TD3 Distribution canonique

Le système est en contact thermique avec un 'thermostat' qui lui impose de l'extérieur sa température

Ex 3) Paramagnétisme de Langevin

N molécules, mt magnétique $\vec{\mu}$, chp extérieur $\vec{B} = B\vec{e_3}$: $W = -\vec{\mu}.\vec{B}$

1) 2 situations $\vec{\mu}\uparrow \uparrow\vec{B} \Rightarrow W_\uparrow = -\mu B$

$\vec{\mu}\downarrow \uparrow\vec{B} \Rightarrow W_\downarrow = -(-\mu B) = \mu B$

$$P_\uparrow = \frac{e^{-\beta W_\uparrow}}{e^{-\beta W_\uparrow} + e^{-\beta W_\downarrow}} = \frac{e^{\beta\mu B}}{e^{\beta\mu B} + e^{-\beta\mu B}} \quad \text{avec } \beta = \frac{1}{k_B T}$$

$$P_\downarrow = \frac{e^{-\beta\mu B}}{e^{\beta\mu B} + e^{-\beta\mu B}}$$

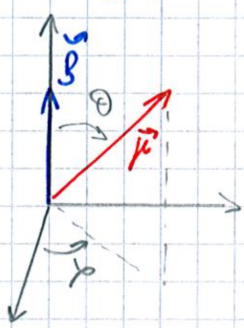
$\Rightarrow$ Valeur moyenne du mt magnétique $\langle \Pi_3(T) \rangle = N(P_\uparrow \mu + P_\downarrow(-\mu))$

$$\langle \Pi_3(T) \rangle = N\mu \frac{(e^{\beta\mu B} - e^{-\beta\mu B})}{e^{\beta\mu B} + e^{-\beta\mu B}}$$

on pose $x = \frac{\mu B}{k_B T} = \beta\mu B$ sans dimension

$$\langle \Pi_3(T) \rangle = N\mu \frac{e^{x} - e^{-x}}{e^{x} + e^{-x}} = N\mu \, th\left(\frac{\mu B}{k_B T}\right)$$

2) a) μ selon Θ et $\Theta + d\Theta$



$W = -\vec{\mu}.\vec{B} = -\mu B\cos\Theta$

syst sphérique

W indep de φ

proba dP que $\vec{\mu}$ pointe dans l'angle solide $d\Omega = \sin\Theta\, d\Theta\, d\varphi = 2\pi \sin\Theta\, d\Theta$

$\equiv$ proportionnelle à $\begin{cases} e^{-\frac{W}{k_B T}} \\ \text{nbre d'états répondant aux cdts fixées par } d\Omega \end{cases}$

$$\Rightarrow \quad dN(\theta) = cste\ e^{-\frac{W}{k_B T}}\ 2\pi \sin\theta\, d\theta$$

$$= cste\ e^{\frac{\mu B \cos\theta}{k_B T}}\ 2\pi \sin\theta\, d\theta$$

Détermination de cste $\Rightarrow \quad N = cste \displaystyle\int_0^{\pi} e^{\frac{\mu B \cos\theta}{k_B T}}\ 2\pi \sin\theta\, d\theta$

$\cos\theta = u$

$-\sin\theta\, d\theta = du$

$$= cste \int_1^{-1} e^{\frac{\mu B u}{k_B T}} (-2\pi)\, du = \frac{2\pi\, cste\, k_B T}{\mu B} \left[e^{\frac{\mu B u}{k_B T}} \right]_{-1}^{1} = \frac{4\pi\, cste}{\mu B} k_B T \left(\frac{e^{\frac{\mu B}{k_B T}} - e^{-\frac{\mu B}{k_B T}}}{2} \right)$$

$$\Rightarrow \quad cste = \frac{\mu B N}{4\pi k_B T\, sh\left(\frac{\mu B}{k_B T}\right)}$$

Soit $\Rightarrow \quad dN(\theta) = \dfrac{\mu B N}{\cancel{4\pi}\,2\, k_B T\, sh\left(\frac{\mu B}{k_B T}\right)}\ e^{\frac{\mu B \cos\theta}{k_B T}}\ \cancel{2\pi} \sin\theta\, d\theta$

$$= \frac{\mu B}{k_B T} \frac{N}{2} \frac{1}{sh\left(\frac{\mu B}{k_B T}\right)} e^{\frac{\mu B \cos\theta}{k_B T}} \sin\theta\, d\theta \quad \text{ou} \quad dP(\theta) = \frac{1}{2} \frac{\mu B}{k_B T} \frac{1}{sh\left(\frac{\mu B}{k_B T}\right)} e^{\frac{\mu B \cos\theta}{k_B T}} \sin\theta\, d\theta$$

b) $\langle M'_z(T) \rangle = \displaystyle\int_0^{\pi} N \mu_z\, dP(\theta) = \int_0^{\pi} N (\mu \cos\theta) \frac{1}{2} \frac{\mu B}{k_B T} \frac{1}{sh\left(\frac{\mu B}{k_B T}\right)} e^{\frac{\mu B \cos\theta}{k_B T}} \sin\theta\, d\theta$

$$= \frac{N \mu^2 B}{2 k_B T} \frac{1}{sh\left(\frac{\mu B}{k_B T}\right)} \int_0^{\pi} e^{\frac{\mu B \cos\theta}{k_B T}} \underbrace{\cos\theta}_{u} \sin\theta\, d\theta$$

c) $u = \cos\theta \qquad du = -\sin\theta\, d\theta$

$v = -\dfrac{k_B T}{\mu B} e^{\frac{\mu B \cos\theta}{k_B T}} \qquad dv = e^{\frac{\mu B \cos\theta}{k_B T}} \sin\theta\, d\theta$ } INTEGRATION PAR PARTIE

$$\langle M'_z(T) \rangle = \frac{N \mu^2 B}{2 k_B T} \frac{1}{sh\left(\frac{\mu B}{k_B T}\right)} \left[\left[-\cos\theta \frac{k_B T}{\mu B} e^{\frac{\mu B \cos\theta}{k_B T}} \right]_0^{\pi} - \frac{k_B T}{\mu B} \int_0^{\pi} e^{\frac{\mu B \cos\theta}{k_B T}} \sin\theta\, d\theta \right]$$

$$= \frac{N \mu^{\cancel{2}} \cancel{B}}{\cancel{2 k_B T}} \frac{1}{sh\left(\frac{\mu B}{k_B T}\right)} \left[\frac{\cancel{2 k_B T}}{\cancel{\mu B}} \underbrace{\left(\frac{e^{\frac{\mu B}{k_B T}} + e^{-\frac{\mu B}{k_B T}}}{2} \right)}_{ch\left(\frac{\mu B}{k_B T}\right)} - \frac{\cancel{2} k_B^2 T^2}{\mu^2 B^2} \underbrace{\left(\frac{e^{\frac{\mu B}{k_B T}} - e^{-\frac{\mu B}{k_B T}}}{2} \right)}_{sh\left(\frac{\mu B}{k_B T}\right)} \right]$$

$$= N\mu \left[\frac{ch\left(\frac{\mu B}{k_B T}\right)}{sh\left(\frac{\mu B}{k_B T}\right)} - \frac{k_B T}{\mu B} \right] = N\mu \left[\coth\left(\frac{\mu B}{k_B T}\right) - \frac{k_B T}{\mu B} \right] = N\mu\, \mathcal{L}\left(\frac{\mu B}{k_B T}\right)$$

fonction de Langevin.

$\mathcal{L}(x) = \coth x - \frac{1}{x}$

3) Comparaison $\langle \Pi_z(T) \rangle$ et $\langle \Pi'_z(T) \rangle$ à h^te température

$\Leftrightarrow \frac{\mu B}{k_B T} = x \ll 1 \qquad e^x \simeq 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cancel{\frac{x^4}{4!}}$

$$\coth x = \frac{e^x + e^{-x}}{e^x - e^{-x}} \simeq \frac{\left(1 + \cancel{x} + \frac{x^2}{2} + \cancel{\frac{x^3}{6}} + \frac{x^4}{24}\right) + \left(1 - \cancel{x} + \frac{x^2}{2} - \cancel{\frac{x^3}{6}} + \frac{x^4}{24}\right)}{\left(\cancel{1} + x + \frac{x^2}{2} + \frac{x^3}{6} + \frac{x^4}{24}\right) - \left(\cancel{1} - x + \frac{x^2}{2} - \frac{x^3}{6} + \frac{x^4}{24}\right)}$$

$$\simeq \frac{(2 + x^2)}{2x + \frac{x^3}{3}} = \frac{1 + \frac{x^2}{2}}{x\left(1 + \frac{x^2}{6}\right)} = \frac{1}{x}\left(1 + \frac{x^2}{2}\right)\left(1 + \frac{x^2}{6}\right)^{-1} \simeq \frac{1}{x}\left(1 + \frac{x^2}{2}\right)\left(1 - \frac{x^2}{6}\right)$$

$$\simeq \frac{1}{x}\left(1 + \frac{x^2}{3}\right) = \frac{1}{x} + \frac{x}{3}$$

soit $\mathcal{L}(x) = \coth x - \frac{1}{x} \simeq \frac{x}{3}$

$$\langle \Pi'_z(T) \rangle = \frac{1}{3} \frac{N\mu^2 B}{k_B T}$$

$$\langle \Pi_z(T) \rangle = N\mu \frac{1}{\coth\left(\frac{\mu B}{k_B T}\right)} = N\mu \coth^{-1}\left(\frac{\mu B}{k_B T}\right) \simeq N\mu \left(\frac{1}{x}\left(1 - \frac{x^2}{3}\right)\right)^{-1}$$

$$= N\mu x = N\frac{\mu^2 B}{k_B T} = 3 \langle \Pi'_z(T) \rangle$$

Ex 1) <u>Gaz parfait dans l'ensemble canonique</u>

équilibre thermodynamique à T, N molécules, masse m, V

1) Fonction de partition d'une molécule : z $\Rightarrow$ q^té sans dimension

$$z = \iiint \iiint e^{-\frac{p^2}{2mk_B T}} \frac{d^3\vec{r}\, d^3\vec{p}}{h^3} = \frac{1}{h^3} \underbrace{\iiint d^3\vec{r}}_{V} \iiint e^{-\frac{(p_x^2 + p_y^2 + p_z^2)}{2mk_B T}} dp_x\, dp_y\, dp_z$$

$$= \frac{V}{h^3} \left[\int_{-\infty}^{+\infty} e^{-\frac{p_x^2}{2mk_B T}} dp_x\right]^3 \qquad \int_0^{\infty} e^{-ax^2} dx = \frac{1}{2}\sqrt{\frac{\pi}{a}} \qquad a = \frac{1}{2mk_B T}$$

$$= \frac{V}{h^3} (2\pi m k_B T)^{3/2}$$

2) Fonction de partition du gaz parfait : Z $\qquad$ N molécules <u>indiscernables</u>

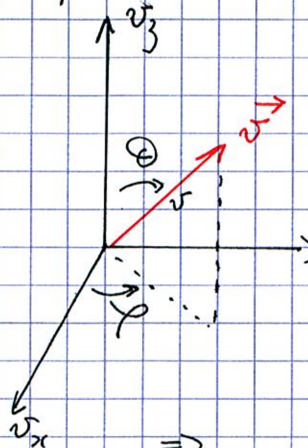
$$Z = \frac{z^N}{N!} \Rightarrow \text{approximation de MB}$$

Ex 5] Pompage cryogénique

N_0 molécules m ds V, contact avec T

$$PV = N_0 k_B T$$

1/ Ss espace des vitesses



$$\underbrace{dP(\vec v)}_{\vec v \text{ à } d^3\vec v \text{ près}} = \underbrace{C e^{-\beta \frac{m v^2}{2}}}_{f(\vec v) \text{ 'densité de proba' ou fct de distribution de } \vec v} d^3\vec v$$

$= \frac{dN(\vec v)}{N_0}$ ← nbre de molécules ayant $\vec v$ à $d^3\vec v$ près ; N_0 ← nbre total de molécules

soit $dN(\vec v) = N_0 C e^{-\beta\frac{mv^2}{2}} \underbrace{d^3\vec v}_{v^2 dv \sin\theta \, d\theta \, d\varphi}$

$\Rightarrow$ $dN(\vec v) = N_0 C e^{-\beta\frac{mv^2}{2}} v^2 dv \sin\theta \, d\theta \, d\varphi$

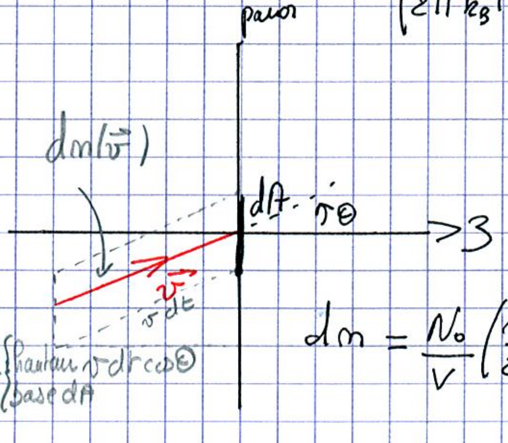
Calcul de C $\Rightarrow \iiint dN(\vec v) = N_0 \Rightarrow C\int_0^\infty v^2 e^{-\beta\frac{mv^2}{2}} dv \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\varphi = 1$

$$4\pi C \underbrace{\int_0^\infty v^2 e^{-\beta\frac{mv^2}{2}} dv}_{\frac14\sqrt{\frac{8\pi k_B^3T^3}{m^3}}} = 1$$

$$\pi C\sqrt{\frac{8\pi k_B^3T^3}{m^3}} = 1 \Rightarrow C = \left(\frac{m}{2\pi k_B T}\right)^{3/2}$$

Finalement $\Rightarrow dN(\vec v) = N_0\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-\frac{mv^2}{2k_BT}} dv \sin\theta \, d\theta \, d\varphi$

2/



cylindre { hauteur $v\,dt\cos\theta$; base dA

$$\frac{dn(\vec v)}{N_0} = \frac{(dA\, v\, dt\cos\theta)}{V} dP(\vec v)$$

$$\Rightarrow dn(\vec v) = \frac{N_0}{V}\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^3 e^{-\frac{mv^2}{2k_BT}} dv \, dA \, dt \sin\theta\cos\theta \, d\theta \, d\varphi$$

3/

$$dn = \frac{N_0}{V}\left(\frac{m}{2\pi k_B T}\right)^{3/2} dA\,dt \underbrace{\int_0^\infty v^3 e^{-\frac{mv^2}{2k_BT}} dv}_{\frac{4k_B^2T^2}{2m^2}} \underbrace{\int_0^{2\pi} d\varphi}_{2\pi} \underbrace{\int_0^{\pi/2} \sin\theta\cos\theta \, d\theta}_{1/2}$$

$$= \frac{N_0}{V}\left(\frac{m}{2\pi k_B T}\right)^{3/2} dA\,dt \times \frac{(2\pi)^2 k_B^2 T^2}{2\pi m^2} = \frac{N_0}{V} dA\,dt \left(\frac{k_B T}{2\pi m}\right)^{1/2}$$

refroidissement de dA $\Rightarrow$ condensation $\Rightarrow$ $P \downarrow$: pompage cryogénique

4) $N(t=0)=N_0$ $dN(t)$ nbre de molécules qui frappent dA pendant dt

$$\frac{dn}{N_0} = -\frac{dN(t)}{N(t)} = \frac{1}{V}\, dA\, dt \left(\frac{k_B T}{2\pi m}\right)^{1/2} \Rightarrow dN(t) = -\frac{N(t)}{V}\, dA\, dt \left(\frac{k_B T}{2\pi m}\right)^{1/2}$$

↑ disparition

ou encore $\dfrac{dN(t)}{dN(t)} = -\alpha\, dt \Rightarrow N(t) = N_0 e^{-\alpha t}$

avec $\alpha = \dfrac{dA}{V}\left(\dfrac{k_B T}{2\pi m}\right)^{1/2}$

Pression $P(t)$ telle que $P(t)V = N(t) k_B T$ (GP)

$$\Leftrightarrow P(t) = \frac{N(t)}{V} k_B T = \frac{N_0}{V} e^{-\alpha t} k_B T = P_0 e^{-\alpha t}$$

AN: $V = \dfrac{4}{3}\pi R^3 = \dfrac{4\pi}{3} 10^{-3} m^3$; $dA = 10^{-4} m^2$

$$\Rightarrow t = \frac{1}{\alpha} \ln \frac{P_0}{P(t)} = \frac{V}{dA}\left(\frac{2\pi m}{k_B T}\right)^{1/2} \ln \frac{P_0}{P(t)}$$

$t = 3{,}3$ s