b.) Zwanzig - Mori Theory : **How calculate relaxation?**

* As stated previously, the goal of Z-M theory is to:

a.) partition the dynamics into $\boxed{\text{relevant}}$ (i.e. usually slow) and irrelevant (i.e. usually fast) variables

b.) project the $\left(\begin{smallmatrix}\text{irrelevant}\\ \text{fast}\end{smallmatrix}\right)$ variables onto the $\left(\begin{smallmatrix}\text{relevant}\\ \text{slow}\end{smallmatrix}\right)$ variables, thereby reducing the effective # of degrees of freedom

c) describe the relevant variables in terms of a
1.) memory function → mixing rate
2.) effective noise →
à la FDT

→ Now, can always write Liouville equation in matrix form, i.e.

Liouville operator

$$\frac{\partial f(x,t)}{\partial t} = -\mathcal{L} f(x,t)$$

↳ dynamical variable

Now, $\varphi_j(x) \equiv$ basis functions for Hilbert space of all functions of x (i.e. states, modes)

i.e. $A(x) = \sum_j \langle j | A(x) | j \rangle \, | j \rangle$

$\langle j | x \rangle = \varphi_j(x)$

of course, this comes with inner product, i.e.

$$(A, B) \equiv \int dx \; f_{eq}(x) \, A(x) \, B^{*}(x)$$

$$\equiv \langle AB \rangle_{eq}.$$

so can write:

$$f(x,t) = f_{eq}(x) \sum_j b_j(t) \, \varphi_j(x)$$

where:

$$b_j(t) = \int dx \; \varphi_j(x) \, f(x,t)$$

$\rightarrow$ projection on φ_j

so

$$\boxed{\frac{\partial b_j(t)}{\partial t} = - \sum_k \underbrace{L_{j,k}}_{\text{Liouvillian Matrix}} b_k(t)}$$

Matrix Liouville Equation

$$L_{j,k} = (\varphi_j, L\varphi_k)$$

Minimal case/limit:

Now, consider case of 2 states/modes:

$$\underbrace{q_1(t)}_{\text{slow}}, \quad \underbrace{q_2(t)}_{\text{fast}}$$

So $$\frac{\partial q_1(t)}{\partial t} = L_{1,1}\, q_1(t) + L_{1,2}\, q_2(t)$$ (absorb sign)

$$\frac{\partial}{\partial t} q_2(t) = L_{2,1}\, q_1(t) + L_{2,2}\, q_2(t)$$

$$\frac{\partial}{\partial t}\begin{pmatrix} q_1(t) \\ q_2(t) \end{pmatrix} = \begin{bmatrix} L_{1,1} & L_{1,2} \\ L_{2,1} & L_{2,2} \end{bmatrix} \begin{pmatrix} q_1(t) \\ q_2(t) \end{pmatrix}$$

To illustrate, associate a characteristic time with each L_{ij}

$$L_{1,1} \to O(1/\tau_{1,1}), \quad L_{1,2} \to O(1/\tau_{1,2})$$

$$L_{2,1} \to O(1/\tau_{2,1}), \quad L_{2,2} \to O(1/\tau_{2,2})$$

and take $\tau_{2,2} \ll \tau_{1,1};\ \tau_{1,2};\ \tau_{2,1}$

then can proceed to simplify q_2 equation ala' Chapman-Enskog: i.e. $\left\{\begin{array}{l}\text{eliminate } q_2 \\ \text{in favor } q_1.\end{array}\right.$
(Relaxation)

$$\frac{\partial q_2(t)}{\partial t} = L_{2,1}\, q_1(t) + L_{2,2}\, q_2(t)$$

$$q_2(t) = q_2^{(0)} + q_2^{(1)} + \cdots$$

$$\frac{\partial}{\partial t}\left(a_2^{(0)} + a_2^{(1)} + \dots\right)$$
$$= L_{3,1} a_1(t) + L_{3,2}\left(a_2^{(0)} + a_2^{(1)} + \dots\right)$$

l.o. **fast** $L_{3,2} a_2^{(0)} = 0$ as $\tau_{3,2} < \tau_{1,1}, \tau_{1,2}, \tau_{3,1}$

$$\Rightarrow \boxed{a_2^{(0)} = a_{2,eq}}$$

existance, structure presumed

1st order: $\cancel{\frac{\partial}{\partial t} a_2^{(0)}}^{\,0} + \frac{\partial}{\partial t} a_2^{(1)} = L_{3,1} a_1(t) + \cancel{L_{3,2} a_2^{(0)}} + L_{3,2} a_2^{(1)}$

then if take $\omega \tau_{3,2} \ll 1$ **to d** → ~~time~~ scale ordering

$$\Rightarrow L_{3,2} a_2^{(1)} = -L_{3,1} a_1(t)$$

$$\boxed{a_2^{(1)} = -L_{3,2}^{-1} L_{3,1} a_1(t)}$$

and,

$$\frac{\partial a_1(t)}{\partial t} = L_{1,1} a_1(t) + L_{1,2}\left(a_{3,eq} - L_{3,2}^{-1} L_{3,1} a_1(t)\right)$$

bare   dressing → fast modes

$$\frac{\partial a_1(t)}{\partial t} - L_{1,1} a_1(t) + \underbrace{L_{1,2} L_{3,2}^{-1} L_{3,1} a_1(t)}_{\text{memory kernel}}$$

$$= \underbrace{L_{1,2} a_{2,eq}}_{\text{effective noise}} \qquad \text{c.e.} - \int^t k(t-s)\, a_1(s)$$

so now have for $q_1(t)$:

$$\boxed{\frac{\partial}{\partial t} q_1(t) - L_{1,1} q_1(t) - \int_0^t \overset{(1)}{K(t-s)\, q_1(s)} = \overset{(2)}{f_{eff}}} \quad *$$

i.e. "renormalized" equation for q_1, where q_2 effects $\underbrace{\text{lumped into}}_{\text{"projected"}}$:

(1) - propagator, with memory function → [relaxation rate

(2) - effective noise.

Notice that while the time scale ordering is the most plausible physical motivation, the procedure is a formal one, i.e.

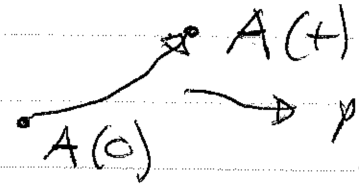
consider q_2 equation:

$$\frac{\partial}{\partial t} q_2(t) = L_{2,1} q_1 + L_{22} q_2$$

then formally solve for q_2 in terms q_1, i.e.

$$q_2(t) = \exp\left[L_{22} t\right] q_2(0) + \int_0^t ds \exp\left(L_{22}(t-s)\right) L_{21}\, q_1(s)$$

N.B.: What does e^{Lt} mean, physically?



→ propagates system in time, along system orbits

and plugging into q_1 equation ⇒

$$\frac{\partial}{\partial t} q_1(t) = L_{1,1} q_1(t) + L_{1,2} \int_0^t ds \, \exp\left[L_{2,2}(t-s)\right] L_{2,1} q_1(s)$$
$$+ L_{1,2} \exp\left[L_{2,2} t\right] q_2(0)$$

i.c. term

memory term.

→ What's the catch? — without scale ordering, renormalized equation for $q_1(t)$ will be intractable.

→ Could generalize and formalize via Projection Operator Theory

i.e. Consider N variables

$n < N$ relevant variables

then can projection operator matrix:

Now, if define:

$$i\Omega = (LA, A)\cdot(A, A)^{-1}$$

$$\underline{K}(t) = -(LF(t), A)\cdot(A, A)^{-1}$$

Now L is anti-Hermitian $(a, Lb) = -(b, La)$
<u>so</u>

$$\underline{\underline{K}}(t) = (F(t), LA)\cdot(A, A)$$

$$= \left(e^{t(1-P)L}\,\underline{(1-P)}\,LA, LA\right)\cdot(A, A)^{-1}$$

Where this leaves us:

thus have:

$$\boxed{\frac{\partial \underline{A}(t)}{\partial t} = i\Omega A(t) - \int_0^t ds\, \underbrace{\underline{\underline{K}}(s)}_{\text{memory kernel}}\cdot A(t-s) + \underbrace{F(t)}_{\text{noise}}}$$

which is form of generalized Langevin equation, a la' Mori.

Notes:

→ Langevin Eqn. depends on time history
⇒ memory! → "Non-Markovian"

i.e. contrast
$$\frac{\partial A(t)}{\partial t} = i\Omega\cdot A(t) - \int_0^t ds\, \underline{K}(s)\cdot A(t-s) + F(t)$$

with:
$$\frac{\partial v}{\partial t} = -\gamma v + \frac{\tilde{f}}{m} \qquad \text{(BM equation)}$$

→ Memory set by time history of irrelevant variables

i.e.
$$\underline{K}(t) = \Big(\underbrace{e^{t(1-P)L}(1-P)LA}_{\sim 1-P \;\to\; \text{irrelevants}},\ LA\Big)\cdot (A,A)^{-1}$$

→ noise also set by irrelevant variables
$$F(t) = \underbrace{e^{t(1-P)L}(1-P)LA}$$

Before proceeding to examples, note two key theoretical questions:

i.) does $F(t)$ really "act like" noise?

i.e. $\langle F(t) \rangle = 0$, for avg. over some non-equilibrium distribution

Yes (can show)

ii.) why does the Langevin equation appear Linear, yet no linearization appeared, explicitly.

(time scale)

see below

First, consider slow variables and some simple applications.

→ Now, often (i.e. usually) variables of interest are "slow"

→ via projection, can 'slave' the dynamics to slow variables (i.e. project out fast variables).

– can simplify Z-M equation in this limit.

$$\underline{\underline{K}}(t) = \left(e^{(1-P)Lt}(1-P)LA, (1-P)LA\right) \cdot (A,A)^{-1}$$

$$\cong \left(e^{Lt}(1-P)LA, (1-P)LA\right) \cdot (A,A)^{-1}$$

so $\quad K(t) = \left(\left((1-P)LA(t)\right), (1-P)LA(0)\right) \cdot (A,A)^{-1}$

so Z-M eqn has form:

$$\boxed{\begin{aligned} \frac{\partial A}{\partial t} &\cong \Theta \cdot A + F(t) \\ \Theta &= i\Omega - \int_0^\infty ds \left(\left((1-P)L\,A(s)\right), (1-P)LA(0)\right) \end{aligned}}$$

which is simple!

$\Rightarrow$

$\rightarrow$ Important Application of Z-M Theory for Slow Variables $\rightarrow$ Hydrodynamics

a.) (Self-Diffusion)

How concentration field evolves?

- seek evolution of $c(x,t)$ $\leftrightarrow$ concentration of tagged particle in case of dependence on x

$$C(x,t) = \sum_q A_q(t)\, e^{iqx}$$

dynamical variables are Fourier modes

tagged particle at R

$C \sim \delta(x-R)$

so $$A_q = \int dx\, \delta(x-R)\, e^{-iq\cdot x}$$

$$= e^{-iqR}$$

$\hookrightarrow$ position of tagged particle

so

$$L A_q = L e^{-iqR}$$

$$= -iq\dot{R}\, e^{-iqR} + h.o.t.$$

$$\equiv -iq V$$

so $$\boxed{K(t) = -q^2 \langle V e^{tL} V \rangle}$$ $\rightarrow$ Memory Kernel

$$= -q^2 \langle V(t) V(0) \rangle$$

$\hookrightarrow$ velocity correlation fnctn.

so
$$\frac{d}{dt} A_q(t) \cong -q^2 \int_0^\infty ds \langle V(s) V(0) \rangle A_q(t)$$

$$= -q^2 D A_q$$

$$D = \int_0^\infty ds \, \langle V(s) V(0) \rangle$$

and
$$\frac{dC(x,t)}{dt} \cong D \nabla^2 C(x,t)$$

Note: $\boxed{\text{Critical element in concentration evolution is long wavelength velocity correlation.}}$

b.) Hydrodynamics – More Generally ...

→ in general, hydrodynamic variables are slow, by construction.

? Why ?

→ for N-body system, can write typical hydrodynamic variables in form: