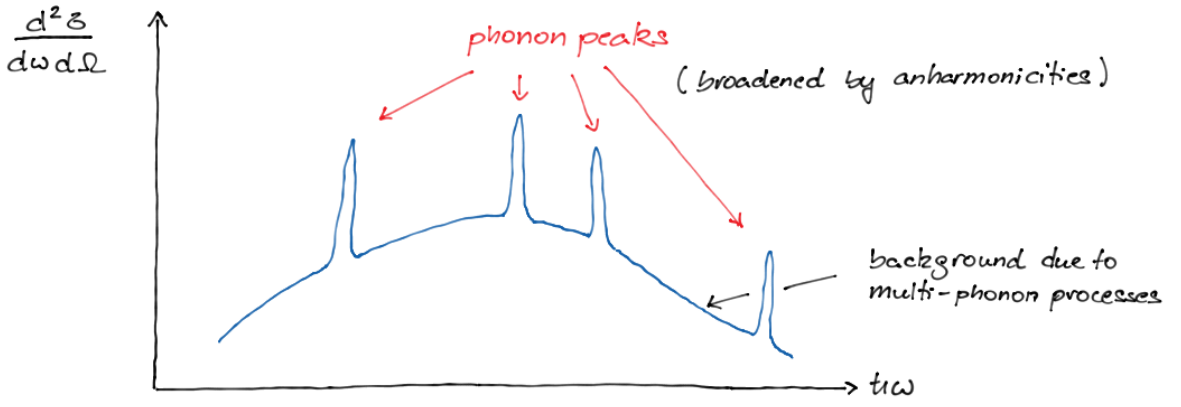
$$\rightarrow \boxed{S^{(1)}(\vec{q},\omega) = e^{-2W} \frac{m}{M} \sum_n |\vec{q}\,\vec{e}_{u\vec{q}}|^2 \frac{1}{2\omega_{uq}} \left[n_B(\omega_{uq})\, 2\pi\delta(\omega-\omega_{uq}) + (1+n_B(\omega_{uq}))\, 2\pi\delta(\omega+\omega_{uq})\right]}$$

absorption of a phonon — spontaneous + stimulated emission of a phonon



The absorption and emission of a phonon during the scattering process results in additional sharp peaks at finite energy $\hbar\omega = \pm\hbar\omega_{u\vec{q}}$

→ measurement of phonon dispersion by <u>inelastic neutron scattering</u>.



Remarks

- neutron scattering method of choice for measuring phonon spectra, X-rays much less suitable due to linear dispersion of photons → difficulty in energy resolution
- photons in the visible range can be used to probe phonons with $\vec{k}=0$ (Γ-point)
  → Raman scattering if phonon is optical
  → Brillouin scattering if phonon is accoustic

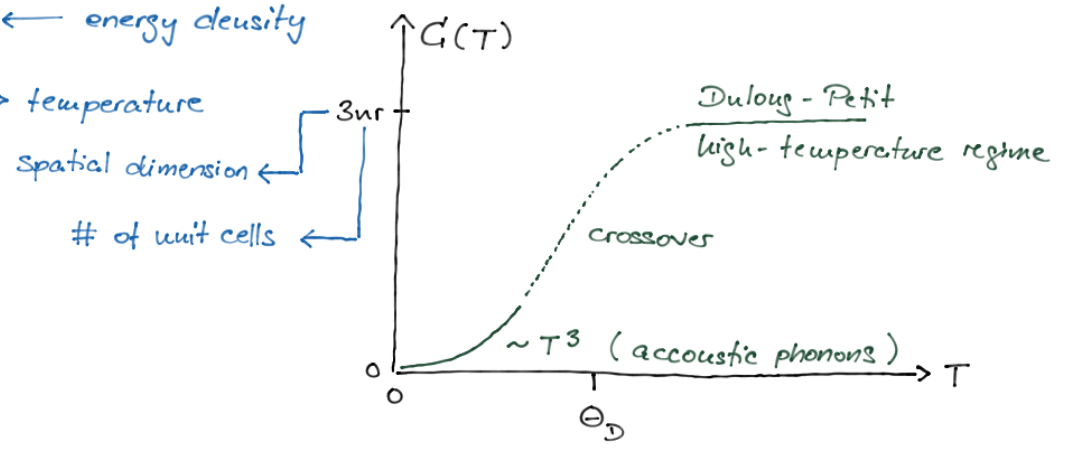
3.4 Thermodynamics of phonons

Here only a quick summary, for more details see exercise(s).

We want to consider the contribution of phonons to the specific heat

$$C = \frac{\partial E}{\partial T}$$

E ← energy density; T → temperature



The thermal crossover between low-temperature and high-temperature regimes is typically described by the Debye-model where the crossover occurs at the Debye temperature Θ_D.

Typical values: $\Theta_D \sim$ 160 K (Au), 350 K (Cu), 470 K (Fe), 1860 K (diamond)