

5. Applications of the canonical ensemble

In this section we present various applications of the canonical ensemble in Statistical Physics.

I. Ideal monatomic gas and Gibbs paradox

We consider the ideal monatomic gas as a classical system so that the partition function for the $N = \text{fixed}$ molecules is

$$\tilde{Z} = \int e^{-\beta E} \frac{d^3 \vec{r}_1 \cdots d^3 \vec{r}_N d^3 \vec{p}_1 \cdots d^3 \vec{p}_N}{h_0^{3N}}$$

with

$$E = \sum_{i=1}^N \frac{|\vec{p}_i|^2}{2m} + U(\vec{r}_1, \dots, \vec{r}_N)$$

Therefore

$$\tilde{Z} = \frac{1}{h_0^{3N}} \int e^{-\frac{\beta}{2m} |\vec{p}_1|^2} d^3 \vec{p}_1 \cdots \int e^{-\frac{\beta}{2m} |\vec{p}_N|^2} d^3 \vec{p}_N \int e^{-\beta U(\vec{r}_1, \dots, \vec{r}_N)} d^3 \vec{r}_1 \cdots d^3 \vec{r}_N$$

↑
complicated in general

If $U = 0$ (diluted) or $U = \begin{cases} 0 & (\text{inside box}) \\ \infty & (\text{outside box}) \end{cases}$ then

$$\int e^{-\beta U(\vec{r}_1, \dots, \vec{r}_N)} d^3 \vec{r}_1 \cdots d^3 \vec{r}_N = V^N \Rightarrow \tilde{Z} = \underbrace{\left(\frac{V}{h_0^3} \int e^{-\frac{\beta}{2m} |\vec{p}|^2} d^3 \vec{p} \right)^N}_{\tilde{Z}^N}$$

To evaluate the general integral

$$\int_{-\infty}^{\infty} e^{-\frac{\beta}{2m} |\vec{p}|^2} d^3 \vec{p} = \int_{-\infty}^{\infty} e^{-\frac{\beta}{2m} p_x^2} dp_x \int_{-\infty}^{\infty} e^{-\frac{\beta}{2m} p_y^2} dp_y \int_{-\infty}^{\infty} e^{-\frac{\beta}{2m} p_z^2} dp_z$$

$$= \left[2 \frac{\sqrt{\pi}}{2} \left(\frac{\beta}{2m} \right)^{-\frac{1}{2}} \right]^3 = \left(\sqrt{\frac{2m\pi}{\beta}} \right)^3$$

NOTE: $\int_0^{\infty} e^{-\alpha x^2} dx = \frac{\sqrt{\pi}}{2} \alpha^{-\frac{1}{2}}$

Therefore

$$\tilde{Z} = Z^N = \left[V \left(\frac{2m\pi}{\beta h_0^2} \right)^{\frac{3}{2}} \right]^N$$

$$\Rightarrow \ln \tilde{Z} = N \ln Z = N \ln \left[V \left(\frac{2m\pi}{\beta h_0^2} \right)^{\frac{3}{2}} \right]$$

$$= N \left[\ln V - \frac{3}{2} \ln \beta + \frac{3}{2} \ln \left(\frac{2m\pi}{h_0^2} \right) \right]$$

Equipped with the partition function \tilde{Z} we can compute the thermodynamical mean values and the equation of state

- $\bar{p} = \frac{1}{\beta} \frac{\partial \ln \tilde{Z}}{\partial V} = \frac{1}{\beta} \frac{N}{V} \Rightarrow \bar{p} V = N k T$ "Eq. of state"

- $\bar{E} = - \frac{\partial \ln \tilde{Z}}{\partial \beta} = \frac{3}{2} N \frac{1}{\beta} = N \frac{3}{2} k T = N \bar{\epsilon}$
 $\bar{\epsilon} = \frac{3}{2} k T \equiv \text{mean energy / molecule}$

• Heat capacity : $C_V = \left(\frac{\partial \bar{E}}{\partial T} \right)_V = \frac{3}{2} N K = \frac{3}{2} n R \Rightarrow c_v = \frac{C_V}{n} = \frac{3}{2} R$
 nR molar specific heat

• Energy dispersion : $\overline{(\Delta E)^2} = - \frac{\partial \bar{E}}{\partial \beta} = \frac{3}{2} N \frac{1}{\beta^2} = K C_V \cdot T^2$

• $\tilde{S} = K \left[\ln \tilde{Z} + \beta \bar{E} \right]$

$= K N \left[\ln V - \frac{3}{2} \ln \beta + \frac{3}{2} \ln \left(\frac{2m\pi}{h_0^2} \right) + \frac{3}{2} \right]$

$= K N \left[\ln V + \frac{3}{2} \ln T + \frac{3}{2} \ln \left(\frac{2m\pi}{h_0^2} K \right) + \frac{3}{2} \right]$

$\sigma \equiv$ independent of T, V, N

$= K N \left[\ln V + \frac{3}{2} \ln T + \sigma \right]$

Not correct!!

• Entropy must be an extensive quantity :

$V \rightarrow \gamma V, N \rightarrow \gamma N \Rightarrow \tilde{S} \rightarrow \gamma \tilde{S}$

3rd law thermod.

• $\tilde{S} \rightarrow -\infty$ when $T \rightarrow 0$: It should go to $\tilde{S}_0 = \text{cte}$

• \tilde{S} is not an additive quantity for systems A and A'

[Gibbs paradox]

Question : What is going wrong ?

Answer : We treated the gas molecules as individually distinguishable !!
wrong !!

This is a consequence of the classical treatment we applied. If we had done a quantum mechanical treatment we should have considered the molecules as completely indistinguishable !!
 correct !!

Therefore we must use

$$Z = \frac{\tilde{z}^N}{N!} = \frac{z^N}{N!} \Rightarrow \ln Z = N \ln z - \ln N!$$

Stirling $\xrightarrow{N \gg 1}$ $\approx N \ln z - N \ln N + N$

so that only the entropy gets affected and

$$S = kN \left[\ln V + \frac{3}{2} \ln T + \sigma \right] + k(-N \ln N + N)$$

$$= kN \left[\underbrace{\ln \left(\frac{V}{N} \right)} + \frac{3}{2} \ln T + \sigma_0 \right] \quad \text{with} \quad \sigma_0 \equiv \sigma + 1$$

- Now entropy is extensive and additive
- $S \rightarrow -\infty$ when $T \rightarrow 0$: Classical approximation not valid at low T !!
few
quantum states

* Validity of classical approximation: Is it valid to use classical physics to study gases?

• Criterion : amount of action involved $\Rightarrow \Delta q \Delta p \geq \hbar$?

"Heisenberg"

• Estimating Δq and Δp :

i) $\Delta q \sim$ mean separation between molecules \bar{L}

ii) $\Delta p \sim$ mean value of momentum \bar{p}

Classical behaviour $\Leftrightarrow \bar{L} \cdot \bar{p} \gg \hbar$

\Downarrow

$$\bar{L} \gg \frac{\hbar}{\bar{p}} = \frac{1}{2\pi} \frac{h}{\bar{p}} = \frac{1}{2\pi} \lambda$$

$\lambda =$ de Broglie wavelength

Important : When $\bar{L} \gg \lambda$ the quantum description is equivalent to the motion of wave packages describing individual particles which move independently in a quasi-classical manner. If $\bar{L} \ll \lambda$ then the whole gas is described by a single wave function encoding the quantum correlations between particles even if no forces exist between them.

i) \bar{L} : Each molecule is viewed as a cube of size \bar{L}



$$\approx \text{volume} = \bar{L}^3 \Rightarrow$$

$$N \cdot \bar{L}^3 = V$$

$$\Rightarrow \bar{L} = \left(\frac{V}{N}\right)^{\frac{1}{3}}$$

ii) \bar{p} : We estimate it from the mean energy

$$\frac{\bar{p}^2}{2m} = \bar{\epsilon} \approx \frac{3}{2} kT \Rightarrow \bar{p} \approx (3mkT)^{\frac{1}{2}}$$

Therefore one has that

$$\bar{\lambda} = \frac{h}{\bar{p}} \approx \frac{h}{\sqrt{3mkT}}, \quad \bar{L} = \left(\frac{V}{N}\right)^{\frac{1}{3}}$$

and

$$\bar{L} \gg \bar{\lambda} \Leftrightarrow \left(\frac{V}{N}\right)^{\frac{1}{3}} \gg \frac{h}{\sqrt{3mkT}}$$

Important: The classical approximation is valid at:

Low density $\left(\frac{N}{V}\right) \oplus$ High temperature $T \oplus$ m not too small

* Numerical estimations:

a) He gas at room temperature T and pressure \bar{p}

- $T = 300 \text{ K} \Rightarrow kT \approx 4 \times 10^{-14} \text{ ergs}$
 - $\bar{p} = 760 \text{ mm Hg}$
 - molecular mass $m = \frac{4}{6 \times 10^{23}} \approx 7 \times 10^{-24} \text{ grams}$
- $$\left. \begin{array}{l} \cdot T = 300 \text{ K} \Rightarrow kT \approx 4 \times 10^{-14} \text{ ergs} \\ \cdot \bar{p} = 760 \text{ mm Hg} \end{array} \right\} \frac{N}{V} = \frac{\bar{p}}{kT} = 2.5 \times 10^{19} \frac{\text{molecules}}{\text{cm}^3}$$

$$\Rightarrow \begin{array}{l} \bar{L} = 34 \times 10^{-8} \text{ cm} \\ \bar{\lambda} = 6 \times 10^{-9} \text{ cm} \end{array} \Rightarrow \bar{L} \gg \bar{\lambda} \quad \text{classical } \checkmark$$

b) Electrons in a typical metal (no interaction \approx ideal gas)

• electron mass $m = 10^{-27}$ grams

$$\Rightarrow \begin{aligned} \bar{L} &= 2 \times 10^{-8} \text{ cm} \\ \bar{\lambda} &= 5 \times 10^{-7} \text{ cm} \end{aligned} \quad \Rightarrow \quad \bar{L} \ll \bar{\lambda} \quad \text{classical } \times$$

II. Real monatomic gas

Our starting point now is the classical partition function in the previous section

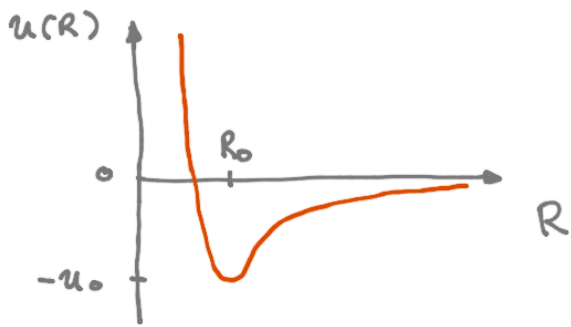
$$Z = \frac{1}{N!} \left(\frac{2m\pi}{\beta h_0^2} \right)^{\frac{3}{2}N} \underbrace{\int e^{-\beta U(\vec{r}_1, \dots, \vec{r}_N)} d^3\vec{r}_1 \dots d^3\vec{r}_N}_{Z_U}$$

This time we address the problem of having $U \neq 0$. The potential can be modelled as

$$U = u_{12} + u_{13} + \dots + u_{N-1N} = \overbrace{\sum_{i < j} u_{ij}}^{\frac{1}{2}N(N-1) \text{ terms}} = \frac{1}{2} \sum_{i \neq j} u_{ij}$$

with $u_{ij} = u(|\vec{r}_i - \vec{r}_j|)$. The potential between two molecules at distance R has a "semi-empirical" form

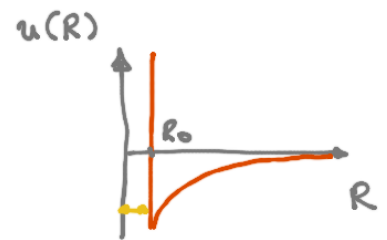
$$u(R) = u_0 \left[\left(\frac{R_0}{R} \right)^{12} - 2 \left(\frac{R_0}{R} \right)^6 \right] \quad \text{"Lennard-Jones" potential}$$



- $R < R_0 \Rightarrow$ strong electric repulsion
- $R > R_0 \Rightarrow$ weak gravitational attraction

The potential $u(R)$ can be less accurately modelled as

$$u(R) = \begin{cases} \infty & \text{if } R < R_0 \\ -u_0 \left(\frac{R_0}{R}\right)^s & \text{if } R > R_0 \end{cases}$$



intermolecular distance R_0

NOTE: The choice $s=6$ is usually the most realistic

In order to compute Z_U let us consider the effective potential U_e felt by a molecule as a consequence of the rest [separability \Leftrightarrow canonical ensemble]. Then

$$Z_U = \left[\int e^{-\beta U_e(\vec{r})} d^3 \vec{r} \right]^N \quad \Rightarrow N \text{ independent molecules !!}$$

- There is a region of space V_x (per molecule) which is excluded in the integral.
For each pair of molecules, one of them cannot be where the other is.
- In $(V - V_x)$ the potential is smooth: $U_e \approx \bar{U}_e$

Therefore

$$Z_U \approx \left[(V - V_x) e^{-\beta \bar{U}_e} \right]^N \approx \rightarrow (V_x, \bar{U}_e) \text{ to be determined by some self-consistency checks}$$

i) Determination of \bar{U}_e :

Total mean potential $N \bar{U}_e \stackrel{!}{=} \overbrace{\frac{1}{2} N(N-1)}^{\text{pairs of molecules}} \underbrace{\bar{u}}_{\text{mean intermolecular potential}} \approx \frac{1}{2} N^2 \bar{u}$ $N \gg 1$

$$\Rightarrow \bar{U}_e = \frac{1}{2} N \bar{u}$$

$$= \frac{1}{2} N \int_{R_0}^{R^*} \underbrace{\frac{4\pi R^2 dR}{V}}_{\substack{\uparrow \\ \text{Probability of intermolecular distance to be between } R \text{ and } R+dR}} u(R)$$

Probability of intermolecular distance to be between R and $R+dR$

NOTE: $V = \frac{4}{3} \pi R^3 \Rightarrow dV = 4\pi R^2 dR$

$$= \frac{1}{2} \frac{N}{V} 4\pi \int_{R_0}^{R^*} R^2 \underbrace{u(R)}_{-u_0 \left(\frac{R_0}{R}\right)^s} dR = -\frac{1}{2} \frac{N}{V} 4\pi u_0 \int_{R_0}^{R^*} \left(\frac{R_0}{R}\right)^s R^2 dR$$

$$= -\frac{1}{2} \frac{N}{V} 4\pi u_0 R_0^s \left[\frac{R^{3-s}}{3-s} \right]_{R_0}^{R^*}$$

$$= -\frac{1}{2} \frac{N}{V} 4\pi u_0 R_0^s \left[\frac{R^{*3-s}}{3-s} - \frac{R_0^{3-s}}{3-s} \right]$$

$$= \frac{1}{2} \frac{N}{V} 4\pi u_0 \frac{1}{s-3} \left[\underbrace{R_0^s \cdot R^{3-s}}_{s>3 \text{ and } R^s \rightarrow \infty} - R_0^3 \right]$$

$s > 3$ and $R^s \rightarrow \infty$

$$= - \frac{N}{V} \left(\underbrace{\frac{2\pi}{3} R_0^3 u_0 \frac{3}{s-3}}_{a'} \right) = - \frac{N}{V} a'$$

ii) Determination of V_x :



$$\underbrace{\frac{1}{2} N(N-1)}_{\text{\# of pairs of interacting molecules}} \times \underbrace{\frac{4}{3} \pi R_0^3}_{\text{Region excluded for each interacting pair of molecules}} \stackrel{N \gg 1}{\approx} \frac{2}{3} N^2 \pi R_0^3 \stackrel{!}{=} \underbrace{N V_x}_{\text{Total excluded region}}$$

$$\Rightarrow V_x = N \left(\underbrace{\frac{2\pi}{3} R_0^3}_{b'} \right) = N \cdot 4 \left[\underbrace{\frac{4}{3} \pi \left(\frac{R_0}{2} \right)^3}_{\text{molecule volume}} \right]$$

$$= N b'$$

Now we can readily compute the equation of state for the real gas using the partition function

$$Z = \frac{1}{N!} \left[\left(\frac{2m\pi}{\beta h_0^2} \right)^{\frac{3}{2}} (V - V_x) e^{-\beta \bar{u}_e} \right]^N$$

One finds

$$\begin{aligned}\bar{p} &= \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} = \frac{1}{\beta} \frac{\partial}{\partial V} \left[N \ln(V - v_x) - N \beta \bar{u}_e \right] \\ &= \frac{N \kappa T}{V - N b'} - \frac{N^2}{V^2} a' \Rightarrow \bar{p} + a' \frac{N^2}{V^2} = \frac{N}{V - N b'} \kappa T \\ &\quad \underbrace{\hspace{10em}}_{\left(\frac{V}{N} - b'\right)^{-1}}\end{aligned}$$

$$\Rightarrow \left(\bar{p} + a' \frac{N^2}{V^2} \right) \left(\frac{V}{N} - b' \right) = \kappa T$$

Equivalently

$$\boxed{\left(\bar{p} + \frac{a}{\sigma^2} \right) (\sigma - b) = R T}$$

"van der Waals law"
(1873)

with $a = a' N_A^2$, $b = b' N_A$, $N = \underbrace{n \cdot N_A}_{\text{mols}}$ and $\sigma = \frac{V}{n}$.

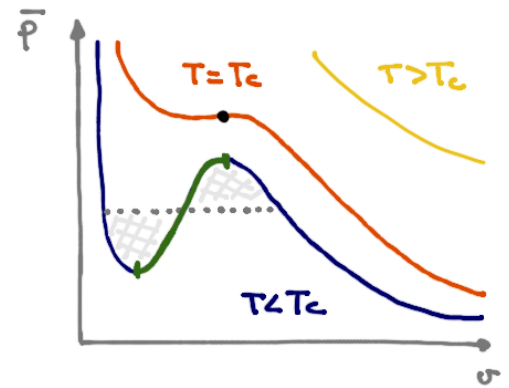
* **Critical point**: The van der Waals equation of state predicts the existence of a **critical point** located at $(T_c, \bar{p}_c, \sigma_c)$ where

$$\left(\frac{\partial \bar{p}}{\partial \sigma} \right)_T \Big|_{T_c, \bar{p}_c, \sigma_c} = 0, \quad \left(\frac{\partial^2 \bar{p}}{\partial \sigma^2} \right)_T \Big|_{T_c, \bar{p}_c, \sigma_c} = 0$$

Using the vdW equation of state one finds a unique critical point at

$$T_c = \frac{8a}{27bR}, \quad \bar{p}_c = \frac{a}{27b^2}, \quad v_c = 3b$$

NOTE: "....." \equiv Maxwell's area line to eliminate discontinuity in $v = \frac{\partial G}{\partial p} \Rightarrow$ 1st order phase transition where $\left(\frac{\partial \bar{p}}{\partial v}\right) > 0$ [instability]



III. Equipartition theorem and simple applications

It is a very powerful theorem in classical statistical physics about the mean value $\bar{\epsilon}_i$ of the energy associated with a quadratic generalised coordinate / momentum. This is

$$E = E(q_1, \dots, q_f, p_1, \dots, p_f) = \begin{cases} \underbrace{c p_i^2}_{\epsilon_i(p_i)} + E'(q_1, \dots, p_f) \\ \underbrace{c q_i^2}_{\epsilon_i(q_i)} + \underbrace{E'(q_1, \dots, p_f)}_{\text{rest of the energy}} \end{cases}$$

If the classical system is in equilibrium at temperature $\beta = (kT)^{-1}$ then

$$\bar{\epsilon}_i = \frac{\int_{-\infty}^{\infty} e^{-\beta E} \epsilon_i dq_1 \dots dp_f}{\int_{-\infty}^{\infty} e^{-\beta E} dq_1 \dots dp_f} = \frac{\int_{-\infty}^{\infty} e^{-\beta(\epsilon_i + E')} \epsilon_i dq_1 \dots dp_f}{\int_{-\infty}^{\infty} e^{-\beta(\epsilon_i + E')} dq_1 \dots dp_f}$$

$$\begin{aligned} \overline{\epsilon_i} &= \frac{\int_{-\infty}^{\infty} e^{-\beta \epsilon_i} \epsilon_i dp_i \int_{-\infty}^{\infty} e^{-\beta \epsilon'} dq_1 \dots dp_f}{\int_{-\infty}^{\infty} e^{-\beta \epsilon_i} dp_i \int_{-\infty}^{\infty} e^{-\beta \epsilon'} dq_1 \dots dp_f} \end{aligned}$$

↗ independent of p_i

↘ independent of p_i

$$= \frac{\int_{-\infty}^{\infty} e^{-\beta \epsilon_i} \epsilon_i dp_i}{\int_{-\infty}^{\infty} e^{-\beta \epsilon_i} dp_i} = \frac{-\frac{\partial}{\partial \beta} \left(\int_{-\infty}^{\infty} e^{-\beta \epsilon_i} dp_i \right)}{\int_{-\infty}^{\infty} e^{-\beta \epsilon_i} dp_i}$$

$$= -\frac{\partial}{\partial \beta} \ln \left[\int_{-\infty}^{\infty} e^{-\beta \epsilon_i} dp_i \right]$$

If $\epsilon_i = c p_i^2$ then

$$\int_{-\infty}^{\infty} e^{-\beta c p_i^2} dp_i = \beta^{-\frac{1}{2}} \int_{-\infty}^{\infty} e^{-c y^2} dy$$

$p_i = \frac{1}{\sqrt{\beta}} y$

$$= -\frac{\partial}{\partial \beta} \ln \left[\beta^{-\frac{1}{2}} \cdot \int_{-\infty}^{\infty} e^{-c y^2} dy \right] = -\frac{\partial}{\partial \beta} \left[-\frac{1}{2} \ln \beta \right]$$

independent of β

"Equipartition theorem"

$$= \frac{1}{2} \frac{1}{\beta} = \frac{1}{2} k T$$

$$\Rightarrow \boxed{\overline{\epsilon_i} = \frac{1}{2} k T}$$

for quadratic variables p_i^2 or q_i^2

Message: The mean value of each independent quadratic term in the energy is equal to $\frac{1}{2} kT$ for classical systems.

Comment: The classical approximation is justified whenever

$$\underbrace{\Delta E}_{\text{separation of quantum energy levels}} \ll \underbrace{\beta^{-1}}_{\text{thermal energy}} = kT$$

so that E looks like a continuous quantity instead of a discrete (quantised) one.

We will discuss now some simple applications of the equipartition theorem.

* Mean kinetic energy of a molecule in a gas: Consider a molecule in a gas so that

$$K = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) \Rightarrow \bar{K} = \sum_{i=1}^3 \underbrace{\frac{1}{2m} p_i^2}_{\frac{1}{2} kT} = \frac{3}{2} kT$$

The mean energy of the full (ideal and monatomic) gas is

$$\bar{E} = N \left(\frac{3}{2} kT \right) = \frac{3}{2} nRT \Rightarrow c_v = \frac{1}{n} \left(\frac{\partial \bar{E}}{\partial T} \right)_v = \frac{3}{2} R$$

↳ molar specific heat

* **Brownian motion** : Consider a macroscopic particle of mass m immersed in a liquid at temperature T .

Since the motion is random then $\overline{v_x} = \overline{v_y} = 0$

gravity along z axis

However

$$\overline{K} = \overline{\frac{1}{2} m v_{x,y}^2} = \frac{1}{2} k T \Rightarrow \overline{v_{x,y}^2} = \frac{k T}{m}$$

- Heavy particles with $m \gg k T$ look at rest

- Light particles with $m \approx k T$ perpetually move in a random manner \Rightarrow Brownian motion

[particle in contact with thermal bath (other particles in the medium)]

* **Harmonic oscillator** : Consider a 1D classical harmonic oscillator with

$$E = \underbrace{\frac{p^2}{2m}}_{\text{quadratic}} + \underbrace{\frac{1}{2} k_0 x^2}_{\text{quadratic}}$$

so that

$$\overline{E} = \underbrace{\frac{1}{2m} \overline{p^2}}_{\frac{1}{2} k T} + \underbrace{\frac{1}{2} k \overline{x^2}}_{\frac{1}{2} k T} = k T \Rightarrow \text{Classical result}$$

Let us look now at the quantum energy levels

$$E_n = \hbar \omega \left(\frac{1}{2} + n \right), \text{ with } \omega^2 = \frac{k_0}{m}$$

so the canonical partition function reads

$$\begin{aligned} Z &= \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-(n+\frac{1}{2})\beta\hbar\omega} \\ &= e^{-\frac{1}{2}\beta\hbar\omega} \cdot \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega} \\ &= e^{-\frac{1}{2}\beta\hbar\omega} \left[1 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + \dots \right] \\ &= e^{-\frac{1}{2}\beta\hbar\omega} \frac{1}{1 - e^{-\beta\hbar\omega}} = \frac{1}{2} \operatorname{csch} \left[\frac{\beta\hbar\omega}{2} \right] \end{aligned}$$

NOTE: $1 + x + x^2 + \dots = \sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$, with $x \equiv e^{-\beta\hbar\omega} < 1$

$$\Rightarrow \ln Z = -\frac{1}{2}\beta\hbar\omega - \ln \left[1 - e^{-\beta\hbar\omega} \right]$$

$$\Rightarrow \bar{E} = -\frac{\partial \ln Z}{\partial \beta} = -\left[-\frac{1}{2}\hbar\omega - \frac{e^{-\beta\hbar\omega} \hbar\omega}{1 - e^{-\beta\hbar\omega}} \right]$$

$$= \hbar\omega \left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right) \Rightarrow \text{Quantum result}$$

Q: How do we reconcile classical vs quantum results?

i) Limit $\beta \hbar \omega = \frac{\hbar \omega}{kT} = \frac{\Delta E}{kT} \ll 1$ (High T) : This is a classical limit

$$\Delta E \ll kT$$

and consequently

$$\bar{E} = \hbar \omega \left(\frac{1}{2} + \frac{1}{(1 + \beta \hbar \omega + \dots)^{-1}} \right) \approx \hbar \omega \left(\frac{1}{2} + \frac{1}{\beta \hbar \omega} \right)$$
$$\approx \hbar \omega \frac{kT}{\hbar \omega} = kT \Rightarrow \bar{E} \approx kT$$

↳ In agreement with the equipartition theorem

(i) Limit $\beta \hbar \omega = \frac{\hbar \omega}{kT} = \frac{\Delta E}{kT} \gg 1$ (Low T) : This is not a classical limit

$$\Delta E \gg kT$$

and then

$$\bar{E} = \hbar \omega \left(\frac{1}{2} + \frac{1}{\underbrace{e^{\beta \hbar \omega} - 1}_{\gg 1}} \right) \approx \hbar \omega \left(\frac{1}{2} + e^{-\beta \hbar \omega} \right)$$

- Different from equipartition theorem
- Approaches the "zero point" energy $\bar{E} = \frac{1}{2} \hbar \omega$ when $T \rightarrow 0$

* General form of equipartition theorem: We show now that a more general form of equipartition theorem is

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \delta_{ij} kT \quad \text{with } x_i = q_i, p_i$$

Let us start from the classical canonical probability distribution

$$P(\epsilon) = C e^{-\beta H(p, q)}$$

so that

$$C \int e^{-\beta H(p, q)} \underbrace{dq_1 \dots dq_f dp_1 \dots dp_f}_{d\Gamma \equiv \prod_i dq_i dp_i} = 1 \quad \rightarrow \text{Normalisation}$$

Integrating by parts with $x_k = q_k$ or p_k one finds

$$C \int d \left[e^{-\beta H(p, q)} x_k \right] \frac{d\Gamma}{dx_k} - C \int d \left[e^{-\beta H(p, q)} \right] x_k \frac{d\Gamma}{dx_k} = 1$$

integration over all coordinates but $x_k \Rightarrow H \rightarrow \infty$ when $p_i, q_i \rightarrow \pm\infty (i \neq k)$

$$- e^{-\beta H(p, q)} \beta \frac{\partial H}{\partial x_i} dx_i$$

$$\Rightarrow C \int e^{-\beta H(p, q)} \left(x_k \underbrace{\frac{dx_i}{dx_k}}_{\delta_{ki}} \frac{\partial H}{\partial x_i} \right) d\Gamma = \frac{1}{\beta} = kT$$

$$\Rightarrow \left\langle x_k \frac{\partial H}{\partial x_i} \right\rangle = \delta_{ki} kT$$

IV. Specific heats of solids



Let us consider a solid with $N_A = 6.023 \times 10^{23} \frac{\text{atoms}}{\text{mol}}$. Each atom vibrates about its equilibrium position with three position coordinates and three momentum coordinates. The appropriate coordinates after diagonalising the Hamiltonian are referred to as "normal mode coordinates" in terms of which

$$E = \sum_{i=1}^{3N_A} \left(\frac{p_i^2}{2m} + \frac{1}{2} \kappa_i q_i^2 \right) \equiv \frac{\text{Energy}}{\text{mol}}$$

around equilibrium (minimum)

* Equipartition theorem [classical] :

$$\bar{E} = 3N_A \left[\frac{1}{2} kT + \frac{1}{2} kT \right] = 3RT$$

$$\Rightarrow c_v = \left(\frac{\partial \bar{E}}{\partial T} \right)_v = 3R \sim 25 \frac{\text{joules}}{\text{mol} \cdot \text{K}}$$

"Dulong-Petit law, 1819"
[experimental]

* Quantum vibrations with $\kappa_i = \kappa_0 = m \cdot \omega^2$ [Einstein, 1907] :

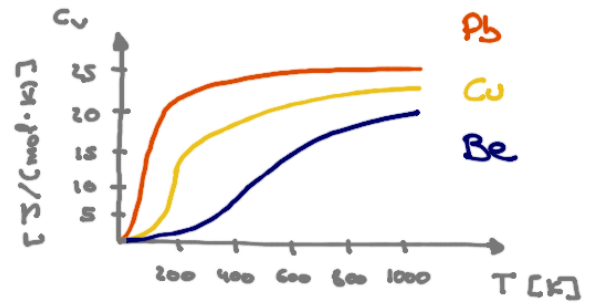
$$\bar{E} = 3N_A \hbar \omega \left(\frac{1}{2} + \frac{1}{e^{\beta \hbar \omega} - 1} \right)$$

$$\Rightarrow c_v = \left(\frac{\partial \bar{E}}{\partial T} \right)_v = \left(\frac{\partial \bar{E}}{\partial \beta} \right)_v \cdot \left(\frac{\partial \beta}{\partial T} \right) = -\frac{1}{kT^2} \left(\frac{\partial \bar{E}}{\partial \beta} \right)$$

$$= -\frac{3N_A}{kT^2} \hbar \omega \left[-\frac{e^{\beta \hbar \omega} \hbar \omega}{(e^{\beta \hbar \omega} - 1)^2} \right]$$

NOTE: $R = N_A k$, $\Theta_E \equiv \frac{\hbar \omega}{k}$ (Einstein temperature = characteristic param.)

$$= 3R \left(\frac{\Theta_E}{T} \right)^2 \frac{e^{-\frac{\Theta_E}{T}}}{\left(e^{-\frac{\Theta_E}{T}} - 1 \right)^2}$$



Let us look at two limiting cases :

i) High $T \Leftrightarrow \frac{kT}{\hbar\omega} \gg 1 \Leftrightarrow \frac{\Theta_E}{T} \ll 1$ [classical]

$$c_v = 3R \left(\frac{\Theta_E}{T} \right)^2 \frac{1 + \frac{\Theta_E}{T} + \dots}{\left(\frac{\Theta_E}{T} + \dots \right)^2} \approx 3R$$

ii) Low $T \Leftrightarrow \frac{kT}{\hbar\omega} \ll 1 \Leftrightarrow \frac{\Theta_E}{T} \gg 1$ [not classical]

$$c_v = 3R \left(\frac{\Theta_E}{T} \right)^2 \underbrace{e^{-\frac{\Theta_E}{T}}}$$

- Exponential decrease as $T \rightarrow 0$
- Experimentally $c_v \sim T^3$ as $T \rightarrow 0$ due to "phonons"

* Remark on 3rd law of thermodynamics vs Dulong-Petit :

TdS equation : $TdS = C_v dT + T \left(\frac{\partial P}{\partial T} \right)_V \frac{0}{dV} \Rightarrow C_v = T \left(\frac{dS}{dT} \right)_V$

3rd law of thermodynamics : $T \rightarrow 0 \Rightarrow S = S_0 = \text{cte}$

Therefore $\frac{dS}{dT} \Big|_{T \rightarrow 0} = \text{finite} \Rightarrow C_v \Big|_{T \rightarrow 0} = 0 \Rightarrow$ Dulong-Petit most fail at low T !!
↳ indep of V

* Remark on phonons: Einstein made an oversimplification by modelling the solid with $\kappa_i = m\omega^2 \forall i$. The structure of vibrations of atoms in the solid is more complex and gives rise to collective excitations called "phonons". These phonons are responsible for the $c_v \sim T^3$ behaviour at $T \rightarrow 0$.

=> Below any small T there will be collective excitations with frequency $\hbar\omega \ll kT$ contributing to c_v . [Debye]
 long wavelength \equiv global

V. Paramagnetism for arbitrary spin

Before we studied a system of N_0 magnetic atoms with $s = \frac{1}{2}$ in presence of an external magnetic field at temperature T . We now generalise the study to arbitrary total angular momentum \vec{J}

each atom: $E = -\underbrace{\vec{\mu}}_{\text{magnetic moment}} \cdot \vec{H} = -g\mu_0 \underbrace{\vec{J} \cdot \vec{H}}_{\text{pointing in z-direction}} = -g\mu_0 H J_z$

with magnetic moment $\vec{\mu}$ given by

$$\vec{\mu} = g\mu_0 \vec{J} \quad \left\{ \begin{array}{l} g \equiv \text{"g-factor" of the atom} \quad [\text{Landé g factor}] \\ \mu_0 = \frac{e\hbar}{2m_e c} \equiv \text{Bohr magneton} \\ \vec{J} \equiv \text{total angular momentum} \\ \quad \text{orbital + spin} \end{array} \right.$$

and where

2J+1 possible values

$$J_z \equiv m = -J, -J+1, \dots, J-1, J$$

Therefore

$$E_m = -g \mu_0 H m \Rightarrow P_m \propto e^{-\beta E_m} = e^{\beta g \mu_0 H m}$$

NOTE: If $J = \frac{1}{2}$ then $m = \pm \frac{1}{2}$ and we recover the pure $S = \frac{1}{2}$ case

The z-component of $\vec{\mu}$ and its mean value read

$$\mu_z = g \mu_0 m \Rightarrow \bar{\mu}_z = \frac{\sum_{m=-J}^J e^{\beta g \mu_0 H m} g \mu_0 m}{\sum_{m=-J}^J e^{\beta g \mu_0 H m}}$$

$$= \frac{1}{\beta} \frac{1}{z} \frac{\partial z}{\partial H} = \frac{1}{\beta} \frac{\partial \ln z}{\partial H}$$

with

$$z = \sum_{m=-J}^J e^{\beta g \mu_0 H m} = \sum_{m=-J}^J e^{\eta m} \Rightarrow \text{Partition function}$$

Therefore

$$z = e^{-\eta J} + e^{-\eta(J-1)} + e^{-\eta(J-2)} + \dots + e^{\eta J}$$

(reversing ordering)

$$= e^{\eta J} \cdot (1 + e^{-\eta} + \dots + e^{-\eta 2J} + \dots) - e^{-\eta(J+1)} (1 + e^{-\eta} + e^{-2\eta} + \dots)$$

terms to be subtracted !!

NOTE: $\frac{1}{1-x} = 1 + x + x^2 + \dots \quad (|x| < 1)$

$$= \frac{e^{\eta J} - e^{-\eta(J+1)}}{1 - e^{-\eta}} \stackrel{\frac{-e^{\eta}}{-e^{\eta}}}{=} \frac{e^{-\eta J} - e^{\eta(J+1)}}{1 - e^{\eta}}$$

$$\frac{e^{-\frac{\eta}{2}}}{e^{-\frac{\eta}{2}}} = \frac{e^{-\eta(J+\frac{1}{2})} - e^{\eta(J+\frac{1}{2})}}{e^{-\frac{1}{2}\eta} - e^{\frac{1}{2}\eta}} = \frac{\sinh[\eta(J+\frac{1}{2})]}{\sinh[\frac{1}{2}\eta]}$$

$$\Rightarrow \ln Z = \ln \sinh[(J+\frac{1}{2})\eta] - \ln \sinh[\frac{1}{2}\eta]$$

Using the above partition function we can readily compute

$$\overline{\mu_z} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial H} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \eta} \frac{\partial \eta}{\partial H} = \frac{\partial \ln Z}{\partial \eta} \quad (g\mu_0)$$

↳ external parameter

$$= g\mu_0 \left[\frac{(J+\frac{1}{2}) \cosh[(J+\frac{1}{2})\eta]}{\sinh[(J+\frac{1}{2})\eta]} - \frac{\frac{1}{2} \cosh[\frac{1}{2}\eta]}{\sinh[\frac{1}{2}\eta]} \right]$$

$$= g\mu_0 J B_J(\eta) \Rightarrow \overline{\mu_z} = g\mu_0 \overline{J_z} = g\mu_0 J B_J(\eta)$$

$$\Rightarrow \overline{J_z} = J B_J(\eta)$$

with $B_J(\eta) = \frac{1}{J} \left[(J+\frac{1}{2}) \coth[(J+\frac{1}{2})\eta] - \frac{1}{2} \coth[\frac{1}{2}\eta] \right]$

"Brillouin function"

Let us look at the two limiting cases :

i) Limiting case $T \rightarrow 0 \Leftrightarrow \eta \gg 1$

$$B_J(\eta) = \frac{1}{J} \left[\left(J + \frac{1}{2} \right) - \frac{1}{2} \right] = 1$$

NOTE: $\coth y = \frac{e^y + e^{-y}}{e^y - e^{-y}} \approx 1$
 $y \gg 1$

ii) Limiting case $T \rightarrow \infty \Leftrightarrow \eta \ll 1$

$$\begin{aligned} B_J(\eta) &= \frac{1}{J} \left\{ \left(J + \frac{1}{2} \right) \left[\frac{1}{\left(J + \frac{1}{2} \right) \eta} + \frac{1}{3} \left(J + \frac{1}{2} \right) \eta \right] - \frac{1}{2} \left[\frac{2}{\eta} + \frac{\eta}{6} \right] \right\} \\ &= \frac{1}{J} \left\{ \frac{1}{3} \left(J + \frac{1}{2} \right)^2 \eta - \frac{1}{12} \eta \right\} = \frac{\eta}{3J} \left[J^2 + \frac{1}{4} + J - \frac{1}{4} \right] \\ &= \frac{\eta}{3J} J(J+1) = \frac{(J+1)}{3} \eta \end{aligned}$$

NOTE: $\coth y = \frac{e^y + e^{-y}}{e^y - e^{-y}} = \frac{(1+y+\frac{y^2}{2}+\dots) + (1-y+\frac{y^2}{2}-\dots)}{(1+y+\frac{y^2}{2}+\dots) - (1-y+\frac{y^2}{2}-\dots)}$

$$= \frac{(1+\frac{y^2}{2}+\dots)}{y \cdot (1+\frac{y^2}{6}+\dots)} \approx (1+\frac{y^2}{2}) \frac{1}{y} (1-\frac{y^2}{6})$$

$$\approx \frac{1}{y} + y \left(\frac{1}{2} - \frac{1}{6} \right)$$

$$= \frac{1}{y} + \underline{\underline{\frac{y}{3}}}$$

important to keep this subleading order !!

The magnetisation of the substance is then defined as

no interactions

$$\bar{M}_0 = N_0 \cdot \bar{\mu}_z = N_0 g \mu_0 J B_J(\eta)$$

and takes the limiting expressions

$$i) T \rightarrow 0 \Leftrightarrow \eta = \frac{g \mu_0 H}{kT} \gg 1$$

$$\bar{M}_0 = N_0 g \mu_0 J \quad (\text{independent of } H)$$

maximum μ_z an atom can have \Leftrightarrow saturation

$$ii) T \rightarrow \infty \Leftrightarrow \eta = \frac{g \mu_0 H}{kT} \ll 1$$

$$\bar{M}_0 = N_0 g \mu_0 J \frac{(J+1)}{3} \frac{g \mu_0 H}{kT}$$

$$= \underbrace{N_0 g^2 \mu_0^2 \frac{J(J+1)}{3kT}}_X H = X H$$

so that $X \propto T^{-1}$ "Curie Law" for arbitrary J

Comment: We used $\mu_0 = \frac{e\hbar}{2me}$ as this example considered unpaired electrons in the atom as the source of J (ex: iron atoms). If atoms have no unpaired electrons and the source of J is

the nucleus (ex: He³ atom) then all the results hold for $\mu_n \equiv$ nuclear magneton which is smaller than $\mu_0 \equiv$ Bohr magneton by the ratio $\frac{\mu_n}{\mu_0} \propto \frac{m_e}{m_n}$

VI. Interaction between spins and ferromagnetism

We consider now a system with N_0 magnetic atoms with arbitrary total angular momentum $\vec{J} = \vec{L} + \vec{S}$ and let them interact according to "exchange interaction" [Quantum nature]

"Exchange interaction"

Increases (decreases) the distance between fermions (bosons) compared to when they are distinguishable.

- Same spin orientation $\uparrow\uparrow \Rightarrow$ Pauli's exclusion principle \Rightarrow Not too close
- Different spin orientation $\uparrow\downarrow \Rightarrow$ No Pauli's exclusion principle \Rightarrow Arbitrary close

Overlapping of wave functions: $\Psi_{\text{elec}} = \Psi_s \cdot \Psi_r$ $\begin{cases} \Psi_s (\text{sym}) \Leftrightarrow \Psi_r (\text{anti}) \\ \Psi_s (\text{anti}) \Leftrightarrow \Psi_r (\text{sym}) \end{cases}$
spin \leftarrow Ψ_s orbital \leftarrow Ψ_r

Important: Since different spatial separation implies different electrostatic interaction \Rightarrow interaction term depending on spin orientation !!

Simplification: We will consider only spin degrees of freedom $\Rightarrow \vec{J} = \underbrace{\vec{L}}_0 + \vec{S} = \vec{S}$
0 orbital momentum

each atom : $E = -g \mu_0 H S_z - 2 J S_z \underbrace{\sum_{k=1}^n S_{kz}}$

NOTE: This interaction term is the simplest. It can be generalised to $\vec{S}_i \cdot \vec{S}_j$ couplings [O(2), O(3), ...]
 XY model Heisenberg model

Interaction term

- n nearest neighbours
- $J \equiv$ strength of the exchange interaction [not to be confused with $|J|$]

The total energy of the system then reads

$$E_{tot} = \sum_{i=1}^{N_0} E_i = -g \mu_0 H \sum_{i=1}^{N_0} S_{iz} + \frac{1}{2} (-2 J \sum_{i=1}^{N_0} \sum_{k=1}^n S_{iz} S_{kz})$$

Q: What is the mean magnetic moment $\bar{M}(T, H)$ now that the atoms have exchange interaction?

Approach: As for the case of real gases, we will approximate the interaction with neighbours by an **effective potential (interaction) term** given by the mean value

$$2 J \sum_{k=1}^n S_{kz} \equiv g \mu_0 \underbrace{H_m}_{\text{mean field theory}} \quad [\text{Weiss}] \quad (1907)$$

One then has

$$\begin{aligned} \text{each atom : } E &= -g \mu_0 H S_z - g \mu_0 H_m S_z \\ &= -g \mu_0 S_z (H + H_m) \end{aligned}$$

where

$$S_z \equiv m = -S, -S+1, \dots, S-1, S$$

Therefore

$$E_m = -g \mu_0 (H + H_m) m \Rightarrow P_m = e^{-\beta E_m} = e^{g \mu_0 (H + H_m) m}$$

The z-component of $\vec{\mu}$ and its mean value read

- $\mu_z = g \mu_0 S_z$
- $\bar{\mu}_z = g \mu_0 S B_S(\eta) \equiv$ Result from the non-interacting case with:

$$\eta = \beta g \mu_0 (H + H_m) = \frac{g \mu_0 (H + H_m)}{kT}$$

to be determined

$$\Rightarrow \bar{S}_z = \frac{\bar{\mu}_z}{g \mu_0} = S B_S(\eta)$$

Depends on H_m

Determination of H_m :

To determine H_m we go back to the relation

$$2J \sum_{k=1}^n S_{kz} \stackrel{!}{=} g \mu_0 H_m$$

$\underbrace{\hspace{10em}}$

$n \bar{S}_z \equiv$ There is no special atom and any neighbour can be considered the central atom

$$\underbrace{S B_s(\eta)}$$

$$\Rightarrow 2nJ \bar{S}_z = 2nJS B_s(\eta) = g \mu_0 H_m$$

$$\Rightarrow B_s(\eta) = \frac{g \mu_0}{2nJS} H_m$$

NOTE: $\eta = \beta g \mu_0 (H + H_m) \Rightarrow H_m = \frac{\eta}{\beta g \mu_0} - H$

$$\Rightarrow B_s(\eta) = \frac{g \mu_0}{2nJS} \left[\frac{\eta}{\beta g \mu_0} - H \right]$$

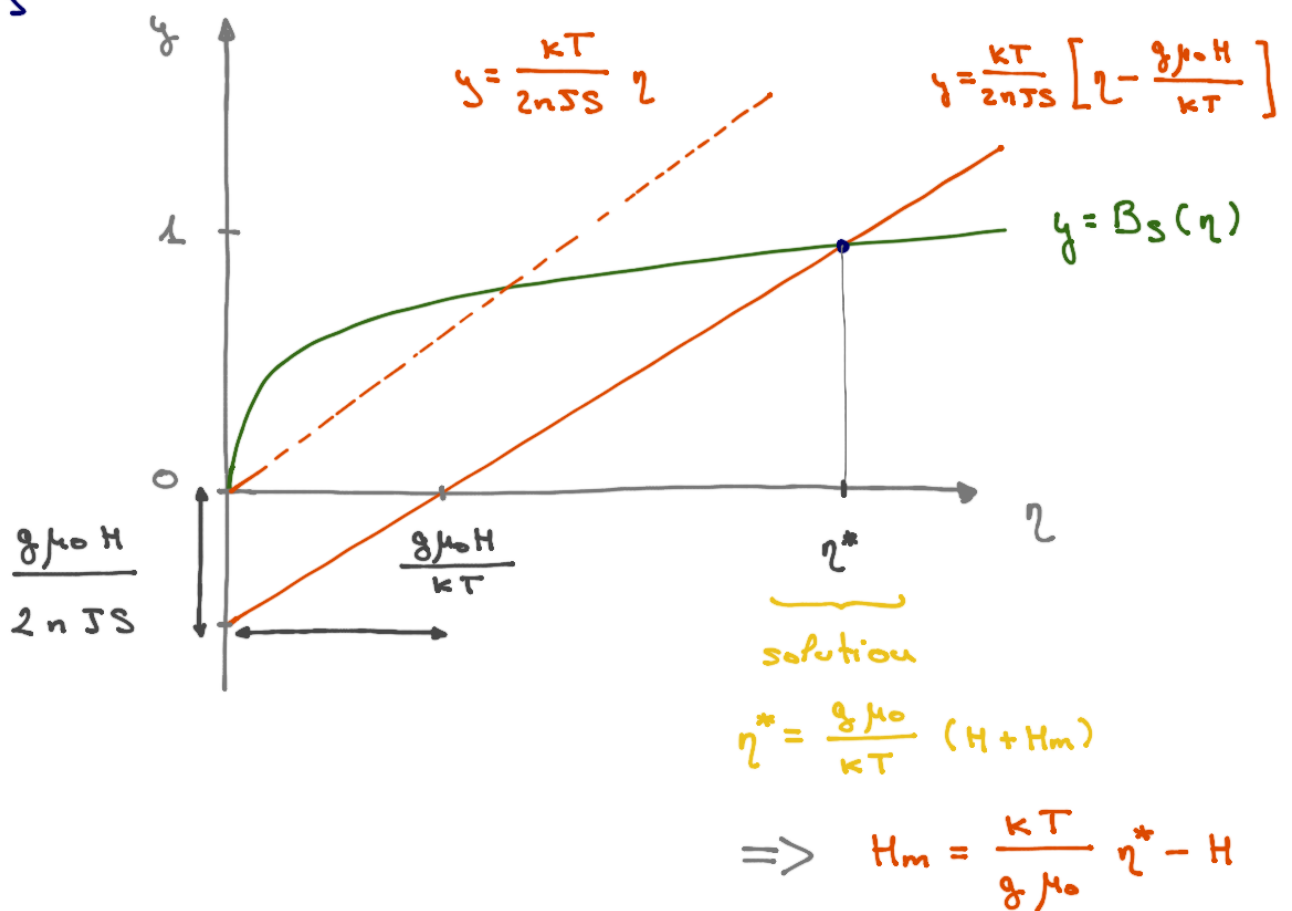
$$= \frac{kT}{2nJS} \left[\eta - \frac{g \mu_0 H}{kT} \right] \Rightarrow \text{This equation determines } \eta \text{ and therefore } H_m$$

NOTE: $B_s(\eta) = \frac{1}{S} \left[(S + \frac{1}{2}) \coth \left[(S + \frac{1}{2}) \eta \right] - \frac{1}{2} \coth \left[\frac{1}{2} \eta \right] \right]$

Unfortunately the equation to determine $\eta = \eta^*$ (solution)

$$\frac{1}{S} \left[\left(S + \frac{1}{2} \right) \coth \left[\left(S + \frac{1}{2} \right) \eta^* \right] - \frac{1}{2} \coth \left[\frac{1}{2} \eta^* \right] \right] = \frac{kT}{2nJS} \left[\eta^* - \frac{g\mu_0 H}{kT} \right]$$

cannot be solved analytically. However it can be solved by drawing



The magnetisation of the substance is then defined as

$$\bar{M} = \sum_{i=1}^{N_0} \bar{\mu}_{i,z} = g\mu_0 \sum_{i=1}^{N_0} \bar{S}_{i,z} = N_0 g\mu_0 S B_S(\eta^*)$$

* Case $H=0$: By looking at the plot it becomes clear that there is the solution

$$\eta^* = 0 \Rightarrow H_m = 0 \Rightarrow \bar{M} = 0$$

But there is a second solution whenever

$$\underbrace{\frac{kT}{2nJS}}_{\text{slope of } \nearrow} < \left. \frac{dB_S}{d\eta} \right|_{\eta=0} \Rightarrow \text{For an intersection to exist}$$

Using the expansion

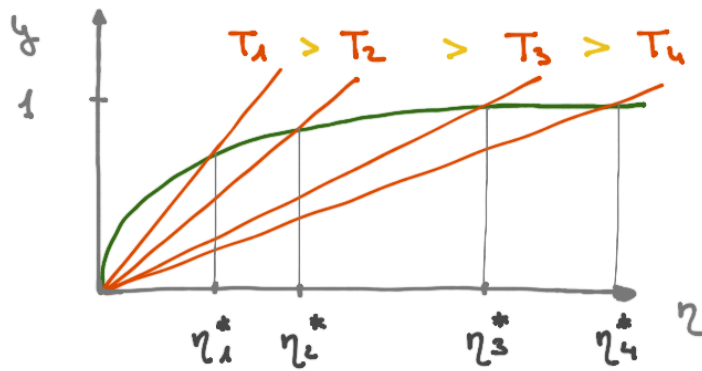
$$B_S(\eta) \stackrel{\eta \ll 1}{\approx} \frac{S(S+1)}{3} \eta$$

one finds

$$\frac{kT}{2nJS} < \frac{S+1}{3} \Rightarrow kT < \underbrace{2nJ \frac{S(S+1)}{3}}_{T_c = 2nJ \frac{S(S+1)}{3K} \text{ "Curie/critical temperature"}} \equiv kT_c$$

- **Ferromagnetism:** There is a spontaneous magnetisation \bar{M} originated by $H_m \neq 0$ ($\eta^* \neq 0$) whenever $T < T_c$ in absence of an external field. [$S = \frac{1}{2} \Rightarrow$ "Ising model"]

As long as T decreases the situation becomes as depicted



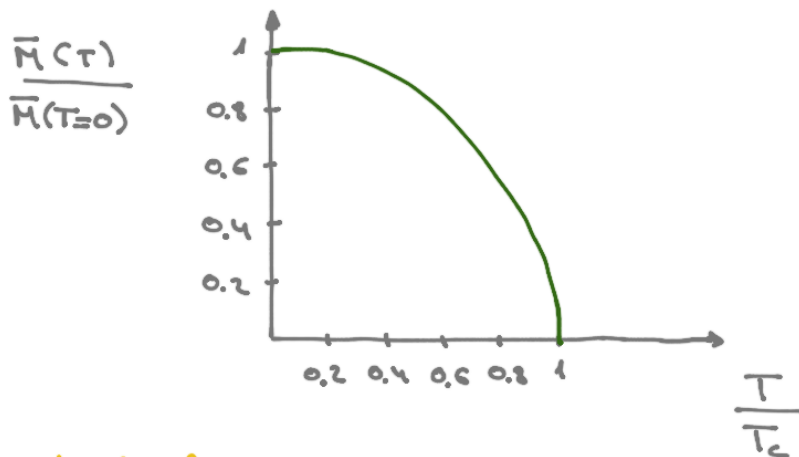
so that

$$T \rightarrow 0 \Rightarrow \eta^* \rightarrow \infty \Rightarrow B_s(\infty) = 1$$

$$\Rightarrow \bar{M}(T=0) = N_0 g \mu_0 S$$

all spins
parallel !!

- For arbitrary $T < T_c$ one finds
a magnetisation curve $[S = \frac{1}{2}]$



order/disorder
transition

- Helmholtz potential :

$$[H=0 \text{ \& } V, T = \text{cte}]$$

$$F(T, V) = \bar{E} - TS$$

$$\Rightarrow T \rightarrow 0 \Rightarrow \bar{E} \text{ minimised} \Rightarrow \uparrow\uparrow\uparrow \dots \text{ alignment}$$

$$T \text{ increases} \Rightarrow S \text{ maximised} \Rightarrow \uparrow\downarrow\downarrow \dots \text{ disorder}$$

* Case $H \ll 1$ and $T > T_c$ [$\eta \ll 1$]: As soon as $H \neq 0$ there is always an intersection point $\eta = \eta^*$ with magnetisation

$$\bar{M} = N_0 g \mu_0 S B_S(\eta^*)$$

Using $B_S(\eta) \stackrel{\eta \ll 1}{\approx} \frac{1}{3} (S+1) \eta$ then η^* is determined from

$$\frac{1}{3} (S+1) \eta^* = \frac{kT}{2nJS} \left[\eta^* - \frac{g \mu_0 H}{kT} \right]$$

$$\Rightarrow \eta^* = \frac{g \mu_0 H}{k(T - T_c)}$$

Therefore the magnetisation takes the form

$$\bar{M} = N_0 g \mu_0 S B_S(\eta^*)$$

$$= N_0 g \mu_0 S \frac{1}{3} (S+1) \eta^*$$

$$= \frac{N_0 g^2 \mu_0^2 S(S+1)}{3k(T - T_c)} H = \chi H$$

$\chi \equiv$ susceptibility "Curie - Weiss law"

Remark : $\chi \rightarrow \infty$ when $T \rightarrow T_c$ and the substance becomes ferromagnetic \Rightarrow 2nd order phase transition
 $\chi \propto (T - T_c)^{-1} \rightsquigarrow$ critical exponent \Leftrightarrow Correlation length $\xi \rightarrow \infty$ at T_c

$$\langle S_{zi} S_{zj} \rangle - \langle S_{zi} \rangle \langle S_{zj} \rangle \sim e^{-\frac{|r_i - r_j|}{\lambda}}$$

VII. Kinetic theory of diluted gases

Our starting point is the $P(\vec{r}, \vec{p})$ of finding a molecule in phase space within the range \vec{r} and $\vec{r} + d\vec{r}$ as well as \vec{p} and $\vec{p} + d\vec{p}$

$$P(\vec{r}, \vec{p}) d^3\vec{r} d^3\vec{p} \propto \left(\frac{d^3\vec{r} d^3\vec{p}}{h_0^3} \right) e^{-\beta \frac{|\vec{p}|^2}{2m}}$$

We are now interested in determining this quantity in full detail for N molecules. To this end we define

- $f(\vec{r}, \vec{v}) d^3\vec{r} d^3\vec{v} \equiv$ Mean number of molecules with position between \vec{r} and $\vec{r} + d\vec{r}$ and velocity between \vec{v} and $\vec{v} + d\vec{v}$

so that

$$f(\vec{r}, \vec{v}) d^3\vec{r} d^3\vec{v} = c e^{-\beta \frac{m|\vec{v}|^2}{2}} d^3\vec{r} d^3\vec{v}$$

$$\Rightarrow c \int \int e^{-\beta \frac{m|\vec{v}|^2}{2}} d^3\vec{r} d^3\vec{v} \stackrel{!}{=} N \text{ (normalisation)}$$

This yields

$$N \stackrel{!}{=} c V \underbrace{\int_{-\infty}^{\infty} e^{-\beta \frac{m\sigma_x^2}{2}} d\sigma_x}_{\left(\frac{2\pi}{\beta m}\right)^{\frac{1}{2}}} \underbrace{\int_{-\infty}^{\infty} e^{-\beta \frac{m\sigma_y^2}{2}} d\sigma_y}_{\left(\frac{2\pi}{\beta m}\right)^{\frac{1}{2}}} \underbrace{\int_{-\infty}^{\infty} e^{-\beta \frac{m\sigma_z^2}{2}} d\sigma_z}_{\left(\frac{2\pi}{\beta m}\right)^{\frac{1}{2}}} = c V \left(\frac{2\pi}{\beta m}\right)^{\frac{3}{2}}$$

$$\Rightarrow C = \underbrace{\frac{N}{V}}_{n = \frac{N}{V}} \left(\frac{\beta m}{2\pi} \right)^{\frac{3}{2}}$$

Therefore

$$f(\vec{r}, \vec{v}) d^3\vec{r} d^3\vec{v} = \underbrace{f(\vec{v})}_{f(|\vec{v}|)} d^3\vec{r} d^3\vec{v} = n \left(\frac{\beta m}{2\pi} \right)^{\frac{3}{2}} e^{-\frac{1}{2} \beta m |\vec{v}|^2} d^3\vec{r} d^3\vec{v}$$

$$\Rightarrow \boxed{f(\vec{v}) = n \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{m |\vec{v}|^2}{2kT}}$$

"Maxwell velocity distribution"

* Distribution of a component velocity: Integrating over the other components one finds:

$$\begin{aligned} \bullet \quad g(v_x) dv_x &= \int_{(v_y)} \int_{(v_z)} f(\vec{v}) d^3\vec{v} \\ &= n \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{m v_x^2}{2kT}} dv_x \underbrace{\int_{-0}^0 e^{-\frac{m v_y^2}{2kT}} dv_y}_{\left(\frac{2\pi kT}{m} \right)^{\frac{1}{2}}} \underbrace{\int_{-0}^0 e^{-\frac{m v_z^2}{2kT}} dv_z}_{\left(\frac{2\pi kT}{m} \right)^{\frac{1}{2}}} \\ &= n \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{m v_x^2}{2kT}} dv_x \left(\frac{2\pi kT}{m} \right) \\ &= n \left(\frac{m}{2\pi kT} \right)^{\frac{1}{2}} e^{-\frac{m v_x^2}{2kT}} dv_x \Rightarrow \text{Gaussian distrib.} \end{aligned}$$

mean # of molec. per unit volume

The Gaussian parameters are

- $\overline{v_x} = 0$
- $\overline{(\Delta v_x)^2} = \overline{v_x^2} = \underbrace{\sigma^2}_{\text{(Gaussian distribution)}} = \frac{kT}{m}$

NOTE: Equipartition th: $\frac{1}{2} m \overline{v_x^2} = \frac{1}{2} kT \Rightarrow \overline{v_x^2} = \frac{kT}{m}$

* Distribution of $|\vec{v}| \equiv v$: Integrating over a shell $v < |\vec{v}| < v + dv$ one finds

$$F(v) dv = \int_{\text{shell}} f(\vec{v}) d^3\vec{v} = 4\pi v^2 dv f(v)$$

$\int d^3\vec{v} = dv \, v d\theta \, v \sin\theta d\phi = v^2 dv d\Omega$

mean # of molec.
per unit volume

$$f(\vec{v}) = f(|\vec{v}|) \equiv f(v)$$

$$= 4\pi n \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2kT}} dv \Rightarrow \text{Non-Gaussian}$$

* Mean values: We calculate some relevant mean values

$$\cdot \overline{|\vec{v}|} \equiv \overline{v} = \frac{1}{n} \int_0^{\infty} F(v) v dv$$

$$= 4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \int_0^{\infty} e^{-\frac{mv^2}{2kT}} v^3 dv$$

$$= 4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \cdot \frac{1}{2} \left(\frac{m}{2kT} \right)^{-2} = \sqrt{\frac{8}{\pi} \frac{kT}{m}}$$

$$\begin{aligned}
 \bullet \overline{|\vec{v}|^2} &= \overline{v^2} = \frac{1}{n} \int_0^{\infty} F(v) v^2 dv \\
 &= 4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \int_0^{\infty} e^{-\frac{mv^2}{2kT}} v^4 dv \\
 &= 4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \frac{3}{8} \sqrt{\pi} \left(\frac{m}{2kT} \right)^{-\frac{5}{2}} = 3 \frac{kT}{m}
 \end{aligned}$$

NOTE: Equipartition th: $\frac{1}{2} m \overline{v^2} = \frac{1}{2} m (\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}) = \frac{3}{2} kT$

NOTE: $I(3) = \frac{1}{2} \alpha^{-2}$, $I(4) = \frac{3}{8} \sqrt{\pi} \alpha^{-\frac{5}{2}}$ $\Rightarrow \overline{v^2} = 3 \frac{kT}{m}$

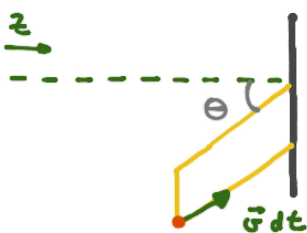
* Most likely $|\vec{v}|$: We have to maximise $F(v)$

$$\left. \frac{dF}{dv} \right|_{\tilde{v}} = 0 \Rightarrow 2\tilde{v} e^{-\frac{m\tilde{v}^2}{2kT}} - \tilde{v}^2 \frac{m}{kT} e^{-\frac{m\tilde{v}^2}{2kT}} = 0$$

$$\Rightarrow 1 - \tilde{v}^2 \frac{m}{2kT} = 0 \Rightarrow \tilde{v} = \underbrace{\sqrt{\frac{2kT}{m}}}_{\neq \overline{v}}$$

* Number of molecules striking a surface: We introduce

$\Phi_0 \equiv$ Total number of molecules which strike a unit area of the wall per unit of time



$$dt dA \Phi_0 = \int_{v_z > 0} d^3 \vec{v} f(\vec{v}) v dt dA \cos \theta$$

$$\begin{aligned}
 \Rightarrow \Phi_0 &= \int_{\sigma_z > 0} \overbrace{v^2 d\sigma \sin\theta d\theta d\varphi}^{d^3\vec{\sigma} \text{ (spherical)}} f(v) v \cos\theta \\
 &= \int_0^\infty v^3 f(v) dv \int_0^{\frac{\pi}{2}} \sin\theta \cos\theta d\theta \int_0^{2\pi} d\varphi \\
 &= \int_0^\infty v^3 f(v) dv \left[\frac{1}{2} \sin^2\theta \right]_0^{\frac{\pi}{2}} (2\pi) \\
 &= \pi \int_0^\infty v^3 f(v) dv = \pi \frac{n\bar{v}}{4\pi} = \frac{1}{4} n \bar{v}
 \end{aligned}$$

$\sqrt{\frac{8}{\pi} \frac{kT}{m}}$
 \downarrow
 $\frac{\bar{p}}{kT}$

NOTE:

$$\begin{aligned}
 \bar{v} &= \frac{1}{n} \int d^3\vec{\sigma} f(v) v = \frac{1}{n} \int_0^\infty \int_0^\pi \int_0^{2\pi} (v^2 dv \sin\theta d\theta d\varphi) f(v) v \\
 &= \frac{4\pi}{n} \int_0^\infty v^3 f(v) dv
 \end{aligned}$$

NOTE: Equation of state : $\bar{p} = n kT \Rightarrow n = \frac{\bar{p}}{kT}$

$$\Rightarrow \Phi_0 = \frac{1}{4} \frac{\bar{p}}{kT} \sqrt{\frac{8}{\pi} \frac{kT}{m}} = \frac{\bar{p}}{\sqrt{2\pi m kT}}$$

Message: Pressure can be understood as the number of molecules striking a unit area surface in a unit of time.

Appendix: Debye theory of collective excitations ("phonons")

Let us consider the $3N_A$ normal modes of a mol of solid with energy

$$E_{\text{tot}} = \sum_{i=1}^{3N_A} \hbar \omega_i \left(\frac{1}{2} + n_i \right) = \frac{1}{2} \hbar \sum_{i=1}^{3N_A} \omega_i + \hbar \sum_{i=1}^{3N_A} n_i \omega_i$$
$$= E_0 + E_{N_A}(n_i)$$

with $n_i = 0, 1, 2, \dots$, where ω_i is the vibrational frequency of the normal mode "i".

* We will consider a box of size $L_{x,y,z}$ so that $\vec{k} \equiv$ quantised with

$$k_{x,y,z} = \frac{2\pi}{L_{x,y,z}} n_{x,y,z}$$

with $|\vec{k}| < k_D$. ^{Debye} For each \vec{k} there are three vibrational modes:

• Longitudinal $\Rightarrow \omega_1(\vec{k}) = c_L |\vec{k}|$

• Transversal $\Rightarrow \omega_2(\vec{k}) = \omega_3(\vec{k}) = c_T |\vec{k}|$

where c_L, c_T are the speed of longitudinal/transversal sound waves.

i) Determination of Debye frequency as the one below which the total number of modes is $3NA$.

NOTE: Continuum limit:

$$\sum_{k_x} g(k_x) = \frac{1}{\Delta k_x} \sum_{k_x} \Delta k_x g(k_x) \approx \frac{1}{\Delta k_x} \int_{-\infty}^{\infty} dk_x g(k_x)$$

$$\Delta k_x = \frac{2\pi}{L_x}$$

and $L_x \rightarrow \infty \Leftrightarrow \Delta k_x \rightarrow 0$

The number of wave vectors \vec{k} with $|\vec{k}|$ between $|\vec{k}|$ and $|\vec{k}| + d|\vec{k}|$ is given by

$$\frac{1}{\Delta k_x \Delta k_y \Delta k_z} \sum_{k_x k_y k_z} \Delta k_x \Delta k_y \Delta k_z = 1$$

$$\Rightarrow \underbrace{\frac{L_x L_y L_z}{(2\pi)^3}}_{\frac{V}{(2\pi)^3}} \int d^3 \vec{k} = \frac{V}{(2\pi)^3} (4\pi) \int |\vec{k}|^2 d|\vec{k}|$$

$$\Rightarrow \begin{aligned} \# \text{ wave vectors} &= \frac{V}{(2\pi)^3} 4\pi |\vec{k}|^2 d|\vec{k}| \\ \text{between } |\vec{k}| \text{ and } |\vec{k}| + d|\vec{k}| &= \frac{V}{2\pi^2} |\vec{k}|^2 d|\vec{k}| \end{aligned}$$

Changing variables to longitudinal / transversal frequencies $\omega_1 = c_L |\vec{k}|$ and $\omega_2 = \omega_3 = c_T |\vec{k}|$ we can obtain the number of longitudinal / transversal modes with frequency between $|\vec{\omega}|$ and $|\vec{\omega}| + d|\vec{\omega}|$:

- Longitudinal modes : $\frac{V}{2\pi^2} \frac{1}{c_L^3} |\vec{\omega}|^2 d|\vec{\omega}|$

- Transversal modes : $\frac{V}{2\pi^2} \frac{2}{c_T^3} |\vec{\omega}|^2 d|\vec{\omega}|$

$$\Rightarrow \text{Total number of modes : } \frac{V}{2\pi^2} \left(\frac{1}{c_L^3} + \frac{2}{c_T^3} \right) |\vec{\omega}|^2 d|\vec{\omega}|$$

$$= \frac{3V}{2\pi^2 c_s^3} |\vec{\omega}|^2 d|\vec{\omega}|$$

NOTE: c_s reduces to speed of sound if $c_L = c_T$.

The Debye frequency is defined as the one for which

$$\frac{3V}{2\pi^2 c_s^3} \int_0^{\omega_D = c_s k_D} |\vec{\omega}|^2 d|\vec{\omega}| \stackrel{!}{=} 3NA \quad \equiv \text{total number of modes are below } \omega_D$$

$$\Rightarrow \frac{3V}{2\pi^2 c_s^3} \frac{\omega_D^3}{3} = 3NA \quad \Rightarrow \quad \omega_D^3 = 6\pi^2 c_s^3 \underbrace{\frac{NA}{V}}_{n \equiv \text{molar density}}$$

ii) Computation of specific heat per mol in the Debye approximation

$$\bar{E} = \sum_{i=1}^{3N_A} \hbar \omega_i \left[\frac{1}{2} + \frac{1}{e^{\beta \hbar \omega_i} - 1} \right]$$

normal modes
are independent
=> Z factorises

$$\Rightarrow c_v = \left(\frac{\partial \bar{E}}{\partial T} \right)_V = \left(\frac{\partial \bar{E}}{\partial \beta} \right)_V \cdot \frac{\partial \beta}{\partial T} = -\frac{1}{kT^2} \left(\frac{\partial \bar{E}}{\partial \beta} \right)$$

$$= \frac{1}{kT^2} \sum_{i=1}^{3N_A} \frac{e^{\beta \hbar \omega_i} \hbar^2 \omega_i^2}{(e^{\beta \hbar \omega_i} - 1)^2} = k \sum_{i=1}^{3N_A} \frac{e^{\beta \hbar \omega_i} (\beta \hbar \omega_i)^2}{(e^{\beta \hbar \omega_i} - 1)^2}$$

Continuum

limit =>

$$c_v = k \int_0^{\omega_D} \frac{e^{\beta \hbar |\vec{\omega}|}}{(e^{\beta \hbar |\vec{\omega}|} - 1)^2} \underbrace{(\beta \hbar |\vec{\omega}|)^2}_{x \equiv \beta \hbar |\vec{\omega}|} \underbrace{\frac{3V}{2\pi^2 c_s^3} |\vec{\omega}|^2 d|\vec{\omega}|}_{\text{total number of modes}}$$

"Debye approximation"

of modes



$$= k \int_0^{x_D} \frac{e^x}{(e^x - 1)^2} x^4 \frac{3V}{2\pi^2 c_s^3} \frac{1}{(\beta \hbar)^3} dx$$

$$= k \frac{3V}{2\pi^2 (c_s \beta \hbar)^3} \int_0^{\beta \hbar \omega_D} \frac{e^x}{(e^x - 1)^2} x^4 dx$$

NOTE: Recall that $\omega_D^3 = 6\pi^2 c_s^3 \frac{NA}{V}$

$$= \frac{3k}{2\pi^2 (c_s \beta \hbar)^3} 6\pi^2 NA \left(\frac{c_s}{\omega_D}\right)^3 \int_0^{\beta \hbar \omega_D} \frac{e^x}{(e^x - 1)^2} x^4 dx$$

$$= 9k NA \left(\frac{1}{\beta \hbar \omega_D}\right)^3 \int_0^{\beta \hbar \omega_D} \frac{e^x}{(e^x - 1)^2} x^4 dx$$

$$= 3 \underbrace{k NA}_R \underbrace{f_D(\beta \hbar \omega_D)}_{y = \beta \hbar \omega_D} = 3R \underbrace{f_D\left(\frac{\hbar \omega_D}{kT}\right)}_{\Theta_D \equiv \frac{\hbar \omega_D}{k}}$$

$$= 3R f_D\left(\frac{\Theta_D}{T}\right) \quad \text{"Debye temperature"}$$

$$\text{with } f_D(y) = \frac{3}{y^3} \int_0^y \frac{e^x}{(e^x - 1)^2} x^4 dx \quad \equiv \quad \text{"Debye function"}$$

iii) Evaluation of c_v at high / low temperature and comparison with Einstein theory of solids

$$a) T \rightarrow \infty \Leftrightarrow x = \frac{\hbar \omega}{kT} \rightarrow 0$$

In this case

$$e^x \approx 1+x \Rightarrow f_D(\gamma) \approx \frac{3}{\gamma^3} \int_0^{\hbar \omega} \frac{1+x}{x^2} x^4 dx$$

$$\approx \frac{3}{\gamma^3} \int_0^{\hbar \omega} x^2 dx = 1$$

$$\Rightarrow c_v \approx 3R \quad [\text{equipartition theorem}]$$

$$b) T \rightarrow 0 \Leftrightarrow \gamma = \frac{\hbar \omega_D}{kT} \rightarrow \infty$$

In this case

$$\int_0^{\infty} \frac{e^x}{(e^x - 1)^2} x^4 dx = 4 \int_0^{\infty} \frac{x^3}{e^x - 1} dx = \frac{4\pi^4}{15}$$

$$\Rightarrow f_D(\gamma) = \frac{4\pi^4}{5} \frac{1}{\gamma^3}$$

$$\Rightarrow c_v \approx 3R \frac{4\pi^4}{5} \left(\frac{kT}{\hbar \omega_D} \right)^3 = \frac{12\pi^4}{5} R \left(\frac{T}{\Theta_D} \right)^3$$

NOTE: Einstein model:

$$c_v \approx 3R \left(\frac{\Theta_E}{T} \right)^2 \underbrace{e^{-\frac{\Theta_E}{T}}}_{\text{exponential decrease}}$$

$$T \rightarrow 0 \Rightarrow c_v \sim T^3$$

[Experimentally]