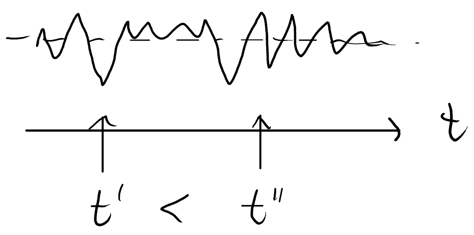
Funzione di autocorrelazione della velocità



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

Equilibrio:

- $\langle v \rangle = 0$
- C_v dipende da $t'' - t' = t$

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

In 3d:

$$C_v(t) = \frac{1}{3} \langle \vec{v}(t') \cdot \vec{v}(t'+t) \rangle \overset{t'=0}{=} \frac{1}{3} \langle \vec{v}(t) \cdot \vec{v}(0) \rangle$$

Langevin:

$$\vec{v}(t) = \vec{v}_0\, e^{-\xi/m\, t} + \frac{1}{m} \int_0^t ds\, e^{-\xi/m (t-s)}\, \vec{\theta}(s)$$

$$\vec{v}(t) = \vec{v}(t_0)\, e^{-\xi/m (t-t_0)} + \frac{1}{m} \int_{t_0}^t ds\, e^{-\xi/m (t-s)}\, \vec{\theta}(s) \qquad t_0 \to -\infty$$

$$= \int_{-\infty}^t ds\, e^{-\xi/m (t-s)}\, \vec{\theta}(s)$$

(es.) ... $\langle \vec{v}(t) \cdot \vec{v}(0) \rangle$

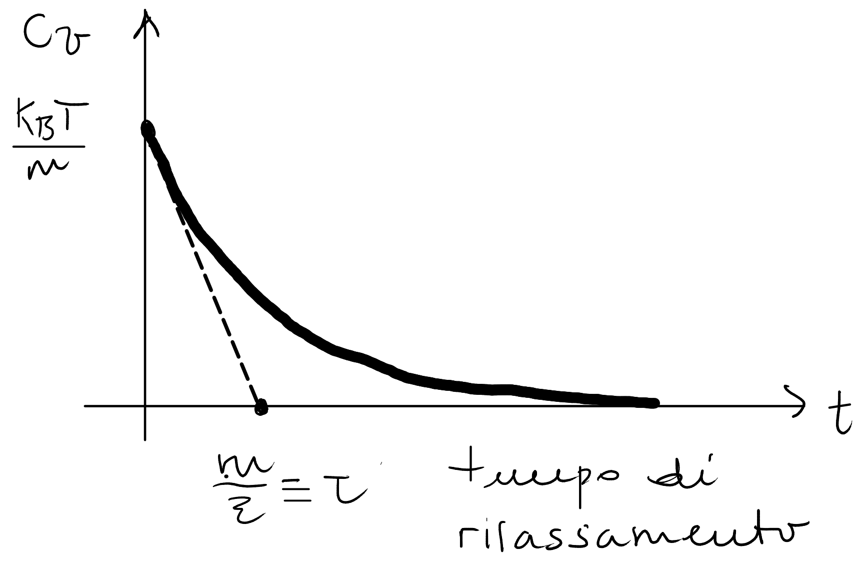
$$\frac{d\vec{v}}{dt} = -\xi/m\,\vec{v} + \frac{1}{m}\vec{\Theta}(t)$$

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

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

$$\langle \vec{v}(t)\cdot\vec{v}(0)\rangle = \langle |\vec{v}|^2\rangle\, e^{-\xi/m\,t} \qquad \langle v^2\rangle = \frac{3K_BT}{m}$$

$$C_v = \frac{1}{3}\langle \vec{v}(t)\cdot\vec{v}(0)\rangle = \frac{K_BT}{m}\, e^{-\xi/m\,t}$$

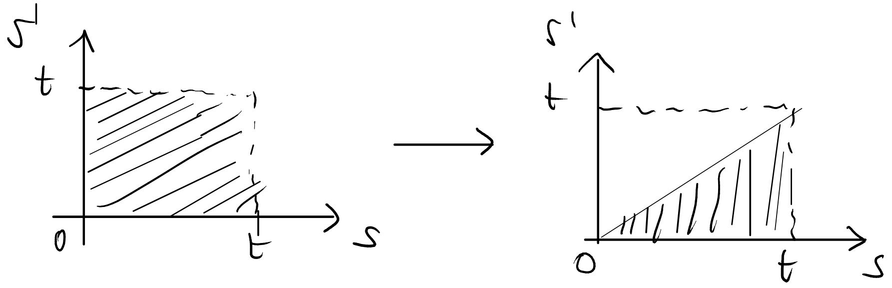


Spostamento quadratico medio

→ moto diffusivo

$$\Delta\vec{r} = \vec{r}(t) - \vec{r}(0) = \int_0^t \vec{v}(s)\, ds$$

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



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

$$\langle \vec{v}(s) \cdot \vec{v}(s') \rangle = 3\, C_v(s-s')$$

↙ Equilibrio

$t' = s - s'$

cambio variabile

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

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

Langevin:

$$C_v(t) = \frac{K_B T}{m} e^{-\xi/m\, t} \quad \underset{\text{es.}}{\rightarrow} \quad \langle |\Delta\vec{r}|^2 \rangle = 6 \frac{K_B T}{\xi} \left[t + \frac{m}{\xi} \left(e^{-\xi/m\, t} - 1 \right) \right]$$

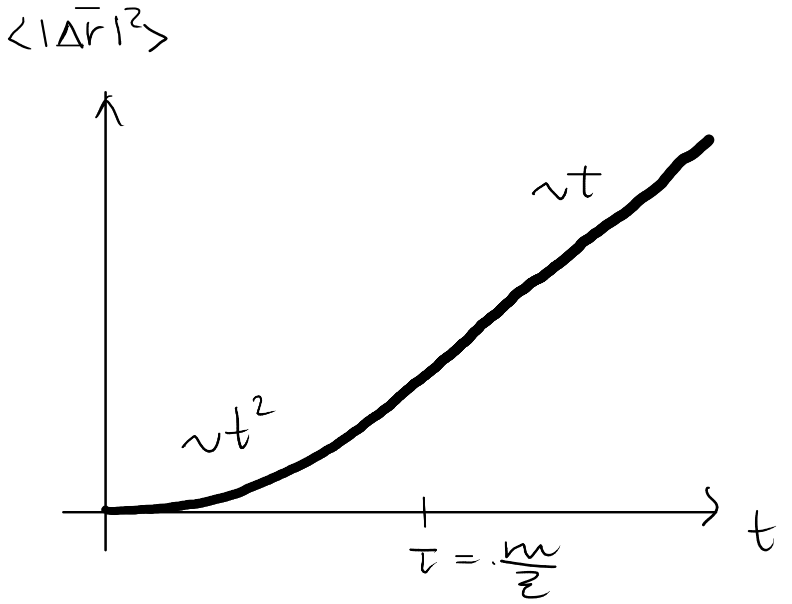
- $t \ll \frac{m}{\xi}$: $\langle |\Delta \vec{r}|^2 \rangle \approx 6 \frac{k_B T}{\xi} \left[t + \frac{m}{\xi} \left(-\frac{\xi}{m} t + \frac{1}{2} \frac{\xi^2}{m^2} t^2 \right) \right] = 3 \frac{k_B T}{\xi} \cdot \frac{\xi}{m} t^2 = \underbrace{\frac{3 k_B T}{m}}_{\langle v^2 \rangle} t^2$

  $\sim t^2$ <u>balistico</u>

- $t \gg \frac{m}{\xi}$: $\langle |\Delta r^2| \rangle \approx 6 \frac{k_B T}{\xi} t$ coefficiente di diffusione D

  $\sim t$ <u>diffusivo</u>

  $= 2 \cdot d \cdot D \cdot t$



EQUAZIONE DI LANGEVIN SOVRA-AMORTITA

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

trascurabile rispetto agli altri se $\xi \to \infty$, $\xi \sim \theta_0$

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

eq. Langevin sovra-amortita $\to$ dinamica Browniana

Caso libero

$$\vec{r}(t) = \vec{r}(0) + \frac{1}{\xi}\int_0^t ds\,\vec{\theta}(s) \qquad \Delta\vec{r} = \vec{r}(t) - \vec{r}(0) \qquad \theta_0 = k_B T \cdot \xi$$

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

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

coeff. diffusione

Esempi

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

Algoritmo di Ermak: potenziale generico

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

Eulero I ordine: intervallo Δt

$$x(t+\Delta t) = x(t) + \frac{1}{\xi}\int_t^{t+\Delta t} F(x)\,dt + \frac{1}{\xi}\int_t^{t+\Delta t}\theta(t)\,dt \approx x(t) + \frac{F(x)}{\xi}\Delta t + \underbrace{\frac{1}{\xi}\int_t^{t+\Delta t}\theta(t)\,dt}_{\tilde{\theta}}$$

$$\tilde{\theta}(t;\Delta t) = \frac{1}{\xi}\int_t^{t+\Delta t}\theta(t)\,dt$$

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

Teor. limite centrale $\Rightarrow$ $\tilde{\theta}$ ha distribuzione gaussiana

$$p(\tilde{\theta}) = \frac{1}{\sqrt{4\pi D\,\Delta t}}\, e^{-\frac{\tilde{\theta}^2}{4D\Delta t}} \xrightarrow[3d]{} p(\vec{\tilde{\theta}}) = \frac{1}{(4\pi D \Delta t)^{3/2}}\, e^{-\frac{|\tilde{\theta}|^2}{4D\Delta t}}$$

APPROCCIO DI FOKKER - PLANCK

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

eq. diff. ordinaria
<u>stocastica</u>

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

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

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

eq. diff. derivate parziali
<u>deterministica</u>