Zwanzig-Mori (formalism): An introduction (formally)

Related papers:

A large variety of scientific problems involve seeking to resolve many degrees of freedom; e.g., variables in weather prediction, multiscale description of materials.

Scope: To reduce "complexity," some methods aim to achieve dimensional reduction: resolve variables only partially (resolve fewer variables).

This task is pursued by elaborate "projection methods."

Idea: Pick variables, e.g., particle positions, to resolve (by "projection" in some subspace).

Use some probability density to describe data for other ("unresolved") variables. The choice of this density follows from physical criteria.

[In this way: A deterministic problem $\Rightarrow$ stochastic dynamics]

Seeds of this approach can be traced to works of van Hove (1955, 59); and Prigogine (56, 59);

Abstract theory (in some generality):
- Zwanzig (1960) and Mori (1965).

Some modern implications are described by Chorin and Hald (2009).

Here, we attempt a pedagogical exposition; our focus is Hamiltonian dynamics.
Example \( \text{Particle in a potential}\) [Chorin, Hold, 2009]

Consider \( N \) other particles, which we don't care about.

Resolved Particle \((x,v)\); other particles \( \{ (q_j, p_j) \}_{j=1}^{N} \)

System Hamiltonian:

- 1-pot. kin. en.
- 1-pot. pot. energy

\[
H = \frac{1}{2} v^2 + U(x) + \frac{1}{2} \sum_{j=1}^{N} p_j^2 + \frac{1}{2} \sum_{j=1}^{N} f_j^2 \left( q_j - \frac{\gamma_j}{f_j} x \right)^2
\]

- \( U \): velocity
- \( Unperturbed energy of resolved particle \)

(Hamilton's)

Equations of motion:

\[
\dot{x} = v = \frac{\partial H}{\partial p} \quad \quad (p = v)
\]

\[
\dot{v} = -\frac{dU}{dx} + \sum_{j=1}^{N} \gamma_j \left( q_j - \frac{\gamma_j}{f_j} x \right) = -\frac{\partial H}{\partial x}
\]

\[
\dot{q}_j = \frac{\partial H}{\partial p_j} = p_j
\]

\[
\dot{p}_j = -\frac{\partial H}{\partial q_j} = -f_j^2 \left( q_j - \frac{\gamma_j}{f_j} x \right) = -f_j^2 q_j + \gamma_j x
\]

Prescription: Eliminate \( \{ (q_j, p_j) \} \)

Solving for \( q_j \) from last 2 eqns:

\[
q_j(t) = q_j(0) \cos(f_j t) + \frac{p_j(0)}{f_j} \frac{\sin(f_j t)}{f_j} + \frac{\gamma_j}{f_j} \int_{0}^{t} x(s) \sin(f_j(t-s)) \, ds
\]

Resulting eqns of motion for \((x,v)\):

- \( x(t) = v(t) \)
- \( \dot{x}(t) = -U'(x) + \int_{0}^{t} K_s(t-s) v(s) \, ds + F_\text{fl}(t) \)
- \( \dot{v}(t) = -U'(x) + \int_{0}^{t} K_s(t-s) v(s) \, ds + F_\text{fl}(t) \)

- "Fluctuation" (from known random processes)

- "Noise" if \( q_j(0) \) and \( p_j(0) \) are random
1) Suppose \( x(0) \) is non-random, and the joint prob. density

\[
\rho_j(x(0)) \quad \text{for} \quad \sqrt{p_j(0)} \quad \text{is} \quad Z^{-1} e^{-H/\tilde{T}} \quad (Z = \text{const.})
\]

(Exercise) \( \Rightarrow IE \rho_j(0) \rho_k(0) \) \( = T \delta_{jk} \), \( IE \left[ \left( \frac{\partial_j}{\partial_j} x(0) \right) \left( \frac{\partial_k}{\partial_k} x(0) \right) \right] \) \( = \frac{T \delta_{jk}}{f_j^2} \)

Then, compute \( IE \left[ F(t) F(t') \right] = -TK(t-t') \) \( \leftarrow \text{colored noise} \)

This is an instance of a "fluctuation-dissipation theorem".

2) In most practical applications, the computation of the memory kernel is a great challenge. This \( K \) signifies the non-Markovian nature of the reduced system.

3) The above example can be generalized in a formal manner by use of projection operators. In the above example, the "projection" is for the reduction of \( N+1 \) degrees of freedom to 1 degree.

We show the abstract formalism in context of quantum stat. mech. [Zwanzig, 1960]

Let \( \mathcal{H} \) be a Hilbert space with a fixed number of particles. The state (or, ensemble of states) of a system is described by the "density matrix" (operator), \( \rho(t) : \mathcal{H} \rightarrow \mathcal{H} \) \( (\mathcal{H} : \text{Hilbert sp.}) \)

Average of dynamical variable \( \mathcal{H} : \text{Hermition, Time Independent} \)

\[
\text{Liouville's eqn: } i \frac{\partial \rho}{\partial t} = H \rho - \rho H \]

Introduce projection op. \( P \):

Split \( \rho(t) \) into a "resolved" part and an "unresolved" part

\[
\rho(t) = \rho_r(t) + \rho_u(t) \quad \left\{ \begin{array}{l}
\rho_r(t) = P \rho(t) \quad (P^2 = P) \\
\rho_u(t) = (1-P) \rho(t)
\end{array} \right.
\]

Assume: \( \frac{\partial}{\partial t} P = 0 \) \( \Rightarrow [P, \frac{\partial}{\partial t}] = 0 \) \( \Rightarrow P \) linear, bounded
\[ P \left( \frac{\partial e}{\partial t} \right) = i \frac{\partial e}{\partial t} = PL (P_t + P_a) \]

\[(1-P) \left( i \frac{\partial e}{\partial t} \right) = i \frac{\partial e}{\partial t} = (1-P) L (P_t + P_a) \Rightarrow \text{solve in terms of } P_a(0), P_r(t) \]

\[ \Rightarrow P_a(t) = e^{-i(1-P)L t} P_a(0) - i \int_0^t ds e^{-i(1-P)L} (1-P)L P_r(s) ds \]

Duhamel's principle

Replace in Eq. (1): random

\[ i \frac{\partial e}{\partial t} = PL e^{-i(1-P)L} P_a(0) + PL P_r(t) \]

\[ - i \int_0^t ds PL e^{-i(1-P)L} (1-P)L P_r(s) \]

This can be put/recast into the form

\[ \downarrow \quad \text{IRREVERSIBILITY} \]

\[ i \frac{\partial e}{\partial t} = PL P_r(t) - i \int_0^t K(t-s) P_r(s) ds + F(t) \]

\[ \Rightarrow \text{fluctuation} \quad \text{REDUCED} \]

\[ \text{EQ. OF MOTION} \]

where

\[ K(t) = PL e^{-i(1-P)L} \]

\[ F(t) = PL e^{-i(1-P)L} P_a(0) \]

This abstract formalism can be given also for classical Hamiltonian dynamics.

(Then \([\cdot,\cdot]\) is replaced by Poisson bracket)

This type of dimensional reduction is pursued today in the context of Molecular Dynamics.

A good choice of \(K\)?

One can assume something reasonable about \(P_a(0)\) [missing information].

Prediction methods based on Zwanzig-Mori formalism are "optimal prediction"