3D harmonic oscillator – qm.

We had:

$$H = \sum_{I=1}^{M} \frac{\underline{P}_I^2}{2M_I} + V^{BO}(\{\underline{R}_I\})$$

$$+ \frac{1}{2} \sum_{I,J}^{M,M} \sum_{\mu,\nu}^{3,3} s_{I,\mu} \, \Phi_{\mu\nu}(\underline{R}_I, \underline{R}_J) \, s_{J,\nu}$$

transform to eigenmodes $s_I(\underline{k})$:

$$H_{vib} = \sum_{i=1}^{3} \sum_{\underline{k}} \frac{p_i^2(\underline{k})}{2M_I} + \frac{1}{2} \sum_{i=1}^{3} \sum_{\underline{k}} \omega_i(\underline{k}) \, |s_i(\underline{k})|^2$$

$+ \text{const.}$

(monatomic case)

So far: classical H transformed

but: H_{vib} now $3M$ decoupled

harmonic oscillators

Like in case of 1D harmonic oscillator:

$\hat{p}$, $\hat{s}$ become operators

can define

$$a_i(\underline{k}) = \sqrt{\frac{M\omega_i(\underline{k})}{2\hbar}} \, s_i(\underline{k}) + i \sqrt{\frac{1}{2\hbar M_I \omega_i(\underline{k})}} \, p_i(\underline{k})$$

$$a_i^\dagger(\underline{k}) = \quad \ldots \quad -i \quad \ldots$$

go through a lot of algebra (see 1D case)

and find:

$$H_{vib} = \sum_{i=1}^{3} \sum_{\underline{k}} \hbar\omega_i(\underline{k}) \left[a_i^\dagger(\underline{k})\, a_i(\underline{k}) + \frac{1}{2} \right]$$

and $$E_{vib} = \sum_{i=1}^{3} \sum_{\underline{k}} \hbar\omega_i(\underline{k}) \left[n_i(\underline{k}) + \frac{1}{2} \right]$$

This is a fundamental insight:

Algebraically, the eigenmodes of the harmonic crystal behave as if they were composed of individual particles

Momentum $\underline{k}$, energy $\hbar\omega_i(\underline{k})$

So: **phonons** $\equiv$ independent excitations of a harmonic crystal, V^{BO}

in principle: ∞ many excitations of each mode possible

$T=0$: $n_i(\underline{k}) = 0$ but

$$E_{zero} = \sum_{i=1}^{3} \sum_{\underline{k}} \frac{\hbar\omega(\underline{k})}{2} \neq 0$$

$T \neq 0$: $n_i(\underline{k})$ determined by T – how?

Lattice Energy at finite T:

for given mode $\underline{k}$, $\omega_i(\underline{k})$

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega_i(\underline{k})$$

Excitation probability of n phonons at finite T

$$P_n(T) = \frac{e^{-\frac{E_n}{k_B T}}}{\sum_l e^{-\frac{E_l}{k_B T}}} = \frac{\left(e^{-\frac{\hbar\omega_i(\underline{k})}{k_B T}}\right)^n}{\sum_l \left(e^{-\frac{\hbar\omega_i(\underline{k})}{k_B T}}\right)^l}$$

$$=: \frac{x^n}{\sum_l x^l}$$

$\sum_{l=0}^{\infty} x^l = \frac{1}{1-x}$ geometrical series

$$\rightarrow P_n(T) = x^n (1-x)$$

Energy average of crystal at T

$$\bar{E}_i(T, \omega(\underline{k})) = \sum_{n=0}^{\infty} E_n \cdot P_n(T)$$

$$= \frac{\hbar\omega_i(k)}{2} + \hbar\omega_i(k) \sum_n n P_n(T)$$

$$= \frac{\hbar\omega_i(k)}{2} + \hbar\omega_i(k) \cdot (1-x) \underbrace{\sum_{n=0}^{\infty} n x^n}_{\frac{x}{(1-x)^2}}$$

$$= \hbar\omega_i(k) \left[\frac{1}{e^{\frac{\hbar\omega_i(k)}{k_B T}} - 1} + \frac{1}{2} \right]$$

$$\bar{n}_i(k) = \frac{1}{e^{\frac{\hbar\omega(k)}{k_B T}} - 1}$$

Bose-Einstein statistics!

Total energy of the lattice

$$E_{vib}(T) = \sum_{i=1}^{3} \sum_{k} \hbar\omega_i(k) \left(\frac{1}{e^{\frac{\hbar\omega_i(k)}{k_B T}} - 1} + \frac{1}{2} \right)$$

Can we make this look simpler?

Phonon density of states:

Number of phonons in a given interval $[\omega, \omega+d\omega]$:

$$g(\omega)\,d\omega = \frac{1}{(2\pi)^3}\sum_i \int d^3\underline{k}\;\delta(\omega-\omega_i(\underline{k}))$$

and $$\int_0^\infty d\omega\, g(\omega) = \frac{3M}{V}$$

Thus: $$E_{vib} = V\cdot \int_0^\infty d\omega\; g(\omega)\left(\frac{1}{e^{\frac{\hbar\omega}{k_BT}}-1}+\frac{1}{2}\right)\hbar\omega$$

What is this good for?

- either calculate $g(\omega)$ exactly (DFT, ..)
- make appropriate generic models for $g(\omega)$

exact formulation (just like for electrons):

$g(\omega)$ from
1) $\omega(\underline{k})$
2) The surface which is defined by $\omega=\omega(\underline{k})$ in $\underline{k}$-space

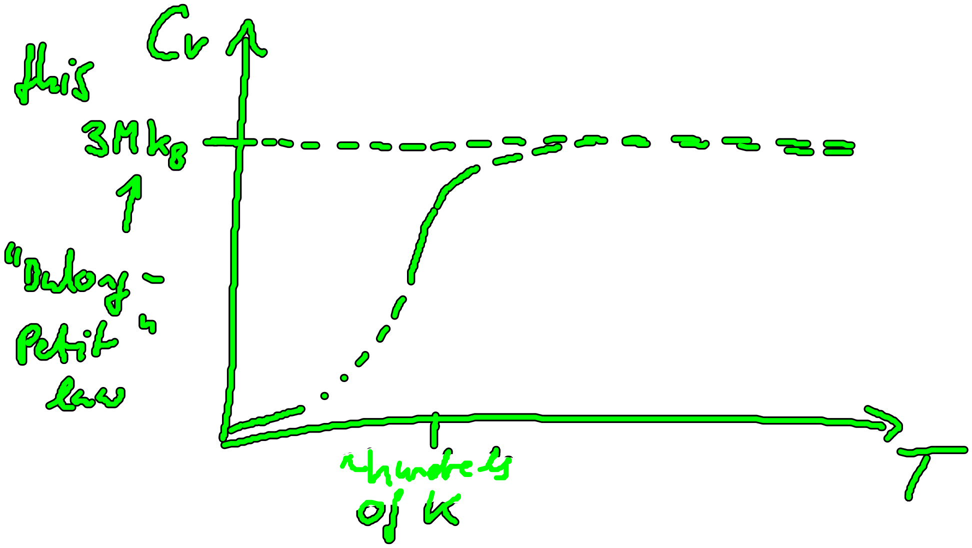
$$g(\omega) = \sum_i \int \frac{d^2S}{(2\pi)^3}\,\frac{1}{|\underline{\nabla}\omega(\underline{k})|}$$

integral over surface of constant ω

$\underline{\nabla}\omega(\underline{k}) = 0$ van Hove singularity

Specific of a Harmonic Crystal

We can measure this



$$C_V = \frac{\partial E}{\partial T}\bigg|_V$$

$$c_V = \frac{1}{V}\frac{\partial E}{\partial T}\bigg|_V$$

equipartition theorem (classical):

harmonic system has $6M$ degrees of freedom

each gets $\frac{k_B T}{2}$ $\rightarrow$ $E_{class} = 3Mk_B T$

$\rightarrow C_V = 3Mk_B$.

Darn.

But we know $E_{vib}(T)$.

(at constant volume V)

Equipartition theorem has no continuous $\omega(\underline{k})$ to distribute $\frac{k_B T}{2}$ to!

$$c_V^{vib}(T) = \frac{1}{V}\frac{\partial E_{vib}}{\partial T}\bigg|_V$$

$$= \frac{\partial}{\partial T}\int^{\infty} d\omega\, g(\omega)\, \hbar\omega \left(\frac{1}{e^{\frac{\hbar\omega}{k_B T}}-1}+\frac{1}{2}\right)$$

Limiting cases:

1. Einstein model:

3M independent oscillators, 1 at each site, ω_E:

$$g_{\text{Einstein}} = \left(\frac{3M}{V}\right) \delta(\omega - \omega_E)$$

$$C_V = \frac{3Mk_B}{V} \frac{x^2 e^x}{(e^x - 1)} \qquad x = \frac{\hbar\omega_E}{k_B T}$$

[$T \to \infty$: Dulong-Petit]

$T \to 0$: $x \to \infty$

$$\Rightarrow C_V \to \frac{3Mk_B}{V} \frac{x^2}{e^x}$$

exponential decay towards zero!

Experiment: too fast!

2. high-temperature limit (general $g(\omega)$)

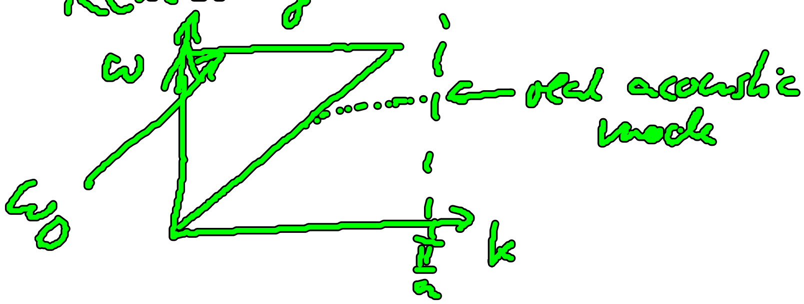
$$\frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1} \xrightarrow{T \to \infty} \frac{1}{1 + \frac{\hbar\omega}{k_B T} + \ldots - 1} = \frac{k_B T}{\hbar\omega}$$

$$C_V^{vib}(T) = \frac{1}{V} \int_0^\infty d\omega \, g(\omega) \frac{\partial}{\partial T}(k_B T)$$

$$= \frac{3M k_B}{V} \quad \text{Dulong-Petit (general)}$$

(2) "Debye model"

Remembering the acoustic modes



Debye: $\omega_i(\underline{k}) = v_g \cdot k$

but $\frac{1}{(2\pi)^3} \int_0^{\omega_D} d\omega \; \delta(\omega - \omega(k)) = 3M \rightarrow$ yields ω_D

$$g_D(\omega) = \frac{3}{2\pi^2 (v)^3} \cdot \omega^2 \cdot \Theta(\omega - \omega_D)$$

ω_D enforces $3M$ modes

Exercise:

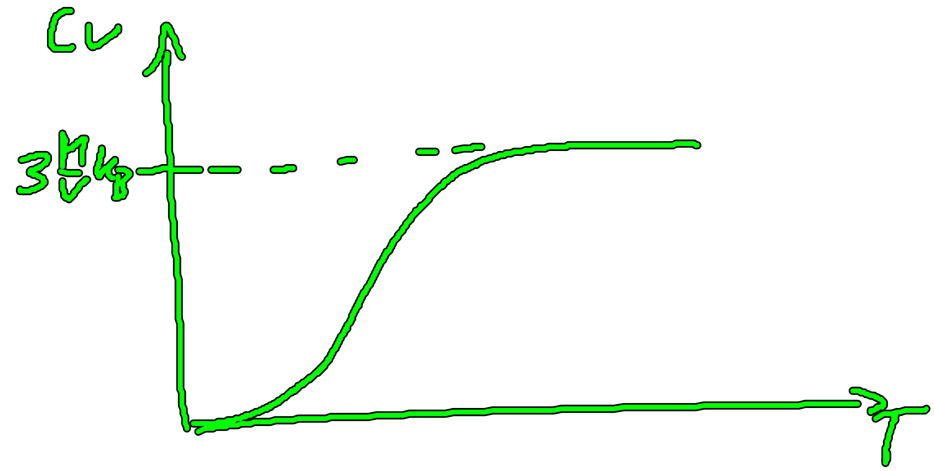
$$C_V^{\text{Debye}} = \frac{9 k_B M}{V} \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\frac{\Theta_D}{T}} dx \, \frac{x^4 e^x}{(e^x - 1)^2}$$

$T \to \infty$: Dulong-Petit

$T \to 0$: $C_V^{\text{Debye}} \sim T^3$.

Real solids:

- high T ✓
- low T : acoustic modes $\rightarrow \sim T^3$ Debye
- intermediate T :

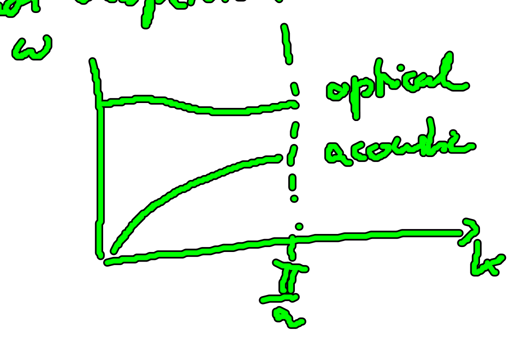


(a) take Debye law and fit ω_D

$$\hbar\omega_D =: k_B \Theta_D$$

$$\Theta_D = \frac{\hbar\omega_D}{k_B} \quad \text{Debye temperature}$$

(b) Phonon dispersion



optical, top of acoustic modes: $\omega \sim$ const.

$\rightarrow$ Einstein model describes intermediate range

Anharmonic effects in crystals

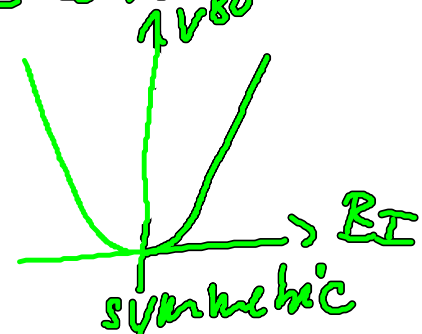
So far : • $\omega(\underline{k})$ dispersion – harmonic

• phonons – behave as independent particle-like entities

• Thermal expansion

$a = a(T)$ lattice constant

but PES, V^{BO}



no harmonic thermal expansion!

• heat transport

harmonic phonons are eigenstates of H^{vib}_{harm}

→ travel forever

→ infinite heat conductivity ? No.

Phonon – Phonon interaction!

Thermal expansion

a) thermodynamic considerations

$$\alpha = \frac{1}{3V}\left(\frac{\partial V}{\partial T}\right)_p$$

thermal expansion coefficient

We know:

bulk modulus $\quad \frac{1}{B} = \frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$

pressure: $\quad P = -\left(\frac{\partial U}{\partial V}\right)_T \quad$ (thermodynamics)

$$U \equiv E_{vib} \quad \text{here}$$

Put all this together:

$$\alpha = \frac{1}{3V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{3V}\left(\frac{\partial V}{\partial p}\right)_T \cdot \left(\frac{\partial P}{\partial T}\right)_V$$

$$= \frac{1}{3B}\left(\frac{\partial P}{\partial T}\right)_V$$

and $\quad U = E_{vib} = \sum_i \sum_{\underline{k}} \hbar\omega_i(\underline{k})\left(n_i(\underline{k}) + \frac{1}{2}\right)$

$$\Rightarrow P = \sum_i \sum_{\underline{k}} \left(\frac{\partial \hbar\omega_i(\underline{k})}{\partial V}\right)_T \left(n_i(\underline{k}) + \frac{1}{2}\right)$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \sum_i \sum_{\underline{k}} \left(\frac{\partial \hbar\omega_i(\underline{k})}{\partial V}\right)_T \left(\frac{\partial n_i(\underline{k})}{\partial T}\right)_V$$

$$\alpha = -\frac{1}{3B} \sum_{i,\underline{k}} \left(\frac{\partial \hbar\omega_i(\underline{k})}{\partial V}\right)_T \cdot \left(\frac{\partial n_i(\underline{k})}{\partial T}\right)_V$$

Common rewrite:

$$\alpha = \frac{\gamma}{3B} C_V$$

γ : total Grüneisen parameter

often ~ 1 (NaCl: 1.6)

and can show that

$\alpha \sim T^3$ low T

$\alpha \sim$ const. high T

($\sim$ Debye model)

we know: $$C_V = \sum_{i\underline{k}} \frac{\hbar \omega_i(\underline{k})}{V} \frac{\partial}{\partial T} n_i(T)$$

so $$\alpha = -\frac{1}{3B} \sum_{i\underline{k}} \underbrace{\frac{\hbar \omega_i(\underline{k})}{V} \frac{\partial \omega_i(\underline{k})}{\partial V}}_{\gamma_{i,\underline{k}}} c_{v,i}(\underline{k})$$

$\gamma_{i,\underline{k}}$ Grüneisen parameter mode dependent.

and $$\gamma = \frac{\sum_{\underline{k},i} \gamma_{\underline{k}i} \, c_{v,i}(\underline{k})}{\sum_{\underline{k},i} c_{v,i}(\underline{k})}$$

(b) Quantitative theories;

DFT et al.

can <u>calculate</u> α, et al.

"quasiharmonic approximation":

$\hbar\omega_i(\underline{k})$ depends on V

but not on T.

This we can calculate:

- $\hbar\omega_i(\underline{k})$ at $T \simeq 0$ for different V of the same solid.

works well in modern electronic structure theory (DFT)

also for C_p (heat capacity at constant pressure → measured!)

<u>Heat transport</u>: (qualitatively)

a) purely harmonic crystals: infinite heat conductivity.

b) anharmonicities: Phonon-Phonon interactions

qualitatively: perturbation theory

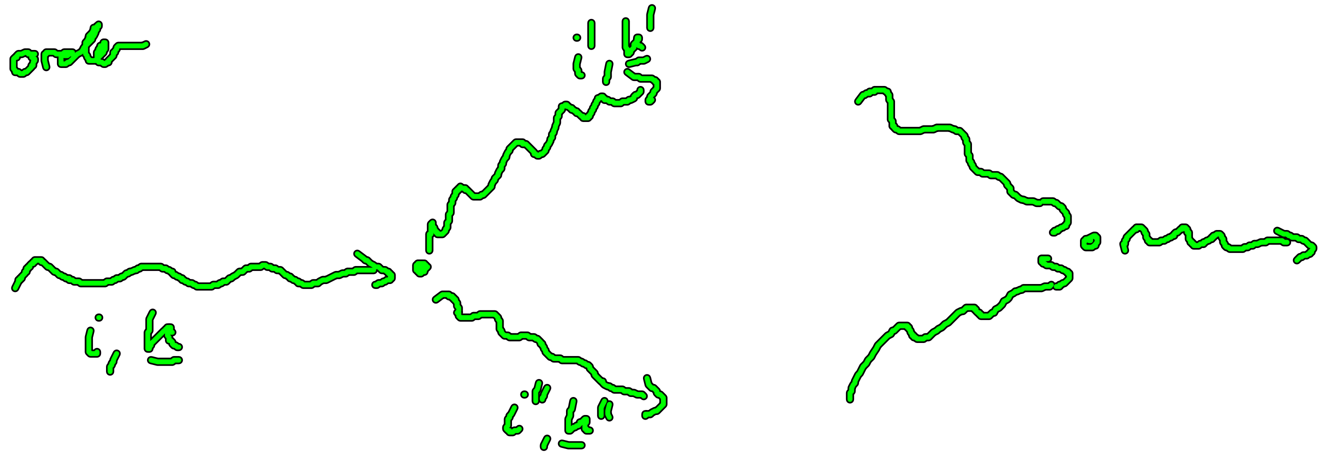
phonons remain <u>approximate</u> eigenstates with lifetime:

if crystal at time t were exactly in mode $(i, \underline{k})$

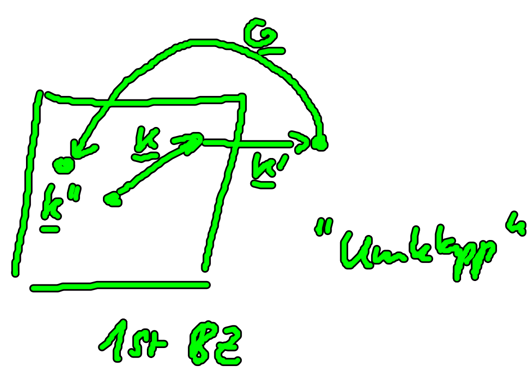
→ as t progresses, deviations become larger and larger

quantum-mechanically:
3rd order terms in $V^{BO}(\{\underline{R}_I\})$
lead to 3 phonon processes,
4th order to 4 ph-processes
etc

3rd order



energy conservation
momentum conservation



through "Umklapp",
limit the th conductivity
at high T

low T: surface reflection etc
becomes important.