

Aplicações no ensemble canônico.

$$\hat{\rho}_B = \frac{e^{-\beta \hat{H}}}{Z}$$

$$Z = \text{tr} e^{-\beta \hat{H}}$$

$$\hat{\rho}_B = \frac{1}{Z} \sum_n |n\rangle \langle n| e^{-\beta E_n}$$

e: $x \equiv \{x_i\}$ tais que $\hat{H} = \hat{H}(x)$

$$E(\beta, x) = \text{tr} \hat{\rho}_B \hat{H} = - \left. \frac{\partial \ln Z}{\partial \beta} \right|_x$$

$$X_i(\beta, x) = \text{tr} \hat{\rho}_B \frac{\partial \hat{H}}{\partial x_i} \Big|_{x_{j \neq i}} = - \frac{1}{\beta} \left. \frac{\partial \ln Z}{\partial x_i} \right|_{\beta, x_{j \neq i}}$$

$$S_B = -k \text{tr} \hat{\rho}_B \ln \hat{\rho}_B = -k \text{tr} \hat{\rho}_B (-\beta \hat{H} - \ln Z)$$

$$= +k\beta \text{tr} \hat{\rho}_B \hat{H} + k \ln Z \Rightarrow \frac{S}{k} = \ln Z + \beta E$$

$$\Rightarrow \ln Z = \frac{S}{k} - \beta E$$

$$\frac{1}{k} dS = d \ln Z + \beta dE + E d\beta$$

$$= \frac{\partial \ln Z}{\partial \beta} d\beta + \sum_i \frac{\partial \ln Z}{\partial x_i} dx_i + \beta dE + E d\beta$$

$$= - \cancel{E d\beta} - \sum_i \beta X_i dx_i + \beta dE + \cancel{E d\beta}$$

$$\Rightarrow \frac{dS}{k} = - \sum_i \beta X_i dx_i + \beta dE$$

$$\Rightarrow T dS = - \sum_i X_i dx_i + dE$$

$$\Rightarrow \beta \rightarrow T \quad d(E - TS) = -S dT + \sum_i X_i dx_i + \dots$$

$$F \equiv E - TS = -kT \ln Z = - \frac{1}{\beta} \ln Z$$

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$$\Rightarrow T dS = dE + p dV - \mu dN$$

$$dF = -S dT - p dV + \mu dN$$

$$\Rightarrow \frac{\partial F}{\partial T} = -S \quad \frac{\partial F}{\partial V} = -p \quad \frac{\partial F}{\partial N} = \mu$$

$$\Rightarrow \frac{\partial kT \ln Z}{\partial T} = S \quad \frac{\partial kT \ln Z}{\partial V} = +p \quad \frac{\partial kT \ln Z}{\partial N} = -\mu$$

$$\downarrow$$

$$F = E - TS$$

$$\downarrow$$

$$-\frac{1}{\beta} \frac{\partial \ln Z}{\partial x_i} = \langle x_i \rangle$$

$$\downarrow$$

$$\frac{1}{\beta} \frac{\partial \ln Z}{\partial N} = \mu$$

Teorema da flutuação - resposta:

$$\frac{\partial^2 \ln Z}{\partial \lambda_i \partial \lambda_j} = \frac{\partial a_i}{\partial \lambda_j} = \langle (\hat{A}_i - a_i)(\hat{A}_j - a_j) \rangle$$

$$\Rightarrow \langle (\hat{H} - E)^2 \rangle = \langle \hat{H}^2 \rangle - E^2 = \frac{\partial^2 \ln Z}{\partial \beta^2} \Big|_{x, N} \geq 0$$

$$\frac{\partial \ln Z}{\partial \beta} = -E \Rightarrow \frac{\partial^2 \ln Z}{\partial \beta^2} = -\frac{\partial E}{\partial \beta}$$

$$\text{mas } \frac{\partial E}{\partial \beta} = \frac{\partial E}{\partial T} \left(\frac{\partial \beta}{\partial T} \right)^{-1} = -kT^2 \frac{\partial E}{\partial T} \Big|_x = -kT^2 C_x$$

$$\Rightarrow kT^2 C_x \geq 0 \Rightarrow \text{estabilidade}$$

Gás ideal

N moléculas de um gás ideal

$$H = \sum_{i=1}^N H_i = \sum_i \frac{p_i^2}{2m}$$

$\Rightarrow Z_N = Z^N \rightarrow$ partículas independentes, $\vec{p} = \hbar \vec{k}$

$$Z = \sum_{\vec{p}} \langle \vec{p} | e^{-\beta \frac{p^2}{2m}} | \vec{p} \rangle = \frac{V}{(2\pi)^3} \frac{1}{\hbar^3} \int d^3p e^{-\beta p^2/2m}$$

$$= V \left(\frac{m}{2\pi\beta\hbar^2} \right)^{3/2} \Rightarrow Z_N = V^N \left(\frac{m}{2\pi\hbar^2\beta} \right)^{3N/2} = V^N \left(\frac{1}{\lambda_T^3} \right)^N$$

$$\lambda_T^{-1} = \sqrt{\frac{2\pi m k_B T}{\hbar^2}} = \sqrt{\frac{m k_B T}{2\pi\hbar^2}} \quad \text{Mas, indistingui-$$

$$\text{bilidade} \Rightarrow \frac{1}{N!} \Rightarrow Z_N = \frac{V^N}{N!} \left(\frac{1}{\lambda_T^3} \right)^N$$

$$Z_N^{(cl)} = \int \prod_{i=1}^N d^3r_i d^3p_i e^{-\beta \sum_i p_i^2/2m} \Rightarrow \sigma = \frac{1}{N! \lambda_T^{3N}}$$

$$S = k_B \ln Z_N - k_B \beta \frac{\partial \ln Z_N}{\partial \beta} =$$

$$= k_B N \left[\ln \frac{V}{N} + \frac{3}{2} \ln \left(\frac{2\pi m k_B T}{\hbar^2} \right) + \frac{5}{2} \right] \text{ note as usual}$$

$$\ln N! \approx N \ln N - N \Rightarrow \text{extensividade de } S!$$

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Dois gases distintos = m_1 e m_2 $\left\{ \begin{array}{l} N = N_1 + N_2 \\ V = V_1 + V_2 \end{array} \right.$

$$Z_N^{(i)}(T, V) = \frac{V_1^{N_1}}{N_1!} \left(\frac{1}{\lambda_T^{(1)}} \right)^{\exists N_1} \frac{V_2^{N_2}}{N_2!} \left(\frac{1}{\lambda_T^{(2)}} \right)^{\exists N_2}$$

$$Z_N^{(f)}(T, V) = \frac{V^{N_1}}{N_1!} \left(\frac{1}{\lambda_T^{(1)}} \right)^{\exists N_1} \frac{V^{N_2}}{N_2!} \left(\frac{1}{\lambda_T^{(2)}} \right)^{\exists N_2}$$

$$S^{(f)} - S^{(i)} = k_B \ln \frac{Z_N^{(f)}}{Z_N^{(i)}} = k_B \left[N_1 \ln \frac{V}{V_1} + N_2 \ln \frac{V}{V_2} \right] > 0$$

\Rightarrow aumento da entropia da mistura

Mas, se as partículas são idênticas = $m_1 = m_2$

$$\text{e } \lambda_T^{(1)} = \lambda_T^{(2)} = \lambda_T$$

$$Z_N^{(f)} = \frac{V^N}{N!} \left(\frac{1}{\lambda_T} \right)^{\exists N} \neq \frac{V^N}{N_1! N_2!} \left(\frac{1}{\lambda_T} \right)^{\exists N}$$

$$\text{Como } \frac{V_i}{V} = \frac{N_i}{N}$$

$$S^{(f)} - S^{(i)} = k_B \left[N_1 \ln \frac{N_1 V}{N V_1} + N_2 \ln \frac{N_2 V}{N V_2} \right] = 0$$

Origem da indistingüibilidade:

Energia B.E. $E \Rightarrow$ energia/partícula $\sim \frac{E}{N} \equiv \epsilon$

ocupação média de um nível $\epsilon_r \Rightarrow \langle n_r \rangle \sim \frac{N}{\phi(\epsilon)}$

$\phi(\epsilon) = \#$ de níveis ocupados abaixo de ϵ

$$\phi(\epsilon) = \frac{4\pi V}{3h^3} (2m\epsilon)^{3/2} = \int_0^\epsilon \rho(\epsilon') d\epsilon'$$

$$\Rightarrow \langle n_r \rangle \sim \frac{N}{\frac{4\pi V}{3h^3} (2m\epsilon)^{3/2}} ; d \sim \left(\frac{V}{N}\right)^{1/3} = n^{-1/3}$$

$$d^3 = n^{-1} \Rightarrow \frac{N}{V} = \frac{1}{d^3} \Rightarrow N = \frac{V}{d^3}$$

$$\langle n_r \rangle \sim \frac{h^3}{d^3} \frac{1}{(2m\epsilon)^{3/2}} = \frac{\lambda_T^3}{d^3} \quad \lambda_T = \frac{h}{\sqrt{2\pi m k_B T}}$$

Quando T é tal que $\lambda_T \ll d \Rightarrow$ estatística clássica (distingüibilidade)

$$Z_N = \frac{V^N}{N!} \left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} = \frac{1}{N!} \left(\frac{V}{\lambda_T^3}\right)^N$$

Podemos considerar $\frac{V}{\lambda_T^3} \equiv M$ (# de caixas n)

volume $V \Rightarrow \left(\frac{V}{\lambda_T^3}\right)^N = M^N$ maneiras de se distribuir

N partículas distingüíveis em M caixas $\Rightarrow \langle n_r \rangle = \frac{N}{M}$

e $\langle n_r \rangle \ll 1 \rightarrow$ limite clássico (justificativa mais forte)

de maneiras B.E. $(M-1+N)! / (M-1)! N! \xrightarrow{N/M \ll 1} M^N / N!$
de maneiras F.D. $M! / N! (M-N)! \xrightarrow{N/M \ll 1} M^N / N!$

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Voltando ao gás ideal

$$\begin{aligned} \Rightarrow \ln Z_N &= N \ln \frac{V}{\lambda_T^3} - N \ln N + N \\ &= N \left(\ln \frac{V}{\lambda_T^3} + 1 \right) \\ &= N \left(\ln \frac{V}{N} + \frac{3}{2} \ln \left(\frac{2\pi m}{\beta h^2} \right) + 1 \right) \end{aligned}$$

$$\begin{aligned} \Rightarrow \langle E \rangle &= - \frac{\partial \ln Z}{\partial \beta} = + \frac{3N}{2} \frac{\beta h^2}{2\pi m} \frac{2\pi m}{h^2} \frac{1}{\beta^2} \\ &= \frac{3}{2} N k T \end{aligned}$$

$$\Rightarrow C_V = \frac{d\langle E \rangle}{dT} = \frac{3}{2} N k > 0 \Rightarrow \text{estável}$$

Pela 3ª lei: $S(T, V) = S_0 + \int_0^T \frac{C_V(T')}{T'} dT'$ não pode divergir

$$\Rightarrow C_V(T') \rightarrow 0 \text{ se } T' \rightarrow 0$$

De fato:

$$F(T, V, N) = - kT \ln Z_N = - N k T \left[\ln \frac{V}{N} + \frac{3}{2} \ln \left(\frac{2\pi m k T}{h^2} \right) + 1 \right]$$

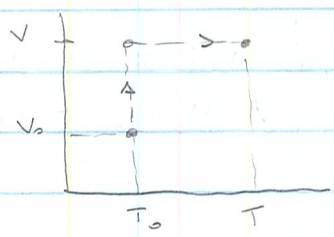
$$S = - \left. \frac{\partial F}{\partial T} \right|_V = N k \left[\ln \frac{V}{N} + \frac{3}{2} \ln \left(\frac{2\pi m k T}{h^2} \right) + \frac{5}{2} \right]$$

$\Rightarrow S(T=0) \rightarrow \infty$, ou seja, aproximação clássica não funciona a baixas temperaturas.

$$P = - \left. \frac{\partial F}{\partial V} \right|_T = \frac{N}{V} k T \Rightarrow PV = N k T$$

$$\text{ou } PV = \frac{2}{3} \langle E \rangle$$

$$S(T, V) = S(T_0, V_0) + nR \ln \frac{V}{V_0} + \frac{lRn}{2} \ln \frac{T}{T_0}$$



$$C_V = nR \frac{l}{2} \quad l=3$$

$\Rightarrow S(T_0, V_0)$ é determinado no cálculo microscópico.

Potencial químico:

$$\mu = - \left. \frac{\partial F}{\partial N} \right|_{T, V} = -kT \left[\ln \frac{V}{N} + \frac{3}{2} \ln \left(\frac{2\pi m k T}{h^2} \right) + 1 \right] + kT$$

$$\Rightarrow \mu = -kT \ln \left\{ \frac{V}{N} \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \right\} = -kT \ln \frac{n}{\lambda_T^3} = kT \ln \lambda_T^3 n$$

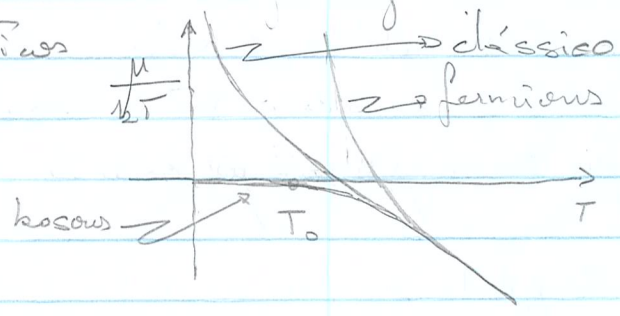
$n \gg \lambda_T^3 \Rightarrow \mu < 0!$

Pode-se entender o que ocorre por:

$$\left. \frac{\partial S}{\partial N} \right|_{E, V} = - \frac{\mu}{T} \quad \Rightarrow \quad S(N+1) - S(N) = - \frac{\mu}{T}$$

mas $S(N+1) - S(N) > 0 \Rightarrow \mu < 0$ (acréscimo de 1 molécula com energia cinética = 0). Se há interação, $E \neq$ constante e não vale o argumento acima \Rightarrow pode haver $\mu > 0$.

Gases quânticos



Estabilidade: $C_V \geq 0$ e $\kappa_T \geq 0$

Gibbs-Duhem $G = \mu N$ e $dG = -SdT + VdP + \mu dN$

$$\Rightarrow N d\mu + SdT - VdP = 0 \quad (\text{Gibbs-Duhem}) \Rightarrow \left. \frac{\partial \mu}{\partial n} \right|_T = \frac{1}{n^2 \kappa_T}$$

mas $\mu = kT \ln n \lambda_T^3 \Rightarrow \left. \frac{\partial \mu}{\partial n} \right|_T = kT \frac{\lambda_T^3}{n \lambda_T^3} \Rightarrow \kappa_T = \frac{1}{n kT} \geq 0$ estável!

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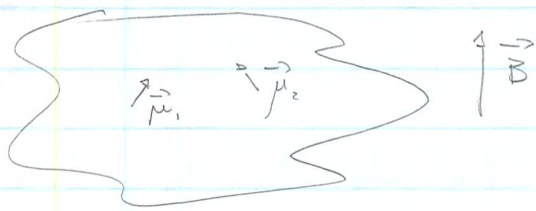
CNTP \rightarrow vol molar: 22,4 litros $\Rightarrow n \sim 2.7 \times 10^{25}$ molecules / m^3

$$\Rightarrow d \sim n^{-1/3} \sim 3 \times 10^{-9} \text{ m} = 3 \text{ nm.}$$

$$\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}} \sim 2 \times 10^{-10} \text{ m}$$

$$\left. \begin{array}{l} \sqrt{\langle v^2 \rangle} \approx 2 \times 10^3 \text{ m/s} \\ p / \text{H}_2 \approx 300 \text{ K.} \end{array} \right\}$$

ii) Paramagnetismus:



$$H = - \sum_i \vec{\mu}_i \cdot \vec{B} = \sum_i H_i$$

$$H_i = - \vec{\mu}_i \cdot \vec{B}$$

classicamente: $\vec{\mu} = \frac{e}{2mc} \vec{L}$

quanticamente: $\vec{\mu} = \frac{e}{2mc} \sqrt{l(l+1)} \hbar \hat{l} \sim \frac{e\hbar}{2mc} l \hat{l}$

$$\frac{e\hbar}{2mc} \equiv \mu_B$$

Spin: $\vec{\mu} = g \mu_B \vec{S}$ $g \approx 2$ p/ electron.

$$S_z |1/2, \pm m_s\rangle = \pm m_s \hbar |1/2, \pm m_s\rangle \quad m_s = \pm 1/2.$$

$$\Rightarrow H_i = - \vec{\mu}_i \cdot \vec{B} = - \mu_B \sigma_z.$$

$$H_i | \pm \rangle = \mp \mu_B | \pm \rangle.$$

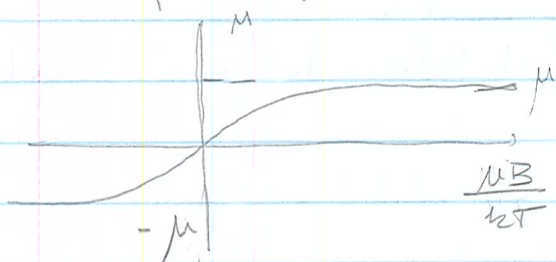
$$Z = e^{\beta \mu_B} + e^{-\beta \mu_B} = 2 \cosh \beta \mu_B \quad Z = Z^N$$

$$M^N = + \frac{1}{\beta} \frac{\partial \ln Z}{\partial B} = N \mu_B \tanh(\beta \mu_B)$$

$$p_{\pm} = \frac{1}{\mathcal{Z}} e^{\pm \beta \mu B} = \frac{1}{\mathcal{Z}} e^{\pm \mu B / kT}$$

$$\langle \mu_m \rangle = \mu (p_+ - p_-) = \mu \frac{2 \sinh \frac{\mu B}{kT}}{2 \cosh \frac{\mu B}{kT}} = \mu \tanh \frac{\mu B}{kT}$$

$$\Rightarrow \mathcal{M} = N \langle \mu \rangle$$



→ competição energia-entropia.

T - constante \Rightarrow sistema \rightarrow mínimo de F

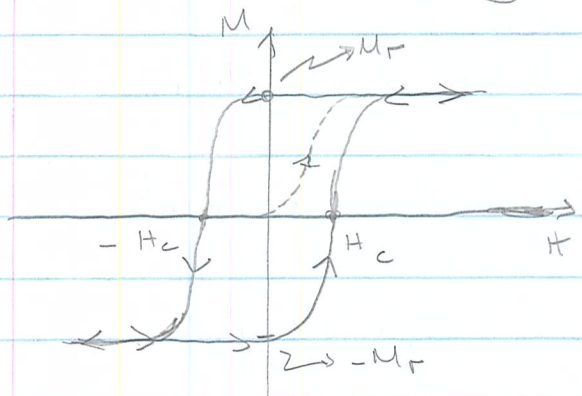
$\Rightarrow \min F \left\{ \begin{array}{l} kT \gg \mu B \Rightarrow E - TS \Rightarrow \text{aumenta entropia} \\ kT \ll \mu B \Rightarrow E - TS \Rightarrow \text{diminui energia} \end{array} \right.$

↙ Lei de Curie.

Se $kT \gg \mu B$ $M = \frac{\mathcal{M}}{V} \approx \frac{n \mu^2 B}{kT}$ e $\chi = \frac{\partial M}{\partial B} = \frac{n \mu^2}{kT}$

$$\chi_0 \equiv \lim_{B \rightarrow 0} \chi(B) = \frac{n \mu^2}{kT}$$

iii) Modelo de Ising e o ferromagnetismo



M_r - magnetização remanescente
 H_c → campo de coercividade
 comportamento ferromagnético
 abaixo de T_c - temperatura
 de Curie $\sim 10^3 K \rightarrow Fe$

Transição de 2º ordem

$M=0$ (desordem) \rightarrow M - finito (ordem)

$B=0$