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# Dynamical Coarse Graining -Principle and Applications-

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## Outline

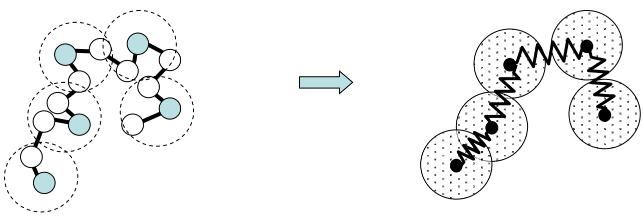
- Introduction
  - Coarse graining in statics and dynamics
- Classical example of dynamical coarse graining
  - Brownian motion
- Principle of dynamical coarse graining
  - Fluctuation dissipation theorem
- Applications
- Conclusion

05/03 Eric Vanden-Eijnden
“Mori-Zwanzig Formalism as a Practical Computational Tool

# Introduction

# Coarse graining

To describe the system with reduced degrees of freedom



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

# Static coarse graining

Ensure equilibrium properties

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

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

This is exact in the sense:

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

$$\psi_{eq}(\Gamma) = \frac{1}{Z}e^{-\beta H(\Gamma)} \qquad \psi_{eq}(x) = \frac{1}{Z}e^{-\beta A(x)}$$

# Dynamical coarse graining

Ensure the time evolution of x(t)

$$\dot{q}_i = \frac{\partial H}{\partial p_i}$$

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

$$\Rightarrow \dot{x}_i = V_i(x_1,..x_n) + V_i^r(t)$$

$$\Downarrow \qquad\qquad \Downarrow$$

$$\langle \hat{x}_i(t) \rangle = \int d\Gamma \hat{x}_i(\Gamma)\psi(\Gamma, t) \qquad \langle x_i(t) \rangle$$

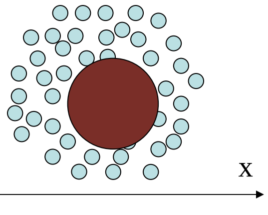
Brownian motion
-Classical example of dynamical coarse graining-

# Theory of Brownian motion:
## Prototype of dynamical coarse graining

Microscopic equation

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

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




Langevin equation

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

$$m/\zeta << \tau \quad \downarrow$$

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

# Fluctuation dissipation theorem

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

$$\langle F_r(t) F_r(t') \rangle = 2A\delta(t-t')$$

Impose that the distribution of x at equilibrium is given by $\psi_{eq}(x) \propto \exp\left(-\frac{U(x)}{k_B T}\right)$

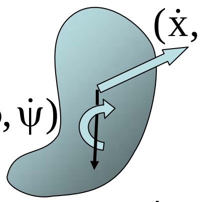
$$A = \int_0^\infty dt \langle F_r(t) F_r(0) \rangle$$

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

# Brownian Motion of Rigid Particle

Particles moving in a viscous fluid

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



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

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

$U(x_i)$ Potential energy

Time evolution of the particle state

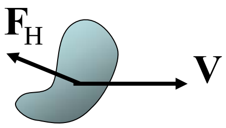
$$-\sum \zeta_{ij}(x)\dot{x}_j - \frac{\partial U(x)}{\partial x_i} + F_{ri}(t) = 0$$

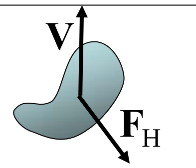
$$\langle F_{ri}(t) F_{ri}(t') \rangle = 2\zeta_{ij} k_B T \delta(t-t')$$

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

# Reciprocal relation

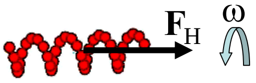
Hydrodynamic drag $F_{Hi} = -\sum \zeta_{ij}(x)\dot{x}_j$ $\boxed{\zeta_{ij}(x) = \zeta_{ji}(x)}$

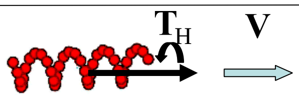



$F_{Hy} = -\zeta_{yx} V_x$ $F_{Hx} = -\zeta_{xy} V_y$

$\boxed{\zeta_{yx} = \zeta_{xy}}$




$F_H = -\zeta_{tr}\omega$ $T_H = -\zeta_{rt} V$

$\boxed{\zeta_{tr} = \zeta_{rt}}$

# Onsager's proof for the reciprocal relation

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

Fluctuation dissipation theorem

$$\zeta_{ij}(x) = \beta \int_0^\infty dt \left\langle F_{ri}(t) F_{rj}(0) \right\rangle$$

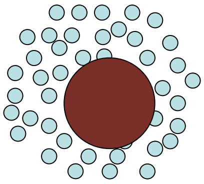
Time reversal symmetry

$$\left\langle A(t)B(0) \right\rangle = \left\langle A(-t)B(0) \right\rangle$$

$\boxed{\zeta_{ij}(x) = \zeta_{ji}(x)}$

No hydrodynamics is used

# Formal proof by stat-mech



$H(\Gamma;x)$

- $x$ → Parameters representing the configuration of Brownian particles
- $\Gamma$ → 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

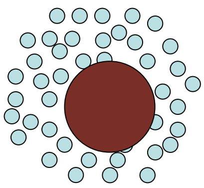
$$\langle F_i(t)\rangle = \left\langle -\frac{\partial H}{\partial x_i}\right\rangle = -\int d\Gamma\, P(\Gamma;x,t)\frac{\partial H}{\partial x_i}$$

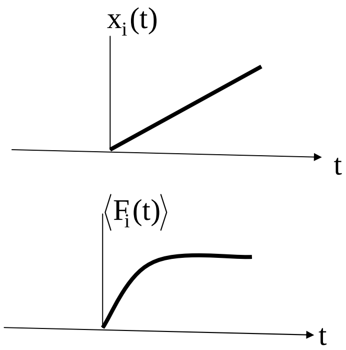
At equilibrium

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

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

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






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

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

## 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

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

$$\zeta_{ij}(x) = \frac{1}{k_B T}\int_0^\infty dt' \langle F_{ri}(t')F_{rj}(0)\rangle_0$$

# Principle of dynamical coarse graining

# What we have learned

$$\dot{q}_i = \frac{\partial H}{\partial p_i}$$

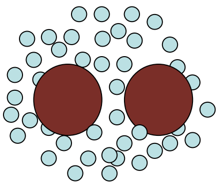
$$\dot{p}_i = -\frac{\partial H}{\partial q_i}$$

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

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

$$\zeta_{ij} = \frac{1}{2k_B T}\int_{-\infty}^{\infty} dt \langle F_{ri}(t) F_{rj}(0) \rangle$$

# The procedure



Fix the particle position at x and measure the force acting on the particle

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

$$\langle \hat{F}_i \rangle = -\frac{\partial A}{\partial x_i} \qquad \zeta_{ij} = \frac{1}{2k_B T}\int_{-\infty}^{\infty} dt \langle F_{ri}(t) F_{rj}(0) \rangle$$

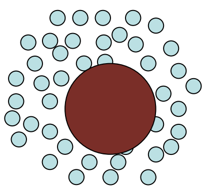
$$\sum \zeta_{ij}(x)\dot{x}_j = -\frac{\partial A(x)}{\partial x_i} + F_{ri}(t)$$

$$\dot{x}_i = -\sum \mu_{ij}(x)\frac{\partial A(x)}{\partial x_j} + V_{ri}(t)$$

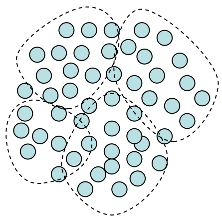
# Application

May 3, Hydroweek KITP

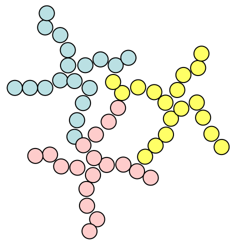
Eric Vanden-Eijnden (with Pep Espanol, Rafael Delgado Buscalioni)
“Mori-Zwanzig Formalism as a Practical Computational Tool



Brownian
dynamics

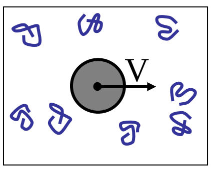


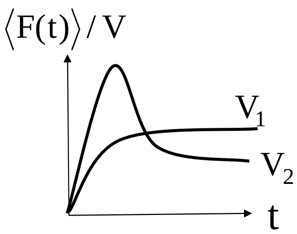
Dssipative
particle
dynamics



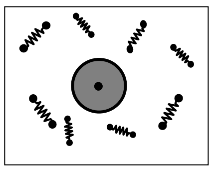
Liquid of star polymer

# Brownian motion in polymer solutions




Introduce polymer conformation



$$\zeta(\mathbf{r}_i - \kappa \bullet \mathbf{r}_i) = -k\mathbf{r}_i + \mathbf{f}_{ri}(t)$$

Introduce internal variable

$$\mathbf{Q} = \langle \mathbf{r}\mathbf{r} \rangle$$

$$\dot{\mathbf{Q}} = -\mathbf{F}(\mathbf{Q}, \boldsymbol{\kappa})$$

# Conclusion

- Brownian motion theory is the classical example of dynamical coarse graining.
- Onece slow variables are given, it tells us how to obtain the equation of motion

$$\dot{x}_i = -\sum \mu_{ij}(x) \frac{\partial A(x)}{\partial x_j} + V_{ri}(t)$$

Onsager type time evolution equation

Is it appropriate to call this Mori-Zwanzig formalism?