Mori-Zwanzig formalism

Let $Z(t) = \{q_i(t), r_i(t)\} \in \mathbb{R}^{6N}$ be the phase-space coordinate for a Hamiltonian molecular system of N particles. The restriction to Hamiltonian dynamics is not necessary, for example, the dynamics of $Z(t)$ could be a stochastic Markov process as well. We are interested in a coarse-grained variable (observable) $A(Z(t))$,

$$A(Z(t)) = \{A_1(z), \ldots, A_M(z)\} \in \mathbb{R}^m$$

We follow the notation / derivation by Pep Español here, but do not bother with distinguishing capital $Z(t)$ with lower-case z.

Assume we have measured (observed) the value of $A(Z)$ at $t=0$. We still do not know the exact value of the micro-variables z, so we need a statistical (physics) model.

Consider the ensemble of trajectories $\{z(t)\}$ generated by using initial conditions from the conditioned or constrained equilibrium ensemble

$$z \sim \rho_{eq}(z) \;\Big|\; A(z) = \alpha = a(t=0, z)$$

Recall the fundamental assumption of statistical mechanics that all microstates z compatible with $A(z)=\alpha$ are equally probable. (entropy maximization). Here we assume a known prior distribution

Denote

$$\boxed{\Omega(\alpha) = \int \rho_{eq}(z)\, \delta\left[A(z) - \alpha\right] dz}$$

which "counts" the volume in phase space of microstates compatible with the macrostate $A(z) = \alpha$, which is also the equilibrium distribution of the macroscopic observables.

$$\begin{cases} \Omega(\alpha) = e^{-F(\alpha)/k_B T} \\ \text{where } F \equiv H \text{ is the coarse-grained} \\ \text{"free energy" or "Hamiltonian".} \end{cases}$$

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Then the constrained equilibrium ensemble, i.e., our assumed ensemble of initial conditions is

$$\rho_\alpha(z) = \frac{\rho_{eq}(z) \cdot \delta\left[A(z) - \alpha\right]}{\Omega(\alpha)}$$

We now want to know what happens to this ensemble as we run the microscopic dynamics to time t.

We can do this by looking at evolution of distributions or the observables directly (recall forward-backward Kolmogorov, Denote the <u>macroscopic</u> variable

$$a(t,z) \equiv A(z(t))$$

z ← initial condition from constrained eq. ensemble

Being an observable, this follows the backward Kolmogorov equation

$$\boxed{\partial_t a = \underbrace{iL}_{\text{Liouville operator}} a} \quad \text{where } iL = -\frac{\partial H}{\partial z} \cdot L_0 \frac{\partial}{\partial z}$$

where $L_0 = \begin{bmatrix} 0 & I \\ -I & 0 \end{bmatrix}$ is the canonical symplectic matrix

The formal solution is

$$a(t,z) = \exp(iLt)\, A(z)$$

and our goal is to split this into three parts:

1. Part only involving macro variables (deterministic coarse-grained dynamics,
2. Part only involving microscopic variables (noise)
3. Part involving cross-terms (diffusion)

The key idea of the Mori-Zwanzig formalism is to introduce the conditional expectation projection operator that gives the expectation value of an arbitrary phase function $F(z)$ in the constrained equilibrium ensemble:

$$\boxed{P_\alpha F = \Omega^{-1}(\alpha) \int F(z)\, \rho^{eq}(z)\, \delta\left[A(z)-\alpha\right] dz}$$

This is a projection because $P_\alpha^2 = P_\alpha$

$\Rightarrow$ $\boxed{Q_\alpha = I - P_\alpha}$ obeys $Q_\alpha^2 = Q_\alpha$, $P_\alpha Q_\alpha = 0$

The coarse-grained equation is

$$\partial_t a = iL\,a = iL \exp(iLt) A$$

$$\boxed{\partial_t a = \mathcal{L} e^{\mathcal{L}t} A}, \quad \mathcal{L} = iL$$

Because $\mathcal{L}$ and $e^{\mathcal{L}t}$ commute,

$$\partial_t a = e^{\mathcal{L}t}(\mathcal{L}A) = e^{\mathcal{L}t}\underbrace{(P+Q)}_{\text{identity}}\mathcal{L}A$$

$$\begin{cases} \partial_t a = \exp\left[(P\mathcal{L} + Q\mathcal{L})t\right](P\mathcal{L} + Q\mathcal{L})A \\ \text{which splits the dynamics into a projected} \end{cases}$$

and orthogonal dynamics

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We now use the following identity, called the <u>Duhamel - Dyson formula</u>

$$\exp\left[(A+B)t\right] = \exp\left[At\right] + \int_0^t e^{(t-s)(A+B)} B e^{sA} ds$$

for <u>any</u> operators A and B, in order to rewrite

$$\exp\left[(P\alpha + Q\alpha)t\right]$$

into pieces containing P only and other cross terms.

After some algebra and rearrangement...

We obtain the <u>formal</u> (exact) rewriting of the microscopic dynamics as the

<u>Mori-Zwanzig equation</u>:

$$
\begin{cases}
\partial_t a = e^{tL} P L A \\
\quad + \int_0^t e^{(t-s)L} P L \tilde{R}(s) \, ds \quad \leftarrow \text{memory kernel} \\
\quad + \tilde{R}(t) \leftarrow \text{stochastic contribution}
\end{cases}
$$

where $\tilde{R}(t) = Q e^{tQL} L A$

see Español, Vanden-Eijnden et al.

Here $\tilde{R}(t)$ is the unresolved dynamics or the noise, since

$$P\tilde{R}(t) = 0 \quad \text{for all } t$$

and it is clear that we will need some sort of approximation to model it. The interesting term is the memory term; which features:

$$PL\tilde{R}(s) = -M(\alpha, s) \cdot \frac{\partial H(\alpha)}{\partial \alpha} + (k_B T) \frac{\partial}{\partial \alpha} \cdot M^*(\alpha, s)$$

(see Español for complicated derivation) where the <u>mobility</u> operator

$$M(\alpha, s) = \frac{1}{k_B T} P\left(\underbrace{\tilde{R}(t) \otimes \tilde{R}(0)}_{} \right)$$

time correlation function of noise

and $H(\alpha) = -k_B T \ln[\Omega(\alpha)]$ is the coarse-grained Hamiltonian or free-energy

Using the obvious property

$$e^{\mathcal{L}t} f[A(z)] = f[a(t,z)]$$

it can then be shown that

the Mori-Zwanzig equation becomes:

$$\begin{cases} \partial_t a(t) = v(a) + \tilde{R}(t) \\ + \int_0^t ds\, M\left[a(t-s), s\right] \cdot \frac{\partial H}{\partial \alpha}(a(t-s)) \\ + k_B T \int ds\, \frac{\partial}{\partial \alpha} \cdot M^*\left[a(t-s), s\right] \end{cases}$$

where the drift

$$v(\alpha) = P \mathcal{L} A$$

is the projected deterministic dynamics, and $\tilde{R}(t)$ is the "noise"

The Mori-Zwanzig formalism thus gives us explicitly and formally-exact a Generalized Langevin equation (GLE) in which the process $a(t)$ is non-Markovian due to the dependence on history via the memory integrals.

Formally, $\tilde{R}(t)$ is a zero-mean random process whose statistical properties are those of

$$Q e^{tQL} L A(z) \text{ where } z \sim \rho_{a(0)}(z)$$

CONSTRAINED ENSEMBLE

The GLE is not useful in practice:

1. $U(\alpha)$ and $\frac{\partial H}{\partial \alpha}$ can be computed using constrained molecular dynamics, but not $\tilde{R}(t)$ or $M(\alpha, t)$

2. In general $\tilde{R}(t)$ is <u>not Gaussian</u> and only if we <u>assume</u> it is can we get it from its two-point correlation function M

3. Integro-differential equations are hard!

There are two ways to make the GLE useful:

1. Make some modeling assumptions about the time correlations of $\tilde{R}(t)$, for example, exponentially-decaying

2. By far the most used and practical is the so-called Markovian approximation:

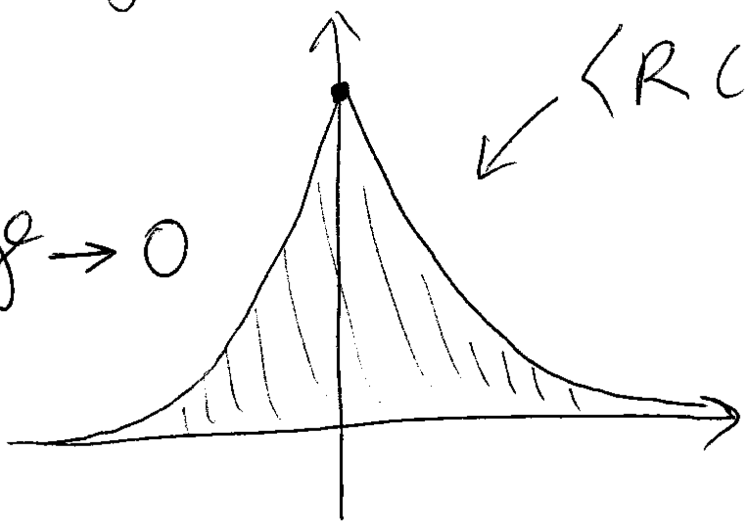
$$R(t) = \left[2 k_B T M(a)\right]^{1/2} W(t) \leftarrow \text{white-noise}$$

$$M(a,t) \simeq M(a)\,\delta(t)$$

This is really assuming SEPARATION of TIME SCALE

Note that the prefactor 2 in the noise covariance comes from the fact that all the integrals are one-sided $(t>0)$ but we can think of white noise as a limit of a symmetric covariance:

$$\langle R(t)R(0)\rangle = C \cdot e^{-\gamma t} \rightarrow \delta(0)$$



$\gamma \rightarrow 0$ t

$$M(\alpha) = \int_0^\infty dt \langle R(t)R(0)\rangle = C\,\gamma^{-1}$$

In limit $\langle R(t)R(0)\rangle \rightarrow 2M(\alpha)\,\delta(0)$

With the Markovian approximation the GLE becomes our familiar Langevin equation (in Ito form)

$$\begin{cases} \partial_t a = v(a) + M(a) \cdot \frac{\partial H}{\partial a} + (k_B T) \frac{\partial}{\partial a} \cdot M^*(a) \\ \qquad + \sqrt{2 k_B T M(a)} \cdot W(t) \end{cases}$$

This can be justified rigorously as a leading order asymptotic expansion in the separation of time scales (see Vanden-Eijnden et. al.)

In principle, we can try to obtain the drift and mobility (diffusion coefficient) from microscopic simulations:

1. We could assume that the coarse variables follow the Ito SDE and measure the first and second moments of the displacement over a time Δt short compared to macroscale but long compared to decorrelation time $\bar{\tau}$. (hard to do for second moments!)

(2) We could <u>assume</u> that the Markovian assumption is correct and use

$$M(\alpha) \simeq \int_0^T dt \; P\left[R(t) \otimes R(0)\right]$$

Green-Kubo formula

approximation of "projected" dynamics

Here T needs to be chosen carefully and has to fall inside a "<u>plateau</u>".

This also requires care and does not ensure convergence as we would like

(3) (see paper by Español, Vanden-Eijnden & Delgado-Buscalioni)

We can <u>enforce</u> (not assume) that the Markovian model is exact by enforcing a strict (infinite) <u>separation of time scale</u>

Perform <u>constrained molecular dynamics</u> with constraint $A(z) = a$

Denote:

$$\tilde{v}(t) \equiv \left[i\mathcal{L} A(\tilde{Z}(t)) \right]_{\text{constrained}}$$

This modifies the natural dynamics!

and then define

drift $\quad v = \lim_{T\to\infty} \frac{1}{T} \int_0^T dt \cdot \tilde{v}(t)$

diffusion tensor/ mobility
$$\left\{ M = \lim_{T\to\infty} \frac{1}{k_B T} \int_0^\infty dt' \, \frac{1}{T} \int_0^T dt \left[\tilde{v}(t+t') \otimes \tilde{v}(t) \right] \right.$$

Discuss on board example of a colloidal suspension at the diffusive level (Smoluchowski).

(A)

$$\exp[-\beta V(Q)] \sim \exp[-\beta V^{cc}(Q)] \int dq \cdot \exp[-\beta V^{s}(q,Q)]$$

effective potential

compute using "static" Monte Carlo or model

(B)

diffusion tensor

$$D_{ij} = \int_0^\infty dt \, \langle V_j(t) \, V_i(0) \rangle_Q$$

Here $[iLA]_Q = [iLQ]_Q = V$

but we do not actually move Q!