Quantum Theory of Harmonic Crystals

$$H^{harm} = \sum_{\vec{R}} \frac{\vec{P}(\vec{R})^2}{2M} + \frac{1}{2}\sum_{\vec{R},\vec{R}'} D_{\mu\nu}(\vec{R}-\vec{R}')\, u_\mu(\vec{R})\, u_\nu(\vec{R}')$$

Classical Description

$\vec{P}(\vec{R})$, $\vec{u}(\vec{R})$

continuous vector functions

Quantum Theory

$$[\hat{P}_\mu(\vec{R}), u_\nu(\vec{R}')] = -i\hbar\,\delta_{\mu\nu}\,\delta_{\vec{R},\vec{R}'}$$

operators

Normal Modes 3N

$\vec{\epsilon}_s(\vec{k})$, $\omega_s(\vec{k})$ - - - - - - - - - > 3N quantum oscillators "PHONONS"

$$\vec{u}(\vec{R},t) = \sum_{\vec{k},s} A_s(\vec{k}) \cdot \vec{\epsilon}_s(\vec{k}) \cdot \exp\{i\vec{k}\cdot\vec{R} - i\omega_s(\vec{k})\cdot t\}$$

dimensionless amplitude of the $(s,\vec{k})$ mode

continuous function

operator

Energy

$$E = \sum_{\vec{k},s} |A_s(\vec{k})|^2\, \omega_s(k)$$

valid when $n_s(\vec{k}) \gg 1$

$$E = \sum_{\vec{k},s} \hbar\omega_s(\vec{k})\left[n_s(\vec{k}) + \tfrac{1}{2}\right]$$

$n_s(\vec{k}) = 0, 1, 2, \ldots$

number of phonons of sort $(s,\vec{k})$

LATTICE SPECIFIC HEAT

Classical Statistical Physics: averaging in phase space

for now $\boxed{k_B = 1}$!

$$\langle \dots \rangle = \frac{\int d\Gamma \, e^{-\frac{K}{T} - \frac{U}{T}} \dots}{\int d\Gamma \, e^{-\frac{K}{T} - \frac{U}{T}}}$$

$$d\Gamma = \frac{d\vec{P}_1 \dots d\vec{P}_N \, d\vec{R}_1 \dots d\vec{R}_N}{(2\pi\hbar)^{3N}}$$ phase-space element

Two difficulties in Quantum Approach:

① $\hat{\vec{P}}_i$ become operators, do not commute with $\vec{R}_i$

② $\hat{K} = \sum_i \hat{P}_i^2 / 2M_i$, $U = \sum_{i \neq j} U(\vec{R}_i - \vec{R}_j)$

$$[\hat{K}, U] \neq 0$$

$$e^{-\frac{\hat{K}}{T} - \frac{U}{T}} \neq e^{-\frac{\hat{K}}{T}} \cdot e^{-\frac{U}{T}}$$

Recipe: use exact QM energies E_i and QM eigenstates $|i\rangle$

$$\langle \dots \rangle = \frac{1}{Z} \sum_i \langle i | \dots | i \rangle \exp(-E_i / T)$$

$$Z = \sum_i \exp(-E_i / T)$$ statistical sum

Partition Function

$Z = Z(T)$ contains <u>all</u> information about thermodynamics of the system

fundamentally important!

Free energy $F = F(T, V) = -T \ln Z$

Internal energy $U = U(S, V)$ — ?

entropy

$F = U - T \cdot S$ $\quad dF = -S \cdot dT - P \cdot dV$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V$$

$$U = F - T\left(\frac{\partial F}{\partial T}\right)_V$$

$$U = -T \ln Z + T \frac{\partial}{\partial T}(T \ln Z)$$

$$U = T^2 \frac{\partial \ln Z}{\partial T} = \boxed{-\frac{\partial \ln Z}{\partial \beta}}$$

$\beta = \frac{1}{T}$

$Z(T)$ for a single oscillator

$$Z = \sum_{n=0}^{\infty} \exp\left(-\frac{\hbar\omega_0[n+1/2]}{T}\right)$$

$$Z = e^{-\frac{\hbar\omega_0}{2T}} \cdot \sum_{n=0}^{\infty} e^{-\frac{\hbar\omega_0}{T}\cdot n} =$$

$$= e^{-\frac{\hbar\omega_0}{2T}} \cdot \left\{ 1 + e^{-\frac{\hbar\omega_0}{T}} + e^{-2\frac{\hbar\omega_0}{T}} + \dots \right\}$$

geometric progression

$$= e^{-\frac{\hbar\omega_0}{2T}} \cdot \frac{1}{1 - e^{-\frac{\hbar\omega_0}{T}}}$$

$$Z(T) = \frac{1}{e^{+\frac{\hbar\omega_0}{2T}} - e^{-\frac{\hbar\omega_0}{2T}}} = \frac{1}{2\,\mathrm{sh}\left(\frac{\hbar\omega_0}{2T}\right)}$$

(Mean) thermal energy

$$U = -\frac{\partial \ln Z}{\partial \beta} \qquad \beta = 1/T$$

$$-\ln Z = \ln 2 + \ln\left[\mathrm{sh}\left(\frac{\hbar\omega_0}{2}\cdot\beta\right)\right]$$

$$-\frac{\partial \ln Z}{\partial \beta} = \frac{1}{2}\hbar\omega_0 \frac{\partial}{\partial x}\ln(\mathrm{sh}\,x) = \frac{1}{2}\hbar\omega_0 \frac{\mathrm{ch}\,x}{\mathrm{sh}\,x}$$

$$x = \frac{1}{2}\hbar\omega_0 \cdot \beta$$

$$\boxed{U = \frac{1}{2}\hbar\omega_0 \,\mathrm{cth}\left(\frac{\hbar\omega_0}{2T}\right)}$$

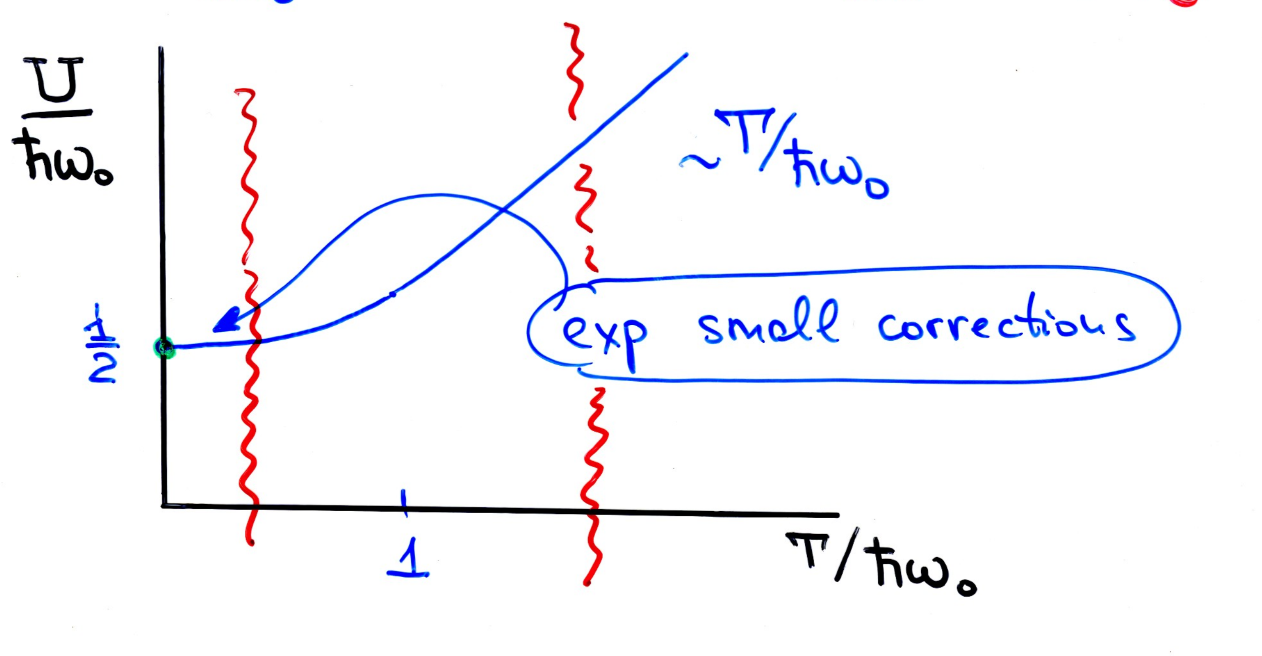
Another representation:

$$\boxed{U = \hbar\omega_0\left[\frac{1}{2} + \langle n \rangle\right]}$$

Bose-Einstein distribution function

$$\langle n \rangle = \frac{1}{\exp\left(\frac{\hbar\omega_0}{T}\right) - 1}$$

$$\langle n \rangle = \begin{cases} \exp\left(-\frac{\hbar\omega_0}{T}\right) \ll 1, & T \ll \hbar\omega_0 \text{ quantum regime} \\ \frac{T}{\hbar\omega_0} \gg 1, & T \gg \hbar\omega_0 \text{ classical regime} \end{cases}$$

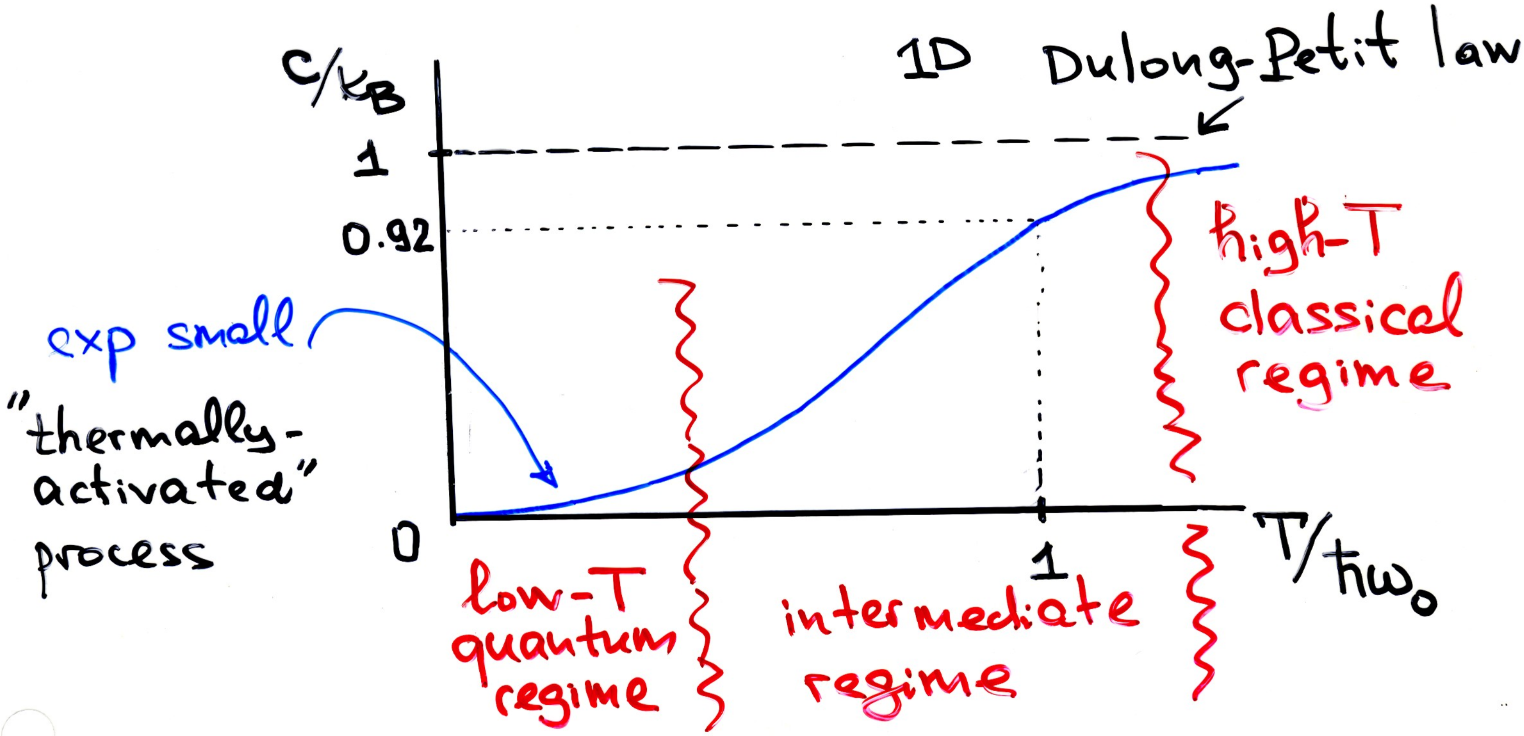


Specific heat/per one oscillator/

$$C = \frac{\partial U}{\partial T} = \frac{\partial}{\partial T}\left(\hbar\omega_0 \frac{1}{e^{\frac{\hbar\omega_0}{T}}-1}\right)$$

$$C = \left(\frac{\hbar\omega_0}{T}\right)^2 \frac{\exp(\hbar\omega_0/T)}{\left[\exp(\hbar\omega_0/T)-1\right]^2}$$

$$C = \begin{cases} 1 - \frac{1}{12}\cdot\left(\frac{\hbar\omega_0}{T}\right)^2, & T \gg \hbar\omega_0 \\ \left(\frac{\hbar\omega_0}{T}\right)^2 e^{-\frac{\hbar\omega_0}{T}}\left[1+2e^{-\frac{\hbar\omega_0}{T}}+\dots\right], & T \ll \hbar\omega_0 \end{cases}$$



3D Crystal vibrations: 3N normal modes

$\equiv$ 3N independent oscillators

with eigenfrequencies $\omega_s(\vec{k})$

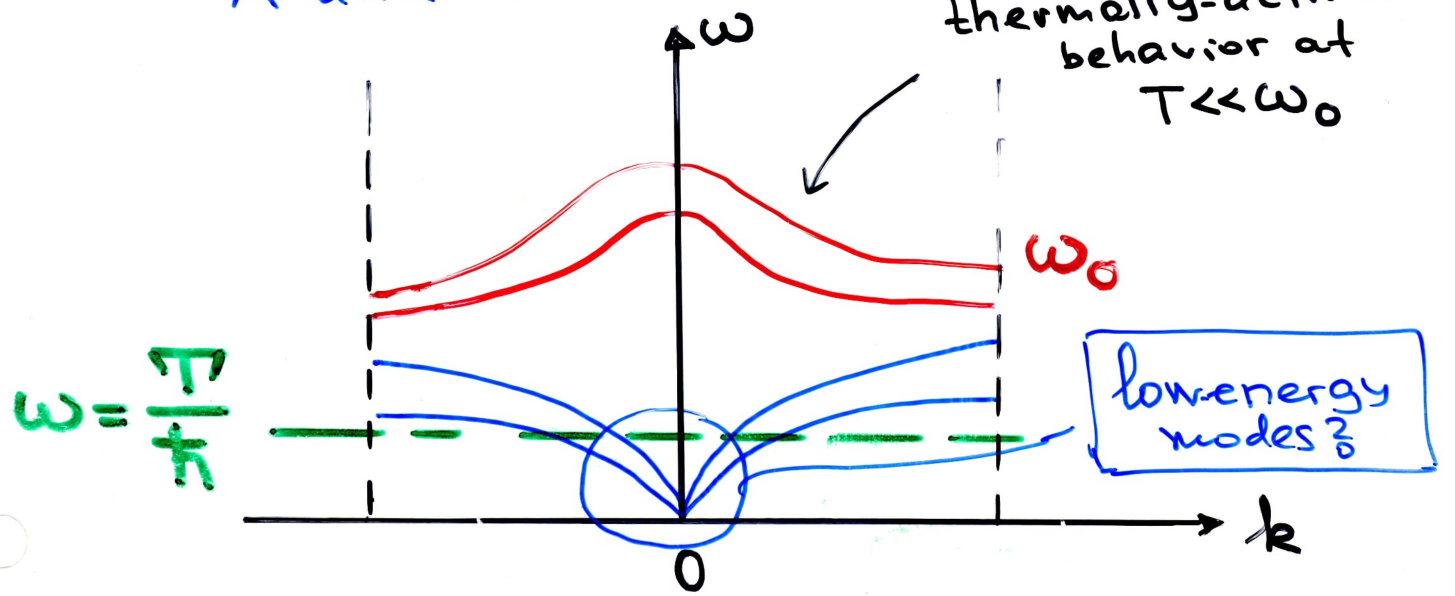
$$U = \sum_{s=1}^{3p} \sum_{\vec{k} \in BZ} \hbar\omega_s(\vec{k}) \left[1/2 + \frac{1}{\exp\left(\frac{\hbar\omega_s(\vec{k})}{T}\right) - 1} \right]$$

Energy density $u = U/V$

Specific heat

$$C_v = \frac{1}{V} \sum_{s\vec{k}} \frac{\partial}{\partial T} \frac{\hbar\omega_s(\vec{k})}{\exp\left(\frac{\hbar\omega_s(\vec{k})}{T}\right) - 1}$$

How to deal with contributions from A and O modes?



1. At $T \ll \hbar\omega_0$ contribution of optical modes $\sim e^{-\frac{\hbar\omega_0}{T}} \ll 1$

neglect!

2. For acoustic modes

$$\omega_s(\vec{k}) \simeq c_s k \qquad [c_s = c_s(\hat{k})]$$

linearize!

3. $\vec{k} \in BZ \longrightarrow$ integrate the whole $\vec{k}$-space!

$$C_v = \frac{\partial}{\partial T} \sum_{s=1}^{3} \int \frac{d^3k}{(2\pi)^3} \cdot \frac{\hbar c_s(\hat{k}) k}{\exp\left(\frac{\hbar c_s(\hat{k}) k}{T}\right) - 1}$$

$d^3k = k^2 dk \, d\Omega(\hat{k})$ spherical coordinates

$$\frac{\hbar c_s(\hat{k}) k}{T} = x$$

$$C_v = \frac{\partial}{\partial T} \sum_{s=1}^{3} \frac{1}{(2\pi)^3} \cdot \int d\Omega \frac{T^4}{(\hbar c_s(\hat{k}))^3} \times$$

$$\times \int_0^\infty x^2 dx \frac{x}{\exp(x) - 1}$$

$$C_v = \frac{\partial}{\partial T}\left[\frac{T^4}{(\hbar c)^3} \cdot \frac{3}{2\pi^2} \cdot \int_0^\infty dx \, \frac{x^3}{e^x - 1}\right]$$

① $$\frac{1}{c^3} = \frac{1}{3}\sum_{s=1}^{3} \int \frac{d\Omega}{4\pi} \frac{1}{[c_s(\hat{k})]^3}$$ averaged speed of sound

② $$\int_0^\infty dx \, \frac{x^3}{e^x - 1} = \sum_{n=1}^{\infty} \int_0^\infty dx \, x^3 e^{-nx}$$

$$= \sum_{n=1}^{\infty} \frac{1}{n^4} \int_0^\infty dy \, y^3 e^{-y} \qquad = \sum_{n=1}^{\infty} \frac{\Gamma(4)}{n^4} = 3! \sum_{n=1}^{\infty} \frac{1}{n^4} = 6\zeta(4) =$$

$$= \frac{\pi^4}{15} \checkmark$$

$$C_v = \frac{\pi^2}{10} \frac{1}{(\hbar c)^3} \frac{\partial}{\partial T} T^4$$

$$\boxed{C_v = \frac{2\pi^2}{5} k_B \cdot \left(\frac{k_B T}{\hbar c}\right)^3 \sim T^3}$$

power-law! not exponential

quantum low-T behavior