

VPŠF cvičení

Jaynes' principle of maximal entropy (in quantum domain)

- state space $\mathcal{H}$... Hilbert space, $\dim \mathcal{H} < \infty$
- pure state $|\psi\rangle \in \mathcal{H}$
- density operator ρ - ensemble of systems in different states
 - $\rho \geq 0$
 - $\text{Tr} \rho = 1$
- $\rightarrow \rho = \sum p_i |\psi_i\rangle\langle\psi_i|$, $p_i \geq 0$, p_i - probabilities

$$\rho = \sum p_i |\psi_i\rangle\langle\psi_i|$$

- mean value of observable $A = A^\dagger$ $\langle A \rangle_\rho = \text{Tr} \{ A \rho \}$
- Measure of uncertainty - von Neumann entropy $S(\rho) = -k \text{Tr} (\rho \ln \rho) \stackrel{!}{=} -k \sum p_i \ln p_i$
 - $S(|\psi\rangle\langle\psi|) = 0$
 - $S(\rho) = 0 \Leftrightarrow \rho = |\psi\rangle\langle\psi|$
 - $S(\rho_A \otimes \rho_B) = S(\rho_A) + S(\rho_B)$
 - $S(\frac{1}{N} I) \geq S(\rho) \quad \forall \rho$, $\frac{1}{N} I$ - maximally mixed state
 - $S(\sum p_i \rho_i) \geq \sum p_i S(\rho_i)$ $\alpha p_i \leq 1$, $\sum p_i = 1$

- $\rho(0) \xrightarrow{t} \rho_{eq}$ (0th principle of thermodynamics)

$$\rho_{eq} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \rho(t) dt$$

- 1957 Jaynes - information approach

- we have information about equilibrium state - mean values of observables $\{A_i\}$, $A_i = A_i^\dagger$, $\langle A_i \rangle_{\rho_{eq}} = \text{Tr} \{ A_i \rho_{eq} \} = \alpha_i$

- "Among all states satisfying the conditions above, the one with maximal entropy represents the state of the system in the best way."

Mathematical intermezzo

- variation of functional $\text{Tr} f(X)$, where $X = X^\dagger$ and f is analytical

$$X = \sum x_i |e_i\rangle\langle e_i| \rightarrow f(X) = \sum f(x_i) |e_i\rangle\langle e_i|$$

$$\delta \text{Tr} f(X) = \text{Tr} f(X + \delta X) - \text{Tr} f(X), \quad f(x) = \sum_{n=0}^{\infty} \frac{f^{(n)}(x_0)}{n!} (x - x_0)^n$$

$$= \sum_{n=0}^{\infty} \frac{f^{(n)}(x_0)}{n!} \text{Tr} [(X + \delta X - x_0 I)^n - (X - x_0 I)^n]$$

$$= \sum_{n=0}^{\infty} \frac{f^{(n)}(x_0)}{n!} \left[\text{Tr} (X - x_0 I)^n + n \text{Tr} \{ (X - x_0 I)^{n-1} \delta X \} + \mathcal{O}(\delta X^2) - \text{Tr} (X - x_0 I)^n \right]$$

$$= \sum_{n=1}^{\infty} \frac{f^{(n)}(x_0)}{(n-1)!} \text{Tr} \{ (X - x_0 I)^{n-1} \delta X \} + \mathcal{O}(\delta X^2)$$

$$= \text{Tr} \left\{ \sum_{n=0}^{\infty} \frac{(f')^{(n)}(x_0)}{n!} (X - x_0 I)^n \delta X \right\} + \mathcal{O}(\delta X^2) = \text{Tr} \{ f'(X) \delta X \} + \mathcal{O}(\delta X^2)$$

- Klein inequality: Let f be convex and differentiable function on interval I .
Then for hermitian operators A and B , $f(A), f(B) \in I$, it holds that

$$\text{Tr} \{ f(A) - f(B) - (A-B)f'(B) \} \geq 0$$

If f is strictly convex then the equality holds iff $A=B$

Proof: $A|e_i\rangle = a_i|e_i\rangle$, $\langle e_i, f_j \rangle = c_{ij}$
 $B|f_j\rangle = b_j|f_j\rangle$, $\sum_i |c_{ij}|^2 = \sum_j |c_{ij}|^2 = 1$

$$\begin{aligned} \langle e_i | f(A) - f(B) - (A-B)f'(B) | e_i \rangle &= f(a_i) - \sum_j f(b_j) |c_{ij}|^2 - \underbrace{(a_i - \sum_j b_j |c_{ij}|^2) \sum_j f'(b_j) |c_{ij}|^2}_{=0} \\ &= \sum_j |c_{ij}|^2 (f(a_i) - f(b_j) - (a_i - b_j) f'(b_j)) \geq 0 \end{aligned}$$

if f is strictly convex then we get equality

$$\Leftrightarrow |c_{ij}| = 0 \text{ or } a_i = b_j$$

$$\text{Tr} \{ A-B \}^2 = \sum_{ij} |c_{ij}|^2 (a_i - b_j)^2 = 0 \Leftrightarrow c_{ij} = 0 \text{ or } a_i = b_j$$

f is convex

$$f(y) - f(x) = (y-x) f'(\xi) \geq (y-x) f'(x)$$

f is strictly convex

$$f(y) - f(x) - (y-x) f'(x) > 0 \quad x \neq y$$

In particular for $f(x) = \begin{cases} x \ln x & \text{for } x > 0 \\ 0 & \text{for } x = 0 \end{cases}$

$$\rightarrow f'(x) = 1 + \ln x \text{ for } x > 0$$

$$\begin{aligned} \rightarrow \text{Tr} A \ln A - \text{Tr} B \ln B &\geq \text{Tr} \{ (A-B)(I + \ln B) \} \\ \text{Tr} A \ln A - \text{Tr} A \ln B &\geq \text{Tr} A - \text{Tr} B, \quad A \geq 0, B > 0 \end{aligned}$$

Lagrange functional: $\Lambda(\rho, \lambda_i) = -k \text{Tr}(\rho \ln \rho) - \sum \lambda_i \text{Tr} \{ A_i \rho \} - k\alpha \text{Tr} \rho$

$$\delta \Lambda = k \text{Tr} \left\{ \rho \left[-I - \ln \rho - \sum \lambda_i A_i - \alpha I \right] \right\} = 0$$

$$\Rightarrow (1+\alpha)I + \ln \rho + \sum \lambda_i A_i = 0 \Rightarrow \rho_{eq} = \exp \left(-(\alpha+1)I - \sum \lambda_i A_i \right) = \frac{1}{Z} e^{-\sum \lambda_i A_i}$$

$$Z = \text{Tr} \left\{ \exp \left(-\sum \lambda_i A_i \right) \right\}$$

$\rightarrow$ the solution is strictly positive - for finite A_i we always get mixed state

- for infinite λ_i we can reach zero

$$\bullet S(\rho_{eq}) = -k \text{Tr} [\rho_{eq} \ln \rho_{eq}] = -k \left\{ \text{Tr} [\rho_{eq} (-\ln Z - \sum \lambda_i A_i)] \right\} = -k \ln Z + k \sum \lambda_i \langle A_i \rangle_{eq}$$

$\rightarrow$ is it really the state of maximal entropy

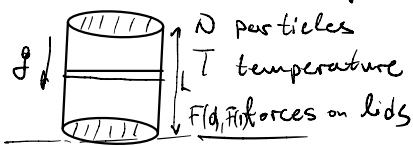
$$\text{let us have } \rho \neq \rho_{eq}, \text{Tr}(A_i \rho') = \text{Tr}(A_i \rho_{eq}) = A_i$$

$$\text{Tr} X \ln Y - \text{Tr} X \ln X \leq \text{Tr} Y - \text{Tr} X$$

$$\text{we plug in } X = \rho', Y = \rho_{eq} \rightarrow S(\rho') \leq -k \text{Tr} \rho' \ln \rho_{eq} = -k [-\ln Z - \sum \lambda_i A_i] = S(\rho_{eq})$$

$\bullet$ We want to check if we have $\langle A_i \rangle_{eq} = - \left(\frac{\partial \ln Z}{\partial \lambda_i} \right)_{\lambda_{j \neq i}}$ in quantum regime

Ex) Classical ideal gas



State equation $pV = NkT$

$$\rightarrow p(z) S dz = n(z) dz kT, \quad n(z) = N \psi(z)$$

$$\psi(\vec{p}, \vec{q}) = \frac{1}{Z_1} e^{-\beta H_1} = \frac{1}{Z_1} e^{-\beta \left(\frac{\vec{p}^2}{2m} + mgz \right)}$$

$$\rightarrow \psi(z) = \frac{1}{Z_1} \int d\vec{p} \int dx dy e^{-\beta \left(\frac{\vec{p}^2}{2m} + mgz \right)} = \frac{1}{Z_1} \left(\frac{2\pi m}{\beta} \right)^{3/2} S e^{-\beta mgz}$$

$$1 = \int_0^L \psi(z) dz = \frac{1}{Z_1} \left(\frac{2\pi m}{\beta} \right)^{3/2} S \frac{1 - e^{-\beta mgL}}{\beta mg} \Rightarrow Z_1 = \left(\frac{2\pi m}{\beta} \right)^{3/2} S \frac{1 - e^{-\beta mgL}}{\beta mg}$$

$$\rightarrow \psi(z) = \frac{\beta mg}{1 - e^{-\beta mgL}} e^{-\beta mgz}$$

$$\rightarrow p(z) = \frac{NkT}{S} \frac{\beta mg}{1 - e^{-\beta mgL}} e^{-\beta mgz} = \frac{Nmg}{S} \frac{e^{-\beta mgz}}{1 - e^{-\beta mgL}}$$

$$F(0) = Sp(0) = Nmg \frac{1}{1 - e^{-\beta mgL}}, \quad F(L) = Sp(L) = Nmg \frac{e^{-\beta mgL}}{1 - e^{-\beta mgL}} = \frac{Nmg}{e^{\beta mgL} - 1}$$

Ex) Uranium enrichment

Uranium natural sample $\begin{cases} c_1 = 0,72\% \text{ } ^{235}\text{U} \\ c_2 = 99,27\% \text{ } ^{238}\text{U} \end{cases}$

$\text{UF}_6 - 330^\circ\text{K}$ we insert this into cylindric vessel in gravitational field

Calculate concentrations $c_i(z)$ and determine the maximal enrichment of ^{235}U

$$c_i(z) = \frac{n_i(z)}{n_1(z) + n_2(z)} \quad n_i(z) = N_i \frac{\beta m_i g}{1 - e^{-\beta m_i gL}} e^{-\beta m_i g z}$$

$$c_1(z) = \frac{1}{1 + \frac{n_2(z)}{n_1(z)}} \quad \frac{n_1(z)}{n_2(z)} = \frac{N_1}{N_2} \frac{m_1}{m_2} \frac{1 - e^{-\beta m_2 gL}}{1 - e^{-\beta m_1 gL}} e^{-\beta (m_1 - m_2) g z}$$

$$c_1(z) = \left(1 + \frac{c_2 m_2}{c_1 m_1} \frac{1 - \exp(-\beta m_1 gL)}{1 - \exp(-\beta m_2 gL)} e^{-\beta (m_2 - m_1) g z} \right)^{-1} \quad \begin{matrix} \frac{c_1}{c_2} \\ m_2 > m_1 \end{matrix} \rightarrow \text{maximum for } z = L$$

$$c_1(L) = \left(1 + \frac{c_2}{c_1} \frac{m_2}{m_1} \frac{e^{\beta m_1 gL} - 1}{e^{\beta m_2 gL} - 1} \right)^{-1} \quad (\text{note: for enrichment of 4\% you need } L \approx 10^5 \text{ m})$$

Ex) Classical ideal gas in vessel with a piston of mass M

- system has temperature T

- N molecules

- homogeneous gravitational field

a) formulate the first principle of thermodynamics for this system

b) formulate the corresponding statistical ensemble

c) determine the mean height, variation of height and internal energy

Grandcanonical ensemble

• can exchange energy and particles with its environment $\rightarrow$ observables: H, N

$$[H, N] = 0 \Rightarrow H = \bigoplus_N H_N, \quad H = \bigoplus_N H_N, \quad g = \bigoplus_N g_N$$

$$U = \text{Tr}_H H g = \sum_N \text{Tr}_N g_N H_N \dots \beta$$

$$\langle N \rangle = \text{Tr}_H N g = \sum_N N \text{Tr}_N g_N \dots - \alpha$$

$$\rightarrow g_T = \frac{1}{Z_G} e^{-\beta H + \alpha N}, \quad Z_G = \text{Tr}_H e^{-\beta H + \alpha N} = \sum_N \text{Tr}_N e^{-\beta H + \alpha N} = \sum_N e^{\alpha N} \text{Tr}_N e^{-\beta H_N}$$

$$= \sum_N e^{\alpha N} Z_c(N)$$

$$dS = k\beta dU - k\alpha dN \rightarrow dU = \underbrace{\frac{1}{k\beta}}_T dS + \underbrace{\frac{k\alpha}{k\beta}}_\mu dN \rightarrow \frac{1}{k\beta} = T, \quad \alpha = \frac{\mu}{kT}$$

$$S = k \ln Z_G + k\beta U - k\alpha N \rightarrow -kT \ln Z_G = U - TS - \mu N = \Omega$$

$$d\Omega = -SdT - pdV - Nd\mu \Rightarrow p = -\left(\frac{\partial \Omega}{\partial V}\right)_{T, \mu} = kT \left(\frac{\partial \ln Z_G}{\partial V}\right)_{T, \mu}$$

Classical ideal gas

$$Z_G = \sum_{N=0}^{\infty} e^{\alpha N} Z_c(N) = \sum_{N=0}^{\infty} e^{\alpha N} \frac{1}{N!} z_1^N = \exp(e^{\alpha} z_1)$$

• More types of particles - non-interacting

$$\langle N_1 \rangle \dots - \alpha_1 \quad H = H_1 + H_2 \quad [H_1, H_2] = 0$$

$$\langle N_2 \rangle \dots - \alpha_2 \quad N = N_1 + N_2 \quad [N_1, N_2] = 0$$

$$Z_G = \text{Tr} e^{-\beta H_1 - \beta H_2 + \alpha_1 N_1 + \alpha_2 N_2} = \left(\text{Tr} e^{-\beta H_1 + \alpha_1 N_1} \right) \left(\text{Tr} e^{-\beta H_2 + \alpha_2 N_2} \right) = Z_G^{(1)} Z_G^{(2)}$$

⊗ Two ideal classical gases (m_1, m_2) with chemical potentials μ_1, μ_2 are kept in vessel with volume V and with temperature T . Calculate pressure of each gas and prove Dalton's law

$$z_1^{(1)} = \frac{V}{h^3} \left(\frac{2\pi m_1}{\beta} \right)^{3/2} \rightarrow Z_G^{(1)} = \exp \left(e^{\alpha_1} \frac{V}{h^3} \left(\frac{2\pi m_1}{\beta} \right)^{3/2} \right) = \exp \left(e^{\frac{\mu_1}{kT}} \frac{V}{h^3} (2\pi m_1 kT)^{3/2} \right)$$

$$Z_G = Z_G^{(1)} Z_G^{(2)} \rightarrow p = kT \left(\frac{\partial}{\partial V} \ln Z_G \right)_{T, \mu} = kT \left[\frac{\partial}{\partial V} \ln Z_G^{(1)} + \frac{\partial}{\partial V} \ln Z_G^{(2)} \right] =$$

$$p_i = kT \frac{\partial \ln Z_G^{(i)}}{\partial V} = kT \left[e^{\frac{\mu_i}{kT}} \left(\frac{2\pi m_i}{h^2} kT \right)^{3/2} + e^{\frac{\mu_2}{kT}} \left(\frac{2\pi m_2}{h^2} kT \right)^{3/2} \right] = p_1 + p_2$$

$$= kT e^{\frac{\mu_i}{kT}} \left(\frac{2\pi m_i}{h^2} kT \right)^{3/2}$$

$$N_i = \frac{\partial \ln Z_G^{(i)}}{\partial \mu_i} \cdot \frac{\partial \mu_i}{\partial \alpha_i} = \frac{1}{kT} e^{\frac{\mu_i}{kT}} V \left(\frac{2\pi m_i}{h^2} kT \right)^{3/2} \cdot kT$$

$$p_i = \frac{kT}{V} N_i$$

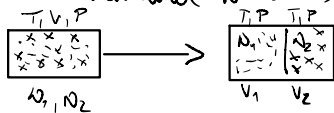
$$p = \frac{kT}{V} N_1 + \frac{kT}{V} N_2$$

Def: Specific volume $\equiv$ volume which gas occupies if it is alone under the pressure P

$$V_i = \frac{N_i kT}{P} = \frac{N_i kT}{\frac{N_i kT}{V}} = \frac{N_i}{N} V$$

Ex) Minimal work to separate two types of particles

- Two mixed gases with two different masses m_1, m_2 with number of molecules N_1 and N_2
- Assume system has temperature T and volume of the vessel V .
- What minimal work has to be done to separate gases?



2nd principle of thermodynamics: Transition between two equilibrium states A and B of closed system is accompanied with increase of entropy $S_B \geq S_A \Rightarrow \Delta S = S_B - S_A \geq 0$



system connected to bath with temperature T

$$\Delta S + \Delta S_{\text{bath}} \geq 0$$

$$\Delta Q + \Delta Q_{\text{bath}} = 0$$

$$T \Delta S_{\text{bath}} = \Delta Q_{\text{bath}}$$

$$\Rightarrow \Delta S \geq -\Delta S_{\text{bath}} = -\frac{\Delta Q_{\text{bath}}}{T} = \frac{\Delta Q}{T}$$

$$\left. \begin{array}{l} \Delta Q_1 = \Delta U_1 + \delta W_1 \\ \Delta Q_2 = \Delta U_2 + \delta W_2 \end{array} \right\} \oplus \underbrace{\Delta Q_1 + \Delta Q_2}_{\Delta Q} = \underbrace{\Delta U_1 + \Delta U_2}_{\Delta U} + \underbrace{\delta W_1 + \delta W_2}_{\Delta W}$$

for ideal gas $Z_G = \exp(e^{\alpha} z_1)$, $z_1 = \frac{V}{h^3} \left(\frac{2\pi m}{\beta} \right)^{3/2} \rightarrow U = -\frac{\partial \ln Z_G}{\partial \beta} = e^{\alpha} \frac{3}{2} \frac{z_1}{\beta} = \frac{3}{2} N k T$
 $N = \frac{\partial \ln Z_G}{\partial \alpha} = e^{\alpha} z_1$

$\Delta U = 0 \rightarrow T \Delta S \geq \Delta Q = \Delta W'$ work done by the system

$\Delta W = -\Delta W' \geq -T \Delta S$ work done on the system

entropy $S = k \ln Z_G + \frac{1}{T} U - \frac{1}{T} N = k e^{\alpha} z_1 + \frac{1}{T} \frac{3}{2} N k T - \frac{k T N}{T} \ln \frac{N}{z_1} = \frac{5}{2} k N - k N \ln \left[\frac{N}{V} \frac{h^3}{(2\pi m)^{3/2}} \right]$

$$-\Delta S = -k N_1 \ln \frac{N_1}{V} - k N_2 \ln \frac{N_2}{V} + k N_1 \ln \frac{N_1}{V_1} + k N_2 \ln \frac{N_2}{V_2} = \left| \frac{V_1}{N_1} = \frac{k T}{P} = \frac{V}{N} \right|$$

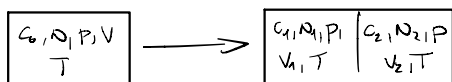
initial entropy final entropy of 1 final entropy of 2

$$= k N_1 \ln \left(\frac{N_1 + N_2}{N_1} \right) + k N_2 \ln \left(\frac{N_1 + N_2}{N_2} \right) \approx k \ln \left(\frac{N_1 + N_2}{N_1} \right)$$

Ex) Starting from natural uranium with $c_0 = 0,0072$ of ^{235}U and $\tilde{c}_0 = 1 - c_0$ of ^{238}U

One uses isotope separation of the UF_6 to produce enriched uranium with $c_1 = 0,032$ of ^{235}U which is accompanied with production of depleted uranium $c_2 = 0,002$ of ^{235}U

a) how much natural uranium must be treated in order to produce 1kg of nuclear fuel



$$N = N_1 + N_2$$

$$m = 1 \text{ kg} = N_1 (c_1 \cdot 235 u_p + (1 - c_1) 238 u_p)$$

$$c_0 N = c_1 N_1 + c_2 N_2 \rightarrow N_1 = 2,5 \cdot 10^{24}$$

$$m_{\text{in}} = N (c_0 m(^{235}\text{U}) + (1 - c_0) m(^{238}\text{U})) = 5,77 \text{ kg}$$

b) what is the minimal work to achieve this enrichment

$$\Delta S = S_1 + S_2 - S = -k N_1' \ln \frac{N_1'}{V_1} - k N_1'' \ln \frac{N_1''}{V_1} - k N_2' \ln \frac{N_2'}{V_2} - k N_2'' \ln \frac{N_2''}{V_2} + k c_0 N \ln \frac{c_0 N}{V} + k (1 - c_0) N \ln \frac{(1 - c_0) N}{V}$$

$$= k \left\{ -c_1 N_1 \ln \frac{c_1 N_1}{V_1} - (1 - c_1) N_1 \ln \frac{(1 - c_1) N_1}{V_1} - c_2 N_2 \ln \frac{c_2 N_2}{V_2} - (1 - c_2) N_2 \ln \frac{(1 - c_2) N_2}{V_2} + c_0 N \ln \frac{c_0 N}{V} + (1 - c_0) N \ln \frac{(1 - c_0) N}{V} \right\}$$

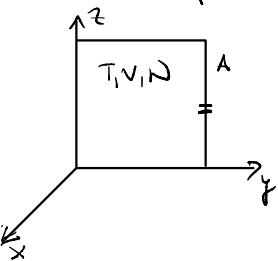
$$= k \left\{ \ln \frac{N}{V} \left[-c_1 N_1 - (1 - c_1) N_1 - c_2 N_2 - (1 - c_2) N_2 + c_0 N + (1 - c_0) N \right] - N_1 (c_1 \ln c_1 + (1 - c_1) \ln (1 - c_1)) \right.$$

$$\left. - N_2 (c_2 \ln c_2 + (1 - c_2) \ln (1 - c_2)) + N (c_0 \ln c_0 + (1 - c_0) \ln (1 - c_0)) \right\} \approx -1,2407 [J K^{-1} \text{ kg}^{-1}]$$

$$W \geq W_{\text{min}} = -T \Delta S = 436 \text{ J kg}^{-1}$$

• in reality is separation by gas diffusion it is $7 \cdot 10^7$ times higher

Gas diffusion



how many particles per second will go through the hole to the other side?

equilibrium $\Leftrightarrow$ size of the hole is much smaller in comparison with the mean free path

$$w(\vec{p}, \vec{q}) = \frac{1}{2} \exp\left(-\beta \frac{\vec{p}^2}{2m}\right), \quad w(\vec{p}) = \frac{V}{h^3} \frac{1}{V} \left(\frac{\beta}{2\pi m}\right)^{3/2} e^{-\beta \frac{\vec{p}^2}{2m}}$$

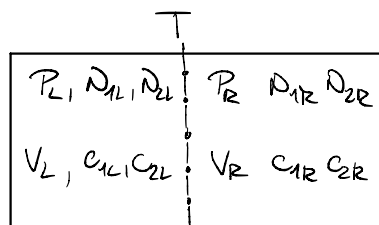
$$\begin{aligned} \int n A v_x dt \left(\frac{\beta}{2\pi m}\right)^{3/2} e^{-\beta \frac{\vec{p}^2}{2m}} d\vec{p} &= n A \left(\frac{\beta}{2\pi m}\right)^{3/2} dt \int_0^\infty dp_x \frac{p_x}{m} \bar{v} \frac{\beta^2}{2m} \int_R dp_y e^{-\beta \frac{p_y^2}{2m}} \int_R dp_z e^{-\beta \frac{p_z^2}{2m}} \\ &= n A \left(\frac{\beta}{2\pi m}\right)^{3/2} \frac{dt}{m} \int_0^\infty -\frac{m}{\beta} e^{-\beta \frac{p_x^2}{2m}} \Big|_0^\infty \frac{2\pi m}{\beta} = n A \left(\frac{1}{2\pi m \beta}\right)^{1/2} dt \\ \Rightarrow \frac{dN}{dt} &= -n A \sqrt{\frac{kT}{2\pi m}} \end{aligned}$$

Ex) Separation by gas diffusion

Natural uranium

index 1 - lighter isotope ^{235}U

index 2 - heavier isotope ^{238}U



Area of holes $\equiv A$

a) determine master equations which drive concentrations on both sides

b) assume stationary value of isotope ^{235}U on the right side and based on that calculate maximal enrichment of this isotope

$$a) -\frac{dN_{1R}}{dt} = \frac{dN_{1L}}{dt} = -\frac{N_{1L}}{V_L} \sqrt{\frac{kT}{2\pi m_1}} + \frac{N_{1R}}{V_R} \sqrt{\frac{kT}{2\pi m_1}} = \sqrt{\frac{kT}{2\pi m_1}} \left(-\frac{N_{1L}}{N_L} \frac{N_L}{V_L} + \frac{N_{1R}}{N_R} \frac{N_R}{V_R} \right) = \frac{1}{\sqrt{2\pi m_1 kT}} (-c_{1L} P_L + c_{1R} P_R)$$

$$-\frac{dN_{2R}}{dt} = \frac{dN_{2L}}{dt} = \frac{1}{\sqrt{2\pi m_2 kT}} (-c_{2L} P_L + c_{2R} P_R)$$

$$b) \frac{dC_{1R}}{dt} = 0 = \frac{d}{dt} \left(\frac{N_{1R}}{N_{1R} + N_{2R}} \right) = \frac{1}{N_{1R} + N_{2R}} \frac{dN_{1R}}{dt} - \frac{N_{1R}}{(N_{1R} + N_{2R})^2} \left(\frac{d}{dt} N_{1R} + \frac{d}{dt} N_{2R} \right) = \frac{(N_{1R} + N_{2R}) \dot{N}_{1R} - N_{1R} (\dot{N}_{1R} + \dot{N}_{2R})}{(N_{1R} + N_{2R})^2}$$

$$\Rightarrow N_{2R} \dot{N}_{1R} = N_{1R} \dot{N}_{2R} \Leftrightarrow \frac{\dot{N}_{1R}}{\dot{N}_{2R}} = \frac{c_{1L} P_L - c_{1R} P_R}{c_{2L} P_L - c_{2R} P_R} \sqrt{\frac{m_2}{m_1}} = \frac{N_{1R}}{N_{2R}} = \frac{c_{1R}}{c_{2R}}$$

$$(c_{1L} P_L - c_{1R} P_R) \sqrt{\frac{m_2}{m_1}} = \frac{c_{1R}}{c_{2R}} c_{2L} P_L - c_{1R} P_R \quad \left| \frac{1}{P_L c_{1R}} \right.$$

$$\left(\frac{c_{1L}}{c_{1R}} - \frac{P_R}{P_L} \right) \sqrt{\frac{m_2}{m_1}} = \frac{c_{2L}}{c_{2R}} - \frac{P_R}{P_L} \Leftrightarrow \frac{c_{1L}}{c_{1R}} \sqrt{\frac{m_2}{m_1}} - \frac{c_{2L}}{c_{2R}} = \frac{P_R}{P_L} \left(\sqrt{\frac{m_2}{m_1}} - 1 \right) \geq 0 \text{ and it is zero for } P_L \gg P_R$$

$$\frac{c_{1L}}{c_{1R}} \sqrt{\frac{m_2}{m_1}} - \frac{c_{2L}}{1 - c_{1R}} \geq 0 \rightarrow (1 - c_{1R}) c_{1L} \sqrt{\frac{m_2}{m_1}} - c_{1R} c_{2L} \geq 0 \rightarrow c_{1L} \sqrt{\frac{m_2}{m_1}} \geq c_{1R} (c_{1L} \sqrt{\frac{m_2}{m_1}} + c_{2L})$$

$$\Rightarrow c_{1R} \leq \frac{c_{1L} \sqrt{\frac{m_2}{m_1}}}{1 + c_{1L} \left(\sqrt{\frac{m_2}{m_1}} - 1 \right)} \rightarrow \text{maximal enrichment } c_{1R} = c_{1L} \sqrt{\frac{m_2}{m_1}}$$

- $P_L \gg P_R$

- $c_{1L} \rightarrow 0$

Ex) Calculate change of entropy for separation by diffusion within time dt

N_{1L}, N_{2L}	N_{1R}, N_{2R}
T, V_L, P_L	T, V_R, P_R

$\xrightarrow{dt}$

$N_{1L}-dN_{1R}, N_{2L}+dN_{2R}$	$N_{1R}+dN_{1R}, N_{2R}+dN_{2R}$
T, P_L, V_L'	T, P_R, V_R'

$$S = \frac{5}{2} kN - kN \ln \left[\frac{N}{V} h^3 \left(\frac{m}{2\pi kT} \right)^{3/2} \right]$$

$$\frac{dS}{k} = -(N_{1R}+dN_{1R}) \ln \frac{N_{1R}+dN_{1R}}{V_R'} - (N_{2R}+dN_{2R}) \ln \frac{N_{2R}+dN_{2R}}{V_R'} - (N_{1L}-dN_{1R}) \ln \frac{N_{1L}-dN_{1R}}{V_L'} - (N_{2L}-dN_{2R}) \ln \frac{N_{2L}-dN_{2R}}{V_L'}$$

$$+ N_{1R} \ln \frac{N_{1R}}{V_R} + N_{2R} \ln \frac{N_{2R}}{V_R} + N_{1L} \ln \frac{N_{1L}}{V_L} + N_{2L} \ln \frac{N_{2L}}{V_L}$$

$$= -dN_{1R} \ln \frac{N_{1R}}{V_R} - (N_{1R}+dN_{1R}) \ln \frac{1+\frac{dN_{1R}}{N_{1R}}}{1+\frac{dN_{2R}}{N_{2R}}} - dN_{2R} \ln \frac{N_{2R}}{V_R} - (N_{2R}+dN_{2R}) \ln \frac{1+\frac{dN_{2R}}{N_{2R}}}{1+\frac{dN_{1R}}{N_{1R}}} + dN_{1R} \ln \frac{N_{1L}}{V_L} - (N_{1L}-dN_{1R}) \ln \frac{1-\frac{dN_{1R}}{N_{1L}}}{1+\frac{dN_{2R}}{N_{2L}}}$$

$$+ dN_{2R} \ln \frac{N_{2L}}{V_L} - (N_{2L}-dN_{2R}) \ln \frac{1-\frac{dN_{2R}}{N_{2L}}}{1+\frac{dN_{1R}}{N_{1L}}} = 1^{st} \text{ order contribution in } dN_{1R}, dN_{2R}$$

$$\approx dN_{1R} \ln \frac{N_{1L}}{V_L} \frac{V_R}{N_{1R}} + dN_{2R} \ln \frac{N_{2L}}{V_L} \frac{V_R}{N_{2R}} - dN_{1R} + \frac{N_{1R}}{N_{2R}} dN_{2R} - dN_{2R} + \frac{N_{2R}}{N_{1R}} dN_{1R} + dN_{1R} + \frac{N_{1L}}{N_{2L}} dN_{2R} + \frac{N_{2L}}{N_{1L}} dN_{1R}$$

$$= dN_{1R} \ln \frac{c_{1L} P_L}{c_{1R} P_R} + dN_{2R} \ln \frac{(1-c_{1L}) P_L}{(1-c_{1R}) P_R}$$

• change of internal energy $dU = 0$

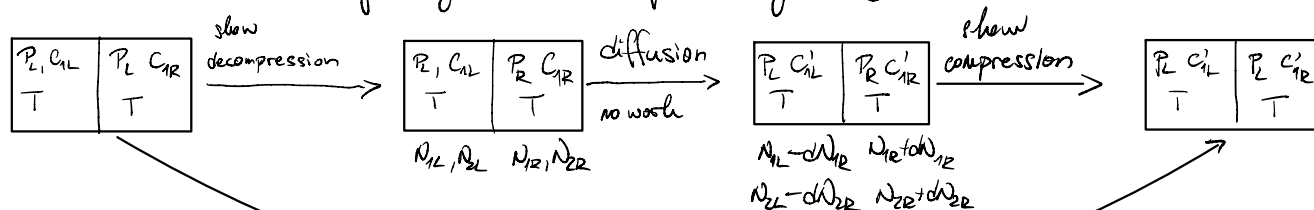
• what is the work done by the gas? $\delta W = P_L dV_L + P_R dV_R = d(P_L V_L + P_R V_R) = d((N_L + N_R) kT) = 0$

$$\rightarrow \delta Q - dU + \delta W = 0 \Rightarrow dS \geq \frac{\delta Q}{T} = 0$$

$$dN_{1R} \ln \frac{c_{1L} P_L}{c_{1R} P_R} = k(c_{1L} P_L - c_{1R} P_R) \ln \frac{c_{1L} P_L}{c_{1R} P_R} = (x-y)(\ln x - \ln y) \geq 0$$

process is reversible $\Leftrightarrow dS = 0 \Leftrightarrow c_{1L} P_L = c_{1R} P_R \Leftrightarrow P_L = P_R$ very inefficient regime
 $(1-c_{1L}) P_L = (1-c_{1R}) P_R \Leftrightarrow c_{1L} = c_{1R}$

• Make estimate of delivered work during separation process by diffusion in comparison with the minimal work given by 2nd law of thermodynamics



$$\Delta Q_1 = \Delta W_1 = \int_{P_L}^{P_R} P dV = \int_{P_L}^{P_R} P d \left(\frac{N_R kT}{P} \right) = - \int_{P_L}^{P_R} \frac{N_R kT}{P} dP = -N_R kT \ln \frac{P_R}{P_L}$$

$$\Delta Q_3 = \Delta W_3 = -(N_R + dN_R) kT \ln \frac{P_L}{P_R} = (N_R + dN_R) kT \ln \frac{P_R}{P_L}$$

$$\Delta W_1 + \Delta W_3 = dN_R kT \ln \frac{P_R}{P_L} \dots \text{delivered heat / work performed by gas}$$

• total change of entropy during all three steps

$$dS + \frac{\Delta Q_1}{T} + \frac{\Delta Q_3}{T} = k dN_{1R} \ln \frac{c_{1L} P_L}{c_{1R} P_R} + k dN_{2R} \ln \frac{(1-c_{1L}) P_L}{(1-c_{1R}) P_R} + k dN_R \ln \frac{P_R}{P_L} = k \left(dN_{1R} \ln \frac{c_{1L}}{c_{1R}} + dN_{2R} \ln \frac{1-c_{1L}}{1-c_{1R}} \right)$$

- work delivered to the system

$$\delta W = -\Delta W = T\delta S - T\delta S_0 \geq -T\delta S_0 = \delta W_0$$

$$\frac{\delta W}{kT dN_{1R}} = \ln \frac{P_L}{P_R} \left(1 + \frac{dN_{2R}}{dN_{1R}} \right) = \left| \frac{dN_{2R}}{dN_{1R}} = \sqrt{\frac{m_1}{m_2}} \frac{c_{1L}P_L - c_{2R}P_R}{c_{1L}P_L - c_{1R}P_R} \stackrel{\text{stationary regime}}{=} \frac{c_{2R}}{c_{1R}} \right| = \ln \frac{P_L}{P_R} \left(1 + \frac{c_{2R}}{c_{1R}} \right) = \left| \frac{P_L}{P_R} = 5 \right| \left| \frac{c_{2R}}{c_{1R}} = \sqrt{\frac{m_2}{m_1}} \frac{c_{1L}}{c_{1R}} \right| 420$$

$$\frac{\delta W_0}{kT dN_{1R}} = -\ln \frac{c_{1L}P_L}{c_{1R}P_R} - \frac{dN_{2R}}{dN_{1R}} \ln \frac{1-c_{1L}}{1-c_{1R}} = \dots = 2 \cdot 10^{-5}$$

$$\frac{\delta W}{\delta W_0} \sim 1,1 \cdot 10^7$$

Surface chemistry

- adsorption $\begin{cases} \text{chemical reactions} \\ \text{intermolecular forces} \end{cases}$

Langmuir adsorption model

- adsorption of ideal gas onto an idealized surface
- surface is homogeneous
- molecules can bond to each site with the same energy $-\epsilon > 0$
- energy of empty site is 0
- monolayer adsorption - each site can only hold one molecule and they are non-interacting
- we assume equilibrium at given temperature T and pressure P

What is efficiency of adsorption $\theta = \frac{n}{N}$ mean value of adsorbed molecules
number of sites

$$\begin{aligned} \bullet \text{ 2 states } & \begin{cases} \text{empty } E=0 & n_0=0 \\ \text{filled } E=-\epsilon & n_\epsilon=1 \end{cases} \\ Z_1 &= e^{\alpha \cdot 0 - \beta \cdot 0} + e^{\alpha + \beta \epsilon} = 1 + e^{\alpha + \beta \epsilon} \\ Z &= (1 + e^{\alpha + \beta \epsilon})^N \end{aligned}$$

Principle: If we remove constraints in constrained equilibrium, the new equilibrium is characterized by the maximum entropy of all possible constrained equilibria

$$dS_i = \frac{1}{T_i} dU_i - \frac{\mu_i}{T_i} dN_i$$

$$dS = dS_1 + dS_2, \text{ constraints } U = \text{const}, N = \text{const. } dU_1 = dU_2, dN_1 = -dN_2$$

$$-\left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU_1 + \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) dN_1 = 0 \Rightarrow T_1 = T_2 \wedge \mu_1 = \mu_2$$

1... gas
2... sites

$$Z_G^{\text{gas}} = \exp\left(e^\alpha \frac{V}{h^3} \left(\frac{2\pi m}{\beta}\right)^{3/2}\right) \quad -kT \ln Z_G = \Omega \quad p = -\frac{\partial \Omega}{\partial V} = kT e^\alpha \left(\frac{2\pi m}{h^2 \beta}\right)^{3/2} \rightarrow e^\alpha = \frac{p}{kT} \left(\frac{h^2 \beta}{2\pi m}\right)^{3/2}$$

$$\theta = \frac{e^\alpha}{e^{-\beta \epsilon} + e^\alpha} = \frac{\frac{p}{kT} h^3 \left(\frac{\beta}{2\pi m}\right)^{3/2}}{e^{-\beta \epsilon} + \frac{p}{kT} h^3 \left(\frac{\beta}{2\pi m}\right)^{3/2}} = \frac{p}{p + e^{-\beta \epsilon} \frac{kT}{h^3} \left(\frac{2\pi m}{\beta}\right)^{3/2}}$$

BET theory of multilayer adsorption (Brunauer, Emmett, Teller 1938)

- more layers
- bond energy to surface: $-\epsilon_1$
- bond energy to molecules: $-\epsilon_L$

$$Z_1 = 1 + \sum_{n=1}^{\infty} e^{\alpha n + \beta \epsilon_1 + (n-1)\beta \epsilon_L} = 1 + \frac{e^{\beta(\epsilon_1 - \epsilon_L)} e^{\alpha + \beta \epsilon_L}}{1 - e^{\alpha + \beta \epsilon_L}}$$

$$= 1 + \frac{e^{\alpha + \beta \epsilon_1}}{1 - e^{\alpha + \beta \epsilon_L}}$$

$$Z_G = \left(1 + \frac{e^{\alpha + \beta \epsilon_1}}{1 - e^{\alpha + \beta \epsilon_L}} \right)^N$$

$$n = \frac{\partial \ln Z_G}{\partial \alpha} = N \left(1 + \frac{e^{\alpha + \beta \epsilon_1}}{1 - e^{\alpha + \beta \epsilon_L}} \right)^{-1} \cdot \frac{e^{\alpha + \beta \epsilon_1} (1 - e^{\alpha + \beta \epsilon_L}) + e^{\alpha + \beta \epsilon_1} e^{\alpha + \beta \epsilon_L}}{(1 - e^{\alpha + \beta \epsilon_L})^2}$$

$$= N \frac{e^{\alpha + \beta \epsilon_1}}{(1 - e^{\alpha + \beta \epsilon_L}) (1 - e^{\alpha + \beta \epsilon_L} + e^{\alpha + \beta \epsilon_1})}$$

$$\theta = \frac{n}{N} = \frac{e^{\alpha + \beta \epsilon_1}}{(1 - e^{\alpha + \beta \epsilon_L}) (1 - e^{\alpha} (e^{\beta \epsilon_1} - e^{\beta \epsilon_L}))}$$

$$x = e^{\alpha + \beta \epsilon_L}$$

$$C = e^{\beta(\epsilon_1 - \epsilon_L)} \text{ BET constant}$$

$$= \frac{Cx}{(1-x)(1+Cx-x)} \rightarrow \frac{x}{n(1-x)} = \frac{1+Cx-x}{Nc} = \frac{1}{Nc} + \frac{C-1}{Nc} x$$

$$\frac{1}{\frac{nkT}{P} \left(\frac{1}{x} - 1 \right)} = \frac{1}{\frac{Nc}{P}} + \frac{C-1}{\frac{Nc}{P}} x, \quad x = \frac{P}{P_0}$$

P — equilibrium pressure of adsorbate (gas)

P_0 — saturation pressure of adsorbate

Statistical model of breathing

- O_2 $\nearrow$ 97% transported by hemoglobin
3% transported in form of dissolved gas

- hemoglobin — hemoprotein — 4 atoms of iron
— chemical reaction — HbO_2 — 1 molecules
 HbO_2 — 4 molecules

- myoglobin — one iron
— responsible for storing oxygen in muscles

- CO_2 — each molecule of hemoglobin can bind just one molecule of CO_2

- 1 Torr — pressure of 1 mm of mercury
 $= 133,33 \text{ Pa}$

- 1 Atm = 760 Torrs

- partial pressures of gases in human body

O_2 : lungs 100 Torrs CO_2 : lungs 35 Torrs
tissues 35 Torrs

Ord muscles 5 Torrs

- partial concentration

atmosphere: N_2 — 78% lungs: O_2 — 15%
 O_2 — 21%
 CO_2 — 0,034%

at room temperature $kT = 0,0267 \text{ eV} \rightarrow \beta = 37,43 \text{ eV}^{-1}$

$$h = 4,1316 \cdot 10^{-15} \text{ eV} \cdot s$$

$$\hbar = 6,582 \cdot 10^{-16} \text{ eV} \cdot s$$

$$m_{O_2} = 2 \cdot 16 \cdot m_n, \quad m_{CO} = 28 \cdot m_n, \quad m_{CO_2} = 44 \cdot m_n$$

1) Assume hemoprotein capable of storing one oxygen

1st state $-E = -0,65 \text{ eV}$ occupied

2nd state 0 non-occupied

Calculate efficiency of saturation of oxygen in hemoprotein (myoglobin)

$$Z^{(1)} = 1 + e^{\alpha + \beta E} \quad \frac{n}{N} = \frac{\partial \ln Z^{(1)}}{\partial \alpha} = \frac{e^{\alpha + \beta E}}{1 + e^{\alpha + \beta E}} \quad e^{\alpha} = \frac{P}{kT} h^3 \left(\frac{\lambda}{2\pi m} \right)^{3/2}$$

$$\Theta = 0,9984 \text{ for } 100 \text{ Torr}, \quad \Theta = 0,9953 \text{ for } 35 \text{ Torr}$$

2) Toxicity of CO - assume presence of CO in atmosphere

• Hemoprotein with one site for oxygen / CO

O_2 - binding energy $0,65 \text{ eV}$

CO - binding energy $0,78 \text{ eV}$

Calculate ratio of occupied hemoglobin by oxygen as a function of concentration of CO $\frac{r}{r}$

• possible states: no O_2 no CO 0 $\langle E \rangle \dots \beta$

one O_2 no CO $-E_1$ $\langle N_1 \rangle \dots \alpha_1 \dots \text{oxygen}$

no O_2 one CO $-E_2$ $\langle N_2 \rangle \dots \alpha_2 \dots \text{CO}$

$$Z^{(1)} = 1 + e^{\alpha_1 + \beta E_1} + e^{\alpha_2 + \beta E_2}$$

$$\langle N_1 \rangle = \frac{\partial \ln Z}{\partial \alpha_1} = N \frac{e^{\alpha_1 + \beta E_1}}{1 + e^{\alpha_1 + \beta E_1} + e^{\alpha_2 + \beta E_2}}$$

$$e^{\alpha_2} = \frac{r}{0,15} \left(\frac{m_{O_2}}{m_{CO}} \right)^{3/2} e^{\alpha_1}$$

$$\Theta_0^{-1} = 1 + e^{-\alpha_1 - \beta E_1}$$

$$\Theta^{-1} = 1 + e^{-\alpha_1 - \beta E_1} + e^{\alpha_2 - \alpha_1 + \beta(E_2 - E_1)}$$

$$= \Theta_0^{-1} + \frac{r}{0,15} \left(\frac{m_{O_2}}{m_{CO}} \right)^{3/2} e^{\beta(E_2 - E_1)}$$

$$\approx 1 + 1000r$$

$$e^{\alpha_1} = \frac{P_{O_2}}{kT} h^3 \left(\frac{1}{2\pi m_{O_2} kT} \right)^{3/2}$$

$$e^{\alpha_2} = \frac{P_{CO}}{P_{O_2}} \frac{P_{O_2}}{kT} h^3 \left(\frac{1}{2\pi m_{O_2} kT} \right)^{3/2} \left(\frac{m_{O_2}}{m_{CO}} \right)^{3/2} = \frac{P_{CO}}{P_{O_2}} \left(\frac{m_{O_2}}{m_{CO}} \right)^{3/2} e^{\alpha_1}$$

$$\frac{P_{CO} V}{kT N_{CO}} \left\{ \Rightarrow \frac{P_{CO}}{P_{O_2}} = \frac{N_{CO}}{N_{O_2}} = \frac{C_{CO}}{C_{O_2}} \approx \frac{r}{0,15} \right.$$

3) Model of gradual occupation of hemoprotein sites

• 4 sites for O_2 with binding energies $E_1 = 0,38 \text{ eV}$, $E_2 = E_3 = \frac{1}{2}(E_1 + E_4) = 0,515 \text{ eV}$, $E_4 = 0,65 \text{ eV}$

a) filling first site $\Theta = \frac{1}{1 + e^{-\alpha - \beta E_1}}$ $\Theta = 0,0243$ $\Theta = 0,0087$

b) filling second site

1st	2nd	E_n	N_n	g_n
0	0	0	0	1
1	0	$-E_1$	1	2
1	1	$-(E_1 + E_2)$	2	1

$$Z_G = \left(1 + 2e^{\alpha + \beta E_1} + e^{2\alpha + \beta(E_1 + E_2)} \right)^N$$

$$\Theta = \frac{n}{N} = \frac{1}{2} \frac{2e^{\alpha + \beta E_1} + 2e^{2\alpha + \beta(E_1 + E_2)}}{1 + 2e^{\alpha + \beta E_1} + e^{2\alpha + \beta(E_1 + E_2)}}$$

$$\Theta = 0,1066$$

$$\Theta = 0,0201$$

c) filling three sites

1st	2nd	3rd	E_n	N_n	g_n
0	0	0	0	0	1
1	0	0	$-E_1$	1	3
1	1	0	$-(E_1 + E_2)$	2	3
1	1	1	$-(E_1 + E_2 + E_3)$	3	1

$$Z_G = \left(1 + 3e^{\alpha + \beta E_1} + 3e^{2\alpha + \beta(E_1 + E_2)} + e^{3\alpha + \beta(E_1 + E_2 + E_3)} \right)^N$$

$$\Theta = \frac{n}{N} = \frac{1}{3} \frac{3e^{\alpha + \beta E_1} + 2e^{2\alpha + \beta(E_1 + E_2)} + e^{3\alpha + \beta(E_1 + E_2 + E_3)}}{1 + 3e^{\alpha + \beta E_1} + 3e^{2\alpha + \beta(E_1 + E_2)} + e^{3\alpha + \beta(E_1 + E_2 + E_3)}}$$

$$\Theta = 0,3433$$

$$\Theta = 0,0453$$

d) 4 sites

1st	2nd	3rd	4th	E_n	N_n	g_n
0	0	0	0	0	0	1
1	0	0	0	$-E_1$	1	4
1	1	0	0	$-(E_1 + E_2)$	2	6
1	1	1	0	$-(E_1 + E_2 + E_3)$	3	4
1	1	1	1	$-(E_1 + E_2 + E_3 + E_4)$	4	1

$$\Theta = 0,9926$$

$$\Theta = 0,7684$$

4) Hemoprotein capable to bind one molecule of oxygen and one molecule of CO_2

$$\langle E \rangle \dots \beta, \langle N_1 \rangle \dots \alpha, \langle N_2 \rangle \dots \alpha''$$

$$\text{binding energy for } \text{O}_2 \quad -\varepsilon = -0.65 \text{ eV}$$

$$\text{CO}_2 \quad -\varepsilon'' = -0.65 \text{ eV}$$

$$\text{energy when both are bound} \quad -(\varepsilon + \varepsilon'' - \delta) = -1.1 \text{ eV} \Rightarrow \delta = 0.2 \text{ eV}$$

Show how concentration of CO_2 helps to transport O_2

O_2	CO_2	E_T
0	0	0
1	0	$-\varepsilon$
0	1	$-\varepsilon''$
1	1	$-(\varepsilon + \varepsilon'' - \delta)$

$$Z_G = (1 + \exp(\alpha + \beta\varepsilon) + \exp(\alpha' + \beta\varepsilon'') + \exp(\alpha + \alpha'' + \beta(\varepsilon + \varepsilon'' - \delta)))^N$$

$$\theta = \frac{N_1}{N} = \frac{\partial \ln Z_G}{\partial \alpha} = \frac{\exp(\alpha + \beta\varepsilon) + \exp(\alpha + \alpha'' + \beta(\varepsilon + \varepsilon'' - \delta))}{1 + \exp(\alpha + \beta\varepsilon) + \exp(\alpha' + \beta\varepsilon'') + \exp(\alpha + \alpha'' + \beta(\varepsilon + \varepsilon'' - \delta))}$$

$$= \frac{1}{1 + e^{-\alpha - \beta\varepsilon} \underbrace{(1 + e^{\alpha'' + \beta(\varepsilon'' - \delta)})^{-1} (1 + e^{\alpha' + \beta\varepsilon'})}_A}$$

$$\text{if } \delta = 0 \quad \theta_0 = \frac{1}{1 + e^{-\alpha - \beta\varepsilon}}$$

$$\frac{1}{\theta_0} - \frac{1}{\theta} = e^{-\alpha - \beta\varepsilon} (1 - A) \Rightarrow \theta - \theta_0 = \theta \theta_0 e^{-\alpha - \beta\varepsilon} (1 - A) = \theta \theta_0 \left(\frac{1}{\theta_0} - 1 \right) (1 - A)$$

$$\Rightarrow \frac{\theta_0}{\theta} = \theta_0 \left(\frac{1}{\theta_0} - 1 \right) (1 - A) + 1 = 1 + (1 - \theta_0)(1 - A) = 1 + (1 - \theta_0) \frac{e^{\alpha' + \beta\varepsilon''} (e^{-\beta\delta} - 1)}{1 + e^{\alpha' + \beta(\varepsilon'' - \delta)}}$$

$$= 1 + (1 - \theta_0) \frac{e^{\beta\delta} - 1}{1 + e^{\alpha' - \beta\varepsilon'' + \beta\delta}}$$

5) Assume Hemoglobin with 4 sites for O_2 and one site for CO_2

$$\text{O}_2: -\varepsilon_1 = -0.35 \text{ eV}$$

$$-\varepsilon_2 = -\varepsilon_3 = -\frac{1}{2}(\varepsilon_1 + \varepsilon_4) = -0.575 \text{ eV}$$

$$-\varepsilon_4 = -0.65 \text{ eV}$$

$$\text{CO}_2: -\varepsilon' = -0.65 \text{ eV} \quad \text{if both occupied} \quad -(\varepsilon_{\text{O}_2} + \varepsilon_{\text{CO}_2} - \delta) \quad \delta = 0.2 \text{ eV}$$

$$Z_G = \dots$$

$$\theta = \frac{n}{N} = \dots$$

1st	2nd	3rd	4th	CO_2	E_T	g_T
0	0	0	0	0	0	1
1	0	0	0	0	$-\varepsilon_1$	4
1	1	0	0	0	$-\varepsilon_1 - \varepsilon_2$	6
1	1	1	0	0	$-\varepsilon_1 - \varepsilon_2 - \varepsilon_3$	4
1	1	1	1	0	$-\varepsilon_1 - \varepsilon_2 - \varepsilon_3 - \varepsilon_4$	1
0	0	0	0	1	$-\varepsilon'$	1
1	0	0	0	1	$-(\varepsilon_1 + \varepsilon' - \delta)$	4
1	1	0	0	1	$-(\varepsilon_1 + \varepsilon_2 + \varepsilon' - \delta)$	6
1	1	1	0	1	$-(\varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \varepsilon' - \delta)$	4
1	1	1	1	1	$-(\varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \varepsilon_4 + \varepsilon' - \delta)$	1

Electric and magnetic properties of matter

• classical description: $H_i = \frac{1}{2m} (\vec{p}_i - q\vec{A})^2 + q\phi(\vec{r}_i)$ $\vec{\pi} = \frac{\vec{p} - q\vec{A}}{m}$

Bohr, van Leeuwen theorem: Magnetization of ensemble of N classical electrons in stationary magnetic field in thermal equilibrium is zero

Proof: classical magnetic moment $\vec{\mu} = \frac{1}{2} q \vec{r} \times \vec{\pi} = \frac{1}{2} \frac{q}{m} \vec{L}$

$$\vec{M} = \sum_{i=1}^N \langle \vec{\mu}_i \rangle = \frac{1}{2} Nq \langle \vec{r} \times \vec{\pi} \rangle$$

$$\vec{a} \cdot \langle \vec{\pi} \rangle = \langle \vec{a} \cdot \vec{\pi} \rangle = \langle \vec{a} \cdot (\vec{r} \times \vec{\pi}) \rangle = \langle \vec{\pi} \cdot (\vec{a} \times \vec{r}) \rangle = \left\langle \frac{\vec{p} - q\vec{A}}{m} \cdot (\vec{a} \times \vec{r}) \right\rangle$$

$$= \frac{1}{Z_1} \int \frac{\vec{p} - q\vec{A}}{m} \cdot \vec{a}(\vec{r}) e^{-\beta \left(\frac{(\vec{p} - q\vec{A})^2}{2m} \right) + \beta q \phi(\vec{r})} d\vec{p} d\vec{r} = 0$$

Ex Classical polarization

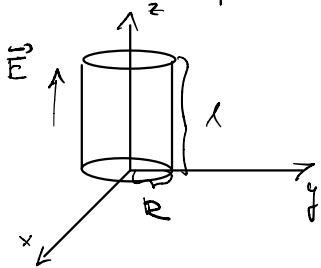
Assume cylindric capacitor with uniform field $\vec{E}$ oriented along the z axis.

(side we have ideal gas consisting of N particles with charge q and with mass m)

We assume low densities therefore no interaction among particles

Calculate partition function, polarization, internal energy

$$(e^{-\beta q E l} - 1)(e^{\beta q E l} - 1)$$



$$H_+ = \frac{p^2}{2m} - q E z$$

$$H_- = \frac{p^2}{2m} + q E z$$

$$Z_{\pm}^{(1)} = \int \frac{d^3 p d^3 x}{h^3} e^{-\beta \left(\frac{p^2}{2m} \mp q E z \right)}$$

$$= \left(\frac{2\pi m}{h^2 \beta} \right)^{3/2} S \cdot \int_{-l}^l e^{\mp \beta q E z} dz = \left(\frac{2\pi m}{h^2 \beta} \right)^{3/2} S \frac{1}{\mp \beta q E} (e^{\mp \beta q E l} - 1)$$

$$Z_k = \frac{1}{N!} Z_+^{(1)N} \frac{1}{N!} Z_-^{(1)N} = \frac{1}{(N!)^2} \left(\frac{2\pi m}{h^2 \beta} \right)^{3N} S^{2N} \frac{1}{(\beta q E)^{2N}} \left(\sinh \frac{\beta q E l}{2} \right)^{2N} 4^N$$

$$1st \text{ law: } \delta Q = T \delta S = dU + \int \vec{P} d\vec{E}_0$$

work done by dielectric with fixed charges

$\vec{E}_0$ field without dielectric

contains interaction between dielectric and field

$$\Rightarrow dF = -S dT - \vec{P} d\vec{E} \rightarrow P_i = - \left(\frac{\partial F}{\partial E_i} \right)_{T,N}$$

$$F = -k_B T \ln Z_k \quad P_z = k_B T \frac{\partial \ln Z_k}{\partial E_z} = S_{13} 2k_B T N \left[\frac{\beta q l}{2 \sinh(\frac{\beta q E l}{2})} - \frac{1}{E} \right] = S_{13} \beta q l N k_B T \left[\coth \frac{\beta q E l}{2} - \frac{2}{\beta q E l} \right]$$

$$U = - \frac{\partial \ln Z_k}{\partial \beta} = 3N k_B T - 2N \left[\coth \frac{\beta q E l}{2} \frac{q E l}{2} - \frac{1}{\beta} \right] = 3N k_B T - N q E l \left[\coth \frac{\beta q E l}{2} - \frac{2}{\beta q E l} \right]$$

$$= 3N k_B T - E \cdot P_z$$

$$-\frac{1}{x} + \coth x \xrightarrow{x \gg 1} \frac{e^x + e^{-x}}{e^x - e^{-x}} \approx 1 \quad P_z = N q l$$

$$P_z = \frac{1}{3} N q l \frac{\beta q E l}{2} = \frac{1}{6} \frac{N q^2 l^2}{k_B T}$$

Hamiltonian of charged particle in EM field

$$\hat{H} = \frac{(\hat{\vec{p}} - q\vec{A})^2}{2m} + q\varphi = \frac{\hat{\vec{p}}^2}{2m} - \frac{q}{m} \vec{A} \cdot \hat{\vec{p}} + \frac{q^2}{2m} A^2 + q\varphi \quad \text{in Coulomb gauge } \vec{\nabla} \cdot \vec{A} = 0$$

homogeneous stationary field $\vec{A} = -\frac{1}{2} \vec{r} \times \vec{B}$

$$\frac{i\hbar q}{m} \vec{A} \cdot \vec{\nabla} = -\frac{i\hbar q}{2m} (\vec{r} \times \vec{B}) \cdot \vec{\nabla} = -\frac{i\hbar q}{2m} (\vec{\nabla} \times \vec{r}) \cdot \vec{B} - \frac{q}{2m} (\vec{r} \times (-i\hbar \vec{\nabla})) \cdot \vec{B} = -\frac{q}{2m} \underbrace{\vec{L}}_{\hat{L}} \cdot \vec{B}$$

for electron we need to include spin ($\vec{B} = (0, 0, B)$)

$$\hat{H} = -\frac{\hbar^2}{2m} \Delta - e\varphi(\vec{r}, t) + \underbrace{\frac{q^2}{2m} A^2}_{\text{diamagnetic term}} + \underbrace{\frac{1}{\hbar} \left(\frac{e\hbar}{2m} \right) B \hat{L}_z + \frac{2\mu_B}{\hbar} B S_z}_{\text{paramagnetic term}}$$

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 - e\varphi(\vec{r}, t) + \frac{\mu_B B}{\hbar} (\hat{L} + 2\hat{S}) \quad , \quad \text{approximation for weak fields } - \vec{\mu} \propto \vec{J}$$

$\{J_z, J^2, L^2, S^2\}$ - commuting set of observables $\rightarrow |j, m\rangle$

$\vec{\mu}_J = g_J \mu_B \hat{J}$, $\vec{J} = \vec{L} + \vec{S}$, $\vec{\mu}_L = g_L \mu_B \hat{L}$, $\vec{\mu}_S = g_S \mu_B \hat{S}$

$g_J J = g_L L + g_S S \rightarrow g_J J^2 = g_L L J + g_S S J$

$2\hat{S} \cdot \hat{S} = \hat{S}^2 = \frac{1}{2}(\hat{J}^2 - \hat{L}^2 - \hat{S}^2)$

Lande factor

$$g_J j(j+1) = \frac{1}{2} (g_L + g_S) j(j+1) + \frac{1}{2} (g_L - g_S) (l(l+1) - s(s+1))$$

$$g_J = \frac{1}{2} (g_L + g_S) + \frac{1}{2} (g_L - g_S) \frac{l(l+1) - s(s+1)}{j(j+1)} = \frac{3}{2} + \frac{s(s+1) - l(l+1)}{2j(j+1)} \quad \text{for electrons}$$

$$\Rightarrow \hat{H} = \hat{H}_0 + \frac{\mu_B B}{\hbar} g_J \hat{J}$$

Ex) Magnetization of paramagnetic salt

assumption: 1) freeze out atomic motions vibrations } sufficiently low temperature

2) non-interacting particles

3) homogeneous magnetic field $\vec{B} = (0, 0, B)$

$$\hat{H} = -\vec{B} \cdot \sum_{i=1}^N \hat{\vec{\mu}}_i = \frac{\mu_B B}{\hbar} g_J \sum_{i=1}^N J_z^{(i)} \quad j_z \in \{-j, \dots, j\}$$

canonical ensemble - calculate Z, M, U

In general: $g = \frac{1}{Z} \exp(-\sum \lambda_i A_i)$ - we are very often not able to express mean values of observables analytically

Method: Choose set of test density operators $\{\tilde{g}\}$ for which we are able to calculate desired mean values
Then we choose the optimal candidate which represents the equilibrium state

$$S(\tilde{g}) \leq k \ln Z + k \sum \lambda_i \langle A_i \rangle_{\tilde{g}} \Leftrightarrow -kT \ln Z \leq -TS(\tilde{g}) + kT \sum \lambda_i \langle A_i \rangle_{\tilde{g}}$$

(Ex) In canonical ensemble $F \leq \tilde{U} - TS(\tilde{g}) = F(\tilde{g})$

We choose the state $\tilde{g}$ which minimizes the potential

• Minimum of potential $\Leftrightarrow$ minimum of quantum relative entropy

$$S(g_1 | g_2) = k \{ \text{Tr } g_1 \ln g_1 - \text{Tr } g_1 \ln g_2 \} \geq 0$$

$$\min S(\tilde{g} | g) = \min \{ k \text{Tr } \tilde{g} \ln \tilde{g} + k \text{Tr } \tilde{g} \ln Z + k \sum \lambda_i \text{Tr} \{ A_i \tilde{g} \} \} \geq 0 \Leftrightarrow -kT \ln Z \leq -TS(\tilde{g}) + kT \sum \lambda_i \langle A_i \rangle_{\tilde{g}}$$

$S(g_1 | g_2)$ - measure of distinguishability of state g_1 from true state of g_2
($P(g_1 = g_2) \sim \exp(-NS(g_1 | g_2))$)

Ferromagnetism

• model: solid ferromagnetic substance - spins with fixed positions which can interact mutually

$$\text{Ising model } \hat{H} = \mu_B B \sum_{i=1}^N \hat{s}_i - \sum_{i,j} V_{ij} \hat{s}_i \hat{s}_j, \quad \hat{s}_i = \frac{2\hat{S}_i^z}{\hbar}, \quad [\hat{s}_i, \hat{s}_j] = 0$$

- N particles with spin $1/2$ in homogeneous field $\vec{B} = (0, 0, B)$

- V_{ij} coupling constants

- Anisotropic magnetic substance with preferred z -axis

$$g = \frac{1}{Z} \exp(-\beta \hat{H}), \quad Z = \sum_{s_i = \pm 1} \exp(-\beta (\mu_B B \sum s_i - \sum_{i,j} V_{ij} s_i s_j))$$

• test set of states

- mean field approximation

- many interactions $\Rightarrow$ resulting homogeneous field B_{eff} , $H_{\text{eff}} = \mu_B B_{\text{eff}} \sum \hat{s}_i$
 $\tilde{g} = \frac{1}{Z} \exp(-\underbrace{\frac{\mu_B B_{\text{eff}}}{kT}}_{\chi} \sum \hat{s}_i)$, $\tilde{Z}(\chi) = \sum_{\{s_i\}} \exp(-\chi \sum_{i=1}^N s_i) = \prod_{i=1}^N (\sum_{s_i} e^{\chi s_i}) = (e^{\chi} + e^{-\chi})^N$

- we minimize $\tilde{F}(\chi)$ with respect to χ

1) Assume $B = 0$

$$\tilde{F}(\chi, B=0) = \tilde{U} - TS(\tilde{g})$$

$$\tilde{U} = \langle \hat{H} \rangle_{\tilde{g}} = \sum_{\{s_i, i=1\}} \frac{1}{Z} \exp(-\chi \sum_{i=1}^N s_i) (-\sum_{i,j} V_{ij} s_i s_j) = -\frac{1}{Z} \sum_{i,j} V_{ij} \sum_{s_i, s_j} s_i s_j \exp(-\chi \sum_{i=1}^N s_i)$$

$$= -\frac{1}{Z} \sum_{i,j} V_{ij} \sum_{s_i} s_i e^{-\chi s_i} \sum_{s_j} s_j e^{-\chi s_j} \left(\sum_{s_k} e^{\chi s_k} \right)^{N-2} = -\frac{1}{Z} \sum_{i,j} V_{ij} (e^{\chi} - e^{-\chi})(e^{\chi} - e^{-\chi})(e^{\chi} + e^{-\chi})^{N-2} = -\tanh^2 \chi \sum_{i,j} V_{ij}$$

$$TS(\tilde{g}) = kT \text{Tr}(\tilde{g} \ln \tilde{g}) = kTN \ln(2 \cosh \chi) - kTN \chi \tanh \chi$$

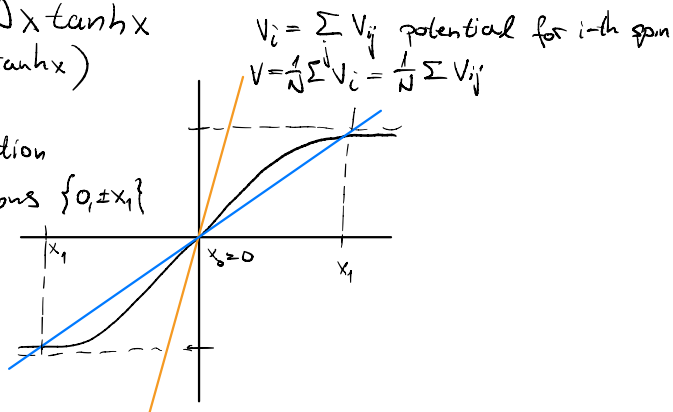
$$\tilde{F} = \tilde{U} - TS(\tilde{g}) = -\tanh^2 \chi \sum_{i,j} V_{ij} - kTN (\ln(2 \cosh \chi) - \chi \tanh \chi)$$

$$\tilde{F}'(\chi) = 0 \rightarrow \frac{kTx}{V} = \tanh x \quad a) \frac{kT}{V} \geq 1 \rightarrow 1 \text{ solution}$$

$$b) T < T_c = \frac{V}{k} \rightarrow 3 \text{ solutions } \{0, \pm x_1\}$$

$$T_c > T: \begin{matrix} x < 0 & \tilde{F}'(x) > 0 \\ x > 0 & \tilde{F}'(x) < 0 \end{matrix}$$

$$T_c < T: \begin{matrix} x < 0 & \tilde{F}'(x) < 0 \\ x > 0 & \tilde{F}'(x) > 0 \end{matrix}$$



Magnetization $M(S_1, \dots, S_N) = -\mu_B \sum_{i=1}^N \hat{S}_i$

$$\langle M \rangle = \text{Tr} \{ g M \} = \frac{1}{2} \sum_{\{S_i\}} \left(-\mu_B \sum_{i=1}^N S_i \exp(-x \sum S_i) \right) = -\frac{\mu_B}{2} \sum_{i=1}^N \sum_{S_i=-1}^1 S_i \exp(-x S_i) \left[\sum_{S_j=-1}^1 \exp(-x S_j) \right]^{N-1}$$

$$= \frac{\mu_B N \sinh x \cosh^{N-1} x}{\cosh^N x} = \mu_B N \tanh x$$

$T > T_c \rightarrow \langle M \rangle = 0$
 $T < T_c \rightarrow \langle M \rangle = \pm \mu_B N \frac{T_c}{T} x_1$
 $T \approx T_c \rightarrow x_1 \sim 0 \rightarrow \tanh x = x - \frac{x^3}{3} \rightarrow x - \frac{x^3}{3} = \frac{T_c}{T} x \rightarrow x \left((1 - \frac{T_c}{T}) - \frac{x^2}{3} \right) = 0 \Rightarrow x = \pm \sqrt{3(1 - \frac{T_c}{T})}$
 $\rightarrow \langle M \rangle = \pm \mu_B N \frac{T_c}{T} \sqrt{3(1 - \frac{T_c}{T})}$

$T \rightarrow 0 \rightarrow x_1 \rightarrow +\infty : \frac{kT}{V} x = \tanh x = \frac{e^x - e^{-x}}{e^x + e^{-x}} = \frac{1 - e^{-2x}}{1 + e^{-2x}} = 1 - 2e^{-2x} \sum_{n=0}^{\infty} (-1)^n e^{-2nx} = 1 - 2e^{-2x} + 2e^{-4x} - 2e^{-6x} + \dots$

$$x = \beta V [1 - 2\exp(-2\beta V(1 - e^{-2x} + \dots)) + 2\exp(-4\beta V(1 - e^{-2x} + \dots)) - \dots]$$

$$= \beta V [1 - 2\exp(-2\beta V) + 2\exp(-4\beta V) - \dots] = \beta V [1 - 2\exp(-2\beta V) \frac{1}{1 + e^{2\beta V}}]$$

$$\langle M \rangle = \pm \mu_B N \frac{T_c}{T} \left(1 - \frac{2\exp(-2\beta V)}{1 + \exp(-2\beta V)} \right) \xrightarrow{T \rightarrow 0} \pm \mu_B N$$

Entropy

x is continuous in temperature

$$S = -kT \text{Tr} \{ g \ln g \} = Nk (\ln(2 \cosh x) - x \tanh x)$$

$T > T_c \rightarrow S_0 = Nk \ln 2$

$T < T_c \rightarrow T \approx T_c \rightarrow x \rightarrow 0 \Rightarrow S \rightarrow S_0$

$T \rightarrow 0 \rightarrow x \rightarrow +\infty : \ln(e^x + e^{-x}) - x \frac{e^x - e^{-x}}{e^x + e^{-x}} = x + \ln(1 + e^{-2x}) - x \frac{e^x - e^{-x}}{e^x + e^{-x}} = e^{-2x} (2x + 1)$
 $S \approx Nk \ln \frac{V}{kT} (1 - 2e^{-2\beta V}) e^{-2\beta V(1 - 2e^{-2\beta V})}$
 $\approx \frac{2NkV}{T} e^{-2\beta V}$

Heat capacity

$T \geq T_c \quad C = 0$

$T < T_c \quad C = T \frac{dS}{dx} \frac{dx}{dT}, \quad \frac{dS}{dx} = Nk \left(\tanh x - \tanh x - \frac{x}{\cosh^2 x} \right) = -\frac{Nkx}{\cosh^2 x}$
 $\frac{kT}{V} = \frac{\tanh x}{x} \rightarrow \frac{k}{V} = \left(\frac{1}{x \cosh^2 x} - \frac{\tanh x}{x^2} \right) \frac{dx}{dT} = \frac{x - \sinh x \cosh x}{x^2 \cosh^2 x} \frac{dx}{dT} \rightarrow \frac{dx}{dT} = \frac{k}{V} \frac{x^2 \cosh^2 x}{x - \frac{1}{2} \sinh 2x}$
 $C = -T \frac{Nkx}{\cosh^2 x} \frac{k}{V} \frac{x^2 \cosh^2 x}{x - \frac{1}{2} \sinh 2x} = -\frac{NkT}{T_c} \frac{x^3}{x - \frac{1}{2} \sinh 2x} = \frac{NkT}{T_c} \frac{x^3}{\frac{1}{2} \sinh 2x - x}$
 $\sinh 2x = 2x + \frac{(2x)^3}{3!} + \dots$

$T \rightarrow 0 \rightarrow C \rightarrow 0$

$T \nearrow T_c \rightarrow x \searrow 0 \quad \frac{NkT}{T_c} \frac{x^3}{x + \frac{2^3 x^3}{3!} - x} = \frac{NkT}{T_c} \frac{3}{2} \rightarrow \frac{3}{2} Nk$

$\Rightarrow C(T \nearrow T_c) = \frac{3}{2} Nk \wedge C(T \searrow T_c) = 0$

2) $B \neq 0$

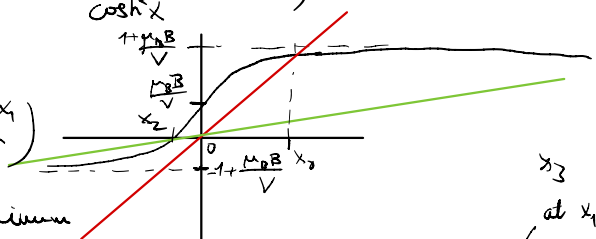
$$\tilde{F}(x) = \sum_{\{S_i\}} \frac{e^{-x \sum S_i}}{2} \left[-\sum_{i,j} V_{ij} S_i S_j + \mu_B B \sum S_i \right] + kT \sum_{\{S_i\}} \frac{e^{-x \sum S_i}}{2} [-x \sum S_i - \ln 2]$$

$$= -\frac{1}{2} NV \tanh^2 x - N \mu_B B \tanh x + NkT (x \tanh x - \ln(2 \cosh x))$$

$$\frac{d\tilde{F}(x)}{dx} = -NV \frac{\tanh x}{\cosh^2 x} - \frac{N \mu_B B}{\cosh^2 x} + NkT \left(\tanh x + \frac{x}{\cosh^2 x} - \tanh x \right) = 0$$

$$\frac{T}{T_c} x = \frac{kT}{V} x = \tanh x + \frac{\mu_B B}{V}$$

a) one candidate $x_0 : \frac{d\tilde{F}}{dx} = \frac{NkT}{\cosh^2 x} \left(x - \frac{\mu_B B}{kT} - \frac{T_c}{T} \tanh x \right)$
 $x \gg 0 \rightarrow \frac{d\tilde{F}}{dx} > 0$
 $x \ll 0 \rightarrow \frac{d\tilde{F}}{dx} < 0 \Rightarrow x_0$ is minimum



b) three intersections $\frac{d^2 \tilde{F}}{dx^2} = -\frac{NkT}{\cosh^2 x} \left[\tanh x \left(x - \frac{\mu_B B}{kT} - \frac{T_c}{T} \tanh x \right) - 1 + \frac{T_c}{T} \frac{1}{\cosh^2 x} \right] = \frac{NkT}{\cosh^4 x} \left[\cosh^2 x - \frac{T_c}{T} \right]$

$\Rightarrow$ if there is inflection, there is only one inflection

$\Rightarrow$ global minimum is always in the direction of the field

$B > 0 \rightarrow x_{\min} > 0$

$B < 0 \rightarrow x_{\min} < 0$

Magnetization: $M = N \mu_B \tanh x$ - paramagnetic

• with increasing B , we gradually achieve saturation of the magnetization $M = N \mu_B$

$$T \gg T_c \wedge B \approx 0 \Rightarrow x \sim 0$$

$$k_B T x = V x + \mu_B B \quad x = \frac{\mu_B B}{k_B T - T_c} \quad \text{Curie-Weiss law}$$

$$T = T_c \quad B \approx 0 \quad x = \left(\frac{\mu_B B}{k_B T_c} \right)^{1/3}$$

$$T < T_c \quad M = N \mu_B \left(\frac{T}{T_c} x - \frac{\mu_B B}{V} \right) \quad \text{for } B \rightarrow 0 \quad x_3 \rightarrow x_1(B=0) \Rightarrow M \rightarrow M_{\text{spontaneous}}$$

Ex) linear chain of interacting spin $\cdots \cdots \cdots V_{i,i+1} \neq 0$
can be calculated analytically and there is no phase transition

Quantum ideal gases

- non-interacting particles
- no magnetic field
- particles with spin S

$$\ln Z_G = - \sum_q \ln(1 - z e^{-\beta \epsilon_q + \alpha})$$

$$f_q = \frac{1}{e^{\beta \epsilon_q - \alpha} - z} \quad \text{--- occupation number}$$

q --- state of one particle

ϵ_q --- energy of the state q

$z < \begin{cases} +1 & \text{bosons} \\ -1 & \text{fermions} \end{cases}$

Quantum ideal gas in a box (L_1, L_2, L_3)

- rigid walls: $V = \begin{cases} 0 & \text{inside} \\ +\infty & \text{outside and on the walls} \end{cases}$

• Schrödinger equation $i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \Delta \psi + V\psi$ solve using separation $\psi(x,y,z,t) = X(x)Y(y)Z(z)T(t)$
 $\{(A_1 \cos k_1 x + B_1 \sin k_1 x)(A_2 \cos k_2 y + B_2 \sin k_2 y)(A_3 \cos k_3 z + B_3 \sin k_3 z) e^{-i\omega t}\}$ $\omega_n = \frac{\hbar}{2m} k^2 = \frac{\hbar}{2m} (k_1^2 + k_2^2 + k_3^2)$

• Boundary conditions $\Rightarrow A_1 = A_2 = A_3 = 0 \wedge k_i = \frac{n_i \pi}{L_i}$, $n_i > 0$

$$E(\vec{n}) = \frac{\hbar^2}{2m} k^2 = \frac{\hbar^2 \pi^2}{2m} \sum \frac{n_i^2}{L_i^2} \quad \text{ground state } E = E_0 = \frac{\hbar^2 \pi^2}{2m} \sum \frac{1}{L_i^2} \neq 0$$

• Classical momentum ($E = \frac{p^2}{2m}$) $\vec{p} = \hbar \vec{k}$

• Large volume limit $\rightarrow$ energies and momenta of 1-particle states are very dense.

• one-particle density of states $-D(E)$ $\int_{E_0}^E D(E) dE = \text{number of energy states in } [E_0, E]$

$$N = \int_{E_0}^{\infty} dE D(E) f(E) \quad U = \int_{E_0}^{\infty} dE E D(E) f(E) \quad f(E) \text{ is known (bosons or fermions) --- occupation number}$$

$D(E)$ depends on system of interest

$$\begin{aligned} N &= \sum_q f(\epsilon_q) = \sum_{n_1, n_2, n_3=1}^{\infty} (2s+1) f(\epsilon(\vec{n})) = \frac{L_1 L_2 L_3}{(h\pi)^3} \sum_{n_1, n_2, n_3=1}^{\infty} (2s+1) f(\epsilon(\vec{n})) \frac{h\pi}{L_1} \frac{h\pi}{L_2} \frac{h\pi}{L_3} \\ &= \frac{V(2s+1)}{(h\pi)^3} \int_{p_0}^{\infty} \int_{p_0}^{\infty} \int_{p_0}^{\infty} dp^3 f(\epsilon(\vec{p})) = \frac{V(2s+1)}{p(h\pi)^3} \int_{\mathbb{R}^3 \text{ cube}(2p_0)} dp^3 f(\epsilon(\vec{p})) = \frac{V(2s+1)}{h} \int_{\mathbb{R}^3 B(p_0)} dp^3 f(\epsilon(\vec{p})) \\ &= \frac{V(2s+1)}{h^3} 4\pi \int_{p_0}^{\infty} dp p^2 f(\epsilon(p)) = \frac{4\pi V(2s+1)}{h^3} \int_{E_0}^{\infty} dE \underbrace{p^2(E) \frac{dp}{dE}}_{D(E)} f(E) \end{aligned}$$

$$\Rightarrow D(E) = \frac{4\pi}{h^3} V(2s+1) p^2(E) \frac{dp}{dE} \quad \text{true for both relativistic and non-relativistic}$$

• non-relativistic particle $E = \frac{p^2}{2m}$ $p = \sqrt{2mE}$

$$D(E) = \frac{4\pi}{h^3} V(2s+1) 2mE \frac{1}{2} \frac{\sqrt{2m}}{\sqrt{E}} = \frac{2\pi}{h^3} V(2s+1) (2m)^{3/2} \sqrt{E} = A \sqrt{E}$$

• relativistic particle $E^2 = p^2 c^2 + m_0^2 c^4$ $p = \frac{\sqrt{E^2 - m_0^2 c^4}}{c}$

$$D(E) = \frac{4\pi}{h^3} V(2s+1) \frac{E^2 - m_0^2 c^4}{c^2} \cdot \frac{2E}{2c\sqrt{E^2 - m_0^2 c^4}} = \frac{4\pi}{h^3 c^3} V(2s+1) E \sqrt{E^2 - m_0^2 c^4}$$

$$\Omega = -PV = -kT \ln Z_G = -\frac{2}{\beta} \sum (2s+1) \ln(1 - z e^{-\beta \epsilon_s + \alpha}) = -\frac{2}{\beta} \int d\epsilon D(\epsilon) \ln(1 - z e^{-\beta \epsilon + \alpha})$$

$$= \left\{ \mathcal{N}(\epsilon) = \int_{\epsilon_0}^{\epsilon} D(\epsilon) d\epsilon, \frac{d}{d\epsilon} \ln(1 - z e^{-\beta \epsilon + \alpha}) = \frac{\beta z e^{-\beta \epsilon + \alpha}}{1 - z e^{-\beta \epsilon + \alpha}} \right\} = -\frac{2}{\beta} \left(\underbrace{\left[\mathcal{N}(\epsilon) \ln(1 - z e^{-\beta \epsilon + \alpha}) \right]_{\epsilon_0}^{\infty}}_{=0} - \int_{\epsilon_0}^{\infty} \mathcal{N}(\epsilon) \frac{\beta z e^{-\beta \epsilon + \alpha}}{1 - z e^{-\beta \epsilon + \alpha}} d\epsilon \right)$$

$$= -\int_{\epsilon_0}^{\infty} \mathcal{N}(\epsilon) f(\epsilon) d\epsilon$$

$$N = \int_{\epsilon_0}^{\infty} d\epsilon D(\epsilon) f(\epsilon) = \overbrace{\left[\mathcal{N}(\epsilon) f(\epsilon) \right]_{\epsilon_0}^{\infty}}^0 - \int_{\epsilon_0}^{\infty} \mathcal{N}(\epsilon) \frac{df}{d\epsilon} d\epsilon$$

Classical limit

$f(\epsilon) \dots$ encodes the nature of particles

in classical system $f(\epsilon) = e^{\alpha - \beta \epsilon} \rightarrow D(\epsilon) = \frac{2\pi V}{h^3} (2m)^{3/2} \sqrt{\epsilon}$

$$\mathcal{N}(\epsilon) = \int_{\epsilon_0=0}^{\epsilon} A \sqrt{\epsilon} d\epsilon = \frac{2}{3} A \epsilon^{3/2} \rightarrow \ln Z_G = \beta \int \frac{2}{3} A \epsilon^{3/2} e^{\alpha - \beta \epsilon} d\epsilon = \left| x = \beta \epsilon \right| = \frac{2}{3} A \beta^{-3/2} \int_0^{\infty} x^{3/2} e^{-x} dx$$

$$\ln Z_G = \frac{4\pi V}{3h^3} (2m kT)^{3/2} \Gamma(5/2) = \frac{V}{h^3} (2\pi m kT)^{3/2} e^{\alpha}$$

$$Z_G = \sum_{N=0}^{\infty} e^{\alpha N} \left[\frac{V}{h^3} (2\pi m kT)^{3/2} \right]^N \cdot \frac{1}{N!} = \sum_{N=0}^{\infty} e^{\alpha N} Z_G(N) \Rightarrow Z_G(N) = \frac{1}{N!} z^N \quad z = \frac{V}{h^3} (2\pi m kT)^{3/2}$$

Why $\frac{1}{e^{\beta \epsilon - \alpha} - z} \rightarrow \frac{1}{e^{\beta \epsilon - \alpha}}$?

$$N = \int_0^{\infty} D(\epsilon) f(\epsilon) d\epsilon = \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^{\infty} \frac{\sqrt{\epsilon} (2s+1)}{e^{\beta \epsilon - \alpha} - z} d\epsilon = \left| \beta \epsilon = x \right| = \frac{2\pi V}{h^3} (2m kT)^{3/2} \int_0^{\infty} \frac{\sqrt{x} (2s+1)}{e^{x-\alpha} - z} dx$$

$$\frac{N}{V} \frac{h^3}{(2\pi m kT)^{3/2}} = (2s+1) \frac{2}{\sqrt{\pi}} \int_0^{\infty} \frac{\sqrt{x}}{e^{x-\alpha} - z} dx \quad \text{Classical limit } \frac{N}{V} \ll 1 \text{ and } T \gg 1$$

$$\Rightarrow e^{-\alpha} \gg 1 \Rightarrow z \text{ is negligible}$$

Helium ^4He and Bose condensation

- no spin $s=0$
- low temperatures - non-relativistic particles $\epsilon = \frac{p^2}{2m}$

$$f_p = \frac{1}{\exp\left(\frac{p^2}{2m} - \mu\right) - 1} \quad \begin{array}{l} \mu < \epsilon_0 \neq 0 \text{ rigid walls} \\ \mu < \epsilon_0 = 0 \text{ periodic boundary} \end{array}$$

$$\mathcal{N}(\epsilon) = \int_{\epsilon_0}^{\epsilon} D(\epsilon) d\epsilon = \frac{2}{3} A (\epsilon^{3/2} - \epsilon_0^{3/2}), \quad \Omega = -PV = -\int_{\epsilon_0}^{\infty} \mathcal{N}(\epsilon) f(\epsilon) d\epsilon = -\frac{2}{3} A \int_{\epsilon_0}^{\infty} \frac{(\epsilon^{3/2} - \epsilon_0^{3/2})}{\exp\left(\frac{\epsilon - \mu}{kT}\right) - 1} d\epsilon$$

$$U = \int_{\epsilon_0}^{\infty} \epsilon f(\epsilon) D(\epsilon) d\epsilon = \int_{\epsilon_0}^{\infty} A f(\epsilon) \epsilon^{3/2} d\epsilon = \frac{2}{3} PV + A \epsilon_0^{3/2} \int_{\epsilon_0}^{\infty} f(\epsilon) d\epsilon$$

$$\int_{\epsilon_0}^{\infty} \frac{d\epsilon}{e^{(\epsilon - \mu)/kT} - 1} = \left| x = \frac{\epsilon - \mu}{kT} \right| = \int_{\frac{\epsilon_0 - \mu}{kT}}^{\infty} \frac{kT}{e^x - 1} dx = kT \left[-x + \ln(e^x - 1) \right]_{\frac{\epsilon_0 - \mu}{kT}}^{+\infty}$$

Condensation

$$N = \frac{2\pi V}{h^3} (2m)^{3/2} \int_{\epsilon_0}^{\infty} d\epsilon \frac{\sqrt{\epsilon}}{e^{\frac{\epsilon - \mu}{kT}} - 1} \rightarrow \rho = \frac{N}{V} = \frac{2\pi}{h^3} (2m)^{3/2} \int_{\epsilon_0}^{\infty} d\epsilon \frac{\sqrt{\epsilon}}{e^{\frac{\epsilon - \mu}{kT}} - 1}$$

ρ constant as $T \searrow 0$ the chemical potential $\mu \uparrow \epsilon_0$ to keep ρ constant

$\rightarrow$ There is a critical point $T = T_c$ defined by $\mu = \epsilon_0$

$$\rho = \frac{(2m)^{3/2}}{(2\pi h^2)^{3/2}} \int_{\epsilon_0}^{\infty} d\epsilon \frac{\sqrt{\epsilon}}{e^{(\epsilon - \epsilon_0)/kT} - 1} = \frac{(2m)^{3/2}}{h^3} e^{-\epsilon_0/kT} (kT_c)^{3/2} \int_0^{\infty} \frac{\sqrt{\epsilon + \frac{\epsilon_0}{kT_c}}}{e^{\epsilon} - 1} d\epsilon \approx \left(\frac{mkT_c}{2\pi h^2} \right)^{3/2} \frac{2}{\sqrt{\pi}} \int_0^{\infty} \frac{\sqrt{\epsilon}}{e^{\epsilon} - 1} d\epsilon$$

What about $T \leq T_c$?

occupation number $f_{\epsilon_0} = \frac{1}{e^{\frac{\epsilon_0 - \mu}{kT}} - 1} \sim \frac{kT}{\epsilon_0 - \mu} = N_0$ number of condensed bosons in ground state (for non-zero temperature)

Correction for $T < T_c$ $N = \sum f(\epsilon_q) = f(\epsilon_{\text{ground}}) + \sum_{\text{rest}} f(\epsilon_q)$

$$\frac{N}{V} = \frac{kT}{(\epsilon_0 - \mu)V} + 2.61 \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2}$$

Non-relativistic Bose-Einstein condensation in 2D

• n_3 is frozen, $s=0$

$$N = \sum_{n_1, n_2} f(\epsilon(n_1, n_2)) = \frac{A}{h^2} \int_{\mathbb{R}^2} d\vec{p} \tilde{f}(\vec{p}) = \frac{A}{h^2} 2\pi \int_{p_0}^{\infty} p \tilde{f}(p) dp = \frac{A}{h^2} 2\pi \int_{\epsilon_0}^{\infty} p(\epsilon) \frac{dp}{d\epsilon} f(\epsilon) d\epsilon$$

$$D(\epsilon) = \frac{A}{h^2} 2\pi p(\epsilon) \frac{dp}{d\epsilon} = \frac{A}{h^2} 2\pi \sqrt{2m\epsilon} \frac{\frac{1}{2} \sqrt{2m}}{\sqrt{2m\epsilon}} = \frac{2\pi A}{h^2} m$$

$$N = \frac{2\pi A}{h^2} m \int_{\epsilon_0}^{\infty} \frac{1}{e^{\frac{\epsilon - \mu}{kT}} - 1} d\epsilon = \frac{2\pi A}{h^2} m kT \int_{\epsilon_0}^{\infty} \frac{e^{\frac{\mu - \epsilon}{kT}} \cdot \frac{1}{kT}}{1 - e^{\frac{\mu - \epsilon}{kT}}} d\epsilon = \frac{2\pi A}{h^2} m kT \left[\ln(1 - e^{\frac{\mu - \epsilon}{kT}}) \right]_{\epsilon_0}^{\infty}$$

$$= - \frac{2\pi A}{h^2} m kT \ln\left(1 - e^{\frac{\mu - \epsilon_0}{kT}}\right) \quad \mu = \epsilon_0 + kT \ln\left[1 - \exp\left(-\frac{N}{A} \frac{h^2}{2\pi m kT}\right)\right]$$

Ultra-relativistic BEC in 2D

• assume $\epsilon_0 = 0$, $\epsilon = pc$

$$D(\epsilon) = \frac{A}{h^2} 2\pi \frac{\epsilon}{c} \cdot \frac{1}{c} = \frac{2\pi A}{c^2 h^2} \epsilon$$

$$n = \frac{N}{A} = \frac{2\pi}{c^2 h^2} \int_0^{\infty} \frac{\epsilon}{e^{\frac{\epsilon - \mu}{kT}} - 1} d\epsilon \quad \text{to keep this constant } \mu \text{ must increase as we decrease temperature}$$

critical temperature is given by $\mu = \epsilon_0 = 0$

$$n = \frac{2\pi}{h^2 c^2} \int_0^{\infty} \frac{\epsilon}{e^{\frac{\epsilon}{kT_c}} - 1} d\epsilon = \frac{2\pi}{h^2 c^2} (kT_c)^2 \int_0^{\infty} \frac{x}{e^x - 1} dx = \frac{\pi^3 k^2 T_c^2}{3 h^2 c^2} \quad \Gamma(2)=1$$

$$\int_0^{\infty} \frac{x}{e^x - 1} dx = \int_0^{\infty} \frac{x e^{-x}}{1 - e^{-x}} dx = \int_0^{\infty} x e^{-x} \sum_{k=0}^{\infty} e^{-xk} dx = \int_0^{\infty} x \sum_{k=1}^{\infty} e^{-xk} dx = \sum_{k=1}^{\infty} \int_0^{\infty} x e^{-xk} dx = \sum_{k=1}^{\infty} \frac{1}{k^2} \int_0^{\infty} t e^{-t} dt = \frac{\pi^2}{6}$$

$$\text{for } T < T_c \quad n = n_0 + \frac{\pi^3}{3 h^2 c^2} (kT)^2$$

Degenerate Fermi gas

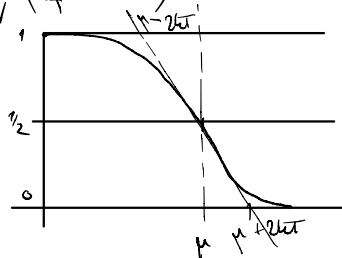
$$f(\epsilon) = \begin{cases} 1 & \epsilon \leq \epsilon_f \\ 0 & \epsilon > \epsilon_f \end{cases} \quad N = N(\epsilon_f) = \int_0^{\epsilon_f} \frac{2\pi (2s+1)V}{h^3} (2m)^{3/2} \sqrt{\epsilon} d\epsilon = \frac{4\pi V}{3h^3} (2m\epsilon_f)^{3/2} (2s+1) = \frac{2}{3} A \epsilon_f^{3/2}$$

$$\epsilon_f = \frac{1}{2m} \left(\frac{3h^3 N}{4\pi V (2s+1)} \right)^{2/3} = \frac{\hbar^2}{2m} \left(\frac{3}{4\pi (2s+1)} \frac{N}{V} \right)^{2/3} \quad \Theta_f = \frac{\epsilon_f}{k}$$

$$U = \int_0^{\epsilon_f} \epsilon D(\epsilon) f(\epsilon) d\epsilon = \int_0^{\epsilon_f} \epsilon A \epsilon^{1/2} d\epsilon = A \frac{2}{5} \epsilon_f^{5/2} = \frac{3}{5} \epsilon_f N$$

$$P = \frac{1}{V} \int_0^{\epsilon_f} N(\epsilon) d\epsilon = \frac{1}{V} \int_0^{\epsilon_f} \frac{2}{3} A \epsilon^{3/2} d\epsilon = \frac{1}{V} \frac{2}{3} A \frac{2}{5} \epsilon_f^{5/2} = \frac{1}{V} \frac{2}{5} \epsilon_f N = \frac{1}{V} (\epsilon_f N - U)$$

Gas can be treated as degenerate if $T \ll \Theta_f$ because



Ultra-relativistic degenerate Fermi gas

$$\epsilon = pc \quad D(\epsilon) = \frac{4\pi(2s+1)}{h^3 c^3} \epsilon^2$$

$$N = \int_0^{\epsilon_f} \frac{4\pi(2s+1)}{h^3 c^3} \epsilon^2 d\epsilon = \frac{4\pi(2s+1)}{3 h^3 c^3} \epsilon_f^3 = \frac{1}{3} B \epsilon_f^3 \Rightarrow \epsilon_f = \left(\frac{3}{4} \frac{h^3 c^3}{\pi(2s+1)} \frac{N}{V} \right)^{1/3}$$

$$U = \int_0^{\epsilon_f} \epsilon B \epsilon^2 d\epsilon = \frac{1}{4} B \epsilon_f^4 = \frac{3}{4} N \epsilon_f$$

$$P = \frac{1}{V} \int_0^{\epsilon_f} \epsilon dN = \frac{1}{V} \int_0^{\epsilon_f} \frac{1}{3} B \epsilon^3 d\epsilon = \frac{1}{V} \frac{1}{12} B \epsilon_f^4 = \frac{1}{V} \frac{1}{4} N \epsilon_f = \frac{1}{V} (c_p N - U)$$

White dwarves

- interior temperature $\sim 10^7 K$
- 0.15 - 1.5 solar mass
- $10^3 km$ radius

classicality $\varphi = \frac{N}{V} \frac{h^3}{(2\pi m k T)^{3/2}} \frac{1}{2s+1} \gg 1$