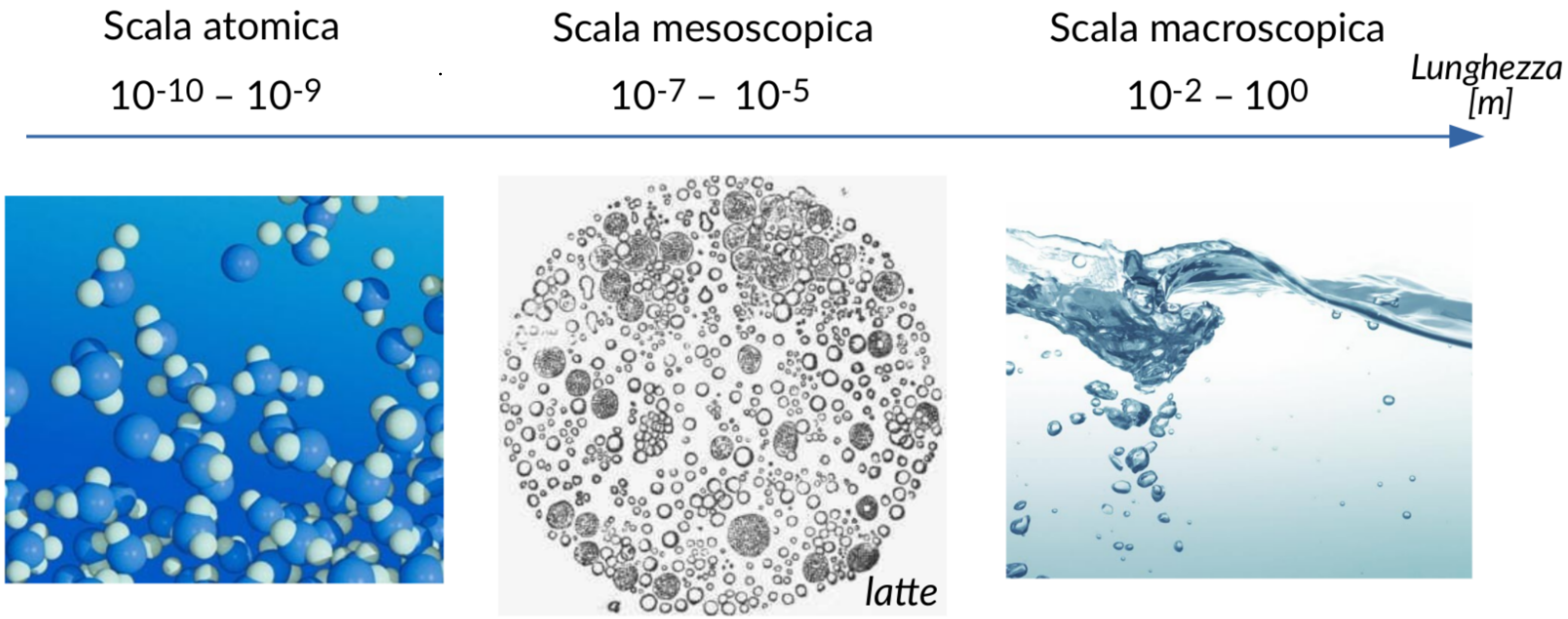
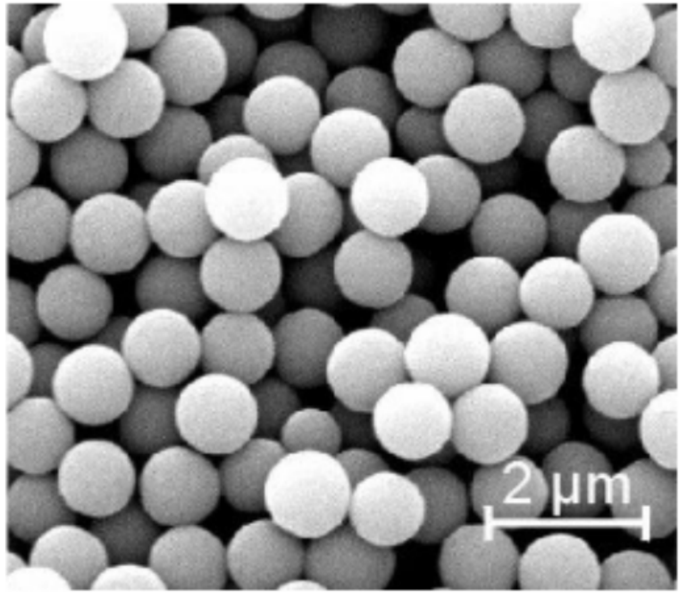
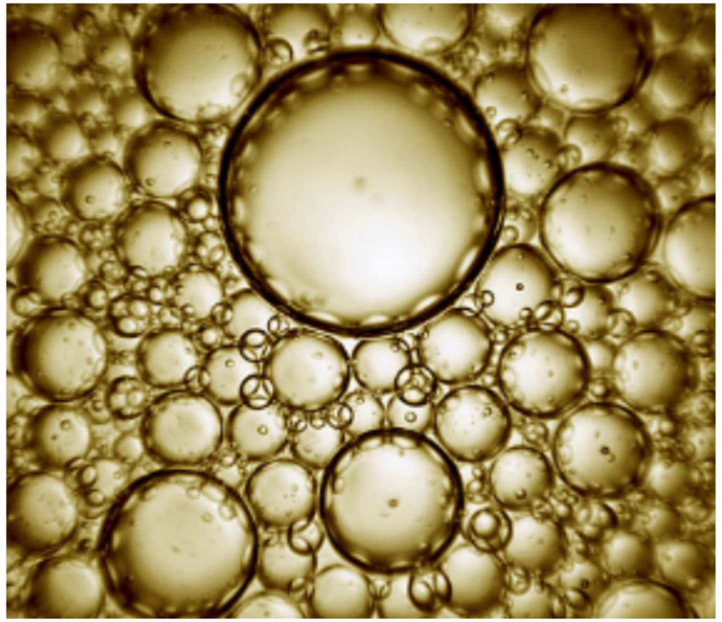

Scala atomica
$10^{-10} – 10^{-9}$
Scala mesoscopica
$10^{-7} – 10^{-5}$
Scala macroscopica
$10^{-2} – 10^{0}$
Lunghezza [m]
latte

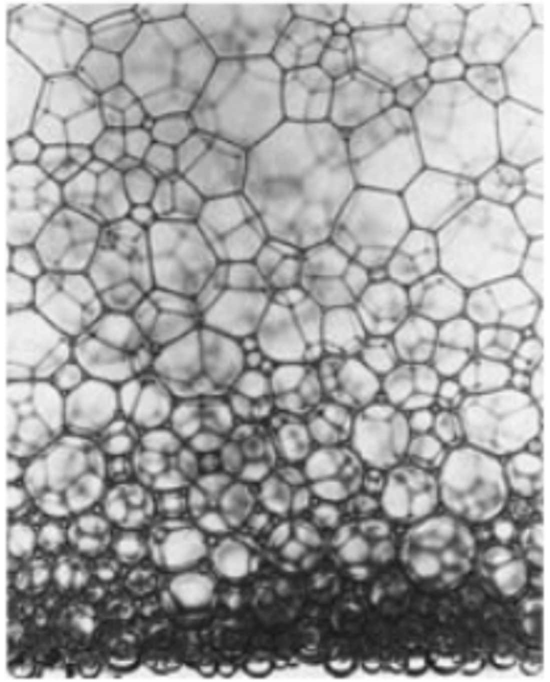
PMMA



SOSPENSIONE COLLOIDALE



EMULSIONE

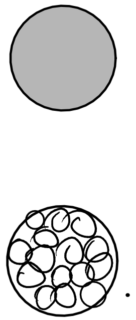


SCHIUME

Sospensione colloidale

Def.: miscela fortemente asimmetrica composta da particelle solide mesoscopiche sospese in un solvente (liquido) microscopico

meso: $10^{-7} - 10^{-5}$ m   micro: $10^{-10} - 10^{-9}$ m



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

$\updownarrow a \quad N \sim \left(\frac{a}{\xi_0}\right)^3 \sim \left(\frac{10^{-6}}{10^{-10}}\right)^3 \sim 10^{12}$

ξ_0

Criterio di stabilità:

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

$\uparrow$
particella colloidale

Es.: grafite $\rho_c \approx 10^3 \frac{Kg}{m^3}$ $T = 300\ K$

$$a \lesssim \left(\frac{10^{-23} \frac{J}{K} \times 3\cancel{0}0\ K}{10^3 \frac{Kg}{m^3} \times \cancel{1}0 \frac{m}{s^2}} \right)^{1/4} \approx \left(3 \times 10^{-25} \right)^{1/4} \approx 7 \times 10^{-7}\ m$$

Materia soffice:

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

$\epsilon_{dura} \sim 100\ k_B T_a$ $\epsilon_{soffice} \sim 10\ k_B T_a$

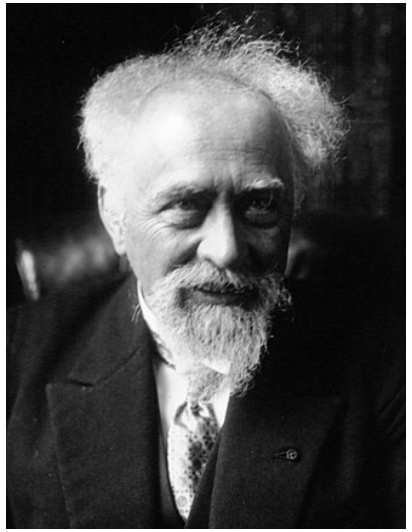
$\sigma_{dura} \sim 10^{-10}\ m$ $\sigma_{soffice} \sim 10^{-6}\ m$

$$\frac{Y_{dura}}{Y_{soffice}} \sim \frac{\epsilon_{duro}}{\epsilon_{soffice}} \cdot \left(\frac{\sigma_{soffice}}{\sigma_{duro}} \right)^3 \sim \frac{100}{10} \cdot \left(\frac{10^{-6}}{10^{-10}} \right)^3 = \underline{10^{13}}$$

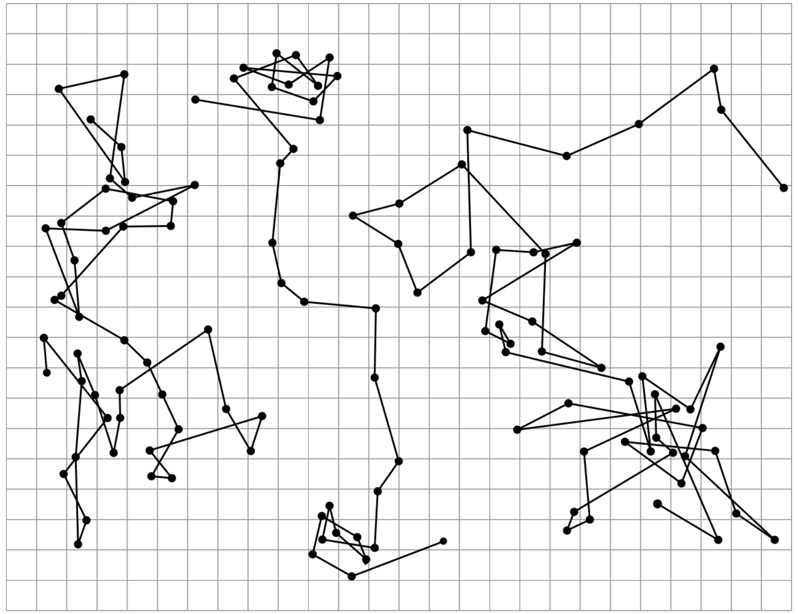
DINAMICA BROWNIANA

1827 : Brown (botanico)
1905 : Einstein
1906 : Smoluchowski
1908 : Langevin
1909 : Perrin (Nobel 1926)

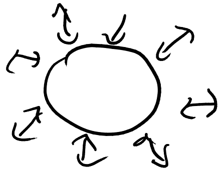
→ teoria dei processi stocastici



J.-B. Perrin



EQUAZIONE DI LANGEVIN



Classica, fenomenologica, stocastica

Particella massa m, forza esterna, sospesa in un solvente (T)

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

attrito viscoso macro — forza stocastica micro

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

$\vec{\theta}$ variabile stocastica

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

$\langle \dots \rangle$ = media sulle realizzazioni forza stocastica

Particella libera

$$\vec{F}_{est} = \vec{0}$$

$$m \frac{d\vec{v}}{dt} = -\xi \vec{v} + \vec{\theta}(t)$$ [processo di Ornstein-Uhlenbeck]

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

$$\frac{dx}{dt} = a x + b(t)$$ → variazione delle costanti $\quad a = -\frac{\xi}{m} \quad b = \frac{1}{m}\theta$

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

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

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

Soluzione formale

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

Relazione di fluttuazione-dissipazione

Solvente = bagno termico a temperatura T $\Rightarrow$ $\xi \leftrightarrow \theta_0$ $\qquad \frac{1}{2} m \langle |\vec{v}|^2 \rangle_{eq} = \frac{3}{2} k_B T$

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

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

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

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

$$= \frac{6\theta_0}{m^2} \int_0^t ds\, e^{-\frac{2\xi}{m}(t-s)} = \frac{6\theta_0}{m^2} \frac{m}{2\xi} \left[e^{\frac{2\xi}{m}(s-t)} \right]_0^t = \frac{3\theta_0}{\xi m} \left(1 - e^{-\frac{2\xi}{m} t} \right)$$

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

Limite $t \to \infty$

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

$$\langle |\bar{v}(\infty)|^2 \rangle = \langle |\bar{v}|^2 \rangle_{eq} \Rightarrow \frac{3\theta_0}{\xi \cdot m} \simeq \frac{3 K_B T}{m}$$

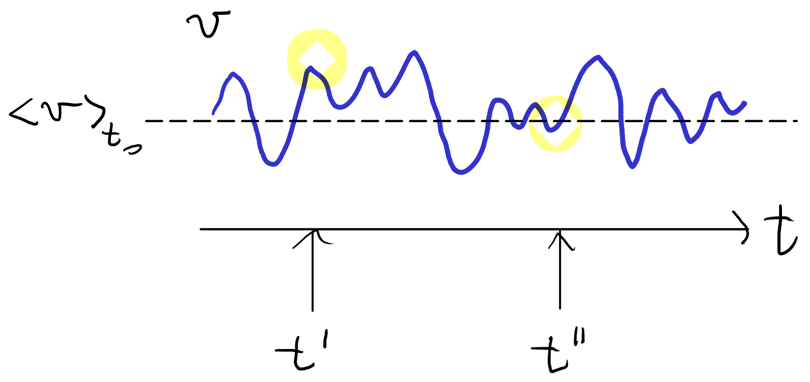
$$\Rightarrow \boxed{\theta_0 = K_B T \cdot \xi}$$

relazione

di fluttuazione - dissipazione

Funzione di correlazione della velocità

1d:



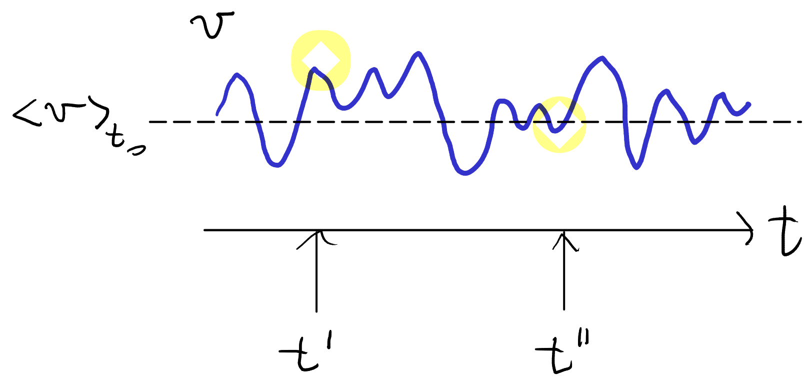
$$C_v(t',t'') = \langle (v(t') - \langle v \rangle) \cdot (v(t'') - \langle v \rangle) \rangle_{t_0}$$

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

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

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

Funzione di correlazione della velocità



1d :

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

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

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

Ergodicità : $\langle \dots \rangle_{t_0} = \langle \dots \rangle_{eq} \rightarrow$ media d'ensemble

$t = t'' - t' \quad (t'' > t')$

$C_v(t) = \langle v(t) \cdot v(0) \rangle_{eq}$ stazionario : invarianza per traslazione temporale

3d :

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

$\langle \dots \rangle \rightarrow$ media sul rumore $\rightarrow$ sulle realizzazioni della forza stocastica

$\langle \dots \rangle_{eq} \rightarrow$ sul rumore e sulle velocità della particella

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

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

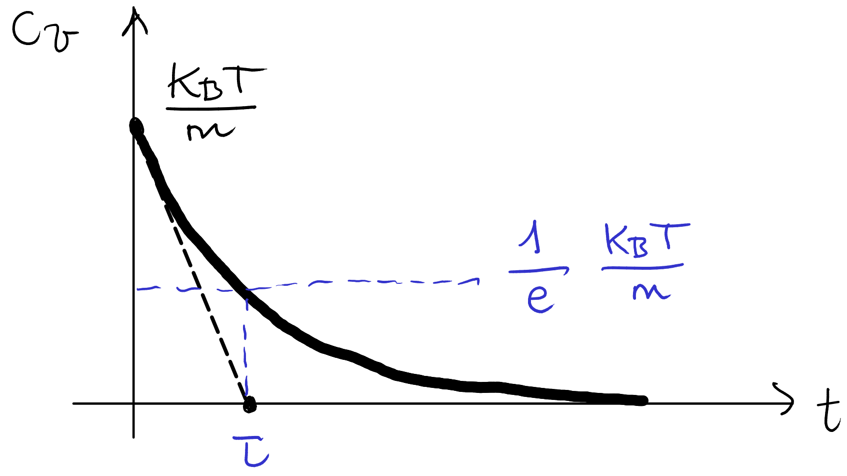
$$= \frac{1}{3}\langle \vec{v}(0)\cdot\vec{v}(0)\rangle_{eq}\, e^{-\frac{\xi}{m}t} + \frac{1}{3m}\int_0^t ds\, e^{-\frac{\xi}{m}(t-s)} \overbrace{\langle \vec{\theta}(s)\cdot\vec{v}(0)\rangle_{eq}}^{=0}$$

$$= \frac{1}{3}\langle |\vec{v}|^2\rangle_{eq}\, e^{-\frac{\xi}{m}t}$$

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

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

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



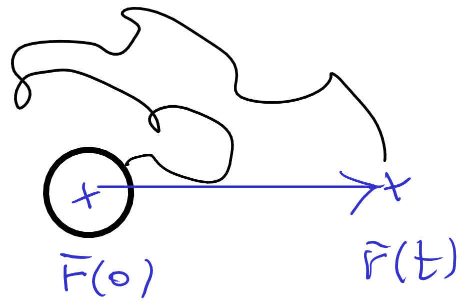
(es.) Mostra che

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

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

Spostamento quadratico medio

→ moto browniano + RW



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

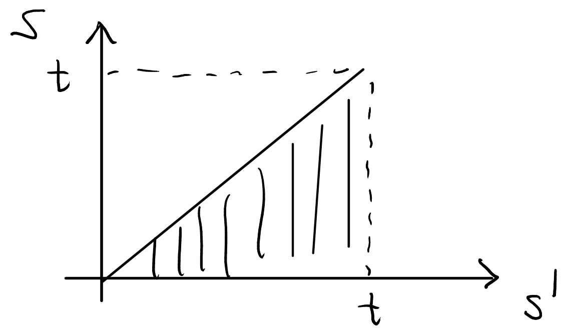
$$\Delta\bar{r}(t) = \int_0^t ds\, \bar{v}(s)$$

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

$$= 2\int_0^t ds \int_0^s ds' \langle \bar{v}(s)\cdot\bar{v}(s')\rangle_{eq}$$

cambio variabile

$t' = s - s'$



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

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

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

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

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

(es.) Mostra che:

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

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

$$\langle|\Delta\vec r|^2\rangle_{eq} = 6\,\frac{K_BT}{\xi}\left[t + \frac{m}{\xi}\left(-\frac{\xi}{m}t + \frac{1}{2}\left(\frac{\xi}{m}\right)^2 t^2\right)\right] \qquad \langle|\vec v(0)|^2\rangle_{eq}$$

$$= \frac{3K_BT}{m}\,t^2 = \langle|\vec v|^2\rangle_{eq}\,t^2$$ balistico

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

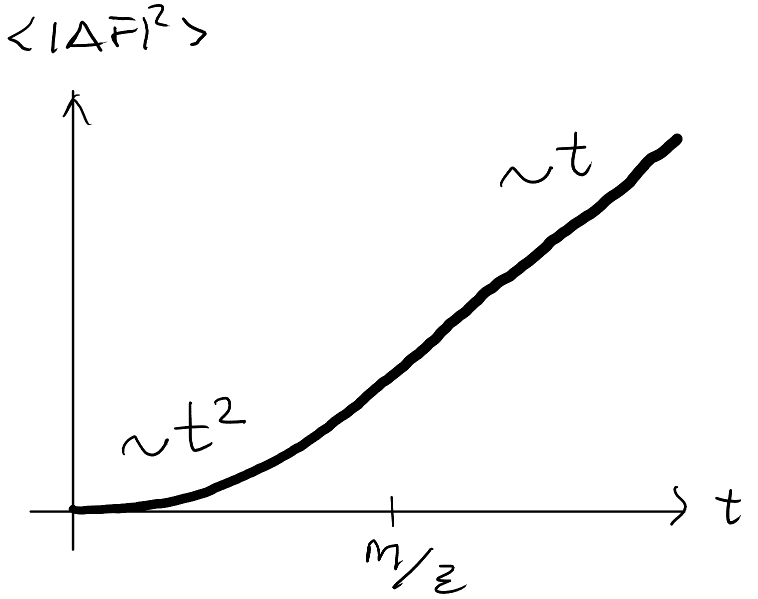
$$\langle|\Delta\vec r|^2\rangle_{eq} = 6\,\frac{K_BT}{\xi}\,t = 2d\,\boxed{\frac{K_BT}{\xi}}\,t$$ diffusivo

$$\langle|\Delta\vec r|^2\rangle_{eq} = 2dDt$$

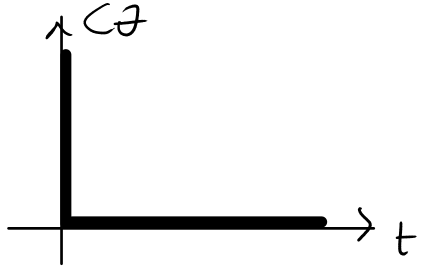
coefficiente di diffusione D

$T\uparrow \quad D\uparrow$

$\xi\uparrow \quad D\downarrow$



1d : $\langle \theta(t) \rangle = 0$ $\quad \langle \theta(t')\,\theta(t'') \rangle = 2\theta_0\, \delta(t'-t'')$ $\quad t = t'-t''$



$C_\theta(t) = 2\theta_0\, \delta(t) \to \tau = 0$!

$\Rightarrow$ markoviana

EQUAZIONE DI LANGEVIN SOVRA-SMORZATA

$$m \frac{d\vec{v}}{dt} = \vec{F}_{est} - \xi \vec{v} + \vec{\theta}(t) \qquad \theta_0 \sim \xi \qquad \text{(equilibrio)}$$

≈ 0 termine inerziale $\ll$ frizione / forza stocastica

fluttuazione dissipazione

$$\xi \frac{d\vec{r}}{dt} = \vec{F}_{est} + \vec{\theta}(t)$$ "overdamped" $\rightarrow$ dinamica browniana $\qquad \theta_0 = k_B T \cdot \xi$

Particella libera:

$$\frac{d\vec{r}}{dt} = \frac{1}{\xi} \vec{\theta}(t) \qquad \vec{r}(t) = \vec{r}(0) + \frac{1}{\xi} \int_0^t ds\, \vec{\theta}(s) \qquad \langle \vec{\theta}(t) \rangle = \vec{0} \qquad \langle \vec{\theta}(t) \cdot \vec{\theta}(t') \rangle = 2\theta_0 \delta_{\alpha p} \delta(t-t')$$

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

$$\langle |\Delta \vec{r}(t)|^2 \rangle_{eq} = 6 \frac{K_B T}{\xi} t$$

Esempi (Notebooks)

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

Algoritmo di Ermak

Eulero I ordine

$$\frac{d\bar{r}}{dt} = \frac{1}{\xi}\bar{F}_{est} + \frac{1}{\xi}\bar{\theta}(t)$$

Passo temporale Δt $\rightarrow$ $\vec{F}_{est} \approx cost$

1d

$$\frac{dx}{dt} = \frac{1}{\xi}F_{est} + \frac{1}{\xi}\theta(t)$$

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

$$x(t+\Delta t) \approx x(t) + \frac{1}{\xi}F_{est}\,\Delta t + \tilde{\theta}(t;\Delta t) \leftarrow \text{Ermak} \quad F_{est} \text{ arbitraria}$$

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

pdf 1d:

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

pdf 3d:

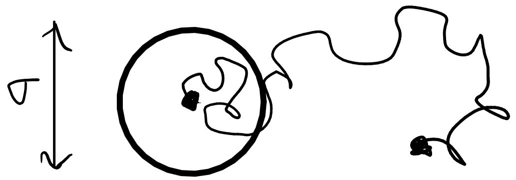
$$p(\vec{\tilde{\theta}}) = \frac{1}{(4\pi D\Delta t)^{3/2}} \exp\left(-\frac{|\vec{\tilde{\theta}}|^2}{4D\Delta t}\right)$$

Eq. Langevin sovra-smorzata: condizione di validità

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

$\tau \ll \tau_D$

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



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

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

$\sigma^2 \simeq D \tau_D$

$\tau_D \approx \frac{\sigma^2}{D}$

Es.: $\langle|\Delta \bar{r}|^2\rangle \approx \langle|\bar{v}|^2\rangle \Delta t^2$

--- o ---

Langevin: $\vec{r}, \vec{v}$		Sovra-smorzata: $\vec{r}$	Eq. diff. ordinarie STOCASTICHE
↙	↘	↓	
Fokker-Planck	Kramers	Smoluchowski	Eq. diff. derivate parziali
$p(\bar{v}, t)$	$p(\bar{r}, \bar{v}, t)$	$p(\bar{r}, t)$	DETERMINISTICHE
	↓	⇑	
	BH		

EQUAZIONE DI SMOLUCHOWSKI.

1d : $\frac{dx}{dt} = \frac{1}{\xi} F(x) + \frac{1}{\xi}\theta(t)$ $\quad \langle \theta(t) \rangle = 0 \quad \langle \theta(t)\theta(t') \rangle = 2\theta_0 \delta(t-t')$ equilibrio: $D = \frac{K_B T}{\xi}$

$\theta_0 = K_B T \xi$

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

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

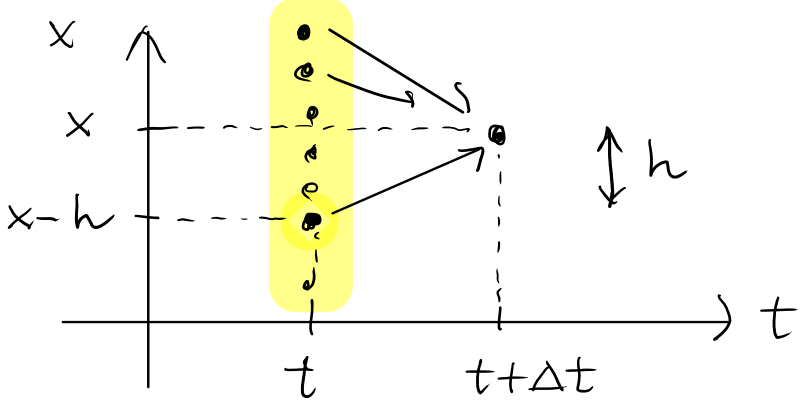
$$\begin{cases} \langle h \rangle = \frac{1}{\xi} F(x)\Delta t \\ \langle (h - \langle h \rangle)^2 \rangle = \langle \delta h^2 \rangle = \frac{1}{\xi^2}\int_t^{t+\Delta t} ds \int_t^{t+\Delta t} ds' \underbrace{\langle \theta(s)\theta(s') \rangle}_{\sim \delta(s-s')} = 2\frac{\theta_0}{\xi^2}\Delta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

Densità di prob. di h

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

Densità di prob.: $p(x,t)$

Master equation per $p(x,t)$



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

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

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

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

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

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

Taylor I ordine in Δt

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

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

Eq. di Smoluchowski

$$\frac{\partial p}{\partial t} = -\underbrace{\frac{\partial}{\partial x}\left(\frac{1}{\xi}Fp\right)}_{\text{deriva}} + \underbrace{\frac{\partial^2}{\partial x^2}(Dp)}_{\text{diffusione}}$$

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

$\to$ deriva-diffusione

$$\frac{\partial p}{\partial t} + \frac{\partial}{\partial x}\left(\frac{1}{\xi}Fp - \frac{\partial}{\partial x}(Dp)\right) = 0 \quad \Rightarrow \quad \frac{\partial p}{\partial t} + \frac{\partial J}{\partial x} = 0$$

eq. continuità

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

3d

$$\Rightarrow \quad \frac{\partial p}{\partial t} + \vec{\nabla}\cdot\underbrace{\left(\frac{1}{\xi}\vec{F}p - \vec{\nabla}(Dp)\right)}_{\vec{J}} = 0$$

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

Casi particolari :

0) **Equilibrio** : $p(x,t) = \frac{1}{Z} \exp\left(-\frac{U(x)}{K_B T}\right)$

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

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

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

1) **Particella libera** : $F = 0$

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

Fourier :

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

$$\frac{\partial p_k}{\partial t} = -k^2 D\, \vec{p}_k(t) \quad \rightarrow \quad p_{\vec{k}}(t) = \vec{p}_{\vec{k}}(0)\, e^{-k^2 D t}$$

condizioni al contorno: sul bordo del dominio

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

condizioni iniziali: $p(\bar{r}, t=0) \rightarrow p(\bar{r}, 0) = \delta(\bar{r})$

$$p(\bar{r}, 0) = \delta(\bar{r}) \rightarrow p_{\bar{k}}(0) = 1$$

Spazio reale:

$$p(\bar{r}, t) = \frac{1}{(4\pi D t)^{3/2}}\, e^{-\frac{|\bar{r}|^2}{4Dt}} \qquad p(\bar{r}, 0) = \delta(\bar{r})$$

2) Forza costante

$$\frac{\partial p}{\partial t} = -\frac{F}{\xi}\frac{\partial p}{\partial x} + D\frac{\partial^2 p}{\partial x} \qquad y = x - \frac{F}{\xi}t \qquad p(x,t) \rightarrow q(y,t) \qquad dx = dy$$

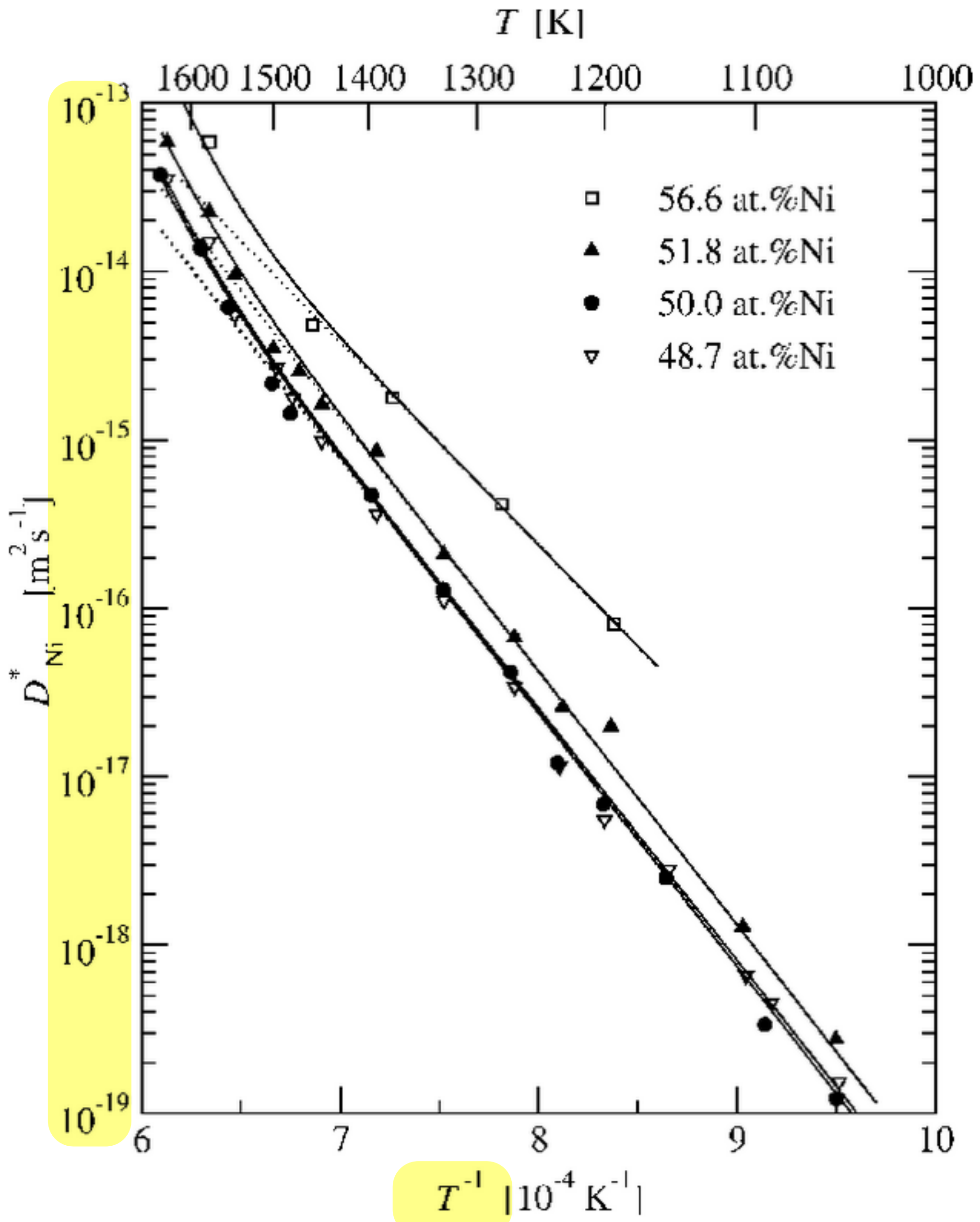
$$p(x,t)\,dx\,dt = q(y,t)\,dy\,dt \Rightarrow p(x,t) = q(y,t) \rightarrow y = y(x,t)$$

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

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

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

$$p(x,t) = \frac{1}{\sqrt{4\pi D t}}\exp\left[-\frac{(x-\frac{F}{\xi}t)^2}{4Dt}\right] \rightarrow \begin{cases} \langle x \rangle = \frac{F}{\xi}t \\ \langle (x(t) - \langle x(t) \rangle)^2 \rangle = 2Dt \end{cases}$$



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.

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

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

legge di Arrhenius

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

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

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

Maxwell:

$$\eta = G_\infty \tau$$

$$\eta \sim \tau$$

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

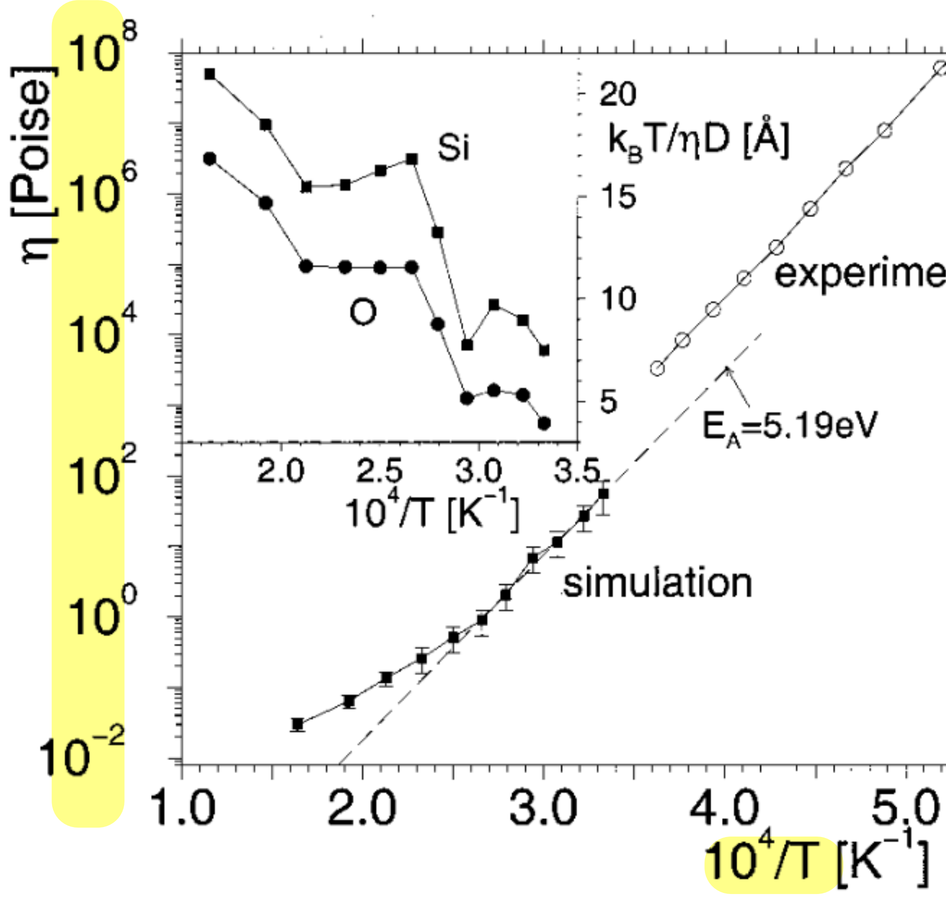
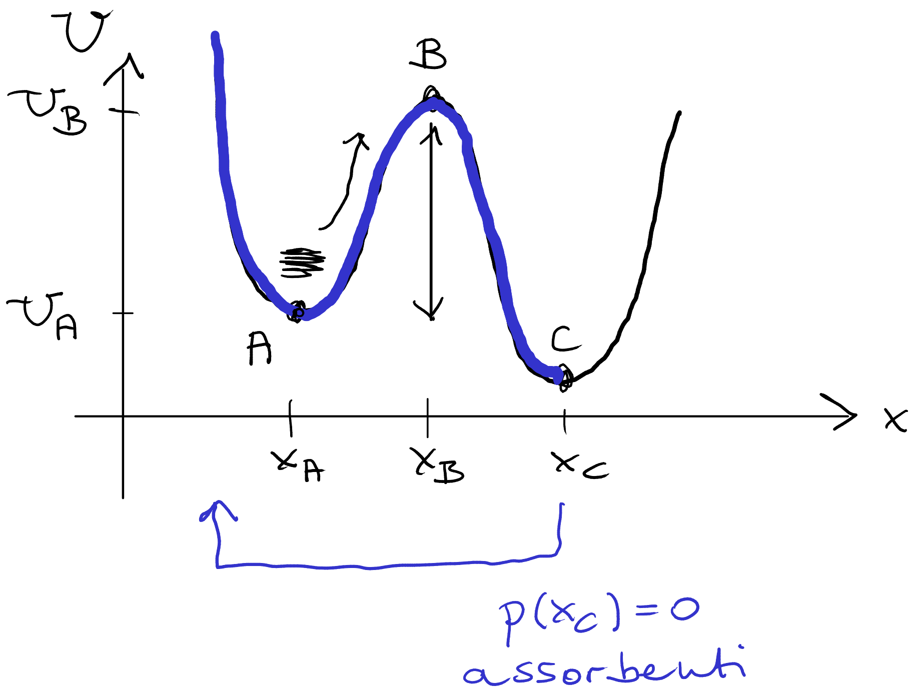


FIG. 10. Main figure: Arrhenius plot of the shear viscosity from the simulation (solid squares). The dashed line is a fit with an Arrhenius law to our low-temperature data. The open circles are experimental data from Urbain *et al.* (Ref. 35). Inset: temperature dependence of the left hand side of Eq.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

4) Attivazione termica: problema di Kramers (1940)



Particella browniana in equilibrio a T in una doppia buca di potenziale 1d

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

Smoluchowski: equilibrio

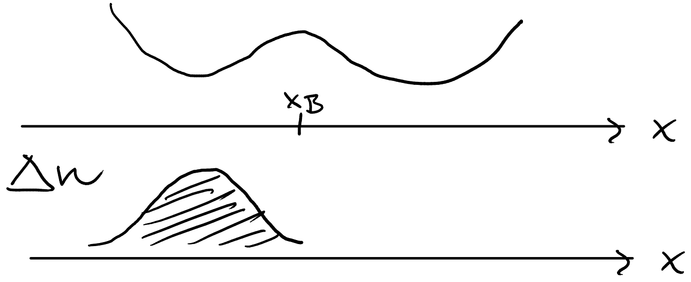
$$\frac{\partial p}{\partial t} = -\frac{1}{\xi} F \frac{\partial p}{\partial x} + D \frac{\partial^2 p}{\partial x^2} \qquad D = \frac{k_B T}{\xi}$$

$$\frac{\partial p}{\partial t} = \frac{\partial}{\partial x}\Big(\underbrace{\frac{1}{\xi}\frac{dU}{dx} p + \frac{k_B T}{\xi}\frac{\partial p}{\partial x}}_{-J} \Big)$$

H. Kramers
1894 – 1952

Goal: tempo di uscita medio τ

Regime stazionario: $\frac{\partial p}{\partial t} = 0 \Rightarrow J = \text{cost}$ $\qquad \rho_N(x,t) \rightarrow J_N$



$$J_N = \frac{\Delta n}{\tau} \qquad \tau = \frac{\Delta n}{J_N}$$

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

$$\frac{1}{\xi}\frac{dU}{dx}p + \frac{K_BT}{\xi}\frac{dp}{dx} = -J = \text{cost} \quad \rightarrow \quad p(x)$$

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

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

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

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

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

Tempo di uscita :

$$\tau = \frac{\Delta p}{J} = \frac{\xi}{K_BT}\int_{-\infty}^{x_B} dx'' \exp\left(-\frac{U(x'')}{K_BT}\right)\underbrace{\int_{x''}^{x_c} dx' \exp\left(\frac{U(x')}{K_BT}\right)}_{\circledast}$$

$$\circledast \quad \int_{x''}^{x_c} dx' \exp\left(\frac{U(x')}{K_BT}\right) \approx \text{cost} \quad \text{se} \quad x'' \approx x_A$$

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

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

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

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

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

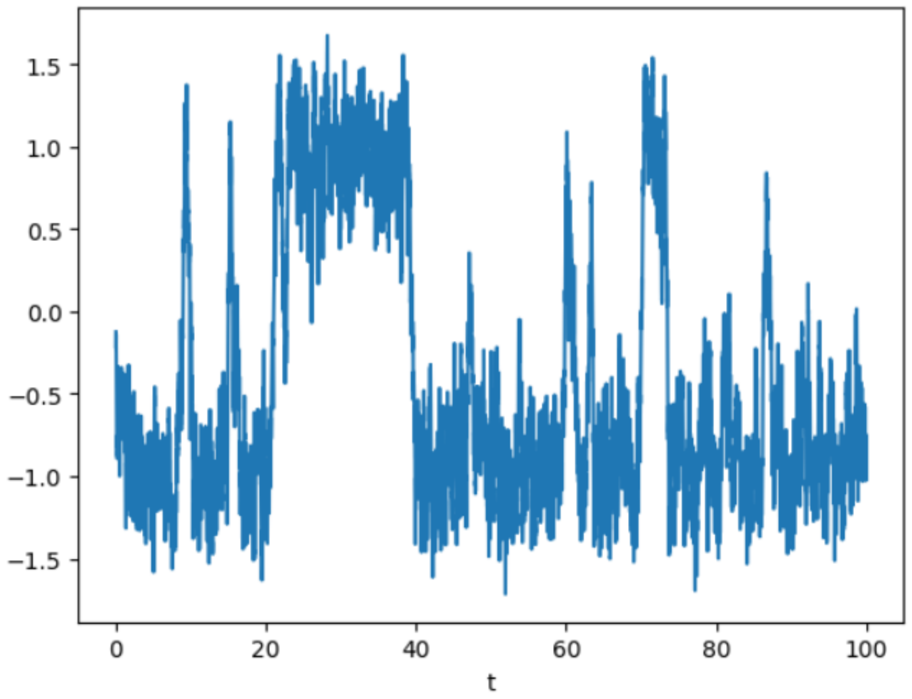
$$\tau = \frac{\varepsilon}{K_B T} \sqrt{\frac{2\pi K_B T}{m\omega_B^2}} \exp\left(\frac{U_B}{K_B T}\right) \exp\left(-\frac{U_A}{K_B T}\right) \int_{-\infty}^{\infty} dx'' \exp\left[-\frac{1}{2}\frac{m\omega_A^2}{K_B T}(x'' - x_A)^2\right]$$

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

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

fattore di Arrhenius

$\omega_A, \omega_B \uparrow \quad \tau \downarrow \qquad \xi \uparrow \quad \tau \uparrow$



Svante Arrhenius
1859 → 1927