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Theory of Brownian Motion Revisited
-Prototype of Dynamic Coarse Graining-

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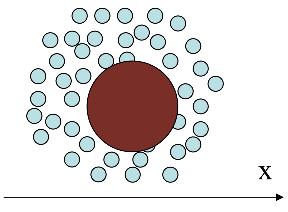
Theory of Brownian Motion:
Prototype of Coarse Graining in Dynamics



Macroscopic equation

$$m\ddot{x} = -\zeta\dot{x} - \frac{\partial U}{\partial x}$$

Langevin equation

$$m\ddot{x} = -\zeta\dot{x} - \frac{\partial U}{\partial x} + F_r(t)$$

Microscopic equation

$$m\ddot{x} = -\frac{\partial U_m(x,\{\mathbf{r}\})}{\partial x} \qquad m_i\ddot{\mathbf{r}}_i = -\frac{\partial U_m(x,\{\mathbf{r}\})}{\partial \mathbf{r}_i}$$

Fluctuation Dissipation Theorem

$$m\ddot{x} = -\zeta\dot{x} - \frac{\partial U}{\partial x} + F_r(t)$$

$$m\ddot{x} = -\zeta\dot{x} + F_r(t)$$

$$\frac{1}{2}m\langle\dot{x}^2\rangle = \frac{1}{2}k_B T$$

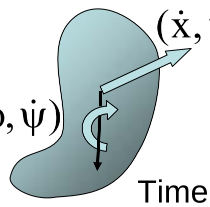
$$\langle F_r(t)F_r(t')\rangle = 2\zeta k_B T\delta(t-t')$$

$$0 = -\zeta\dot{x} - \frac{\partial U}{\partial x} + F_r(t)$$

$$\psi_{eq}(x) \propto \exp\left(-\frac{U(x)}{k_B T}\right)$$

Brownian Motion of Rigid Particle

Particles moving in a viscous fluid



$(\dot{\theta}, \dot{\phi}, \dot{\psi})$

$(\dot{x}, \dot{y}, \dot{z})$ x_i $(i = 1,2,...f)$ Generalized coordinate (position, orientation)

$(x, y, z, \theta, \phi, \psi)$

$U(x_i)$ Potential energy

Time evolution of the particle state

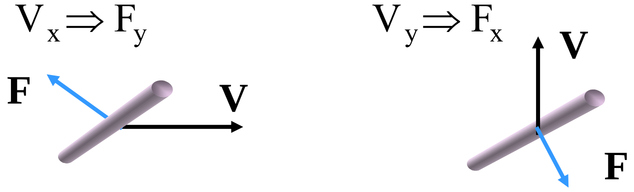
$$-\sum \zeta_{ij}(x)\dot{x}_j - \frac{\partial U(x)}{\partial x_i} + F_{ri}(t) = 0$$

$$\langle F_{ri}(t)F_{rj}(t')\rangle = 2\zeta_{ij}(x)k_B T\delta(t-t')$$

$\zeta_{ij}(x) = \zeta_{ji}(x)$ Hydrodynamic reciprocal relation

Reciprocal relation is NOT a trivial relation

$V_x \Rightarrow F_y$ $\qquad$ $V_y \Rightarrow F_x$



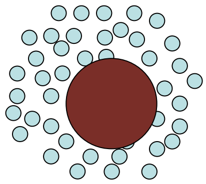
$$F_y / V_x = F_x / V_y$$

$T = \zeta_{rt} V$ $\qquad$ $F = \zeta_{tr} \omega$

Proof of the reciprocal relation

1. Proof by hydrodynamics (Lorentz)
2. Proof by phenomenology (Onsager)
3. Pfoof by statisitical mechanics(Kubo,…)

Statisitical mechanical theory for Brownian motion



$H(\Gamma; x)$

- x → Parameters representing the configuration of Brownian particles
- Γ → Phase space variables representing the configuration of solvent molecules

Force exerted on the particle by fluid molecules

$$\hat{F}_i(\Gamma, x) = -\frac{\partial H}{\partial x_i}$$

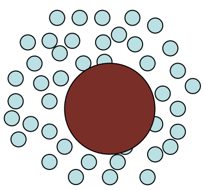
Mean force
$$\langle F_i(t) \rangle = \left\langle -\frac{\partial H}{\partial x_i} \right\rangle = -\int d\Gamma P(\Gamma; x, t) \frac{\partial H}{\partial x_i}$$

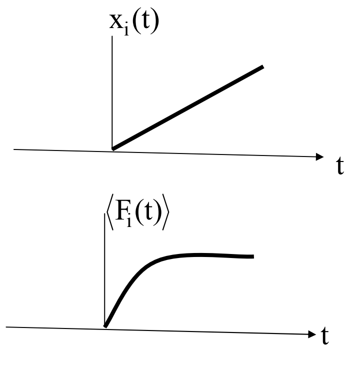
At equilibrium
$$P(\Gamma; x, t) \propto \exp[-\beta H(\Gamma; x)]$$

$$\langle F_i \rangle = -\frac{\partial A(x)}{\partial x_i} \qquad A(x) = -\frac{1}{\beta} \ln \int d\Gamma e^{-\beta H(\Gamma; x)}$$

Free energy, Potential of mean force

Suppose that the particles is pulled with velocity $\dot{x}_i$





$$x_i(t) = x_{i0} + \dot{x}_i t$$

$$\frac{\partial P}{\partial t} = (L + L')P$$

$$\langle F_i(t) \rangle = \left\langle -\frac{\partial H}{\partial x_i} \right\rangle = -\int d\Gamma P(\Gamma; x, t) \frac{\partial H}{\partial x_i}$$

Result of the perturbation solution

$$\langle F_i(t)\rangle = -\frac{\partial A}{\partial x_i} - \sum \tilde{\zeta}_{ij}(x,t)\dot{x}_j$$

$$\tilde{\zeta}_{ij}(x,t) = \frac{1}{k_B T}\int_0^t dt' \langle F_{ri}(t')F_{rj}(0)\rangle_x \qquad F_{ri} = \hat{F}_i(\Gamma,x) - \langle \hat{F}_i(\Gamma,x)\rangle$$

If the correlation time of the force is short

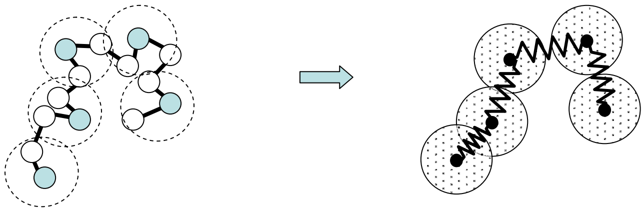
$$\langle F_i(t)\rangle = -\frac{\partial A}{\partial x_i} - \sum \zeta_{ij}(x)\dot{x}_j \qquad \zeta_{ij}(x) = \frac{1}{k_B T}\int_0^\infty dt' \langle F_{ri}(t')F_{rj}(0)\rangle_0$$

$$\langle F_{ri}(t)F_{rj}(0)\rangle = 2\zeta_{ij}(x)k_B T\delta(t)$$

No hydrodynamics involved

So, what do we learn?

Static coarse graining



$$\Gamma = (q_1,..q_f, p_1..p_f) \qquad x = (x_1,..x_n)$$

$$H(\Gamma) \Rightarrow A(x) = -\frac{1}{\beta}\ln\int d\Gamma e^{-\beta H(\Gamma)}\delta(x - \hat{x}(\Gamma))$$

$$Z = \int d\Gamma e^{-\beta H(\Gamma)} \qquad Z = \int dx\, e^{-\beta A(x)}$$

$$\psi_{eq}(\Gamma) \propto e^{-\beta H(\Gamma)} \qquad \psi_{eq}(x) \propto e^{-\beta A(x)}$$

Dynamic coarse graining

If $x = (x_1,..x_n)$ is the set of slow variables

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i}$$

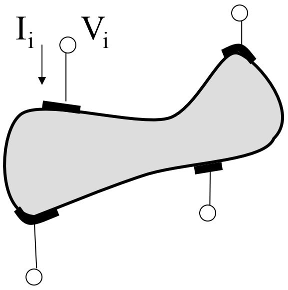
$$\Rightarrow \quad 0 = -\sum \zeta_{ij}(x)\dot{x}_j - \frac{\partial A(x)}{\partial x_i} + F_{ri}(t)$$

$$\langle F_{ri}(t)F_{rj}(0)\rangle = 2\zeta_{ij}(x)k_B T\delta(t)$$

$$\zeta_{ij}(x) = \frac{1}{k_B T}\int_0^\infty dt' \langle F_{ri}(t')F_{rj}(0)\rangle$$

$\zeta_{ij}(x) = \zeta_{ji}(x)$ Reciprocal relation

Reciprocal relation in Ohmic conductor



$$V_i = \sum_j R_{ij} I_j$$

$$R_{ij} = R_{ji}$$

The Onsager principle

Onsager 1931

If fluctuations are ignored

$$\sum \zeta_{ij} \dot{x}_j = -\frac{\partial A}{\partial x_i}$$

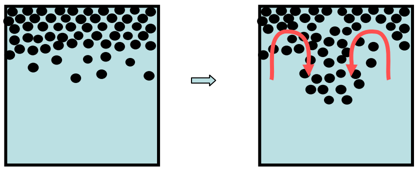
$$\zeta_{ij} = \zeta_{ji}$$

Time evolution of the system is determined by the minimization condition of Rayleighian

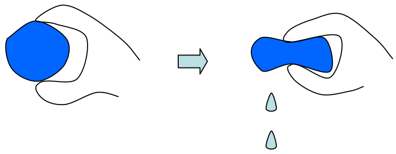
$$R = \frac{1}{2} \sum \zeta_{ij} \dot{x}_i \dot{x}_j + \sum \frac{\partial A}{\partial x_i} \dot{x}_i$$

Onsager principle is central in soft matter dynamics

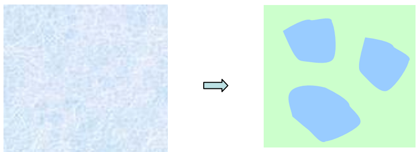
Dynamics of colloidal particles



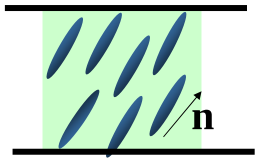
Gel dynamics



Dynamics of phase separation



Nemato hydrodynamics



Introduction to soft matter physics