# EQUAZIONE DI SMOLUCHOWSKI.

$$\xi \frac{dx}{dt} = F(x) + \theta(t) \qquad \langle \theta(t) \rangle = 0 \qquad \langle \theta(s')\theta(s) \rangle = 2\theta_0\, \delta(s-s') \underset{\uparrow}{=} 2\, k_B T \cdot \xi\, \delta(s-s')$$

equilibrio

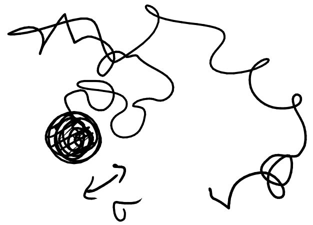
$$\frac{1}{2} m \langle v^2 \rangle = \frac{1}{2} k_B T \qquad \theta_0 = k_B T \cdot \xi$$

$$\sqrt{\langle v^2 \rangle} = \sqrt{\frac{k_B T}{m}}$$

$$\sigma = \sqrt{\langle v^2 \rangle} \cdot \tau_D = \sqrt{\frac{k_B T}{m}}\, \tau_D$$

Condizione di validità:

$$\tau = \boxed{\frac{m}{\xi}} \ll \tau_D = \boxed{\frac{\xi \sigma^2}{k_B T}}$$



$$\sigma \gg \frac{\sqrt{k_B T\, m}}{\xi}$$

$$\xi \gg \frac{\sqrt{k_B T \cdot m}}{\sigma}$$

$$\langle \Delta x^2 \rangle \sim D t$$

$$\sigma^2 \sim D \tau_D = \frac{k_B T}{\xi} \tau_D$$

Intervallo $\Delta t$ → Taylor I ordine per lo spostamento $h$

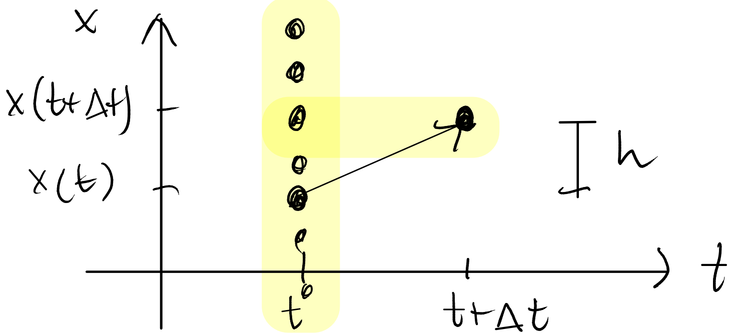
$$h \approx \frac{F(x)}{\xi} \Delta t + \frac{1}{\xi} \int_t^{t+\Delta t} ds\, \theta(s) \; ; \; \langle h \rangle = \frac{F(x)}{\xi} \Delta t \; ; \; \langle (h - \langle h \rangle)^2 \rangle = \frac{1}{\xi^2} \int_t^{t+\Delta t} ds \int_t^{t+\Delta t} ds' \underset{\sim \delta(s-s')}{\langle \theta(s)\theta(s') \rangle}$$

$$= \frac{2\theta_0}{\xi^2} \Delta t = 2 D \Delta t$$

Densità prob. di $h$

$$\Pi(x,h) = \frac{1}{\sqrt{4\pi D \Delta t}} \exp\left[ - \frac{\left(h - \frac{F(x)}{\xi}\Delta t\right)^2}{4 D \Delta t} \right]$$

Master equation per $p(x,t)$




$$p(x,t+\Delta t) \simeq \int_{-\infty}^{\infty} dh\, \overbrace{\Pi(x-h,h)\, p(x-h,t)}^{\varphi(x-h)}$$

Taylor di $\Pi \cdot p$ nella variabile $x-h$ attorno a $h=0$

$$p(x,t+\Delta t) \approx \int_{-\infty}^{\infty} dh \left[ \varphi(x) + \frac{d\varphi}{dh}\, h + \frac{1}{2}\frac{d^2\varphi}{dh^2}\, h^2 \right]$$

$$= \int_{-\infty}^{\infty} dh \left[ \varphi(x) - \frac{d\varphi}{dx}\, h + \frac{1}{2}\frac{d^2\varphi}{dx^2}\, h^2 \right] \qquad \left( \frac{d\varphi}{dh} = -\frac{d\varphi}{dx} \right)$$

$$\simeq p(x,t)\int_{-\infty}^{\infty} dh\, \Pi(x,t) - \int_{-\infty}^{\infty} dh\, \frac{\partial}{\partial x}\Big( \Pi(x,h)\, p(x,t) \Big) h + \frac{1}{2}\int_{-\infty}^{\infty} dh\, \frac{\partial^2}{\partial x^2}\Big( \Pi(x,h)\, p(x,t) \Big) h^2$$

$$= p(x,t)\underbrace{\int_{-\infty}^{\infty} dh\, \Pi(x,t)}_{=1} - \frac{\partial}{\partial x}\left[ \left( \int_{-\infty}^{\infty} dh\, \Pi(x,h)\, h \right) p \right] + \frac{1}{2}\frac{\partial^2}{\partial x^2}\left[ \underbrace{\left( \int_{-\infty}^{\infty} dh\, \Pi\, h^2 \right)}_{2D\Delta t + \langle h\rangle^2} p \right]$$

$$\cancel{p(x,t)} + \frac{\partial p}{\partial t}\Delta t + O(\Delta t^2) = \cancel{p(x,t)} - \frac{\partial}{\partial x}\left( \frac{F(x)}{\xi}\cancel{\Delta t}\, p(x,t) \right) + \frac{1}{2}\frac{\partial^2}{\partial x^2}\Big[ \cancel{2} D \cancel{\Delta t}\, p(x,t) \Big] + \underbrace{\frac{1}{2}\frac{\partial^2}{\partial x^2}\left( \frac{F^2}{\xi^2} p \right) \Delta t^2}_{O(\Delta t^2)}$$

$$\frac{\partial p}{\partial t} = -\frac{\partial}{\partial x}\left( \frac{F(x)}{\xi}\, p(x,t) \right) + \frac{\partial^2}{\partial x^2}\Big( D\, p(x,t) \Big) \Rightarrow \frac{\partial p}{\partial t} = -\frac{\partial}{\partial x}\left( \frac{F(x)}{\xi}\, p \right) + D\frac{\partial^2 p}{\partial x^2}$$

eq. Smoluchowski $\qquad \rightarrow$ convezione − diffusione

$$\frac{\partial p}{\partial t} + \frac{\partial}{\partial x}\Big( \underbrace{\frac{F(x)}{\varepsilon} p(x,t) - D \frac{\partial p}{\partial x}}_{\text{corrente di prob. } J(x,t)} \Big) = 0$$

eq. di continuità per $p(x,t)$

Condizioni al contorno ai bordi di un dominio:

→ $p=0$ assorbenti

→ $J=0$ riflettenti

3d : $$\frac{\partial p}{\partial t} + \vec{\nabla}\cdot\Big( \frac{\vec{F}(\vec{r})}{\varepsilon} p(\vec{r},t) - D\,\vec{\nabla}\cdot p \Big) = 0$$

Fokker – Planck : $$\frac{\partial p}{\partial t} = \frac{\partial}{\partial v}\Big( \frac{\varepsilon}{m} v(t)\, p(v,t) + \frac{\varepsilon^2}{m^2} D \frac{\partial p}{\partial v} \Big) \rightarrow p(v,t)$$

## Casi particolari

1) Regime stazionario : $\frac{\partial p}{\partial t} = 0$ $\qquad \frac{F(x)}{\varepsilon} p(x) - D \frac{\partial p}{\partial x} = J = \text{cost}$

$F(x) = -\frac{dU}{dx}$ $\qquad p(x) \sim \exp\Big(-\frac{U(x)}{K_B T}\Big)$ Boltzmann è soluzione stazionaria

$$-\frac{dU}{dx}\frac{1}{\varepsilon} p(x) - \frac{\cancel{K_B T}}{\varepsilon}\Big(-\frac{dU}{dx}\Big)\frac{1}{\cancel{K_B T}} p(x) \simeq J = 0 \Leftarrow D = \frac{K_B T}{\varepsilon}$$

2) <u>Particella libera</u> : $F(x) = 0$

$$\frac{\partial p}{\partial t} = D \frac{\partial^2 p}{\partial x^2}$$ eq. diffusione $p(x,t)$

Trasf. Fourier

$$p_k(t) = \int_{-\infty}^{\infty} dx\, e^{-ikx}\, p(x,t)$$

$$\frac{\partial p_k}{\partial t} = -Dk^2 p_k(t) \rightarrow p_k(t) = p_k(0) \exp(-Dk^2 t)$$

Antitrasf. Fourier

$$p(x,t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk\, e^{ikx} \overbrace{p_k(0)}^{=1} \exp(-Dt\, k^2)$$

Condizione iniziale : $p(x,0) = \delta(x) \rightarrow p_k(0) = 1$

$$p(x,t) = \frac{1}{\sqrt{4\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right) \qquad \langle x^2 \rangle = 2Dt \Rightarrow \langle \Delta x^2 \rangle = 2Dt$$

3) <u>Forza costante</u>

$$\frac{\partial p}{\partial t} = \frac{\partial}{\partial x}\left( - \frac{F}{\xi} p(x,t) + D \frac{\partial p}{\partial x} \right)$$

Cambio variabile: $y = x - \frac{F}{\xi} t \quad \rightarrow \quad q(y,t)$

$$p(x,t)\, \cancel{dx}\, \cancel{dt} = q(\underset{\substack{\uparrow \\ y(t)}}{y},t)\, \cancel{dy}\, \cancel{dt} \qquad dx = dy \quad \Rightarrow \quad \frac{\partial p}{\partial x} = \frac{\partial q}{\partial y}$$

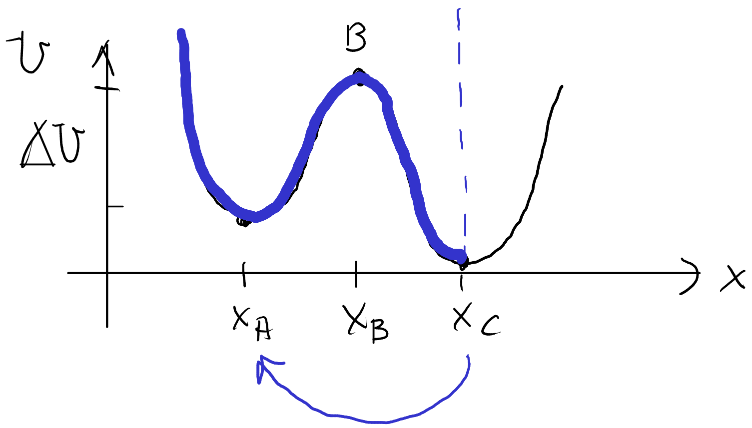
$$\frac{\partial q}{\partial t} + \cancel{\frac{\partial q}{\partial y} \underbrace{\frac{\partial y}{\partial t}}_{-\frac{F}{\xi}}} = \cancel{- \frac{F}{\xi} \frac{\partial q}{\partial y}} + D \frac{\partial^2 q}{\partial y^2} \quad \Rightarrow \quad \frac{\partial q}{\partial t} = D \frac{\partial^2 q}{\partial y^2}$$

$$q(y,t) = \frac{1}{\sqrt{4\pi D t}} \exp\left( - \frac{y^2}{4Dt} \right) \quad \Rightarrow \quad p(x,t) = \frac{1}{\sqrt{4\pi D t}} \exp\left( - \frac{(x - \frac{F}{\xi} t)^2}{4Dt} \right)$$

$$\langle x \rangle = \frac{F}{\xi} t \qquad \langle (x - \langle x \rangle)^2 \rangle = 2Dt$$

## 4) Attivazione termica : problema di Kramers (1940)

Smoluchowski : $\dfrac{\partial p}{\partial t} = -\dfrac{\partial}{\partial x}\left(\dfrac{F(x)}{\xi}\, p(x,t)\right) + D\,\dfrac{\partial^2 p}{\partial x^2} = \dfrac{\partial}{\partial x}\left(-\dfrac{F(x)}{\xi}\, p(x,t) + D\dfrac{\partial p}{\partial x}\right) = \dfrac{\partial}{\partial x}\Big(\underbrace{\dfrac{1}{\xi}\dfrac{\partial U}{\partial x}\, p + D\,\dfrac{\partial p}{\partial x}}_{-J(x)}\Big)$




condizioni assorbenti in C : $p(x_c) = 0$

$$\Delta U = U_B - U_A \gg k_B T$$

Regime stazionario : $\dfrac{\partial p}{\partial t} = 0 \;\Rightarrow\; -J = \dfrac{1}{\xi}\dfrac{dU}{dx}\, p(x) + D\,\dfrac{dp}{dx} = \text{cost}$

Goal : calcolare tempo di uscita $\tau$ dalla buca in A

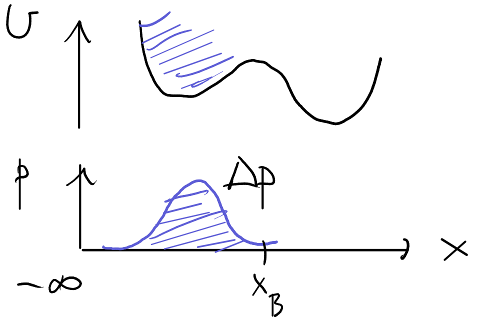
Soluzione nella forma :

$$p(x) = \psi(x)\exp\left(-\frac{U(x)}{k_B T}\right) \qquad D = \frac{k_B T}{\xi}$$

$$\frac{1}{\xi}\frac{dU}{dx}\,\psi(x)\exp\left(-\frac{U(x)}{k_B T}\right) + \frac{k_B T}{\xi}\frac{d\psi}{dx}\exp\left(-\frac{U(x)}{k_B T}\right) + \frac{\cancel{k_B T}}{\xi}\,\psi(x)\left(-\frac{dU}{dx}\right)\frac{1}{\cancel{k_B T}}\exp\left(-\frac{U(x)}{k_B T}\right) = -J$$

$$\frac{d\psi}{dx} = -\frac{J\xi}{k_B T}\exp\left(\frac{U(x)}{k_B T}\right) \;\Rightarrow\; \psi(x_c) - \psi(x) = -\frac{J\xi}{k_B T}\int_x^{x_c} dx' \exp\left(\frac{U(x')}{k_B T}\right)$$

$$\psi(x) = \frac{J\xi}{k_B T}\int_x^{x_c} dx' \exp\left(\frac{U(x)}{k_B T}\right) \;\Rightarrow\; p(x) = \frac{J\xi}{k_B T}\exp\left(-\frac{U(x)}{k_B T}\right)\int_x^{x_c} dx' \exp\left(\frac{U(x)}{k_B T}\right)$$




$$J = \frac{\Delta p}{\tau} \Rightarrow \tau = \frac{\int_{-\infty}^{x_B} p(x)\,dx}{J} \qquad \text{tempo di uscita}$$

$$\frac{J\varepsilon}{k_B T} \int_{-\infty}^{x_B} dx'' \exp\left(-\frac{U(x'')}{k_B T}\right) \int_{x''}^{x_C} dx' \exp\left(\frac{U(x')}{k_B T}\right)$$

Nell' intorno di $x_A$

$$\int_{x''}^{x_C} dx' \exp\left(\frac{U(x')}{k_B T}\right)$$

non dipende molto da $x$ ed è dominato dal contributo attorno a $x_B$

$$U(x) \approx U(x_B) - \frac{1}{2} m\omega_B^2 (x - x_B)^2 \qquad \text{per } x \approx x_B$$

$$\int_{x''}^{x_C} dx' \exp\left(\frac{U_B}{k_B T}\right) \exp\left(-\frac{1}{2}\frac{m\omega_B^2}{k_B T}(x-x_B)^2\right) \approx \int_{-\infty}^{\infty} dx' \exp\left(-\frac{1}{2}\frac{m\omega_B^2}{k_B T}(x-x_B)^2\right) \cdot \exp\left(\frac{U_B}{k_B T}\right)$$

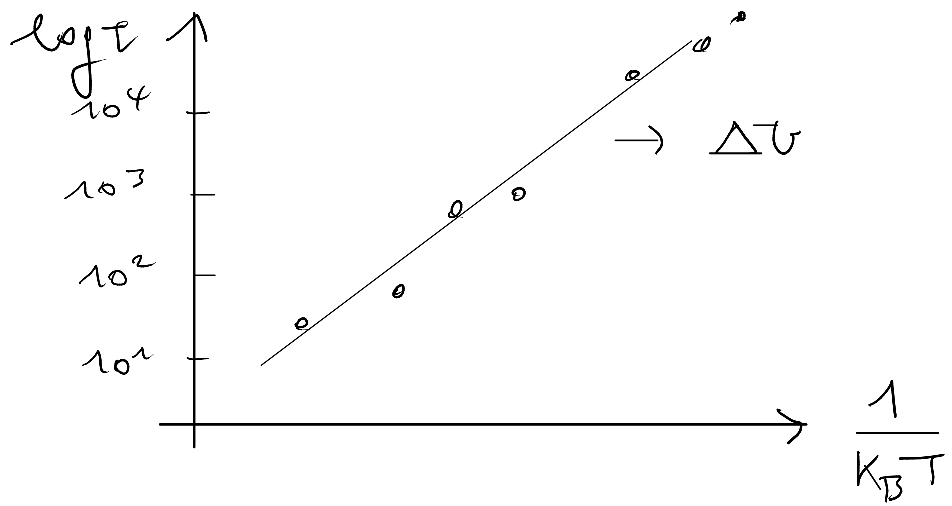
$$= \sqrt{\frac{2\pi k_B T}{m\omega_B^2}} \cdot \exp\left(\frac{U_B}{k_B T}\right)$$

Approssimazione per $x \approx x_A$: $U(x) \approx U(x_A) + \frac{1}{2} m\omega_A^2 (x - x_A)^2$

$$\int_{-\infty}^{x_B} dx'' \exp\left(-\frac{U_A}{K_BT}\right)\exp\left(-\frac{1}{2}\frac{m\omega_A^2}{K_BT}(x-x_A)^2\right) \approx \int_{-\infty}^{\infty} dx'' \left(-\frac{1}{2}\frac{m\omega_A^2}{K_BT}(x-x_A)^2\right)\cdot\exp\left(-\frac{U_A}{K_BT}\right)$$

$$= \sqrt{\frac{2\pi K_BT}{m\omega_B^2}}\exp\left(-\frac{U_A}{K_BT}\right)$$

$$\tau = \frac{\Delta p}{J} = \frac{\cancel{J}\,\varepsilon}{\cancel{K_BT}}\,\frac{1}{\cancel{J}}\,\frac{2\pi\,\cancel{K_BT}}{m\,\omega_A\,\omega_B}\exp\left(\frac{U_B-U_A}{K_BT}\right)$$




$$\tau = \frac{2\pi\,\varepsilon}{m\omega_A\omega_B}\exp\left(\frac{\Delta U}{K_BT}\right)$$ ← fattore di Arrhenius

$\omega_A \searrow \quad \tau \nearrow$

$\omega_B \searrow \quad \tau \nearrow$

$\varepsilon \nearrow \quad \tau \nearrow$