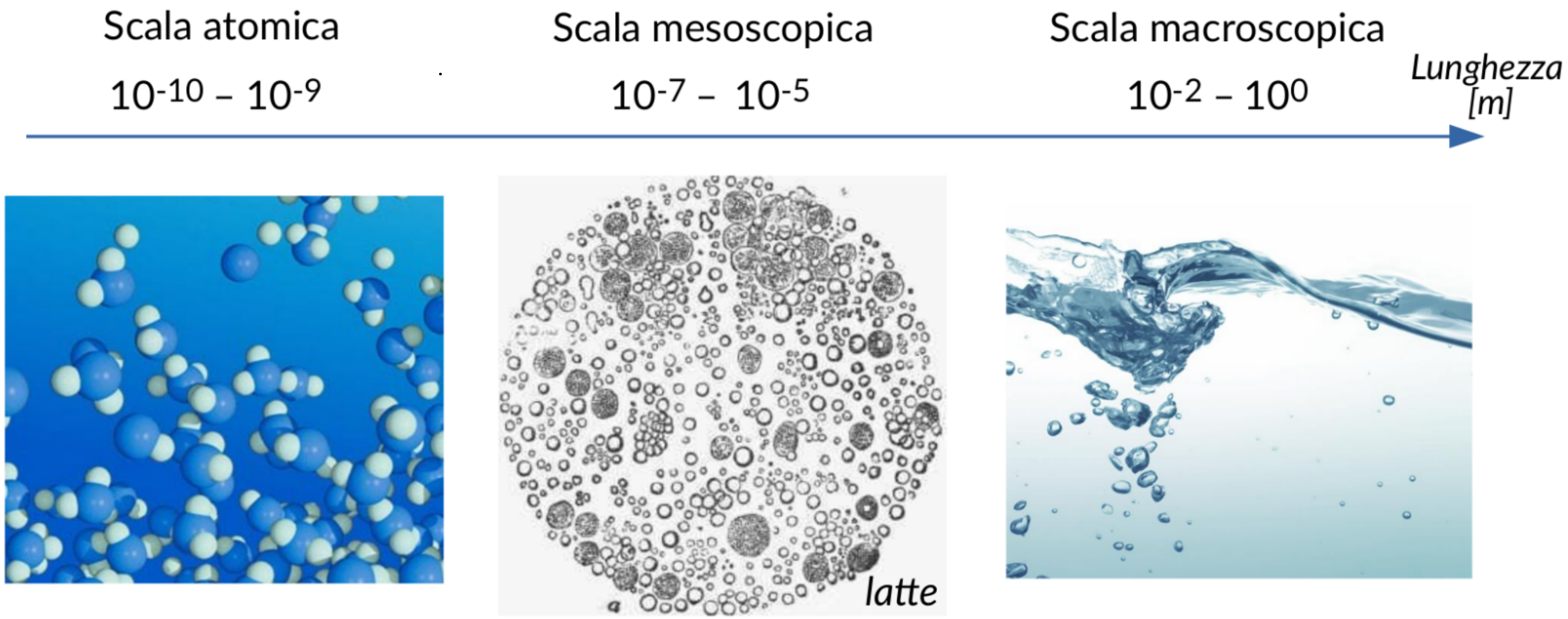
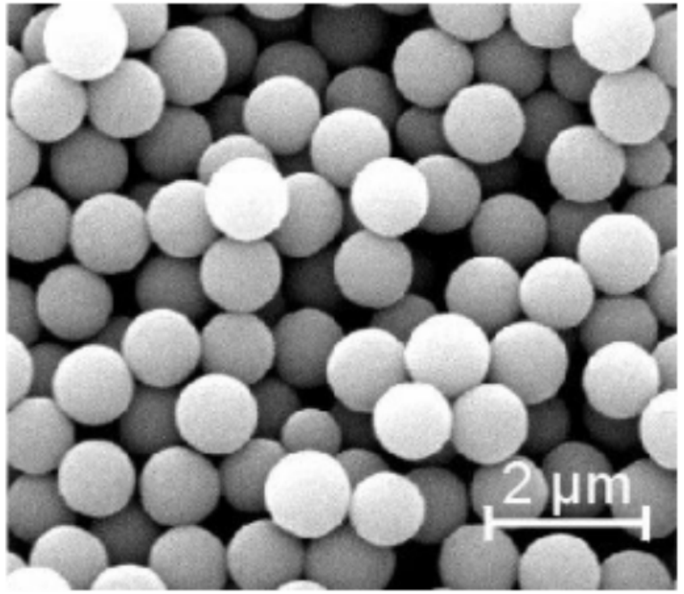
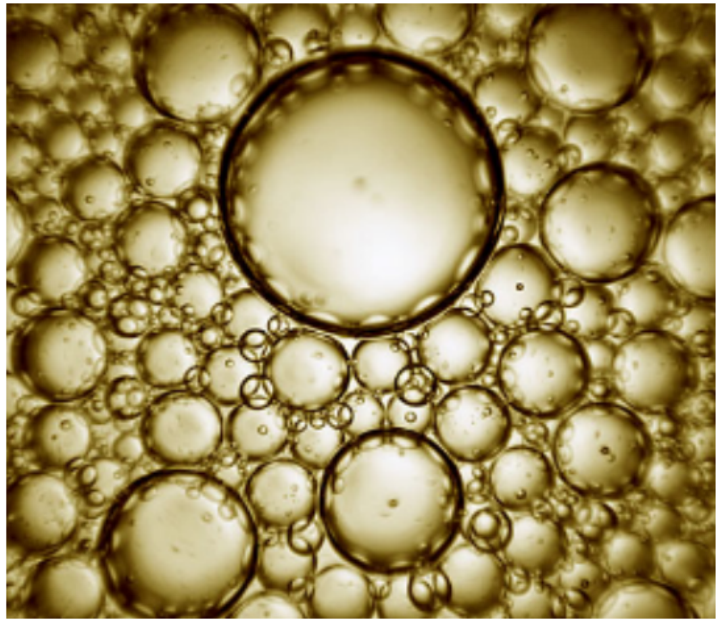


Scala atomica
10^{-10} – 10^{-9}
Scala mesoscopica
10^{-7} – 10^{-5}
Scala macroscopica
10^{-2} – 10^{0}
Lunghezza [m]
latte

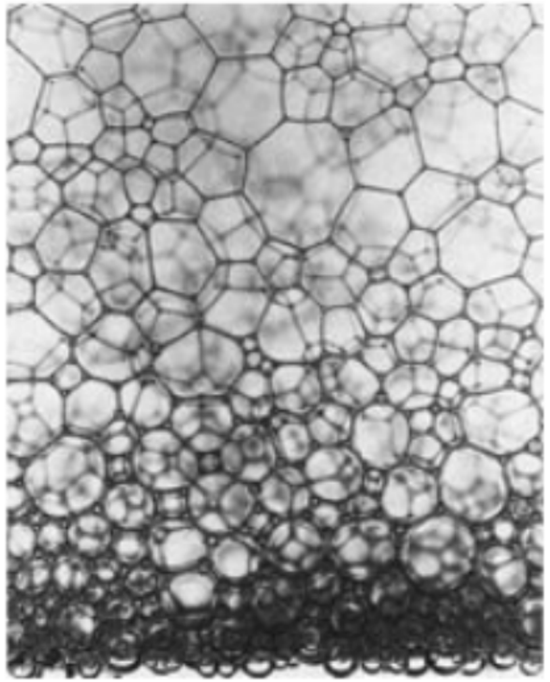
PMMA



SOSPENSIONE COLLOIDALE



EMULSIONE



SCHIUMA

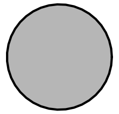
Def: sistema eterogeneo composto da particelle solide mesoscopiche sospese in un liquido micro

micro

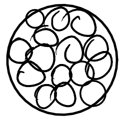
$10^{-10} - 10^{-9}$ m

meso

$10^{-7} - 10^{-5}$ m



$\updownarrow z_0 \quad N \sim N_A \sim 10^{23}$



$\updownarrow z_0 \quad N \sim \left(\frac{z_0}{a}\right)^3 \sim 10^{12}$

a

Criterio di stabilità

$$\xi_0 \lesssim \left(\frac{K_B T}{\rho_c g} \right)^{1/4}$$

$\uparrow$ densità della particella

Es.: grafite $\rho_c \sim 10^3 \; kg/m^3$ $\quad K_B T_a \approx 4 \times 10^{-21} \; J$

$$\xi_0 \lesssim \left(\frac{4 \times 10^{-21}}{10^3 \times 10} \right)^{1/4} m \approx \left(10^{-24} \right)^{1/4} m \sim \underline{10^{-6} \; m}$$

Materia soffice vs. dura

$$[G] = [Y] = \frac{E}{V^3} \sim \frac{\epsilon}{\sigma^3}$$

$\epsilon_{dura} \sim 10 - 100 \; K_B T_a$ $\quad \epsilon_{soffice} \sim 10 \; K_B T_a$

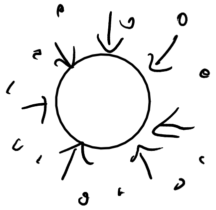
$\sigma_{dura} \sim 10^{-10} \; m$ $\quad \sigma_{soffice} \sim 10^{-6} \; m$

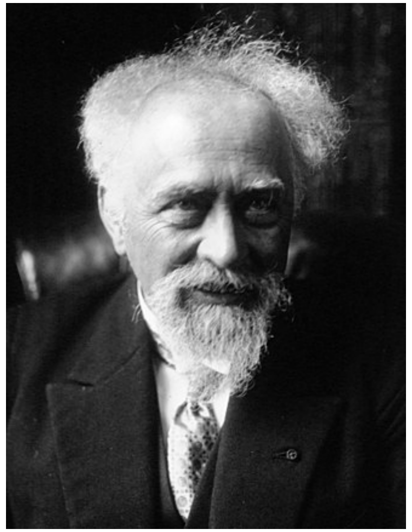
$$\frac{Y_{dura}}{Y_{soffice}} \sim \left(\frac{\epsilon_{dura}}{\epsilon_{soffice}} \right) \left(\frac{\sigma_{soffice}}{\sigma_{dura}} \right)^3 \sim 10 \cdot 10^{12} \sim \underline{10^{13}}$$

DINAMICA BROWNIANA

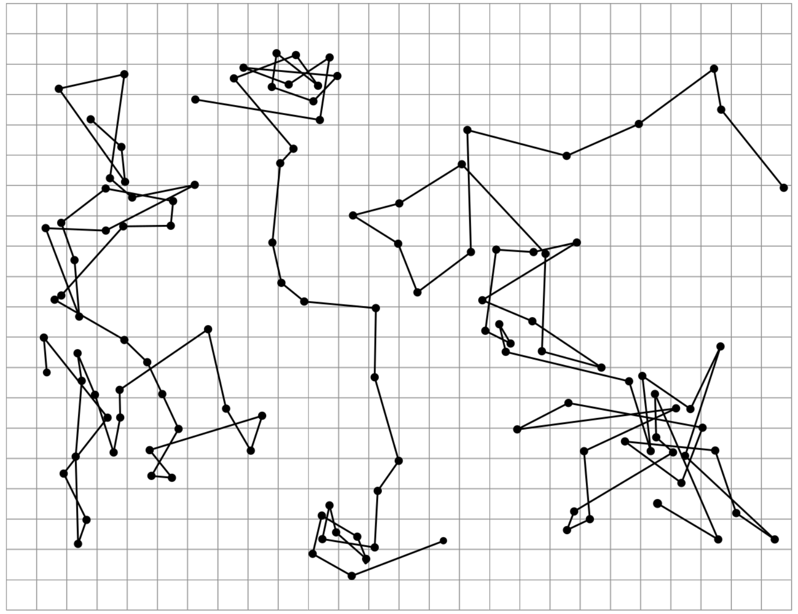
1827 : Brown
1905 : Einstein
1906 : Smoluchowski
1907 : Langevin
1909 : Perrin → N_A → 1926 Nobel

→ processi stocastici





J.-B. Perrin



EQUAZIONE DI LANGEVIN

Particella massa m, sospesa in un solvente (temperatura T), altrito viscoso, F_{est}

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

ξ: coeff. attrito $\vec{\theta}(t)$: forza stocastica

[Ornstein – Uhlenbeck]

$\hat{\theta}$ variabile stocastica $\langle \dots \rangle$ media sulle realizzazioni della forza stocastica

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

$$\begin{cases} \langle \vec{\theta}(t) \rangle = \vec{0} \\ \langle \theta_\alpha(t)\, \theta_\beta(t') \rangle = 2\theta_0\, \delta_{\alpha\beta}\, \delta(t-t') \end{cases}$$

Particella libera

$$\frac{d\vec{v}}{dt} = -\frac{\xi}{m}\vec{v} + \frac{1}{m}\vec{\theta}(t) \qquad F_{est} = 0$$

Variazione delle costanti

$$\frac{dx}{dt} = ax + b(t) \qquad a = -\xi/m \qquad b(t) = \frac{1}{m}\theta(t)$$

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

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

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

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

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 di fluttuazione-dissipazione

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

$$= |\vec{v}(0)|^2 \, e^{-2\xi/m\, t}$$

$$\vec{v}(0) \cdot \underbrace{\langle \vec{\theta}(s) \rangle}_{=0} = 0$$

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

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

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

$$\frac{6\theta_0}{m^2} \int_0^t ds \, e^{-2\xi/m(t-s)} = \frac{3\cancel{6}\theta_0}{m^{\cancel{2}}} \, \frac{\cancel{m}}{\cancel{2}\xi} \left[e^{\frac{2\xi}{m}(s-t)} \right]_0^t$$

$$\frac{3\theta_0}{m\xi} \left(1 - e^{-\frac{2\xi}{m} t} \right)$$

$$\langle |\vec{v}(t)|^2 \rangle = |\vec{v}(0)|^2 \, e^{-2\xi/m\, t} + \frac{3\theta_0}{m\xi} \left(1 - e^{-\frac{2\xi}{m} t} \right)$$

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

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

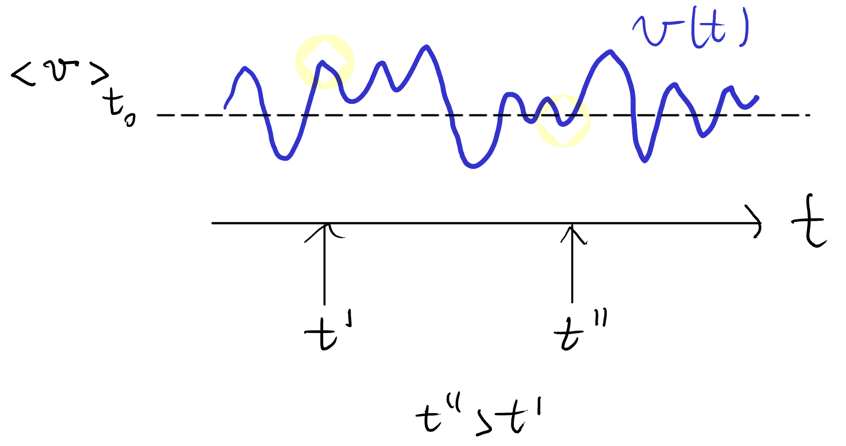
$$\langle |\vec{v}|^2 \rangle_{eq} = \frac{3 K_B T}{m}$$

$$\langle |\vec{v}(\infty)|^2 \rangle = \underbrace{|\vec{v}(0)|^2 e^{-2\xi/m\, t}}_{\to 0} + \frac{3\theta_0}{m\xi}\Big(1 - \underbrace{e^{-\frac{2\xi}{m} t}}_{\longrightarrow 0}\Big) = \frac{3\theta_0}{m\xi} = \frac{3 K_B T}{m}$$

Relazione di fluttuazione - dissipazione : $\boxed{\theta_0 = K_B T \cdot \xi}$

Funzione di correlazione della velocità

1d



$$C_v(t', t'') = \langle (v(t') - \langle v \rangle_{t_0})(v(t'') - \langle v \rangle_{t_0}) \rangle_{t_0}$$

$$C_v(t', t'') = \langle v(t') v(t'') \rangle_{t_0}$$

$$\langle v(t') v(t'') \rangle_{t_0} = \lim_{T \to \infty} \frac{1}{T} \int_0^T dt_0 \, v(t_0 + t') \, v(t_0 + t'')$$

Stazionario : $t'' - t' = t$

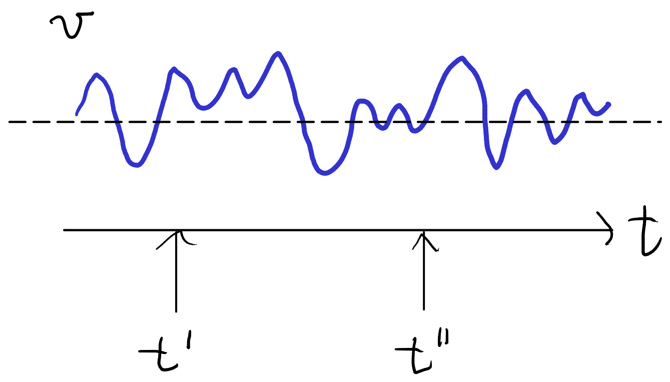
$$C_v(t) = \langle v(t) v(0) \rangle_{t_0}$$

Ergodicità : $\langle \dots \rangle_{t_0} = \langle \dots \rangle_{eq}$

3d

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

Soluzione formale dell' equazione di Langevin



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

$\langle \ldots \rangle$ → forza stocastica (solvente)

$\langle \ldots \rangle_{eq}$ → particella + forza stocastica $\qquad \langle\langle \ldots \rangle_\theta \rangle_v$

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

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

Funzione di correlazione della velocità

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

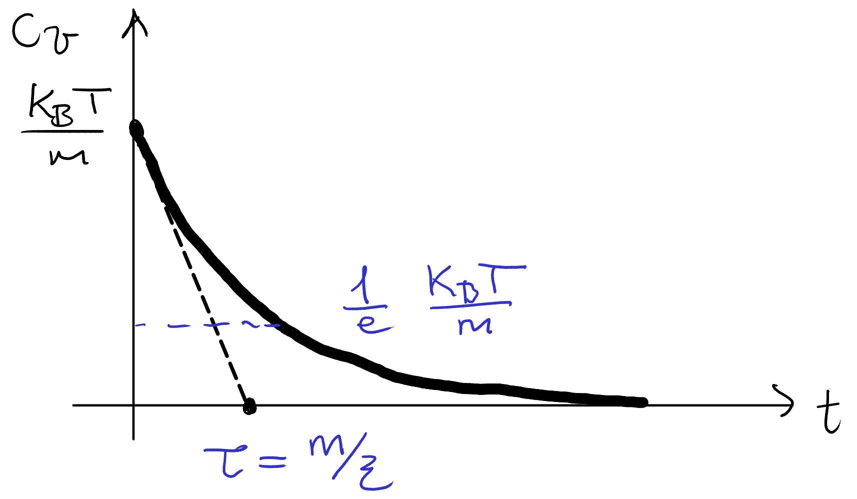
$$= \frac{1}{3}\langle |\vec v(0)|^2 \rangle_{eq}\, e^{-\xi/m\, t} + \frac{1}{3m}\int_0^t ds\, e^{-\xi/m\,(t-s)} \overbrace{\langle \vec v(0) \cdot \vec\theta(s) \rangle_{eq}}^{=\vec 0}$$

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

τ = tempo di correlazione $\quad \tau \uparrow \quad m \uparrow \quad \xi \downarrow$

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

τ = tempo di rilassamento



(es.) Mostra che

$$\langle \vec{v}(t') \cdot \vec{v}(t'') \rangle = \frac{3\,\theta_0}{m\,\xi}\, e^{-\xi/m\, |t''-t'|} \qquad \text{se } t' \gg 0,\ t'' \gg 0 \qquad \text{[zwanzig]}$$

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

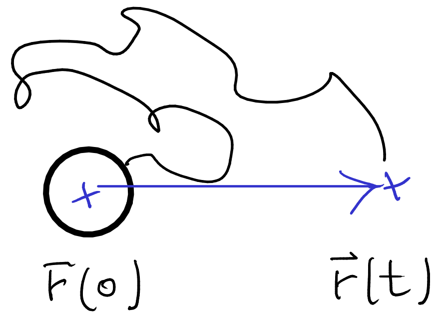
1d: $\langle \theta(s)\, \theta(s') \rangle = 2\,\theta_0\, \delta(s-s') \qquad s - s' = t$

$$C_\theta(t) = 2\,\theta_0\, \delta(t)$$

markoviana

Spostamento quadratico medio

Dinamica browniana, RW

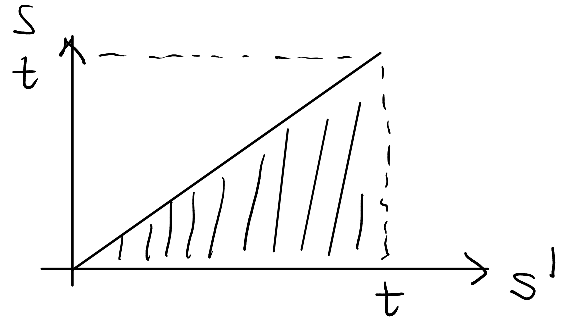


$$\langle|\Delta\vec r|^2\rangle = \langle|\vec r(t)-\vec r(0)|^2\rangle$$

$$\vec r(t) = \vec r(0) + \int_0^t ds\, \vec v(s)$$

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

$$= 2\cdot 3 \int_0^t ds\int_0^s ds'\, C_v(s-s')$$



$$C_v(s-s') = C_v(s'-s)$$

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

$$= 6\int_0^t ds \int_s^0 (-dt')\, C_v(t') = 6\int_0^t ds\, 1\cdot\int_0^s dt'\, C_v(t')$$

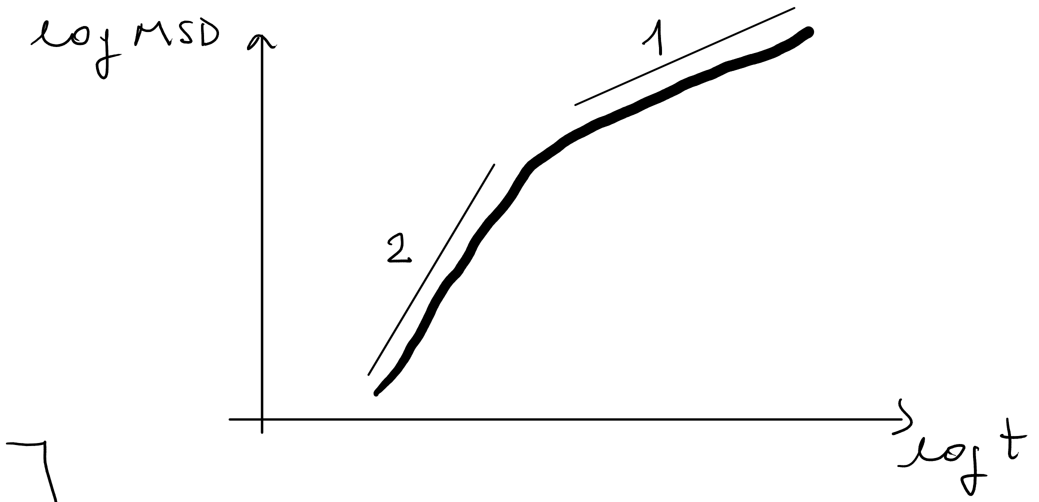
$$= 6\left\{\left[s\int_0^s dt'\, C_v(t')\right]_0^t - \int_0^t ds\, s\, C_v(s)\right\}$$

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

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

(es.) Mostra che:

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



Tempi corti: $t \ll \tau = \frac{m}{\xi}$ Taylor II ordine

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

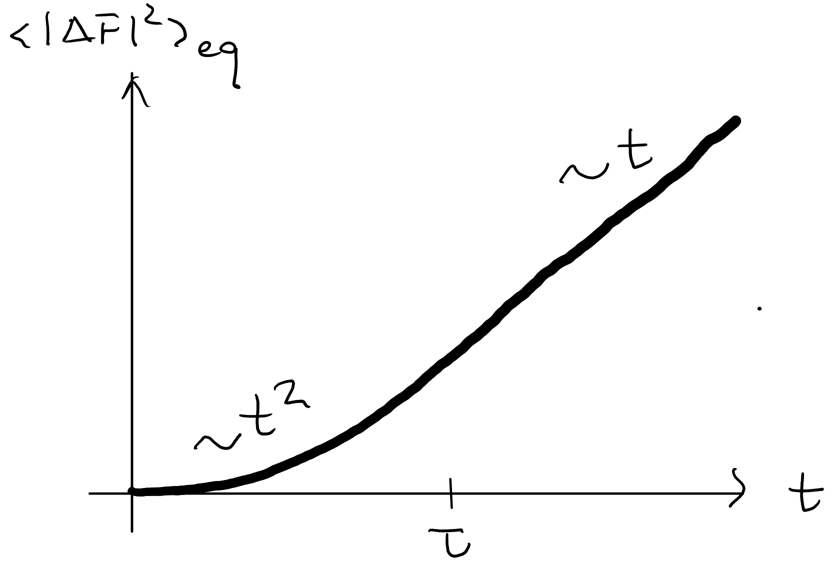
$$= 6 \frac{K_B T}{\xi} \left[\frac{1}{2} \frac{\xi}{m} t^2 \right] = \frac{3 K_B T}{m} t^2 = \langle |\vec{v}|^2 \rangle_{eq} t^2 \sim t^2$$ balistico

Tempi lunghi: $t \gg \tau$

$$\langle |\Delta \vec{r}|^2 \rangle_{eq} \approx 6 \frac{K_B T}{\xi} t = 2 \cdot d \cdot \frac{K_B T}{\xi} t = 2 d D t$$

= coeff. diffusione

$\sim t$ diffusivo $\uparrow D$ $\uparrow T$ $\searrow \xi$



EQUAZIONE DI LANGEVIN SOVRA-SMORZATA

$$m \frac{d\vec{v}}{dt} = \vec{F}_{est} - \xi \vec{v} + \vec{\theta} \qquad \langle \vec{\theta} \rangle = \vec{0} \qquad \langle \theta_\alpha(s)\, \theta_\beta(s') \rangle = 2\theta_0\, \delta(s-s')\, \delta_{\alpha\beta}$$

inerzia << attrito e forza stocastica $\quad \theta_0 \sim \xi \quad$ FD (eq.)

$$\xi \frac{d\vec{r}}{dt} = \vec{F}_{est} + \vec{\theta} \qquad \text{sovra-smorzata} \qquad [\ F_{est} = 0 \ \ \text{processo di Wiener}\ ]$$

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

<u>Particella libera</u>: $\quad F_{est} = 0$

coeff. diffusione

$$\langle |\Delta \vec{r}|^2 \rangle = \frac{1}{\xi^2} \int_0^t ds \int_0^t ds' \langle \vec{\theta}(s) \cdot \vec{\theta}(s') \rangle = 2\, \frac{3\theta_0}{\xi^2} \int_0^t ds = 6\, \frac{\theta_0}{\xi^2}\, t \qquad \theta_0 = k_B T \cdot \xi$$

$$\langle |\Delta \vec{r}|^2 \rangle_{eq} = 6\, \frac{k_B T}{\xi}\, t \qquad D = \frac{k_B T}{\xi}$$

<u>Esempi</u> (Notebooks)

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

Algoritmo di Ermak

Δt passo temporale ("timestep") tale che $F_{est} \approx$ cost

Eulero I ordine

1d : $\dfrac{dx}{dt} = \dfrac{1}{\xi} F_{est} + \dfrac{1}{\xi}\,\theta$

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

$$x(t+\Delta t) \approx x(t) + \frac{1}{\xi} F_{est}\,\Delta t + \tilde{\theta}(t)$$ algoritmo di Ermak

$\theta_0 = k_B T \cdot \xi$

$$\begin{cases} \langle \tilde{\theta} \rangle = 0 \\ \langle \tilde{\theta}^2 \rangle = \dfrac{1}{\xi^2}\displaystyle\int_t^{t+\Delta t} ds \int_t^{t+\Delta t} ds' \underbrace{\langle \theta(s)\,\theta(s')\rangle}_{\sim\,\delta(s-s')} = \dfrac{2\theta_0}{\xi^2}\int_t^{t+\Delta t} ds = \dfrac{2\theta_0}{\xi^2}\Delta t = 2\,\dfrac{k_B T}{\xi}\,\Delta t \end{cases}$$

$$= 2D\,\Delta t$$

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

3d :

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

Condizione di validità

Tempo di correlazione: $\tau = m/\xi$

Tempo di diffusione: $\tau_D = \sigma^2/D$

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

$\sigma^2 \approx D \tau_D$

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

$$\tau \ll \tau_D$$

$$\frac{m}{\xi} \ll \frac{\sigma^2 \xi}{k_B T} \qquad \xi \gg \left(\frac{m k_B T}{\sigma^2}\right)^{1/2} = \frac{\sqrt{m k_B T}}{\sigma}$$

(es.): $\langle|\Delta\vec{r}|^2\rangle \sim \langle|\vec{v}|^2\rangle t^2$

o

Langevin: $\vec{r}, \vec{v}$

Langevin sovra-smorzata: $\vec{r}$

Eq. differenziali ordinarie STOCASTICHE

Fokker-Planck $p(\vec{v})$

Kramers $p(\vec{r}, \vec{v})$ $\uparrow$ BH

Smoluchowski $p(\vec{r})$ $\Uparrow$

Eq. differenziali alle derivate parziali DETERMINISTICHE

EQUAZIONE DI SMOLUCHOWSKI.

1α: $\quad \frac{dx}{dt} = \frac{1}{\xi} F(x) + \frac{1}{\xi}\theta(t) \qquad \langle\theta\rangle = 0 \qquad \langle \theta(s)\theta(s')\rangle = 2\theta_0\,\delta(s-s') \qquad \theta_0 = k_B T\cdot\xi \qquad D = \frac{k_B T}{\xi}$

Spostamento h durante Δt t.c. $F \approx$ cost

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

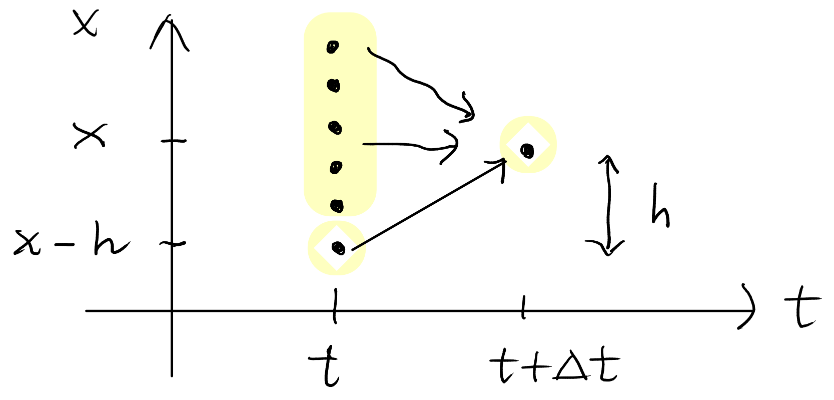
$$\begin{cases} \langle h \rangle = \dfrac{F(x)}{\xi}\,\Delta t \\ \langle (h - \langle h\rangle)^2\rangle = \langle \delta h^2\rangle = \dfrac{1}{\xi^2}\displaystyle\int_t^{t+\Delta t} ds \int_t^{t+\Delta t} ds' \underbrace{\langle \theta(s)\theta(s')\rangle}_{\sim\,\delta(s-s')} = 2\,\dfrac{\theta_0}{\xi^2}\,\Delta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

$$\begin{cases} \langle h^2\rangle - \langle h\rangle^2 = \langle \delta h^2\rangle \\ \langle h^2 \rangle = 2D\,\Delta t + \dfrac{F^2}{\xi^2}\,\Delta t^2 \end{cases}$$

Densità di probabilità di h

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

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 di φ attorno a $y_0 = x$ in $\Delta y = -h$; $\frac{d\varphi}{dx} = \frac{d\varphi}{dy}$

$$p(x,t+\Delta t) = \int_{-\infty}^{\infty} dh \left[\varphi(y_0) - \frac{d\varphi}{dy} h + \frac{1}{2} \frac{d^2\varphi}{dy^2} h^2 \right] + O(h^3)$$

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

$\varphi(x) = p(x,t)\,\Pi(h,x)$

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

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

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

Taylor I ordine in Δt

$$\underset{\sim\sim}{p(x,t)} + \frac{\partial p}{\partial t}\cancel{\Delta t} \approx \underset{\sim\sim}{p(x,t)} - \frac{\partial}{\partial x}\left(\frac{1}{\xi}F(x)\,p(x,t)\right)\cancel{\Delta t} + \frac{\partial^2}{\partial x^2}\left(D\,p(x,t)\right)\cancel{\Delta t}$$

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

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

velocità di deriva ↑   diffusione ↑   → eq. deriva-diffusione

$$\frac{\partial p}{\partial t} + \frac{\partial}{\partial x}\Big(\underbrace{\frac{F(x)}{\xi}\,p(x,t) - D\frac{\partial p}{\partial x}}_{J}\Big) = 0$$ → eq. continuità

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

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

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

0) **Equilibrio** : $p(x,t) = \frac{1}{Z} \exp(-\beta U(x))$ $\qquad F(x) = -\frac{dU}{dx}$

$$\frac{\partial p}{\partial t} + \frac{\partial}{\partial x}\Big(\underbrace{\frac{F(x)}{\xi} p(x,t) - D \frac{\partial p}{\partial x}}_{J} \Big) = 0$$

$$J = \frac{F(x)}{\xi} p(x,t) - \frac{K_B T}{\xi}\left(-\frac{1}{K_B T}\right) \underbrace{\frac{dU}{dx}}_{-F} p(x,t) = 0 \Rightarrow \frac{\partial p}{\partial t} = 0 \quad \text{stazionario}$$

1) **Particella libera**

$$\frac{\partial p}{\partial t} = D \frac{\partial^2 p}{\partial x^2} \quad 1d$$

$$\frac{\partial p}{\partial t} = D \nabla^2 p \quad 3d$$

eq. diffusione

Condizioni al contorno
- $J=0$ riflessive
- $p=0$ assorbenti

condizioni iniziali

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

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

$$\frac{\partial}{\partial x} \to ik_x \qquad \nabla^2 \to -k^2$$

$$\frac{\partial p_{\vec{k}}}{\partial t} = -Dk^2 p_{\vec{k}}(t) \qquad p(\vec{r},0) = \delta(\vec{r}) \quad \to \quad p_{\vec{k}}(0) = 1$$

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

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

2) Forza costante

1d : $\frac{\partial p}{\partial t} = -\frac{1}{\xi}F\frac{\partial p}{\partial x} + D\frac{\partial^2 p}{\partial x^2}$ $\qquad y = x - \frac{F}{\xi}t$ cambio variabile $q(y,t)$

$p(x,t)\,dx\,\cancel{dt} = q(y,t)\,dy\,\cancel{dt}$ $\qquad dy = dx \quad \longrightarrow \quad p(x,t) = q(y,t) \qquad y = y(x,t)$

⚠ conservazione della prob. a t fissato : $\int_{-\infty}^{\infty} dx\, p(x,t) = 1$

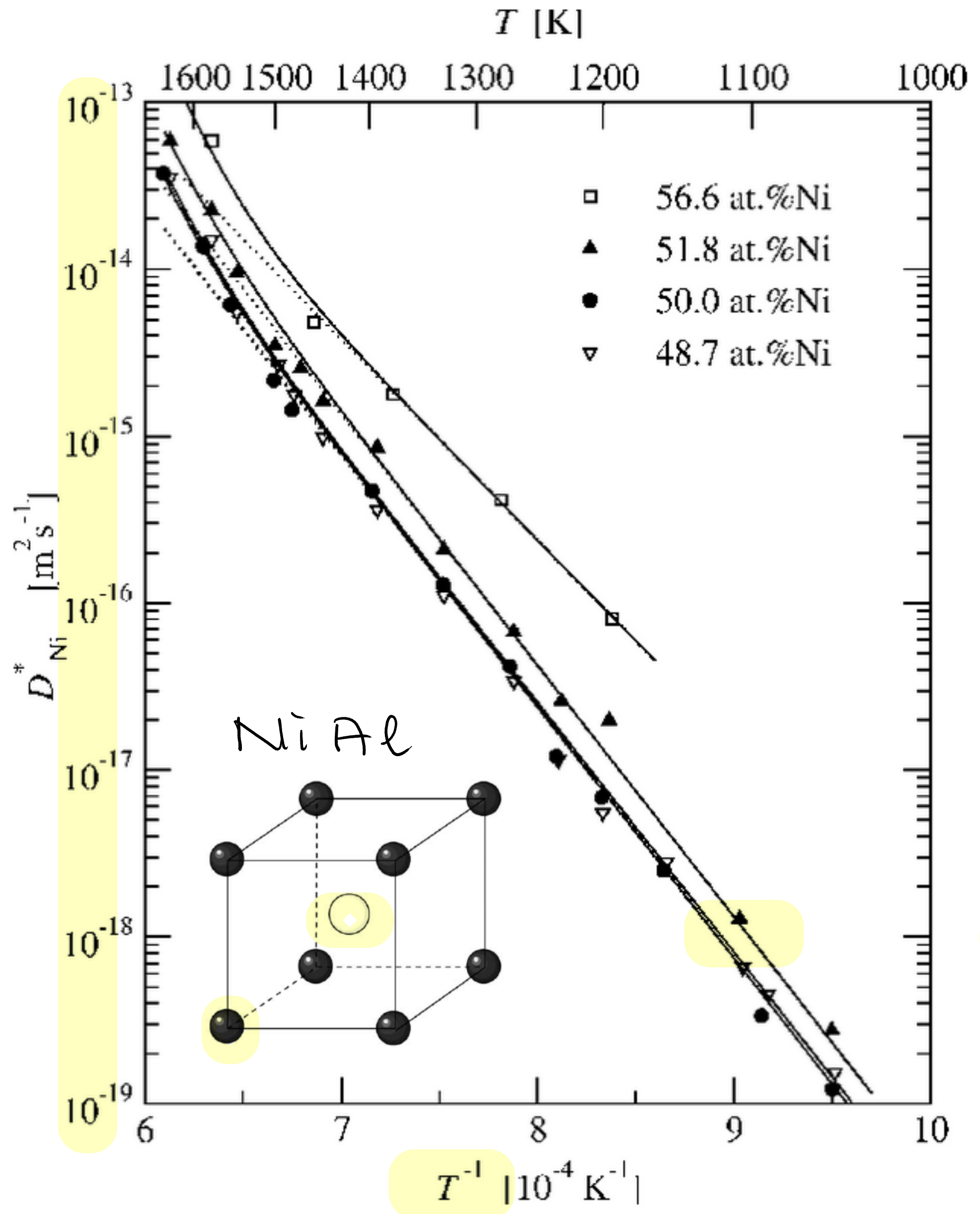
$$\frac{\partial q}{\partial t} + \cancel{\frac{\partial q}{\partial y} \cdot \underbrace{\frac{\partial y}{\partial t}}_{-\frac{F}{\xi}}} = \cancel{-\frac{1}{\xi} F \frac{\partial q}{\partial y}} + D \frac{\partial^2 q}{\partial x^2} \quad \Rightarrow \quad \frac{\partial q}{\partial t} = D \frac{\partial^2 q}{\partial x^2}$$

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

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

$$\begin{cases} \langle x \rangle = \frac{F}{\xi} t \\ \langle (x - \langle x \rangle)^2 \rangle = 2Dt = \langle x^2 \rangle - \langle x \rangle^2 \\ \langle x^2 \rangle = \langle (x - \underset{\approx 0}{\underset{\uparrow}{x(0)}})^2 \rangle = 2Dt + \frac{F^2}{\xi^2} t^2 \end{cases}$$

spostamento quadratico medio



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.

Herzig, Divinski 2004

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

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

legge di Arrhenius

$$\langle |\Delta \vec{r}|^2 \rangle = 6Dt$$

$$\sigma^2 = 6D\tau_D$$

$$\tau_D = \sigma^2/6D \sim 1/D$$

$$\tau_D = \frac{9 \times 10^{-20}}{6 \times 10^{-18}} \, s \simeq 10^{-2} s$$

Modello di Maxwell

$$\eta = G_0 \tau$$

$$\tau = \frac{\eta}{G_0} \sim \eta$$

$$\tau = \frac{10^8 \, Pa \cdot s}{10^{10} \, Pa} \approx 10^{-2} s$$

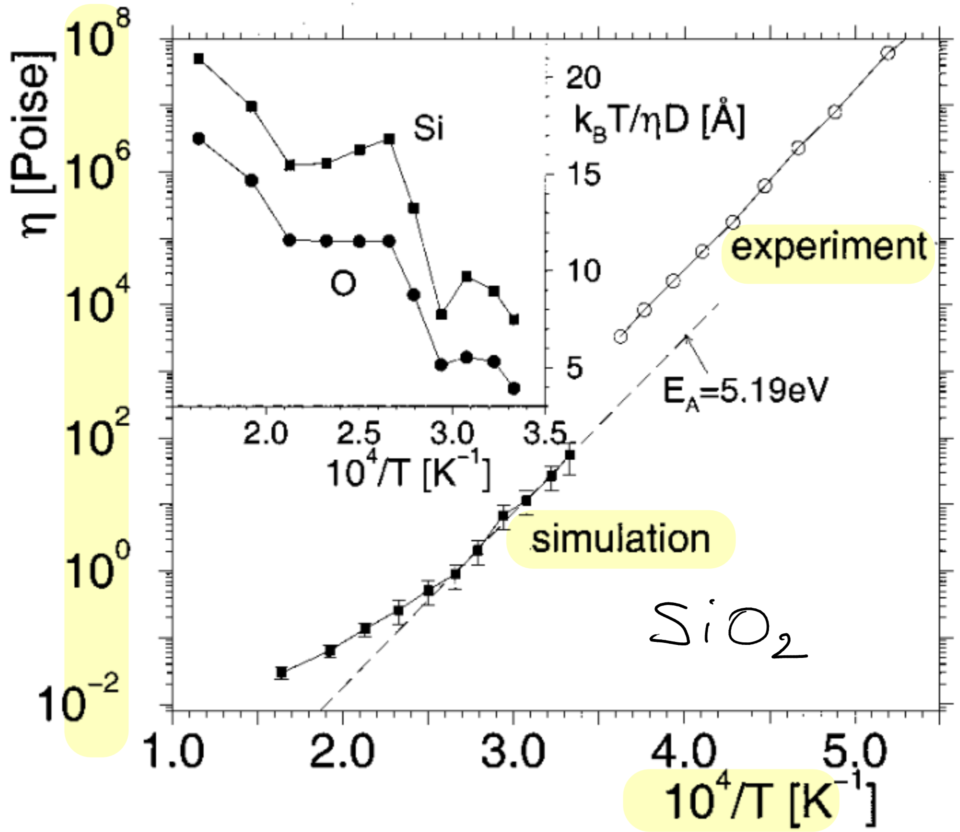
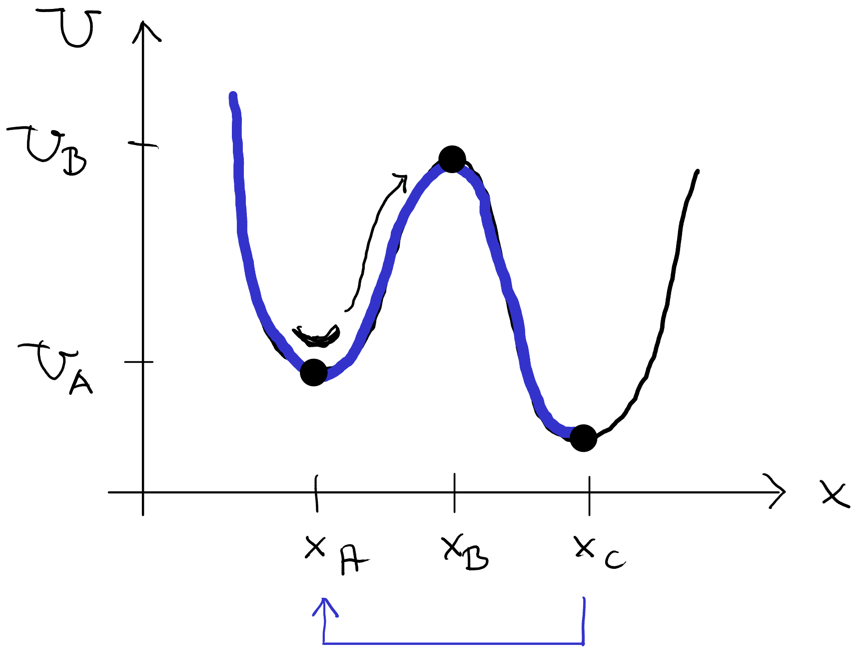


FIG. 10. Main figure: Arrhenius plot of the shear viscosity from the simulation (solid squares). The dashed line is a fit with an Arrhenius law to our low-temperature data. The open circles are experimental data from Urbain *et al.* (Ref. 35). Inset: temperature dependence of the left hand side of Eq.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

Horbach, Kob 1999

3) Problema di Kramers : attivazione termica (1940)



particella browniana, sovrasmorzata in un solvente a temperatura T

equilibrio : $D = k_B T/\xi$ (FD)

doppia buca 1d

$$U_B - U_A \gg k_B T$$

H. Kramers
1894 – 1952

Smoluchowski 1d

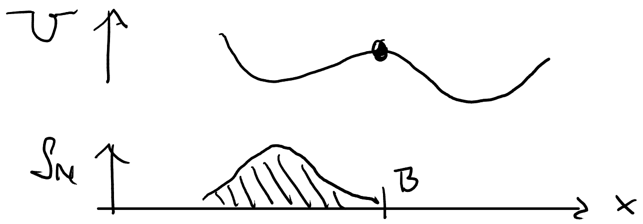
$$\frac{\partial p}{\partial t} = -\frac{1}{\xi} F \frac{\partial p}{\partial x} + D \frac{\partial^2 p}{\partial x^2}$$

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

condizioni al contorno :
assorbenti in c : $p(x_c) = 0$

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

Goal: tempo di uscita medio τ $\qquad \rho_N(x,t) \rightarrow J_N$



$$\Delta n = \int_{-\infty}^{x_B} dx'' \rho_N(x'') \qquad J_N = \frac{\Delta n}{\tau}$$

$$\Delta p = \int_{-\infty}^{x_B} dx'' p(x'') \qquad J = \frac{\Delta p}{\tau} \qquad \tau = \frac{\Delta p}{J}$$

$$\frac{1}{\varepsilon}\frac{dU}{dx}\,p + \frac{K_B T}{\varepsilon}\frac{dp}{dx} = -J$$

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

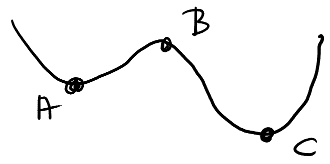
$$\frac{1}{\varepsilon}\frac{dU}{dx}\varphi\exp\left(-\frac{U}{K_BT}\right) + \frac{\cancel{K_BT}}{\varepsilon}\left(-\frac{1}{\cancel{K_BT}}\right)\frac{dU}{dx}\exp\left(-\frac{U}{K_BT}\right)\varphi + \frac{K_BT}{\varepsilon}\frac{d\varphi}{dx}\exp\left(-\frac{U}{K_BT}\right) = -J$$

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

$$\varphi(x) = \underbrace{\varphi(x_c)}_{=0} - \frac{\varepsilon J}{K_BT}\int_{x_c}^{x} dx'\exp\left(\frac{U(x')}{K_BT}\right) \Rightarrow p(x) = \frac{\varepsilon J}{K_BT}\,e^{-\frac{U(x)}{K_BT}}\int_{x}^{x_c} dx'\exp\left(\frac{U(x')}{K_BT}\right)$$

Tempo di uscita

$$\tau = \frac{\Delta p}{J} = \frac{\varepsilon}{K_BT}\int_{-\infty}^{x_B} dx''\,e^{-\frac{U(x'')}{K_BT}}\underbrace{\int_{x''}^{x_c} dx'\,e^{\frac{U(x')}{K_BT}}}_{*}$$



$*$ $\approx$ cost se $x'' \approx x_A$

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

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

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

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

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

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

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

$$= \frac{2\pi \varepsilon}{m\omega_A \omega_B} \exp\left(\frac{U_B - U_A}{K_B T}\right)$$

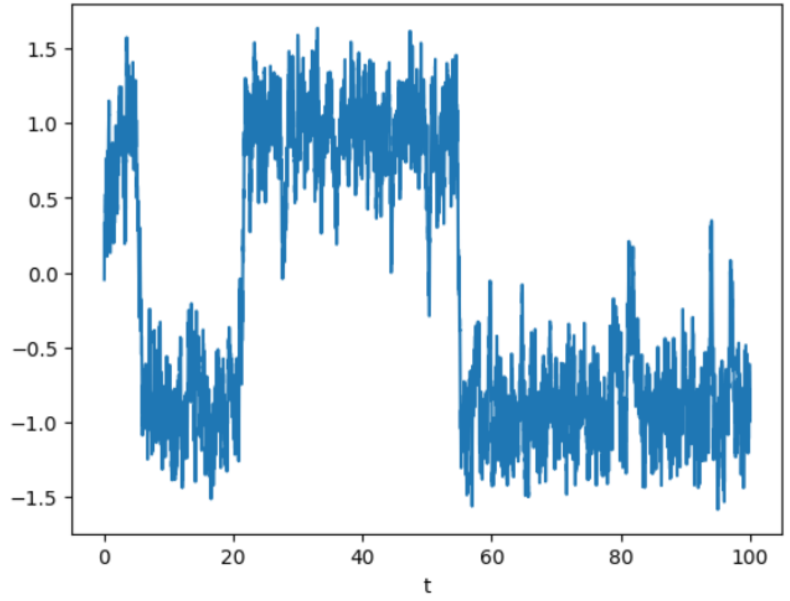
Legge di Arrhenius

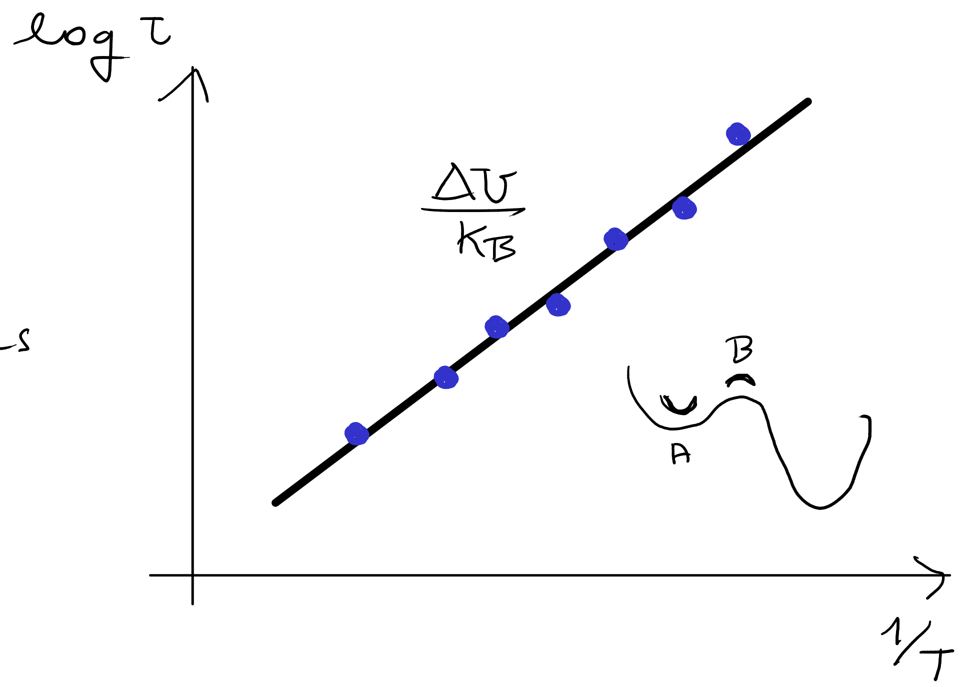
$$\tau = \frac{2\pi\xi}{m\omega_A\omega_B}\exp\left(\frac{\Delta U}{k_B T}\right)$$

$\uparrow$ fattore di Arrhenius

$\uparrow\xi \ \uparrow\tau \qquad \uparrow\omega_A \ \downarrow\tau$

$$\tau = \tau_0 \exp\left(\frac{\Delta E}{k_B T}\right)$$





Svante Arrhenius
1859 — 1927