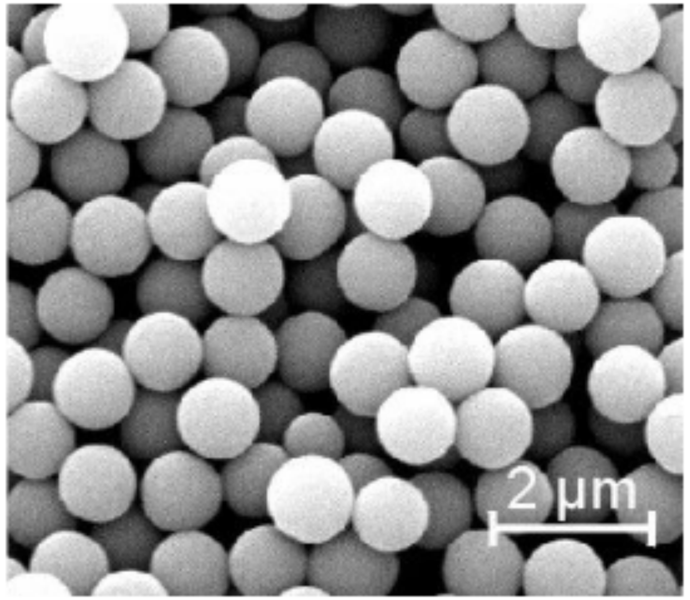
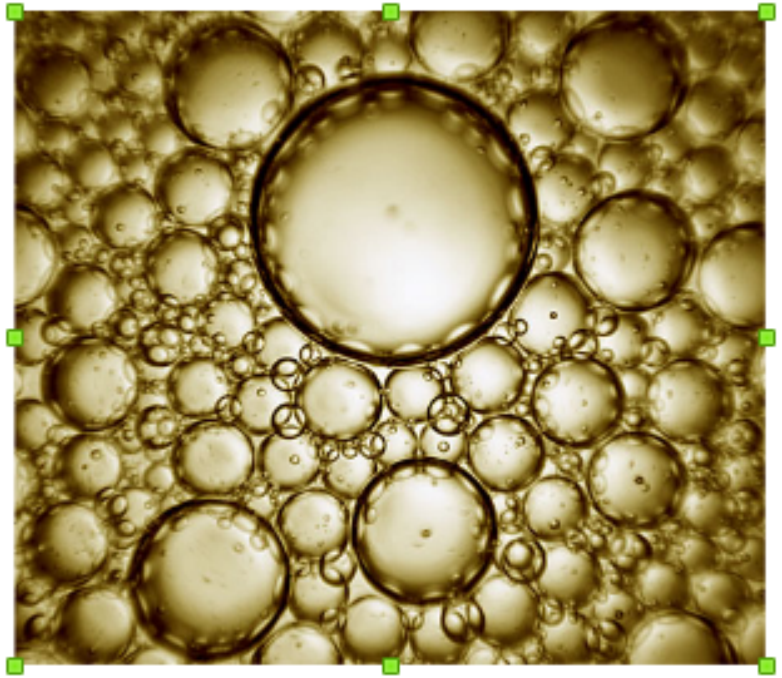
dispersione colloidale
Silica, PMMA



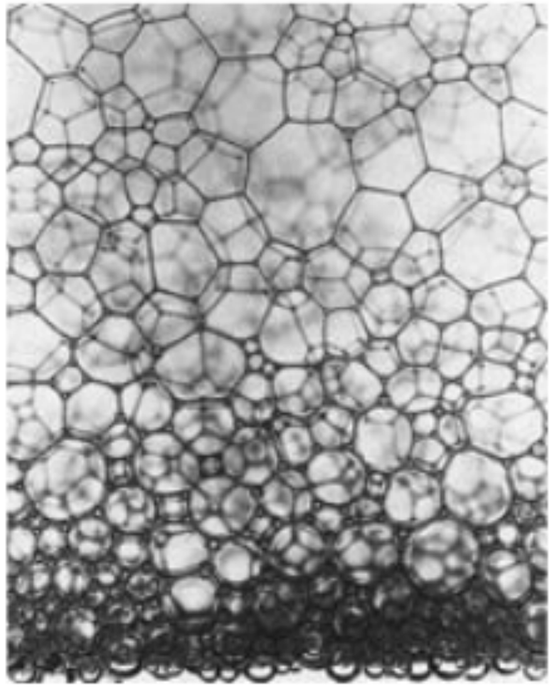
particelle solide

emulsione
mayo, latte



particelle liquide

schiuma



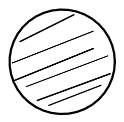
particelle gassose

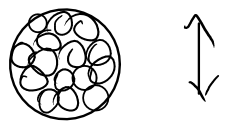
COLLOIDI

Def.: miscela fortemente asimmetrica composta da particelle **solide** di taglia **mesoscopica** disperse in un **solvente liquido**.

Microscopica: 0.1 nm – 10 nm
Mesoscopica: 10 nm – 10 μm ~ μm

Stabilità → no sedimentazione! → agitazione termica



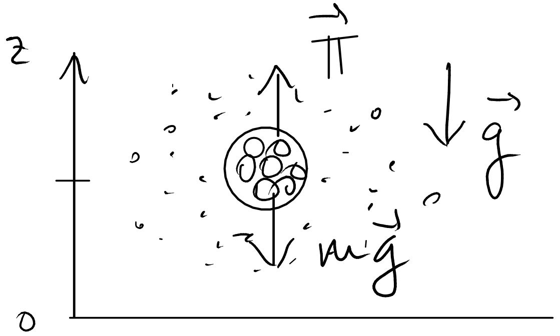


μm

macro
$N \sim N_A \sim 10^{23}$

meso
$N \sim \left(\frac{L}{\sigma}\right)^3 \sim \left(\frac{10^{-6}}{10^{-10}}\right)^3 \sim 10^{12}$

Criterio quantitativo



- σ dim. lineari
- ρ_c densità colloide
- T temperatura solvente
- equilibrio

$$H = H_0 + U(z)$$

$H_0 \to K_0,\ U_0$: particella colloidale libera

$U(z)$: campo esterno

Prob. di trovare la particella ad altezza z : $\quad p(z) \sim \exp(-\beta U(z))$

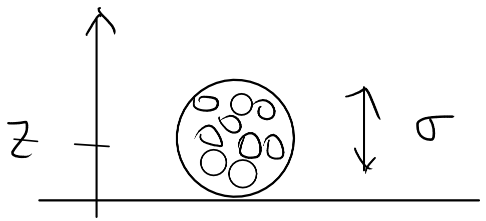
$$p(z) = \mathrm{Tr}_0\left[\frac{\exp(-\beta H)}{\mathrm{Tr}[\exp(-\beta H)]}\right] \qquad \mathrm{Tr}[\dots] = \mathrm{Tr}_z[\,\mathrm{Tr}_0[\dots]\,]$$

$\nearrow \Delta\rho$

$$= \frac{\mathrm{Tr}_0[\exp(-\beta H)]}{\mathrm{Tr}_0[\,\mathrm{Tr}_z[\exp(-\beta H)]\,]} = \frac{\exp(-\beta U(z))}{\mathrm{Tr}_z[\exp(-\beta U(z))]} = \frac{\exp(-\overbrace{\beta\, \rho_c \sigma^3 g}^{K} z)}{\int_0^\infty dz\, \exp(-\beta \rho_c \sigma^3 g z)}$$

$$\langle z \rangle = \frac{\int_0^\infty dz\, z\, e^{-Kz}}{\int_0^\infty dz\, e^{-Kz}} = \frac{\overbrace{\left[-\frac{1}{K} z e^{-Kz}\right]_0^\infty}^{=0} + \frac{1}{K}\int_0^\infty dz\, e^{-Kz}}{\frac{1}{K}} = \int_0^\infty dz\, e^{-Kz} = \frac{1}{K}$$

$$\langle z \rangle = \frac{k_B T}{\rho_c \sigma^3 g} > \sigma \Rightarrow \sigma < \sqrt[4]{\frac{k_B T}{\rho_c g}}$$



Es.: grafite $\rho_c \sim 10^3 \frac{kg}{m^3}$ @ $T_a \sim 300\,K$ $\quad k_B T_a \sim 10^{-23} \times 300\, J \simeq 4\times 10^{-21}\, J$

$$\sigma < \left(\frac{4\times 10^{-21}}{10^4}\right)^{1/4} \sim (4\times 10^{-25})^{1/4} \sim 10^{-6}\, m = 1\,\mu m$$

DINAMICA COLLOIDALE

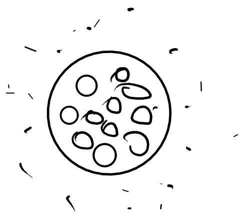
1827 : Brown (botanico) → moto browniano
1904 : Pearson (biologo)
1905 : Einstein → solvente ↔ particella colloidale
1906 : Langevin → eq. Langevin
1909 : Perrin → misura N_A → Nobel

EQUAZIONE DI LANGEVIN

Fenomenologica, classica

Particella di massa m in un solvente, coeff. attrito ξ, in campo esterno

$$m \frac{d\vec{v}}{dt} = - \underset{\substack{\uparrow \\ \text{attrito viscoso} \\ \text{macro}}}{\xi \vec{v}} + \vec{F}_{est} + \underset{\substack{\uparrow \\ \text{forza stocastica} \\ \text{micro}}}{\vec{\theta}(t)}$$



$\vec{\theta}(t)$ è una variabile stocastica

$$\langle \vec{\theta}(t) \rangle = \vec{0}$$

$$\langle \theta_\alpha(t)\, \theta_\beta(t') \rangle = 2\theta_0\, \delta_{\alpha\beta}\, \delta(t-t')$$

$\alpha, \beta = x, y, z$ $\qquad \langle \ldots \rangle$ sulle realizzazioni della forza stocastica

Particella libera : $\vec{F}_{est} = \vec{0}$

$$\frac{d\vec{v}}{dt} = -\frac{\xi}{m}\vec{v} + \frac{1}{m}\vec{\theta}(t) \quad \rightarrow \quad \text{eq. diff. stocastica} \quad (\text{Ito, Stratonovic})$$

$$\frac{dx}{dt} = a\,x(t) + b(t)$$

$$x(t) = e^{at}\,y(t)$$

$$\cancel{a\,e^{at}\,y(t)} + e^{at}\frac{dy}{dt} = \cancel{a\,e^{at}\,y(t)} + b(t)$$

$$\frac{dy}{dt} = e^{-at}\,b(t)$$

$$y(t) = \underbrace{y(0)}_{x(0)} + \int_0^t ds\, e^{-as}\, b(s)$$

$$x(t) = e^{at}x(0) + \int_0^t ds\, e^{-a(s-t)}\, b(s) \qquad a = -\frac{\xi}{m} \qquad b = \frac{1}{m}\vec{\theta}$$

Soluzione formale:

$$\vec{v}(t) = e^{-\xi/m\, t}\,\vec{v}(0) + \frac{1}{m}\int_0^t ds\, e^{-\xi/m\,(t-s)}\,\vec{\theta}(s)$$

Relazione fluttuazione – dissipazione

ξ e $\vec{\theta}$ non sono indipendenti. Equilibrio $\Rightarrow$ $\xi \leftrightarrow \vec{\theta}$

$\langle |\bar{v}|^2 \rangle = \langle v^2 \rangle$

$$\langle |\vec{v}(t)|^2 \rangle = \langle \vec{v}(t) \cdot \vec{v}(t) \rangle = e^{-\frac{2\xi}{m}t} \langle |\vec{v}(0)|^2 \rangle + \frac{2}{m} \int_0^t ds\, e^{-\frac{\xi}{m}(2t-s)} \underbrace{\langle \bar{v}(0) \cdot \bar{\theta}(s) \rangle}_{= \langle \bar{v}(0) \rangle \cdot \langle \bar{\theta}(s) \rangle = 0}$$

$$+ \underbrace{\frac{1}{m^2} \int_0^t ds \int_0^t ds'\, e^{-\xi/m(2t-s-s')} \langle \vec{\theta}(s) \cdot \bar{\theta}(s') \rangle}_{\frac{1}{m^2} \int_0^t ds \int_0^t ds'\, e^{-\xi/m(2t-s-s')}\, 6\theta_0 \delta(s-s')}$$

$$\frac{6\theta_0}{m^2} \int_0^t ds\, e^{-\frac{2\xi}{m}(t-s)}$$

$$\lim_{t\to\infty} \langle |\bar{v}(t)|^2 \rangle = \underbrace{e^{-\frac{2\xi}{m}t}}_{\to 0} \langle |\bar{v}(0)|^2 \rangle + \frac{6\theta_0}{m^2} \int_0^\infty ds\, e^{-\frac{2\xi}{m}(t-s)} = \frac{6\theta_0}{m^2} \frac{m}{2\xi} \underbrace{\left[e^{-\frac{2\xi}{m}(t-s)} \right]_0^t}_{1 - e^{-\frac{2\xi}{m}t},\ \to 0}$$

$$= \frac{3\theta_0}{\xi m}$$

$$\lim_{t\to\infty} \langle |\vec{v}(t)|^2 \rangle = \langle v^2 \rangle_{eq}$$

Teor. equipartizione energia :

$$\frac{1}{\cancel{2}} m \langle v^2 \rangle_{eq} = \frac{3}{\cancel{2}} K_B T$$

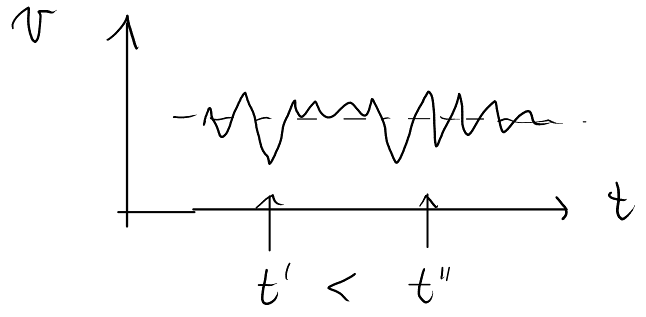
$$\frac{\cancel{3} K_B T}{\cancel{m}} = \frac{\cancel{3}\, \theta_0}{\xi\, \cancel{m}}$$

$$\boxed{\theta_0 = K_B T \cdot \xi}$$

$\uparrow$ fluttuazioni $\qquad$ $\uparrow$ dissipazione

<u>relazione di fluttuazione dissipazione</u>

Funzione di autocorrelazione della velocità



$$\langle v(t)\rangle = \lim_{T\to\infty} \frac{1}{T}\int_0^T dt_0\, v(t_0+t)$$

$$C_v(t',t'') = \langle (v(t') - \langle v\rangle)(v(t'') - \langle v\rangle)\rangle$$

Equilibrio : $\langle v\rangle = 0$, stazionario $t = t'' - t'$

$$C_v(t) = \langle v(t)\, v(0)\rangle = \langle v(t)\, v(0)\rangle_{eq}$$

In 3d

$$C_v(t) = \frac{1}{3}\langle \vec{v}(t)\cdot\vec{v}(0)\rangle$$

Eq. Langevin : (es.)

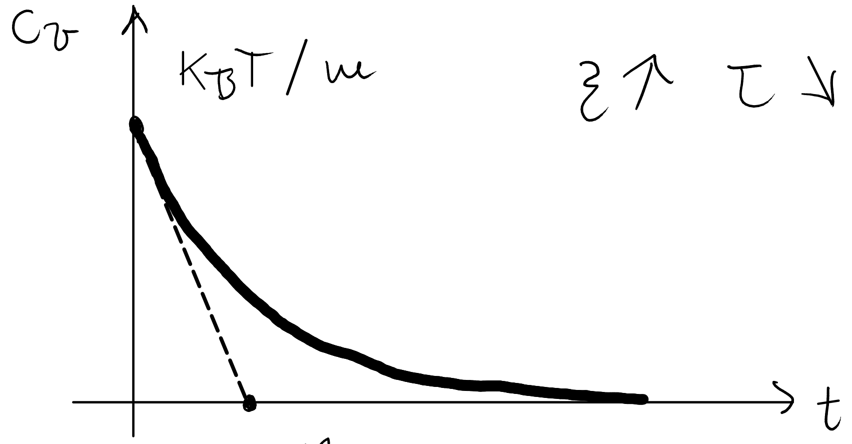
$$\frac{d\vec{v}}{dt} = -\frac{\xi}{m}\vec{v} + \frac{1}{m}\vec{\theta}(t)$$

$$\langle \vec{v}(0)\cdot\frac{d\vec{v}}{dt}\rangle = -\frac{\xi}{m}\langle\vec{v}(t)\cdot\vec{v}(0)\rangle + \frac{1}{m}\underbrace{\langle\vec{v}(0)\cdot\vec{\theta}(t)\rangle}_{=0}$$

$$\frac{d}{dt}\langle \vec{v}(t)\cdot\vec{v}(0)\rangle = -\frac{\xi}{m}\langle \vec{v}(t)\cdot\vec{v}(0)\rangle$$

$$C_v(t) = \frac{1}{3}\langle|\vec{v}(0)|^2\rangle \exp\left(-\frac{\xi}{m}t\right) = \frac{K_B T}{m}\exp\left(-\frac{\xi}{m}t\right) \rightarrow \text{eq.}$$

$$\langle\vec{v}(t)\rangle = \langle\vec{v}(0)\rangle \exp\left(-\frac{\xi}{m}t\right)$$



$\xi \uparrow \quad \tau \downarrow$

$\tau = \frac{m}{\xi}$ tempo di correlazione

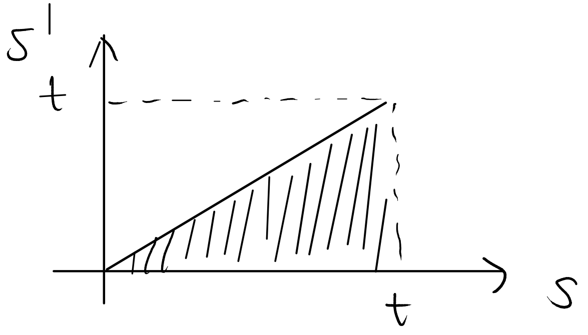
Spostamento quadratico medio

$$\langle |\Delta\vec{r}(t)|^2\rangle = \langle |\vec{r}(t)-\vec{r}(0)|^2\rangle$$

$$\Delta\vec{r}(t) = \int_0^t ds\, \vec{v}(s)$$

$$\langle |\Delta\vec{r}(t)|^2\rangle = \int_0^t ds \int_0^t ds' \langle \vec{v}(s)\cdot\vec{v}(s')\rangle$$

$$= 2\int_0^t ds \int_0^s ds' \langle \vec{v}(s)\cdot\vec{v}(s')\rangle$$



Equilibrio : variabile $t' = s-s'$

$$= 6\int_0^t ds \int_0^s ds'\, C_v(s-s') = 6\int_0^t ds \int_0^s dt'\, C_v(t')$$

$$\simeq 6\left\{ \left[s\int_0^s dt'\, C_v(t')\right]_0^t - \int_0^t ds\, s\, C_v(s)\right\}$$

$$\simeq 6\left\{ t\int_0^t dt'\, C_v(t') - \int_0^t ds\, s\, C_v(s)\right\}$$

$$\langle |\Delta\vec{r}(t)|^2\rangle = 6t\int_0^t ds\, C_v(s)\left(1-\frac{s}{t}\right)$$

(es.) : Langevin

$$\langle|\Delta\vec r|^2\rangle = 6\,\frac{K_BT}{\xi}\left[t+\frac{m}{\xi}\left(e^{-\xi/m\,t}-1\right)\right]$$

Tempi corti: $t \ll \frac{m}{\xi}$

$$\langle|\Delta\vec r|^2\rangle \approx 6\,\frac{K_BT}{\xi}\left[t+\frac{m}{\xi}\left(\cancel{1}-\frac{\xi}{m}t+\frac{1}{2}\frac{\xi^2}{m^2}t^2-\cancel{1}\right)\right]$$

$$\approx 3\,\frac{K_BT}{\xi}\,\frac{\xi}{m}\,t^2 = 3\,\underbrace{\frac{K_BT}{m}}_{\langle|\vec v(0)|^2\rangle}\,t^2$$

balistico $\sim t^2$

Tempi lunghi: $t \gg \frac{m}{\xi}$

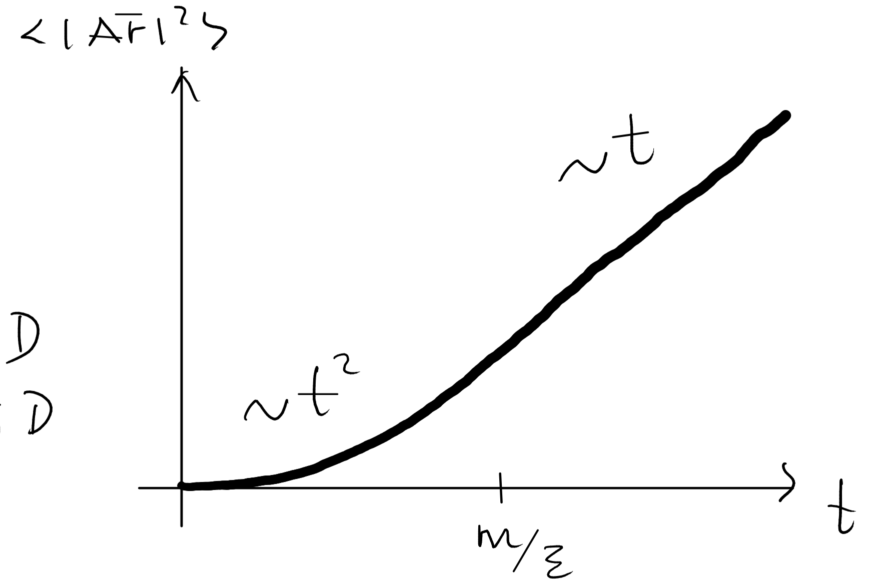
$$\langle|\Delta\vec r|^2\rangle \approx 6\,\frac{K_BT}{\xi}\,t$$

diffusivo $\sim t$

$$\langle|\Delta\vec r|^2\rangle = 2\,\underset{\substack{\uparrow\\ \text{dimensioni spaziali}}}{d}\,D\,t \quad\Rightarrow\quad D=\frac{K_BT}{\xi}$$

$\uparrow T \ \uparrow D$

$\uparrow \xi \ \downarrow D$



EQUAZIONE DI LANGEVIN SOVRA-AMORTITA

$$m \underbrace{\frac{d\vec{v}}{dt}}_{\text{inerziale}} = -\xi \vec{v} + \vec{\theta}(t) \qquad \xi \to \infty \qquad \theta_0 \sim \xi \ (\text{eq.})$$

Regime sovra-amortito particella libera:

$$\frac{d\vec{r}}{dt} = \frac{1}{\xi} \vec{\theta}(t)$$

Soluzione formale:

$$\vec{r}(t) = \vec{r}(0) + \frac{1}{\xi} \int_0^t \vec{\theta}(s)\, ds$$

$$\to 3 \cdot 2 \cdot \theta_0\, \delta(s-s') \qquad \theta_0 = K_B T \cdot \xi$$

$$\langle |\Delta \vec{r}(t)|^2 \rangle = \frac{1}{\xi^2} \int_0^t ds \int_0^t ds' \langle \vec{\theta}(s) \cdot \vec{\theta}(s') \rangle = \frac{6\theta_0}{\xi^2} \int_0^t ds = 6 \frac{\theta_0}{\xi^2} t \sim 6 \underbrace{\frac{K_B T}{\xi}}_{D} t$$

Applicazioni

- forza costante
- potenziale armonico
- forzante sinusoidale
- particella attiva

Dinamica Browniana:

$$\xi \frac{d\vec{r}}{dt} = \vec{F}_{est}(\vec{r}(t)) + \vec{\theta}(t)$$

Algoritmo di Ermak: potenziale generico

$$\xi \frac{dx}{dt} = F(x) + \theta(t) \qquad \langle \theta(t) \rangle = 0 \qquad \langle \theta(t)\theta(t') \rangle = 2\theta_0 \delta(t-t')$$

Eulero: breve intervallo Δt

$$x(t+\Delta t) \approx x(t) + \frac{1}{\xi}\int_t^{t+\Delta t} F(x)\,dt' + \frac{1}{\xi}\int_t^{t+\Delta t} \theta(t')\,dt'$$

$$\approx x(t) + \frac{F(x)}{\xi}\Delta t + \underbrace{\frac{1}{\xi}\int_t^{t+\Delta t} \theta(t')\,dt'}_{\tilde{\theta}(t;\Delta t)}$$

$\tilde{\theta}(t;\Delta t) \to$ gaussiana

$\theta_0 = K_B T \cdot \xi$

$$\begin{cases} \langle \tilde{\theta} \rangle = 0 \\ \langle \tilde{\theta}(t;\Delta t)^2 \rangle = \frac{1}{\xi^2}\int_t^{t+\Delta t} dt' \int_t^{t+\Delta t} dt'' \underbrace{\langle \theta(t')\theta(t'') \rangle}_{2\theta_0 \delta(t'-t'')} = \frac{2\theta_0}{\xi^2}\int_t^{t+\Delta t} dt' = 2\frac{\theta_0}{\xi^2}\Delta t \end{cases}$$

$$= 2D\Delta t$$

Distrib. prob. per $\tilde{\theta}$

$$p(\tilde{\theta}) = \frac{1}{\sqrt{4\pi D \Delta t}} \exp\left(-\frac{\tilde{\theta}^2}{4D\Delta t}\right) \qquad ⚠ \quad \Delta t$$

3d :

$$p(\vec{\tilde{\theta}}) = \frac{1}{(4\pi D \Delta t)^{3/2}} \exp\left(-\frac{|\vec{\tilde{\theta}}|^2}{4D\Delta t}\right)$$

LANGEVIN → FOKKER–PLANCK $p(\vec{v})$ $(\vec{F}_{est} = \vec{0})$

LANGEVIN → KRAMERS $p(\vec{r}, \vec{v})$

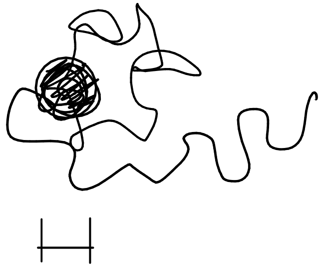
LANGEVIN SOVRA-AMORTITA → SMOLUCHOWSKI $p(\vec{r})$

eq. diff. ordinarie STOCASTICHE → eq. diff. alle derivate parz. DETERMINISTICHE

Condizione di validità di Langevin sovra-amortita

$\frac{m}{\xi} \rightarrow$ tempo di correlazione

$$\frac{m}{\xi} \ll \frac{\sigma^2 \xi}{K_B T} \Rightarrow \xi \gg \sqrt{\frac{K_B T \cdot m}{\sigma^2}}$$



σ

$$\langle |\Delta \vec{r}(\tau)|^2 \rangle \sim D\tau$$

$$\sigma^2 \sim D\tau$$

$$\tau \sim \frac{\sigma^2}{D} = \frac{\sigma^2 \xi}{K_B T}$$

(es.) balistico $\langle v^2 \rangle$

EQUAZIONE DI SMOLUCHOWSKI.

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

Spostamento dopo intervallo Δt

$$h = \frac{1}{\xi} F \Delta t + \frac{1}{\xi} \int_t^{t+\Delta t} \theta(s)\, ds \qquad \triangle\!\!\!\!\!\,\cdot\ F = F(x)$$

Densità di prob. di h sia gaussiana

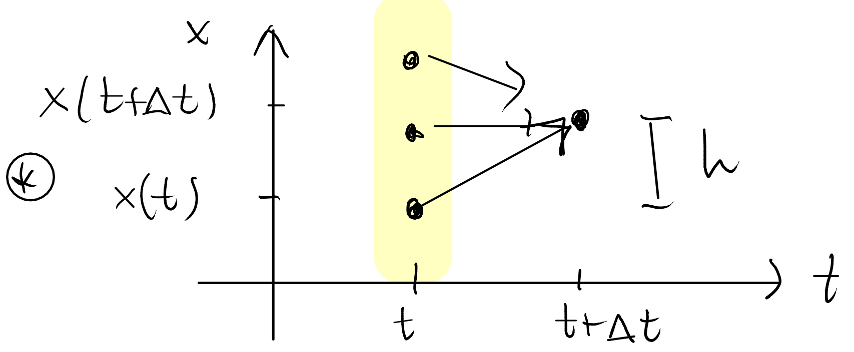
$$D = \frac{k_B T}{\xi}$$

$$\begin{cases} \langle h \rangle = \dfrac{F}{\xi} \Delta t \\ \langle (h - \langle h \rangle)^2 \rangle = \dfrac{1}{\xi^2} \displaystyle\int_t^{t+\Delta t} ds \int_t^{t+\Delta t} ds' \, \langle \theta(s)\,\theta(s') \rangle = 2 \frac{\theta_0}{\xi^2} \Delta t = 2 D \Delta t \end{cases}$$

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

Master equation per $p(x,t)$

$$p(x,t+\Delta t) = \int_{-\infty}^{\infty} dh\; \underbrace{p(x-h,t)\,\Pi(h,x-h)}_{\varphi(x-h)\,=\,\varphi(y)} = (*)$$



Taylor II ordine : $y = x \qquad \Delta y = -h$

$$\langle \delta h^2 \rangle = \langle h^2 \rangle - \langle h \rangle^2$$

$$(*) = \int_{-\infty}^{\infty} dh \left[\varphi(x) + \frac{d\varphi}{dy}\Delta y + \frac{1}{2}\frac{d^2\varphi}{dy^2}\Delta y^2 \right]$$

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

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

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

Taylor I ordine in Δt

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

Eq. Smoluchowski

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

$$\frac{\partial p}{\partial t} = \frac{\partial}{\partial x}\left[-\frac{1}{\xi}Fp\right] + D\frac{\partial^2 p}{\partial x^2} \qquad D = \text{cost} \qquad \rightarrow \text{ drift} - \text{diffusion}$$

deriva diffusione

$$\frac{\partial p}{\partial t} + \frac{\partial}{\partial x}\Big[\underbrace{\frac{1}{\xi}Fp - D\frac{\partial p}{\partial x}}\Big] = 0$$

J = densità di corrente

3d: $\frac{\partial p}{\partial t} = -\vec{\nabla}\cdot\left(\frac{1}{\xi}p\vec{F}\right) + \nabla^2[Dp]$

condizioni contorno: $p = 0$; $J = 0$

condizione iniziale: $p(x,0) = \delta(x)$

Fokker-Planck: $\frac{\partial p}{\partial t} = \frac{\partial}{\partial v}\left(\frac{\xi}{m}v(t)\,p(v,t) + \frac{\xi^2}{m^2}D\frac{\partial p}{\partial v}\right) \rightarrow p(v,t)$ (es.)

Casi particolari

1) Equilibrio

$$\frac{\partial p}{\partial t} = 0 \qquad F = -\frac{dU}{dx} \qquad p(x) \sim \exp\left(-\frac{U(x)}{K_B T}\right) \qquad D = \frac{K_B T}{\xi}$$

$$\frac{1}{\xi}\left(-\frac{dU}{dx}\right) p(x) - \frac{\cancel{K_B T}}{\xi}\left(-\frac{dU}{dx}\right)\frac{1}{\cancel{K_B T}} p(x) = 0$$ (corrente nulla)

2) Particella libera

$$\frac{\partial p}{\partial t} = D \frac{\partial^2 p}{\partial x^2}$$ eq. diffusione $\rightarrow$ $$\frac{\partial p}{\partial t} = D \nabla^2 p$$ 3d

Trasf. Fourier

$$p_{\vec{k}}(t) = \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}}\, p(\vec{r},t)$$

Anti-trasf. Fourier

$$p(\vec{r},t) = \frac{1}{(2\pi)^3} \int d\vec{k}\, e^{i\vec{k}\cdot\vec{r}}\, p_{\vec{k}}(t)$$

$$\frac{\partial p_{\vec{k}}}{\partial t} = -K^2 D\, p_{\vec{k}} \qquad |\vec{K}|^2 = K^2$$

$$p_{\vec{k}}(t) = p_{\vec{k}}(0)\, \exp(-K^2 D t)$$

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

$p_{\vec{k}}(0) = 1$

$$p(\vec{r},t) = \frac{1}{(4\pi D t)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right)$$

3) Forza costante 1d

$F = \text{cost} \to p(x,t)$

$$\frac{\partial p}{\partial t} = -\frac{\partial}{\partial x}\left[\frac{1}{\zeta} F p\right] + D \frac{\partial^2 p}{\partial x^2}$$

Cambio variabile: $y = x - \frac{F}{\zeta} t \qquad dx = dy$

$y = y(t)$

$$p(x,t)\, dx\, dt = q(y,t)\, dy\, dt \Rightarrow p(x,t) = q(y,t) \to \frac{\partial p}{\partial x} = \frac{\partial q}{\partial y}$$

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

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

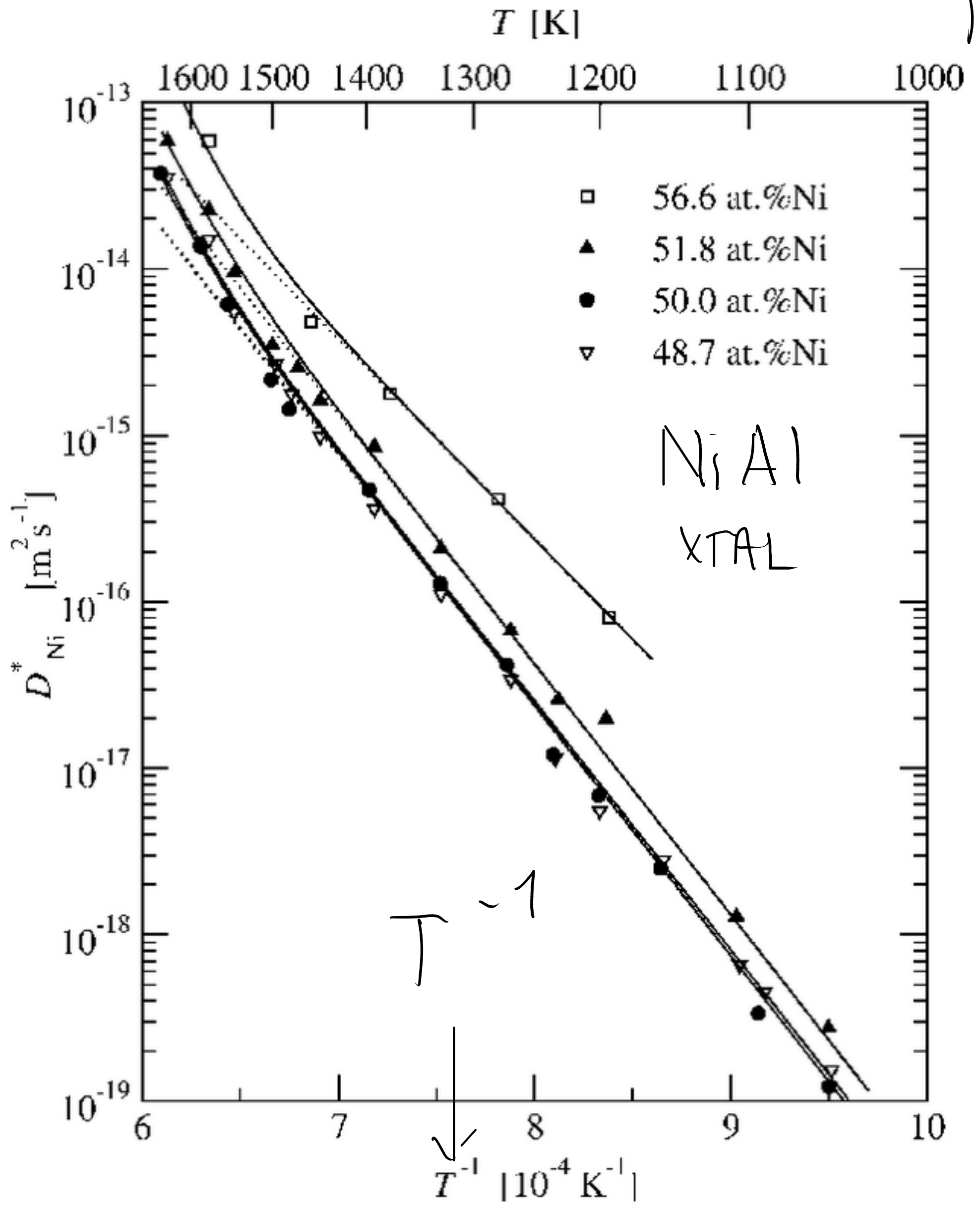
$$p(x,t) = \frac{1}{\sqrt{4\pi D t}} \exp\left[-\frac{(x-\frac{F}{z}t)^2}{4Dt}\right]$$

$$\begin{cases} \langle x \rangle = \frac{F}{z} t & \rightarrow \text{deriva} \\ \langle (x - \langle x \rangle)^2 \rangle = 2Dt & \rightarrow \text{diffusione} \end{cases}$$

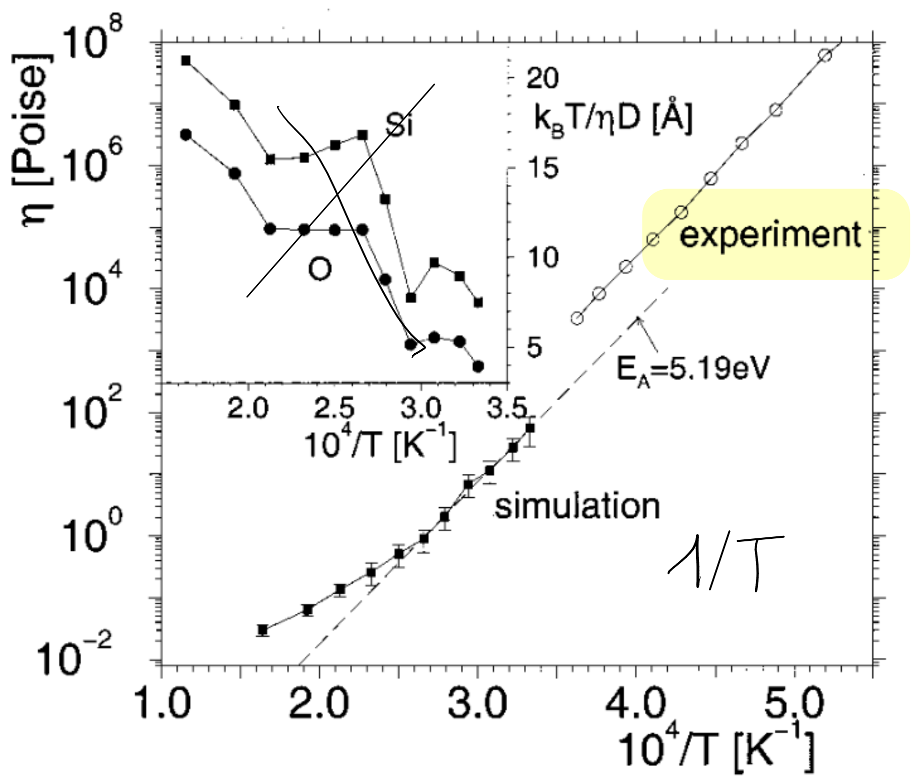
$e^{-\frac{A}{T}}$

$\eta \sim e^{\frac{\Delta E}{K_B T}}$ legge di Arrhenius

$e^{\frac{A}{T}}$



The Arrhenius diagram of Ni diffusion in different NiAl alloys (the composition is indicated in at.%Ni). The dotted lines present the extrapolation of the Arrhenius fits obtained in the low-temperature interval, T , 1500 K, of the experiments.



SiO_2

silice

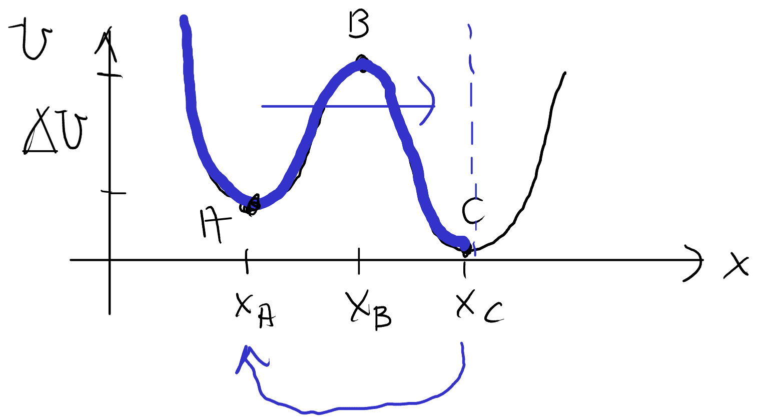
amorfa

FIG. 10. Main figure: Arrhenius plot of the shear viscosity from the simulation (solid squares). The dashed line is a fit with an Arrhenius law to our low-temperature data. The open circles are experimental data from Urbain *et al.* (Ref. 35). Inset: temperature dependence of the left hand side of Eq. (12) to check the validity of the Stokes-Einstein relation.

4) Attivazione termica : problema di Kramers (1940)

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

$$\frac{\partial p}{\partial t} = \frac{\partial}{\partial x}\left[-\frac{F}{\xi}p + D\frac{\partial p}{\partial x}\right] = \frac{\partial}{\partial x}\Big[\overbrace{\frac{1}{\xi}\frac{dU}{dx}p + D\frac{\partial p}{\partial x}}^{\sim J}\Big]$$



$$D = \frac{k_B T}{\xi} \quad (\Leftarrow \text{rel. fluttuazione dissip.})$$

Regime stazionario : $\frac{\partial p}{\partial t} = 0$

$$\frac{1}{\xi}\frac{dU}{dx}p + \frac{k_B T}{\xi}\frac{dp}{dx} = -J = \text{cost}$$

$p(x_C) = 0$ assorbenti

Goal: tempo di uscita

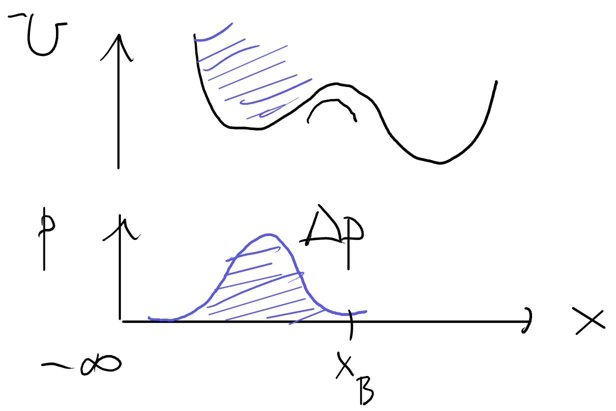
$$p(x) = \psi(x)\exp\left(-\frac{U(x)}{k_B T}\right) \Rightarrow \frac{1}{\xi}\frac{dU}{dx}p + \frac{k_B T}{\xi}\frac{d\psi}{dx}\exp\left(-\frac{U(x)}{k_B T}\right)$$

$$+ \frac{\cancel{k_B T}}{\xi}\left(-\frac{dU}{dx}\right)\frac{1}{\cancel{k_B T}}p = -J$$

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

$$p(x_c) = 0 \Rightarrow \psi(x_c) = 0$$

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



$$\Delta p = \int_{-\infty}^{x_B} p(x)\, dx = \underset{\text{densità di corrente}}{J}\ \underset{\text{tempo di uscita}}{\tau}$$

$$\tau = \frac{\xi}{k_B T} \int_{-\infty}^{x_B} dx'' \exp\left(- \frac{U(x'')}{k_B T} \right) \int_{x''}^{x_c} dx' \exp\left(\frac{U(x')}{k_B T} \right)$$

$\int_{x''}^{x_c} dx' \exp\left(\frac{U(x')}{k_B T} \right)$ è $\approx$ cost per $x'' \approx x_A$

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

$$\exp\left(\frac{U(x_B)}{K_B T}\right) \int_{x''}^{x_c} dx' \exp\left[-\frac{1}{2}\frac{m\omega_B^2}{K_B T}(x-x_B)^2\right] \approx \exp\left(\frac{U_B}{K_B T}\right) \int_{-\infty}^{\infty} dx' \exp\left[-\frac{1}{2}\frac{m\omega_B^2}{K_B T}(x-x_B)^2\right]$$

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

$$\tau \approx \frac{\xi}{K_B T} \sqrt{\frac{2\pi K_B T}{m\omega_B^2}} \exp\left(\frac{U_B}{K_B T}\right) \int_{-\infty}^{x_B} dx'' \exp\left(-\frac{U(x'')}{K_B T}\right)$$

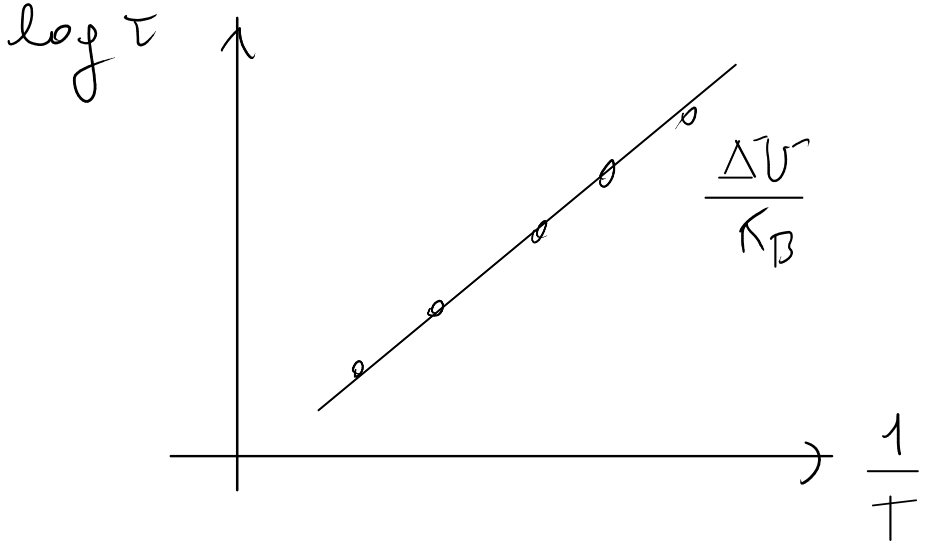
$$U(x'') \approx U_A + \frac{1}{2} m\omega_A^2 (x-x_A)^2$$

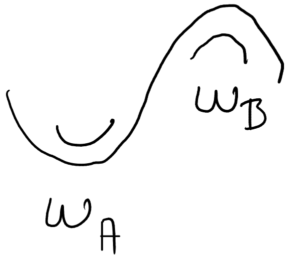
$$\tau \approx \frac{\xi}{K_B T} \sqrt{\frac{2\pi K_B T}{m\omega_B^2}} \exp\left(\frac{U_B}{K_B T}\right) \exp\left(-\frac{U_A}{K_B T}\right) \int_{-\infty}^{\infty} dx'' \exp\left[-\frac{1}{2}\frac{m\omega_A^2}{K_B T}(x-x_A)^2\right]$$

$$\approx \frac{\xi}{\cancel{K_B T}} \frac{2\pi \cancel{K_B T}}{m\,\omega_A \omega_B} \exp\left(\frac{U_B - U_A}{K_B T}\right)$$

Tempo di uscita

$$\tau \approx \frac{2\pi\xi}{m\,\omega_A\,\omega_B}\exp\left(\frac{\Delta U}{K_B T}\right)$$ → fattore di Arrhenius





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

$\nearrow \xi \quad \nearrow \tau$