Mecânica Estatística

18/03/24

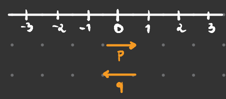
→ Resolução de problemas: problema "dual"

* Permutações: $\begin{cases} \text{Elementos distintos: } \boxed{P = n!} \ (\text{nº de perm.}) \\ \text{Elementos repetidos: } \boxed{P = \dfrac{n!}{\Sigma(k_i!)}} \end{cases}$ k_i → nº de elementos idênticos do i-ésimo conj.

* Combinações: $\boxed{C = \binom{n}{m} = \dfrac{n!}{m!\,(n-m)!}}$

Problema do caminho aleatório

→ $P_N(m) = ?$ → probabilidade de que o caminhante pare na posição m após N passos → difusão



↳ $p + q = 1$

↳ Sequência: $\left.\begin{matrix} \overset{p}{\rightarrow} \overset{p}{\rightarrow} \overset{p}{\rightarrow} \overset{q}{\leftarrow} \overset{q}{\leftarrow} \\ \overset{p}{\rightarrow} \overset{q}{\leftarrow} \overset{p}{\rightarrow} \overset{p}{\rightarrow} \overset{q}{\leftarrow} \end{matrix}\right\} P = p^3 q^2$

↳ $\rightarrow : N_1, \quad \leftarrow : N_2$

↳ N passos totais: $N = N_1 + N_2$

Prob. de que em N passos, N_1 sejam p/ a direita: $\boxed{W_N(N_1) = \dfrac{N!}{N_1!\,N_2!} p^{N_1} q^{N_2} = \dfrac{N!}{N_1!\,(N-N_1)!} p^{N_1} q^{(N-N_1)}}$

$$\boxed{1 = \sum_{N_1=0}^{N} W_N(N_1) = \sum_{N_1=0}^{N} \binom{N}{N_1} p^{N_1} q^{N-N_1} = (p+q)^N \Rightarrow p+q = 1}$$

↳ expansão binomial: $(x+y)^N = \sum_{m=0}^{N} \binom{N}{m} x^m y^{N-m}$

{ Adicionar prob. r de que caminhante permaneça no lugar: $p + q + r = 1$
etc.

↳ Posição m: $\left.\begin{matrix} m = N_1 - N_2 \\ N = N_1 + N_2 \end{matrix}\right\}$ $\boxed{\begin{matrix} N_1 = \dfrac{m+N}{2} \\ N_2 = \dfrac{N-m}{2} \end{matrix}}$

$$\boxed{P_N(m) = \frac{N!}{\left(\frac{m+N}{2}\right)!\left(\frac{N-m}{2}\right)!} p^{\frac{N+m}{2}} q^{\frac{N-m}{2}}}$$

※20/03/24

Equação de difusão

cadeia de Markov

$$\rightarrow P_{N+1}(m) = \overset{\text{p/ direita}}{p}\, \underbrace{P_N(m-1)}_{\text{pos. anterior}} + \overset{\text{p/ esquerda}}{q}\, \underbrace{P_N(m+1)}_{\text{pos. posterior}} \rightarrow \text{eq. diferenças}$$

$$\begin{cases} \text{Posição: } & x = m\ell \\ \text{Tempo entre passos: } & t = N\tau \end{cases} \Rightarrow P_N(m) \rightarrow P(t,x)$$

→ Expressão para a distribuição contínua: $P(t+\tau, x) = pP(t, x-\ell) + qP(t, x+\ell)$

↳ $\tau \to 0$: $P(t+\tau, x) = P(t,x) + \frac{\partial P}{\partial t}\tau + O(\tau^2)$

↳ $\ell \to 0$: $P(t, x\pm\ell) = P(t,x) \pm \frac{\partial P}{\partial x}\ell + \frac{1}{2}\frac{\partial^2 P}{\partial x^2}\ell^2 + O(\ell^3)$

$$\boxed{P(t,x) + \frac{\partial P}{\partial t}\tau = p\left[P(t,x) - \frac{\partial P}{\partial x}\ell + \frac{1}{2}\frac{\partial^2 P}{\partial x^2}\ell^2\right] + q\left[P(t,x) + \frac{\partial P}{\partial x}\ell + \frac{1}{2}\frac{\partial^2 P}{\partial x^2}\ell^2\right]}$$

isotrópico

$$\rightarrow p = q = \frac{1}{2}: \quad P(t,x) + \frac{\partial P}{\partial t}\tau = \frac{1}{2}\left[P(t,x) - \frac{\partial P}{\partial x}\ell + \frac{1}{2}\frac{\partial^2 P}{\partial x^2}\ell^2\right] + \frac{1}{2}\left[P(t,x) + \frac{\partial P}{\partial x}\ell + \frac{1}{2}\frac{\partial^2 P}{\partial x^2}\ell^2\right]$$

$$\cancel{P(t,x)} + \frac{\partial P}{\partial t}\tau = \cancel{P(t,x)} + \frac{1}{2}\frac{\partial^2 P}{\partial x^2}\ell^2$$

$$\frac{\partial P}{\partial t} = \underbrace{\boxed{\frac{\ell^2}{2\tau}}}_{\text{coef. difusão } D}\frac{\partial^2 P}{\partial x^2} \rightarrow \boxed{\frac{\partial P}{\partial t} = D\frac{\partial^2 P}{\partial x^2}}$$

$$\begin{cases} \text{o limite } \ell \to 0,\ \tau \to 0 \\ \text{é tal que } \frac{\ell^2}{2\tau} = D = \text{cte} \end{cases}$$

* Mais dimensões: $p = \frac{1}{2d}$ → dimensões do espaço

↳ prob. do passo

$$P(t+\tau, \vec{x}) = \frac{1}{2d}\left[P(t, x-\ell, y, z) + P(t, x+\ell, y, z) + P(t, x, y-\ell, z) + P(t, x, y+\ell, z) + P(t, x, y, z-\ell) + P(t, x, y, z+\ell)\right]$$

$$P(t,\vec{x}) + \frac{\partial P}{\partial t}\tau = \frac{1}{2d}\left[P(t, x-\ell, y, z) + P(t, x+\ell, y, z) + P(t, x, y-\ell, z) + P(t, x, y+\ell, z) + P(t, x, y, z-\ell) + P(t, x, y, z+\ell)\right]$$

$$\vdots$$

$$\boxed{\frac{\partial P}{\partial t} = \frac{\ell^2}{2d\tau}\nabla^2 P(t,x)} \qquad D = \frac{\ell^2}{2d\tau} \qquad P(t=0, x) = \delta(x)$$

↳ Resolução

① Transf. de similaridade

semelhança

$$\rightarrow \frac{\partial P}{\partial t} = D\frac{\partial^2 P}{\partial x^2}, \quad D = \frac{\ell^2}{2\tau} \qquad \begin{cases} [P(t,x)] = \frac{1}{L} \\ [D] = \frac{L^2}{T} \end{cases}$$

→ densidade de probabilidade

$$\rightarrow [Dt] = L^2$$

$$[x] = L \rightarrow \left[\frac{x^2}{Dt}\right] = L^0 \Rightarrow \boxed{P(t,x) = \frac{1}{(Dt)^{\frac{1}{2}}} f\overbrace{\left(\frac{x^2}{Dt}\right)}^{\text{adimensional}}} \rightarrow \text{"Ansatz" da análise dimensional}$$

$$\rightarrow \left.\begin{matrix} P_1 \text{ dado}, & x = 2, & t = 4 \\ P_2 = ?, & x = 4, & t = 16 \end{matrix}\right\} \quad \frac{x^2}{Dt} = \frac{4}{4D} = \frac{1}{D} \qquad \left.\begin{matrix} P_1 = \frac{1}{(4D)^{\frac{1}{2}}} f\left(\frac{1}{D}\right) \\ P_2 = \frac{1}{(16D)^{\frac{1}{2}}} f\left(\frac{1}{D}\right) \end{matrix}\right\} \quad \boxed{\frac{P_2}{P_1} = \frac{1}{2}}$$

$$\rightarrow u = \frac{x^2}{Dt} \rightarrow P(t,x) = \frac{1}{(Dt)^{\frac{1}{2}}} f(u)$$

$$\left.\begin{matrix} \frac{\partial P}{\partial t} = \frac{1}{\sqrt{Dt}} f'(u)\left(-\frac{x^2}{Dt^2}\right) + \frac{1}{\sqrt{D}\,t^{3/2}}\left(-\frac{1}{2}\right) f(u) \\ \frac{\partial P}{\partial x} = \frac{1}{\sqrt{Dt}} f'(u)\frac{2x}{Dt} \\ \frac{\partial^2 P}{\partial x^2} = \frac{1}{\sqrt{Dt}}\left[f''(u)\left(\frac{2x}{Dt}\right)^2 + f'(u)\frac{2}{Dt}\right] \end{matrix}\right\}$$

$$4uf''(u) + 2f'(u) + uf'(u) + \frac{1}{2}f(u) = 0$$

Chute: $f(u) = e^{-au}$, $a = \frac{1}{4}$

$$\boxed{P(x,t) \propto \frac{1}{(Dt)^{\frac{1}{2}}} e^{-\frac{1}{4}\frac{x^2}{Dt}}} \rightarrow \text{Gaussiana}$$

$\rightarrow P(t,x) = (Dt)^{-\frac{1}{2}} f(u) \quad \Big| \quad u = \frac{x^2}{Dt} \rightarrow \frac{\partial u}{\partial t} = -\frac{x^2}{Dt^2}, \quad \frac{\partial u}{\partial x} = \frac{2x}{Dt}, \quad \frac{\partial^2 u}{\partial x^2} = \frac{2}{Dt}$

$\frac{\partial f}{\partial t} = \frac{\partial f}{\partial u}\frac{\partial u}{\partial t}$

$\rightarrow \frac{\partial P}{\partial t} = -\frac{1}{2} D^{-\frac{1}{2}} t^{-\frac{3}{2}} f(u) + (Dt)^{-\frac{1}{2}} f'(u) \left(-\frac{x^2}{Dt^2}\right)$

$\rightarrow \frac{\partial P}{\partial x} = (Dt)^{-\frac{1}{2}} f'(u) \left(\frac{2x}{Dt}\right), \quad \frac{\partial P}{\partial x} = (Dt)^{-\frac{1}{2}} f''(u) \left(\frac{2x}{Dt}\right)^2 + (Dt)^{-\frac{1}{2}} f'(u) \left(\frac{2}{Dt}\right)$

$\rightarrow \frac{\partial P}{\partial t} = D \frac{\partial^2 P}{\partial x^2} \Rightarrow -\frac{1}{2} D^{-\frac{1}{2}} t^{-\cancel{\frac{3}{2}}\ t^{-1}} f(u) + D^{-\frac{1}{2}} \cancel{t^{-\frac{1}{2}}} f'(u) \left(-\frac{x^2}{Dt^2}\right) = \cancel{D^{\frac{1}{2}}} \cancel{t^{-\frac{1}{2}}} f''(u) \left(\frac{2x}{Dt}\right)^2 + \cancel{D^{\frac{1}{2}}} \cancel{t^{-\frac{1}{2}}} f'(u) \left(\frac{2}{Dt}\right)$

$D^{-1}\left[-\frac{1}{2} \overset{1/t}{t^{-1}} f(u) + f'(u) \overset{\frac{1}{t}}{\left(-\frac{x^2}{Dt^2}\right)}\right] = f''(u) \overset{1/t}{\left(\frac{2x}{Dt}\right)^2} + f'(u) \overset{1/t}{\left(\frac{2}{Dt}\right)}$

$-\frac{x^2}{Dt} \cdot \frac{1}{t} = -\frac{u}{t} \qquad \frac{4x^2}{D^2t^2} = \frac{4}{Dt}\frac{x^2}{Dt} = \frac{4}{Dt} u$

$\cancel{D^{-1}}\left[-\frac{1}{2} f(u) - u f'(u)\right] = \frac{4}{\cancel{D}} u f''(u) + \frac{2}{\cancel{D}} f'(u)$

$\therefore 4u f''(u) + 2f'(u) + u f'(u) + \frac{1}{2} f(u) = 0$

$\rightarrow f(u) = Ae^{-\alpha u} \rightarrow f'(u) = -\alpha A e^{-\alpha u} \rightarrow f''(u) = \alpha^2 A e^{-\alpha u}$

$4u\alpha^2 A e^{-\alpha u} - 2\alpha A e^{-\alpha u} - u\alpha A e^{-\alpha u} + \frac{1}{2} A e^{-\alpha u} = 0$

$\alpha \neq 0 \quad \underbrace{(4\alpha^2 - \alpha)}_{4\alpha = 1 \Rightarrow \alpha = \frac{1}{4}} u + \underbrace{\left(\frac{1}{2} - 2\alpha\right)}_{2\alpha = \frac{1}{2} \Rightarrow \alpha = \frac{1}{4}} = 0$

$\therefore \boxed{f(u) = Ae^{-\frac{1}{4}u}}$

$\rightarrow$ Normalização: $1 = \int_{-\infty}^{+\infty} P(x,t)\,dx \rightarrow A = \frac{1}{\sqrt{4\pi}}$ $\qquad \boxed{P(x,t) = \frac{1}{\sqrt{4\pi Dt}} e^{-\frac{1}{4}\frac{x^2}{Dt}}}$

$P(x,t) = A(Dt)^{-\frac{1}{2}} e^{-\frac{1}{4}\frac{x^2}{Dt}}$

$\int_{-\infty}^{+\infty} e^{-a(x+b)^2} dx = \sqrt{\frac{\pi}{a}}$

$1 = \int_{-\infty}^{+\infty} A(Dt)^{-\frac{1}{2}} e^{-\frac{1}{4}\frac{x^2}{Dt}} dx = A(Dt)^{-\frac{1}{2}} \int_{-\infty}^{+\infty} e^{-\frac{1}{4}\frac{x^2}{Dt}} dx = A(Dt)^{-\frac{1}{2}} (4Dt\pi)^{\frac{1}{2}} = A(4\pi)^{\frac{1}{2}} \Rightarrow A = \frac{1}{\sqrt{4\pi}}$

* Em termos de densidade de caminhantes: $\begin{cases} \frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2} \\ \rho(t=0,x) = N\delta(x) \end{cases}$

$\rightarrow$ Eq. continuidade: $\frac{\partial \rho}{\partial t} = -\vec{\nabla} \cdot \vec{J}$

↳ na difusão:  $\vec{J} = -D\nabla\rho \rightarrow \frac{\partial \rho}{\partial t} = D\nabla^2\rho$

※ 22/03/24

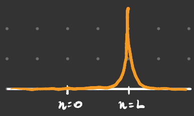
(1)

$\rightarrow \frac{\partial \rho}{\partial t} = D\nabla^2 \rho$

$\rightarrow \vec{J} = -D\nabla\rho$

$\frac{\partial \rho}{\partial t} = -\nabla \cdot \vec{J}$ → condições de contorno para sistemas mais complicados

$\rightarrow \frac{\partial \rho}{\partial t} = D\frac{\partial^2 \rho}{\partial x^2}$



→ sistema aberto

$\rightarrow \rho(x, t=0) = N\delta(x-L)$

② Transf. Fourier: $\rho(x,t) = \int_{-\infty}^{+\infty} \tilde{\rho}(k,t)\, e^{-ikx} \frac{dk}{2\pi}$ (*)

$\rightarrow N\delta(x-L) = \int_{-\infty}^{+\infty} \tilde{\rho}(k,0)\, e^{-ikx}\frac{dk}{2\pi}$ → c.i.

$\rightarrow \delta(x) = \int_{-\infty}^{+\infty} e^{-ikx}\frac{dk}{2\pi} \rightarrow \delta(x-L) = \int_{-\infty}^{+\infty} e^{-ik(x-L)}\frac{dk}{2\pi}$

$\hookrightarrow \int_{-\infty}^{+\infty} N e^{-ik(x-L)}\frac{dk}{2\pi} = \int_{-\infty}^{+\infty} N e^{ikL} e^{-ikx}\frac{dk}{2\pi} = N\delta(x-L)$

$\therefore \boxed{\tilde{\rho}(k,0) = Ne^{ikL}}$

Fazer $\frac{\partial^2 \rho}{\partial x^2} \rightarrow \frac{\partial^2}{\partial x^2}\left[e^{ikx}\right] = -k^2 e^{ikx}$

↓ (*) em (1):

$\rightarrow \int_{-\infty}^{+\infty} \frac{\partial\tilde{\rho}}{\partial t}(k,t)\, e^{-ikx}\frac{dk}{2\pi} = D\int_{-\infty}^{+\infty} -k^2\tilde{\rho}(k,t)\, e^{ikx}\frac{dk}{2\pi} \Rightarrow \int_{-\infty}^{+\infty}\left(\frac{\partial\tilde{\rho}}{\partial t} + Dk^2\tilde{\rho}\right) e^{-ikx}\frac{dk}{2\pi} = 0 \quad \forall x \in \mathbb{R}$

em princípio $A = A(k)$ $\therefore \boxed{\frac{\partial\tilde{\rho}}{\partial t} = -Dk\tilde{\rho}}$ parâmetro

eq. continuidade

$\rightarrow \frac{d\tilde{\rho}}{\tilde{\rho}} = -Dk^2 dt \Rightarrow \boxed{\tilde{\rho} = A(k)e^{-Dk^2 t}}$

$\rightarrow \tilde{\rho}(k,t=0) = A(k) = Ne^{ikL} \Rightarrow A(k) = Ne^{ikL}$

$\tilde{\rho}(k,0)$ $\therefore \boxed{\tilde{\rho}(k,t) = Ne^{ikL}e^{-Dk^2 t}}$

transformada

$\rightarrow \rho(x,t) = N\int_{-\infty}^{+\infty} e^{-Dk^2 t + ikL} e^{-ikx}\frac{dk}{2\pi}$

$\rho(x,t) = N\int_{-\infty}^{+\infty} e^{-Dk^2 t + ik(L-x)}\frac{dk}{2\pi}$

$u = ak - \frac{b}{2a} \rightarrow k = \pm\infty \rightarrow u = \pm\infty$

$du = a\,dk$

→ Integral gaussiana: $I = \int_{-\infty}^{+\infty} e^{-a^2k^2 + bk}\, dk = ?$

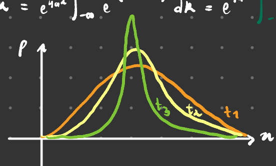
$-a^2k^2 + bk = -\left[\left(ak - \frac{b}{2a}\right)^2 - \frac{b^2}{4a^2}\right] \Rightarrow I = \int_{-\infty}^{+\infty} e^{-\left(ak-\frac{b}{2a}\right)^2} e^{\frac{b^2}{4a^2}}\, dk = e^{\frac{b^2}{4a^2}}\int_{-\infty}^{+\infty} e^{-\left(ak-\frac{b}{2a}\right)^2} dk = e^{\frac{b^2}{4a^2}}\int_{-\infty}^{+\infty} e^{-u^2}\frac{du}{a} = \frac{1}{a}e^{\frac{b^2}{4a^2}}\sqrt{\pi}$

$\sqrt{\pi}$

$\hookrightarrow a^2 = Dt,\ b = i(L-x) \Rightarrow \rho(x,t) = \frac{N}{2\pi}\frac{\sqrt{\pi}}{\sqrt{Dt}} e^{-\frac{(L-x)^2}{4Dt}}$

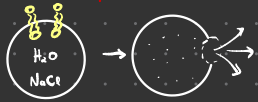
$\therefore \boxed{\rho(x,t) = \frac{N}{(4\pi Dt)^{\frac{1}{2}}} e^{-\frac{(L-x)^2}{4Dt}}}$

$P(x,t) = \frac{\rho(x,t)}{N}$



$\rho(x, t\rightarrow\infty) \rightarrow \delta(x)$

→ Exemplo: lipossoma



tempo para perder conteúdo?

↳ Versão simplificada: 1D

$$\begin{cases} \frac{\partial \rho}{\partial t} = D\frac{\partial^2 \rho}{\partial x^2} \\ \frac{\partial \rho}{\partial x}\Big|_{x=0} = 0 \quad (*) \\ \rho(x=L,t) = 0 \\ \rho(x,t=0) = \rho_0 \end{cases}$$

(*) densidade máxima (muda com o tempo)

ρ_0 → não homogêneo

→ Troca de variáveis: $\Delta(x,t) \equiv \rho_0 - \rho(x,t)$

$$\begin{cases} \frac{\partial \Delta}{\partial t} = D\frac{\partial^2 \Delta}{\partial x^2} \\ \frac{\partial \Delta}{\partial x}\Big|_{x=0} = 0 \\ \Delta(x=L,t) = \rho_0 \\ \Delta(x,t=0) = 0 \end{cases}$$

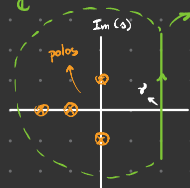
troca de variável

Tempo para ficar em equilíbrio?

problema "dual"

③ Transf. Laplace: $\mathcal{L}[f(t)] = F(s) = \int_0^\infty f(t)e^{-st}\,dt$ → inverter transformada → $\mathbb{C}$

$\mathcal{L}[f'(t)] = s\mathcal{L}[f(t)] - f(0)$



→ teorema dos resíduos: $\oint f(s)\,ds = \frac{1}{2\pi i}\sum \text{Res.}$

→ Integral de inversão de Mellin: $f(t) = \frac{1}{2\pi i}\int_{\gamma - i\infty}^{\gamma + i\infty} e^{ts} F(s)\,ds$

※ 25/03/24

→ Em Δ: $\frac{\partial \Delta(x,t)}{\partial t} = D\frac{\partial^2 \Delta(x,t)}{\partial x^2}$

→ $\mathcal{L}\left[\frac{\partial \Delta}{\partial t}\right] = \mathcal{L}\left[D\frac{\partial^2 \Delta}{\partial x^2}\right] \Rightarrow s\tilde{\Delta}(x,s) - \cancel{\Delta(x,0)}^{\,0} = D\frac{\partial^2 \tilde{\Delta}(x,s)}{\partial x^2} \Rightarrow D\frac{\partial^2 \tilde{\Delta}}{\partial x^2} = s\tilde{\Delta}$

ℒ em t   ℒ em t   cte   parâmetro

$\frac{\partial^2 \tilde{\Delta}}{\partial x^2} - \frac{s}{D}\tilde{\Delta} = 0 \Rightarrow \tilde{\Delta} = C\cosh\left(\sqrt{\frac{s}{D}}\,x\right) + D\,\mathrm{senh}\left(\sqrt{\frac{s}{D}}\,x\right)$

$$\boxed{\tilde{\Delta}(x,s) = A(s)e^{kx} + B(s)e^{-kx}}$$

→ $\Delta(x=L,t) = \rho_0 \Rightarrow \mathcal{L}[\Delta(x=0,t)] = \int_0^\infty \rho_0 e^{-st}\,dt = \frac{\rho_0}{s}$ ($\frac{1}{s}$)

→ $\frac{\partial \Delta}{\partial x}\Big|_{x=0} = 0 \Rightarrow \frac{\partial \tilde{\Delta}}{\partial x}\Big|_{x=0} = 0$ ⇒ C.C.: $\begin{cases} \tilde{\Delta}(L,s) = \frac{\rho_0}{s} \\ \frac{\partial \tilde{\Delta}}{\partial x}\Big|_{x=0} = 0 \end{cases}$

→ $\frac{\partial \tilde{\Delta}}{\partial x} = Ak e^{kx} - Bk e^{-kx} \Rightarrow \frac{\partial \tilde{\Delta}}{\partial x}\Big|_{x=0} = Ak - Bk = 0 \Rightarrow A = B$

→ $\tilde{\Delta}(L,s) = Ae^{kL} + Be^{-kL} = A(e^{kL} + e^{-kL}) = \frac{\rho_0}{s} \Rightarrow 2A\left[\frac{e^{kL}+e^{-kL}}{2}\right] = \frac{\rho_0}{s} \Rightarrow 2A\cosh(kL) = \frac{\rho_0}{s}$

→ $A(s) = \frac{\rho_0}{2s\cosh(kL)}$, $k = \sqrt{\frac{s}{D}}$

$$\therefore \boxed{\tilde{\Delta}(x,s) = \frac{\rho_0\cosh\left(\sqrt{\frac{s}{D}}\,x\right)}{s\cosh\left(\sqrt{\frac{s}{D}}\,L\right)}}$$

→ Singularidades:

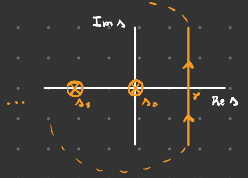
↳ $s = 0$: polo simples

↳ $\cosh(kL)$ → $k = i\omega$: $\cosh(i\omega L) = \cos(\omega L) = 0$ → $\omega_m L = \frac{m\pi}{2}$, m ímpar

$k_m^2 = -\omega_m^2 = -\frac{m^2\pi^2}{4L^2} = \frac{s_m}{D} \Rightarrow s_m = -\frac{m^2\pi^2 D}{4L^2}$ → polos simples

→ Inversão: $\Delta(t) = \frac{1}{2\pi i}\int_{\gamma - i\infty}^{\gamma + i\infty} \tilde{\Delta}(s)\, e^{ts}\, ds$

↳ comportamento temporal



$s_0 = 0$

$s_1 = -\frac{\pi^2 D}{4L^2}$

$s_2 = -\frac{9\pi^2 D}{4L^2}$

$\gamma > 0 \in \mathbb{R}$

$\cosh(ix) = \cos x$

$\operatorname{senh}(ix) = i \operatorname{sen} x$

↳ T. Resíduos: $\oint f(z)\, dz = 2\pi i \sum \text{Res}$

↳ $\text{Res}(s_m) = \lim_{s \to s_m} (s - s_m)\, \tilde{\Delta}(x, s)$ → polo simples

comportamento espacial

→ $\text{Res}(s_0) = \lim_{s \to 0} \cancel{(s-0)} \frac{p_0 \cosh\left[\sqrt{\frac{s}{D}}\, x\right]}{\cancel{s} \cosh\left[\sqrt{\frac{s}{D}}\, L\right]} e^{ts} = p_0 \cdot \frac{1}{1} = p_0$ ← $s \to 0 \Leftrightarrow t \to \infty$

→ $f(s) = \frac{g(s)}{h(s)} \Rightarrow \text{Res}\, f_m = \frac{g(s)}{h'(s)}\Big|_{s = s_m}$ → $\tilde{\Delta}(x, s) = \frac{p_0 \cosh\left[\sqrt{\frac{s}{D}}\, x\right] e^{ts}}{s} \cdot \frac{1}{\cosh\left[\sqrt{\frac{s}{D}}\, L\right]}$

$g(s)$: não singular para s_m, $m > 0$

$h(s)$: singular para s_m, $m > 0$

→ $h'(s) = \sqrt{\frac{1}{D}}\, L\, \frac{1}{2} s^{-\frac{1}{2}} \operatorname{senh}\left[\sqrt{\frac{s}{D}}\, L\right]$

→ $\frac{g(s)}{h'(s)} = \frac{p_0 \cosh\left[\sqrt{\frac{s}{D}}\, x\right] e^{ts}}{s} \frac{1}{\frac{1}{2\sqrt{Ds}} L \operatorname{senh}\left[\sqrt{\frac{s}{D}}\, L\right]} = \sqrt{\frac{D}{s}} \cdot \frac{2 p_0 \cosh\left[\sqrt{\frac{s}{D}}\, x\right] e^{ts}}{L \operatorname{senh}\left[\sqrt{\frac{s}{D}}\, L\right]}$

→ $s_1 = -\frac{\pi^2 D}{4L^2} \Rightarrow \text{Res}(s_1) = \sqrt{\frac{\cancel{D}}{-\frac{\pi^2 \cancel{D}}{4L^2}}} \cdot \frac{2 p_0 \cosh\left[\sqrt{-\frac{\pi^2 \cancel{D}}{4L^2} \frac{1}{\cancel{D}}}\, x\right] e^{-\frac{\pi^2 D t}{4L^2}}}{L \operatorname{senh}\left[\sqrt{-\frac{\pi^2 \cancel{D}}{4L^2} \frac{1}{\cancel{D}}}\, L\right]} = \frac{2\cancel{L}}{i\pi} \cdot \frac{2 p_0 \cosh\left[i\left(\frac{\pi}{2L} x\right)\right] e^{-\frac{\pi^2 D t}{4L^2}}}{\cancel{L} \operatorname{senh}\left[i\left(\frac{\pi}{2\cancel{L}} \cancel{L}\right)\right]} = -\cancel{i}\, \frac{4 p_0}{\pi} \frac{\cos\left(\frac{\pi}{2L} x\right)}{\cancel{i} \operatorname{sen}\left(\frac{\pi}{2}\right)} e^{-\frac{\pi^2 D t}{4L^2}}$

$\therefore \boxed{\text{Res}(s_1) = -\frac{4 p_0}{\pi} \cos\left(\frac{\pi}{2L} x\right) e^{-\frac{t}{\tau_1}}}$

⋮

$\Delta(x,t) = \overset{s_0}{p_0} + A e^{t \overset{s_1}{s_1}} \cosh\sqrt{\frac{s_1}{D}}\, x = p_0 + A e^{-\frac{\pi^2 D}{4L^2} t} \cos\left(\frac{\pi}{2L} x\right)$

Extrapolar a física

$\tau \sim \frac{L^2}{D}$ $\begin{cases} [D] = \frac{L^2}{T} \\ [L] = L \\ [\tau] = T \end{cases}$

$\therefore \boxed{\Delta(x,t) = p_0 - \frac{4 p_0}{\pi} e^{-\frac{t}{\tau_1}} \cos\left(\frac{\pi}{2L} x\right) + B e^{-\frac{t}{\tau_2}} \cos\left(\frac{3\pi}{2L} x\right) + \dots}$, $\boxed{\tau_1 = \frac{4}{\pi^2} \frac{L^2}{D}}$

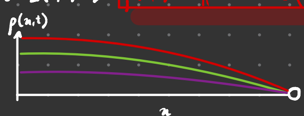
polo 0: $t \to \infty$

polo 1: $t > \tau_1$

polo 2: $t > \tau_2$

p/ determinar: resolver problema

→ $p(x,t) = p_0 - \Delta(x,t) \Rightarrow \boxed{p(x,t) = \frac{4 p_0}{\pi} e^{-\frac{t}{\tau_1}} \cos\left(\frac{\pi}{2L} x\right) + \dots}$

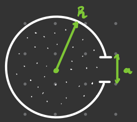


Perfil de densidade exponencial → onda estacionária

↳ Diminui amplitude com o tempo

↳ Mantém a forma

→ Lipossoma real



$a \ll R$ → nova quantidade → comprimento (2D, 3D)

$\tau \sim L^2/D$ → 1D

$N(t) \sim e^{-t/\tau}$ → tempos grandes

$$\boxed{\tau = \frac{R^2}{D} \underbrace{f\left(\frac{a}{R}\right)}_{\text{adimensional}}}$$

→ $\frac{\partial \rho}{\partial t} = D\nabla^2 \rho$

→ $\hat{n}\cdot\nabla\rho = 0$

→ $\rho(\vec{r})\big|_{\text{buraco}} = 0$

} c.c. mistas

↳ Ex.: $R = 200\,Å$, $a = 5\,Å$ $\xrightarrow{\text{escalar}}$ $R = 400\,Å$, $a = 10\,Å$

$$\tau_5 = \frac{200^2}{D} f\left(\frac{5}{200}\right)$$
$$\tau_{10} = \frac{400^2}{D} f\left(\frac{10}{400}\right) \Rightarrow \frac{\tau_{10}}{\tau_5} = \frac{400^2}{200^2} = 4 \; //$$

→ Tempo p/ cozinhar peru

↳ Ex.: $m = 2\,kg \longrightarrow t = 2h$

$m = 3\,kg \longrightarrow t = ?$

Eq. difusão do calor: $\frac{\partial T}{\partial t} = \underset{\text{cond. térmica}}{\kappa} \nabla^2 T$

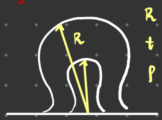
$[T] = K$, $\nabla^2 \to \frac{1}{L^2}$ → $\frac{K}{t} = [\kappa]\frac{K}{L^2} \Rightarrow [\kappa] = \frac{L^2}{t}$

$$\kappa \sim \frac{R^2}{t} \Rightarrow t_c \sim \frac{R^2}{\kappa}$$

Peru esférico: $\rho = \frac{M}{\frac{4}{3}\pi R^3} \Rightarrow R \sim M^{\frac{1}{3}}$, $\boxed{t_c \sim M^{\frac{2}{3}}}$

$$t_{c,2} = A M_2^{\frac{2}{3}} = A\,2^{\frac{2}{3}}$$
$$t_{c,3} = A M_3^{\frac{2}{3}} = A\,3^{\frac{2}{3}} \Rightarrow \boxed{\frac{t_{c,3}}{t_{c,2}} = \frac{3^{\frac{2}{3}}}{2^{\frac{2}{3}}} = \left(\frac{3}{2}\right)^{\frac{2}{3}}}$$

→ Energia de uma bomba



R

t

ρ

$[E] = kg\,\frac{m}{s^2}\,m$

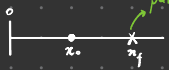
$[\rho] = kg/m^3$

$[Et^2] = kg\,m^2$

$\frac{[Et^2]}{[\rho]} = m^5 \Rightarrow \boxed{R \sim \left(\frac{Et^2}{\rho}\right)^{\frac{1}{5}}}$

※ 01/04/24

Tempo Médio de 1ª Passagem (MFPT)



partícula removida

$$P(x, t=0) = \delta(x - x_0)$$

→ Prob. de chegar em x pela primeira vez?

→ Ensemble de partículas

→ Em termos de densidade: $\frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2}$

$$\begin{cases} \rho(x, t=0) = N\delta(x - x_0) & \to \text{c.i.} \\ \left.\frac{\partial \rho}{\partial x}\right|_{x=0} = 0 & \to \text{parede} \\ \rho(x = x_f, t) = 0 & \to \text{pos. final} \end{cases} \Bigg\} \text{ c.c.}$$

Nº de partículas: $n(t) = \int_0^{x_f} \rho(x,t)\, dx$

$$dn(t) = dt \int_0^{x_f} \frac{\partial \rho}{\partial t}(x,t)\, dx \quad \leftarrow \rho(x, t+dt) - \rho(x,t)$$

→ $t \to \infty$: todas as partículas saem do sistema

→ $P(t)\,dt = \dfrac{\overset{dn < 0}{\ominus dn(t)}}{\underbrace{-\int_{t=0}^{\infty} dn}_{-N}} = \dfrac{-dn(t)}{N}$

→ τ: Tempo médio de 1ª passagem → $\boxed{\text{MFPT} \equiv \tau = \int_0^{\infty} t\, P(t)\, dt}$

funções bem comportadas
sem divergências

$$\tau = \int_0^{\infty} t P(t) dt = -\frac{1}{N} \int_0^{\infty} t\, dn(t) = -\frac{1}{N} \int_0^{\infty} t\, dt \int_0^{x_f} \frac{\partial \rho}{\partial t} dx = -\frac{1}{N} \int_0^{x_f} dx \int_0^{\infty} dt\, t \frac{\partial \rho}{\partial t}$$

$$\left.\begin{matrix} u = t & dv = \frac{\partial \rho}{\partial t} dt \\ du = dt & v = \rho(x,t) \end{matrix}\right\} \quad \int_0^{\infty} dt\, t \frac{\partial \rho}{\partial t} = \cancel{t\rho(x,t)}\Big|_0^{\infty} - \int_0^{\infty} \rho(x,t)\, dt = -\int_0^{\infty} \rho(x,t)\, dt$$

$\rho(x,t) \sim e^{-\alpha t} f(x)$: $\left. t\rho(x,t)\right|_{t=\infty} \to 0$

$$\therefore \boxed{\tau = \frac{1}{N} \int_0^{x_f} dx \int_0^{\infty} dt\, \rho(x,t)}$$

Caminhante Aleatório Generalizado

→ Tamanho de passo aleatório: $\int_{-\infty}^{\infty} w(s)\,ds$ → mesma distribuição para todos os passos

→ $p(x, N)$, $x = \sum_{i=1}^{N} s_i$ → passos (N passos)

→ $\int_{-\infty}^{\infty} p(x,N)\,dx = 1$ | $\int_{-\infty}^{\infty} w(s)\,ds = 1$

$w(s_1)$ $w(s_2)$ $w(s_3)$ $w(s_4)$ $w(s_N)$

⋮

$$p(x,N) = \int_{x \leq s_1 + s_2 + \cdots + s_N \leq x + dx} w(s_1)\,w(s_2)\cdots w(s_N)\,ds_1\,ds_2\cdots ds_N$$

→ vínculo

↳ caso contrário, integral seria 1

→ $p(x,N)dx = \int_{-\infty}^{\infty} ds_1 \ldots \int_{-\infty}^{\infty} ds_N\; w(s_1)\cdots w(s_N)\,\delta\Big(x - \sum_{i=1}^{N} s_i\Big)\,dx$ (vínculo)

→ $\delta(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-ikx}\,dk$

$$p(x,N)\,dx = \frac{dx}{2\pi}\int_{-\infty}^{\infty} ds_1 \cdots \int_{-\infty}^{\infty} ds_N\; w(s_1)\cdots w(s_N)\int_{-\infty}^{\infty} e^{-ik\left(x - \sum_{i=1}^{N} s_i\right)}\,dk$$

↳ $e^{-ikx}\,e^{iks_1}\,e^{iks_2}\cdots e^{iks_N}$

$\tilde{\omega}(k) = \int_{-\infty}^{\infty} ds_i\, w(s_i)\, e^{iks_i}$

1 p/ cada s_i

→ $p(x,N)\,dx = \frac{dx}{2\pi}\int_{-\infty}^{\infty} dk\, e^{-ikx}\left[\tilde{\omega}(k)\right]^N$ ⇒ $\boxed{p(x,N) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-ikx}\left[\tilde{\omega}(k)\right]^N dk}$, $\tilde{\omega}(k) = \int_{-\infty}^{\infty} e^{iks}\,w(s)\,ds$

※ 03/04/24

* Caminhante de passo ℓ: $\boxed{w(s) = p\,\delta(s-\ell) + q\,\delta(s+\ell)}$

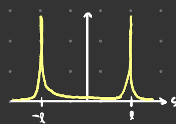
$w(s) = \int_{-\infty}^{\infty} e^{-iks}\,\tilde{\omega}(k)\,\frac{dk}{2\pi}$

$\tilde{\omega}(k) = \int_{-\infty}^{\infty} e^{iks}\,w(s)\,ds$

$= p\int_{-\infty}^{\infty} e^{iks}\,\delta(s-\ell)\,ds + q\int_{-\infty}^{\infty} e^{iks}\,\delta(s+\ell)\,ds$

$= pe^{ik\ell} + qe^{-ik\ell}$

$\boxed{\tilde{\omega}(k) = pe^{ik\ell} + qe^{-ik\ell}}$



↳ $\left[\tilde{\omega}(k)\right]^N = \left[pe^{ik\ell} + qe^{-ik\ell}\right]^N$

↳ $(x+y)^N = \sum_{n=0}^{N} \frac{N!}{n!(N-n)!}\,x^n y^{N-n} = \sum_{n=0}^{N}\binom{N}{n} x^n y^{N-m}$

$$\left[\tilde{\omega}(k)\right]^N = \sum_{n=0}^{N}\binom{N}{n}\left(pe^{ik\ell}\right)^n\left(qe^{-ik\ell}\right)^{N-n}$$

↳ $p(x,N) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk\, e^{-ikx}\left[\sum_{n=0}^{N}\binom{N}{n} p^n q^{N-n}\, e^{ik\ell n - ik\ell(N-n)}\right]$

$= \frac{1}{2\pi}\int_{-\infty}^{\infty} dk \sum_{n=0}^{N}\binom{N}{n} p^n q^{N-n}\, e^{-ik[x - 2n\ell + N\ell]}$

$\int_{-\infty}^{\infty} e^{-iky}\,\frac{dk}{2\pi} = \delta(y)$

$= \sum_{n=0}^{N}\binom{N}{n} p^n q^{N-n}\,\delta(x - 2n\ell + N\ell)$ ← densidade de probabilidade

↳ Somente são permitidas posições onde $x - 2n\ell + N\ell = 0$

↳ $x = 2n\ell - N\ell = n\ell - (N-n)\ell$

→ Probabilidade binomial: $P_N(m) = \int_{2n\ell - N\ell - \varepsilon}^{2n\ell - N\ell + \varepsilon} p(x,N)\,dx$

$= \int_{2n\ell - N\ell - \varepsilon}^{2n\ell - N\ell + \varepsilon} \sum_{n=0}^{N}\binom{N}{n} p^n q^{N-n}\,\delta(x - 2n\ell + N\ell)\,dx$

∴ $\boxed{P_N(n) = \frac{N!}{n!(N-n)!}\,p^n q^{N-n}}$

↳ Integral em x: para cada x, faz o somatório em n

↳ Apenas um valor de n que satisfaz $x = 2n\ell - N\ell$

↳ Para qualquer outro x, o somatório não satisfará o vínculo

↳ $\delta \to 0$

↳ Para o valor correto de x, apenas um valor de n satisfará o vínculo

↳ $\delta \to 1$, $\Sigma \to$ 1 termo

* Processo markoviano: $p(x, N+1) = \int_{-\infty}^{\infty} \underbrace{p(x-s, N)}_{\text{posição anterior}} \overbrace{w(s)}^{\text{passo do tamanho correto}} ds$ } convolução

$$\mathcal{F}\{p(x, N+1)\} = \mathcal{F}\{p(x,N)\}\, \mathcal{F}\{w(s)\}$$
$$\tilde{p}(k, N+1) = \tilde{p}(k,N)\, \tilde{w}(k)$$

↳ $p(x,0) = \delta(x) \Rightarrow \tilde{p}(k,0) = 1 \rightarrow \tilde{p}(k,0) = \int_{-\infty}^{\infty} e^{ikx}\delta(x)\,dx = e^{ik\cdot 0} = 1$ // $\Rightarrow \mathcal{F}\{\delta(x-a)\} = e^{ika}$

↳ Solução recursiva: $\tilde{p}(k,1) = \tilde{p}(k,0)\,\tilde{w}(k) = \tilde{w}(k)$

$$\tilde{p}(k,2) = \tilde{p}(k,1)\,\tilde{w}(k) = [\tilde{w}(k)]^2$$
$$\vdots$$
$$\boxed{\tilde{p}(k,N) = [\tilde{w}(k)]^N}$$

$$p(x,N) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{-ikx}\, \tilde{p}(k,N) \Rightarrow \boxed{p(x,N) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{-ikx} [\tilde{w}(k)]^N}$$

* Teorema do Limite Central:

↳ $p(x,N) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-ikx}[\tilde{w}(k)]^N dk$

↳ $N \rightarrow \infty$ → distribuição deixa de ser aleatória

↳ $x = \sum_{i=1}^{N} s_i$ ← $w(s)$

↳ $\tilde{w}(k) = \int_{-\infty}^{\infty} e^{iks} w(s)\, ds$ — e^{iks} oscilatório → valor máximo para $k=0$

$[\tilde{w}(k)]^N$ → função fica estreita (valores $<1 \rightarrow 0$)

Expansão em torno de $k=0$: $\tilde{w}(k) = \int_{-\infty}^{\infty} e^{iks} w(s)\, ds$

$$= \int_{-\infty}^{\infty} w(s) \left\{ 1 + iks - \frac{1}{2}k^2 s^2 + \cdots \right\} ds$$

(1, $ik\langle s\rangle$, $-\frac{1}{2}k^2\langle s^2\rangle$)

$\frac{d}{dx}\ln(1+x) = \frac{1}{1+x}$
$\frac{d^2}{dx^2}\ln(1+x) = -\frac{1}{(1+x)^2}$

$\ln(1+x) \approx \ln(1) + 1\cdot x - \frac{1}{2}\cdot x^2 \approx x - \frac{x^2}{2}$

$\tilde{w}(k) = 1 + ik\langle s\rangle - \frac{1}{2}k^2\langle s^2\rangle + \cdots$ (1: $w(s)$ normalizada; $\langle s\rangle$ ↳ 1º mom.; $\langle s^2\rangle$ ↳ 2º mom.)

↳ $\ln[\tilde{w}(k)]^N = N\ln[\tilde{w}(k)] = N\ln[1 + \overbrace{ik\langle s\rangle - \frac{1}{2}k^2\langle s^2\rangle}^{\equiv x \,\rightarrow\, \text{até ordem 2}} + \cdots] \approx N[ik\langle s\rangle - \frac{1}{2}k^2\langle s^2\rangle - \frac{1}{2}(-1)k^2\langle s\rangle^2]$

$$\left.\begin{aligned} [\tilde{w}(k)]^N &= e^{N\ln[\tilde{w}(k)]} \\ \ln(1+x) &= x - \frac{x^2}{2} + \cdots \end{aligned}\right\} p(x,N) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk\, e^{-ikx + Nik\langle s\rangle + \frac{1}{2}Nk^2 \underbrace{(\langle s\rangle^2 - \langle s^2\rangle)}_{-\langle(\Delta s)^2\rangle}}$$

Variável estocástica: $\langle(\Delta s)^2\rangle = \langle(s-\langle s\rangle)^2\rangle = \langle s^2 - 2s\langle s\rangle + \langle s\rangle^2\rangle = \langle s^2\rangle - 2\langle s\rangle^2 + \langle s\rangle^2 = \langle s^2\rangle - \langle s\rangle^2 \geq 0 \Rightarrow \langle s^2\rangle \geq \langle s\rangle^2$

$$\Rightarrow p(x,N) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk\, e^{-ikx + Nik\langle s\rangle - \frac{1}{2}Nk^2\langle(\Delta s)^2\rangle}$$

$$\therefore \boxed{p(x, \overset{N \text{ passos}}{N}) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}} \qquad \mu = N\langle s\rangle, \quad \sigma^2 = N\langle(\Delta s)^2\rangle$$

Gaussiana

$$\int_{-\infty}^{\infty} e^{-ak^2+bk} dk = \sqrt{\frac{\pi}{a}}\, e^{\frac{b^2}{4a}} \rightarrow p(x,N) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk\, e^{-\frac{1}{2}N\langle(\Delta s)^2\rangle k^2 + i(N\langle s\rangle - x)k} = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk\, e^{-\overbrace{\frac{1}{2}\sigma^2}^{a} k^2 + \overbrace{i(\mu - x)}^{b} k} = \frac{1}{2\pi}\sqrt{\frac{\pi}{\frac{\sigma^2}{2}}}\, e^{-\frac{(\mu-x)^2}{2\sigma^2}} = \frac{1}{\sqrt{2\pi\sigma}} e^{-\frac{(x-\mu)^2}{2\sigma^2}} \quad //$$

* Exemplo: Caminhante de passo ℓ

→ $w(s) = p\delta(s-\ell) + q\delta(s+\ell)$, $p+q=1$

→ $\langle s\rangle = \int_{-\infty}^{\infty} s\,w(s)\,ds = \int_{-\infty}^{\infty} s\,p\,\delta(s-\ell)\,ds + \int_{-\infty}^{\infty} s\,q\,\delta(s+\ell)\,ds = \ell p - \ell q \Rightarrow \langle s\rangle = (p-q)\ell$

→ $\langle s^2\rangle = \int_{-\infty}^{\infty} s^2 p\,\delta(s-\ell)\,ds + \int_{-\infty}^{\infty} s^2 q\,\delta(s+\ell)\,ds = \ell^2 p + (-\ell)^2 q = (p+q)\ell^2 \Rightarrow \langle s^2\rangle = \ell^2$

→ $p(x,N) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$, $\mu = N\langle s\rangle \Rightarrow \mu = N(p-q)\ell \rightarrow p-q \neq 0 \Rightarrow$ "drift"

$\sigma^2 = N\langle(\Delta s)^2\rangle = N\left(\langle s^2\rangle - \langle s\rangle^2\right) = N\left[\ell^2 - (p-q)^2\ell^2\right] \Rightarrow \sigma^2 = N\ell^2\left[1-(p-q)^2\right]$

→ $\langle x\rangle = \int_{-\infty}^{\infty} x\,p(x,N)\,dx \Rightarrow \langle x\rangle = \mu = N(p-q)\ell$ → fazer ✓

→ $\langle x^2\rangle = \int_{-\infty}^{\infty} x^2 p(x,N)\,dx = \sigma^2 + \langle x\rangle^2 \Rightarrow \langle x^2\rangle = \sigma^2+\mu^2 = N\ell^2 + (p-q)^2\ell^2 N(N-1)$

→ P. binomial: $W_N(N_1) = \frac{N!}{N_1!\,N_2!} p^{N_1} q^{N-N_1}$

$$\sum_{N_1=0}^{N} W_N(N_1) = 1$$

$$\langle N_1\rangle = \sum_{N_1=0}^{N} N_1 W_N(N_1) = \sum_{N_1=0}^{\infty} N_1 \frac{N!}{N_1!\,(N-N_1)!} p^{N_1} q^{N-N_1}$$

$$p\frac{\partial}{\partial p}\underbrace{\sum_{N_1=0}^{N} W_N(N_1)}_{=(p+q)^N} = \sum_{N_1=0}^{N} \frac{N!}{N_1!\,(N-N_1)!} N_1 p^{N_1-1+1} q^{N-N_1}$$

tratamos p e q como independentes
↳ válido para quaisquer p e q

$\langle N_1\rangle = p\frac{\partial}{\partial p}(p+q)^N$

$\boxed{\langle N_1\rangle = Np(p+q)^{N-1}\big|_{p+q=1}}$ $\boxed{\langle N_2\rangle = Nq(p+q)^{N-1}\big|_{p+q=1}}$

↳ No nosso caso: $p+q=1 \Rightarrow \boxed{\langle N_1\rangle = Np}$ $\boxed{\langle N_2\rangle = Nq}$ $\Rightarrow \boxed{\langle x\rangle = \langle N_1\rangle\ell - \langle N_2\rangle\ell = N(p-q)\ell}$

$x = y+\mu$
$y = x-\mu \rightarrow dx = dy$

→ $\langle x\rangle = \int_{-\infty}^{\infty} x\,p(x,N)\,dx = \int_{-\infty}^{\infty} x \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}dx = \frac{1}{\sqrt{2\pi\sigma^2}}\left[\int_{-\infty}^{\infty} y\,e^{-\frac{y^2}{2\sigma^2}}dy + \mu\int_{-\infty}^{\infty} e^{-\frac{y^2}{2\sigma^2}}dy\right] = \frac{1}{\sqrt{2\pi\sigma^2}}\left[-\sigma^2\int_{-\infty}^{\infty}\frac{\partial}{\partial y}e^{-\frac{y^2}{2\sigma^2}}dy + \mu\sqrt{2\pi\sigma^2}\right]$

$\frac{\partial}{\partial y}e^{-\frac{y^2}{2\sigma^2}} = \frac{\partial}{\partial y}\left(-\frac{y^2}{2\sigma^2}\right)e^{-\frac{y^2}{2\sigma^2}} = -\frac{1}{\sigma^2}\,y\,e^{-\frac{y^2}{2\sigma^2}}$

$= \mu - \sigma^2 e^{-\frac{y^2}{2\sigma^2}}\Big|_{-\infty}^{\infty} = \mu$ //

→ $\langle N_1^2\rangle = \sum_{N_1=0}^{N} N_1^2 W_N(N_1) = p\frac{\partial}{\partial p}p\frac{\partial}{\partial p}(p+q)^N\Big|_{p+q=1} \Rightarrow \langle N_1^2\rangle = pN + p^2N(N-1)$ ← fazer

$\langle N_2^2\rangle = \sum_{N_1=0}^{N} N_2^2 W_N(N_1) = q\frac{\partial}{\partial q}q\frac{\partial}{\partial q}(p+q)^N\Big|_{p+q=1}$ $\langle N_2^2\rangle = qN + q^2N(N-1)$

$p\frac{\partial}{\partial p}p\frac{\partial}{\partial p}(p+q)^N = p\frac{\partial}{\partial p}Np(p+q)^{N-1}$
$= Np\left[(p+q)^{N-1} + p(N-1)(p+q)^{N-2}\right]$
$p+q=1 \rightarrow Np + N(N-1)p^2$

→ $\langle N_1N_2\rangle = \sum_{N_1=0}^{N} N_1N_2 W_N(N_1) = q\frac{\partial}{\partial q}p\frac{\partial}{\partial p}(p+q)^N\Big|_{p+q=1} \Rightarrow \langle N_1N_2\rangle = pqN(N-1)$

$= q\frac{\partial}{\partial q}Np(p+q)^{N-1} = pqN(N-1)(p+q)^{N-2}\Big|_{p+q=1}$

→ $x = (N_1-N_2)\ell$

↳ $\langle x\rangle = \langle(N_1-N_2)\ell\rangle = \langle N_1\rangle\ell - \langle N_2\rangle\ell$

↳ $\langle x^2\rangle = \langle(N_1-N_2)^2\ell^2\rangle = \langle N_1^2\rangle\ell^2 + \langle N_2^2\rangle\ell^2 - 2\langle N_1N_2\rangle\ell^2$

2º mom. da dist. binomial para N arbit.
é igual ao 2º mom. da gaussiana

→ $\left\langle\left(\frac{x}{\ell}\right)^2\right\rangle = \langle N_1^2\rangle + \langle N_2^2\rangle - 2\langle N_1N_2\rangle = pN + p^2N(N-1) + qN + q^2N(N-1) - 2pqN(N-1) = \left[(p+q)N + (p-q)^2N(N-1)\right]$

$\left\langle\left(\frac{x}{\ell}\right)^2\right\rangle = N + (p-q)^2N(N-1)$

Termodinâmica

※ 08/04/24

→ Mec. Est.: justificar a Termodinâmica

decaimento rápido: $\frac{1}{r^\alpha}$, $\alpha > d$

* 1º Postulado: o estado de um fluido é completamente caracterizado por $U, V, \{N_i\}$

* 2º Postulado: ∃ uma função dos parâmetros extensivos chamada entropia definida para todos os sistemas em equilíbrio: $S(U,V,N)$

↳ aditiva: $S_T = S_1(U_1, V_1, N_1) + S_2(U_2, V_2, N_2) + \cdots$ → não há interação significativa entre subsistemas

↳ entropia da interface << entropia dos subs.

} interação entre partículas de curto alcance

forças de van der Waals ← curto

energia ∝ área → $U \propto N^{\frac{2}{3}} << N \sim 10^{23}$

* 3º Postulado: a entropia é uma função aditiva

↳ função homogênea de grau 1: $S(\lambda U, \lambda V, \lambda N) = \lambda S(U,V,N)$

a entropia é função monotonicamente crescente da energia: $\frac{\partial S}{\partial U} > 0$

↳ função inversível: $S(U,V,N) \rightarrow U(S,V,N)$

→ Representação homogênea:

$$\lambda = \frac{1}{N} \rightarrow S(\lambda U, \lambda V, \lambda N) = S\left(\frac{U}{N}, \frac{V}{N}, 1\right) = \frac{S}{N}(u,v) \Rightarrow s \equiv \frac{S}{N},\ u \equiv \frac{U}{N},\ v \equiv \frac{V}{N}$$

$\boxed{s = s(u,v)}$ entropia por partícula

* 4º Postulado: a entropia se anula num estado $\left(\frac{\partial U}{\partial S}\right)_{V,N} = T = 0$: $S \rightarrow 0$ p/ $T \rightarrow 0$

→ Equação fundamental: $U = U(S,V,N) \Rightarrow \boxed{dU = \left.\frac{\partial U}{\partial S}\right|_{V,N} dS + \left.\frac{\partial U}{\partial V}\right|_{S,N} dV + \left.\frac{\partial U}{\partial N}\right|_{S,V} dN}$

$$\boxed{dU = \text{đ}Q + \text{đ}W_{mec} + \text{đ}W_{quim} = TdS - pdV + \mu dN}$$

→ $dQ = TdS$ → Ciclo de Carnot (reversível): $\oint dS = \oint \frac{dQ}{T} = 0$

→ $dW = -pdV$ $\begin{cases} dV > 0 \Rightarrow dW < 0 \Rightarrow dU < 0 \rightarrow \text{sistema faz trabalho e diminui energia interna} \\ dV < 0 \Rightarrow dW > 0 \Rightarrow dU > 0 \rightarrow \text{sistema sofre trabalho e aumenta energia interna} \end{cases}$

→ $dW_q = \mu dN$

→ Relacionando as derivadas: $\begin{cases} \left.\frac{\partial U}{\partial S}\right|_{V,N} = T \rightarrow V \text{ e } N \text{ fixos} \\ \left.\frac{\partial U}{\partial V}\right|_{S,N} = -p \rightarrow S \text{ e } N \text{ fixos} \\ \left.\frac{\partial U}{\partial N}\right|_{S,V} = \mu \rightarrow S \text{ e } V \text{ fixos} \end{cases}$

→ Equações de estado: $\begin{cases} T = T(S,V,N) \\ p = p(S,V,N) \\ \mu = \mu(S,V,N) \end{cases}$ → inverter relações → $S = S(U,V,N)$

→ $\bar{U} = U(\lambda S, \lambda V, \lambda N) = \lambda U(S,V,N)$ → homogênea de 1ª ordem → variáveis extensivas

↳ $\frac{U}{N} = u(s,v)$

→ $U(\lambda S, \lambda V, \lambda N) = \bar{U}(\bar{S}, \bar{V}, \bar{N})$, com $\bar{U} = \lambda U$, $\bar{S} = \lambda S$, $\bar{V} = \lambda V$, $\bar{N} = \lambda N$

↳ $\bar{T} = \left.\frac{\partial \bar{U}}{\partial \bar{S}}\right|_{\bar{V},\bar{N}} = \left.\frac{\partial \lambda U}{\partial \lambda S}\right|_{\bar{V},\bar{N}} = \left.\frac{\partial U}{\partial S}\right|_{V,N} = T \Rightarrow \bar{T} = T(\lambda S, \lambda V, \lambda N) = T$ → homogênea de ordem 0 → variáveis intensivas

$\rightarrow dU + p\,dV - \mu\,dN = T\,dS \Rightarrow \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN = dS$

$$\rightarrow dS(U,V,N) = \frac{\partial S}{\partial U}dU + \frac{\partial S}{\partial V}dV + \frac{\partial S}{\partial N}dN \quad \begin{cases} \left.\frac{\partial S}{\partial U}\right|_{V,N} = \frac{1}{T} = \left.\left(\frac{\partial U}{\partial S}\right)^{-1}\right|_{V,N} \\ \left.\frac{\partial S}{\partial V}\right|_{U,N} = \frac{p}{T} = \left.\left(\frac{\partial U}{\partial V}\right)^{-1}\right|_{S,N} \\ \left.\frac{\partial S}{\partial N}\right|_{U,V} = -\frac{\mu}{T} = \left.\left(\frac{\partial U}{\partial N}\right)^{-1}\right|_{S,V} \end{cases} \longrightarrow \boxed{U(S,V,N) \longleftrightarrow S(U,V,N)}$$

$\rightarrow u(s,v) \rightarrow du(s,v) = \left.\frac{\partial u}{\partial s}\right|_v ds + \left.\frac{\partial u}{\partial v}\right|_s dv$

N fixo

$$\hookrightarrow \left.\frac{\partial u}{\partial s}\right|_v = \left.\frac{\partial\left(\frac{U}{N}\right)}{\partial\left(\frac{S}{N}\right)}\right|_v = \left.\frac{\partial\left(\frac{U}{\cancel{N}}\right)}{\partial\left(\frac{S}{\cancel{N}}\right)}\right|_{V,N} = \left.\frac{\partial U}{\partial S}\right|_{V,N} = T \longrightarrow \left.\frac{\partial u}{\partial s}\right|_v = T$$

v pode ser fixo com V e N variando na mesma proporção

{ situações diferentes em que a mesma derivada é a temperatura

$$\hookrightarrow \left.\frac{\partial u}{\partial v}\right|_s = \left.\frac{\partial\left(\frac{U}{N}\right)}{\partial\left(\frac{V}{N}\right)}\right|_s = \left.\frac{\partial\left(\frac{U}{\cancel{N}}\right)}{\partial\left(\frac{V}{\cancel{N}}\right)}\right|_{S,N} = \left.\frac{\partial U}{\partial V}\right|_{S,N} = -p \longrightarrow \left.\frac{\partial u}{\partial v}\right|_s = -p$$

Gás ideal

→ $PV = Nk_BT$ → $pv = k_BT$

→ $U = \frac{3}{2}Nk_BT$ → $u = \frac{3}{2}k_BT$ → não há energia de interação → única fonte de energia é a cinética ↗ T. equipartição

→ $s(u,v) = ?$

→ $ds = \frac{\partial s}{\partial u}\Big|_v du + \frac{\partial s}{\partial v}\Big|_u dv$
$ds = \frac{1}{T}du + \frac{p}{T}dv$

→ $\left.\begin{array}{l} \frac{\partial s}{\partial u}\Big|_v = \frac{1}{T(u)} \\ T = \frac{2}{3}\frac{u}{k_B} \end{array}\right\}$ $\frac{\partial s}{\partial u}\Big|_v = \frac{3}{2}\frac{k_B}{u}$ ⇒ $s(u,v) = \frac{3}{2}k_B\ln u + f(v)$

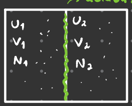
→ $\left.\begin{array}{l} \frac{\partial s}{\partial v}\Big|_u = \frac{p}{T} \\ \frac{p}{T} = \frac{k_B}{v} \end{array}\right\}$ $\frac{\partial s}{\partial v}\Big|_u = \frac{k_B}{v}$ ⇒ $f'(v) = \frac{k_B}{v}$ ⇒ $f(v) = k_B\ln v + A$

$s(u,v) = \frac{3}{2}k_B\ln u + k_B\ln v + A$

$\therefore \boxed{s(u,v) = k_B\ln(u^{\frac{3}{2}}v) + A}$

→ Sistema composto:

→ adiabática



V_i, N_i fixos

$U_t = U_1 + U_2 = cte$
$\delta U_t = \delta U_1 + \delta U_2 = 0$ ⇒ $\delta U_1 = -\delta U_2$

$S_t = S_1(U_1, V_1, N_1) + S_2(U_2, V_2, N_2)$
$\delta S_t = \frac{\partial S_1}{\partial U_1}\Big|_{V_1,N_1}\delta U_1 + \frac{\partial S_2}{\partial U_2}\Big|_{V_2,N_2}\delta U_2 = \left(\frac{\partial S_1}{\partial U_1}\Big|_{V_1,N_1} - \frac{\partial S_2}{\partial U_2}\Big|_{V_2,N_2}\right)\delta U_1 = 0$ → equilíbrio: máxima entropia
$(T_1 - T_2) = 0$ ⇒ $\boxed{T_1 = T_2}$

↳ Mudando o volume: $\delta U = \delta U_1 + \delta U_2 = 0$ ⇒ $\delta U_1 = -\delta U_2$
$\delta V = \delta V_1 + \delta V_2 = 0$ ⇒ $\delta V_1 = -\delta V_2$

$\delta S = \delta S_1 + \delta S_2 = \frac{\partial S_1}{\partial U_1}\delta U_1 + \frac{\partial S_1}{\partial V_1}\delta V_1 + \frac{\partial S_2}{\partial U_2}\delta U_2 + \frac{\partial S_2}{\partial V_2}\delta V_2 = 0$ → equilíbrio: $\delta S = 0$
$= \left(\frac{\partial S_1}{\partial U_1} - \frac{\partial S_2}{\partial U_2}\right)\delta U_1 + \left(\frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2}\right)\delta V_2 = 0$

↳ $\frac{\partial S_1}{\partial U_1} - \frac{\partial S_2}{\partial U_2} = 0$ ⇒ $\frac{1}{T_1} = \frac{1}{T_2}$ ⇒ $\boxed{T_1 = T_2}$ Equilíbrio térmico

↳ $\frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2} = 0$ ⇒ $\frac{p_1}{T_1} = \frac{p_2}{T_2}$ ⇒ $\boxed{p_1 = p_2}$ Equilíbrio mecânico

※ 12/04/24

→ $U(\lambda S, \lambda V, \lambda N) = \lambda^1 U(S, V, N)$

→ $dU = T dS - p dV + \mu dN$

→ $$\frac{d}{d\lambda} U(\lambda S, \lambda V, \lambda N) = \frac{\partial U}{\partial(\lambda S)}\frac{d(\lambda S)}{d\lambda} + \frac{\partial U}{\partial(\lambda V)}\frac{d(\lambda V)}{d\lambda} + \frac{\partial U}{\partial(\lambda N)}\frac{d(\lambda N)}{d\lambda}$$
$$= \frac{\partial U}{\partial(\lambda S)} S + \frac{\partial U}{\partial(\lambda V)} V + \frac{\partial U}{\partial(\lambda N)} N \quad \forall \lambda$$
$$= \frac{\partial U}{\partial S} S + \frac{\partial U}{\partial V} V + \frac{\partial U}{\partial N} N \quad (\text{escolha } \lambda = 1)$$
$$= TS - pV + \mu N$$

homogênea de 1ª ordem

→ Mas $\frac{d}{d\lambda} U(\lambda S, \lambda V, \lambda N) = \frac{d}{d\lambda} \lambda U(S, V, N) = U(S, V, N)$

$$\therefore \boxed{U(S, V, N) = TS - pV + \mu N}$$

→ Processo mais geral:

Energia: $U = TS - pV + \mu N$
1ª lei: $dU = TdS - pdV + \mu dN$
Derivada completa: $dU = TdS + SdT - pdV - Vdp + \mu dN + Nd\mu$

$$\Bigg\} \quad \begin{aligned} &SdT - Vdp + Nd\mu = 0 \\ &sdT - vdp + d\mu = 0 \end{aligned}$$

apenas duas variáveis independentes

$\therefore \boxed{d\mu = vdp - sdT}$ Relação de Gibbs-Duhem

→ v constante: $V = vN$, v fixo, S fixo por simplicidade
$\delta V = v\,\delta N$

↳ $\delta\left(\frac{U}{N}\right) = \frac{1}{N}\delta U - \frac{U}{N^2}\delta N$ (*)
↳ $\delta\left(\frac{S}{N}\right) = -\frac{S}{N^2}\delta N$

$\delta U = T\cancel{\delta S}^{\,0} - p\overbrace{\delta V}^{v\delta N} + \mu\,\delta N$
$\frac{\delta U}{N} = (\mu - pv)\frac{\delta N}{N}$ (1)

$U = TS - pV + \mu N$
$\frac{U}{N} = Ts - pv + \mu$ (2)

(1) e (2) em (*)

$$\Rightarrow \delta\left(\frac{U}{N}\right) = (\mu - pv - TS + pv - \mu)\frac{\delta N}{N} = -TS\frac{\delta N}{N}$$

$$\therefore \frac{\delta\left(\frac{U}{N}\right)}{\delta\left(\frac{S}{N}\right)} = \frac{-TS\frac{\delta N}{N}}{-S\frac{\partial N}{N}} = T \longrightarrow \boxed{\left.\frac{\partial u}{\partial s}\right|_v = \left.\frac{\delta\left(\frac{U}{N}\right)}{\delta\left(\frac{S}{N}\right)}\right|_{V,N} = T}$$

Potenciais Termodinâmicos

→ $U(S,V,N)$

→ $dU = TdS - pdV + \mu dN$

$$\left.\frac{\partial U}{\partial S}\right|_{V,N} = T \qquad \left.\frac{\partial U}{\partial V}\right|_{S,N} = -p \qquad \left.\frac{\partial U}{\partial N}\right|_{V,S} = \mu$$

A energia é uma função "natural" de S, V e N porque suas derivadas são equações de estado simples

→ $S(T,V,N) \rightarrow U(S(T,V,N),V,N) \rightarrow U(T,V,N)$

derivada: perda de informação

→ $U(S(T,V,N),V,N) \rightarrow dU = \frac{\partial U}{\partial S}\frac{\partial S}{\partial T}dT + \frac{\partial U}{\partial S}\frac{\partial S}{\partial V}dV + \frac{\partial U}{\partial S}\frac{\partial S}{\partial N}dN + \frac{\partial U}{\partial V}dV + \frac{\partial U}{\partial N}dN$

↳ situações em que dT seja mais relevante do que dS

Transformada de Legendre

→ Mudar a dependência a uma variável extensiva para uma intensiva

① Energia (livre) de Helmholtz → útil para sistemas em contato com res. térmico

→ $F = U - TS = F(T,V,N)$

$dF = dU - TdS - SdT = -SdT - pdV + \mu dN$

$$\boxed{\left.\frac{\partial F}{\partial T}\right|_{V,N} = -S \qquad \left.\frac{\partial F}{\partial V}\right|_{T,N} = -p \qquad \left.\frac{\partial F}{\partial N}\right|_{T,V} = \mu}$$

→ recupera a informação termodinâmica completa

② Entalpia → res. de pressão

→ $H = U - (-pV) = U + pV = TS + \mu N = H(S,p,N)$

$dH = TdS - \cancel{pdV} + \mu dN + \cancel{pdV} + Vdp = TdS + Vdp + \mu dN$

③ Energia (livre) de Gibbs → res. térmico e de pressão

→ $G = F + pV = G(T,p,N)$

$dG = -SdT - pdV + \mu dN + pdV + Vdp = -SdT + Vdp + \mu dN$

$G = F + pV = U - TS + pV = TS - pV + \mu N - TS + pV$

$\therefore \boxed{G = \mu N} \qquad g = \frac{G}{N} = \mu$

④ Gran potencial

→ $\Phi = U - TS - \mu N = TS - pV - TS - \mu N \Rightarrow \boxed{\Phi = -pV}$

$d\Phi = -SdT - pdV - Nd\mu$

Relações de Maxwell

→ $F = F(T,V,N)$

$dF = -SdT - pdV + \mu dN$

etc

$$\left.\frac{\partial F}{\partial T}\right|_{V,N} = -S, \quad \left.\frac{\partial F}{\partial V}\right|_{T,N} = -p, \quad \left.\frac{\partial F}{\partial N}\right|_{T,V} = \mu$$

→ $\frac{\partial^2 F}{\partial T \partial V} = \frac{\partial^2 F}{\partial V \partial T} \Rightarrow -\left.\frac{\partial p}{\partial T}\right|_{V,N} = -\left.\frac{\partial S}{\partial V}\right|_{T,N}$ → dois experimentos diferentes devem produzir o mesmo resultado

→ $\frac{\partial^2 F}{\partial V \partial N} = \frac{\partial^2 F}{\partial N \partial V} \Rightarrow \left.\frac{\partial \mu}{\partial V}\right|_{T,N} = -\left.\frac{\partial p}{\partial N}\right|_{T,V}$

→ $\frac{\partial^2 F}{\partial T \partial N} = \frac{\partial^2 F}{\partial N \partial T} \Rightarrow \left.\frac{\partial \mu}{\partial T}\right|_{V,N} = -\left.\frac{\partial S}{\partial N}\right|_{T,V}$

$\rightarrow G(T, p, N)$

$dG = -SdT + Vdp + \mu dN$

$\rightarrow -\left.\frac{\partial S}{\partial p}\right|_{T,N} = \left.\frac{\partial V}{\partial T}\right|_{p,N}$

$\rightarrow \left.\frac{\partial V}{\partial N}\right|_{p,T} = \left.\frac{\partial \mu}{\partial p}\right|_{N,T}$

$\rightarrow -\left.\frac{\partial S}{\partial N}\right|_{T,p} = \left.\frac{\partial \mu}{\partial T}\right|_{N,p}$

Gás ideal

$\rightarrow s(u, v) = \frac{3}{2} k_B \ln u + k_B \ln v + k_B C$

$\rightarrow u(s, v) = ?\quad f(T, v) = ?$

$\rightarrow \frac{3}{2} k_B \ln u = (s - k_B C) - k_B \ln v \Rightarrow u = v^{-\frac{2}{3}}\, e^{\frac{2}{3}\left(\frac{s}{k_B} - c\right)}$

$\rightarrow f(T, v) = \frac{U - TS}{N} = u - Ts = u(T, v) - Ts(T, v)$

$df = -sdT - pdv$

$du = Tds - pdv$

$\rightarrow T = \left.\frac{\partial u}{\partial s}\right|_{v},\quad \frac{1}{T} = \left.\frac{\partial s}{\partial u}\right|_{v} = \frac{3}{2} k_B \frac{1}{u} \Rightarrow u = \frac{3}{2} k_B T$

$\rightarrow s(T, v) = \frac{3}{2} k_B \ln\left(\frac{3}{2} k_B T\right) + k_B \ln v + k_B C$

$\therefore f(T, v) = \frac{3}{2} k_B T - T \frac{3}{2} k_B \ln\left(\frac{3}{2} k_B T\right) + T k_B \ln v + T k_B C \Rightarrow f(T, v) = k_B T \left\{\frac{3}{2}\left[1 - \ln\left(\frac{3}{2} k_B T\right)\right] + \ln v + C\right\}$

Relações entre derivadas

$\rightarrow dU = TdS - pdV + \mu dN \qquad \rightarrow U = TdS - pdV + 0$

$\rightarrow \left.\frac{\partial S}{\partial V}\right|_{U,N} = \frac{p}{T}$

$$\left.\begin{aligned} &\rightarrow \left.\frac{\partial U}{\partial V}\right|_{S,N} = -p \\ &\rightarrow \left.\frac{\partial U}{\partial S}\right|_{V,N} = T \end{aligned}\right\} \left.\frac{\partial S}{\partial V}\right|_{U,N} = \frac{-\left.\frac{\partial U}{\partial V}\right|_{S,N}}{\left.\frac{\partial U}{\partial S}\right|_{T,N}} \rightarrow \left.\frac{\partial S}{\partial V}\right|_{U,N} \left.\frac{\partial U}{\partial S}\right|_{V,N} \left.\frac{\partial V}{\partial U}\right|_{S,N} = -1$$

$\rightarrow 0 = T \left.\frac{\partial S}{\partial p}\right|_{U,N} - p \left.\frac{\partial V}{\partial p}\right|_{U,N}$

$\left.\frac{\partial S}{\partial p}\right|_{U,N} \left.\frac{\partial p}{\partial V}\right|_{U,N} = \frac{p}{T} = \left.\frac{\partial S}{\partial V}\right|_{U,N} \rightarrow \left.\frac{\partial S}{\partial p}\right|_{U,N} \left.\frac{\partial p}{\partial V}\right|_{U,N} \left.\frac{\partial V}{\partial S}\right|_{U,N} = 1$

※ 17/04/23

Respostas Termodinâmicas

* Coeficiente de expansão térmica: $\boxed{\alpha = \frac{1}{V}\frac{\partial V}{\partial T}\Big|_{p,N} = \frac{1}{v}\frac{\partial v}{\partial T}\Big|_{p}}$

* Compressibilidade isotérmica: $\boxed{K_T = -\frac{1}{V}\frac{\partial V}{\partial p}\Big|_{T,N} = -\frac{1}{v}\frac{\partial v}{\partial p}\Big|_{T}}$

* Calor específico a pressão constante: $\boxed{c_p = \frac{1}{N}\frac{dQ}{dT}\Big|_{p,N} = T\frac{\partial s}{\partial T}\Big|_{p}}$

"fundamentais"

* Calor específico a volume constante: $\boxed{c_v = \frac{1}{N}\frac{dQ}{dT}\Big|_{V,N} = T\frac{\partial s}{\partial T}\Big|_{v}}$ $c_v < c_p$ $\left\{ \text{parte da energia é necessária para fazer trabalho (aumentar o volume)} \right.$

→ Como relacionar outras derivadas a essas?

$$s(T,p) \rightarrow \frac{\partial T}{\partial p}\Big|_s \frac{\partial s}{\partial T}\Big|_p \frac{\partial p}{\partial s}\Big|_T = -1 \Rightarrow \frac{\partial T}{\partial p}\Big|_s = -\frac{\frac{\partial s}{\partial p}\Big|_T}{\frac{\partial s}{\partial T}\Big|_p}$$

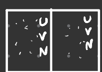
encontrar algum potencial com termos do tipo Sdx e Zdp

$$dU = TdS - pdV + \mu dN$$
$$d(U-TS) = -SdT - pdV + \mu dN$$
$$d(U-TS+pV) = -SdT + Vdp + \mu dN \Rightarrow -\frac{\partial s}{\partial p}\Big|_T = \frac{\partial v}{\partial T}\Big|_p = v\alpha$$

$$\therefore \frac{\partial T}{\partial p}\Big|_s = -\frac{\frac{\partial s}{\partial p}\Big|_T}{\frac{\partial s}{\partial T}\Big|_p} = \frac{T\frac{\partial v}{\partial T}\Big|_p}{T\frac{\partial s}{\partial T}\Big|_p} \Rightarrow \frac{\partial T}{\partial p}\Big|_s = \frac{\alpha v T}{c_p}$$

Extremização: 2ª derivada

→ $\delta S|_{U,V,N} = 0$



→ Estado inicial: $2S(U,V,N)$ (equilíbrio)

→ Estado final: Parede adiabática (fora do equilíbrio)

↳ flutuação

$$2S(U,V,N) \geq S(U-\Delta U, V, N) + S(U+\Delta U, V, N)$$

$\left\{ \text{possibilidade de retornar ao estado de equilíbrio} \right.$

↳ Movendo parede: $2S(U,V,N) \geq S(U-\Delta U, V-\Delta V, N) + S(U+\Delta U, V+\Delta V, N)$

→ Série de Taylor: $\cancel{2S} \geq \cancel{S} - \cancel{\frac{\partial S}{\partial U}\delta U} - \cancel{\frac{\partial S}{\partial V}\delta V} + \frac{1}{2}\left[\frac{\partial^2 S}{\partial U^2}(\delta U)^2 + \frac{\partial^2 S}{\partial V^2}(\delta V)^2 + \frac{2\partial^2 S}{\partial U \partial V}\delta U \delta V\right] + \cancel{S} + \cancel{\frac{\partial S}{\partial U}\delta U} + \cancel{\frac{\partial S}{\partial V}\delta V} + \frac{1}{2}\left[\frac{\partial^2 S}{\partial U^2}(\delta U)^2 + \frac{\partial^2 S}{\partial V^2}(\delta V)^2 + \frac{2\partial^2 S}{\partial U \partial V}\delta U \delta V\right]$

$$\delta^2 S = \frac{\partial^2 S}{\partial U^2}(\delta U)^2 + \frac{\partial^2 S}{\partial V^2}(\delta V)^2 + 2\frac{\partial^2 S}{\partial U \partial V}\delta U \delta V \leq 0$$

Válido $\forall\ \delta U, \delta V$ $\begin{cases} \delta V = 0 \rightarrow \boxed{\frac{\partial^2 S}{\partial U^2} \leq 0} \quad \text{(i)} \\ \delta U = 0 \rightarrow \boxed{\frac{\partial^2 S}{\partial V^2} \leq 0} \quad \text{(ii)} \end{cases}$

→ Condição sobre a derivada mista:

$$\delta^2 S = (\delta U, \delta V) \underbrace{\begin{pmatrix} \frac{\partial^2 S}{\partial U^2} & \frac{\partial^2 S}{\partial V \partial U} \\ \frac{\partial^2 S}{\partial U \partial V} & \frac{\partial^2 S}{\partial V^2} \end{pmatrix}}_{\bar{M}} \begin{pmatrix} \delta U \\ \delta V \end{pmatrix}$$

↗ simétrica → diagonalizável

$$\begin{pmatrix} \delta z \\ \delta w \end{pmatrix} = U_M \begin{pmatrix} \delta U \\ \delta V \end{pmatrix} \quad \Bigg| \quad \begin{aligned} (\delta z, \delta w) &= (\delta U, \delta V)\, U_M^{-1} \\ (\delta z, \delta w)\, U_M &= (\delta U, \delta V) \end{aligned}$$

$$\delta^2 S = (\delta z, \delta w) \underbrace{U_M \bar{M} U_M^{-1}}_{\begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix}} \begin{pmatrix} \delta z \\ \delta w \end{pmatrix} \longrightarrow \delta^2 S = \lambda_1 (\delta z)^2 + \lambda_2 (\delta w)^2 \leq 0$$

eliminamos termos cruzados

$$\therefore \boxed{\lambda_1 \leq 0,\ \lambda_2 \leq 0} \rightarrow \text{autovalores devem ser negativos}$$

$$\mathrm{Tr}(\bar{M}) = \mathrm{Tr}(U_M \bar{M} U_M^{-1}) = \lambda_1 + \lambda_2 \leq 0 \Rightarrow \frac{\partial^2 S}{\partial U^2} + \frac{\partial^2 S}{\partial V^2} \leq 0$$

$$\det(\bar{M}) = \det(U_M \bar{M} U_M^{-1}) = \lambda_1 \lambda_2 \geq 0 \Rightarrow \boxed{\frac{\partial^2 S}{\partial U^2} \frac{\partial^2 S}{\partial V^2} - \left(\frac{\partial^2 S}{\partial U \partial V}\right)^2 \geq 0} \quad \text{(iii)}$$

※ 19/04/24

Estabilidade

$\rightarrow \left.\frac{\partial^2 S}{\partial U^2}\right|_{V,N} = \frac{\partial}{\partial U}\left(\frac{1}{T}\right)\Big|_{V,N} = -\frac{1}{T^2}\left.\frac{\partial T}{\partial U}\right|_{V,N} \leq 0$

$\therefore \boxed{\left.\frac{\partial T}{\partial U}\right|_{V,N} \geq 0} \quad \boxed{\left.\frac{\partial U}{\partial T}\right|_{V,N} \geq 0}$

$\rightarrow dU = TdS - p\cancel{dV} + \mu \cancel{dN} \Rightarrow \left.\frac{\partial U}{\partial T}\right|_{V,N} = T\left.\frac{\partial S}{\partial T}\right|_{V,N} = C_V \Rightarrow \boxed{C_V \geq 0}$

{ Sistema deve voltar ao equilíbrio após uma flutuação

$\rightarrow$ 

$V = V_1 + V_2$

$\delta S|_U = 0$

$\delta^2 S|_{U,V} \leq 0$

$\rightarrow S_t = S(V_1) + S(V - V_1)$

$\left.\frac{\partial S_t}{\partial V_1}\right|_{U,V} = 0, \quad \left.\frac{\partial^2 S_t}{\partial V_1^2}\right|_{U,V} \leq 0 \Leftrightarrow \left.\frac{\partial U_t}{\partial V_1}\right|_{S,V} = 0, \quad \left.\frac{\partial^2 U_t}{\partial V_1^2}\right|_{S,V} \geq 0$

$\rightarrow$ Princípio variacional para a energia: $\boxed{\begin{array}{l} \delta U|_{S,V,N} = 0 \\ \delta^2 U|_{S,V,N} \geq 0 \end{array}}$ Estado de equilíbrio tem energia mínima

$\rightarrow U_t(\underbrace{S, V}_{\text{fixos}}, V_1) \rightarrow U_t(V_1) = U(V_1) + U(\overbrace{V - V_1}^{V_2})$

$\left.\frac{\partial U_t}{\partial V_1}\right|_{V,S} = \underbrace{\frac{\partial U(V_1)}{\partial V_1}}_{-p_1} + \underbrace{\frac{\partial U}{\partial V_2}}_{-p_2}\underbrace{\frac{\partial V_2}{\partial V_1}}_{-1}$

$-\frac{\partial U_t}{\partial V_1} = p_1 - p_2$

$\therefore \frac{\partial U_t}{\partial V_1} = p_2 - p_1$

$\rightarrow \left.\frac{\partial U_t}{\partial V_1}\right|_S \left.\frac{\partial S}{\partial U_t}\right|_{V_1} \left.\frac{\partial V_1}{\partial S}\right|_{U_t} = -1$

$\left.\frac{\partial U}{\partial V_1}\right|_S = -\frac{\left.\frac{\partial S}{\partial V_1}\right|_U}{\left.\frac{\partial S}{\partial U}\right|_{V_1}} = -\frac{\left.\frac{\partial S}{\partial V_1}\right|_U}{\frac{1}{T}} = -T\underbrace{\left.\frac{\partial S}{\partial V_1}\right|_U}_{=0} = 0$

$\therefore \boxed{\left.\frac{\partial U}{\partial V_1}\right|_S = 0}$

$\rightarrow \left.\frac{\partial^2 U}{\partial V_1^2}\right|_S = -\left.\frac{\partial \Delta p}{\partial V_1}\right|_S$

$\Delta p = -\left.\frac{\partial U}{\partial V_1}\right|_S = p_1 - p_2 \rightarrow \Delta p(U, V_1)$

0 no equilíbrio

$\rightarrow \left.\frac{\partial \Delta p}{\partial V_1}\right|_S = \left.\frac{\partial \Delta p}{\partial U}\right|_{V_1}\left.\frac{\partial U}{\partial V_1}\right|_S + \left.\frac{\partial \Delta p}{\partial V_1}\right|_U \overbrace{\left.\frac{\partial V_1}{\partial V_1}\right|_S}^{1}$

$\rightarrow \left.\frac{\partial U}{\partial V_1}\right|_S \left.\frac{\partial V_1}{\partial S}\right|_U \left.\frac{\partial S}{\partial U}\right|_{V_1} = -1$

$-\Delta p = \left.\frac{\partial U}{\partial V_1}\right|_S = -\frac{\left.\frac{\partial S}{\partial V_1}\right|_U}{\left.\frac{\partial S}{\partial U}\right|_{V_1}} \Rightarrow \Delta p = \frac{\left.\frac{\partial S}{\partial V_1}\right|_U}{\left.\frac{\partial S}{\partial U}\right|_{V_1}}$

0 no equilíbrio

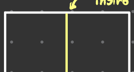
$\rightarrow \left.\frac{\partial^2 U}{\partial V_1^2}\right|_S = -\left.\frac{\partial \Delta p}{\partial V_1}\right|_U = -\frac{\partial}{\partial V_1}\left[\frac{\left.\frac{\partial S}{\partial V_1}\right|_U}{\left.\frac{\partial S}{\partial U}\right|_{V_1}}\right]_U = \frac{-\left.\frac{\partial^2 S}{\partial V_1^2}\right|_U}{\left.\frac{\partial S}{\partial U}\right|_{V_1} \rightarrow \frac{1}{T}} + \frac{\left.\frac{\partial S}{\partial V_1}\right|_U}{\left(\frac{\partial S}{\partial U}\right)^2_{V_1}}\frac{\partial^2 S}{\partial U \partial V_1} = -\underset{>0}{T}\underset{\leq 0}{\left.\frac{\partial^2 S}{\partial V_1^2}\right|_U}$

$\therefore \boxed{\left.\frac{\partial^2 U}{\partial V_1^2}\right|_S \geq 0}$

Concavidade da energia

$\rightarrow U(S + \overbrace{\Delta S, V + \Delta V}^{\text{flutuações}}, N) + U(S - \Delta S, V - \Delta V, N) \geq 2U(S, V, N)$

insiro parede adiabática

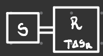


$\left.\begin{array}{l} \Delta S \rightarrow 0 \\ \Delta V \rightarrow 0 \end{array}\right\} \boxed{\begin{array}{l} \left.\frac{\partial^2 U}{\partial S^2}\right|_{V,N} = \left.\frac{\partial T}{\partial S}\right|_{V,N} \geq 0 \\ \left.\frac{\partial^2 U}{\partial V^2}\right|_{S,N} = -\left.\frac{\partial p}{\partial V}\right|_{S,N} \geq 0 \\ \frac{\partial^2 U}{\partial S^2}\frac{\partial^2 U}{\partial V^2} - \left(\frac{\partial U}{\partial S \partial V}\right)^2 \geq 0 \end{array}}$

※ 22/04/24

Consequências da 1ª e 2ª leis

→ $\Delta E = \Delta Q - W_q - p_0 \Delta V$



Calor sai do reservatório → entropia diminui → $\Delta Q = -T\Delta S_R$

processo reversível apenas para o reservatório

trabalho químico (na forma de energia elétrica)

→ $\left.\begin{array}{l} \Delta E = -T\Delta S_R - W_q - p_0 \Delta V \\ \Delta S_S + \Delta S_R \geq 0 \Rightarrow T\Delta S_S \geq -T\Delta S_R \end{array}\right\}$ $\begin{array}{l} \Delta E + W_q + p_0 \Delta V = -T\Delta S_R \leq T\Delta S_S \\ W_q \leq T\Delta S_S - p_0 \Delta V - \Delta E \end{array}$

→ $\left.\begin{array}{l} V = cte \Rightarrow \Delta V = 0 \\ T = cte \end{array}\right\}$ $\boxed{W_q \leq -\Delta(E - TS) = -\Delta F}$ → em um estado de equilíbrio, não há mais trabalho disponível

$\Delta F = 0 \Rightarrow W_q = 0$

→ V variável ⇒ $\boxed{W_q \leq -\Delta G}$, $G = E - T_R S + p_R V$

Concavidade dos potenciais

→ $U(S, V, N)$
$F(T, V, N)$

→ $dU = TdS - pdV + \mu dN$

→ $F = U - TS \Rightarrow dF = -SdT - pdV + \mu dN$

→ $\left.\frac{\partial F}{\partial T}\right|_{V,N} = -S$

→ $\left.\begin{array}{l} \left.\frac{\partial^2 F}{\partial T^2}\right|_{V,N} = -\left.\frac{\partial S}{\partial T}\right|_{V,N} = -\left[\left.\frac{\partial T}{\partial S}\right|_{V,N}\right]^{-1} \\ T = \left.\frac{\partial U}{\partial S}\right|_{V,N} \geq 0 \end{array}\right\}$ $\boxed{\frac{\partial^2 F}{\partial T^2} = -\frac{1}{\left.\frac{\partial^2 U}{\partial S^2}\right|_{V,N}} \leq 0}$ $\boxed{\left.\frac{\partial^2 U}{\partial S^2}\right|_{V,N} \geq 0 \leftrightarrow \left.\frac{\partial^2 F}{\partial T^2}\right|_{V,N} \leq 0}$

→ $T\left.\frac{\partial^2 F}{\partial T^2}\right|_{V,N} = -\underbrace{T\left.\frac{\partial S}{\partial T}\right|_{V,N}}_{C_V} \leq 0 \overset{(T \geq 0)}{\Rightarrow} \boxed{C_V \geq 0}$

→ $\frac{\partial^2 F}{\partial V^2} = ?$

→ $\begin{array}{l} \left.\frac{\partial F}{\partial V}\right|_{T,N} = -p \\ \left.\frac{\partial^2 F}{\partial V^2}\right|_{T,N} = -\left.\frac{\partial p}{\partial V}\right|_{T,N} \end{array}$ | $p = -\left.\frac{\partial U}{\partial V}\right|_{S,N}$ → $\left.\begin{array}{l} p(S, V, N) \\ S(T, V, N) \end{array}\right\}$ $p(S(T, V, N), V, N)$

→ $\left.\frac{\partial p}{\partial V}\right|_{T,N} = \left.\frac{\partial p}{\partial S}\right|_{V,N} \left.\frac{\partial S}{\partial V}\right|_{T,N} + \left.\frac{\partial p}{\partial V}\right|_{S,N}$

→ $\left.\frac{\partial S}{\partial V}\right|_T \left.\frac{\partial V}{\partial T}\right|_S \left.\frac{\partial T}{\partial S}\right|_V = -1$

$\left.\begin{array}{l} \left.\frac{\partial S}{\partial V}\right|_T = -\left.\frac{\partial T}{\partial V}\right|_S \left.\frac{\partial S}{\partial T}\right|_V \\ \\ \left.\frac{\partial T}{\partial V}\right|_S = -\left.\frac{\partial p}{\partial S}\right|_V \end{array}\right\}$ $\left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial p}{\partial S}\right|_V \left.\frac{\partial S}{\partial T}\right|_V = \left.\frac{\partial p}{\partial T}\right|_V$

$\left.\frac{\partial p}{\partial V}\right|_{T,N} = \left(\left.\frac{\partial p}{\partial S}\right|_{V,N}\right)^2 \left.\frac{\partial S}{\partial T}\right|_{V,N} + \left.\frac{\partial p}{\partial V}\right|_{S,N}$

$\left.\frac{\partial^2 F}{\partial V^2}\right|_{T,N} = -\left.\frac{\partial p}{\partial V}\right|_{T,N} = \frac{\left(\left.\frac{\partial p}{\partial S}\right|_{V,N}\right)^2 + \left.\frac{\partial p}{\partial V}\right|_{S,N} \left.\frac{\partial T}{\partial S}\right|_{V,N}}{\left.\frac{\partial T}{\partial S}\right|_V} = \frac{\overbrace{\frac{\partial^2 U}{\partial V^2}\frac{\partial^2 U}{\partial S^2} - \left(\frac{\partial^2 U}{\partial V \partial S}\right)^2}^{\geq 0}}{\frac{\partial^2 U}{\partial S^2}} \geq 0$

$\therefore \boxed{\left.\frac{\partial^2 F}{\partial V^2}\right|_{T,N} \geq 0}$

Transformada de Legendre inverte a concavidade apenas das variáveis trocadas

→ $F(T, V - \Delta V, N - \Delta N) + F(T, V + \Delta V, N + \Delta N) \geq 2F(T, V, N) \quad \forall \Delta V, \Delta N$

→ $\left.\frac{\partial^2 F}{\partial V^2}\right|_{T,N} \geq 0$, $\left.\frac{\partial^2 F}{\partial N^2}\right|_{T,V} \geq 0$, $\frac{\partial^2 F}{\partial N^2}\frac{\partial^2 F}{\partial V^2} - \left(\frac{\partial^2 F}{\partial N \partial V}\right)^2 \geq 0$