Mecânica Estatística Clássica

Ensemble Microcanônico

→ Quaisquer arranjos de mesma energia são igualmente prováveis

→ $\Omega(E, V, N; \{x_i\})$

→ $P_r(\{x_i\}) \propto \frac{1}{\Omega}$

E_1 V_1 N_1	E_2 V_2 N_2

$\Omega(E_1, V_1, N_1)\,\Omega(E_2, V_2, N_2)$

↳ $E_T = E_1 + E_2$ → vínculo (V, N fixos)

↳ $\Omega(0)\,\Omega(E) = ?$

$$\boxed{\Omega_t = \sum_{E_1=0}^{E} \Omega(E_1)\,\Omega(E-E_1)}$$ → nº de configurações total

↳ Uma configuração particular: $$\boxed{P(E_1) = \frac{\Omega(E_1)\,\Omega(E-E_1)}{\sum_{E_1'=0}^{E} \Omega(E_1')\,\Omega(E-E_1')}}$$

∃ um máximo de $P(E_1)$ para $E = E_1$ → estado de equilíbrio

→ Números muito grandes → olhamos o ln

$$f(E_1) = \ln[\Omega(E_1)] + \ln[\Omega(E-E_1)] - \ln \Omega_t$$

$$\left.\frac{\partial f}{\partial E_1}\right|_E = \left.\frac{\partial \ln[\Omega(E_1)]}{\partial E_1}\right|_E + \left.\frac{\partial \ln[\Omega(\overbrace{E-E_1}^{E_2})]}{\partial E_1}\right|_E \quad (E \text{ fixo})$$

$$= \left.\frac{\partial \ln[\Omega(E_1)]}{\partial E_1}\right|_E - \left.\frac{\partial \ln[\Omega(E_2)]}{\partial E_2}\right|_E$$

→ Estado de equilíbrio: $\frac{\partial S(E_1)}{\partial E_1} - \frac{\partial S(E_2)}{\partial E_2} = 0$, $S = S(E_1) + S(E-E_1)$

↳ Sugestão: associar entropia a $\ln \Omega$

* Relação de Boltzmann: $\boxed{S(E) = k_B \ln \Omega(E)}$

* Exemplo: modelo de paramagneto

↳ $\mathcal{H} = -\mu_0 H \sum_{j=1}^{N} \sigma_j$, $\sigma_j = \pm 1$

↑ ↓ ↑ ↑

↑ ↑ ↑ ↑

↳ Magnetização: $M = \sum_{i=1}^{N} \sigma_i$

$m = \frac{M}{N}$

↳ N_1: ↑, N_2: ↓

↳ Energia: $E = -\mu_0 H N_1 - (-1)\,\mu_0 H N_2$

$E(N_1) = -\mu_0 H N_1 + \mu_0 H (N - N_1) = \mu_0 H N - 2\mu_0 H N_1$

↳ Configurações diferentes: $\Omega(N_1) = \frac{N!}{N_1!\,(N-N_1)!}$

$$\left.\begin{aligned} N_1 &= \tfrac{1}{2}\left(N - \tfrac{E}{\mu_0 H}\right) \\ N_2 &= \tfrac{1}{2}\left(N + \tfrac{E}{\mu_0 H}\right) \end{aligned}\right\} \quad \boxed{\Omega(E) = \frac{N!}{\left[\frac{1}{2}\left(N - \frac{E}{\mu_0 H}\right)\right]!\,\left[\frac{1}{2}\left(N + \frac{E}{\mu_0 H}\right)\right]!}}$$

↳ $S(E) = k_B \ln \Omega(E)$

↳ $\ln \Omega = \ln N! - \ln\left[\frac{1}{2}\left(N-\frac{E}{\mu_0 H}\right)\right]! - \ln\left[\frac{1}{2}\left(N+\frac{E}{\mu_0 H}\right)\right]!$

↳ Aproximação de Stirling: $\ln N! \approx N\ln N - N$, para N grande

↳ $\ln \Omega \approx N\ln N - \cancel{N} - \frac{1}{2}\left(N-\frac{E}{\mu_0 H}\right)\ln\left[\frac{1}{2}\left(N-\frac{E}{\mu_0 H}\right)\right] + \cancel{\frac{1}{2}}\left(N-\cancel{\frac{E}{\mu_0 H}}\right) - \frac{1}{2}\left(N+\frac{E}{\mu_0 H}\right)\ln\left[\frac{1}{2}\left(N+\frac{E}{\mu_0 H}\right)\right] + \cancel{\frac{1}{2}}\left(N+\cancel{\frac{E}{\mu_0 H}}\right)$

$= N\ln N - \frac{N}{2}\left(1-\frac{E}{\mu_0 HN}\right)\ln\left[\frac{N}{2}\left(1-\frac{E}{\mu_0 HN}\right)\right] - \frac{N}{2}\left(1+\frac{E}{\mu_0 HN}\right)\ln\left[\frac{N}{2}\left(1+\frac{E}{\mu_0 HN}\right)\right]$

$= N\ln N - \frac{N}{2}\left(1-\frac{u}{\mu_0 H}\right)\left[\ln N + \ln\frac{1}{2} + \ln\left(1-\frac{u}{\mu_0 H}\right)\right] - \frac{N}{2}\left(1+\frac{u}{\mu_0 H}\right)\left[\ln N + \ln\frac{1}{2} + \ln\left(1+\frac{u}{\mu_0 H}\right)\right]$

$= \left\{\cancel{N} - \cancel{\frac{N}{2}}\left[\left(1-\cancel{\frac{u}{\mu_0 H}}\right) + \left(1+\cancel{\frac{u}{\mu_0 H}}\right)\right]\ln N\right\} - \frac{N}{2}\left[\left(1-\cancel{\frac{u}{\mu_0 H}}\right) + \left(1+\cancel{\frac{u}{\mu_0 H}}\right)\right]\ln\frac{1}{2} - \frac{N}{2}\left[\left(1-\frac{u}{\mu_0 H}\right)\ln\left(1-\frac{u}{\mu_0 H}\right) + \left(1+\frac{u}{\mu_0 H}\right)\ln\left(1+\frac{u}{\mu_0 H}\right)\right]$

$= N\left\{\ln 2 - \frac{1}{2}\left[\left(1-\frac{u}{\mu_0 H}\right)\ln\left(1-\frac{u}{\mu_0 H}\right) + \left(1+\frac{u}{\mu_0 H}\right)\ln\left(1+\frac{u}{\mu_0 H}\right)\right]\right\}$

↳ $s(u) = \frac{S}{N} = \frac{1}{N} k_B \ln\Omega$

$$\therefore \boxed{s(u) = k_B \ln 2 - \frac{k_B}{2}\left(1+\frac{u}{\mu_0 H}\right)\ln\left(1+\frac{u}{\mu_0 H}\right) - \frac{k_B}{2}\left(1-\frac{u}{\mu_0 H}\right)\ln\left(1-\frac{u}{\mu_0 H}\right)}$$

→ $\frac{\partial s}{\partial u} = \frac{1}{T} = \frac{k_B}{2\mu_0 H}\ln\left[\frac{\mu_0 H - u}{\mu_0 H + u}\right] \Rightarrow \gamma \equiv e^{\frac{2\mu_0 H}{k_B T}} = \frac{\mu_0 H - u}{\mu_0 H + u}$

$\gamma(\mu_0 H + u) = \mu_0 H - u$

$\gamma u + u = \mu_0 H - \gamma\mu_0 H$

$u = \mu_0 H\left(\frac{1-\gamma}{1+\gamma}\right)$

$u(T) = \frac{\mu_0 H\left(1-e^{\frac{2\mu_0 H}{k_B T}}\right)}{1+e^{\frac{2\mu_0 H}{k_B T}}} \cdot \frac{e^{-\frac{\mu_0 H}{k_B T}}}{e^{-\frac{\mu_0 H}{k_B T}}} = \mu_0 H \frac{\left(e^{-\frac{\mu_0 H}{k_B T}} - e^{\frac{\mu_0 H}{k_B T}}\right)}{\left(e^{-\frac{\mu_0 H}{k_B T}} + e^{\frac{\mu_0 H}{k_B T}}\right)}$

$\tanh x = \frac{e^{x}-e^{-x}}{e^{x}+e^{-x}}$

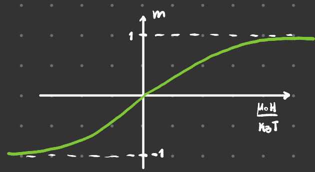
$$\therefore \boxed{u(T) = -\mu_0 H \tanh\left(\frac{\mu_0 H}{k_B T}\right)}$$

→ $M = N_1 - N_2$

$E = -\mu_0 H N_1 + \mu_0 H N_2 = -\mu_0 H(N_1 - N_2) = -\mu_0 H M$

$M = -\frac{E}{\mu_0 H}$, $m = -\frac{u}{\mu_0 H}$, $u = -\mu_0 H m$

$$\therefore \boxed{m(T, H) = \tanh\left(\frac{\mu_0 H}{k_B T}\right)}$$



01/07/24

* Modelo com energia contínua

$$\mathcal{H} = \sum \frac{\vec{p}^2}{2m} \rightarrow \Omega \rightarrow \text{densidade de energia}$$

→ Contagem de estados: $\Omega(E,V,N)\,\delta E$

$$\Omega(E,V,N)\,\delta E = \overbrace{\int d^3r_1\, d^3r_2 \cdots d^3r_N}^{\text{Volume}} \; \overbrace{\int_{2mE \leq p_1^2 + \cdots + p_N^2 \leq 2m(E+\delta E)} d^3p_1\, d^3p_2 \cdots d^3p_N}^{\text{Energia}}$$

$2mE \leq p_1^2 + \cdots + p_N^2 \leq 2m(E+\delta E)$ → Restrição sobre momentos: "energy shell"

$$= V^N \boxed{\int d^3p_1 \cdots d^3p_N}_{V_{in}}$$

→ integral em 3N dimensões → como calcular? → volume de uma casca esférica de 3N dimensões

* Volume de hiperesfera em n dimensões: $V_n(R) = \int_{0 \leq x_1^2 \cdots x_n^2 \leq R^2} dx_1 \cdots dx_n$ → vínculo

↳ Transformação para coordenadas "esféricas" → inviável para dimensões maiores

↳ Por análise dimensional, devemos ter $\boxed{V_n(R) = A_n R^n}$ → o problema se torna determinar A_n

↳ Integrais gaussianas: $$\left(\frac{\pi}{a}\right)^n = \left(\int_{-\infty}^{\infty} e^{-ax^2}\,dx\right)^n = \int_{-\infty}^{\infty} \underbrace{e^{-ax_1^2 - ax_2^2 \cdots - ax_n^2}}_{\text{1 coord. radial: } e^{-ar^2}} \underbrace{dx_1\, dx_2 \cdots dx_n}_{\text{elemento de hipervolume: } r^{n-1}\,dr\, d\theta_1\, d\theta_2 \cdots d\theta_{n-1}}$$

área de uma hiperesfera de raio unitário: $\overbrace{d\theta_1\, d\theta_2 \cdots d\theta_{n-1}}$

$V_n(R) = A_n R^n$ — variação do volume

$$\delta V_n(R) = \begin{cases} A_n\, n\, R^{n-1}\,\delta R \\ S_n(R)\,\delta R \end{cases}$$

área

$\longrightarrow \boxed{S_n = n A_n R^{n-1}}$

↳ $V_3 = \frac{4\pi}{3} r^3 \rightarrow \delta V_3 = \overbrace{4\pi r^2}^{S_3}\,\delta r$

$$\Rightarrow \left(\frac{\pi}{a}\right)^n = \int_0^{\infty} e^{-ar^2} r^{n-1}\, n A_n\, dr = \left(2a^{\frac{n}{2}}\right)^{-1} n A_n\, \Gamma\!\left(\frac{n}{2}\right)$$

$\Gamma(m) = (m-1)!\,, \quad m \in \mathbb{Z}$

$$\therefore \boxed{A_n = \frac{2\pi^{\frac{n}{2}}}{n\,\Gamma\left(\frac{n}{2}\right)}}\,, \quad \boxed{S_n(R) = \frac{2\pi^{\frac{n}{2}}}{\Gamma\left(\frac{n}{2}\right)} R^{n-1}}$$

→ Retornando à integral: $$I = \int_{\underbrace{(2mE)}_{R^2} \leq \vec{p}_1^{\,2} + \cdots + \vec{p}_N^{\,2} \leq \overbrace{2m(E+\delta E)}^{R^2 + \delta R^2}} d^3p_1 \cdots d^3p_N \Rightarrow I = S_{3N}(R)\,\delta R = C_{3N} R^{3N-1}\,\delta R$$

$N \rightarrow \infty$: $R^{3N-1} \approx R^{3N}$

$$R = (2mE)^{\frac{1}{2}} \Rightarrow \delta R = \frac{1}{2}(2m)^{\frac{1}{2}} E^{-\frac{1}{2}}\,\delta E \Rightarrow \boxed{I = \frac{1}{2} C_{3N} (2m)^{\frac{3N}{2}} E^{\frac{3N}{2}}\,\delta E}$$

→ $$\left.\begin{aligned} &\Omega(E)\,\delta E = V^N \frac{C_{3N}}{2} (2m)^{\frac{3N}{2}} E^{\frac{3N}{2}}\,\delta E \\ &S = k_B \ln \Omega \end{aligned}\right\}$$

$$\ln C_{3N} \sim \frac{3N}{2}\ln\pi - \ln\left(\frac{3N}{2}\right)! = \frac{3N}{2}\ln\pi - \frac{3N}{2}\ln\left(\frac{3N}{2}\right) + \frac{3N}{2}$$

$$S = k_B\left[\boxed{N \ln V} + \frac{3}{2} N \ln\frac{E}{N} + \tilde{A}N\right]$$

(eliminamos termos constantes → "subextensivos")

↳ não extensivo

→ Problema: entropia não é extensiva

Solução: considerar as partículas indistinguíveis (mec. quântica resolve o problema)

↳ Introduzimos o termo $\frac{1}{N!}$ → usamos a aproximação de Stirling

$$\boxed{\Omega(E)\,\delta E = \frac{1}{N!} V^N \frac{C_{3N}}{2} (2m)^{\frac{3N}{2}} E^{\frac{3N}{2}}\,\delta E} \Rightarrow \boxed{S = k_B\left[N \ln\frac{V}{N} + \frac{3}{2} N \ln\frac{E}{N} + \check{3}N\right]}$$

→ Exemplo:

E_1	E_2
$\Omega(E_1)$	$\Omega(E_2)$

$$\Omega(E)\,\Omega(E-E_1)$$
$$\Omega_t = \sum_{E_1=0}^{E} \Omega(E_1)\,\Omega(E-E_1)$$

$$P(E_1) = \frac{\Omega(E_1)\,\Omega(E-E_1)}{\Omega_t}, \qquad \Omega(E) = \frac{C_{3N} V^N}{N!} E^{\frac{3N}{2}}$$

→ Qual a distribuição de energia mais provável?

$$\frac{\partial \ln P(E)}{\partial E_1} = 0 \Rightarrow \frac{\partial}{\partial E_1}\left[\ln \Omega(E_1) + \ln \Omega(E-E_1) - \ln \Omega_t\right] = \frac{1}{k_B}\overbrace{\frac{\partial S_1}{\partial E_1}}^{\frac{1}{T_1}} - \frac{1}{k_B}\overbrace{\frac{\partial S_2}{\partial E_2}}^{\frac{1}{T_2}} = 0 \Rightarrow \boxed{T_1 = T_2}$$

→ Todas essas conclusões valem para o limite termodinâmico: $N \to \infty$ reduz as flutuações

→ $S = k_B \ln \Omega = k_B \frac{3}{2} N \ln E + f(V,N)$

$$\frac{\partial S}{\partial E} = \frac{3N}{2}\frac{k_B}{E} = \frac{1}{T} \Rightarrow \boxed{E_1 = \frac{3N}{2} k_B T}$$

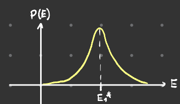
→ $\boxed{\Omega(E) = \frac{1}{N!} C_{3N} V^N E^{\frac{3N}{2}}}$

→ Mostrar que o equilíbrio é estável: $\frac{\partial^2 \ln P(E_1)}{\partial E_1^2} = -\frac{3}{2}\frac{N_1}{E_1^2} - \frac{3}{2}\frac{N_2}{E_2^2}$

↳ $E_1^* = \frac{3}{2} k_B T N_1$

↳ $E_2^* = \frac{3}{2} k_B T N_2$

$$\boxed{\left.\frac{\partial^2 \ln P(E_1)}{\partial E_1^2}\right|_{E^*} = -\frac{2}{3(k_BT)^2}\left(\frac{1}{N_1} + \frac{1}{N_2}\right) < 0}$$



→ Expansão em torno do máximo: $\ln P(E_1) = \ln P(E_1^*) + \overbrace{\left.\frac{\partial \ln P(E_1)}{\partial E_1}\right|_{E_1^*}}^{0}(E_1 - E_1^*) + \frac{1}{2}\frac{\partial^2 \ln P(E_1)}{\partial E_1^2}(E_1 - E_1^*)^2 - \dots$

$$P(E_1) = A e^{-\frac{1}{3k_BT}\frac{N_1+N_2}{N_1N_2}\left(E_1 - \frac{3}{2}k_BTN_1\right)^2}$$

→ Normalização: $\int_0^E P(E_1)\,dE_1 = 1$

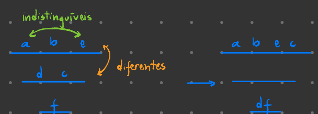
→ Comparamos com gaussiana:
$$\begin{cases} P(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-\mu)^2}{2\sigma^2}} \Rightarrow \boxed{\mu = \frac{3}{2}k_BTN_1} \\ \frac{1}{2\sigma^2} = \frac{1}{3k_BT}\frac{N_1+N_2}{N_1N_2}, \quad \sigma^2 = \langle(\Delta x)^2\rangle = \langle(E_1 - E_1^*)^2\rangle \Rightarrow \boxed{\sigma^2 = \frac{3}{2}(k_BT)^2\frac{N_1N_2}{N_1+N_2}} \end{cases}$$

→ Comparação adimensional (flutuação relativa): $\frac{\sigma^2}{\mu^2} = \frac{\langle(E_1-E_1^*)^2\rangle}{\langle E_1\rangle^2} \Rightarrow \boxed{\frac{\langle(\Delta E_1)^2\rangle}{\langle E_1\rangle^2} = \frac{2}{3}\frac{N_2}{N_1(N_1+N_2)}}$

↳ No limite termodinâmico: $\boxed{\frac{\langle(\Delta E_1)^2\rangle}{\langle E_1\rangle^2} \to 10^{-23} \sim 0}$ → flutuações microscópicas

* Exemplo: Toymodel de Boltzmann

→ n estados de energia: ε_i, $i \in \{1, \dots, n\}$



Qual estado é mais provável?

(ambos têm a mesma energia)

$$\boxed{\Omega = \frac{6!}{3!\,2!\,1!} = 60} \qquad \Omega = \frac{6!}{4!\,0!\,2!} = 15$$

Mais configurações possíveis

→ $\Omega(E, N, \{N_j\}) = \frac{N!}{N_1! \dots N_n!}$

$$f = \ln \Omega + \lambda_1\left(N - \sum_{j=1}^{n} N_j\right) + \lambda_2\left(E - \sum_{j=1}^{n}\varepsilon_j N_j\right)$$

$$f(\{N_j\}) = -\sum_j (N_j \ln N_j - N_j) - \lambda_1 \sum_j N_j - \lambda_2 \sum_j \varepsilon_j + C$$

maximizar: encontrar distribuição com maior degenerescência

→ $\frac{\partial N_j}{\partial N_k} = \delta_{jk}$, $\frac{\partial f}{\partial N_k} = 0 \Rightarrow -\ln N_k - \lambda_1 - \lambda_2 \varepsilon_k = 0$

$$\boxed{N_k = e^{-\lambda_2\varepsilon_k - \lambda_1}}$$

Geral

→ $N = \sum_k N_k = \sum_k e^{-\lambda_2\varepsilon_k - \lambda_1} = e^{-\lambda_1}\sum_k e^{-\lambda_2\varepsilon_k} \Rightarrow \boxed{e^{-\lambda_1} = \frac{N}{\sum_k e^{-\lambda_2\varepsilon_k}} = \frac{N}{Z}}$ $\quad Z(\lambda_2) = \sum_k e^{-\lambda_2\varepsilon_k}$

→ gás ideal: $\left.\begin{aligned} &\varepsilon_k \to \tfrac{1}{2}mv^2 \\ &\textstyle\sum_k N_k\varepsilon_k = E = \tfrac{3}{2}k_BTN \end{aligned}\right\}$ $\frac{\partial \ln Z}{\partial \lambda_2} = \frac{1}{Z}\frac{\partial Z}{\partial \lambda_2} = \frac{N\sum_k \varepsilon_k e^{-\lambda_2\varepsilon_k}}{\sum_k e^{-\lambda_2\varepsilon_k}} \Rightarrow \boxed{E = -N\frac{\partial \ln Z}{\partial \lambda_2} = \frac{3}{2}k_BTN}$

$$Z = \sum_k e^{-\lambda_2\varepsilon_k} \to \int d^3v\, e^{-\lambda_2\frac{1}{2}mv^2} = \left(\frac{2\pi}{\lambda_2 m}\right)^{\frac{3}{2}}$$

$$\ln Z = -\frac{3}{2}\ln\lambda_2 + C$$

$$\frac{\partial \ln Z}{\partial \lambda_2} = -\frac{3}{2}\frac{1}{\lambda_2} \Rightarrow \frac{3}{2}\frac{N}{\lambda_2} = \frac{3}{2}k_BTN$$

$$\boxed{\lambda_2 = \frac{1}{k_BT} \equiv \beta}$$

distribuição de velocidades

→ $\frac{N_k}{N} \to \rho(v)\,d^3v$

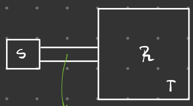
$$\boxed{\rho(\vec{v}) = \left(\frac{2\pi k_BT}{m}\right)^{-\frac{3}{2}} e^{-\frac{mv^2}{2k_BT}}}$$

→ Integrando sobre todos os ângulos: $\int \rho(v)\,d^3v = \int \rho(v)\,4\pi v^2\,dv$

08/07/24

Ensemble Canônico

* Fixamos um microestado do sistema e vemos quantos microestados do reservatório são compatíveis



energia do sistema pode flutuar

↓

média da energia

→ Número de estados dentro do reservatório: $\boxed{P_j = \dfrac{\overbrace{\Omega(E_0 - E_j)}^{E_R}\cdot 1}{\Omega_t}}$

$$\ln P_j = \ln \Omega(E_0 - E_j) - \ln \Omega_t$$
$$= \ln \Omega(E_0) - \frac{\partial \ln \Omega(E)}{\partial E}\Big|_{E_0} E_j + O(E_j^2) + C$$

$$S = k_B \ln \Omega(E) \Rightarrow \frac{\partial S}{\partial E}\Big|_{E_R} = k_B \frac{\partial \ln \Omega}{\partial E}\Big|_{E_R} = \frac{1}{T_R}$$

$E_R = E_0 - E_j \Rightarrow E_R E_j \sim E_0 E_j + O(E_j^2)$

→ Veja que $E_0 \approx E_R$, para E_j pequeno → $\ln P_j = \ln \Omega(E_0) - \frac{\partial \ln \Omega(E)}{\partial E}\Big|_{E_R} E_j + O(E_j^2) = \ln \Omega(E_0) - \frac{E_j}{k_B T} + C$

$$\therefore \boxed{P_j = A e^{-\frac{E_j}{k_B T}}}$$

→ Normalizando: $\sum_j P_j = 1 = A \sum_j e^{-\beta E_j} \Rightarrow A = \dfrac{1}{\sum_j e^{-\beta E_j}}$

$$\therefore \boxed{P_j = \frac{e^{-\beta E_j}}{\sum_k e^{-\beta E_k}}}$$

→ Definimos a função de partição $\boxed{Z(\beta) = \sum_j e^{-\beta E_j}}$

↳ soma sobre microestados do sistema

→ Considerando a degenerescência de estados, reescrevemos: $Z(\beta) = \sum_E \Omega(E) e^{-\beta E} = \sum_E e^{\ln \Omega(E) - \beta E} = \sum_E e^{-\beta[E - T\overbrace{k_B \ln \Omega(E)}^{S(E)}]}$

$$\therefore Z(\beta) = \sum_E e^{-\beta(E - TS)}$$

→ E e S são extensivas: $-\beta(E - TS) = -\beta N(u - Ts) \Rightarrow Z(\beta) = \sum_E e^{-\beta N[u - Ts(u)]}$

↳ No limite termodinâmico: apenas um termo contribui → $u - Ts \to 0 \Rightarrow \boxed{u \to Ts}$

$$\boxed{\sum_u e^{-\beta N(u - Ts)} \sim e^{-\beta N \min_u (u - Ts(u))}}$$

→ $Z(\beta) = e^{-\beta \min_E (E - TS)}$

$\min_E (E - TS) \rightarrow \frac{\partial}{\partial E}[E - TS(E)] = 0 \Rightarrow 1 - T\frac{\partial S}{\partial E} = 0 \Rightarrow \boxed{\frac{\partial S}{\partial E} = \frac{1}{T}}$ Equilíbrio termodinâmico

→ $\min_E (E - TS) = E^*(T) - TS(E^*(T)) = F(T, S)$

$$\therefore \boxed{Z(\beta) = e^{-\beta F(T,S)}}$$

→ $-\beta F(T) = \ln Z \Rightarrow \boxed{F(T) = -\frac{1}{\beta} \ln Z(\beta)}$

→ $\langle E \rangle = \dfrac{\sum_j E_j e^{-\beta E_j}}{\sum_k e^{-\beta E_k}} = \sum_j E_j P_j(E_j)$

→ $\dfrac{\partial \ln Z(\beta)}{\partial \beta} = \dfrac{1}{Z}\dfrac{\partial Z}{\partial \beta} = \left(\sum_k e^{-\beta E_k}\right)\left(-\sum_j E_j e^{-\beta E_j}\right)$

$\langle E \rangle = -\dfrac{\partial \ln Z(\beta)}{\partial \beta}$

$\ln Z(\beta) = -\beta F(T)$

$\Rightarrow \boxed{\langle E \rangle = \dfrac{\partial [\beta F(T)]}{\partial \beta}}$

→ $\beta = \dfrac{1}{k_B T} \Rightarrow \dfrac{\partial \beta}{\partial T} = -\dfrac{1}{k_B T^2}, \quad \dfrac{\partial T}{\partial \beta} = -k_B T^2$

→ $\dfrac{\partial[\beta F(\beta)]}{\partial \beta} = F(\beta) + \beta \dfrac{\partial F(\beta)}{\partial \beta} = F + \dfrac{1}{k_B T}\cdot\dfrac{\partial F}{\partial T}\dfrac{\partial T}{\partial \beta} = F + \dfrac{1}{k_B T}\cdot(-S)\cdot(-k_B T^2) = F + TS = U \Rightarrow \boxed{\langle E \rangle = U}$

→ $\langle (\Delta E)^2 \rangle = \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2$

→ $\langle E^2 \rangle = \sum_j E_j^2 P(E_j)$

$\langle (\Delta E)^2 \rangle = \dfrac{1}{Z}\underbrace{\sum_j E_j^2 e^{-\beta E_j}}_{\frac{\partial^2 Z}{\partial \beta^2}} - \left(\dfrac{1}{Z}\underbrace{\sum_j E_j e^{-\beta E_j}}_{-\frac{\partial Z}{\partial \beta}}\right)^2 = \dfrac{1}{Z}\dfrac{\partial^2 Z}{\partial \beta^2} - \dfrac{1}{Z^2}\left(\dfrac{\partial Z}{\partial \beta}\right)^2 = \dfrac{1}{Z}\dfrac{\partial^2 Z}{\partial \beta^2} - \left[\dfrac{1}{Z^2}\left(\dfrac{\partial Z}{\partial \beta}\right)\left(\dfrac{\partial Z}{\partial \beta}\right)\right] = \dfrac{1}{Z}\dfrac{\partial^2 Z}{\partial \beta^2} + \dfrac{\partial}{\partial \beta}\left[\dfrac{1}{Z}\right]\left(\dfrac{\partial Z}{\partial \beta}\right) = \dfrac{\partial}{\partial \beta}\left[\dfrac{1}{Z}\left(\dfrac{\partial Z}{\partial \beta}\right)\right]$

$\dfrac{\partial}{\partial \beta}\left[\dfrac{1}{Z}\left(\dfrac{\partial Z}{\partial \beta}\right)\right] = \dfrac{\partial}{\partial \beta}\left[\dfrac{\partial \ln Z}{\partial \beta}\right] = \dfrac{\partial}{\partial \beta}[-\langle E \rangle] \Rightarrow \boxed{\langle (\Delta E)^2 \rangle = -\dfrac{\partial \langle E \rangle}{\partial \beta} = -\dfrac{\partial U}{\partial \beta}}$

→ $\langle (\Delta E)^2 \rangle = -\dfrac{\partial U}{\partial \beta} = -\dfrac{\partial U}{\partial T}\dfrac{\partial T}{\partial \beta} = k_B T^2 C_V$

$\langle (\Delta E)^2 \rangle \geq 0$ e $k_B T^2 > 0 \Rightarrow \boxed{C_V \geq 0}$

10/07/24

→ Resultados da aula passada:

$$\boxed{\langle E\rangle = \frac{\partial[\beta F]}{\partial\beta} = -\frac{\partial \ln Z}{\partial\beta} = Nu} \quad \boxed{\langle(\Delta E)^2\rangle = -\frac{\partial\langle E\rangle}{\partial\beta} = -\frac{\partial U}{\partial\beta} = k_B T^2 N c_v \geq 0}$$

→ Observamos o desvio relativo $\boxed{\frac{\sqrt{\langle(\Delta E)^2\rangle}}{\langle E\rangle} \sim \frac{1}{\sqrt{N}}}$

→ Voltando à termodinâmica:

↳ $\beta = \frac{1}{k_B T}$, $F = -\frac{1}{\beta}\ln Z(\beta) \Rightarrow \frac{\partial F}{\partial\beta} = \frac{1}{\beta^2}\ln Z(\beta) - \frac{1}{\beta}\frac{1}{Z}\frac{\partial Z(\beta)}{\partial\beta}$

↳ $S = -\frac{\partial F}{\partial T}\Big|_V = -\frac{\partial F}{\partial\beta}\frac{\partial\beta}{\partial T} = k_B\beta^2\frac{\partial F}{\partial\beta} = k_B\left[\ln Z(\beta) - \frac{\beta}{Z}\frac{\partial Z}{\partial\beta}\right]$

↳ $Z(\beta) = \sum_j e^{-\beta E_j} \Rightarrow \frac{\partial Z}{\partial\beta} = -\sum_j E_j e^{-\beta E_j}$

$$S = k_B\ln Z + \frac{k_B\beta}{Z}\sum_j E_j e^{-\beta E_j}$$
$$= k_B\ln Z + k_B\sum_j\left[-\ln(ZP_j)P_j\right]$$
$$= \cancel{k_B\ln Z} + k_B\sum_j\left[(-\ln Z)P_j - (\ln P_j)P_j\right]$$

$P_j = \frac{1}{Z}e^{-\beta E_j} \Rightarrow ZP_j = e^{-\beta E_j} \Rightarrow -\beta E_j = \ln(ZP_j)$

$\frac{1}{Z}k_B\beta\sum_j E_j e^{-\beta E_j} = k_B\sum_j(\beta E_j)\frac{e^{-\beta E_j}}{Z} = k_B\sum_j\left[-\ln(ZP_j)P_j\right]$

$\therefore \boxed{S = -k_B\sum_j P_j\ln P_j}$ → Entropia de Gibbs ou Entropia de Shannon

→ Microcanônico: $\left.\begin{array}{l} S = -k_B\sum_j P_j\ln P_j \\ P_j = \frac{1}{\Omega}\end{array}\right\}$ $S = k_B\sum_j P_j(\ln\Omega) = k_B\ln\Omega\sum_j P_j$

$\therefore \boxed{S = k_B\ln\Omega}$ Entropia de Boltzmann

→ Maximizar a entropia: $\left\{\begin{array}{l} S = -k_B\sum_j P_j\ln P_j \\ \text{Vínculos: } \sum_j P_j = 1,\ \sum_j E_j P_j = \langle E\rangle = U\end{array}\right.$ $\Rightarrow f = S - \tilde{\lambda}_1\left(\sum_j P_j - 1\right) - \lambda_2\left(\sum_j E_j P_j - U\right)$

↳ $\delta S = 0$

$\delta f = \delta S - \lambda_1\delta\left(\sum_j P_j - 1\right) - \lambda_2\delta\left(\sum_j E_j P_j - U\right)$

↳ Seja um estado k: $\frac{\partial f}{\partial P_k} = 0 = -k_B\ln P_k \underbrace{-k_B - \tilde{\lambda}_1}_{\lambda_1 \equiv \tilde{\lambda}_1 + k_B} - \lambda_2 E_k$

$\lambda_1 + \lambda_2 E_k = -k_B\ln P_k$

$P_k = e^{-\frac{\lambda_1}{k_B}}e^{-\frac{\lambda_2}{k_B}E_k}$

$\frac{\partial f}{\partial P_j} = -k_B\ln P_j - k_B - \tilde{\lambda}_1 - \lambda_2 E_j = 0$

$\ln P_j = -1 - \frac{1}{k_B}\tilde{\lambda}_1 - \frac{1}{k_B}\lambda_2 E_j$

$P_j = e^{-1-\frac{\tilde{\lambda}_1}{k_B} - \frac{\lambda_2 E_j}{k_B}}$

$\sum_j P_j = 1 = e^{-1-\frac{\tilde{\lambda}_1}{k_B}}\sum_j e^{-\frac{\lambda_2 E_j}{k_B}} \Rightarrow e^{-1-\frac{\tilde{\lambda}_1}{k_B}} = \left[\sum_j e^{-\frac{\lambda_2 E_j}{k_B}}\right]^{-1}$ $\boxed{P_j = \frac{e^{-\frac{\lambda_2 E_j}{k_B}}}{\sum_k e^{-\frac{\lambda_2 E_k}{k_B}}}}$

↳ Sendo $\sum_k P_k = 1$: $1 = e^{-\frac{\lambda_1}{k_B}}\sum_k e^{-\left(\frac{\lambda_2}{k_B}\right)E_k} \Rightarrow \boxed{e^{-\frac{\lambda_1}{k_B}} = \left[\sum_k e^{-\frac{\lambda_2}{k_B}E_k}\right]^{-1}}$

$\therefore \boxed{P_j = \frac{e^{-\frac{\lambda_2}{k_B}E_j}}{\sum_k e^{-\frac{\lambda_2}{k_B}E_k}}}$

Para determinar λ_2: usamos o vínculo $\sum_j E_j P_j = U$

$\sum_j E_j P_j = \left[\sum_k e^{-\frac{\lambda_2 E_k}{k_B}}\right]^{-1}\sum_j E_j e^{-\frac{\lambda_2 E_j}{k_B}} = U$?

✳ Exemplo: $\mathcal{H} = -\mu_0 H\sum_{i=1}^N \sigma_i$, $\sigma_i = \pm 1$

$Z = \sum_{\{\sigma_i\}} e^{-\beta\mathcal{H}}$

↳ soma sobre todas as 2^N configurações → inviável

→ Notação: $Z = \sum_{\{\sigma_i\}} e^{-\beta\mathcal{H}} \equiv \mathrm{Tr}\, e^{-\beta\mathcal{H}}$

→ $Z = \sum_{\{\sigma_i\}}\left[e^{\beta\mu_0 H\sigma_1} e^{\beta\mu_0 H\sigma_2}\cdots e^{\beta\mu_0 H\sigma_N}\right] = \sum_{\sigma_N}\cdots\sum_{\sigma_2}\left(\sum_{\sigma_1=\pm1} e^{\beta\mu_0 H\sigma_1}\right)\cdots e^{\beta\mu_0 H\sigma_N}$

$= \left(e^{\beta\mu_0 H\sigma_1} + e^{-\beta\mu_0 H\sigma_1}\right)\left(e^{\beta\mu_0 H\sigma_2} + e^{-\beta\mu_0 H\sigma_2}\right)\cdots\left(e^{\beta\mu_0 H\sigma_N} + e^{-\beta\mu_0 H\sigma_N}\right)$

$= \left[2\cosh(\beta\mu_0 H)\right]^N$

$\therefore \boxed{Z = \left[2\cosh(\beta\mu_0 H)\right]^N = e^{-\beta G(H,T)}}$ → associamos a função de partição a um potencial termodinâmico

→ $-\beta G = N\ln\left[2\cosh(\beta\mu_0 H)\right] \Rightarrow \boxed{g = -\frac{1}{\beta}\ln\left[2\cosh(\beta\mu_0 H)\right]}$

↳ $dg = -s\,dT + \cdots$

$$\rightarrow \frac{\partial \ln Z}{\partial H} = \frac{1}{Z}\frac{\partial Z}{\partial H} = \frac{1}{Z}\,\mathrm{Tr}\,(\beta\mu_0 \overbrace{\Sigma\sigma_i}^{M\{\sigma_i\}})\, e^{-\beta\mu_0 H \Sigma \sigma_i} = \beta\mu_0 \langle M\rangle$$

$\mu_0 = 1?$

$$\boxed{m = -\frac{\partial g}{\partial H} = \frac{1}{N}\left\langle \sum_{i=1}^{N} \sigma_i \right\rangle = \langle \sigma \rangle}$$

$$\therefore \boxed{dg = -s\,dT - m\,dH}$$

12/07/24

$\rightarrow$ Energia interna: $\boxed{u(s,H) = g + sT}$, $g(T,H) = -k_B T \ln\left[2\cosh(\beta\mu_0 H)\right]$

para ser eq. fundamental: $\beta(s)$

$$\rightarrow s = -\frac{\partial g}{\partial T}\bigg|_H = k_B \ln\left[2\cosh(\beta\mu_0 H)\right] - k_B\beta\mu_0 H \tanh(\beta\mu_0 H) \Rightarrow g + sT = \boxed{u(s,H) = -\mu_0 H \tanh(\beta\mu_0 N) = -\mu_0 H m}$$

$\langle\sigma_i\rangle = m \Rightarrow \langle\sum_i \sigma_i\rangle = \sum_i \langle\sigma_i\rangle = \sum_i m = mN$

$$\rightarrow u = \frac{\langle E\rangle}{N} = -\frac{\mu_0 H}{N}\left\langle \sum_i \sigma_i \right\rangle = -\frac{\mu_0 H}{N} mN = -\mu_0 H m$$

$$\rightarrow \frac{\langle E\rangle}{N} = \frac{-\frac{\partial}{\partial\beta}\ln Z(\beta,H)}{N} = u$$

$*$ Dedução alternativa da função de partição: $N = \overset{(\uparrow)}{N_1} + \overset{(\downarrow)}{N_2} \Rightarrow N_2 = N - N_1$

$$\left.\begin{aligned} E(N_1) &= -\mu_0 H N_1 + \mu_0 H (N - N_1) \\ \Omega &= \frac{N!}{N_1!\,(N-N_1)!} \end{aligned}\right\} \quad Z = \mathrm{Tr}\, e^{-\beta\mathcal{H}} = \sum_{N_1=0}^{N} \Omega(N_1)\, e^{-\beta E(N_1)} = \sum_{N_1=0}^{N} \frac{N!}{N!\,(N-N_1)!}\, e^{\beta\mu_0 H N_1 - \beta\mu_0 H (N-N_1)}$$

Sejam $x = e^{\beta\mu_0 H}$ e $y = e^{-\beta\mu_0 H}$ $\rightarrow Z = \sum_{N_1=0}^{N} \frac{N!}{N_1!\,(N-N_1)!} x^{N_1} y^{N-N_1} = (x+y)^N = \left[2\cosh(\beta\mu_0 H)\right]^N$

$*$ Exemplo: Gás de Boltzmann $\begin{cases} N \text{ número de partículas} \\ n+1 \text{ número de níveis de energia} \end{cases}$

soma sobre estados: partículas distinguíveis $\rightarrow$ mesma energia, estados diferentes

$$\rightarrow \mathcal{H} = \sum_{j=0}^{n} \varepsilon_j N_j, \quad Z = \mathrm{Tr}\, e^{-\beta\mathcal{H}}$$

degenerescência de estados

$$\rightarrow \Omega(E, N, \{N_j\}) = \frac{N!}{N_0!\,N_1!\ldots N_n!} \Rightarrow Z = \sum_{\{N_j\}} e^{-\beta\sum_j \varepsilon_j N_j} \frac{N!}{N_0!\,N_1!\ldots N_n!}, \text{ com o vínculo } \sum_j N_j = N$$

$\rightarrow$ Seja $X_j = e^{-\beta\varepsilon_j} \rightarrow X_j^{N_j} = e^{-\beta\varepsilon_j N_j}$

$$\rightarrow Z = \sum_{\{N_j\}} X_0^{N_0} X_1^{N_1} \ldots X_n^{N_n} \frac{N!}{N_0!\,N_1!\ldots N_n!} = (X_0 + X_1 + \cdots + X_n)^N$$

$$\rightarrow Z_1 = e^{-\beta\varepsilon_0} + e^{-\beta\varepsilon_1} + \ldots + e^{-\beta\varepsilon_n} = X_0 + X_1 + \cdots + X_n \Rightarrow \boxed{Z_N = (Z_1)^N}$$

Gás Ideal Clássico (Canônico)

→ $Z = \mathrm{Tr}\, e^{-\beta \mathcal{H}} = \frac{1}{N!}\frac{1}{h^{3N}}\int d^3q_1\, d^3q_2 \cdots d^3q_N \int d^3p_1\, d^3p_2 \cdots d^3p_N\, e^{-\beta\mathcal{H}}$

↳ cte. de Planck → tornar integral adimensional

↳ partículas indistinguíveis → fazer entropia extensiva

→ $\mathcal{H} = \boxed{\sum_{i=1}^{N} \frac{p_i^2}{2m}} + \boxed{\sum_{i<j} V(|\vec{q}_i - \vec{q}_j|)}$ → potencial de interação → posições acopladas

↳ Canônico: energia total não é fixa → momentos desacoplados

→ $\int_{-\infty}^{+\infty} dp\, e^{-\frac{\beta p^2}{2m}} = \left(\frac{2\pi m}{\beta}\right)^{\frac{1}{2}}$ } 3N vezes

$\therefore \boxed{Z = \left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3N}{2}} \frac{Q_N}{N!}}$, $Q_N = \int d^3q_1\, d^3q_2 \cdots d^3q_N\, e^{-\beta\sum_{i<j}\tilde{V}(|\vec{q}_i - \vec{q}_j|)}$ → sem resolução analítica

→ Caso mais simples: $\tilde{V} = 0$ → gás ideal ⇒ $Q_N = \int d^3q_1 \cdots d^3q_N\, e^0 = \left[\int d^3q_1\right]^N = V^N$

$\therefore \boxed{Z_{id} = \frac{1}{N!}\left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3N}{2}} V^N}$

→ Comprimento de de Broglie térmico: $\boxed{\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}}$

→ $e^{-\beta F} = Z_N = \left(\frac{V}{\Lambda^3}\right)\frac{1}{N!}$

$\beta F = -\ln Z_N = -N\ln\left(\frac{V}{\Lambda^3}\right) + N\ln N - N = N\ln(\rho\Lambda^3) - N$

$\sim N \ln\frac{N}{V} \sim -N\ln V$

$\therefore \boxed{f = \frac{1}{\beta}\left[\ln(\rho\Lambda^3) - 1\right]}$

→ $\beta p = -\frac{\partial \beta F}{\partial V}\Big|_{T,N} = \rho \Rightarrow \beta p = \rho \Rightarrow pV = Nk_BT$

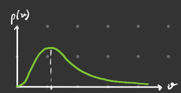
→ $S = -\frac{\partial F}{\partial T}\Big|_{V,N} = \dots$

→ $Z_N = \mathrm{Tr}\, e^{-\beta\mathcal{H}} = \int d^3p_1 \cdots \int d^3p_N \int d^3r_1 \cdots d^3r_N\, e^{-\frac{\beta}{2}\sum_{i=1}^{N}\frac{\vec{p}_i^{\,2}}{m} - \beta\boxed{\sum_{i<j} V(\vec{r}_i - \vec{r}_j)}}$ → sistemas interagentes

→ $f(v) = Ae^{-\frac{1}{2}\frac{mv^2}{k_BT}}$ → $\int d^3v\, Ae^{-\frac{1}{2}\frac{mv^2}{k_BT}} = 1 \Rightarrow \boxed{A = \left(\frac{2\pi k_BT}{m}\right)^{-\frac{3}{2}}}$

"casca esférica" no espaço de momentos

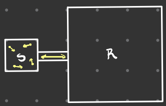
→ Integrando em coordenadas polares: $d^3v = v^2 \operatorname{sen}\theta\, d\theta\, d\varphi\, dv$ ⇒ $\boxed{p_{MB}(v) = 4\pi\left(\frac{2\pi k_BT}{m}\right)^{-\frac{3}{2}} v^2 e^{-\frac{1}{2}\frac{mv^2}{k_BT}}}$



→ $\langle v^2\rangle = \int_0^\infty dv\, v^2 p_{MB}(v) = 3\frac{k_BT}{m} \Rightarrow \boxed{\langle K\rangle = \left\langle\frac{1}{2}mv^2\right\rangle = \frac{3}{2}k_BT}$

15/07/24

Ensemble Grande Canônico



$\begin{cases} E_0 = E_S + E_R \\ N_0 = N_S + N_R \end{cases}$ → reservatório térmico e químico

Sistema: N_j, E_j

→ $P_j \sim \Omega_R(E_0 - E_j ; N_0 - N_j)$ → $\ln P_j = C + \ln\Omega(E_0 - E_j ; N_0 - N_j)$ expansão em série de Taylor

$$= \tilde{C} + \frac{\partial \ln\Omega}{\partial E}(-E_j) + \frac{\partial \ln \Omega}{\partial N}(-N_j) + O(E_j^2, N_j^2)$$

$$\begin{cases} \left.\frac{\partial \ln\Omega}{\partial E}\right|_{E_R, N_R} = \frac{1}{k_B T} \\ \left.\frac{\partial k_B \ln\Omega}{k_B \partial N}\right|_{E_R, N_R} = -\frac{\mu}{k_B T} \end{cases} \Rightarrow \boxed{P_j = A e^{-\beta E_j + \beta\mu N_j}}$$

→ Correção para partículas indistinguíveis: $\boxed{P_j = A \frac{e^{-\beta E_j + \beta \mu N_j}}{N_j!}}$

→ Normalização: $\sum_j P_j = 1$ → Função de grande partição: $\boxed{\Xi = \sum_k \frac{e^{-\beta E_k + \beta\mu N_k}}{N_k!}}$

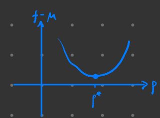
para cada valor de N, somamos todos os estados possíveis; $\therefore \boxed{P_j = \frac{e^{-\beta E_j + \beta\mu N_j}}{N_j!\,\Xi}}$

depois somamos sobre os valores possíveis de N

$$\rightarrow \Xi = \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{N!}\left[\sum_k e^{-\beta E_k(N)}\right]$$
$$= \sum_{N=0}^{\infty} e^{\beta\mu N}\left[\sum_k \frac{e^{-\beta E_k(N)}}{N!}\right] \longrightarrow Z_N(\beta): \text{ função de partição canônica}$$

$Z_N(\beta) = e^{-\beta F}$

$$= \sum_{N=0}^{\infty} e^{\beta\mu N} Z_N(\beta)$$
$$= \sum_{N=0}^{\infty} e^{\beta\mu N - \beta F}$$
$$= \sum_{N=0}^{\infty} e^{-\beta(F - \mu N)} \quad \rightarrow F = Nf \rightarrow F = Nf\left(\frac{N}{V}\right)$$
$$= \sum_{N=0}^{\infty} e^{-\beta N(f-\mu)} \longrightarrow \text{limite termodinâmico} \rightarrow \text{contribuição significativa: } \min_{\rho}(f(\rho) - \mu(\rho))$$
$$\sim e^{-\beta[F(N^*) - \mu N^*]}$$



independente de N (função do reservatório)

→ $\frac{\partial}{\partial N}(F - \mu N) = 0 \Rightarrow \boxed{\frac{\partial F}{\partial N} = \mu}$

inverter para $\mu(N)$

→ $F(N, V, T)$ → $N^*(\mu, V, T)$ → Grande potencial $\boxed{\Phi(\mu, V, T) = F(T, V, N) - \mu N}$

→ $dF = -SdT - pdV + \mu dN$ → $d\Phi = -SdT - pdV - Nd\mu$

→ $U = TS - pV + \mu N$ → $\Phi = U - TS - \mu N = -pV$

$$\therefore \boxed{\Xi = e^{-\beta\Phi} = e^{\beta p(\mu(N), V, T)V}}$$

17/07/24

$$\rightarrow \langle N_j \rangle = \frac{\sum_j N_j \frac{e^{-\beta E_j + \beta\mu N_j}}{N_j!}}{\Xi} \Rightarrow \boxed{\langle N_j \rangle = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln\Xi}$$

$$\rightarrow \langle E_j \rangle = \frac{\sum_j E_j \frac{e^{-\beta E_j + \beta\mu N_j}}{N_j!}}{\Xi} \Rightarrow \boxed{\langle E_j \rangle = -\frac{\partial}{\partial\beta}\ln\Xi - \frac{\mu}{\beta}\frac{\partial}{\partial\mu}\ln\Xi}$$

→ cálculo mais complicado no ensemble grande canônico devido aos termos mistos

$$\langle E_j \rangle = \frac{\partial(\beta\Phi)}{\partial\beta} + \frac{\mu}{\beta}\frac{\partial(\beta\Phi)}{\partial\beta} = U$$

→ Definimos: Fugacidade ou atividade: $z(\beta, \mu) = e^{\beta\mu}$

f. partição canônica

$$\Xi(\beta, z) = \sum_j \frac{e^{-\beta E_j} z^{N_j}}{N_j!} = \sum_{N=0}^{\infty} \frac{z^N}{N!}\sum_k e^{-\beta E_k(N)} \Rightarrow \boxed{\Xi(\beta, z, V) = \sum_{N=0}^{\infty} z^N Z_N(T, V)}$$

$$\therefore \boxed{\begin{aligned} \langle E_j \rangle &= -\frac{\partial}{\partial\beta}\ln\Xi(z,\beta)\Big|_z \\ \langle N_j \rangle &= z\frac{\partial}{\partial z}\ln\Xi(z,\beta)\Big|_\beta \end{aligned}}$$

Valores médios desacoplados

* Flutuações:

→ $\langle(\Delta N)^2\rangle = \langle N^2\rangle - \langle N\rangle^2 = \frac{1}{\beta^2}\frac{\partial^2}{\partial\mu^2}\ln\Xi = \frac{1}{\beta}\frac{\partial\langle N_j\rangle}{\partial\mu} \geq 0$ → estabilidade termodinâmica: $\frac{\partial N}{\partial\mu} \geq 0$

→ Relação de Gibbs-Duhem: $d\mu = -s\,dT + v\,dp$

$$\left.\begin{aligned} \left(\frac{\partial\mu}{\partial N}\right)_{T,V} &= v\left(\frac{\partial p}{\partial N}\right)_{T,V} \\ \left(\frac{\partial\mu}{\partial V}\right)_{T,N} &= v\left(\frac{\partial p}{\partial V}\right)_{T,N} \\ -\left(\frac{\partial p}{\partial N}\right)_{T,V} &= \left(\frac{\partial\mu}{\partial V}\right)_{T,N} \end{aligned}\right\} \left(\frac{\partial\mu}{\partial N}\right)_{T,V} = -v\left(\frac{\partial\mu}{\partial V}\right)_{T,N} = -v^2\left(\frac{\partial p}{\partial V}\right)_{T,N} = \frac{V}{N^2\kappa_T}$$

$$\therefore \boxed{\langle(\Delta N)^2\rangle = N\frac{k_B T\kappa_T}{v} \geq 0}$$

$$\boxed{\kappa_T \geq 0}$$

→ $\frac{\langle(\Delta N)^2\rangle}{\langle N\rangle^2} \sim \frac{1}{N}$ → no limite termodinâmico: flutuação muito pequena (exceto em fenômenos críticos, com $\kappa_T \to \infty$)

* Exemplo: Gás ideal

$\Lambda = h\cdot(2\pi k_B T m)^{-\frac{1}{2}}$

→ $$\left.\begin{aligned} \Xi &= \sum_{N=0}^{\infty} z^N Z_N \\ Z_N(\beta,V) &= \frac{1}{N!}z^N\left(\frac{V}{\Lambda^3}\right)^N \end{aligned}\right\} \Xi = \sum_{N=0}^{\infty}\frac{\left(\frac{zV}{\Lambda^3}\right)^N}{N!} \Rightarrow \boxed{\Xi = e^{\frac{Vz}{\Lambda^3}}}$$

→ $e^{\beta pV} = e^{-\beta\Phi} = \Xi = e^{\frac{Vz}{\Lambda^3}} \Rightarrow \beta pV = \frac{Vz}{\Lambda^3}$

$$\boxed{\beta p = \frac{z}{\Lambda^3} = \frac{e^{\beta\mu}}{\Lambda^3}}$$

fazer: $\frac{\partial\Lambda}{\partial\beta} = \frac{\Lambda}{2\beta}$

→ $U = \langle E\rangle = -\frac{\partial}{\partial\beta}\ln\Xi\Big|_z = \frac{3Vz}{\Lambda^4}\frac{\partial\Lambda}{\partial\beta} = \frac{3}{2}\frac{Vz}{\beta\Lambda^3}$

→ $\langle N\rangle = z\frac{\partial}{\partial z}\ln\Xi\Big|_\beta = \frac{Vz}{\Lambda^3}$

$$\boxed{U = \frac{3}{2}\langle N\rangle k_B T}$$

→ Em termos da densidade: $\beta p = \frac{z}{\Lambda^3}$

19/07/24

Modelo de Ising (d = 1)

→ $\mathcal{H} = -\underbrace{J\sum_i^N \sigma_i \sigma_{i+1}}_{} - H\sum_i \sigma_i \quad , \quad \sigma_i = \pm 1$

J: fixo, carac. do sistema; H: campo externo

↳ interação de curto alcance: primeiros vizinhos apenas

→ $Z = \mathrm{Tr}\, e^{-\beta\mathcal{H}}$

→ Para remover o efeito de borda: condições de contorno periódicas → $\sigma_1 = \sigma_{N+1}$

→ Escrevendo de maneira simétrica: $\mathcal{H} = -J\sum_i \sigma_i\sigma_{i+1} - \frac{H}{2}\sum_i(\sigma_i + \sigma_{i+1})$

→ Função de partição: $\boxed{Z_N = \mathrm{Tr}_{\{\sigma_i\}}\, e^{+\beta J\sum_i \sigma_i\sigma_{i+1} + \frac{\beta H}{2}\sum_i(\sigma_i+\sigma_{i+1})}}$

$\sum_{\{\sigma_i\}} = \sum_{\sigma_1=\pm1}\sum_{\sigma_2=\pm1}\cdots\sum_{\sigma_N=\pm1}$

→ Definimos: $T(\sigma_i, \sigma_{i+1}) = e^{K\sigma_i\sigma_{i+1} + \frac{L}{2}(\sigma_i+\sigma_{i+1})}$, $K \equiv \beta J$, $L \equiv \beta H$

$$\boxed{\bar{T} = \begin{pmatrix} T_{++} & T_{+-} \\ T_{-+} & T_{--} \end{pmatrix}}, \quad \begin{matrix} + \to 1 \\ - \to 2 \end{matrix}$$

* Ex.: $N = 3$

$$Z_3 = \sum_{\{\sigma_i\}} \underbrace{T(\sigma_1, \sigma_2)\, T(\sigma_2, \sigma_3)\, T(\sigma_3, \sigma_1)}_{(\bar{T}_{11})^3}$$

$$\bar{M}_{i\ell}^{\,3} = \sum_{jk} M_{ij} M_{jk} M_{k\ell} \longrightarrow \sum_i \bar{M}_{ii}^{\,3} = \sum_i\sum_{jk} M_{ij}M_{jk}M_{ki} = \mathrm{tr}\,\bar{M}^3$$

$Z_3 = \mathrm{tr}\,\bar{T}^3$

→ Generalizando: $\boxed{Z_N = \mathrm{tr}\,\bar{T}^N}$

→ $\bar{T} = \begin{pmatrix} e^{K+L} & e^{-K} \\ e^{-K} & e^{K-L} \end{pmatrix}$ } matriz simétrica ⇒ diagonalizável → $U\bar{T}U^{-1} = \bar{D}$, $U^{-1} = U^T$, $\bar{D} = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix}$

→ $\mathrm{tr}\,\bar{T}^N = \mathrm{tr}(U^{-1}\bar{D}U)^N = \mathrm{tr}(U^{-1}\bar{D}^N U) \overset{\mathrm{tr}\,\bar{A}\bar{B}\bar{C} = \mathrm{tr}\,\bar{C}\bar{A}\bar{B}}{=} \mathrm{tr}(UU^{-1}\bar{D}^N) = \mathrm{tr}\,\bar{D}^N = \lambda_1^N + \lambda_2^N$

→ Autovalores de $\bar{T}$: $\boxed{\lambda_{1,2} = e^K \cosh L \pm \left[e^{2K}\cosh^2 L - 2\,\mathrm{senh}(2K)\right]^{\frac{1}{2}}}$

$\lambda_1 > \lambda_2$

→ Para estudar o caso de magnetização espontânea, fazemos $H = 0 \Rightarrow L = 0$:

$$\lambda_{1,2} = e^K \pm \left[e^{2K} - 2\,\mathrm{senh}(2K)\right]^{\frac{1}{2}} = e^K \pm \left[e^{2K} - (e^{2K} - e^{-2K})\right]^{\frac{1}{2}} = e^K \pm (e^{-2K})^{\frac{1}{2}} = e^K \pm e^{-K}$$

$$\therefore \boxed{\begin{aligned} \lambda_1(H=0) &= 2\cosh K \\ \lambda_2(H=0) &= 2\,\mathrm{senh}\,K \end{aligned}}$$

→ Como $\lambda_1 > \lambda_2$, escrevemos: $Z_N = \mathrm{tr}\,\bar{D}^N = \lambda_1^N + \lambda_2^N = \lambda_1^N\left[1 + \left(\frac{\lambda_2}{\lambda_1}\right)^N\right]$

↳ No limite $N \to \infty$: $\boxed{\lim_{N\to\infty} Z_N = \lambda_1^N}$

→ $\beta g(T, H=0) = \frac{1}{N}\beta G = -\frac{1}{N}\ln Z_N = -\ln\lambda_1$

$\therefore \boxed{g(T, H=0) = -\frac{1}{\beta}\ln\lambda_1}$

→ Caso geral: $\boxed{g(T,H) = -\frac{1}{\beta}\ln\left\{e^{\beta J}\cosh(\beta H) + \left[e^{2\beta J}\cosh^2(\beta H) - 2\,\mathrm{senh}(2\beta J)\right]^{\frac{1}{2}}\right\}}$

→ Magnetização por partícula:

$$m = -\left.\frac{\partial g}{\partial H}\right|_T = \operatorname{senh}(\beta H)\left[\operatorname{senh}^2(\beta H) + e^{-4\beta J}\right]^{-\frac{1}{2}}$$

→ Observamos que $H \to 0 \Rightarrow m \to 0$: sem transição de fase

$H \neq 0$ quebra a simetria e dá alinhamento preferencial para os spins

→ Fazendo também $T \to 0$, o resultado dependerá da ordem: 1º: $T \to 0$, 2º: $H \to 0$ ou 1º: $H \to 0$, 2º: $T \to 0$

* Não há transição de fase porque em modelos 1D a entropia "vence" a energia na minimização de F; apenas existe fase ferromag. para $T = 0$

* No modelo 2D, existe transição de fase para $T = T_c$

→ $dg = -s\,dT - m\,dH$

→ Calor específico: $c_{H=0} = \frac{J^2}{k_B T^2} \operatorname{sech}^2\left(\frac{J^2}{k_B T}\right)$

→ Função de correlação: $\boxed{\langle \sigma_k \sigma_\ell \rangle = e^{-\frac{r}{\xi}}}$, $r = |\ell - k|$

ξ: comprimento de correlação: $\boxed{\xi = \frac{1}{|\ln|-\tanh \beta J||}}$

determina o quão longe se propaga a influência dos spins

↳ $T \to 0 \Rightarrow \beta \to \infty \Rightarrow \xi \to \infty$

$\therefore \boxed{\langle \sigma_k \sigma_\ell \rangle (T \to 0) \to 1}$

estado fundamental → menor energia

⇒ spins alinhados

↳ Para $d > 1$: $\langle \sigma_k \sigma_\ell \rangle (T = T_c) \sim \frac{1}{r^{d-2+\eta}}$ → expoente crítico (simetrias)

22/07/24

Aproximação de Campo Médio

→ Método aproximado para encontrar quantidades de interesse sem resolver completamente a função de partição

→ $g(T,H,m) = \frac{1}{N}(U - TS)$

→ $\mathcal{H} = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j - H \sum_i \sigma_i$

↳ soma sobre primeiros vizinhos → dimensionalidade do espaço determina quantos "primeiros vizinhos" existem } 2d primeiros vizinhos

→ Energia interna: $U = \langle \mathcal{H} \rangle = -J \sum_{ij} \langle \sigma_i \sigma_j \rangle - H \sum_i \langle \sigma_i \rangle$

↳ C.C.P.: $\langle \sigma_i \rangle = m \quad \forall\, i \in \{1, \dots, N\}$

↳ $\langle \sigma_i \sigma_j \rangle$ → correlação entre primeiros vizinhos → $\langle \sigma_i \sigma_j \rangle = \langle \sigma_1 \sigma_2 \rangle$ ↙ qualquer par de 1º viz.

→ $u = \frac{\langle \mathcal{H} \rangle}{N} = -J \frac{2d}{2} \langle \sigma_1 \sigma_2 \rangle - Hm$ → $u = -Jd \langle \sigma_1 \sigma_2 \rangle - Hm$

↗ vizinhos

↳ termos repetidos na soma

Aproximação de Bragg-Williams

→ Para resolver, fazemos a aproximação de que os spins não estão correlacionados: $\langle \sigma_i \sigma_j \rangle = \underbrace{\langle \sigma_i \rangle \langle \sigma_j \rangle}_{m^2}$ ⇒ $\boxed{u = -Jdm^2 - Hm}$

→ $N = N_+ + N_-$ → $m = \frac{N_+ - N_-}{N}$

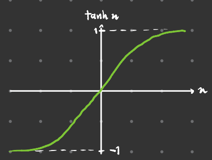
→ $S = k_B \ln\left(\frac{N!}{N_+!\, N_-!}\right) = k_B \ln\left[\frac{N!}{\left(\frac{N+Nm}{2}\right)!\left(\frac{N-Nm}{2}\right)!}\right] = \dots$

$\therefore \boxed{g(T,H,m) = -Jdm^2 - Hm - \frac{\ln 2}{\beta} + \frac{1}{2\beta}\left[(1+m)\ln(1+m) + (1-m)\ln(1-m)\right]}$

→ Estado de equilíbrio: $\frac{\partial g}{\partial m} = 0$

$-2dJm - H + \frac{1}{2\beta} \ln\left[\frac{(1+m)}{(1-m)}\right] = 0$

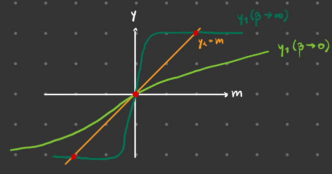
J = 0: recuperamos o paramagneto ← $m = \tanh(2dJ\beta m + \beta H)$ → equação transcendental



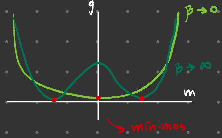
↳ "Campo médio": $H' = 2dJm$ → "campo" gerado pela interação entre vizinhos

→ Fazendo $H = 0$ → $m = \tanh(2dJ\beta m)$

Análise gráfica: $y_1 = \tanh(2dJ\beta m)$, $y_2 = m$ → encontramos o ponto onde $y_1 = y_2$



$\begin{cases} \beta \to 0 \Rightarrow T \to \infty: \; m = 0 \\ \beta \to \infty \Rightarrow T \to 0: \; m = \pm y \quad (m = 0 \text{ se torna um máximo}) \end{cases}$



momento em que mínimo se torna máximo

$y_1'(m) = 2d\beta J\, \mathrm{sech}^2(2d\beta J m)$

$\left.\begin{cases} y_1'(m=0) = 2d\beta J \\ y_2'(m=0) = 1 \end{cases}\right\}$ $2d\beta J = 1$

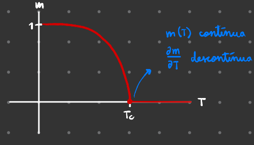
$\beta_c = \frac{1}{k_B T_c} = \frac{1}{2dJ}$

$\therefore \boxed{T_c = \frac{2dJ}{k_B}}$

→ $2dJ\beta = \tanh^{-1} m$ → 0 p/ m ≪ 1

$\frac{\beta}{\beta_c} m \approx m + \frac{1}{3}m^3 + \frac{1}{5}m^5$

$\frac{1}{3}m^2 = \left(\frac{\beta}{\beta_c} - 1\right) = \left(\frac{T_c}{T} - 1\right)$



→ Definimos: $t = \frac{T_c - T}{T} > 0$ p/ $T < T_c$ ⇒ $\boxed{m = (3t)^{\frac{1}{2}}}$ } Expoente "real" de t^α: $\alpha \approx \frac{1}{3}$

→ Susceptibilidade magnética: $\chi = \left.\frac{\partial m}{\partial H}\right|_{T,\, H\to 0}$

↳ Para $H \neq 0$: $m + \frac{1}{3}m^3 \approx \frac{\beta}{\beta_c} m + \beta H \quad \Big\downarrow \frac{\partial}{\partial m}$

$$1 + m^2 = \frac{\beta}{\beta_c} + \beta \left.\frac{\partial H}{\partial m}\right|_T \quad \frac{1}{\chi}$$

↳ $T > T_c$: $m = 0$

$$1 - \frac{\beta}{\beta_c} = \frac{\beta}{\chi_0}$$

$$\left(1 - \frac{T_c}{T}\right) = \frac{T - T_c}{T} \approx \frac{\beta_c}{\chi_0}$$

$$\chi_0 = \frac{\beta_c}{(-t)}$$ → χ_0 diverge para $t \to 0$

$$\boxed{\chi_0 = \frac{C_-}{(-t)^\gamma}} \begin{cases} C_- = \beta_c \\ \gamma = 1 \end{cases}$$

↳ $T < T_c$: $m = (3t)^{\frac{1}{2}}$

$$1 + 3t = \frac{T_c}{T} + \frac{\beta}{\chi_0}$$

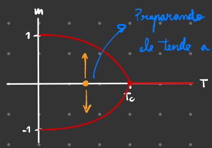
$$-t + 3t = \frac{\beta}{\chi_0}$$

$$2t = \frac{\beta}{\chi_0}$$

$$\chi_0 = \frac{\beta_c}{2t}$$

$$\boxed{\chi_0 = \frac{C_+}{t^\gamma}} \begin{cases} C_+ = \frac{\beta_c}{2} \\ \gamma = 1 \end{cases}$$

* Em ambos os casos χ_0 diverge perto de T_c, mas a "amplitude" da divergência é diferente → $\frac{C_+}{C_-} = \frac{1}{2}$



Preparando o sistema "no meio" das duas fases ele tende a uma coexistência de estados nas duas fases possíveis

↳ estado "homogêneo" é instável

* Expoente crítico depende, por exemplo, das simetrias do Hamiltoniano → propriedades globais do sistema

24/07/24

→ Na transição $T = T_c$:

↳ $m = \tanh(2dJ\beta m + \beta H) \Rightarrow m + \frac{1}{3}m^3 = \frac{\beta}{\beta_c} m + \beta H$

↳ $\beta = \beta_c$: $\cancel{m} + \frac{1}{3}m^3 = \cancel{m} + \beta_c H$

$$\boxed{m = (3\beta_c H)^{\frac{1}{3}}}$$

Desigualdade de Gibbs-Bogoliubov

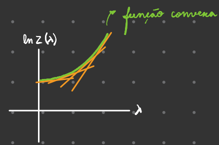
→ Maneira de aproximar a função de partição com um Hamiltoniano factível → ex.: $\mathcal{H}$ sem interação entre partículas

→ Seja: $\mathcal{H}(\lambda) = \mathcal{H}_0 + \lambda(\mathcal{H} - \mathcal{H}_0)$

↳ $\mathcal{H}(0) = \mathcal{H}_0$

↳ $\mathcal{H}(1) = \mathcal{H}$

→ Campo externo "efetivo"



→ $Z(\lambda) = \mathrm{Tr}\, e^{-\beta[\mathcal{H}_0 + \lambda(\mathcal{H} - \mathcal{H}_0)]}$

→ $\dfrac{\partial \ln Z(\lambda)}{\partial \lambda} = \dfrac{1}{Z(\lambda)} \dfrac{\partial Z(\lambda)}{\partial \lambda} = -\beta \langle \mathcal{H} - \mathcal{H}_0 \rangle$

→ $\dfrac{\partial^2 \ln Z(\lambda)}{\partial \lambda^2} = -\beta^2 \langle \mathcal{H} - \mathcal{H}_0 \rangle^2 + \beta^2 \langle (\mathcal{H} - \mathcal{H}_0)^2 \rangle$

→ Tangente em $\lambda = 0$: $y(\lambda) = \ln Z(0) + \lambda \left.\dfrac{\partial \ln Z(\lambda)}{\partial \lambda}\right|_{\lambda=0}$ ⇒ $\ln Z(\lambda) \geq \ln Z(0) + \lambda \left(\underbrace{\dfrac{\partial}{\partial \lambda} \ln Z(\lambda)}_{-\beta\langle \mathcal{H} - \mathcal{H}_0\rangle|_{\lambda=0}}\right)\Big|_{\lambda=0}$

→ Válido para λ arbitrário → fazemos $\lambda = 1$: $\ln Z(1) \geq \ln Z(0) - \beta \langle \mathcal{H} - \mathcal{H}_0 \rangle|_{\lambda=0}$

→ Mas $Z = e^{-\beta G}$: $-\beta G \geq -\beta G_0 - \beta \langle \mathcal{H} - \mathcal{H}_0 \rangle|_{\lambda=0}$

$\therefore \boxed{G \leq G_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle|_{\lambda=0}}$ → limite superior para a energia

* Com o modelo de Ising:

→ $\mathcal{H} = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j - H \sum \sigma_i$

→ $\mathcal{H}_0 = -\eta \sum \sigma_i$ → facilmente solúvel

↗ parâmetro variacional (η)

→ $e^{-\beta G_0} = Z_0 = \mathrm{Tr}\, e^{-\beta \mathcal{H}_0} = (2 \cosh \beta \eta)^N$

→ $\langle \mathcal{H} - \mathcal{H}_0 \rangle_0 = \langle \mathcal{H} - \mathcal{H}_0 \rangle|_{\lambda=0} = \langle (-J \sum_{\langle ij \rangle} \sigma_i \sigma_j - H \sum_i \sigma_i - \eta \sum_i \sigma_i) \rangle_0$ → média com respeito a $\mathcal{H}_0$

↳ $\langle \sigma_i \rangle_0 = \dfrac{e^{\beta\eta} - e^{-\beta\eta}}{e^{\beta\eta} + e^{-\beta\eta}} = \tanh(\beta\eta)$

↳ $\langle \sigma_i \sigma_j \rangle_0 = \langle \sigma_i \rangle_0 \langle \sigma_j \rangle_0 = \tanh^2(\beta\eta)$ → sem correlação (não há interação)

$\therefore \langle \mathcal{H} - \mathcal{H}_0 \rangle_0 = -J d N \tanh^2(\beta\eta) - H N \tanh(\beta\eta) + \eta N \tanh(\beta\eta)$

→ $\Phi_0 = N \left[-\frac{1}{\beta} \ln Z - \frac{1}{\beta} \ln \cosh(\beta\eta) - J d \tanh^2(\beta\eta) + (\eta - H) \tanh(\beta\eta) \right]$

↳ Minimização do parâmetro: $\dfrac{\partial \Phi_0}{\partial \eta} = 0$ → η é um "campo externo" que considera o efeito da interação

→ $m = \langle \sigma_i \rangle_0 = \tanh(\beta\eta) = \dfrac{e^{\beta\eta} - e^{-\beta\eta}}{e^{\beta\eta} + e^{-\beta\eta}} \times \dfrac{e^{-\beta\eta}}{e^{-\beta\eta}} = \dfrac{1 - e^{-2\beta\eta}}{1 + e^{-2\beta\eta}}$ ⇒ $\beta\eta = -\frac{1}{2} \ln\left(\frac{1-m}{1+m}\right)$

→ $\ln \cosh(\beta\eta) = -\frac{1}{2} \ln(1-m) - \frac{1}{2} \ln(1+m)$

$\therefore \boxed{\Phi_0 = -J d m^2 - H m + \frac{1}{2\beta} \left[(1-m) \ln(1-m) + (1+m) \ln(1+m) \right]}$

→ Logo, minimizar com relação a η corresponde a minimizar em relação a m, e obtemos o resultado anterior: $\boxed{m = \tanh(2 J d \beta m + \beta H)}$

melhor limite superior