Thermodynamics of harmonic oscillators

The harmonic oscillator is playing a crucial role in physics

Why? As soon as the energy has a minimum over some distance $\vec{r}^*$, we can expand around $r \sim r^*$

such that $E_p(\vec{r}) = E_p(r^*) + \frac{1}{2}(\vec{r}-\vec{r}^*)^2 \frac{\partial^2 E_p}{\partial r^2}\Big|_{r^*} + \dots$

The quadratic expansion provides a natural harmonic potential.

Applications : - mechanical oscillators, vibration of molecules
- vibration of solids, electronic oscillators
- Electromagnetic fields
- Etc..

I) The 1D harmonic oscillator

We met the Hamiltonian $H = \frac{1}{2} m \omega^2 q^2 + \frac{p^2}{2m}$

where q = position ; p = momentum

Classical : $Z = \frac{1}{h} \int dq \int dp \; e^{-\beta H(q,p)} = \frac{1}{\beta \hbar \omega} = \frac{T}{T_{osc}}$ with $T_{osc} = \frac{\hbar\omega}{k_B}$

$\bar{\mathcal{E}}^c = \frac{1}{2} k_B T + \frac{1}{2} k_B T = k_B T$ (equipartition thm)

$f = k_B T \ln\left(\frac{\hbar\omega}{k_B T}\right)$; etc...

All that assumes $T \gg T_{osc}$

Application : Vibration of the diatomic molecule

Quantum : The eigenenergies are $\mathcal{E}_n = \hbar\omega\left(n+\frac{1}{2}\right)$ with $n \in \mathbb{N}$

$$Z = \sum_{n=0}^{\infty} e^{-\beta \mathcal{E}_n} = e^{-\beta\hbar\omega/2} \sum_n e^{-\beta\hbar\omega n}$$

$$= \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}} = \left[2\sinh\left(\beta\frac{\hbar\omega}{2}\right)\right]^{-1}$$

$$\bar{\varepsilon}^c = -\frac{\partial \ln Z}{\partial \beta} = \frac{\hbar\omega}{2}\coth\left(\frac{\hbar\omega}{2k_BT}\right)$$

and $\coth x = \dfrac{e^x + e^{-x}}{e^x - e^{-x}} = \dfrac{e^x - e^{-x} + 2e^{-x}}{e^x - e^{-x}} = 1 + \dfrac{2}{e^{2x} - 1}$

Therefore $\bar{\varepsilon}^c = \dfrac{\hbar\omega}{2} + \dfrac{\hbar\omega}{e^{\frac{\hbar\omega}{k_BT}} - 1} = \hbar\omega\left(\bar{n}_\omega + \frac{1}{2}\right)$

where $\boxed{\bar{n}_\omega = \dfrac{1}{e^{\frac{\hbar\omega}{k_BT}} - 1}}$ Bose-factor

Average # of quanta in the oscillator

Limits : • For $T \ll \hbar\omega \Rightarrow \bar{n}_\omega \sim 0$

$\frac{5\hbar\omega}{2}$

$\frac{3\hbar\omega}{2}$ and $\bar{\varepsilon}^c \simeq \frac{\hbar\omega}{2}$ → The oscillator is in its ground state

$\frac{\hbar\omega}{2}$ ← quantum freezing

• For $T \gg \hbar\omega \Rightarrow$ we excite many levels

$$\bar{\varepsilon} = \frac{\hbar\omega}{2}\coth\left(\frac{\hbar\omega}{2k_BT}\right) \approx \frac{\hbar\omega}{2}\,\frac{1}{\frac{\hbar\omega}{2k_BT}} \approx k_BT$$

we recover the classical result!

$$C(T) = \frac{\partial \bar{\varepsilon}}{\partial T} = k_B\left(\frac{\hbar\omega}{2k_BT}\right)^2 \frac{1}{\sinh^2\left(\frac{\hbar\omega}{2k_BT}\right)}$$

with $C(T) \simeq k_B \times \begin{cases} 1 & \text{for } k_BT \gg \hbar\omega \\ \left(\frac{\hbar\omega}{2k_BT}\right)^2 e^{-\frac{\hbar\omega}{k_BT}} & \text{for } k_BT \ll \hbar\omega \end{cases}$

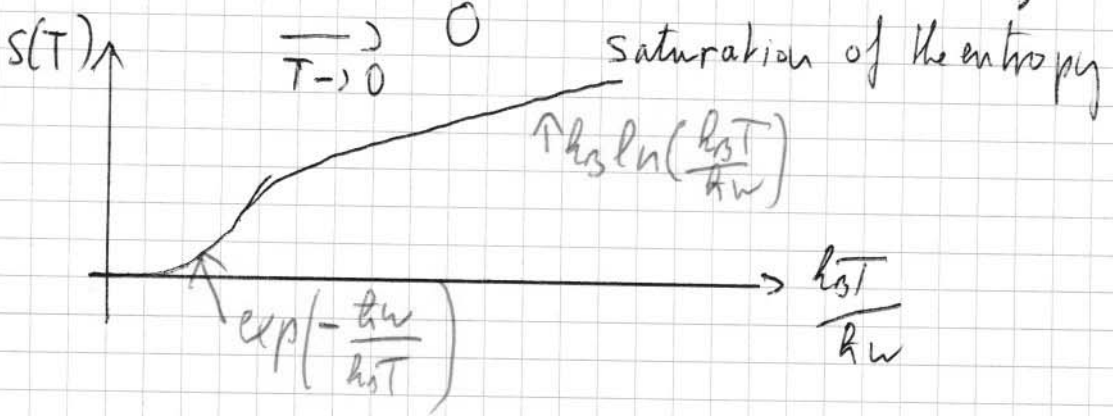
$\Delta = \hbar\omega$ At low T, $C(T) \propto \exp\left(-\dfrac{\Delta}{k_BT}\right)$ with $\Delta = \hbar\omega$

This corresponds at low T to a thermal activation factor due to the gap Δ between the ground state and 1st excited state.

$$f(T) = -k_B T \ln Z = k_B T \ln\left(2\sinh\left(\frac{\hbar\omega}{2k_B T}\right)\right)$$

$$\underset{\text{exact}}{\approx} \underbrace{\frac{\hbar\omega}{2}}_{\text{ground state}} + \underbrace{k_B T \ln\left(1 - e^{-\frac{\hbar\omega}{k_B T}}\right)}_{\text{excitation}} \xrightarrow[T\to 0]{} \frac{\hbar\omega}{2}$$

And $$s(T) = -\frac{\partial f}{\partial T} = k_B\left(\frac{\hbar\omega}{k_B T}\bar{n}_\omega - \ln\left(1 - e^{-\frac{\hbar\omega}{k_B T}}\right)\right)$$

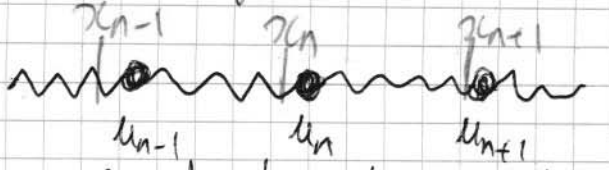


II) Vibrations in a solid

2.1) A chain of springs

At equilibrium $u_n^{(0)} = x_n = n a$

Consider N objects (atoms) related with each-other by elastic coupling



$x_n = n a$

u_n = displacement around $x_n = na$

Assumes periodic boundary condition $u_{N+1} = u_1$

Classical eq. of motion $m \frac{d^2 u_n}{dt^2} = K(u_{n+1} - u_n) + K(u_{n-1} - u_n)$

(m: mass, K: elastic constant)

set of N differential eqs

We go to Fourier space $u_n = \sum_q e^{i(q x_n - \omega t)} \tilde{u}_q$

$u_{N+1} = u_1 \Rightarrow e^{iqNa} = 1 \Rightarrow q = \frac{2\pi}{Na} j \quad j = 1, \dots, N$

$$\sum_q -m\omega^2 \tilde{u}_q e^{i(qna - \omega t)} = \sum_q K \tilde{u}_q e^{i(qna - \omega t)} \left(e^{iqa} + e^{-iqa} - 2\right)$$

$$\Rightarrow -m\omega^2 + 2K(1 - \cos(qa)) = 0$$

$$\Rightarrow \omega_q^2 = \frac{2K}{m}(1 - \cos(qa)) = \frac{4K}{m}\sin^2\left(\frac{qa}{2}\right)$$

where $q = \frac{2\pi}{Na} j$ is quantized.

We thus have N modes (acoustic modes)

Each mode describes a vibration at a specific frequency

At low q $\omega_q \underset{q \to 0}{\sim} 2\sqrt{\frac{K}{m}}\,(qa) = \omega_0 (qa)$

$\omega_0 = c_s q$

where $c_s = a\omega_0$ sound velocity

Quantum treatment

$$\hat{H} = \sum_{\ell=1}^{N} \left(\frac{\hat{p}_\ell^2}{2m} + \frac{k}{2} \left(\hat{u}_{\ell+1} - \hat{u}_\ell \right)^2 \right)$$

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

Again we Fourier transform $\begin{cases} \hat{u}_\ell = \frac{1}{\sqrt{N}} \sum_q e^{iq\ell a}\, \hat{u}_q \\ \hat{p}_\ell = \frac{1}{\sqrt{N}} \sum_q e^{iq\ell a}\, \hat{p}_q \end{cases}$

Periodic boundary condit° : $q = \frac{2\pi}{L} j$ with $j = 1, \dots, N$

and here $L = Na$

check that $[\hat{u}_q, \hat{p}_{q'}] = i\hbar\, \delta_{q,q'}$

$$\begin{cases} u_q^\dagger = u_{-q} \\ p_q^\dagger = p_{-q} \end{cases}$$

After algebra (parseval-plancherel) $\hat{H} = \sum_q \left[\frac{\hat{p}_q^\dagger \hat{p}_q}{2m} + \frac{1}{2} m \omega_q^2 u_q^\dagger u_q \right]$

where $\omega_q = 2\sqrt{\frac{k}{m}} \left| \sin\left(\frac{qa}{2}\right) \right|$

(Here we used $\sum_\ell e^{i Q \cdot \ell a} = N \delta_{Q,0}$

Again in Fourier space, $\hat{H}$ describes a collection of

N <u>independent</u> modes

2.2 Energy of a solid

$$H_{solid} = H_{ions} + H_{el}$$

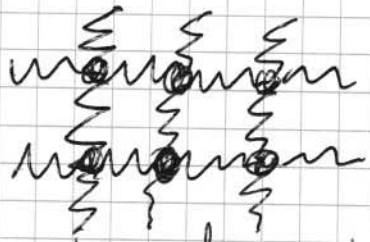
Since electrons are fast, we again use the Born-Oppenheimer approx $\Rightarrow$ decoupling of time scales. An atom will be seen as a "ball"

Consider N atoms on a lattice

$$H_{vib} = \underbrace{\sum_{a=1}^{N} \frac{\vec{p}_a^{\,2}}{2m}}_{\text{kinetic}} + \underbrace{\frac{1}{2} m\omega_0^2 \sum_{\langle a,b \rangle} (\vec{r}_a - \vec{r}_b)^2}_{\text{bonding energy due to electrons exchang}}$$

$\langle a,b \rangle \rightarrow$ means nearest neighbour

Here we treat the interactions between atoms as springs



If we denote the position of one atom by $\vec{r}_i = (x, y, z)$ we have $3N$ spatial ∞ of freedom

We can always write the bonding term H_{bond} as

$$H_{bond} = \frac{1}{2m} \underbrace{\left(\cdots x_i\, y_i\, z_i \cdots \right)}_{3N \text{ vector}} \hat{\Omega} \underbrace{\begin{pmatrix} \ddots & & \\ & x_i & \\ & y_i & \\ & z_i & \\ & & \ddots \end{pmatrix}}_{3N \times 3N \text{ symetric matrix}}$$

We can always diagonalize the $\mathcal{R}$ matrix

This is what we did for the 1D periodic chain by going in Fourier space. ⇒ We do the same here.

we obtain for the bonding Hamiltonian

$$H = \sum_{k} \sum_{\lambda} \left[\frac{\hat{p}_{k,\lambda}^2}{2m} + \frac{1}{2} m \omega_{k,\lambda}^2 \hat{q}_{k,\lambda}^2 \right]$$

where $k \sim \frac{2\pi}{L} j$ and $\lambda = x, y, z$

≈> A collection of $3N$ modes ($3N$ harmonic oscillators)

Notice that the kinetic term is unaffected (we rewrite it in Fourier space)

Because N is large ($N \sim \mathcal{N}_A$), we often introduce

$$\boxed{g(\omega) = \sum_{i} \delta(\omega - \omega_i)} \Rightarrow \underline{\text{classical quantity}}$$

spectral density of modes

$g(\omega)\, d\omega$ = # of modes between ω and $\omega + d\omega$

Because we have $3N$ d° of freedom (spatial)

$$\int_0^{+\infty} g(\omega)\, d\omega = 3N$$

- At low frequency or low q, $\omega_k \sim c_s k$

The frequency spectrum is such that

$$\omega \in \left[0, \omega_{max} \sim \frac{\pi c_s}{a} \right]$$

a ← average distance between 2 neighbors

Let us estimate the behaviour of $g(\omega)$ at low energy

$$g(\omega) = 3 \sum_{k} \delta(\omega - \omega_k) \simeq 3V \int \frac{d^3\vec{k}}{(2\pi)^3} \delta(\omega - \omega_k)$$

↑ 3 modes (isotropic)

Assumes $\omega_k \sim c_s k$

then $$g(\omega) \simeq 3V \int \frac{d^3k}{(2\pi)^3} \delta(\omega - c_s k)$$

$$g(\omega) = \frac{3V}{2\pi^2} \frac{\omega^2}{c_s^3}$$

At low energy, all the complexity is encoded into c_s

RQ: For anisotropic crystal, we define $\frac{3}{c_s^2} = \frac{1}{c_L^2} + \frac{2}{c_\perp^2}$

3 modes = 2 transverse modes + 1 longitudinal mode

At low T, these modes are quantized

$$E_{\{n_i\}} = \sum_{i} \hbar \omega_i \left(n_i + \frac{1}{2}\right)$$

↑ 3N modes

They are called phonons

2.3 Thermodynamics of a solid

We have a collection of $3N$ independent oscillators

$$Z_{vib} = \prod_{i=1}^{3N} z_i \quad \text{where } z_i = \left[2\sinh\left(\frac{\beta\hbar\omega_i}{2}\right)\right]^{-1}$$

$$\overline{E_{vib}} = \sum_{i=1}^{3N}\left(\frac{\hbar\omega_i}{2} + \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i}-1}\right)$$

$$\simeq \int_0^{\omega_{max}} d\omega\, g(\omega)\left(\frac{\hbar\omega}{2} + \hbar\omega\,\overline{n_\omega}\right)$$

↑ Bose factor

Ground state energy → $E_0 = \int_0^{\omega_{max}} d\omega\, g(\omega)\frac{\hbar\omega}{2}$

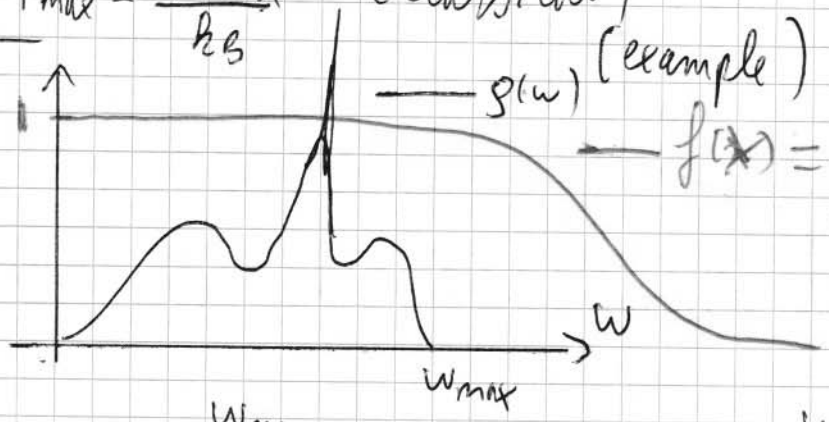
Eccitat° energy → $E_{exc} = \int_0^{\omega_{max}} d\omega\, g(\omega)\,\hbar\omega\,\overline{n_\omega}$

$$C_v = \frac{\partial \overline{E_{vib}}}{\partial T} = k_B\int_0^{\omega_{max}} d\omega\, g(\omega)\,\hbar\omega\,\frac{\partial \overline{n_\omega}}{\partial T}$$

$$= k_B\int_0^{\omega_{max}} d\omega\, g(\omega)\left(\frac{\hbar\omega}{2k_BT}\right)^2\frac{1}{\sinh^2\left(\frac{\hbar\omega}{2k_BT}\right)}$$

We met two situations

* If $T \gg T_{max} = \frac{\hbar\omega_{max}}{k_B}$ (classical)

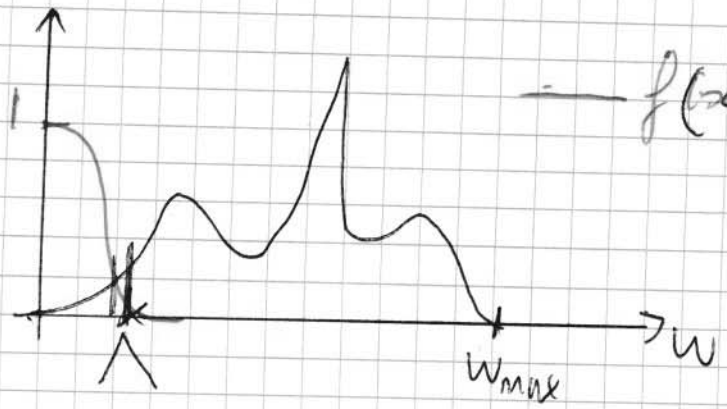


Then $C_v = k_B\int_0^{\omega_{max}} d\omega\, g(\omega)\, f\left(\frac{\hbar\omega}{2k_BT}\right) \simeq k_B\int_0^{\omega_{max}} d\omega\, g(\omega) = 3Nk_B$

⇒ Dulong-Petit law

$$C_v(T) \simeq k_B\,\frac{2\pi^2}{5}V\left(\frac{k_BT}{\hbar c}\right)^3$$

If $T \ll T_{max}$



$$C_v \simeq k_B \int_0^{\Lambda} d\omega\, g(\omega)\, f\left(\frac{\hbar\omega}{2k_B T}\right)$$

where $\Lambda \ll \omega_{max}$

In this low range of frequency $g(\omega) \sim \frac{3V\omega^2}{2\pi^2 c_s^3}$

Therefore $C_v(T) \simeq k_B \frac{3V}{2\pi^2 c_s^3} \int_0^{\Lambda} d\omega\, \omega^2 f\left(\frac{\hbar\omega}{2k_B T}\right)$

$$\simeq k_B \left(\frac{2k_B T}{\hbar}\right)^3 \frac{3V}{2\pi^2 c_s^3} \int_0^{\frac{\hbar\Lambda}{2k_B T}} dx^2 f(x)\, dx$$

$$\int_0^{\frac{\hbar\Lambda}{2k_B T}} dx\, x^2 f(x) \triangleq \int_0^{+\infty} dx\, \frac{x^4}{\sinh^2 x} = \frac{\pi^4}{30}$$

$$C_v(T) \simeq k_B \frac{2\pi^2}{5} V \left(\frac{k_B T}{\hbar c_s}\right)^3 \quad \text{for } k_B T \ll \hbar\omega_{max}$$

This is well verified experimentally

* How to understand $C_v \sim (k_B T)^3$ or equivalently $E \sim (k_B T)^4$?

At low T, only the modes such that $\hbar\omega \lesssim k_B T$ are excited

The excitation energy of these modes is

$$E_{exc} \sim \int_0^{k_B T/\hbar} d\omega\, g(\omega)\, \hbar\omega \propto \int_0^{\frac{k_B T}{\hbar}} d\omega\, \omega^2\, \hbar\omega$$

$$\propto (k_B T)^4$$

This should be contrasted with $C_v \sim e^{-\frac{\Delta}{k_B T}}$

The point is that we have a continuum of excitations without any gap Δ $\quad C_v(T) \propto T^3 \neq e^{-\hbar\omega/k_B T}$

Order of magnitude: For Al: $\frac{\hbar\omega_{max}}{k_B} \simeq 430K \rightarrow$ case (2) quantum behaviour

For Pb: $\frac{\hbar\omega_{max}}{k_B} = 100K \rightarrow$ case (1) classical behaviour

RQ: $F(T,V) = E_{vide} + k_B T \underbrace{\int_0^{\omega_{max}} d\omega\, g(\omega) \ln\left(1 - e^{-\hbar\omega/k_B T}\right)}$

Free energy of the phonon gas

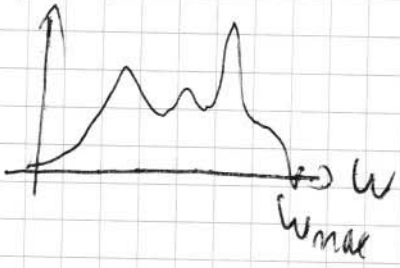
Phonons are excitations energies → no mass

The free energy is independent of their number $\mu = \frac{\partial F}{\partial N} = 0$

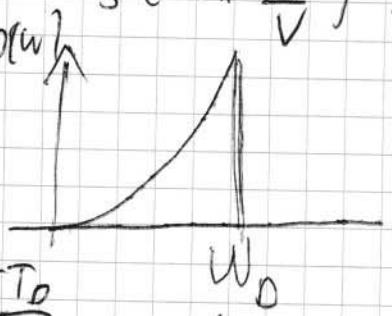
Debye model: Debye assumed $g(\omega) = \frac{3V}{2\pi^2 c_s^3}\omega^2$ everywhere for $\omega \leq \omega_D$

ω_D = Debye frequency such that $\int_0^{\omega_D} g(\omega)\,d\omega = 3N$

$\Rightarrow \omega_D = c_s\left(6\pi^2 \frac{N}{V}\right)^{1/3} \Rightarrow T_D = \frac{\hbar\omega_D}{k_B}$



Debye model



$$C_v(T) = 3N k_B \left(\frac{\pi}{T_D}\right)^3 \int_0^{\frac{T_D}{2T}} dx\, \frac{3x^4}{\sinh^2 x} \simeq \frac{12\pi^4}{5} N k_B \left(\frac{T}{T_D}\right)^3$$

Z	solid	T_D	$\hbar\omega_{max}/k_B = T_m$
6	Carbon	1860	—
13	Al	394	430
29	Cu	315	—
46	Pd	88	100
47	Ag	215	—

$\Rightarrow$ A piece of carbon at room T is described by the Quantum behaviour