The Theory of Coarse-Graining also known as Non-Equilibrium Statistical Mechanics

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IWNET
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The art of using fewer degrees of freedom to describe a system, but still retaining realism

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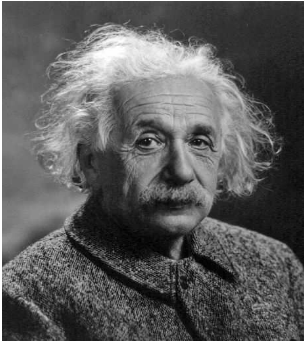

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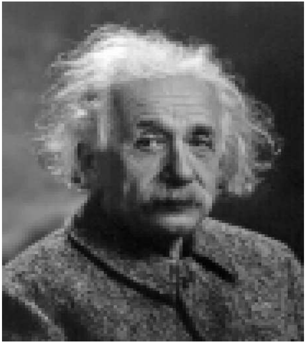

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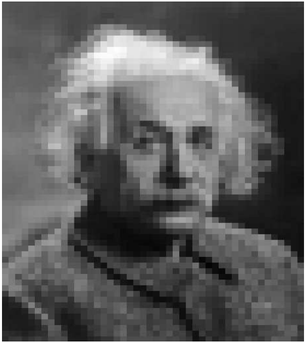

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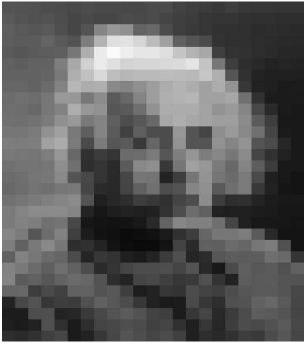

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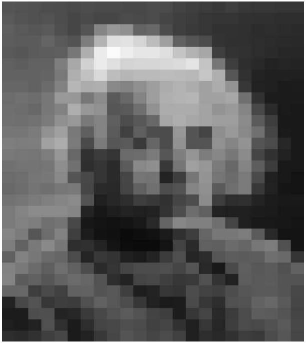
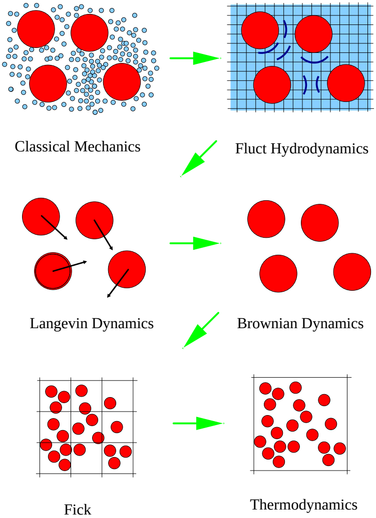


A. Einstein: "Everything should be made as simple as possible, but not simpler"

Levels of description



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Each level of description

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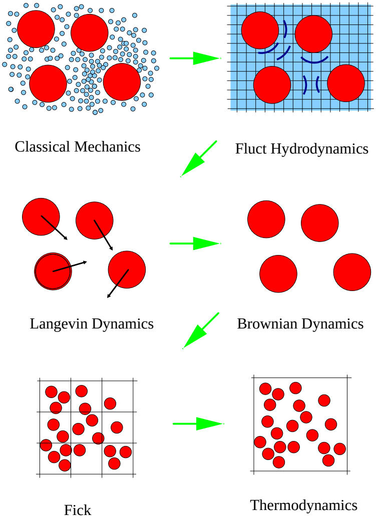

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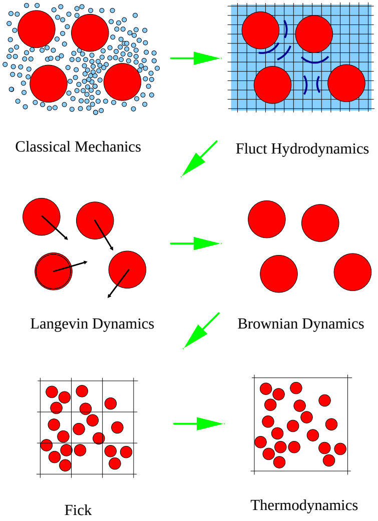

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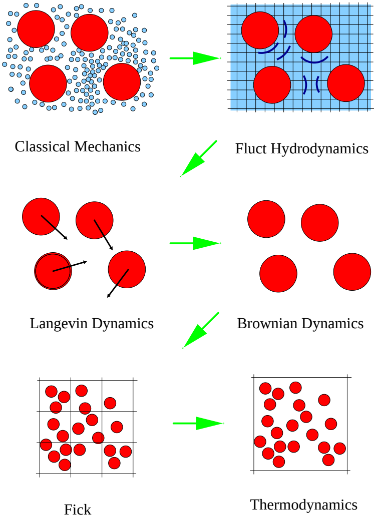
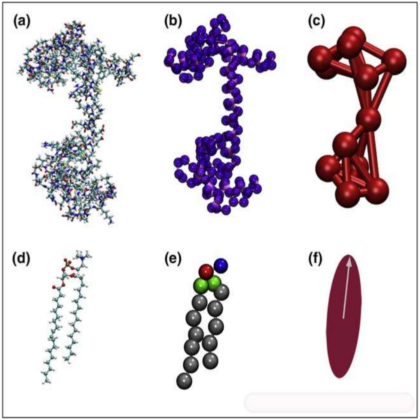


Consider a colloidal suspension.
Each level of description

- is defined by a set of relevant variables
- with characteristic time scales
- ...well separated

Levels of description



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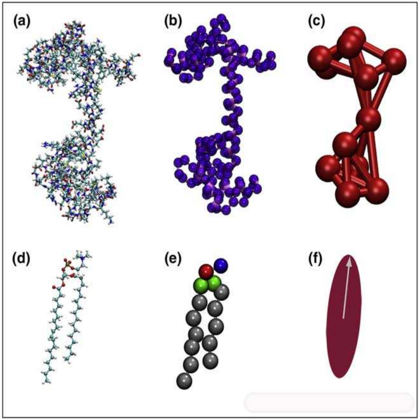

The challenge is to obtain the CG interactions *from* the the microscopic dynamic.

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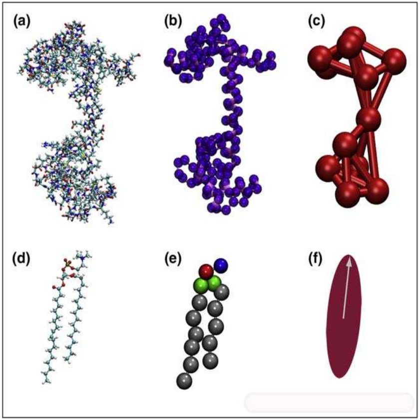

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Run MD to find the CG interactions

Non-Equilibrium Statistical Mechanics

Based on the concept of microstates and macrostates.

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Objective: to obtain the dynamics of the macrostates from the dynamics of the microstates.

Outline

- Microscopic dynamics

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  - M. Green's approach: the macro dynamics is a Markov process

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Microscopic dynamics

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Full atomistic description. The **microstate** of the system is $z = \{\mathbf{q}_i, \mathbf{p}_i, i = 1, \cdots, N\}$.

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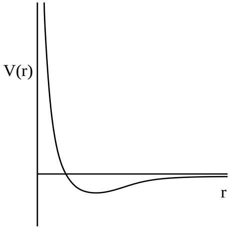
The Hamiltonian

$$H(z) = \sum_i^N \frac{\mathbf{p}_i^2}{2m_i} + V(\mathbf{q}_1, \cdots, \mathbf{q}_N)$$



Microscopic dynamics

Hamilton's equations can also be written as

$$\begin{pmatrix} \dot{\mathbf{q}}_i \\ \\ \dot{\mathbf{p}}_i \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ \\ -1 & 0 \end{pmatrix} \begin{pmatrix} \frac{\partial H}{\partial \mathbf{q}_i} \\ \\ \frac{\partial H}{\partial \mathbf{p}_i} \end{pmatrix}$$

$$\dot{z} = J\frac{\partial H}{\partial z} = -\frac{\partial H}{\partial z} J \frac{\partial}{\partial z} z = Lz$$

where L is the Liouville operator.
The solution of Hamilton's equation with initial condition z is

$$z_t = \exp\{Lt\}z = T_t z$$

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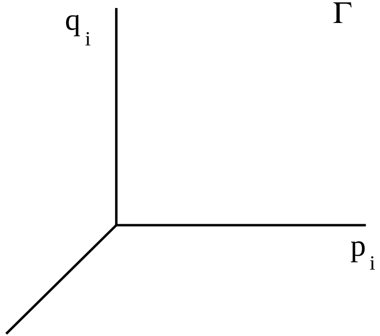

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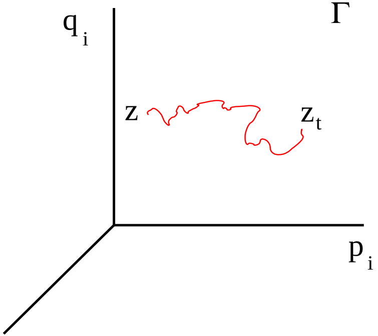

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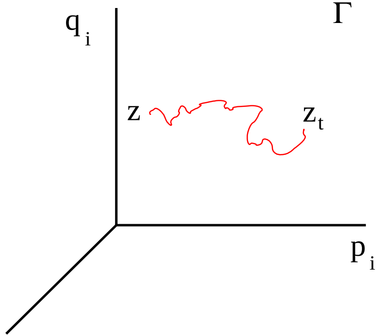

Noether theorem: symmetries in Hamiltonian lead to conserved quantities (energy, linear, angular momentum)

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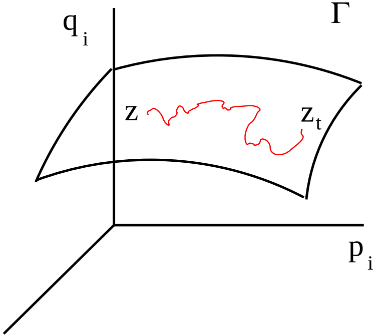

Submanifold of dynamic invariants.

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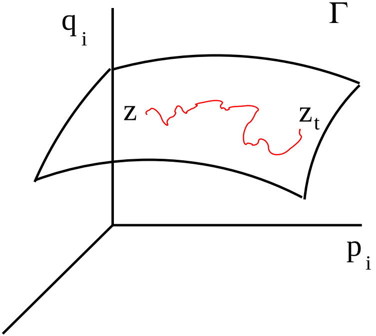

Chaos, volume preserving

Statistical Mechanics

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- Given by Liouville theorem

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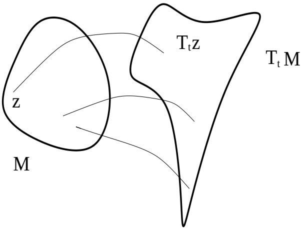

Statistical Mechanics

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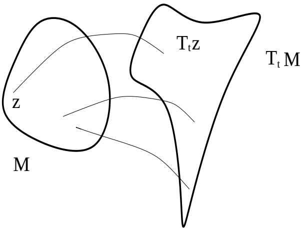

$$\int_M \rho_0(z)dz = \int_{T_tM} \rho_t(z)dz.$$

$$z' = T_t z \to = \int_M \rho_t(T_t z')dz'.$$

$$\rho_0(z) = \rho_t(T_t z)$$

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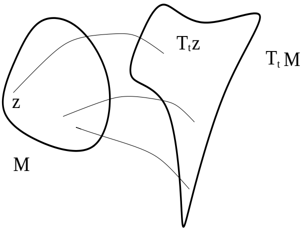

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"The probability at time t is the one that it had initially"

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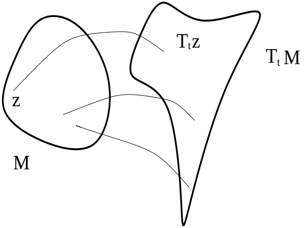

Note that

$$\rho_t(z) = \rho_0(T_{-t}z)$$

implies

$$\partial_t \rho_t(z) = L\rho_t(z)$$

Liouville equation

(Eq) Statistical Mechanics

"Experimental observation": Many Hamiltonians are mixing

$$\lim_{t\to\infty} \rho_t(z) = \rho^{\mathrm{eq}}(z) = \Phi(H(z))$$

for some $\Phi(E)$, in weak sense.

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"All microstates (with the same energy) are equiprobable (in the long run)".

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where

$$\Omega(E) = \int dz \delta(H(z) - E)$$

(Eq) Statistical Mechanics

The result is intuitive

$$\rho_{\mathrm{eq}}(z) = \frac{P_0(H(z))}{\Omega(H(z))}$$

The probability of being at z is the probability that the system has the energy $H(z)$ divided by the “number of microstates” compatible with that energy.

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If $P_0(E) = \delta(E - E_0)$ we obtain the microcanonical ensemble

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(Eq) Statistical Mechanics

Now a magical trick:

The Principle of Maximum Entropy (PME)

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Assume you know $P(E)$, but not $\rho(z)$

$$P(E) = \int dz \rho(z) \delta(H(z) - E) \tag{1}$$

Many $\rho(z)$ give the same $P(E)$. Which one is the "correct" one?

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Consider the **Gibbs-Jaynes entropy functional**

$$S[\rho] = -k_B \int dz \rho(z) \ln \frac{\rho(z)}{\rho_0}$$

PME: The least biased $\rho(z)$ is the one that maximizes the GJ entropy subject to (1).

(Eq) Statistical Mechanics

The solution is

$$\rho(z) = \frac{P(H(z))}{\Omega(H(z))}$$

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Therefore, the Principle of Maximum Entropy gives the same kind of "equiprobability" as mixing Hamiltonians.

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- This ensemble may also be obtained with the Principle of Maximum Entropy.

Macroscopic dynamics

The dynamics of macrostates

Other names for **macrostates**:
Macroscopic variables, slow variables, gross variables, collective variables, coarse-grained variables, reaction coordinates, order parameters, internal variables, structural variables, etc.

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Macroscopic variables, slow variables, gross variables, collective variables, coarse-grained variables, reaction coordinates, order parameters, internal variables, structural variables, etc.
The macrostates are phase functions $A(z)$. There is a mapping

$$\begin{array}{rcl} \mathbb{R}^{6N} & \to & \mathbb{R}^{M} \\ z & \to & a = A(z) \end{array}$$

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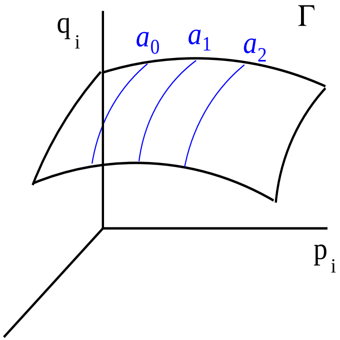
The dynamics of macrostates



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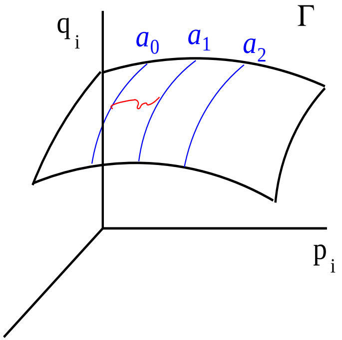

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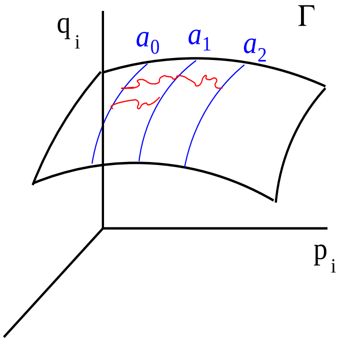

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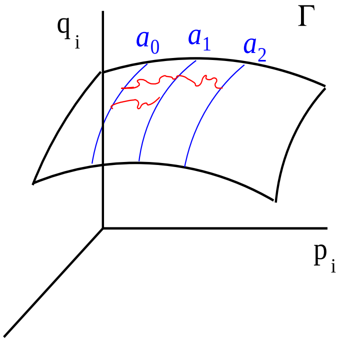

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This implies a stochastic description and we need $P(a, t)$

The dynamics of macrostates

The relation between micro and macro probabilities

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$$\textbf{PME:} \quad \rightarrow \quad \rho_0(z) = \frac{P(A(z),0)}{\Omega(A(z))}$$

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Back to the macroscopic probability

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$$P(a,t) = \int dz \rho_0(z)\delta(A(T_t z) - a)$$
$$= \int dz \frac{P(A(z),0)}{\Omega(A(z))}\delta(A(T_t z) - a)$$

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The dynamics of macrostates

Back to the macroscopic probability

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&= \int da_0 P(a_0, 0) \frac{1}{\Omega(a_0)} \int dz \delta(A(z) - a_0)\delta(A(T_t z) - a)
\end{aligned}
$$

The dynamics of macrostates

Back to the macroscopic probability

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The dynamics of macrostates

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$$

This tells us how to evolve $P(a,0) \to P(a,t)$.

The dynamics of macrostates

The transition probability is

$$P(a_0, 0|a_1, t) = \frac{1}{\Omega(a_0)} \int dz \delta(A(z) - a_0)\delta(A(T_t z) - a_1)$$

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This is the fundamental **micro-macro** link between microscopic and macroscopic dynamics.

(only assumption: initial microstates are equiprobable)

The dynamics of macrostates

The geometric interpretation is simple

$$P(a_0, 0|a_1, t) = \frac{\int dz\delta(A(z) - a_0)\delta(A(T_t z) - a_1)}{\int dz\delta(A(z) - a_0)}$$

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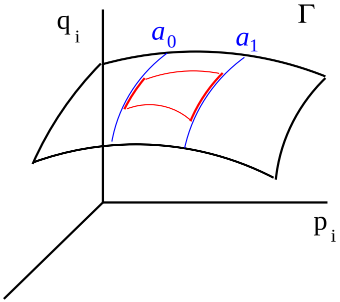

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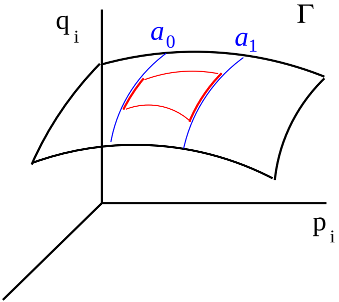

The transition probability is the fraction of microstates of a_0 that land on a_1 after time t.

The dynamics of macrostates

Summary of Macrodynamics:

- The dynamics of macrostates is necesarily stochastic $P(a, t)$.

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- Micro-Macro dynamics link.

$$P(a_0, 0|a,t) = \frac{1}{\Omega(a_0)} \int dz \delta(A(z) - a_0)\delta(A(T_t z) - a)$$

Looking for a dynamic equation

Imagine that the macrostate $A(z)$ is a **quasi-invariant** of the dynamics:

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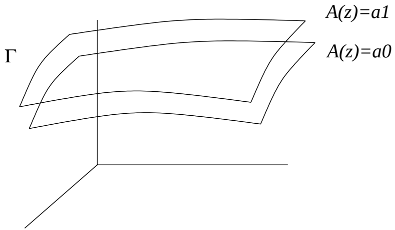

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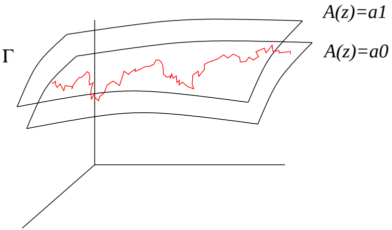

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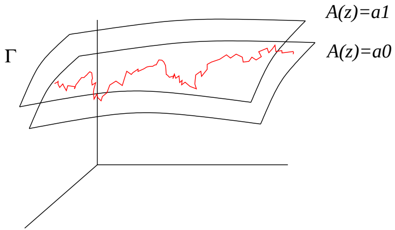

The flow is quasi-stratified in phase space and we expect that, after short time the ensemble becomes a quasi-equilibrium ensemble

$$\rho_t(z) \simeq \overline{\rho}_t(z) = \frac{P(A(z),t)}{\Omega(A(z))}$$

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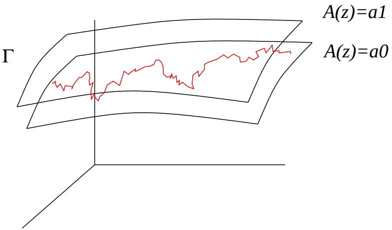

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In the time scale in which $P(a,t)$ has hardly changed, the system has reached (conditional) equilibrium.

Looking for a dynamic equation

The time derivative of the probability is

$$\partial_t P(a,t) = \int dz \partial_t \rho_t(z) \delta(A(z) - a)$$

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The time derivative of the probability is

$$\begin{aligned}\partial_t P(a,t) &= \int dz \partial_t \rho_t(z)\delta(A(z)-a) \\ &= \int dz \rho_t(z) L\delta(A(z)-a)\end{aligned}$$

Looking for a dynamic equation

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\partial_t P(a,t) &= \int dz \partial_t \rho_t(z) \delta(A(z)-a) \\
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&= -\frac{\partial}{\partial a} v(a) P(a,t)
\end{aligned}
$$

Looking for a dynamic equation

In the quasi-equilibrium approximation

$$\partial_t P(a,t) = -\frac{\partial}{\partial a} v(a) P(a,t)$$

with the drift term is given by the microscopic expression

$$v(a) = \langle LA \rangle_a = \frac{1}{\Omega(a)} \int dz \delta(A(z) - a) LA(z)$$

Wow! Closed equation for $P(a,t)$ in microscopic terms!

Looking for a dynamic equation

Unfortunately, the quasi-equilibrium approximation is not very good in general.

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It is a *deterministic* equation:

If $P(a,0)=\delta(a-a_0)$ then $P(a,t)=\delta(a-a(t))$
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There is no widening of $P(a,t)$...

Green's approach to CG

Green's approach

Melville Green 1952 proposed that the stochastic process of macrostates is a **Markov process**:

$$P(a_1 t_1, a_2, t_2, \ldots, a_n t_n) = P(a_1, t_1)P(a_1, t_1|a_2, t_2)\cdots P(a_{n-1}, t_{n-1}|a_n, t_n)$$

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A mathematical result: for a continuum Markov process, the transition probability obeys the **Fokker-Planck equation**

$$\frac{\partial}{\partial t} P(a_0 t_0 | a, t) = -\frac{\partial}{\partial a} D^{(1)}(a) P(a_0 t_0 | a, t) + \frac{1}{2} \frac{\partial^2}{\partial a \partial a} D^{(2)}(a) P(a_0 t_0 | a, t)$$

with initial condition

$$P(a_0, t_0 | a, t_0) = \delta(a - a_0)$$

Green's approach

For sufficiently short times Δt

$$\frac{\partial}{\partial t}P(a_0 t_0|a,t) = -\frac{\partial}{\partial a}D^{(1)}(a)P(a_0 t_0|a,t) + \frac{1}{2}\frac{\partial^2}{\partial a \partial a}D^{(2)}(a)P(a_0 t_0|a,t)$$

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Which is a diffusion equation with constant coefficients with a Gaussian solution

$$\begin{aligned}
&P(a_0,t_0|a_1,t_0+\Delta t)\\
&= \exp\left\{-\frac{1}{2\Delta t}\left(a_1 - a_0 - \Delta t D^{(1)}(a_0)\right) D^{-1}_{(2)}(a_0)\left(a_1 - a_0 - \Delta t D^{(1)}(a_0)\right)\right\}\\
&\times \frac{1}{(2\pi\Delta t)^{M/2}\det(D^{(2)}(a_0))^{1/2}}
\end{aligned}$$

Green's approach

The moments of the transition probability give the drift and diffusion matrix

$$\int da_1(a_1 - a_0)P(a_0, t_0|a_1, t_0 + \Delta t) = D^{(1)}(a_0)\Delta t$$
$$\int da_1(a_1 - a_0)(a_1 - a_0)P(a_0, t_0|a_1, t_0 + \Delta t) = D^{(2)}(a_0)\Delta t$$

These are known as Kramers-Moyal coefficients.

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These are known as Kramers-Moyal coefficients.
Use the micro-macro link

$$P(a_0, 0|a_1, t) = \frac{1}{\Omega(a_0)} \int dz \delta(A(z) - a_0)\delta(A(T_t z) - a_1)$$

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Green's approach

By using the fundamental micro-macro link we obtain microscopic expressions for drift and diffusion

$$D^{(1)}(a_0) = \left\langle \frac{A(\Delta t) - A(0)}{\Delta t} \right\rangle^{a_0}$$

$$D^{(2)}(a_0) = \frac{1}{\Delta t} \left\langle [A(\Delta t) - a_0]^2 \right\rangle^{a_0} = \textbf{Einstein-Helfand}$$

Green's approach

Summary of Green's approach:

- The dynamics of the macrostates is assumed to be described by a Markov diffusion process.

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- The dynamics of the macrostates is assumed to be described by a Markov diffusion process.
- The transition probability obeys the Fokker-Planck equation
- The Fokker-Planck equation contains a drift and a diffusion term
- By using the fundamental micro-macro link the drift and diffusion can be, in principle, computed from MD simulations.

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Zwanzig's approach to CG

Zwanzig's approach

Zwanzig (1961): The relevant ensemble is obtained from the real ensemble through a *projector*:

$$
\begin{aligned}
\overline{\rho}_t(z) &= \frac{P(A(z),t)}{\Omega(A(z))} \\
&= \int da\delta(A(z)-a)\frac{P(a,t)}{\Omega(a)} \\
&= \int da\delta(A(z)-a)\frac{1}{\Omega(a)}\int dz'\delta(A(z')-a)\rho_t(z') \\
&= \mathcal{P}^{\dagger}\rho_t(z)
\end{aligned}
$$

Then

$$
\rho_t(z) = \overline{\rho}_t(z) + (\rho_t(z) - \overline{\rho}_t(z)) + (1-\mathcal{P}^{\dagger})\rho_t(z)
$$

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Zwanzig's approach

The trick:

$$\partial_t \overline{\rho}_t(z) = \partial_t \mathcal{P}^\dagger \rho_t(z) = \mathcal{P}^\dagger L \overline{\rho}_t(z) + \mathcal{P}^\dagger L \delta\rho_t(z)$$
$$\partial_t \delta\rho_t(z) = \mathcal{Q}^\dagger L \rho_t(z) = \mathcal{Q}^\dagger L \overline{\rho}_t(z) + \mathcal{Q}^\dagger L \delta\rho_t(z)$$

The formal solution of the second Eq is

$$\delta\rho_t(z) = \underbrace{\exp\{\mathcal{Q}^\dagger L t\}\delta\rho_0(z)}_{=0} + \int_0^t dt' \exp\{\mathcal{Q}^\dagger L(t-t'\}\mathcal{Q}^\dagger L \overline{\rho}_{t'}(z)$$

Inserting into the first equation leads to a closed equation for $\overline{\rho}_t(z)$

$$\partial_t \overline{\rho}_t(z) = \mathcal{P}^\dagger L \overline{\rho}_t(z) + \int_0^t dt' \mathcal{P}^\dagger L \exp\{\mathcal{Q}^\dagger L(t-t'\}\mathcal{Q}^\dagger L \overline{\rho}_{t'}(z)$$

Zwanzig's approach

The final exact and closed equation for $P(a,t)$ is

$$\begin{aligned}\partial_t P(a,t) &= -\frac{\partial}{\partial a}\mathbf{v}(a)P(a,t)\\ &+ \int_0^t dt'\int da'\Omega(a')\frac{\partial}{\partial a}\mathbf{D}(a,a',t-t')\frac{\partial}{\partial a'}\frac{P(a',t')}{\Omega(a')}\end{aligned}$$

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$$\begin{aligned}\Omega(a) &= \int dz \delta(A(z)-a)\\ \mathbf{v}(a) &= \langle LA\rangle^a\\ \mathbf{D}(a,a',t) &= \langle (LA-\langle LA\rangle^{a'})\exp\{L\mathcal{Q}t\}\delta(A-a)(LA-\langle LA\rangle^a)\rangle^{a'}\end{aligned}$$

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\end{aligned}$$

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\end{aligned}$$

This is just a rewriting of Liouville's theorem!!

Zwanzig's approach

Markov approximation: The crucial approximation now is the separation of time scales between $A(z)$ and the memory kernel.

Zwanzig's approach

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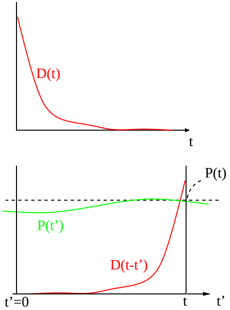

$$\int_0^t dt' D(t-t')P(t') \approx P(t)\int_0^\infty D(t')dt'$$

$$D(t-t') \approx \delta(t-t')\int_0^\infty D(t'')dt''$$

Zwanzig's approach

Final Zwanzig-Fokker-Planck Equation

$$\partial_t P(a,t) = \frac{\partial}{\partial a}\mathbf{v}(a)P(a,t) + k_B\frac{\partial}{\partial a}\Omega(a)\mathbf{M}(a)\cdot\frac{\partial}{\partial a}\frac{P(a,t)}{\Omega(a)}$$

Zwanzig's approach

Final Zwanzig-Fokker-Planck Equation

$$\partial_t P(a,t) = \frac{\partial}{\partial a}\left[\mathbf{v}(a) + \mathbf{M}(a)\cdot\frac{\partial S}{\partial a}(a)\right] P(a,t) + k_B \frac{\partial}{\partial a}\mathbf{M}(a)\cdot\frac{\partial}{\partial a}P(a,t)$$

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$$\Omega(a) = \int dz\delta(A(z)-a) \propto P^{\mathrm{eq}}(a)$$ Equilibrium prob.

$$S(a) = k_B \ln \Omega(a)$$ Entropy

$$\mathbf{v}(a) = \langle LA\rangle^a$$ Rev. Drift

$$\mathbf{M}(a) = \frac{1}{k_B}\int_0^\infty dt' \langle (LA - \langle LA\rangle^a)\exp\{Lt'\}(LA-\langle LA\rangle^a)\rangle^a$$ **Green-Kubo**

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This FPE is identical to the one obtained by Green. In particular **Green-Kubo $\Leftrightarrow$ Einstein-Helfand**

Zwanzig's approach

Summary of Zwanzig's approach:

- Exact equation obtained with a projection operator

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Zwanzig's approach

Summary of Zwanzig's approach:

- Exact equation obtained with a projection operator
- The Markov property assumes a white noise model for the projected current.
- The resulting equation is the FPE by Green

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GENERIC

The GENERIC framework

When the Hamiltonian of the system is expressible in terms of the macrostates

$$H(z) = E(A(z))$$

then a powerful structure emerges.

The GENERIC framework

Note

$$L A_\mu(z) = \frac{\partial A_\mu}{\partial z} J_0 \frac{\partial \mathcal{H}}{\partial z} = \frac{\partial A_\mu}{\partial z} J_0 \frac{\partial E}{\partial a_\nu}(A(z)) \frac{\partial A_\nu}{\partial z}(z)$$

$$= \{A_\mu, A_\nu\} \frac{\partial E}{\partial a_\nu}(A(z))$$

The GENERIC framework

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then

$$v_\mu(a) = \langle LA_\mu \rangle^a = L_{\mu\nu}(a) \frac{\partial E}{\partial a_\nu}(a)$$

where the reversible matrix is

$$L_{\mu\nu}(a) \equiv \left\langle \frac{\partial A_\mu}{\partial z} J_0 \frac{\partial A_\nu}{\partial z} \right\rangle^a = \langle \{A_\mu, A_\nu\} \rangle^a$$

The FPE

The Fokker-Planck Equation is

$$\partial_t P(a,t) = -\frac{\partial}{\partial a}\left[\left[L\frac{\partial E}{\partial a} + M\frac{\partial S}{\partial a}\right]P(a,t)\right] + k_B\frac{\partial}{\partial a}M\frac{\partial}{\partial a}P(a,t)$$

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Two theorems

$$M\frac{\partial E}{\partial a} = 0$$

$$\frac{\partial E}{\partial a}L\frac{\partial S}{\partial a} = k_B\frac{\partial L}{\partial a}\frac{\partial E}{\partial a}$$

The FPE

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Two theorems

$$M\frac{\partial E}{\partial a} = 0$$
$$L\frac{\partial S}{\partial a} = 0$$

The GENERIC framework

Summary of the GENERIC framework:

- When the Hamiltonian may be expressed in terms of the relevant variables, GENERIC emerges.

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The GENERIC framework

Summary of the GENERIC framework:

- When the Hamiltonian may be expressed in terms of the relevant variables, GENERIC emerges.
- There are a number of restrictions to be satisfied by any possible model for the building blocks.
- Typically, whenever you look for non-isothermal models, look for GENERIC.

Examples

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- Brownian Dynamics
- Thermal Blobs

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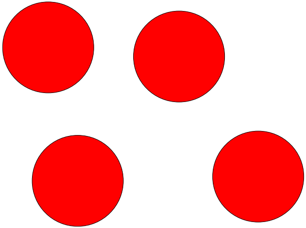
- Brownian Dynamics
- Thermal Blobs

Black box: “You give me the CG variables, I tell you how the move” (if...)

Brownian Dynamics

Consider a colloidal suspension



(1) The Hamiltonian

$$H(z) = \sum_i \left(\frac{p_i^2}{2m_i} + \frac{P_i^2}{2M_i} \right) + \frac{1}{2} \sum_{ij} \left(V_{ij}^{SS}(q) + V_{ij}^{SC}(q, Q) + V_{ij}^{CC}(Q) \right)$$

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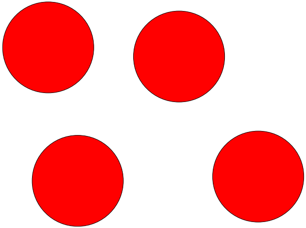

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MD simulation unfeasible

Brownian Dynamics

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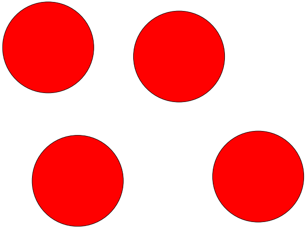

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MD simulation unfeasible

(2) The relevant variables $A(z) \rightarrow \{H(z), \mathbf{Q}_i\}$ (Smoluchowski level)

Brownian Dynamics

(3) The equilibrium solution

$$
\begin{aligned}
\Omega(\overline{Q}) &= \int dz \delta(H(z) - E)\delta(Q_i - \overline{Q}_i) \\
&\approx \int dz \exp\{-\beta H(z)\}\delta(Q_i - \overline{Q}_i) \\
&\propto \int dq \exp\{-\beta V(\overline{Q}, q)\} \\
&\equiv \exp\{-\beta \overline{V}^{\mathrm{PMF}}(\overline{Q})\}
\end{aligned}
$$

The potential of mean force $V^{\mathrm{PMF}}(\overline{Q})$ captures the effective interaction between colloids due to the solvent.

Brownian Dynamics

The potential of mean force gives the mean force

$$
\begin{aligned}
\mathbf{F}_i^{MF}(Q) &= -\frac{\partial}{\partial \mathbf{Q}_i}\overline{V}^{\mathrm{PMF}}(Q) \\
&= -\frac{\partial}{\partial \mathbf{Q}_i}\left(-k_B T \ln \int dq \exp\{-\beta V(Q,q)\}\right) = \\
&= \int dq \frac{\exp\{-\beta V(Q,q)\}}{\int dq \exp\{-\beta V(Q,q)\}}\left[-\frac{\partial}{\partial \mathbf{Q}_i} V(Q,q)\right]
\end{aligned}
$$

$$
= \langle \mathbf{F}_i \rangle^Q
$$

Brownian Dynamics

(4) The time derivative is $LA \to \mathbf{V}_i$

Brownian Dynamics

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(5) The drift term. The conditional expectation

$$\langle \dots \rangle^a = \frac{1}{\Omega(a)} \int dz \delta(A(z) - a) \dots$$

becomes

$$\langle \dots \rangle^{\overline{Q}} = \frac{1}{\Omega(\overline{Q})} \int dq dp dQ dP \delta(H(z) - E) \delta(Q - \overline{Q}) \dots$$

$\mathbf{v}(a) = \langle LA \rangle^a$ is the conditional expectation of particle's momentum. It vanishes by symmetry.

Brownian Dynamics

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$\mathbf{v}(a) = \langle LA \rangle^a$ is the conditional expectation of particle's momentum. It vanishes by symmetry.
(6) The friction matrix $M(x)$ becomes the diffusion tensor.

$$\mathbf{D}_{ij}(Q) = \frac{1}{k_B T} \int_0^\tau dt' \langle \mathbf{V}_i \mathbf{V}_j(t') \rangle^Q$$

Brownian Dynamics

(7) The dynamic equation is the Smoluchowski equation

$$\partial_t P(Q,t) = \frac{\partial}{\partial Q_i}\left[\mathbf{D}_{ij}(Q)\mathbf{F}_j^{MF}(Q)P(Q,t)\right] + k_B T \frac{\partial}{\partial Q_i}\mathbf{D}_{ij}(Q)\cdot\frac{\partial}{\partial Q_j}P(Q,t)$$

equivalent to the SDE

$$d\mathbf{Q}_i = \sum_j \mathbf{D}_{ij}(Q)\mathbf{F}_i^{MF}(Q)dt + k_B T \sum_j \frac{\partial \mathbf{D}_{ij}}{\partial Q}_j(Q)dt + d\tilde{\mathbf{Q}}_i$$

with the Fluctuation-Dissipation theorem

$$d\tilde{\mathbf{Q}}_i d\tilde{\mathbf{Q}}_j = 2k_B T\mathbf{D}_{ij}(Q)dt$$

Brownian Dynamics

(8) Model, model, model:

- $\mathbf{F}_i(Q)$ and $\mathbf{D}_{ij}(Q)$ are many-body functions.

Brownian Dynamics

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- $\mathbf{F}_i(Q)$ and $\mathbf{D}_{ij}(Q)$ are many-body functions.
- No way we can sample the 3M-dimensional space of Q's

Brownian Dynamics

(8) Model, model, model:

- $\mathbf{F}_i(Q)$ and $\mathbf{D}_{ij}(Q)$ are many-body functions.
- No way we can sample the 3M-dimensional space of Q's
- We will assume pair-wise forms.

Brownian Dynamics

(8) Pair wise assumption

$$\mathbf{F}_i(Q) = \sum_j \langle \mathbf{F}_{ij} \rangle^Q \approx \sum_j \langle \mathbf{F}_{ij} \rangle^{\mathbf{Q}_{ij}}$$

$$\mathbf{D}_{ij}(Q) \approx \frac{1}{k_B T} \int_0^\tau dt' \langle \mathbf{V}_i \mathbf{V}_j(t') \rangle^{\mathbf{Q}_{ij}}$$

Brownian Dynamics

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For very dilute suspension, it is simple

$$\mathbf{D}_{ij}(Q) = \delta_{ij} \frac{1}{k_B T} \int_0^\tau dt' \langle \mathbf{V}_i \mathbf{V}_i(t') \rangle^{\mathrm{eq}} = \delta_{ij} \mathbf{1} D_0$$

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For concentrated suspensions, the diffusion tensor describes all the interactions mediated by the solvent.

Brownian Dynamics

(9) Micro$\to$macro transfer of parameters.

Method 1: Run a short MD for two colloidal particles at a given distance, compute average force and correlation of the fluctuations of the force. Repeat for other distances.

Brownian Dynamics

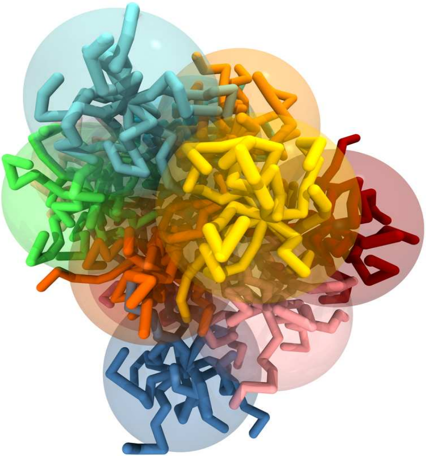
(9) Micro→macro transfer of parameters.

Method 1: Run a short MD for two colloidal particles at a given distance, compute average force and correlation of the fluctuations of the force. Repeat for other distances.
Method 2: Run a short MD for M fixed colloidal particles. Compute average force and correlation of the fluctuations of the force. Sort by distances.

The crucial point of the exercise is that we need to run short simulations to compute the mean force and diffusion tensor.

Thermal Blobs

What are thermal blobs?



- Complex molecules...

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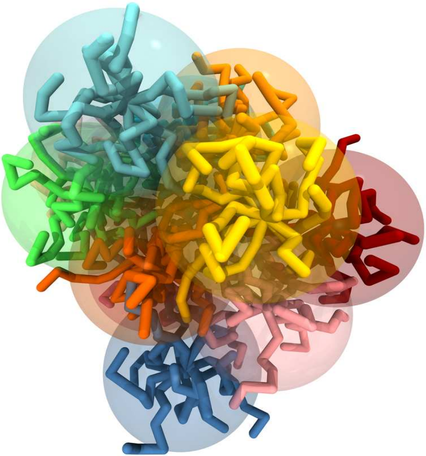

- Complex molecules...
- ... described at a CG level with the CoM ...

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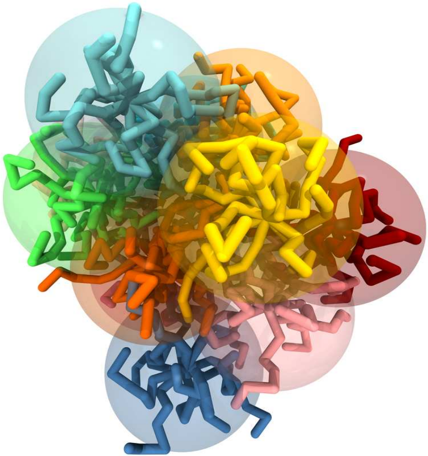

- Complex molecules...
- ... described at a CG level with the CoM ...
- ... and the internal energy

The CG variables

We choose as the CG variables

$$\hat{\mathbf{R}}_\mu(z) = \frac{1}{M_\mu}\sum_i^N m_i \mathbf{r}_i \delta_\mu(i)$$

$$\hat{\mathbf{P}}_\mu(z) = \sum_i^N \mathbf{p}_i \delta_\mu(i)$$

$$\hat{\mathcal{E}}_\mu(z) = \sum_i^N \frac{m_i}{2}(\mathbf{v}_i - \hat{\mathbf{v}}_\mu(z))^2 \delta_\mu(i) + \phi_\mu(z)$$

$$M_\mu = \sum_i^N m_i \delta_\mu(i)$$

$$\hat{\mathbf{v}}_\mu(z) = \frac{\hat{\mathbf{P}}_\mu(z)}{M_\mu}$$

$$\phi_\mu(z) = \frac{1}{2}\sum_{ij}^N \phi_{ij}\delta_\mu(i)$$

UNED

The CG variables

We choose as the CG variables

$$\hat{\mathbf{R}}_\mu(z) = \frac{1}{M_\mu}\sum_i^N m_i \mathbf{r}_i \delta_\mu(i) \qquad M_\mu = \sum_i^N m_i \delta_\mu(i)$$

$$\hat{\mathbf{P}}_\mu(z) = \sum_i^N \mathbf{p}_i \delta_\mu(i) \qquad \hat{\mathbf{v}}_\mu(z) = \frac{\hat{\mathbf{P}}_\mu(z)}{M_\mu}$$

$$\hat{\mathcal{E}}_\mu(z) = \sum_i^N \frac{m_i}{2}(\mathbf{v}_i - \hat{\mathbf{v}}_\mu(z))^2 \delta_\mu(i) + \phi_\mu(z) \qquad \phi_\mu(z) = \frac{1}{2}\sum_{ij}^N \phi_{ij}\delta_\mu(i)$$

Energy and momentum are functions of the CG variables

$$\hat{H}(z) = \sum_i^N \frac{p_i^2}{2m_i} + \frac{1}{2}\sum_{ij}^N \phi_{ij} = \sum_\mu^M \left[\frac{\hat{\mathbf{P}}_\mu^2(z)}{2M_\mu} + \hat{\mathcal{E}}_\mu(z)\right]$$

$$\hat{\mathbf{P}}(z) \equiv \sum_i^N \mathbf{p}_i = \sum_\mu^M \hat{\mathbf{P}}_\mu(z)$$

Time derivatives of CG variables

The time derivatives are

$$L\hat{\mathbf{R}}_\mu(z) = \mathbf{V}_\mu(z)$$

$$L\hat{\mathbf{P}}_\mu(z) = \sum_\nu^M \hat{\mathbf{F}}_{\mu\nu}(z)$$

$$L\hat{\mathcal{E}}_\mu(z) = \sum_\nu^M \left[\hat{Q}_{\mu\nu}(z) - \frac{1}{2}\hat{\mathbf{F}}_{\mu\nu}(z)\cdot\mathbf{V}_{\mu\nu}(z)\right]$$

$$\hat{\mathbf{F}}_{\mu\nu}(z) \equiv \sum_{ij}^N \delta_\mu(i)\delta_\nu(j)\mathbf{F}_{ij} = -\hat{\mathbf{F}}_{\nu\mu}(z)$$

$$\hat{Q}_{\mu\nu}(z) \equiv \sum_{ij}^N \mathbf{F}_{ij}\left(\frac{(\mathbf{v}_i - \mathbf{v}_\mu) + (\mathbf{v}_j - \mathbf{v}_\nu)}{2}\right)\delta_\mu(i)\delta_\nu(j) = -\hat{Q}_{\nu\mu}(z)$$

The equilibrium probability

$$P^{\mathrm{eq}}(\mathbf{R},\mathbf{P},\mathcal{E}) = \Phi(E,\mathbf{P}_T)\exp\left\{\frac{1}{k_B}S(\mathbf{R},\mathbf{P},\mathcal{E})\right\}$$

$$S(\mathbf{R},\mathcal{E}) \equiv k_B \ln \Omega(\mathbf{R},\mathcal{E})$$

$$\Omega(\mathbf{R},\mathcal{E}) = \int dz \prod_{\mu}^{M} \delta(\mathbf{R}_\mu - \hat{\mathbf{R}}_\mu(z))\delta(\mathbf{P}_\mu - \hat{\mathbf{P}}_\mu(z))\delta(\mathcal{E}_\mu - \hat{\mathcal{E}}_\mu(z))$$

The conditional expectations

The conditional averages are of the form

$$\langle \cdots \rangle^{\mathbf{RP}\mathcal{E}} = \frac{1}{\Omega(\alpha)} \int dz \prod_{\mu}^{M} \delta(\mathbf{R}_\mu - \hat{\mathbf{R}}_\mu(z)) \delta(\mathbf{P}_\mu - \hat{\mathbf{P}}_\mu(z)) \delta(\mathcal{E}_\mu - \hat{\mathcal{E}}_\mu(z)) \cdots$$

The final SDE

The final SDE equations are

$$
\begin{aligned}
\dot{\mathbf{R}}_\mu &= \mathbf{V}_\mu \\
\dot{\mathbf{P}}_\mu &= \sum_\nu^M \langle \hat{\mathbf{F}}_{\mu\nu} \rangle^{\mathbf{R}\mathcal{E}} - \frac{1}{2} \sum_{\nu\mu'\nu'}^M \mathbf{\Gamma}_{\mu\mu'\nu\nu'} \cdot \mathbf{V}_{\nu\nu'} \frac{\partial S}{\partial \mathcal{E}_\nu} + \sum_\nu^M \tilde{\mathbf{F}}_{\mu\nu} \\
\dot{\mathcal{E}}_\mu &= -\frac{1}{2} \sum_\nu^M \langle \mathbf{F}_{\mu\nu} \rangle^{\mathbf{R}\mathcal{E}} \cdot \mathbf{V}_{\mu\nu} + \sum_{\nu\mu'\nu'}^M \kappa_{\mu\mu'\nu\nu'} \frac{\partial S}{\partial \mathcal{E}_\nu} + \frac{1}{4} \sum_{\nu\mu'\nu'}^M \mathbf{V}_{\mu\mu'} \cdot \mathbf{\Gamma}_{\mu\mu'\nu\nu'} \cdot \mathbf{V}_{\nu\nu'} \frac{\partial S}{\partial \mathcal{E}_{\nu'}} \\
&\quad + \sum_\nu^M \left[\tilde{Q}_{\mu\nu} - \mathbf{V}_{\mu\nu} \cdot \tilde{\mathbf{F}}_{\mu\nu} \right]
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&\quad + \sum_{\nu}^{M} \left[\tilde{Q}_{\mu\nu} - \mathbf{V}_{\mu\nu} \cdot \tilde{\mathbf{F}}_{\mu\nu} \right]
\end{aligned}
$$

where we have introduced the Green-Kubo transport coefficients

$$
\begin{aligned}
\mathbf{\Gamma}_{\mu\mu'\nu\nu'} &\equiv \frac{1}{k_B} \int_0^\infty dt \left\langle \delta \mathbf{F}_{\mu\mu'} \delta \mathbf{F}_{\nu\nu'}(t) \right\rangle^\alpha \\
\kappa_{\mu\mu'\nu\nu'} &\equiv \frac{1}{k_B} \int_0^\infty dt \left\langle \delta Q_{\mu\mu'} \delta Q_{\nu\nu'}(t) \right\rangle^\alpha
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&\quad + \sum_\nu^M \left[\tilde{Q}_{\mu\nu} - \mathbf{V}_{\mu\nu} \cdot \tilde{\mathbf{F}}_{\mu\nu} \right]
\end{aligned}
$$

Galilean invariant, conserve momentum and energy, random terms satisfy Fluctuation-Dissipation

Model for the entropy

Whatever model for $S(\alpha)$ and $\langle \mathbf{F}_{\mu\nu} \rangle^\alpha$ should satisfy the GENERIC restriction

$$\frac{\partial E}{\partial \alpha} L \frac{\partial S}{\partial \alpha} = k_B \frac{\partial L}{\partial \alpha} \frac{\partial E}{\partial \alpha}$$

which for the present CG description is

$$\frac{\partial S}{\partial \mathbf{R}_\mu} = \frac{1}{2} \sum_\nu^M \mathbf{F}_{\mu\nu} \left(\frac{1}{T_\mu} + \frac{1}{T_\nu} \right) + k_B \sum_\nu^M \frac{1}{2} \left[\frac{\partial}{\partial \mathcal{E}_\mu} + \frac{\partial}{\partial \mathcal{E}_\nu} \right] \mathbf{F}_{\mu\nu}$$

This shows that the entropy plays now the role of a (minus) "potential of mean force".

Model for the entropy

Recall the definition of internal energy

$$
\begin{aligned}
\hat{\mathcal{E}}_\mu(z) &\equiv \sum_i^N \frac{m_i}{2}(\mathbf{v}_i - \hat{\mathbf{v}}_\mu(z))^2 \delta_\mu(i) + \frac{1}{2}\sum_{ij}^N \phi_{ij}\delta_\mu(i) \\
&= \sum_i^N \frac{m_i}{2}(\mathbf{v}_i - \hat{\mathbf{v}}_\mu(z))^2 \delta_\mu(i) + \frac{1}{2}\sum_{ij}^N \phi_{ij}\delta_\mu(j)\delta_\mu(i) + \sum_{\nu\neq\mu}\frac{1}{2}\sum_{ij}^N \phi_{ij}\delta_\nu(j)\delta_\mu(i) \\
&\approx \mathcal{E}_\mu^{\rm int}(z) + \sum_{\nu\neq\mu}\Phi_{\mu\nu}(R_{\mu\nu}(z))
\end{aligned}
$$

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&= \sum_i^N \frac{m_i}{2}(\mathbf{v}_i - \hat{\mathbf{v}}_\mu(z))^2\delta_\mu(i) + \frac{1}{2}\sum_{ij}^N \phi_{ij}\delta_\mu(j)\delta_\mu(i) + \sum_{\nu\neq\mu}\frac{1}{2}\sum_{ij}^N \phi_{ij}\delta_\nu(j)\delta_\mu(i) \\
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$$

The entropy

$$
\begin{aligned}
S(\mathbf{R},\mathcal{E}) &\equiv k_B \ln \int dz \prod_\mu^M \delta(\mathbf{R}_\mu - \hat{\mathbf{R}}_\mu(z))\delta(\mathbf{P}_\mu - \hat{\mathbf{P}}_\mu(z))\delta(\mathcal{E}_\mu - \hat{\mathcal{E}}_\mu(z)) \\
&= k_B \ln \prod_\mu^M \int dz_\mu \delta(\mathbf{R}_\mu - \hat{\mathbf{R}}_\mu(z_\mu))\delta(\mathbf{P}_\mu - \hat{\mathbf{P}}_\mu(z))\delta(\mathcal{E}_\mu - \Phi_\mu - \hat{\mathcal{E}}^{\rm int}_\mu(z)) \\
&= \sum_\mu S_\mu(\mathcal{E}_\mu - \Phi_\mu(R))
\end{aligned}
$$

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&\approx \mathcal{E}_\mu^{\rm int}(z) + \sum_{\nu\neq\mu}\Phi_{\mu\nu}(R_{\mu\nu}(z))
\end{aligned}
$$

The entropy is given by the sum of entropies of isolated blobs!

$$
\begin{aligned}
S(\mathbf{R},\mathcal{E}) &\equiv k_B \ln \int dz \prod_\mu^M \delta(\mathbf{R}_\mu - \hat{\mathbf{R}}_\mu(z))\delta(\mathbf{P}_\mu - \hat{\mathbf{P}}_\mu(z))\delta(\mathcal{E}_\mu - \hat{\mathcal{E}}_\mu(z)) \\
&= k_B \ln \prod_\mu^M \int dz_\mu \delta(\mathbf{R}_\mu - \hat{\mathbf{R}}_\mu(z_\mu))\delta(\mathbf{P}_\mu - \hat{\mathbf{P}}_\mu(z))\delta(\mathcal{E}_\mu - \Phi_\mu - \hat{\mathcal{E}}_\mu^{\rm int}(z)) \\
&= \sum_\mu S_\mu(\mathcal{E}_\mu - \Phi_\mu(R))
\end{aligned}
$$

Model for the entropy

This model is OK, because it satisfies the GENERIC restriction

$$\frac{\partial S}{\partial \mathbf{R}_\mu} = \frac{1}{2}\sum_{\nu}^{M} \mathbf{F}_{\mu\nu}\left(\frac{1}{T_\mu} + \frac{1}{T_\nu}\right) + k_B \sum_{\nu}^{M} \frac{1}{2}\left[\frac{\partial}{\partial \mathcal{E}_\mu} + \frac{\partial}{\partial \mathcal{E}_\nu}\right]\mathbf{F}_{\mu\nu}$$

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provided that the average force defined as

$$\mathbf{F}_{\mu\nu}(\mathbf{R}) = -\frac{\partial \Phi_\mu}{\partial \mathbf{R}_\nu}$$

Model for the transport coefficients

The Green-Kubo coefficients

$$\Gamma_{\mu\mu'\nu\nu'} \equiv \frac{1}{k_B}\int_0^\infty dt \left\langle \delta \mathbf{F}_{\mu\mu'}\delta \mathbf{F}_{\nu\nu'}(t)\right\rangle^\alpha$$
$$\kappa_{\mu\mu'\nu\nu'} \equiv \frac{1}{k_B}\int_0^\infty dt \left\langle \delta Q_{\mu\mu'}\delta Q_{\nu\nu'}(t)\right\rangle^\alpha$$

Model projected currents with the following white noise

$$\delta\hat{\mathbf{F}}_{\mu\nu} \equiv \hat{\mathbf{F}}_{\mu\nu} - \langle\hat{\mathbf{F}}_{\mu\nu}\rangle^\alpha \qquad \mapsto \qquad \tilde{\mathbf{F}}_{\mu\nu} \equiv A_{\mu\nu}\mathbf{e}_{\mu\nu}\mathcal{W}_{\mu\nu}(t)$$
$$\delta\hat{Q}_{\mu\nu} \equiv \hat{Q}_{\mu\nu} - \langle\hat{Q}_{\mu\nu}\rangle^\alpha \qquad \mapsto \qquad \tilde{Q}_{\mu\nu} \equiv B_{\mu\nu}\mathcal{V}_{\mu\nu}(t)$$

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$$\boldsymbol{\Gamma}_{\mu\mu'\nu\nu'} \equiv \frac{1}{k_B}\int_0^\infty dt\,\left\langle \delta\mathbf{F}_{\mu\mu'}\delta\mathbf{F}_{\nu\nu'}(t)\right\rangle^\alpha$$
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Model projected currents with the following white noise

$$\delta\hat{\mathbf{F}}_{\mu\nu} \equiv \hat{\mathbf{F}}_{\mu\nu} - \langle\hat{\mathbf{F}}_{\mu\nu}\rangle^\alpha \quad \mapsto \quad \tilde{\mathbf{F}}_{\mu\nu} \equiv A_{\mu\nu}\mathbf{e}_{\mu\nu}\mathcal{W}_{\mu\nu}(t)$$
$$\delta\hat{Q}_{\mu\nu} \equiv \hat{Q}_{\mu\nu} - \langle\hat{Q}_{\mu\nu}\rangle^\alpha \quad \mapsto \quad \tilde{Q}_{\mu\nu} \equiv B_{\mu\nu}\mathcal{V}_{\mu\nu}(t)$$

where the white noise satisfies

$$\left\langle \mathcal{W}_{\mu\mu'}(t)\mathcal{W}_{\nu\nu'}(t')\right\rangle = \left[\delta_{\mu\nu}\delta_{\mu'\nu'} + \delta_{\mu\nu'}\delta_{\nu\mu'}\right]\delta(t-t')$$
$$\left\langle \mathcal{V}_{\mu\mu'}(t)\mathcal{V}_{\nu\nu'}(t')\right\rangle = \left[\delta_{\mu\nu}\delta_{\mu'\nu'} + \delta_{\mu\nu'}\delta_{\nu\mu'}\right]\delta(t-t')$$
$$\left\langle \mathcal{W}_{\mu\mu'}(t)\mathcal{V}_{\nu\nu'}(t')\right\rangle = 0$$

Model for the transport coefficients

With these modelling assumptions, the Green-Kubo coefficients

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The prefactors of the white noise are microscopically computable

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The simpler SDE

Under the approximations on the transport coefficients we have

$$\dot{\mathbf{R}}_\mu = \mathbf{V}_\mu$$

$$\dot{\mathbf{P}}_\mu = \sum_\nu^M \langle \mathbf{F}_{\mu\nu} \rangle^{\mathbf{R}\mathcal{E}} - \sum_\nu^M \gamma_{\mu\nu} (\mathbf{e}_{\mu\nu} \cdot \mathbf{V}_{\mu\nu}) \mathbf{e}_{\mu\nu} + \sum_\nu \tilde{\mathbf{F}}_{\mu\nu}$$

$$\dot{\mathcal{E}}_\mu = -\frac{1}{2} \sum_\nu^M \langle \mathbf{F}_{\mu\nu} \rangle^{\mathbf{R}\mathcal{E}} \cdot \mathbf{V}_{\mu\nu} + \sum_\nu^M \kappa_{\mu\nu} \left[\frac{1}{T_\mu} - \frac{1}{T_\nu} \right] + \sum_\nu^M \gamma_{\mu\nu} (\mathbf{V}_{\mu\nu} \cdot \mathbf{e}_{\mu\nu})^2 + \sum_\nu^M \left[\tilde{Q}_{\mu\nu} - \mathbf{V}_{\mu\nu} \cdot \tilde{\mathbf{F}}_{\mu\nu} \right]$$

These are the equations of DPD+E (Español '97, Bonet & Mackie '97) BUT with microscopic foundation.

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- Markov allows you to run short MD simulation to extract macroscopic parameters.

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The theory gives you the structure of the equations. You need to provide the physical insights for proper modelling.