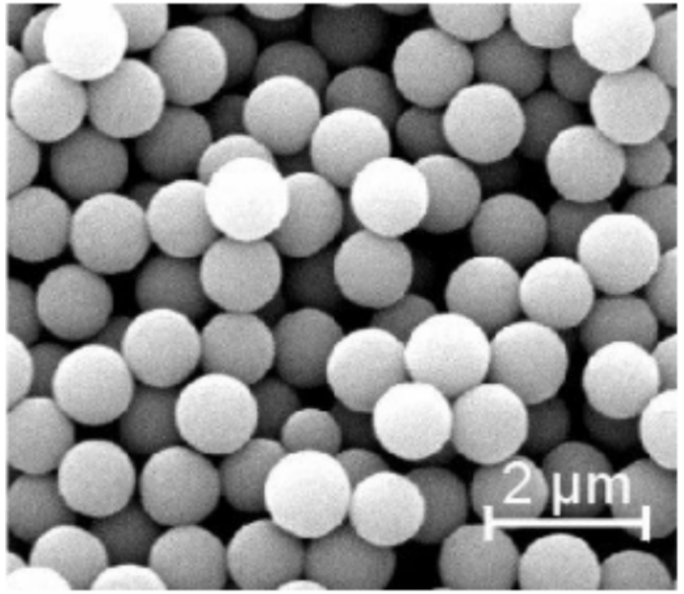
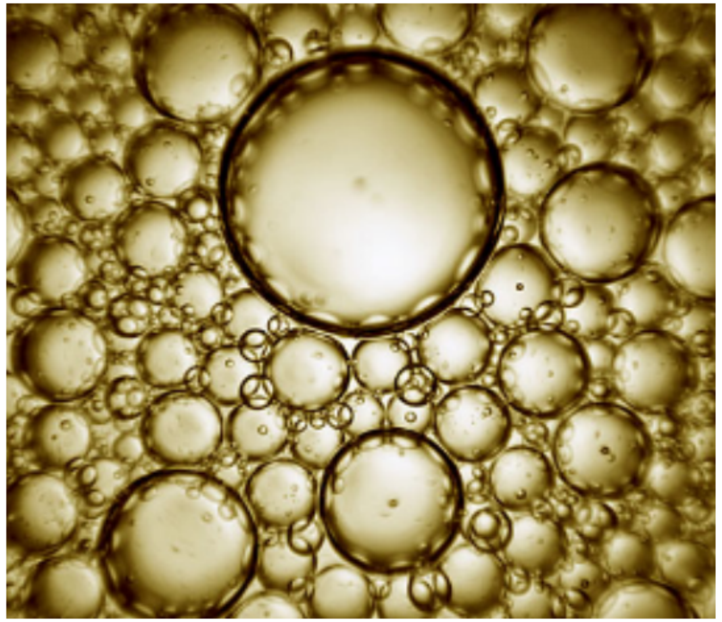
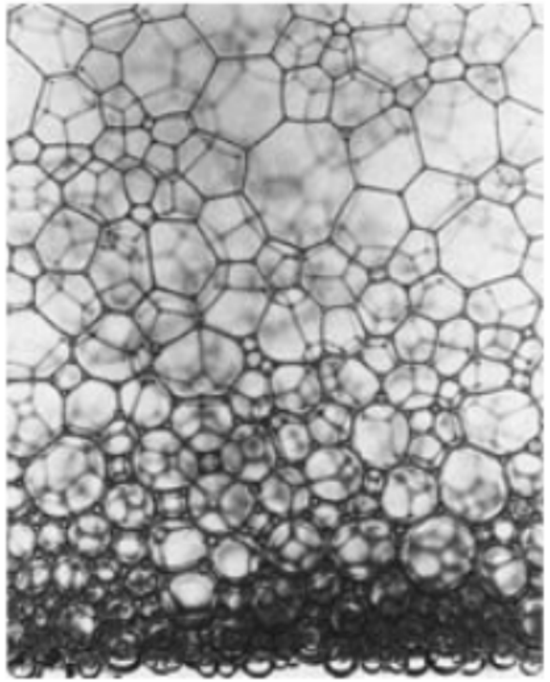


SOSPENSIONE COLLOIDALE



EMULSIONE



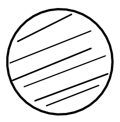
SCHIUMA

COLLOIDI

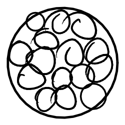
Def: miscela fortemente asimmetrica composta da particelle solide di taglia mesoscopica sospese in un solvente liquido (micro)

micro : $10^{-10} - 10^{-9}$ m

meso : $10^{-9} - 10^{-5}$ m $\sim 10^{-6}$ μm



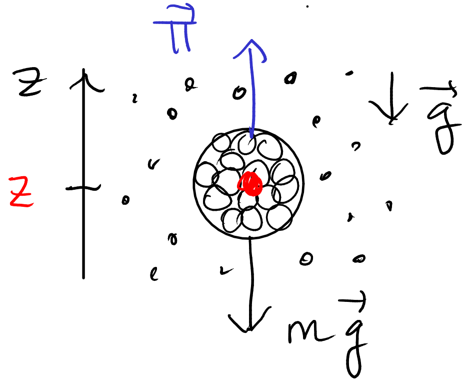
$N \sim N_A \sim 10^{23}$



$N \sim \left(\frac{L}{a}\right)^3 \sim \left(\frac{10^{-6}}{10^{-10}}\right)^3 \sim 10^{12}$ $\Rightarrow$ agitazione termica

Stabilità $\longrightarrow$ sedimentazione

Criterio di stabilità



σ : dim. lineari

ρ_c : densità colloide

ρ_s : densità solvente ($\rho_s \ll \rho_c$)

T : temperatura, equilibrio

$$H = \underbrace{H_0}_{\substack{\uparrow \\ \text{particella colloidale} \\ K_0 + U_0}} + \underbrace{U(z)}_{\substack{\uparrow \\ \text{campo esterno}}}$$

Prob. di trovare la particella ad altezza z

$$\mathrm{Tr}[\ \ ] = \mathrm{Tr}_z[\mathrm{Tr}_0[\ldots]]$$

$$U = \rho_c \sigma^3 g z \to \Delta\rho\, \sigma^3 g z$$

$$p(z) \sim e^{-\beta U(z)}$$

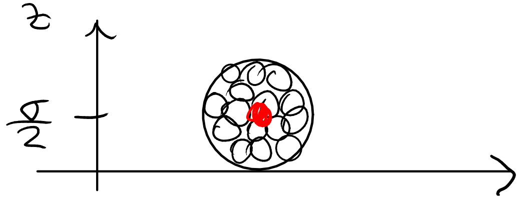
$$p(z) = \frac{\mathrm{Tr}_0[e^{-\beta H}]}{\mathrm{Tr}[e^{-\beta H}]} = \frac{\mathrm{Tr}_0[e^{-\beta H_0} e^{-\beta U(z)}]}{\mathrm{Tr}_z[\mathrm{Tr}_0[e^{-\beta H_0} e^{-\beta U(z)}]]} = \frac{\cancel{\mathrm{Tr}_0[e^{-\beta H_0}]}\, e^{-\beta U(z)}}{\cancel{\mathrm{Tr}_0[e^{-\beta H_0}]}\, \mathrm{Tr}_z[e^{-\beta U(z)}]}$$

$$= \frac{e^{-\beta U(z)}}{\int_0^\infty dz\, e^{-\beta U(z)}} = \frac{e^{-\boxed{\beta \rho_c \sigma^3} z}}{\int_0^\infty dz\, e^{-\beta \rho_c \sigma^3 z}} = \frac{e^{-kz}}{\int_0^\infty dz\, e^{-kz}} \qquad k = \beta \rho_c \sigma^3 g$$

$$\langle z \rangle = \frac{\int_0^\infty dz\, z\, e^{-kz}}{\int_0^\infty dz\, e^{-kz}} = \frac{1}{\frac{1}{k}} \left\{ \underbrace{\left[-\frac{1}{k} e^{-kz} \cdot z \right]_0^\infty}_{=0} + \frac{1}{k} \overbrace{\int_0^\infty dz\, e^{-kz}}^{1/k} \right\} = \frac{1}{k}$$

$$\langle z \rangle = \frac{\boxed{k_B T}}{g \rho_c \sigma^3}$$

$$\frac{k_B T}{g \rho_c \sigma^3} \gtrsim \sigma$$



Stabilità

$$\frac{k_B T}{g \rho_c \sigma^4} \gtrsim 1$$

Es: grafite in H_2O @T_a

$$\rho_c \approx 10^3 \frac{kg}{m^3}$$

$$k_B T_a \approx 10^{-23} \frac{J}{K} \cdot 300K = 4 \times 10^{-21} J$$

$$\sigma = \left(\frac{4 \times 10^{-21}}{10 \times 10^3} m^4 \right)^{1/4} \sim 10^{-6} m$$

DINAMICA COLLOIDALE

1827 : Brown → moto browniano

1904 : Pearson → biologo

1905 : Einstein → particella colloidale ⟷ solvente

1906 : Langevin

1909 : Perrin → N_A ⇒ Nobel

EQUAZIONE DI LANGEVIN

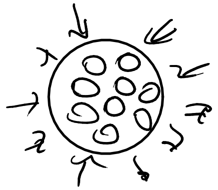
Fenomenologica, classica, stocastica

Particella di massa m in un solvente, forza esterna $\vec{F}_{est}$, II legge Newton

$$\begin{cases} m \dfrac{d\vec{v}}{dt} = -\xi \vec{v} + \vec{F}_{est} + \vec{\theta}(t) \\ \langle \vec{\theta}(t) \rangle = \vec{0} \quad ; \quad \langle \theta_\alpha(t)\, \theta_\beta(t') \rangle = 2\theta_0\, \delta_{\alpha\beta}\, \delta(t-t') \end{cases}$$

ξ ↑ coeff attrito viscoso macro

$\vec{\theta}(t)$ ↑ forza stocastica micro



$\alpha, \beta = x, y, z$

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

$\langle \dots \rangle$ sulle realizzazioni della forza stocastica

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

$$\frac{d\vec{v}}{dt} = -\frac{\xi}{m}\vec{v} + \frac{1}{m}\vec{\theta}(t) \quad \to \quad \text{Ito, Stratonovich}$$

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

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

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

$$\frac{dy}{dt} = e^{-at}\,b(t) \quad \to \quad y(t) = \underbrace{y(0)}_{x(0)} + \int_0^t ds\, e^{-as}\, b(s)$$

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

Soluzione "formale":

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

Relazione fluttuazione – dissipazione

$\vec{\theta} \leftrightarrow \xi$ stato di equilibrio

$$\langle \vec{v}(t)\cdot\vec{v}(t)\rangle = \langle|\vec{v}(t)|^2\rangle$$

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

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

$$\frac{6\theta_0}{m^2}\int_0^t ds\int_0^t ds'\, e^{-\xi/m(2t-s-s')}\,\delta(s-s') = \frac{6\theta_0}{m^2}\int_0^t ds\, e^{-2\xi/m(t-s)}$$

$$= \frac{6\theta_0}{m^2}\,\frac{m}{2\xi}\left[e^{2\xi/m(s-t)}\right]_0^t \qquad 1-0$$

$$\lim_{t\to\infty}\langle|\vec{v}(t)|^2\rangle = \underbrace{\lim_{t\to\infty}\langle|\vec{v}|^2\rangle e^{-2\xi/m\,t}}_{=0} + \lim_{t\to\infty}\frac{3\theta_0}{m\xi}\left[e^{\frac{2\xi}{m}(s-t)}\right]_0^t = \frac{3\theta_0}{m\xi}$$

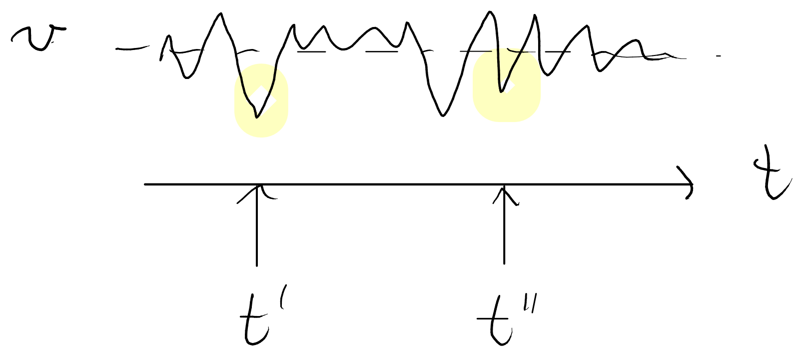
Solvente = bagno termico in eq. a temp. T : teor. equipartizione energia

$$\frac{1}{2} m \langle |\vec{v}|^2 \rangle = \frac{3}{2} K_B T \qquad \langle |\vec{v}|^2 \rangle = \frac{3 K_B T}{m}$$

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

relazione fluttuazione - dissipazione

Funzione di autocorrelazione della velocità



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

1d:

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

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

3d:

$$C_v(t',t'') = \frac{1}{3}\langle \vec{v}(t')\cdot\vec{v}(t'')\rangle$$

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

Equilibrio: $\langle \dots \rangle = \langle \dots \rangle_{eq}$

$$C_v(t) = \frac{1}{3}\langle \vec{v}(t)\cdot\vec{v}(0)\rangle_{eq} \qquad t>0 \qquad (t''>t')$$

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

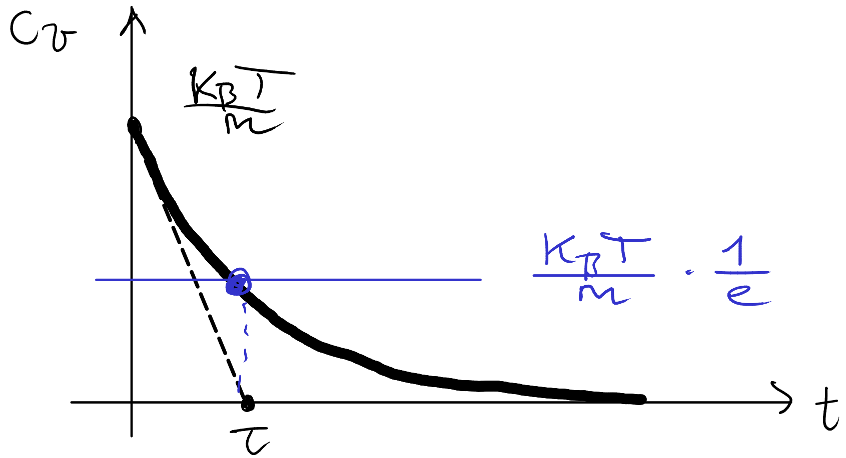
$$= \frac{1}{3}\langle |\vec{v}(0)|^2\rangle_{eq}\, e^{-\xi/m\, t} + \frac{1}{m}\int_0^t ds\, e^{-\xi/m(t-s)}\, \overbrace{\langle \vec{v}(0)\cdot\vec{\theta}(s)\rangle_{eq}}^{=0}$$

$$= \frac{k_B T}{m}\, e^{-\xi/m\, t}$$

Tempo di correlazione: $\tau = \frac{m}{\xi}$

$m \uparrow \quad \tau \uparrow$

$\xi \uparrow \quad \tau \searrow$



$$\langle \vec{v}(t)\rangle = \vec{v}(0)\, e^{-\xi/m\, t}$$

$\uparrow$

tempo di rilassamento

(es.) Mostra che

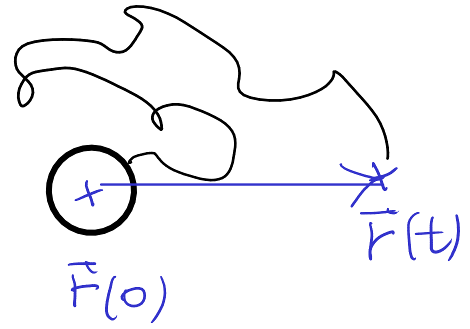
$$\langle \vec{v}(t')\cdot\vec{v}(t'')\rangle = \left[|\vec{v}(0)|^2 - \frac{3\theta_0}{m\xi}\right] e^{-\xi/m(t'+t'')} + \frac{3\theta_0}{m\xi}\, e^{-\xi/m\,|t''-t'|} \leftarrow ⚠$$

$$\langle |\vec{v}(0)|^2\rangle_v = \frac{3\theta_0}{m\xi}$$

Spostamento quadratico medio

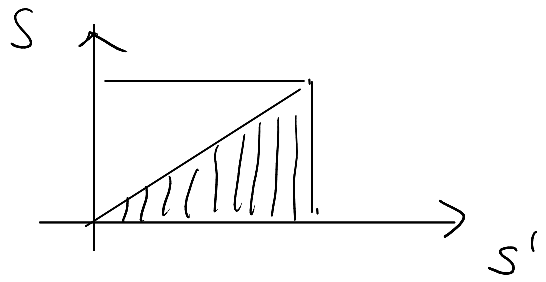
$$\langle |\Delta \vec r(t)|^2 \rangle_{eq} = \langle |\vec r(t) - \vec r(0)|^2 \rangle_{eq}$$

equilibrio $\langle \ldots \rangle = \langle \ldots \rangle_{eq}$



Relazione generale tra $\langle |\Delta \vec r|^2 \rangle$ e $C_v(t)$

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



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

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

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

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

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

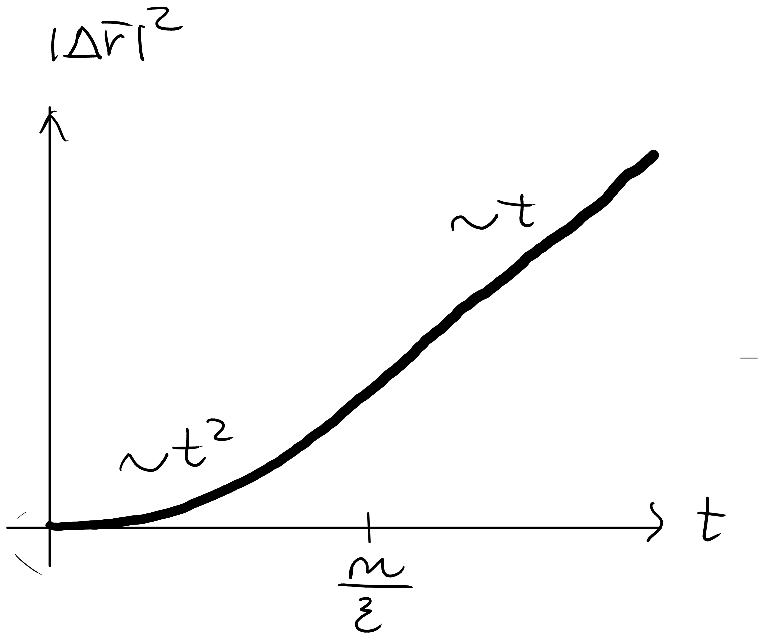
$$= 6 \left\{ t \int_0^t dt'\, C_v(t') - \int_0^t ds\, s\, C_v(s) \right\}$$

$$= 6\, t \left\{ \int_0^t ds \left(1 - \frac{s}{t}\right) C_v(s) \right\} \quad \square$$

(es.) Mostra che:

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

<u>Tempi corti</u>: $t \ll \frac{m}{\xi}$ Taylor II ordine



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

$$= 6 \frac{k_B T}{\xi} \left[\cancel{t} - \cancel{t} + \frac{1}{2} \frac{\xi}{m} t^2 \right]$$

$$= \frac{3 k_B T}{m} t^2 = \langle |\vec{v}|^2 \rangle t^2 \quad \text{balistico}$$

<u>Tempi lunghi</u>: $t \gg \frac{m}{\xi}$

$$\langle |\Delta \vec{r}|^2 \rangle \approx 6 \frac{k_B T}{\xi} t \quad \text{diffusivo}$$

$$= 2 \cdot \underset{\substack{\downarrow \\ =3}}{d} \cdot D \cdot t$$

$\leftarrow$ coeff. di diffusione : $D = \frac{k_B T}{\xi}$

$\nearrow \xi \searrow D$

$\nearrow T \nearrow D$

EQUAZIONE DI LANGEVIN SOVRA-AMORTITA

Sovra-amortito: effetti inerziali trascurabili

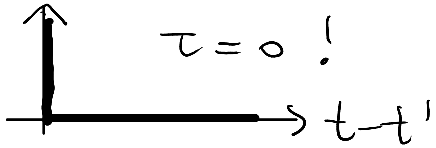
$$\underbrace{m \frac{d\vec{v}}{dt}}_{\approx 0} = -\xi \vec{v} + \vec{\theta}(t) \qquad \theta_0 \sim \xi \qquad \xi \to \infty$$

$$\xi \frac{d\vec{r}}{dt} = \vec{\theta}(t)$$ particella libera, sovra-amortito

1d: $\langle \theta(t)\,\theta(t') \rangle = 2\theta_0\,\delta(t-t')$

$\langle \theta \rangle = 0$

$C_\theta(t-t') = 2\theta_0\,\delta(t-t')$



Solurione formale:

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

$$\langle |\Delta \vec{r}|^2 \rangle = \langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle = \frac{1}{\xi^2}\int_0^t ds \int_0^t ds' \underbrace{\langle \vec{\theta}(s)\cdot\vec{\theta}(s') \rangle}_{\sim\delta(s-s')} = \frac{6\theta_0}{\xi^2}\int_0^t ds = 6\underbrace{\frac{\theta_0}{\xi^2}}_{\to D}\, t$$

$$\xi \frac{d\vec{r}}{dt} = \vec{F}_{est} + \vec{\theta}(t) \qquad \theta_0 = K_B T \cdot \xi \Rightarrow \langle |\Delta \vec{r}|^2 \rangle_{eq} = 6\, \frac{K_B T}{\xi}\, t$$

↳ Langevin

Esempi (Notebooks)

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

Algoritmo di Ermak: potenziale generico

Dinamica browniana:

3d: $\xi \frac{d\vec{r}}{dt} = \vec{F}_{est} + \vec{\theta}(t)$

1d: $\xi \frac{dx}{dt} = F_{est}(x) + \theta(t)$ $\langle \theta(t) \rangle = 0$ $\langle \theta(t') \theta(t'') \rangle = 2\theta_0 \, \delta(t - t')$

Eulero: passo temporale Δt

$$x(t+\Delta t) = x(t) + \frac{1}{\xi} \int_t^{t+\Delta t} ds \, F_{est} + \frac{1}{\xi} \int_t^{t+\Delta t} ds \, \theta(s)$$

$$\approx x(t) + \frac{1}{\xi} F_{est} \Delta t + \tilde{\theta}(t; \Delta t)$$

$\tilde{\theta}$ sia distribuita secondo gaussiana

$$\langle \tilde{\theta}(t; \Delta t) \rangle = 0$$

$$\langle \tilde{\theta}(t; \Delta t) \, \tilde{\theta}(t'; \Delta t) \rangle = \frac{1}{\xi^2} \int_t^{t+\Delta t} ds \int_t^{t+\Delta t} ds' \, \underbrace{\langle \theta(s) \theta(s') \rangle}_{\sim \delta(s-s')}$$

$$= \frac{2\theta_0}{\xi^2}\int_t^{t+\Delta t} ds = \frac{2\theta_0}{\xi^2}\,\Delta t \underset{\substack{\uparrow \\ \text{eq.}}}{=} 2\underbrace{\frac{k_B T}{\xi}}_{D}\,\Delta t$$

Distribuzione di $\tilde{\theta}$

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

3d:

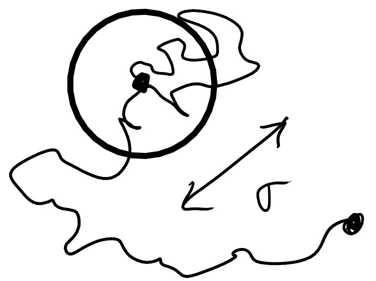
$$p(\vec{\tilde{\theta}}) = \frac{1}{(4\pi D\Delta t)^{3/2}}\exp\left(-\frac{|\tilde{\theta}|^2}{4D\Delta t}\right)$$

Condizione di validità dell'eq. Langevin sovra-smorzata

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

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

es.: $\sqrt{\langle |\vec{v}|^2 \rangle}\, t \approx \sigma$



$$\langle |\Delta \vec{r}(t)|^2 \rangle \approx D t$$
$$\approx \sigma^2$$

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

Langevin

$p(\vec{v})$ — Fokker-Planck — $\vec{F}_{est} = \vec{0}$

$p(\vec{r}, \vec{v})$ — Kramers

Sovra-smorzata

$p(\vec{r})$ — Smoluchowski — $\vec{F}_{est} \neq \vec{0}$

Eq. diff. ordinarie STOCASTICHE

Eq. derivate parziali DETERMINISTICHE

EQUAZIONE DI SMOLUCHOWSKI.

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

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

Spostamento h durante Δt

$$h = \frac{1}{\xi} F(x) \Delta t + \frac{1}{\xi} \int_t^{t+\Delta t} ds \, \langle \theta(s) \rangle = \frac{1}{\xi} F(x) \Delta t$$

Densità di prob. di h

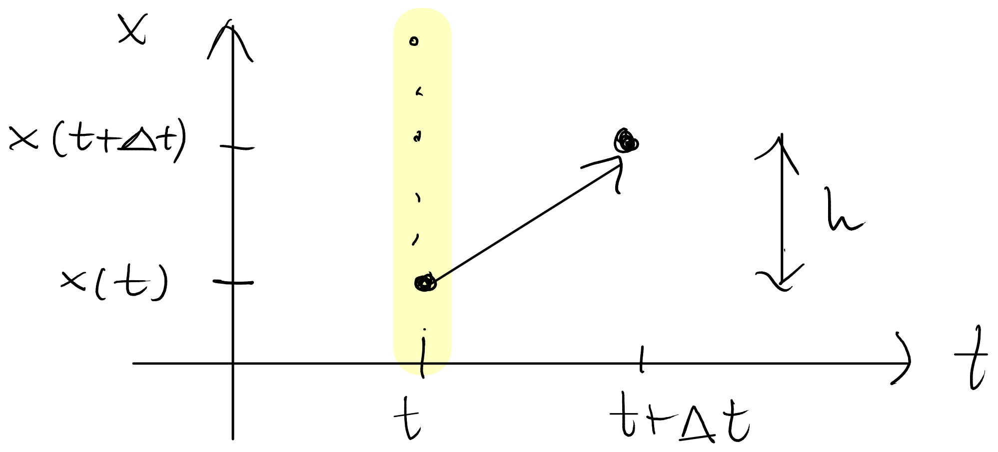
$$\Pi(h, x) = \frac{1}{\sqrt{4\pi D \Delta t}} \exp\left[- \frac{\left(h - \frac{F}{\xi}\Delta t\right)^2}{4 D \Delta t} \right]$$

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

Master equation per $p(x,t)$

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

$$y = x-h$$



Taylor II ordine: $y_0 = x \qquad \Delta y = -h \qquad \frac{d\varphi}{dy} = \frac{d\varphi}{dx}$

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

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

$$= p(x,t) - \frac{\partial}{\partial x}\left[p(x,t) \underbrace{\int_{-\infty}^{\infty} dh\, \Pi(h,x)\, h}_{\frac{1}{3}F(x)\Delta t} \right] + \frac{1}{2}\frac{\partial^2}{\partial x^2}\left[p(x,t) \underbrace{\int_{-\infty}^{\infty} dh\, \Pi(h,x)\, h^2}_{\langle \delta h^2 \rangle - \langle h \rangle^2} \right] \Big\}$$

$$2D\Delta t \qquad O(\Delta t^2)$$

Taylor I ordine in Δt

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

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

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

$$\frac{\partial p}{\partial t} + \vec{\nabla}\cdot\left[\frac{1}{\xi}F(\vec{r})\,p(\vec{r},t)\right] - \vec{\nabla}\cdot\vec{\nabla}\left[D\,p(\vec{r},t)\right] = 0$$ $D = \text{cost}$

$$\frac{\partial p}{\partial t} + \vec{\nabla}\cdot\left[\frac{1}{\xi}F(\vec{r})\,p(\vec{r},t) - \vec{\nabla}\left(D\,p(\vec{r},t)\right)\right] = 0$$ $\rightarrow$ eq. continuità

$$\frac{\partial p}{\partial t} = -\vec{\nabla}\cdot\left[\underbrace{\frac{1}{\xi}\vec{F}}_{\text{deriva}}p\right] + \underbrace{D\nabla^2 p}_{\text{diffusione}}$$

$$\frac{\partial p}{\partial t} = D\frac{\partial^2 p}{\partial x^2}$$ Eq. deriva-diffusione

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

Casi particolari:

1) Equilibrio

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

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

$$-\frac{1}{\xi} F(x) \exp\left(-\frac{U(x)}{K_B T}\right) + \frac{\cancel{K_B T}}{\xi}\left(-\frac{1}{\cancel{K_B T}}\frac{dU}{dx}\right)\exp\left(-\frac{U(x)}{K_B T}\right) = 0 \Rightarrow J = 0$$

$$\Rightarrow \frac{\partial p}{\partial t} = 0 \rightarrow \text{stazionario}$$

2) Particella libera

$$\vec{F} = \vec{0} \quad 3d: \quad \frac{\partial p}{\partial t} = D\nabla^2 p \qquad p = p(\bar{r},t) \rightarrow \text{eq. diffusione}$$

Trasf. Fourier:

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

Anti-trasf. Fourier:

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

$$\frac{\partial p_{\vec{k}}}{\partial t} = -k^2 D\, p_{\vec{k}} \qquad \frac{\partial}{\partial x} \to ik$$

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

Condizioni iniziali : $p(\vec{r}) = \delta(\vec{0})$

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

Condizioni contorno :

- $p=0$: assorbenti
- $J=0$: riflettenti

Condizioni iniziali : $p(\vec{r}, t=0)$

$$p(\vec{r},0) = \delta(\vec{r}=0)$$

In spazio reale :

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

3) Forza costante

$F = \text{cost}$ $\qquad \dfrac{\partial p}{\partial t} = -\dfrac{F}{\xi}\dfrac{\partial p}{\partial x} + D\dfrac{\partial^2 p}{\partial x^2}$ $\qquad y = x - \dfrac{F}{\xi} t$ $\qquad y = y(x,t)$

$p(x,t) \to q(y,t)$ $\qquad p(x,t)\, dx\, dt = q(y,t)\, dy\, dt$ $\qquad p(x,t) = q(y,t)$

$$\frac{\partial q}{\partial t} + \frac{\partial q}{\partial y}\frac{\partial y}{\partial t} = -\frac{F}{\varepsilon}\frac{\partial q}{\partial y} + D\frac{\partial^2 q}{\partial y^2}$$

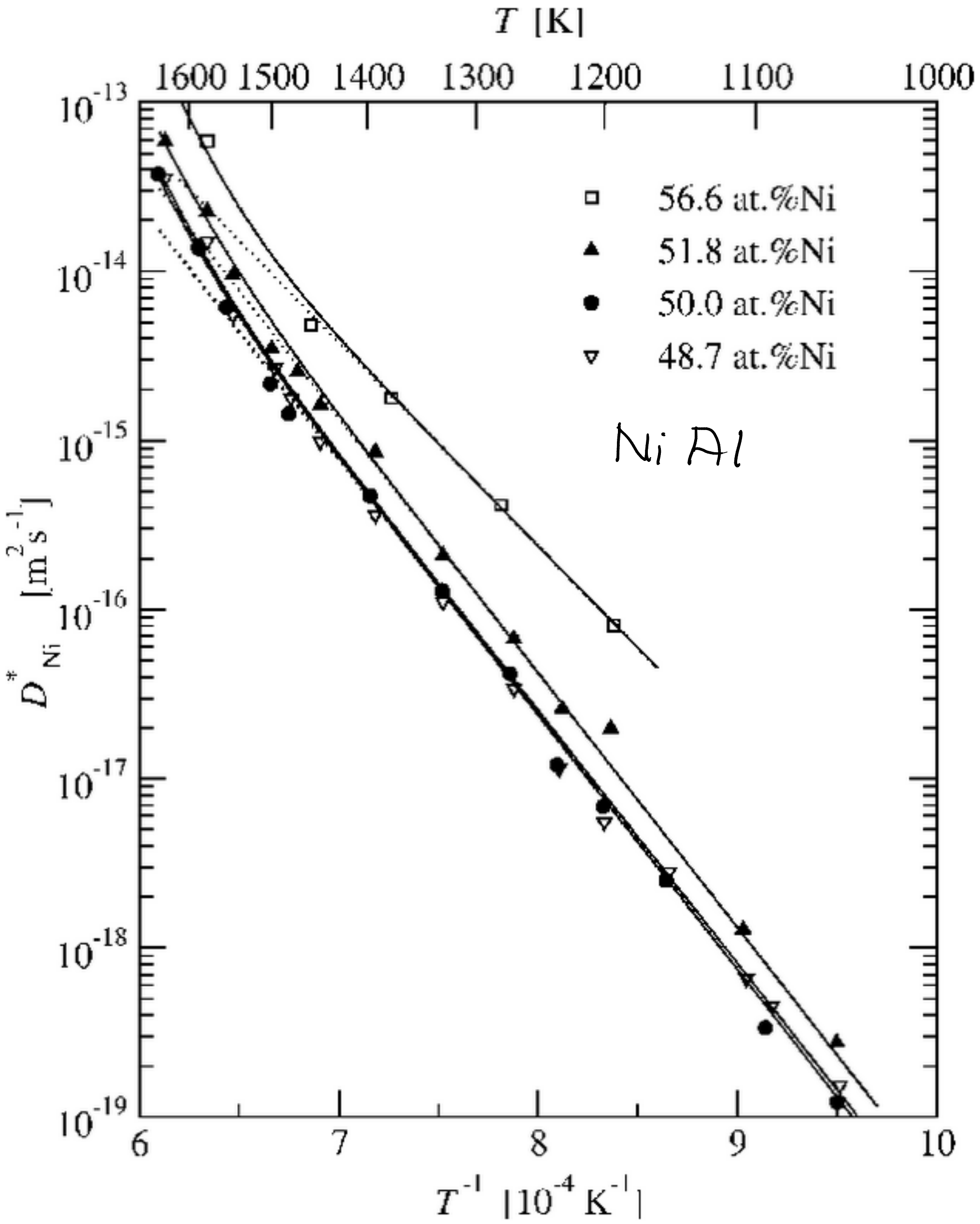
$$\frac{\partial q}{\partial t} - \cancel{\frac{F}{\varepsilon}\frac{\partial q}{\partial y}} = -\cancel{\frac{F}{\varepsilon}\frac{\partial q}{\partial t}} + D\frac{\partial^2 q}{\partial y^2} \Rightarrow \frac{\partial q}{\partial t} = D\frac{\partial^2 q}{\partial t^2}$$

Soluzione:

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

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

$$\begin{cases} \langle x(t)\rangle = \frac{F}{\varepsilon}t \quad \to \text{ deriva} \\ \langle (x(t) - \langle x(t)\rangle)^2\rangle = 2Dt \quad \to \text{ diffusione} \qquad \langle |x(t)-x(0)|^2\rangle \end{cases}$$



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.

$$D \sim \exp\left(-\frac{A}{T}\right)$$

$$\eta \sim \exp\left(\frac{A}{T}\right)$$

$$\langle |\Delta \vec{r}|^2 \rangle \sim D t$$

$$\sigma^2 = D \tau_D$$

$$\tau_D \sim \frac{1}{D}$$

$$\tau_D \sim \exp\left(\frac{A}{T}\right)$$

$$\eta = G_0 \tau$$

$$\tau \sim \exp\left(\frac{A}{T}\right)$$

legge di

ARRHENIUS

silice liquida SiO_2

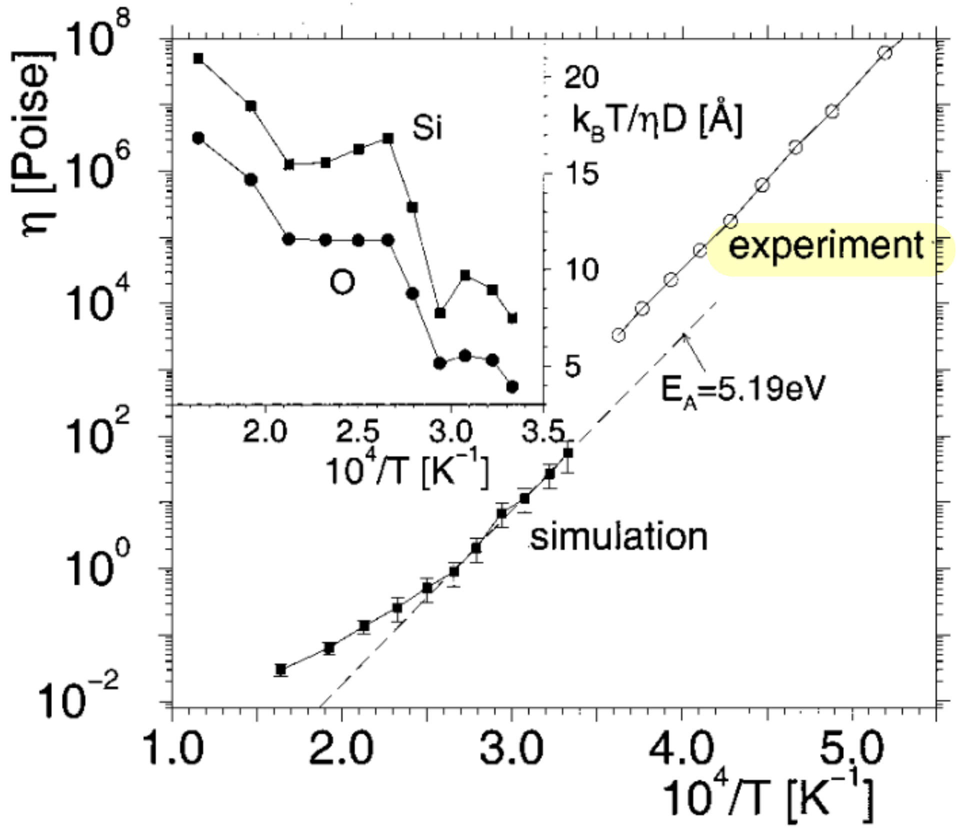
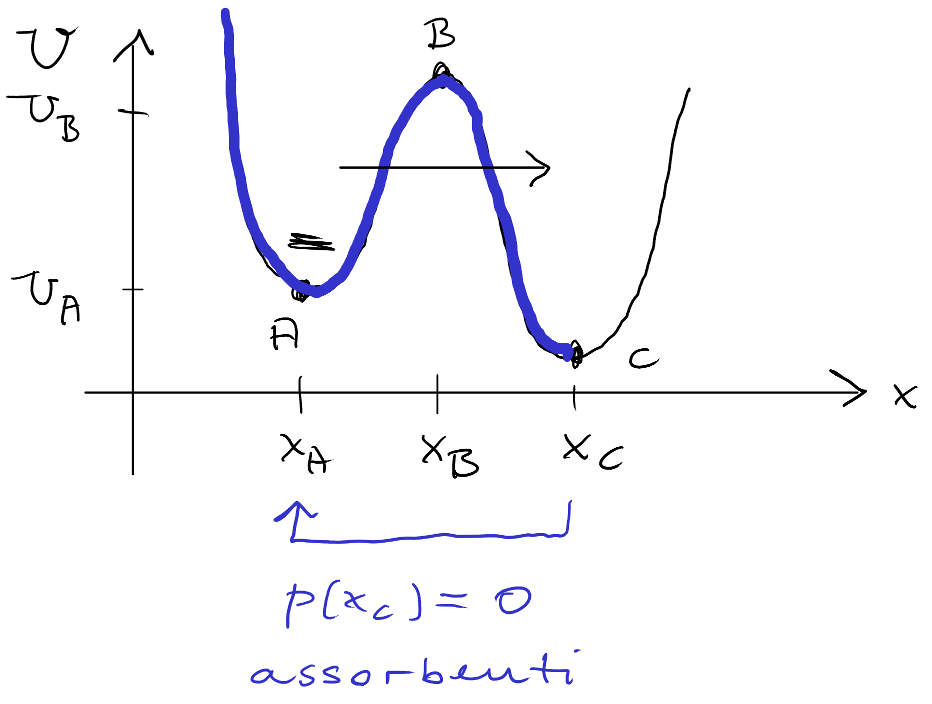


FIG. 10. Main figure: Arrhenius plot of the shear viscosity from the simulation (solid squares). The dashed line is a fit with an Arrhenius law to our low-temperature data. The open circles are experimental data from Urbain *et al.* (Ref. 35). Inset: temperature dependence of the left hand side of Eq.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

4) Attivazione termica: problema di Kramers (1940)



Modello: particella browniana in una doppia buca di potenziale

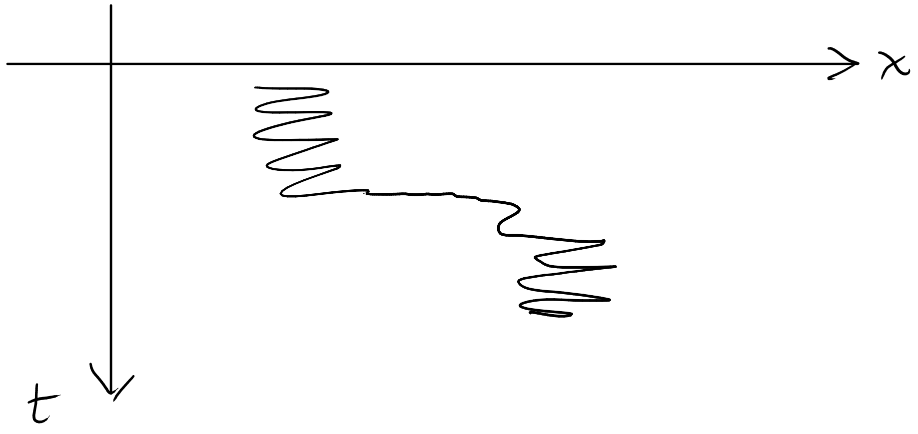
$$\Delta U = U_B - U_A \gg k_B T$$

Goal: tempo di uscita medio

$$\frac{\partial p}{\partial t} = \frac{\partial}{\partial x}\left[-\frac{F}{\xi} p + D \frac{\partial p}{\partial x} \right] \qquad D = \frac{k_B T}{\xi}$$

$$= \frac{\partial}{\partial x} \underbrace{\left[\frac{1}{\xi}\frac{dU}{dx} p + \frac{k_B T}{\xi} \frac{\partial p}{\partial x} \right]}_{-J}$$

H. Kramers
1894 – 1952



Regime stazionario: $\frac{\partial p}{\partial t} = 0 \Rightarrow J = \text{cost}$

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

$$p(x) = \varphi(x) \exp\left(-\frac{U(x)}{k_B T} \right)$$

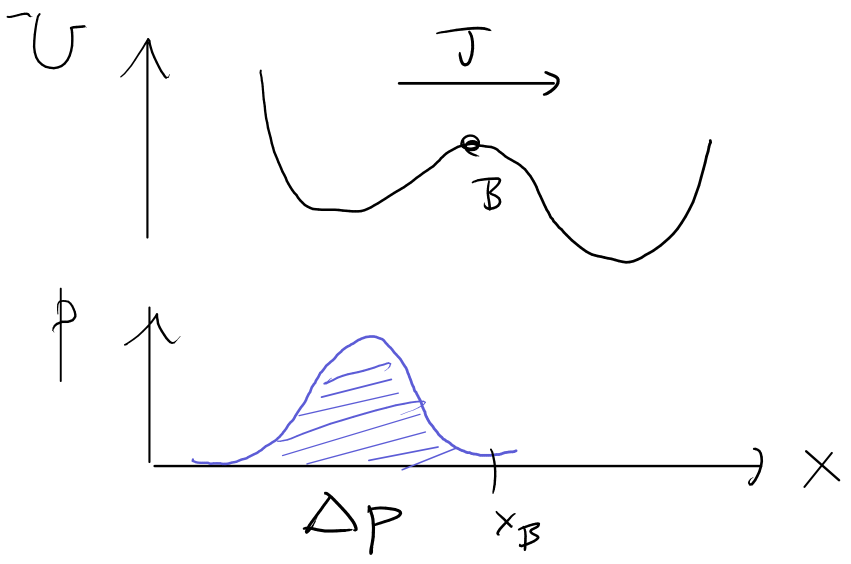
$$\underbrace{\frac{1}{\varepsilon}\frac{dU}{dx}\varphi(x)\exp\left(-\frac{U}{K_BT}\right)} + \frac{K_BT}{\varepsilon}\frac{d\varphi}{dx}\exp\left(-\frac{U}{K_BT}\right) + \underbrace{\frac{\cancel{K_BT}}{\varepsilon}\varphi(x)\left(-\frac{dU}{dx}\right)\frac{1}{\cancel{K_BT}}\exp\left(-\frac{U}{K_BT}\right)} = -J$$

$$\frac{d\varphi}{dx} = -\frac{J\varepsilon}{K_BT}\exp\left(\frac{U}{K_BT}\right)$$

condizioni al contorno : $p(x_c) = 0 \Rightarrow \varphi(x_c) = 0$

$$\varphi(x) = \frac{J\varepsilon}{K_BT}\int_x^{x_c} dx' \exp\left(\frac{U(x')}{K_BT}\right) \rightarrow p(x) = \frac{J\varepsilon}{K_BT}\exp\left(-\frac{U(x)}{K_BT}\right)\int_x^{x_c} dx' \exp\left(\frac{U(x')}{K_BT}\right)$$

Tempo di uscita medio : τ



$$J = \frac{\Delta n}{\tau} \Rightarrow \tau J = \int_{-\infty}^{x_B} dx\, p(x) = \Delta p$$

$$\tau J = \frac{J\varepsilon}{K_BT}\int_{-\infty}^{x_B} dx'' \exp\left(-\frac{U(x'')}{K_BT}\right)\int_{x''}^{x_c} dx' \exp\left(\frac{U(x')}{K_BT}\right)$$

$$\tau = \frac{\varepsilon}{K_BT}\int_{-\infty}^{x_B} dx'' \exp\left(-\frac{U(x'')}{K_BT}\right)\underbrace{\int_{x''}^{x_c} dx' \exp\left(\frac{U(x')}{K_BT}\right)}_{\approx \text{ cost per } x'' \approx x_A} \quad (*)$$

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

$$\textcircled{*} \; \exp\left(\frac{U_B}{K_B T}\right) \int_{x''}^{x_C} dx' \exp\left[-\frac{1}{2}\frac{m\omega_B^2}{K_B T}(x-x_B)^2\right]$$

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

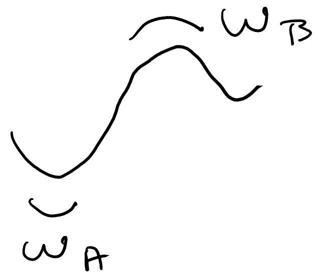
$$\tau = \frac{\varepsilon}{K_B T}\sqrt{\frac{2\pi K_B T}{m\omega_B^2}} \exp\left(\frac{U_B}{K_B T}\right) \int_{-\infty}^{x_B} dx'' \exp\left(-\frac{U(x'')}{K_B T}\right)$$

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

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

$$= \frac{\varepsilon}{K_B T}\sqrt{\frac{2\pi K_B T}{m\omega_B^2}}\sqrt{\frac{2\pi K_B T}{m\omega_A^2}} \exp\left(\frac{\Delta U}{K_B T}\right)$$

$$\boxed{\tau = \frac{2\pi\,\xi}{m\,\omega_A\,\omega_B}\,\exp\left(\frac{\Delta U}{K_B T}\right)}$$



$\omega_A \uparrow \quad \omega_B \uparrow \quad \Rightarrow \quad \tau \searrow$

$\xi \uparrow \quad \Rightarrow \quad \tau \uparrow$

$\uparrow$

fattore di Arrhenius