COLLOIDI

Esempi: industriali, alimentari, biologici

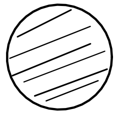
Def.: miscela fortemente asimmetrica composta da particelle solide di taglia mesoscopica sospese in un liquido semplice

- mesoscopico : $10\,nm \longrightarrow 10\,\mu m \sim 1\,\mu m$
- microscopico : $0.1\,nm \longrightarrow 1\,nm$

Stabilità $\rightarrow$ sedimentazione

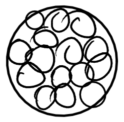
$\uparrow \; \Delta\rho < 0$

$\downarrow \; \Delta\rho > 0$



macroscopico

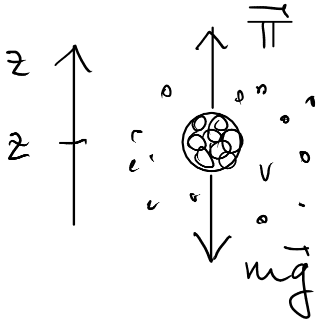
$N \sim N_A \sim 10^{23}$



mesoscopico

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

Criterio quantitativo:



- densità colloidale ρ_c
- —"— solvente ρ_s
- dimensioni lineare σ
- equilibrio T

Hamiltoniana: $H = \underset{\substack{\uparrow \\ K + U_0 \\ \text{particella libera}}}{H_0} + \underset{\substack{\uparrow \\ \text{interazione} \\ \text{ambiente} \\ \text{esterno}}}{U(z)}$

altezza CM

$$U(z) = \rho_c \sigma^3 g z - \rho_s \sigma^3 g z = \Delta\rho\, \sigma^3 g z$$

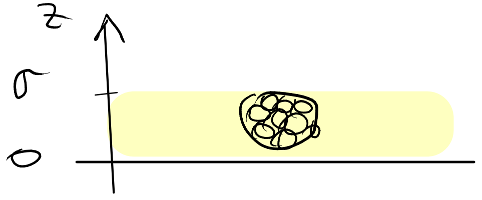
$\uparrow$ gravitazionale

prob. trovare colloide ad altezza z $\qquad Tr[\ldots] = Tr_z[Tr_0[\ldots]]$

$$p(z) = Tr_0\left[\frac{e^{-\beta H}}{Tr[e^{-\beta H}]}\right] = \frac{e^{-\beta U(z)}}{Tr_z[e^{-\beta U(z)}]} \qquad \beta\Delta\rho\,\sigma^3 g = K$$

$$\langle z \rangle = \frac{Tr_z[e^{-\beta U(z)} z]}{Tr_z[e^{-\beta U(z)}]} = \frac{\int_0^\infty dz\, e^{-\beta U(z)} z}{\int_0^\infty dz\, e^{-\beta U(z)}} = \frac{\int_0^\infty dz\, e^{-Kz} z}{\int_0^\infty dz\, e^{-Kz}} = \frac{\underbrace{\left[-\frac{1}{K} e^{-Kz} z\right]_0^\infty}_{=0} + \int_0^\infty \frac{e^{-Kz}}{\cancel{K}} dz}{\frac{1}{\cancel{K}}}$$

$$\langle z \rangle = \int_0^\infty e^{-Kz} dz = \frac{1}{\beta\Delta\rho\,\sigma^3 g} = \frac{k_B T}{\Delta\rho\,\sigma^3 g} > \sigma$$



$\rightarrow$ sedimentazione

$$\langle z \rangle > \sigma \Rightarrow k_B T > \Delta\rho\,\sigma^4 g \Rightarrow \frac{k_B T}{\Delta\rho\,\sigma^4 g} > 1$$

Es: grafite $\rho_s = 10^3 \frac{kg}{m^3} \Rightarrow \Delta\rho \sim 10^3 \frac{kg}{m^3}$ @ $T_{amb} \rightarrow k_B T_{amb} \sim 10^{-23} \cdot 300 \sim 4 \times 10^{-21}$ J

$$\sigma < \sqrt[4]{\frac{4\times 10^{-21}}{10^3 \times 10}}\ m \sim \sqrt[4]{\frac{10^{-21}}{10^4}} \sim 10^{-6}\ m = 1\ \mu m$$

DINAMICA COLLOIDALE

1827: Brown botanico → moto Browniano
1904: Pearson biologo → migrazioni insetti
1905: Einstein modello del moto Browniano: meso → micro
1906: Langevin → eq. Langevin eq. diff. stocastica → Ito, Stratonovic
1909: Perrin → N_A → Nobel

EQUAZIONE DI LANGEVIN

Modellizzazione → fenomenologico → classico

Particella massa m in un solvente e sotto potenziale esterno

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

Ipotesi: separazione di scale di tempo

$t \rightarrow t+dt$

$\vec{\theta}$ è una variabile stocastica

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

↓ effetto "medio" assorbito in $-\xi\vec{v}$

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

↓ $\vec{\theta}$ è scorrelata a istanti ≠

$\langle \dots \rangle$ = realizzazione forza stocastica

modello Caldeira-Leggett

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

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

Struttura :

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

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

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

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

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

Langevin : $a = -\xi/m$, $b = \frac{\theta}{m}$

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

Relazione fluttuazione – dissipazione

ξ, $\vec{\theta}$ non sono indipendenti. Solvente in equilibrio a T.

Fluttuazioni della velocità $\rightarrow$ $\sigma_v^2 = \langle (v - \langle v \rangle)^2 \rangle = \langle v^2 \rangle - \langle v \rangle^2$ es.

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

$$+ \frac{1}{m^2} \int_0^t ds \int_0^t ds'\, e^{-\xi/m (2t - s - s')} \underbrace{\langle \vec{\theta}(s) \cdot \vec{\theta}(s') \rangle}_{3 \cdot 2\theta_0 \cdot \delta(s-s')}$$

$$\langle v^2(t) \rangle = \langle v^2(0) \rangle \underbrace{e^{-2\xi/m\, t}}_{\to 0} + \frac{6\theta_0}{m^2} \int_0^t ds\, e^{-2\xi/m (t-s)}$$

Per $t \to \infty$ il sistema sia in equilibrio

$$\lim_{t\to\infty} \langle v^2(t) \rangle = \langle v^2 \rangle_{eq} = \frac{6\theta_0}{m^2} \lim_{t\to\infty} \left(\frac{m}{2\xi} \right) \underbrace{\left[e^{-\frac{2\xi}{m}(t-s)} \right]_0^t}_{\left(1 - e^{-\frac{2\xi}{m}t}\right),\ e^{-\frac{2\xi}{m}t} \to 0} = \frac{3\theta_0}{m\xi}$$

$$\frac{1}{\cancel{2}} m \langle v^2 \rangle_{eq} = \frac{3}{\cancel{2}} k_B T \quad \text{equipartizione}$$

$$\Rightarrow \frac{3 k_B T}{m} = \frac{3\theta_0}{m\xi} \Rightarrow \boxed{\theta_0 = k_B T \cdot \xi}$$

fluttuazioni (θ_0) — dissipazione (ξ)