How to build a coarse-grained model

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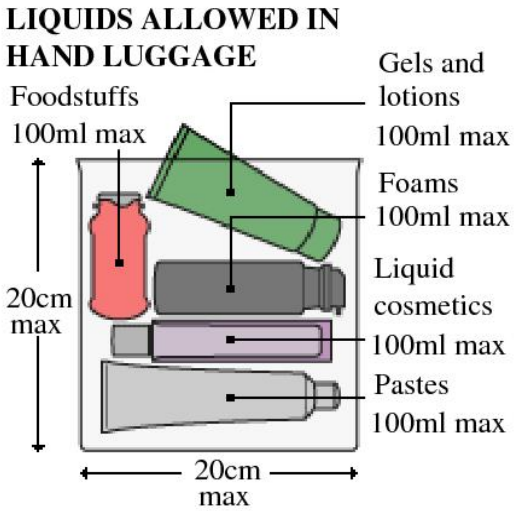
My Background: Soft Matter Physics

Soft Matter



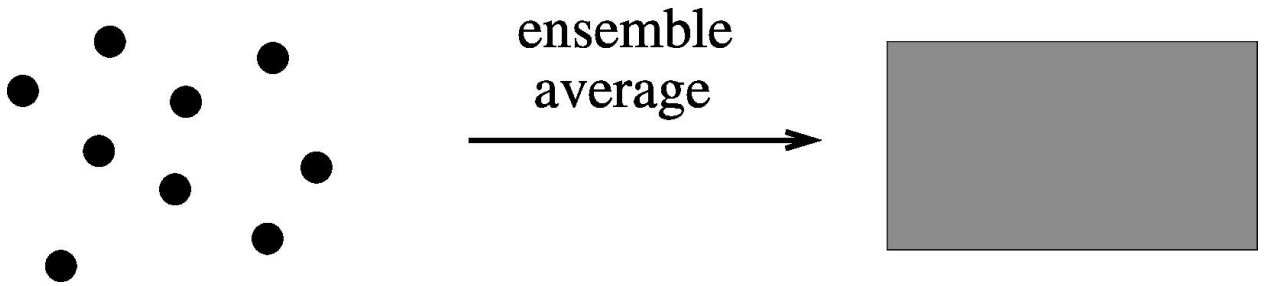
http://www.euromost.info/air_travel/

- Suspensions, Gels, Glasses, Liquid Crystals
- Strongly non-linear response
- Slow relaxation
  $\longrightarrow$ non-equilibrium physics
- **Entropy** matters

Coarse-grained models:

Evolution equations for mesoscopic observables (e.g. local concentrations of solutes, order parameter fields)
or for macroscopic observables (e.g. viscosity, electrical conductivity)

Reminder: Basics of Statistical Mechanics



Microscopic World (classical)

N particles

positions $\vec{r}^N$

momenta $\vec{p}^N$

Fully characterized by Hamiltonian

$$H\left(\vec{r}^N, \vec{p}^N\right) = \sum_{i=1}^{N} \frac{1}{2m_i} \vec{p}_i \cdot \vec{p}_i + V\left(\vec{r}^N\right)$$

Macroscopic World (equilibrium)

internal energy U

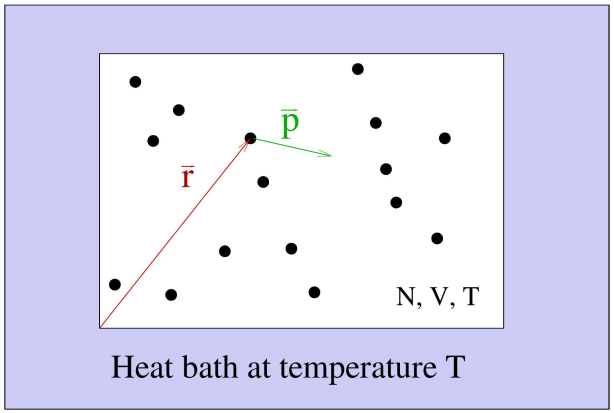
particle number N

volume V

Fully characterized by entropy

$$S = f(U, N, V)$$

Reminder: Basics of Statistical Mechanics



In thermal equilibrium, the probability to find a state $\Gamma = (\vec{r}^N, \vec{p}^N)$ is

$$\rho(\Gamma) = \frac{e^{-\beta H(\Gamma)}}{\int \mathrm{d}\Gamma\, e^{-\beta H(\Gamma)}}$$

where $\beta := \frac{1}{k_B T}$.

Free energy

$$G(N, V, T) = -k_B T \ln \int \mathrm{d}\Gamma\, e^{-\beta H(\Gamma)}$$

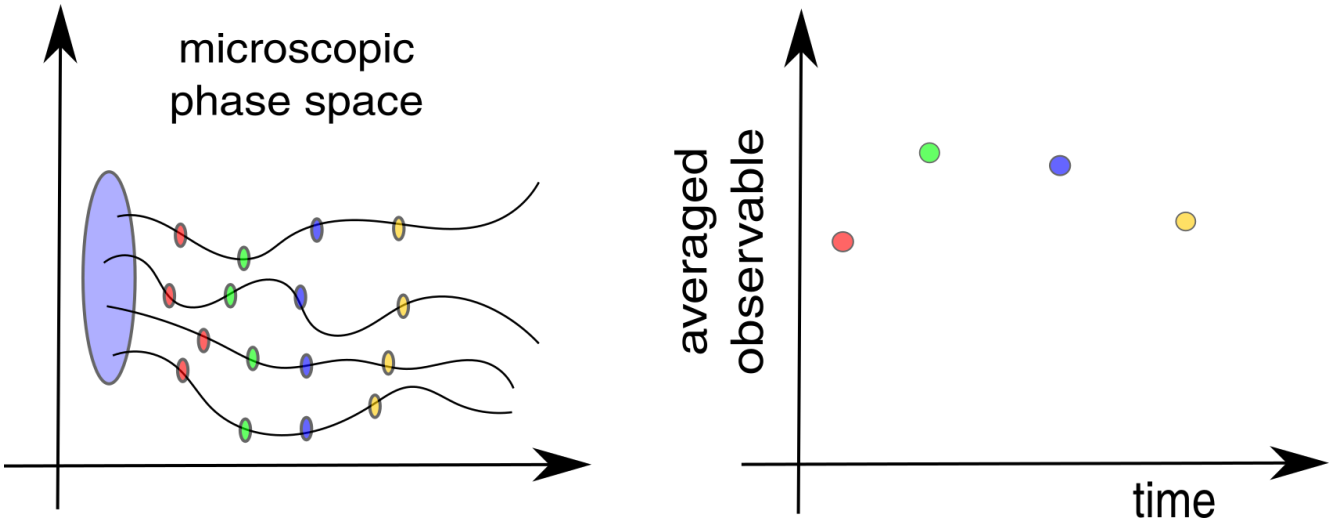
Marcoscopic average of an observable $\mathbb{A}(\Gamma)$

$$\langle A \rangle_{N,V,T} = \frac{\int \mathrm{d}\Gamma\, \mathbb{A}(\Gamma) e^{-\beta H(\Gamma)}}{\int \mathrm{d}\Gamma\, e^{-\beta H(\Gamma)}}$$

Multi-Scale Modelling

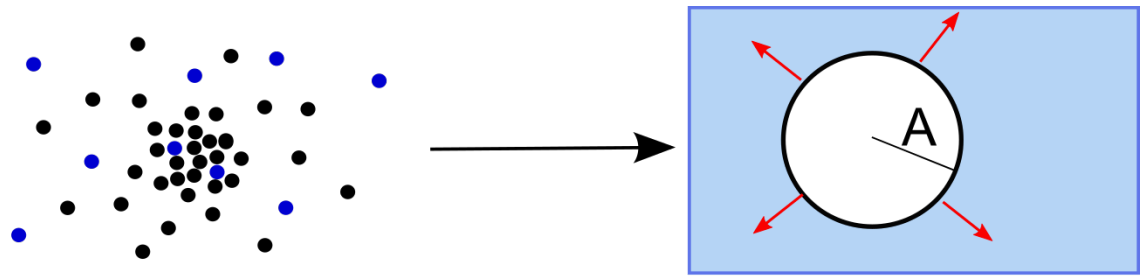
We would like to **"coarse-grain"** dynamics, i.e.

> To derive from the underlying microscopic theory an equation of motion for an observable averaged over non-equilibrium trajectories



... or at least approximate it numerically.

Multi-Scale Modelling



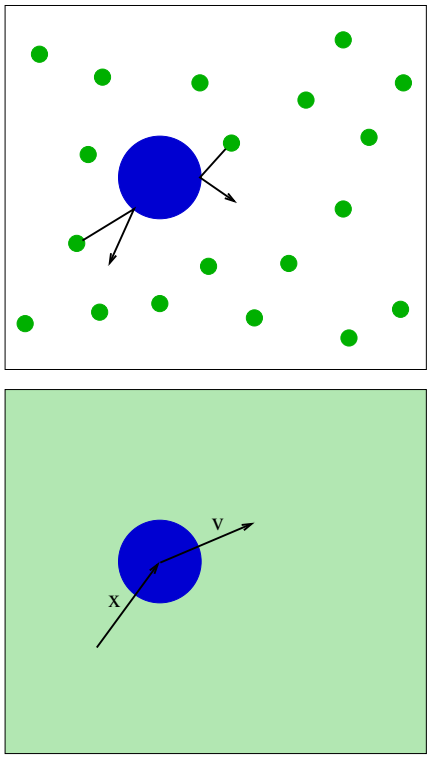
- Classical system, phase space coordinates Γ, Hamiltonian $H(\Gamma)$.
- Liouville equation for the dynamics of the microscopic degrees of freedom

$$\frac{\partial}{\partial t}\rho(\Gamma,t) = \{H,\rho\} = -\mathrm{i}\mathcal{L}\rho$$

- What is the equation of motion of a coarse-grained observable $\mathbb{A}(\Gamma)$?
- **Does it make sense to transfer notions from macroscopic, equilibrium thermodynamics (entropy, free energy etc.) to the non-equilibrium case?**

Example I: Brownian Motion

Task: To find an equation of motion for the position of a solute particle.



- Einstein, Smoluchowski
  Diffusion equation for probability of position

$$\frac{\partial p(x,t)}{\partial t} = D\frac{\partial^2 p(x,t)}{\partial x^2}$$

  D: diffusion constant.

- Langevin
  Stochastic differential equation for velocity

$$m\frac{\mathrm{d}v}{\mathrm{d}t} = -\nu v + \xi(t)$$

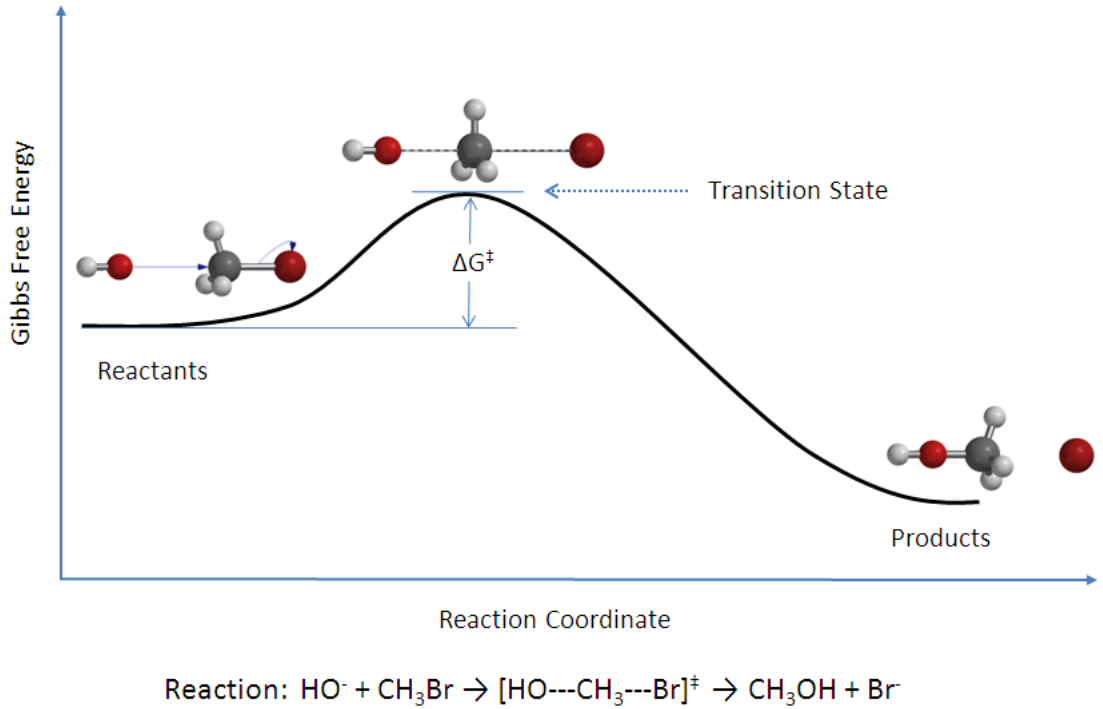
  ν: friction coefficient, $\langle \xi(t)\xi(t')\rangle = 2\nu k_B T\delta(t-t')$

- Descriptions are equivalent: $D\nu = k_B T$

A. Einstein, Annalen der Physik **322** (1905) 549-560, M. M. von Smoluchowski, Bulletin International de l'Académie des Sciences de Cracovie **3** (1906) 202-213) P. Langevin, Compt. Rendus **146** (1908) 530-533

Example II: Rates of Chemical Reactions

Task: To find the rate of a chemical reaction.



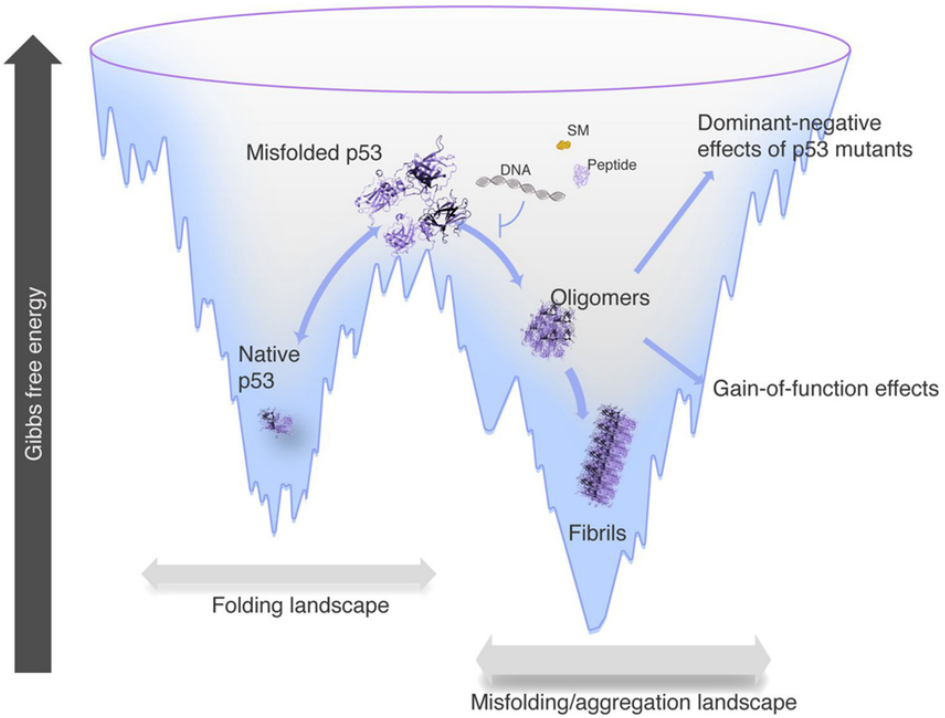
Eyring equation for reaction rate:

$$k = \frac{k_B T}{h} \exp\left(\frac{-\Delta G}{RT}\right)$$

H. Eyring, J. Chem. Phys. **3**, 107 (1935), Source of image: Chem540grp1f08, CC BY-SA 3.0

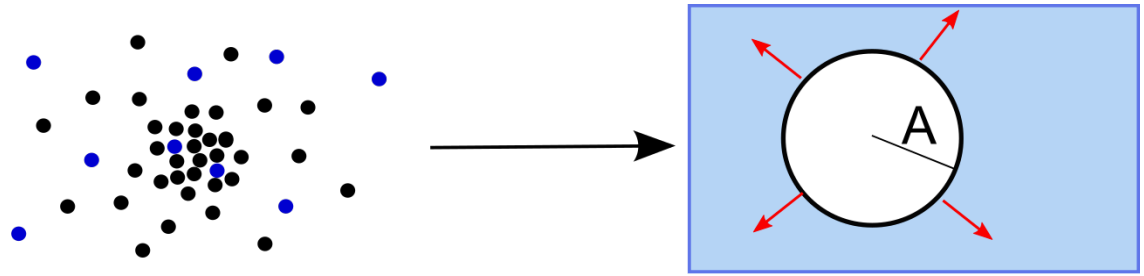
Example III: Transition State Theory

Task: To find equations of motion for reaction coordinates.



Source: Silva, J., Cordeiro, Y., J. Bio. Chemistry **291**, 15482 (2016) 10.1074/jbc.R116.733428.

Principle of "Quasi-Equilibrium" Coarse-Graining



- Pick a coarse-grained observable, a "reaction coordinate" $\mathbb{A}(\Gamma)$
- Compute the **equilibrium probability** to find a certain value A_0 of $\mathbb{A}(\Gamma)$

$$\langle p(A_0)\rangle_{N,V,T} = \frac{\int \mathrm{d}\Gamma\, \delta\left(\mathbb{A}(\Gamma) - A_0\right) e^{-\beta H(\Gamma)}}{\int \mathrm{d}\Gamma\, e^{-\beta H(\Gamma)}}$$

- Interpret $-k_B T \ln(p(A))$ as an **"effective free energy"** $\Delta G(A)$ or a **"potential of mean force"** $W(A)$.
- Model the dynamics as a **stochastic process** in the **free energy landscape**.

Models

In the literature on modelling, we often find an effective equation of motion of the form

$$m\ddot{A}_t = -\left.\frac{\mathrm{d}W(A)}{\mathrm{d}A}\right|_{A=A_t} - \gamma\dot{A}_t + \sqrt{2\gamma k_B T}\,\xi_t$$

A_t	:	coarse-grained variable
m	:	effective mass
ξ_t	:	Gaussian white noise
γ	:	friction coefficient
$W(A)$	:	"potential of mean force"

- The equation is constructed in **analogy to Newtonian mechanics**.
- The potential of mean force or effective free energy is defined as

$$W(A) := -k_B T \ln\left(\rho_{\mathbb{A}}^{\mathrm{eq}}(A)\right) =: \Delta G(A)$$

- γ is related to ξ_t by the **fluctuation dissipation theorem**

$$\langle \xi_t \xi_{t'} \rangle = 2\gamma k_B T \delta(t - t')$$

- Dots indicate time-derivatives, but this is a **stochastic** differential equation.

Models

- Compare Langevin's equation for the velocity of a Brownian particle

$$m\frac{\mathrm{d}v}{\mathrm{d}t} = -\nu v + \xi(t)$$

to

$$m\ddot{A}_t = -\left.\frac{\mathrm{d}W(A)}{\mathrm{d}A}\right|_{A=A_t} - \gamma\dot{A}_t + \sqrt{2\gamma k_B T}\,\xi_t$$

This equation is a version of the **Langevin Equation**.

Models

- Dynamics of coarse-grained observables is also often modelled by **other versions of the Langevin equation**.
- The overdamped case

$$\gamma \dot{A}_t = - \left. \frac{\mathrm{d}W(A)}{\mathrm{d}A} \right|_{A=A_t} + \sqrt{2\gamma k_B T}\xi_t$$

- Phase-field models of phase transitions:

$$\frac{\partial \phi_t(\vec{r})}{\partial t} = -\gamma \left. \frac{\delta G^{\mathrm{PF}}[\phi(\vec{r})]}{\delta \phi} \right|_{\phi(\vec{r})=\phi_t(\vec{r})} + \xi_t(\vec{r})$$

  $\phi_t(\vec{r})$: order parameter field, G^{PF} effective free energy.

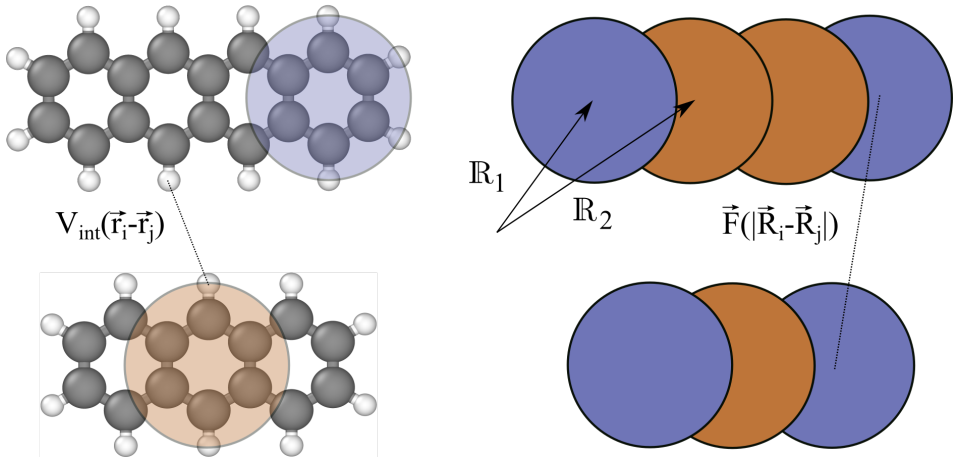
- Dynamic Density Functional Theory

$$\frac{\partial \rho_t(\vec{r})}{\partial t} = \gamma \nabla \cdot \left(\rho_t(\vec{r}) \nabla \left. \frac{\delta G[\rho(\vec{r})]}{\delta \rho} \right|_{\rho(\vec{r})=\rho_t(\vec{r})} \right)$$

  ρ: single particle density

Models

- Dissipative Particle Dynamics



Source: TS, *Coarse-Grained Modelling Out of Equilibrium*, accepted by Physics Reports (2022)

$$m_i \frac{\mathrm{d}^2 \vec{R}_i}{\mathrm{d}t^2} = -\left.\frac{\partial U(\vec{R}^M)}{\partial \vec{R}}\right|_{\vec{R}=\vec{R}_i} - \sum_{j\neq i, j=1}^{M} \gamma \omega^D(R_{ij})(\vec{v}_{ij}\cdot\vec{e}_{ij})\vec{e}_{ij} + \sum_{j\neq i, j=1}^{M} \sigma \nu^R(R_{ij})\vec{e}_{ij}\xi_{ij}$$

R_{ij}: distance between coarse-grained units, $\vec{v}_{ij}$: relative velocity, $\vec{e}_{ij} := \frac{\vec{R}_i - \vec{R}_j}{|\vec{R}_i - \vec{R}_j|}$.

Models

Also frequently encountered in the literature is an **integro-differential equation**

$$m\ddot{A}_t = -\left.\frac{\mathrm{d}W(A)}{\mathrm{d}A}\right|_{A=A_t} - \int_0^t \mathrm{d}s\, K(t-s)\dot{A}_s + \xi_t$$

$K(t)$: the "memory kernel"
ξ_t : the "fluctuating force"

With the generalized **fluctuation-dissipation theorem**,

$$K(t) \propto \langle \xi_0 \xi_t \rangle$$

Can we derive these equations?

Are they controlled approximations to the true dynamics?

Projection Operator Formalisms

We begin with the **Liouville equation**

$$\frac{\partial}{\partial t}\rho(\Gamma,t) = \{H,\rho\} = -\mathrm{i}\mathcal{L}\rho \quad ,$$

which entails the equation of motion of $\mathbb{A}(\Gamma_t)$

$$\frac{\mathrm{d}A_t}{\mathrm{d}t} = \frac{\mathrm{d}\mathbb{A}(\Gamma_t)}{\mathrm{d}t} = \dot{\Gamma}_t \cdot \frac{\partial \mathbb{A}}{\partial \Gamma}(\Gamma_t) = \mathrm{i}\mathcal{L}\mathbb{A}(\Gamma_t) \quad .$$

This is formally solved by

$$\frac{\mathrm{d}A_t}{\mathrm{d}t} = e^{t\mathrm{i}\mathcal{L}}\mathrm{i}\mathcal{L}\mathbb{A}(\Gamma_0) \quad .$$

Projection Operator Formalisms

How do we get from the exact expression

$$\frac{\mathrm{d}A_t}{\mathrm{d}t} = e^{t\mathrm{i}\mathcal{L}}\mathrm{i}\mathcal{L}\mathbb{A}(\Gamma_0)$$

to an equation of motion of the form of the Langevin equation?

We define a **projection operator** $\mathcal{P}$ on the space of phase space functions.

Using $\mathcal{Q} := 1 - \mathcal{P}$ and

$$e^{t\mathrm{i}\mathcal{L}}\circ = e^{t\mathcal{Q}\mathrm{i}\mathcal{L}}\circ + \int_0^t \mathrm{d}s\, e^{(t-s)\mathrm{i}\mathcal{L}}\mathcal{P}\mathrm{i}\mathcal{L}e^{s\mathcal{Q}\mathrm{i}\mathcal{L}}\circ \quad ,$$

we write the exact equation of motion as

$$\frac{\mathrm{d}A_t}{\mathrm{d}t} = e^{t\mathrm{i}\mathcal{L}}\mathcal{P}\mathrm{i}\mathcal{L}\mathbb{A}(\Gamma_0) + \int_0^t \mathrm{d}s\, e^{s\mathrm{i}\mathcal{L}}\mathcal{P}\mathrm{i}\mathcal{L}\mathcal{Q}e^{(t-s)\mathrm{i}\mathcal{L}\mathcal{Q}}\mathrm{i}\mathcal{L}\mathbb{A}(\Gamma_0) + \mathcal{Q}e^{t\mathrm{i}\mathcal{L}\mathcal{Q}}\mathrm{i}\mathcal{L}\mathbb{A}(\Gamma_0) \quad .$$

Now the task is to **choose a suitable projection operator.**
Depending on the choice, we will obtain different versions of the Langevin equation.

Mori's Approach

Mori defined a **linear projection operator**

$$\mathcal{P}^{\mathrm{M}}\mathbb{X}(\Gamma) := \frac{(\mathbb{X},\mathbb{A})}{(\mathbb{A},\mathbb{A})}\mathbb{A}(\Gamma) \quad \text{with} \quad (\mathbb{X},\mathbb{Y}) := \int \mathrm{d}\Gamma\ \mathbb{X}(\Gamma)\mathbb{Y}(\Gamma)\rho_N^{\mathrm{EQ}}(\Gamma) \quad .$$

Application of $\mathcal{P}^{\mathrm{M}}\circ$ to $\frac{\mathrm{d}A_t}{\mathrm{d}t} = e^{t\mathrm{i}\mathcal{L}}\mathrm{i}\mathcal{L}\mathbb{A}(\Gamma_0)$ produces

$$\frac{\mathrm{d}A_t}{\mathrm{d}t} = \omega A_t + \int_0^t \mathrm{d}\tau\ K(t-\tau)A_\tau + f_t$$

The linear, generalized Langevin Equation

with the drift $\omega := \frac{(\mathrm{i}\mathcal{L}\mathbb{A},\mathbb{A})}{(\mathbb{A},\mathbb{A})}$, the fluctuating force $f_t := e^{t\mathcal{Q}_M\mathrm{i}\mathcal{L}}\mathcal{Q}_M\mathrm{i}\mathcal{L}\mathbb{A}(\Gamma_0)$
and the memory kernel

$$K(t) := \frac{\left(\mathrm{i}\mathcal{L}e^{t\mathcal{Q}_M\mathrm{i}\mathcal{L}}\mathcal{Q}_M\mathrm{i}\mathcal{L}\mathbb{A},\mathbb{A}\right)}{(\mathbb{A},\mathbb{A})} \quad .$$

H. Mori, Prog. Theor. Phys **33**, 423 (1965)

Mori's Approach

Notes on the linear generalized Langevin equation

$$\frac{\mathrm{d}A_t}{\mathrm{d}t} = \omega A_t + \int_0^t \mathrm{d}\tau\, K(t-\tau)A_\tau + f_t$$

The equation is

- ... **deterministic**. To obtain the Langevin equation, we need a stochastic interpretation of f_t.
- ... **non-local in time**, resp. non-Markovian in the stochastic interpretation.
- ... **linear**.
- ... invariant under translations in time, i.e. it holds only in **equilibrium**.

The memory kernel is related to the fluctuating force

$$K(t) := \frac{\left(\mathrm{i}\mathcal{L}e^{t\mathcal{Q}_M\mathrm{i}\mathcal{L}}\mathcal{Q}_M\mathrm{i}\mathcal{L}\mathbb{A},\mathbb{A}\right)}{(\mathbb{A},\mathbb{A})} = -\frac{(f_0,f_t)}{(\mathbb{A},\mathbb{A})} \quad .$$

This relation is often called the **second fluctuation dissipation theorem**.

Zwanzig's Approach

Zwanzig defined a **non-linear projection operator**

$$\mathcal{P}^{\mathrm{Z}}\mathbb{X}(\Gamma) := \frac{\int d\Gamma'\ \delta(\mathbb{A}(\Gamma') - \mathbb{A}(\Gamma))\mathbb{X}(\Gamma')}{\int d\Gamma'\ \delta(\mathbb{A}(\Gamma') - \mathbb{A}(\Gamma))}$$

and obtained the equation of motion

$$\begin{aligned}\frac{\partial \rho(A,t)}{\partial t} &= -\frac{\partial}{\partial A}\left(v(A)\rho(A,t)\right) \\ &\quad + \int_0^t \mathrm{d}\tau \int \mathrm{d}A' \frac{\partial}{\partial A}\left(W(A)K(A,A',\tau)\right)\right) \frac{\partial}{\partial A'}\left(\frac{\rho(A',t-\tau)}{W(A')}\right)\end{aligned}$$

with $W(A) := \int \mathrm{d}\Gamma\ \delta(\mathbb{A}(\Gamma) - A)$ and the transport coefficients v and K.
This equation is

- . . . **non-linear**, **deterministic** and **non-local in time**.
- ". . .too complicated to be useful for any but the most formal applications" (R. Zwanzig)

R. Zwanzig, Phys. Rev. **124**, 983 (1961)

Zwanzig II

- How do we construct an equation of this form

$$m\ddot{A}_t = -\left.\frac{\mathrm{d}W(A)}{\mathrm{d}A}\right|_{A=A_t} - \gamma\dot{A}_t + \sqrt{2\gamma k_B T}\,\xi_t \quad ?$$

- Define two observables $\vec{\mathbb{A}} = (\mathbb{A}_1, \mathbb{A}_2)$
  - $\mathbb{A}_1$ is **linear** in the generalized coordinates.
  - $\mathbb{A}_2$ is the **time-derivative** of $\mathbb{A}_1$, i.e. $\vec{\mathbb{A}} = (\mathbb{A}, \mathrm{i}\mathcal{L}\mathbb{A})$.
- Define a "Zwanzig-like projector"

$$\mathcal{P}\mathbb{X}(\Gamma) := \frac{1}{\rho_{\mathbb{A}}\left(\vec{\mathbb{A}}(\Gamma)\right)} \int \mathrm{d}\Gamma'\, \rho^{\mathrm{eq}}(\Gamma')\, \mathbb{X}(\Gamma')\, \delta\left(\vec{\mathbb{A}}(\Gamma) - \vec{\mathbb{A}}(\Gamma')\right)$$

with the "relevant density"

$$\rho_{\mathbb{A}}\left(\vec{A}\right) := \int \mathrm{d}\Gamma\, \rho^{\mathrm{eq}}(\Gamma)\, \delta\left(\vec{\mathbb{A}}(\Gamma) - \vec{\mathbb{A}}(\Gamma')\right)$$

(Recall the definition of the potential of mean force $W(A) = -k_B T \ln\left(\rho^{\mathrm{eq}}_{\mathbb{A}}(A)\right)$.)

Zwanzig II

- We insert these definitions into the equation of motion

$$\frac{\mathrm{d}\vec{A}_t}{\mathrm{d}t} = e^{t\mathrm{i}\mathcal{L}}\mathcal{P}\mathrm{i}\mathcal{L}\vec{\mathbb{A}}(\Gamma_0) + \int_0^t \mathrm{d}s\, e^{s\mathrm{i}\mathcal{L}}\mathcal{P}\mathrm{i}\mathcal{L}\mathcal{Q}e^{(t-s)\mathrm{i}\mathcal{L}\mathcal{Q}}\mathrm{i}\mathcal{L}\vec{\mathbb{A}}(\Gamma_0) + \mathcal{Q}e^{t\mathrm{i}\mathcal{L}\mathcal{Q}}\mathrm{i}\mathcal{L}\vec{\mathbb{A}}(\Gamma_0) \quad .$$

- For the second component of the first term, we obtain

$$e^{t\mathrm{i}\mathcal{L}}\mathcal{P}\mathrm{i}\mathcal{L}\mathbb{A}_2 \propto \frac{\partial}{\partial A_1} \underbrace{k_B T \ln\left(\rho_A(\vec{A})\right)}_{=:W(\vec{A})} \Big|_{\vec{A}_t} \quad .$$

This is a derivative of a potential of mean force.

Details of the calculation can be found in Fabian Glatzel, TS, Europhysics Letters **136** 36001 (2021).

Zwanzig II

- Recall that we intend to construct

$$m\ddot{A}_t = -\left.\frac{\mathrm{d}W(A)}{\mathrm{d}A}\right|_{A=A_t} - \int_0^t \mathrm{d}s\, K(t-s)\dot{A}_s + \xi_t$$

- Up to now we have got

$$\frac{\mathrm{d}A_{2,t}}{\mathrm{d}t} = \frac{\mathrm{d}^2 A_{1,t}}{\mathrm{d}t^2} = -\frac{1}{m}\left.\frac{\partial W(\vec{A})}{\partial A_1}\right|_{\vec{A}=\vec{A}_t} + \left(\int_0^t \mathrm{d}s\, e^{s\mathrm{i}\mathcal{L}}\mathcal{P}\mathrm{i}\mathcal{L}\mathcal{Q}e^{(t-s)\mathrm{i}\mathcal{L}\mathcal{Q}}\mathrm{i}\mathcal{L}\vec{\mathbb{A}} + \mathcal{Q}e^{t\mathrm{i}\mathcal{L}\mathcal{Q}}\mathrm{i}\mathcal{L}\vec{\mathbb{A}}\right)_2$$

- The other two terms are **difficult to tackle by a Zwanzig projector**.
- We construct a work-around. Note that

$$\mathcal{P}\mathbb{X}(\Gamma) = \frac{1}{\rho_A\left(\vec{\mathbb{A}}(\Gamma)\right)}\int \mathrm{d}\Gamma'\, \rho^{\mathrm{eq}}(\Gamma')\,\mathbb{X}(\Gamma')\,\delta\left(\vec{\mathbb{A}}(\Gamma)-\vec{A}\right) = \left.\frac{\left(\delta\left(\vec{\mathbb{A}}-\vec{A}\right),\mathbb{X}\right)}{\left(\delta\left(\vec{\mathbb{A}}-\vec{A}\right),1\right)}\right|_{\vec{A}=\vec{\mathbb{A}}(\Gamma)}$$

with the inner product

$$(\mathbb{X},\mathbb{Y}) := \int \mathrm{d}\Gamma\, \rho^{\mathrm{eq}}(\Gamma)\,\mathbb{X}(\Gamma)\mathbb{Y}(\Gamma) \quad .$$

Zwanzig II

We pick a **basis** $\{f_i(\vec{\mathbb{A}})\}$ for the space of phase space functions, which depend on Γ solely through $\vec{\mathbb{A}}(\Gamma)$, and write the Zwanzig-projector

$$\mathcal{P}\mathbb{X}(\Gamma) = \left.\frac{\left(\delta\left(\vec{\mathbb{A}} - \vec{A}\right), \mathbb{X}\right)}{\left(\delta\left(\vec{\mathbb{A}} - \vec{A}\right), 1\right)}\right|_{\vec{A}=\vec{\mathbb{A}}(\Gamma)}$$

as

$$\mathcal{P}\mathbb{X}(\Gamma) = \sum_{i=1}^{\infty}\left(f_i\left(\vec{\mathbb{A}}\right), \mathbb{X}\right) f_i\left(\vec{A}\right) \quad .$$

Recall the definition by Mori:

$$\mathcal{P}^{\mathrm{M}}\mathbb{X} = \frac{(\mathbb{A}, \mathbb{X})}{(\mathbb{A}, \mathbb{A})}\mathbb{A} \quad .$$

A Zwanzig projector can be expressed as a Mori-projector which projects onto infintely many observables!

Idea taken from: S. Izvekov JCP **138**, 134106 (2013) and S. Kawai and T. Komatsuzaki JCP **134**, 114523 (2011)

Zwanzig II

- We insert $\mathcal{P}\mathbb{X}(\Gamma) = \sum_i \left(f_i\left(\vec{\mathbb{A}}\right), \mathbb{X}\right) f_i\left(\vec{\mathbb{A}}(\Gamma)\right)$ in

$$\frac{\mathrm{d}\vec{A}_t}{\mathrm{d}t} = e^{t\mathrm{i}\mathcal{L}}\mathcal{P}\mathrm{i}\mathcal{L}\vec{\mathbb{A}}(\Gamma_0) + \int_0^t \mathrm{d}s\, e^{s\mathrm{i}\mathcal{L}}\mathcal{P}\mathrm{i}\mathcal{L}\mathcal{Q}e^{(t-s)\mathrm{i}\mathcal{L}\mathcal{Q}}\mathrm{i}\mathcal{L}\vec{\mathbb{A}}(\Gamma_0) + \mathcal{Q}e^{t\mathrm{i}\mathcal{L}\mathcal{Q}}\mathrm{i}\mathcal{L}\vec{\mathbb{A}}(\Gamma_0)$$

- The 2nd component of the orange term is

$$\sum_{i=1}^{\infty}\int_0^t \mathrm{d}s\, K_{2,i}(t-s) f_i\left(\vec{A}_s\right) \quad \text{with} \quad K_{j,i}(t-s) = \left(f_i\left(\vec{\mathbb{A}}\right), \mathrm{i}\mathcal{L}\mathcal{Q}e^{(t-s)\mathrm{i}\mathcal{L}\mathcal{Q}}\mathrm{i}\mathcal{L}\mathbb{A}_j\right)$$

- Compare to

$$m\ddot{A}_t = -\left.\frac{\mathrm{d}W(A)}{\mathrm{d}A}\right|_{A=A_t} - \int_0^t \mathrm{d}s\, K(t-s)\dot{A}_s + \xi_t \quad .$$

The memory term differs considerably.

Details in Fabian Glatzel, TS, Europhysics Letters **136** 36001 (2021)

Zwanzig II

- Choose e.g. **orthonormal polynomials in** $\vec{\mathbb{A}}$ as basis functions $\{f_i\}$.
  Then the memory term of the exact equation

$$\sum_{i=1}^{\infty} \int_0^t \mathrm{d}s\, K_{2,i}(t-s) f_i\left(\vec{A}_s\right) \quad \text{with} \quad K_{j,i}(t-s) = \left(f_i\left(\vec{\mathbb{A}}\right), \mathrm{i}\mathcal{L}\mathcal{Q}e^{(t-s)\mathrm{i}\mathcal{L}\mathcal{Q}}\mathrm{i}\mathcal{L}\mathbb{A}_j\right)$$

  contains powers $(A_s)^n$ **and** $(\dot{A}_s)^n$ **to any order n** – rather than just $K(t-s)\dot{A}_s$!

- Even if there is time-scale separation at all orders

$$K_{j,i}(t-s) \propto \delta(t-s) =: \gamma_{i,j}\, \delta(t-s) \quad ,$$

  we obtain

$$m\ddot{A}_t = -\left.\frac{\mathrm{d}W(A)}{\mathrm{d}A}\right|_{A=A_t} - \sum_{i=1}^{\infty} \gamma_{2,i}\, f_i\left(A_s, \dot{A}_s\right) + \varepsilon_t$$

  rather than

$$m\ddot{A}_t = -\left.\frac{\mathrm{d}W(A)}{\mathrm{d}A}\right|_{A=A_t} - \gamma\dot{A}_t + \sqrt{2\gamma k_B T}\, \xi_t$$

Details in Fabian Glatzel, TS, Europhysics Letters **136** 36001 (2021)

Zwanzig II

- Also recall that most modellers assume

$$K(t) \propto \langle \xi_0 \xi_t \rangle$$

- We define a short-hand for the third term

$$\vec{\varepsilon}_t := \mathcal{Q} e^{t\mathrm{i}\mathcal{L}\mathcal{Q}} \mathrm{i}\mathcal{L}\vec{\mathbb{A}}$$

- As we used a linear projection operator

$$K_{j,i}(t) = -\left(\mathrm{i}\mathcal{L} f_i\left(\vec{\mathbb{A}}\right), \mathcal{Q} e^{t\mathrm{i}\mathcal{L}\mathcal{Q}} \mathrm{i}\mathcal{L}\mathbb{A}_j\right) = -\left(\mathrm{i}\mathcal{L} f_i\left(\vec{\mathbb{A}}\right), \vec{\varepsilon}_{j,t}\right)$$

- This brings us close to a **fluctuation-dissipation theorem** but not quite there...

$$K_{j,i}(t) = -\left(\mathrm{i}\mathcal{L} f_i\left(\vec{\mathbb{A}}\right), \vec{\varepsilon}_{j,t}\right) = -\left\langle \varepsilon_{j,t} \left(\vec{\varepsilon}_0 \cdot \left. \frac{\mathrm{d} f_i(\vec{A})}{\mathrm{d}\vec{A}} \right|_{\vec{A}=\vec{\mathbb{A}}(\Gamma_0)} \right) \right\rangle$$

i.e.

$$K_{2,1}(t) \neq \langle \varepsilon_{2,0} \varepsilon_{2,t} \rangle \quad !$$

Fabian Glatzel, TS, Europhysics Letters **136** 36001 (2021)

The Non-linear Generalized Langevin Equation

In summary, we obtained an equation of the form

$$m\ddot{A}_t = -\left.\frac{\mathrm{d}W(A)}{\mathrm{d}A}\right|_{A=A_t} - \sum_{i=1}^{\infty}\int_0^t \mathrm{d}s\, K_i(t-s) f_i\left(A_s, \dot{A}_s\right) + \varepsilon_t$$

rather than

$$m\ddot{A}_t = -\left.\frac{\mathrm{d}W(A)}{\mathrm{d}A}\right|_{A=A_t} - \int_0^t \mathrm{d}s\, K(t-s)\dot{A}_s + \xi_t$$

- The exact equation contains **all powers of A_s and $\dot{A}_s$** in the memory term.
- The expansion in $\{f_i\}$ is **not an expansion in a small parameter**. Thus the memory term **cannot simply be truncated after the linear term**.
- A potential of mean force is obtained only if the coarse-grained variable is **linear in the generalized coordinates**.
- **Stochastic interpretation of ε_t is difficult** due to lacking FDT.

Non-Equilibrium

- So far we have not allowed for time-dependent external forces.
  We only discussed equilibrium dynamics and relaxation into equilibrium.
- In the case of a **time-dependent Liouvillian** $\mathrm{i}\mathcal{L}(t)$ observables evolve according to

$$\frac{\mathrm{d}A_t}{\mathrm{d}t} = U(0,t)\,\mathrm{i}\mathcal{L}(t)\,\mathbb{A}(\Gamma_0)$$

  with

$$U(0,t)\circ = \exp_{-}\left(\int_0^t \mathrm{d}t'\,\mathrm{i}\mathcal{L}(t')\circ\right) = 1 + \sum_{n=1}^{\infty}\int_0^t \mathrm{d}t_1 \cdots \int_o^{t_{n-1}} \mathrm{d}t_n\,\mathrm{i}\mathcal{L}(t_n)\cdots\mathrm{i}\mathcal{L}(t_1)\circ$$

- Again, we split the equation of motion and choose a suitable projector

$$\frac{\mathrm{d}A_t}{\mathrm{d}t} = U(0,t)\,[\mathcal{P}(t)\,\mathrm{i}\mathcal{L}(t)\mathbb{A}(\Gamma_0) + \mathcal{Q}(t)\,\mathrm{i}\mathcal{L}(t)\mathbb{A}(\Gamma_0)]$$

  Note: $\mathcal{P}(t)$ **is allowed to depend on time**.

S. Nordholm, *Nonlinearities and fluctuations in microscopic transport theory*, Dissertation, U. Maryland (1972)
Grabert, H. *Projection Operator Techniques in Nonequilibrium Statistical Mechanics*, Springer 1982

A. Latz J. Phys. Condens. Mat. **12** 6252 (2000)

The Linear, Non-stationary GLE

One possible approach is to use a **linear ("Mori"-type) projector**

$$\mathcal{P}(t)\mathbb{X} = \frac{(\mathbb{X},\mathbb{A})_t}{(\mathbb{A},\mathbb{A})_t}\mathbb{A}$$

with the inner product

$$(\mathbb{X},\mathbb{Y})_t = \int \mathrm{d}\Gamma \rho_0(\Gamma)\ \left(U(0,t)\mathbb{X}(\Gamma)\right)\left(U(0,t)\mathbb{Y}(\Gamma)\right) \quad .$$

This yields the

linear, non-stationary, Generalized Langevin Equation

$$\frac{\mathrm{d}A_t}{\mathrm{d}t} = \omega(t)A_t + \int_0^t \mathrm{d}\tau K(t,\tau)A_\tau + \varepsilon_{0,t}$$

$\omega(t)$: the generalized, time-dependent "drift"
$K(t,\tau)$: the "memory kernel" (which depends on two times)
$\varepsilon_{0,t}$: the "fluctuating force"

H. Meyer, Th. Voigtmann, TS, J. Chem. Phys. **147**, 214110 (2017), J. Chem. Phys. **150**, 174118 (2019)

The linear non-stationary GLE

$$\frac{\mathrm{d}A_t}{\mathrm{d}t} = \omega(t)A_t + \int_0^t \mathrm{d}\tau K(t,\tau)A_\tau + \varepsilon_{0,t}$$

Due to the linearity, there is a generalized **fluctuation-dissipation theorem**

$$K(t,\tau) = -\frac{\langle \varepsilon_{0,t}\varepsilon_{0,\tau}\rangle}{\langle |A_t|^2\rangle}$$

This equation is **exact**.

It can be used to coarse-grain systems out of thermal equilibrium in practice, see e.g.

H. Meyer et al., Europhysics Letters **128**, 40001 (2019)
H. Meyer et al., Advanced Theory and Simulations **4**, 2000197 (2020)

The Non-Linear Non-Equilibrium Case

- Include **time as a coordinate** $\Gamma^{\mathrm{a}} = (\Gamma, t)$.
- Define Liouvillian on this "augmented" phase space

$$\mathrm{i}\mathcal{L}^{\mathrm{a}} \circ = \dot{\Gamma}^{\mathrm{a}}(\Gamma^{\mathrm{a}}) \cdot \frac{\partial}{\partial \Gamma^{\mathrm{a}}} \circ$$

- Observables evolve according to

$$A_t(\Gamma^{\mathrm{a}}) = \exp\left(\mathrm{i}\mathcal{L}^{\mathrm{a}} t\right) \mathbb{A}^{\mathrm{a}}(\Gamma^{a})$$

- Define inner product

$$(\mathbb{X}^{\mathrm{a}}, \mathbb{Y}^{\mathrm{a}})^{\mathrm{a}}_t = \int \mathrm{d}\Gamma^{\mathrm{a}}\ \rho^{\mathrm{a}}(\Gamma^{\mathrm{a}}, t)\ \mathbb{X}^{\mathrm{a}}(\Gamma^{\mathrm{a}}) \mathbb{Y}^{\mathrm{a}}(\Gamma^{\mathrm{a}})$$

- Define Zwanzig projector

$$\mathcal{P}(t)\mathbb{X}^{\mathrm{a}}(\Gamma^{\mathrm{a}}) = \frac{\int \mathrm{d}\Gamma^{\mathrm{a}\prime} \rho^{\mathrm{a}}(\Gamma^{\mathrm{a}\prime}, t)\ \delta(\mathbb{A}^{\mathrm{a}}(\Gamma^{\mathrm{a}\prime}) - \mathbb{A}^{\mathrm{a}}(\Gamma^{\mathrm{a}}))\ \mathbb{X}^{\mathrm{a}}(\Gamma^{\mathrm{a}\prime})}{\int \mathrm{d}\Gamma^{\mathrm{a}\prime}\ \rho^{\mathrm{a}}(\Gamma^{\mathrm{a}\prime}, t)\ \delta(\mathbb{A}^{\mathrm{a}}(\Gamma^{\mathrm{a}\prime}) - \mathbb{A}^{\mathrm{a}}(\Gamma^{\mathrm{a}}))}$$

The Non-Linear Non-Equilibrium Case

- As before, define a basis $\{f_i^{\mathrm{a}}(\mathbb{A}^{\mathrm{a}}, \tau)\}$.
- Now the basis depends on time

$$\left(f_i^{\mathrm{a}}(\mathbb{A}^{\mathrm{a}}, \tau), f_j^{\mathrm{a}}(\mathbb{A}^{\mathrm{a}}, \tau)\right)_t = \delta_{i,j} \quad \forall t \quad .$$

- Again, Zwanzig projector can be written as

$$\mathcal{P}(t)\mathbb{X}^{\mathrm{a}}(\Gamma^{\mathrm{a}}) = \sum_{i=1}^{\infty} \left(f_i^{\mathrm{a}}(\mathbb{A}^{\mathrm{a}}(\Gamma^{\mathrm{a}}), \tau), \mathbb{X}^{\mathrm{a}}(\Gamma^{\mathrm{a}\prime})\right)_t \; f_i^{\mathrm{a}}(\mathbb{A}^{\mathrm{a}}(\Gamma^{\mathrm{a}}), t) \quad .$$

- This produces an equation of motion of the form

$$\frac{\mathrm{d}A_t}{\mathrm{d}t} = \sum_{i=0}^{\infty} \left(\omega_i(t) f_i^{\mathrm{a}}(A_t, t) + \int_0^t \mathrm{d}s \, K_i(t,s) \; f_i^{\mathrm{a}}(A_s, s) \right) + \varepsilon_t \quad ,$$

  which **differs considerably** from the coarsed-grained models typically used for active matter, biomolecules and other non-equilibrium systems.

Summary

- We discussed equations of motion for coarse-grained observables.
- We recalled the projection operator formalisms by Mori and Zwanzig.
- Versions of the Langevin equation, which contain a potential of mean force (i.e. a non-linear drift term), also require a non-linear friction term. This statement holds true, even if there is time-scale separation.
- When there is a potential of mean force, there is in general no fluctuation-dissipation theorem.
- We showed how to use projection operator formalisms to construct coarse-grained models for systems with explicitly time-dependent Liouvillians.

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Literature

- See also
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  H. Meyer et al., Europhysics Letters **128**, 40001 (2019)
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- And for a **review on coarse-graining**
  TS, *Coarse-grained modelling out of equilibrium*,
  https://arxiv.org/abs/2107.09972