Thermodynamic of harmonic oscillator

I) Lattice vibrat° in a solid

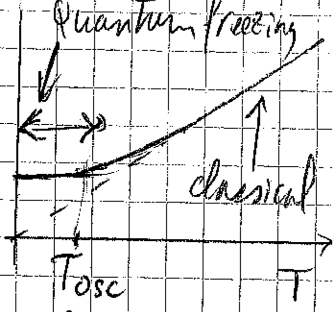
A) Preliminary $\Rightarrow \quad \varepsilon_n = \hbar w\left(n+\frac{1}{2}\right)$

1) $z = \sum_{n=0}^{\infty} e^{-\beta\varepsilon_n} = \dfrac{1}{2\sinh\left(\frac{\beta\hbar w}{2}\right)} \Rightarrow$

2) $\overline{\varepsilon^c} = -\dfrac{\partial \ln z}{\partial\beta} = \dfrac{\hbar w}{2}\coth\left(\dfrac{\beta\hbar w}{2}\right) = \hbar w\left(\overline{n^c}+\frac{1}{2}\right)$

where $\overline{n^c} = \dfrac{1}{e^{\beta\hbar w}-1}$

When $T \to 0$, $\overline{n^c} \to 0$; therefore $\overline{\varepsilon^c} \xrightarrow[T\to 0]{} \dfrac{\hbar w}{2}$



Define $\boxed{T_{osc} = \dfrac{\hbar w}{k_B}}$; For $T \lesssim T_{osc}$

the oscillator is in its ground state $\Rightarrow$ frozen

3) $C_V(T) = \dfrac{\partial\overline{\varepsilon^c}}{\partial T} = k_B\left(\dfrac{\hbar w}{2k_BT}\right)^2 \dfrac{1}{\sinh^2\left(\frac{\beta\hbar w}{2}\right)} = k_B\left(\underbrace{\sinh c}_{\frac{\sinh x}{x}}\left(\dfrac{\beta\hbar w}{2}\right)\right)^{-2}$

$$\frac{C_V(T)}{k_b} = \begin{cases} 1 & \text{if } T \gg T_{osc} \\ \left(\dfrac{\hbar w}{k_BT}\right)^2 e^{-\frac{\hbar w}{k_BT}} & \text{if } T \ll T_{osc} \end{cases}$$

$\rightarrow$ The $e^{-\frac{\hbar w}{kT}}$ is characteristic of a gap in the spectrum

B) Einstein model (1907)

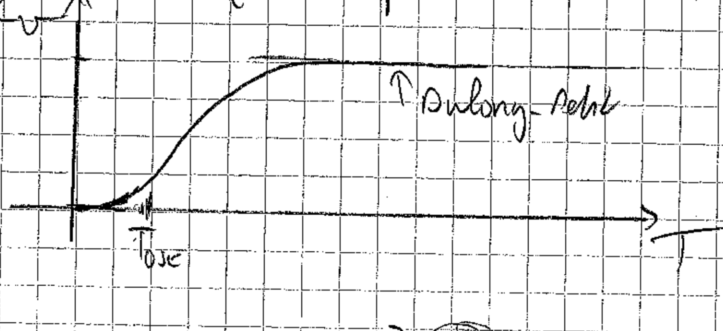
1) Solid of N atoms. Each atom can vibrate around its position

$\Rightarrow H = \sum_{j=1}^{3N}\left(\dfrac{p_j^2}{2m} + \dfrac{1}{2}m w^2 q_j^2\right) \rightarrow 3N$ independent $\delta°$ of freedom

$\Rightarrow$ distinguishable $\Rightarrow Z = z^{3N}$

2) $\overline{E^c} = 3N\,\overline{\varepsilon^c} \Rightarrow C_V = 3Nk_B \operatorname{sinhc}^{-2}\left(\dfrac{\beta\hbar w}{2}\right) \xrightarrow[\beta\to 0]{} 3Nk_B \Rightarrow$ equipartit° thm

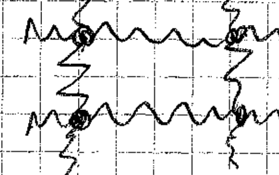
Ahh



3) high T $\rightarrow$ OK

low T, the experiment finds $C_V \simeq aT + bT^3 \neq C_V^{\text{Einstein}}$ $\rightarrow$ bad

c) The Debye model (1912)



Atoms are now coupled $\Rightarrow$ 3N coupled harmonic oscillators

$\hookrightarrow$ diagonalize the quadratic form

$$H=\sum_{i=1}^{3N}\left(\frac{p_i^2}{2m}+\frac{1}{2}m\omega_i^2 q_i^2\right)$$

The $\{\omega_i\}$ form a $\leq$ spectrum $\rightarrow$ spectral density $\rho(\omega)=\sum_i \delta(\omega-\omega_i)$

1) $$C_V^{Debye}(T)=k_B\sum_{i=1}^{3N}\sinh c^{-2}\left(\frac{\hbar\omega_i}{2k_BT}\right)$$

$$=k_B\int_0^{\omega_D} d\omega\,\rho(\omega)\,\sinh c^{-2}\left(\frac{\hbar\omega}{2kT}\right)$$ where $\rho(\omega)$

2) a) ω_D = maximum frequency associate to the shorter length scale $= a \sim \mathcal{O}(\mathring{A})$

$$\omega_D\sim\frac{c_s}{a}$$

b) $\int_0^{\omega_D} d\omega\,\rho(\omega)=3N$

c) $\omega_{\vec{k}}$ = dispersion relat° where $\vec{k}$ = wave vector

$\vec{k}$ belongs to the 1st Brillouin zone

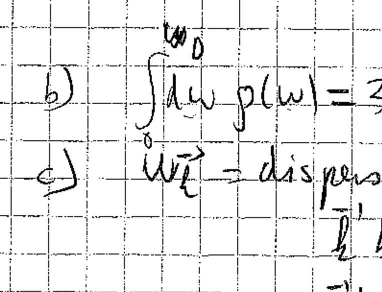
$\omega_{\vec{k}} \underset{k\to 0}{\simeq} c_s|\vec{k}|$: 3 acoustic modes (in the long wavelength limit $k\to 0$).

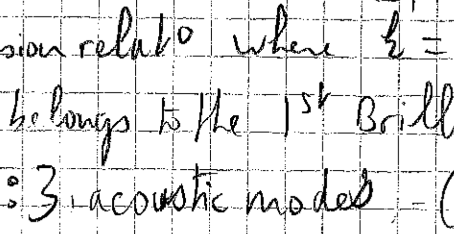
There is typically one longitudinal mode with $c_{/\!/}$ and two transverse modes — $c_\perp$ assume $c_{/\!/}\sim c_\perp\sim c_s$

$$\rho(\omega)\simeq 3\sum_{\vec{k}}\delta(\omega-\omega_{\vec{k}})\simeq 3\sum_{\vec{k}}\delta(\omega-c_s|\vec{k}|)$$

$$\simeq 3V\int\frac{d^3\vec{k}}{(2\pi)^3}\,\delta(\omega-c_s|\vec{k}|)=\frac{3V}{2\pi^2}\frac{\omega^2}{c_s^3}$$

for $\omega\in[0,\omega_D]$



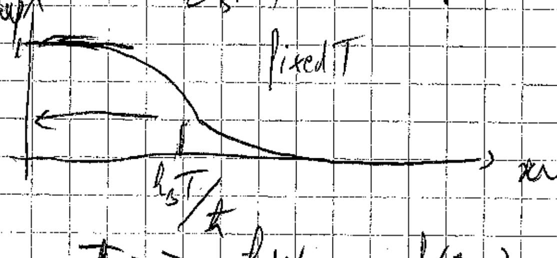


Sum rule $\int_0^{\omega_D} d\omega\,\rho(\omega)=3N \Rightarrow \frac{3V}{2\pi^2}\frac{\omega_D^3}{3c_s^3}=3N$

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

3) $C_v(T) = k_B \int_0^{\omega_D} d\omega\, g(\omega)\, f\left(\frac{\hbar\omega}{2k_BT}\right)$ where $f(x) = \frac{x^2}{\sinh^2(x)}$

a)



At $\frac{\hbar\omega_D}{2k_BT} \ll 1 \Leftrightarrow T \gg \frac{\hbar\omega_D}{2k_B}$ $\quad f(x) \sim 1$

then $C_v(T) \simeq k_B \int_0^{\omega_D} d\omega\, g(\omega) = 3Nk_B$

→ recover Dulong-Petit.

b) Low T $\Rightarrow f\left(\frac{\hbar\omega}{2k_BT}\right)$ selects frequencies such that $\omega \lesssim \frac{k_BT}{\hbar}$

Therefore, the smaller T, the smaller the frequencies are!

Therefore the better the Debye approx should work.

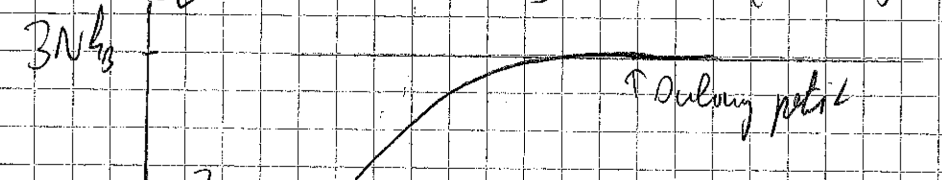
$$C_v(T) \approx k_B \frac{3V}{2\pi^2 c_s^3} \int_0 d\omega\, \frac{\omega^2}{\sinh^2\left(\frac{\hbar\omega}{2k_BT}\right)} \left(\frac{\hbar\omega}{2k_BT}\right)^2$$

$$\simeq k_B \left(\frac{2k_BT}{\hbar}\right)^3 \frac{3V}{2\pi^2 c_s^3} \underbrace{\int_0^{\frac{\hbar\omega_D}{2k_BT}} dx\, x^4 \sinh^{-2}(x)}_{\sim \underbrace{\int_0^{+\infty} dx\, x^4 \sinh^{-2}(x)}_{\frac{\pi^4}{30}}}$$

$$\text{Therefore } C_v(T) \underset{T \ll \frac{\hbar\omega_D}{k_B}}{\simeq} \frac{2\pi^2}{5} k_B V \left(\frac{k_BT}{\hbar c_s}\right)^3$$

$$= \frac{12\pi^4}{5} N k_B \left(\frac{k_BT}{\hbar\omega_D}\right)^3$$

$C_v \sim T^3$



- Einstein model → gap in the spectrum → exp. activated behaviour
- Debye model → Continuous spectrum

At finite T, $E(T) \sim$ (energy available) × (# d° of freedom)

$(k_BT) \times \left(\int_0^T d\omega\, g(\omega)\right) \sim (k_BT)^4$

7.2) Thermodynamics of electromagnetic radiation

1) $\rho(\omega) = \sum_{\vec{k}} 2\, \delta(\omega - \|\vec{k}\|c) = 2V \int \frac{d^3k}{(2\pi)^3}\, \delta(\omega - |\vec{k}|c)$

2 ← polarisat°

$(\vec{k}, \sigma)$: $\vec{k}$ wave vector, $\sigma = \pm$ polarisat°

$$\boxed{\rho(\omega) = \frac{V\omega^2}{\pi^2 c^3}}$$

2) One oscillator → $\varepsilon_n = \hbar\omega(n+\frac{1}{2})$

Here $\overline{E^c_{em}} = \sum_{\vec{k},\sigma} \hbar\omega_{\vec{k}} \left(\overline{n_{\omega_k}} + \frac{1}{2}\right)$

where $\overline{n_{\omega_k}} = \frac{1}{e^{\beta\hbar\omega_k} - 1}$

At low enough T $\overline{n_{\omega_k}} \overset{T \to 0}{=} 0$

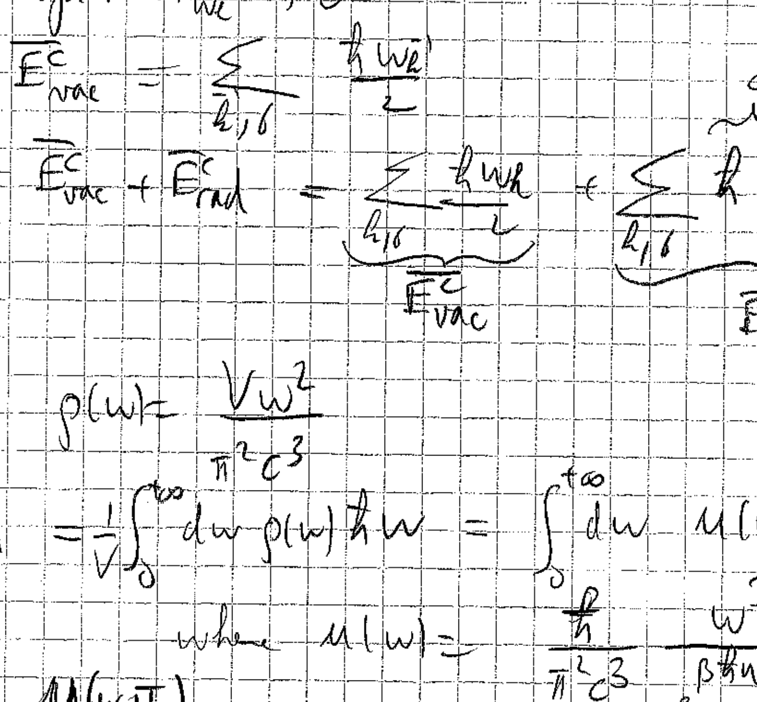
$\hookrightarrow \overline{E^c_{vac}} = \sum_{\vec{k},\sigma} \frac{\hbar\omega_k}{2}$

3) $\overline{E^c_{e\text{-}m}} = \overline{E^c_{vac}} + \overline{E^c_{rad}} = \underbrace{\sum_{k,\sigma} \frac{\hbar\omega_k}{2}}_{\overline{E^c_{vac}}} + \underbrace{\sum_{k,\sigma} \hbar\omega_k \overbrace{\overline{n_{\omega_k}}}^{\text{contribut° from one mode}}}_{\overline{E^c_{rad}}}$

4) See 1) $\rho(\omega) = \frac{V\omega^2}{\pi^2 c^3}$

5) $\frac{1}{V}\overline{E^c_{rad}} = \frac{1}{V}\int_0^{+\infty} d\omega\, \rho(\omega)\hbar\omega = \int_0^{+\infty} d\omega\, u(\omega)$

$$\boxed{\text{where } u(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1}}$$ Planck law spectral energy density



$\omega_M \sim 2.82 \cdot \frac{k_B T}{\hbar}$

6) Photon density $n_\gamma(T)$

$n_\gamma(T) = \frac{1}{V}\int_0^\infty \overline{n_\omega}\, \rho(\omega)\, d\omega = \frac{1}{\pi^2 c^3} \int d\omega\, \omega^2 \frac{1}{e^{\beta\hbar\omega} - 1}$

$= \frac{1}{\pi^2 c^3}\left(\frac{k_B T}{\hbar}\right)^3 \int_0^{+\infty} dx \frac{x^2}{e^x - 1} = \frac{2\zeta(3)}{\pi^2}\left(\frac{k_B T}{\hbar c}\right)^3$

5

$$\Rightarrow \boxed{n_\gamma(T) = \frac{2\zeta(3)}{\pi^2}\left(\frac{k_B T}{\hbar c}\right)^3}$$

Energy density: $u_{tot}(T) = \frac{1}{V}\int_0^{+\infty} d\omega\, \hbar\omega\, \rho(\omega)\, \bar{n}_\omega$

$$= \frac{\hbar}{\pi^2 c^3}\left(\frac{k_B T}{\hbar}\right)^4 \underbrace{\int_0^{+\infty} dx\, \frac{x^3}{e^x - 1}}_{\Gamma(4)\zeta(4) = 6\zeta(4) = \frac{\pi^4}{15}}$$

$$u_{tot}(T) = \frac{\pi^2}{15}\frac{(k_B T)^4}{(\hbar c)^3}$$ Stefan-Boltzmann law!

B) Cosmic microwave background radiation

1) $t_0 \simeq 14 \times 10^9$ years, $T = 2.725\,K$

$$n_\gamma(T) = \frac{2 \times 1.202}{\pi^2} \times \left(\frac{1.38\,10^{-23} \times 2.725}{10^{-34} \times 3\,10^8}\right)^3 \simeq 0.47\,10^9\, m^{-3}$$

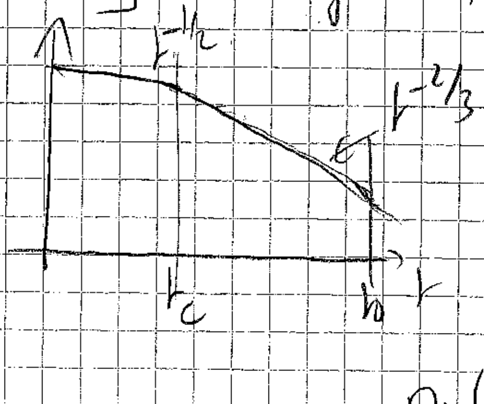
$n_\gamma \simeq 0.5\, mm^{-3}$

$$u_{tot}(T) = \frac{\pi^2}{15}\frac{(1.38\,10^{-23} \times 2.725)^4}{(10^{-34} \times 3.10^8)^3} \text{ in } J\,m^{-3}$$

$$= \frac{\pi^2}{15}\frac{(1.38 \times 2.725)^4}{3^3 \times 1.6}\cdot 10^5 \text{ in } eV\,m^{-3}$$

$$= 2.93\,10^5\, eV\,m^{-3} \simeq 0.3\, eV\,cm^{-3}$$

2) Dark ages $T(t) \propto t^{-2/3}$



$t_c = 380 \times 10^3$ years

$t_0 = 14 \times 10^9$ years

$$T(t_c) = \left(\frac{14 \times 10^9}{380\,10^3}\right)^{2/3} \times 2.725 \simeq 3000\,K$$

$$n_\gamma(t_c) \simeq 0.5\,10^9 \times \left(\frac{3000}{2.725}\right)^3 \simeq 0.7\,10^{18}\, m^{-3} = 0.7\,(\mu m)^{-3}$$

$$u_{tot}(t_c) \simeq 2.93\,10^5 \times \left(\frac{3000}{2.725}\right)^4 \simeq 0.45\,10^{18}\, eV\,m^{-3}$$

$$\simeq 0.45\, eV\,(\mu m)^{-3}$$

$\sim$ comparable to the sun

7.3) Equilibrium between light and matter

1) Atom: $\hbar\omega_0$, $|e\rangle$, $|g\rangle$ $\longleftrightarrow$ thermal radiation

$A_{e\to g}$ (spontaneous emission)

or $A_{e\to g} + B_{e\to g} I(\omega_0)$

spontaneous + stimulated emission

$B_{g\to e} I(\omega_0)$ (absorption)

a) $P_g(t)$ probability for an atom to be in the ground state

$P_e(t)$ ——— excited state.

$$\Rightarrow P_g(t) + P_e(t) = 1$$

$$\frac{dP_e(t)}{dt} = -\frac{dP_g(t)}{dt} = -\left[A_{e\to g} + B_{e\to g} I(\omega_0)\right] P_e(t) + B_{g\to e} I(\omega_0) P_g(t)$$

b) equilibrium $P_e \times \left(A_{e\to g} + B_{e\to g} I(\omega_0)\right) = B_{g\to e} I(\omega_0) P_g$

2) $\frac{P_e^{eq}}{P_g^{eq}} = e^{-\beta\hbar\omega_0}$ (canonical distributⁿ)

3) $u(\omega, T) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1} \Rightarrow$ Assume $I(\omega_0) = u(\omega_0, T)$

4) a) $k_B T \gg \hbar\omega_0 \hookrightarrow u(\omega_0, T) \simeq \frac{\omega_0^2}{\pi^2 c^3}(k_B T)$

and $P_e^{eq} \simeq P_g^{eq}$

$\left[A_{e\to g} + B_{e\to g} I(\omega_0 T)\right] = B_{g\to e} I(\omega_0)$

$\underline{kT \gg \hbar\omega_0}$

Therefore $B_{e\to g} I(\omega_0 T) = B_{g\to e} I(\omega_0 T)$

$$\Rightarrow \underline{B_{e\to g} \simeq B_{g\to e}} \;||$$

b) $P_e\left(A + B u(\omega_0 T)\right) = B u(\omega_0 T) P_g$

$$A + B u(\omega_0 T) = B u(\;)\, e^{\beta \omega_0}$$

$$A = B u(\omega_0 T)\left(e^{\beta\omega_0} - 1\right) \simeq B \frac{\hbar \omega_0^3}{\pi^2 c^3} \Rightarrow \underline{\frac{A}{B} \propto \omega_0^3} \;||$$

c) The larger the frequency, the $\underline{\text{larger } A \text{ is}}$: Dominated by $\underline{\text{Spontaneous emission}}$

MASER → μ wave $O(1\text{ meV}) \sim O(\text{GHz})$

LASER → optical $O(\text{eV}) \sim O(\text{THz})$.