III. Zwanzig – Mori and Projection Operator Methods

General Goal: ① Divide dynamical variables into
- irrelevant: relaxation time scales fast enough to equilibrate
- relevant: relaxation rate slow

② Project irrelevant onto relevant → slow/resolved variables define dynamics.

③ derive kinetic equation for relevant variables → Zwanzig-Mori equation

① - ③ constitute a simple case of "renormalization"
i.e. – treat 'fast' variables as noise
– derive response in presence of noise.

? How is Fokker-Planck theory a "Renormalization"?

→ Z.-M. theory depends on Kubo's Response Theory
so
a.) Linear Response Theory (cf. Zwanzig, 2001)
b.) Z-M. Theory (cf. Zwanzig and R. Serra, et. al.)

a.) Linear Response Theory (Kubo)

Recall from discussion of F.-D. Thm:

$$\underbrace{(x^2)_\omega}_{\text{fluctuation spectrum}} = \hbar\,\alpha_{IM}(\omega)\coth(\hbar\omega/2T)$$

$$\cong \frac{2T}{\omega}\underbrace{\alpha_{IM}(\omega)}_{\text{"dissipation"}} \qquad (\hbar\omega < 2T)$$

where: $\underbrace{x(\omega)}_{\text{displacement}} = \underbrace{\alpha(\omega)}_{\text{response function (linear)}} f(\omega) \hookrightarrow$ forcing

Now "response function" $\leftrightarrow$ { generalized susceptibility, transport coefficients, etc.

{ pose question → expect very general answer / route to answer to question of: "what sets susceptibility (linear) in system at T, near equilibrium"?

⇒ Linear response theory answers that question...

⇒ L.R.T. is yet another approach to the F.-D.T. structure and balance relationships

⇒ why care?

→ Kubo L. R. T. is:
a.) easily generalized to Q.M. problems
b.) especially simple for extracting time + frequency dependent responses

time dependent responses: i.e.

$$\frac{\partial f}{\partial t} + \frac{q}{m} E(t) \frac{\partial f}{\partial v} = C(f) = -\nu(f-f_0)$$

$E(t) = E_0 e^{-i\omega t}$ ⇒ if $\omega < \nu$ (why?)
can ask what is $\sigma(\omega)$
conductivity

now: $C(f) = 0$

(Chapman-Enskog theory is a linear response theory!)

$$\frac{\partial}{\partial t}\delta f + \nu \delta f = -\frac{q}{m} E(t) \frac{\partial f_0}{\partial v}$$

$$\Rightarrow (-i\omega + \nu)\,\delta f_\omega = -\frac{q}{m} E_\omega \frac{\partial f_0}{\partial v}$$

and $J_\omega = \int dv\, n_0 q\, v\, \delta f_\omega$ defines $\sigma(\omega)$.

→ While not "necessary" in strict sense, Kubo L.R.T. often yields insights and reduces labor

Proceed via : i) static response $\left\langle \begin{array}{l} cl \\ QM \end{array}\right.$
ii) dynamic response $\left\langle \begin{array}{l} classical \\ quantum \end{array}\right.$ → skipped.
iii.) frequency dependent response
iv.) applications / examples.

i.) Static Response

Consider system : $H_0(X) \equiv$ unperturbed Hamiltonian, fctn of X → dynamical variable

then $\underline{E}$ → perturbing field
M(X) → function of state of system s/t

$$H = H_0(x) - M(X)\,E$$

i.e. E → electric field $\underline{E}$
M → polarization field $\underline{P}$ or magnetic field $\underline{B}$, Magnetization $\underline{M}$

$$H = H_0 + \frac{\underline{D}\cdot\underline{E}}{8\pi} = \underbrace{H_0}_{\text{unperturbed}} + \underbrace{\frac{\underline{E}^2}{8\pi}}_{\substack{\text{field energy} \\ \text{(not coupled to system)}}} + \underbrace{\underline{P}\cdot\underline{E}}_{\substack{\text{field - system} \\ \text{interaction} \\ (-ME)}}$$

Then trivially,

$$\begin{cases} f(x) = \frac{1}{Z} e^{-H/T} = \frac{1}{Z} e^{-\beta H} \to \text{distribution} \\ Z = \int dx \; e^{-\beta H} \quad \to \text{partition} \end{cases}$$

so

with $E \neq 0 \quad H \to H_0 - ME \quad , \quad M = M(x)$

$$\begin{cases} f(x,E) = \frac{1}{Z(E)} \exp\left[-\beta H_0(x) + \beta M(x) E\right] \\ Z(E) = \int dx \; \exp\left[-\beta H_0(x) + \beta M(x) E\right] \end{cases}$$

so

$$e^{-\beta(H_0 - ME)} \cong \left(1 + \beta M E + (\text{h.o.t.})\right) e^{-\beta H_0}$$

$$Z(E) \cong \int dx \, e^{-\beta H_0} \left\{1 + \beta M(x) E + \text{h.o.t.}\right\}$$

$$= \underbrace{Z_0(E)}_{\to \text{ unperturbed partition}} \left(1 + \beta \langle M(x) \rangle E + \text{h.o.t.}\right\}$$

$$\langle M(x) \rangle = \underbrace{\int dx \; M(x) e^{-\beta H_0}}_{\text{(defines avg.)}} \Big/ \int dx \; e^{-\beta H_0}$$

then

$$f(x,E) \cong \underbrace{f_0(x)}_{\text{unperturbed dist.}} \left\{ 1 + \beta\left(M(x) - \langle M \rangle\right) E \right\} + \cdots$$

Now, clearly can generalize:

$\langle A(x); E \rangle \equiv$ average of any $A(x)$ quantity (for perturbing field E)

$$\langle A(x); E \rangle = \int dx\, A(x) f_0(x) \left\{ 1 + \beta \left(M(x) - \langle M \rangle \right) E \right\}$$

$$= \underbrace{\langle A(x) \rangle}_{\int dx\, A(x) f_0(x) (1 - \langle M \rangle E)} + \beta \int dx\, f_0(x) \left(A(x)\ M(x) \right) E$$

$O(E^2)$, as $\langle M \rangle \sim E$

$$= \langle A(x) \rangle + \beta \langle A(x) M(x) \rangle E$$

$\left(\langle C \rangle = \int dx\, f_0 C \right)$ average

$$\Rightarrow \boxed{\langle A(x) \rangle_E = \langle A(x) \rangle_0 + \beta \langle A(x) M(x) \rangle E}$$

$$\& \quad \boxed{\chi_A = \delta \langle A \rangle / \delta E = \beta \langle AM \rangle}$$

general result of linear susceptibility of A to E

? If unperturbed system is plasma at T and perturbation is field due test charge, what is χ_E ?

→ Extending to QM case: H_0, M → operators

- useful to note Laplace transform of equilibrium distribution is:

→ transform variable

$$\int_0^\infty d\beta\, e^{-(\beta)(H_0 - ME)}\, e^{-y\beta}$$

$$= 1/y + H_0 - ME$$

{ switch on E at $t=0$ ⇒ 1 sided F.T. ⇒ L.T.

for ME small:

$$\cong \frac{1}{y+H_0} + \frac{1}{y+H_0} ME \frac{1}{y+H_0} + O(E^2)$$

so, inverting Laplace Transform:

$$e^{-[\beta H + \beta ME]} = e^{-\beta H} + \int_0^\beta d\lambda\, e^{-\lambda H} ME\, e^{-(\beta-\lambda) H}$$

{ convolution from transform of product...

and

$$e^{-\lambda H} M e^{\lambda H} = M(i\hbar\lambda)$$ → { $i\hbar\lambda$ as imaginary time

from $$e^{-\frac{iHt}{\hbar}} M e^{+\frac{iHt}{\hbar}} = M(t)$$ → from Heisenberg representation....

so have:

$$e^{-\beta(H - ME)} = e^{-\beta H} + \int_0^{\beta} d\lambda \, M(i\hbar\lambda)\, E\, e^{-\beta H}$$

Now can define 'Kubo transform' of operator by:

$$\boxed{\tilde{M} = \frac{1}{\beta}\int_0^{\beta} d\lambda \, M(i\hbar\lambda)}$$ Kubo transform

$$\Rightarrow e^{-\beta(H-ME)} = e^{-\beta H}(1 + \beta \tilde{M} E)$$

so

$$\langle A \rangle_E = \langle A \rangle + \beta \langle A\tilde{M} \rangle E$$

$$\Rightarrow \boxed{\chi_A = \beta \langle A \tilde{M} \rangle}$$

Note:

→ χ_A in QM has same structure as χ_A classical except $M \to \tilde{M}$

→ show if $\langle M \rangle = 0$ then $\langle \tilde{M} \rangle = 0$

c(i) Dynamic Response

Now:

- seek $\langle A(X,t)\rangle = \int dX\, f(X,t)\, A(X)$
  so need $f(X,t)$

- $f(X,t)$ evolves from $f(X,0)$

Now, in general:

$$\frac{\partial f}{\partial t} = -Lf$$

↳ Liouville operator

$$Lf = \{H, f\}$$

$\{\ \} \equiv$ Poisson bracket

i.e. for particle in electric field E_0:

↳ unperturbed here

$$Lf = V\frac{\partial f}{\partial x} + \frac{q}{m}E_0\frac{\partial f}{\partial V}$$

$$H = \frac{1}{2}mv^2 + q\phi_0(x) = \frac{p^2}{2m} + q\phi(x)$$

$$\{H, f\} = \left(\frac{\partial H}{\partial p}\frac{\partial f}{\partial x} - \frac{\partial H}{\partial x}\frac{\partial f}{\partial p}\right)$$

$$= \left(\frac{p}{m}\frac{\partial f}{\partial x} - q\frac{\partial \phi}{\partial x}\frac{\partial f}{\partial p}\right)$$

$$= \left(V\frac{\partial f}{\partial x} + \frac{q}{m}E\frac{\partial f}{\partial V}\right)$$

Now,
$$
\begin{aligned}
(L_0+L_1) f &= \{H_0 - ME(t), f\} \\
&= \{H_0, f\} - \{ME(t), f\} \\
&= \{H_0, f\} - \{M, f\} E(t) \\
&\equiv L_0 f + L_1 E(t) f
\end{aligned}
$$

so
$$\boxed{\frac{\partial f}{\partial t} = -L_0 f - L_1 E(t) f}$$

Perturbed Liouville Eqn.

Proceed ala' Chapman - Enskog Expansion!

$$f = f_0 + f_1$$

$$\frac{\partial}{\partial t}(f_0+f_1) = -L_0(f_0+f_1) - L_1 E(t)(f_0+f_1)$$

l.o. $\quad \dfrac{\partial f_0}{\partial t} = -L_0 f_0$

$C(f) = 0$

$L_0 f_0 = 0$

1st $\quad \dfrac{\partial f_1}{\partial t} = -L_0 f_1 - L_1 E(t) f_0$

$\dfrac{\partial f_1}{\partial t} + L_1 E(t) f_0 = -L_0 f$

$\dfrac{\partial f}{\partial t} + \dfrac{\varepsilon}{m} E \dfrac{\partial f_0}{\partial v} = -\nu \tilde{f}$

¿ Develop precise analogy with C-E. ?

Now $\rightarrow$ assume system at equilibrium at $t=0$
so $f(0) = f_{eq}$.

$$\left.\begin{aligned} f_0(0) &= f_{eq}. \\ f_1(0) &= 0 \end{aligned}\right\} \text{ initial conditions}$$

$\Rightarrow$

l. o. : $\quad \dfrac{\partial f_0}{\partial t} = -L_0 f \qquad f_0(0) = f_{eq}$

$\Rightarrow \quad f_0 = f_{eq} \quad , \quad$ all $t \quad (L_0 f_0 = 0)$.

1 st o: $\quad \dfrac{\partial f_1}{\partial t} + L_0 f_1 = -L_1 E(t)\, f_0$

$$f_1(t) = -\int_0^t ds\; e^{-(t-s)L_0} L_1\, E(s)\, f_0(s)$$
$$= -\int_0^t ds\; e^{-(t-s)L_0} L_1\, E(s)\, f_{eq}$$

but

$$L_1 f_{eq} = -\{M, f_{eq}\}$$
$$= -\left[\frac{\partial M}{\partial \underline{p}} \cdot \frac{\partial f_{eq}}{\partial \underline{q}} - \frac{\partial M}{\partial \underline{q}} \cdot \frac{\partial f_{eq}}{\partial \underline{p}}\right]$$

$\underline{q}, \underline{p}$ are usual Hamiltonian variables

and...

$$f_{eq} = \frac{1}{Z} e^{-\beta H_0}$$

$\Rightarrow$

$$L_1 f_{eq} = \beta f_{eq} \left[\frac{\partial M}{\partial \underline{p}} \cdot \frac{\partial H_0}{\partial \underline{q}} - \frac{\partial M}{\partial \underline{q}} \cdot \frac{\partial H_0}{\partial \underline{p}} \right]$$

$$= -\beta f_{eq} \{ M, H_0 \}$$

but $\{M, H_0\} = \frac{dM}{dt} \equiv \dot{M}$

$\Rightarrow$

$$L_1 E(s) f_{eq} = \qquad -\beta E(s) \dot{M} f_{eq}$$

and finally

$$\boxed{f_1(t) = \int_0^t ds \, \beta E(s) \, e^{-(t-s)L_0} \dot{M} f_{eq}}$$

with $f = f_0 + f_1 = f_{eq} + f_1$

$\to$ dynamical response of f!

Now, for general expression for averages:

$$\langle A \rangle = \int dx \, A \left(f_{eq}(x) + f_1(x,t) \right)$$

thus,

$$\langle A(t)\rangle = \langle A_{eq}\rangle + \int dx\, A(x) \int_0^t ds\, \beta E(s) e^{-(t-s)L_0} \dot{M} f_{eq}$$

$$= \langle A_{eq}\rangle + \beta \int_0^t ds\, E(t) \int dx\, A(x) e^{-(t-s)L_0} \dot{M} f_{eq}.$$

Now $e^{-(t-s)L_0}$ can work "backwards" i.e.:

$$A(x) e^{-(t-s)L_0} = A(x, t-s)$$

{ propagates A backward in time

i.e. l.o. of expansion $A(x) e^{-(t-s)L_0} \cong A(x)\left(1 - (t-s) L_0\right) +$

$$= A(p,q)\left(1 + (t-s)\left(\dot{q}\frac{\partial}{\partial q} + \dot{p}\frac{\partial}{\partial p}\right)\right)$$

so for realization:

$$\int dx\, A(x) \left(1 - (t-s) L_0\right) f_{eq}$$

{ $\nabla \cdot V_{tr}$ assures self-adjointness of L operator

$$= \int d\underline{p}\, d\underline{q}\, A(p,q) \left(1 + (t-s)\left(\dot{q}\cdot\frac{\partial}{\partial \underline{q}} + \dot{p}\cdot\frac{\partial}{\partial \underline{p}}\right)\right) f_{eq}$$

$$= \langle A\rangle + (t-s) \int d\underline{p} \int d\underline{q}\, A(p,q) \left(\dot{\underline{q}}\cdot\frac{\partial}{\partial \underline{q}} + \dot{\underline{p}}\cdot\frac{\partial}{\partial \underline{p}}\right) f_{eq}$$

ibp $\quad (\nabla \cdot \underline{V}_{tr} = 0$ for Liouvillian)

$$= \langle A\rangle - (t-s) \int dp \int dq \left(\dot{q}\cdot\frac{\partial A}{\partial \underline{q}} + \dot{p}\cdot\frac{\partial A}{\partial \underline{p}}\right) f_{eq}$$

$$= \langle A\rangle + (t-s) \left.\frac{\partial \langle A\rangle}{\partial t}\right|_{t=0}$$

and re-assembling the series gives;

$\cong A(t-s)$, as term is l.o. in Taylor series

so

$$\langle A, t\rangle = \langle A_{eq}\rangle + \beta\int_0^t ds\, E(s)\, \langle A(t-s)\,\dot{M}(0)\rangle$$

where $\langle C\rangle = \int dx\, C f_{eq}$, eqbm average

$$\boxed{\phi_{AM}(t) = \beta\langle A(t)\,\dot{M}(0)\rangle_{eq}}$$

→ dynamic analogue of susceptibility

and "Kubo Response Formula"

$$\boxed{\langle A(t)\rangle = \beta\int_0^t ds\, \phi_{AM}(s)\, E(t-s)}$$

→ response at time t

Now, can ask what happens as $t\to\infty$, if E switched on at $t=0$

(causal case)

$$\left.\boxed{\begin{aligned} \langle A, t\to\infty\rangle &= \chi_{AM}\,\underline{E} \\ \chi_{AM} &= \int_0^\infty dt\, \phi_{AM}(t) \\ \phi_{AM}(t) &= \beta\langle A(t)\,\dot{M}(0)\rangle_{eq} \end{aligned}}\right\}\ \text{asymptotic results.}$$

Now, have $\begin{cases} \chi_{AM} = \int_0^\infty dt\, \phi_{AM}(t) \\ \text{\underline{and}: } \chi_{AM} = \beta\langle AM\rangle \end{cases}$

Is the equivalence clear?

Now,

$$\chi_{AM} = \int_0^\infty dt\, \beta\left\langle A(t)\left.\frac{dM}{dt}\right|_0\right\rangle_{eq}$$

$$= \cancel{\beta A(t) M(0)\Big|^\infty} - \int_0^\infty dt\, \beta\langle \dot{A}(t) M(0)\rangle_{eq}$$

$t\to\infty$, A, M uncorrelated → some assumption of ergodicity ...

$$= -\int_0^\infty dt\, \beta \frac{d}{dt}\langle A(t) M(0)\rangle_{eq}$$

at $t=\infty$, A decorrelated from $M(0)$

$$= -\beta\left[\cancel{\langle A(\infty) M(0)\rangle_{eq}} - \langle A(0) M(0)\rangle_{eq}\right]$$

$$\chi_{AM} = \beta\langle A(0) M(0)\rangle = \chi_{static}\ !$$

yes — it works.

in particular, note:

$$\chi_{M,M} = \beta \int_0^\infty dt \, \langle M(t) \dot{M}(0)_{eq} \rangle$$

→ correlation function sets susceptibility.

Now, for frequency-dependent response:

→ useful ↔ often ask E switched on at $t=0$, oscillates at ω.

→ involves causality:

$$E(t) = 0, \quad t<0$$

$$\begin{aligned} \langle A(t) \rangle &= 0, \quad t<0 \\ &\neq 0, \quad t>0 \end{aligned}$$

so

$$E_\omega = \int_{-\infty}^{+\infty} dt \, e^{-i\omega t} E(t) = \int_0^\infty dt \, e^{-i\omega t} E(t)$$

$$\langle A \rangle_\omega = \int_{-\infty}^{+\infty} dt \, e^{-i\omega t} \langle A(t) \rangle = \int_0^\infty dt \, e^{-i\omega t} \langle A(t) \rangle$$

Now, $\langle A(t)\rangle = \beta\int_0^t ds\, \phi_{AM}(s)\, E(t-s)$

then

$$\langle A(t)\rangle_\omega = \underbrace{\int_0^\infty dt\, e^{-i\omega t}}_{\text{Laplace transform}}\, \underbrace{\beta\int_0^t ds\, \phi_{AM}(s)\, E(t-s)}_{\text{convolution } \phi\cdot E}$$

$$\mathcal{L}[\phi\cdot E] = \phi(\omega)\, E(\omega)$$

{ L.T. of convolution is product of L.T.

so

$$\langle A(t)\rangle_\omega = \beta\int_0^\infty dt\, e^{-i\omega t}\int_0^t \phi(s)\, E(t-s)\, ds$$

$$= \int_0^\infty ds\, e^{-i\omega s}\phi(s)\int_0^\infty dt\, e^{-i\omega t}E(t)$$

$\Rightarrow$

$$\boxed{\langle A\rangle_\omega = \sigma_{AM}(\omega)\, E_\omega}$$

$$\boxed{\sigma_{AM}(\omega) = \int_0^\infty dt\, e^{-i\omega t}\, \phi_{AM}(t)}$$

where $\phi_{AM}(t) = \beta\,\langle A(t)\dot{M}(0)\rangle_{eq.}$

Frequency-dependent response fctn.

$\downarrow$

as used in F-D thm

$\sigma \Leftrightarrow \alpha$

N.B. $\rightarrow$ recall can relate real, Im parts via Kramers-Kronig!

$\rightarrow$ general expression.

→ Some Applications

a.) Mobility of Single Ion in Solution when $E(t)$ applied
field

$H = H_0 + H_1$

$H_1 = -q E(t) x \equiv q \phi$

"M" $= q x$

$\therefore -ME = -qxE =$

seek: $V_\omega = \mu(\omega) E_\omega$

↳ mobility → sought

where $\frac{dv}{dt} = -\gamma v + \frac{q}{m} E(t) + \tilde{q}$

damping, perturbation, Brownian noise

$\Rightarrow \langle V_\omega \rangle = \sigma_{V,M} E_\omega$

"A" $= V$ here

$\sigma_{V,M} = \int_0^\infty dt\, e^{-i\omega t} \phi_{V,M}(t)$ → response.

and

$$\phi_{V,M}(t) = \beta \langle V(t) \dot{M}(0) \rangle$$

$$= \beta q \langle V(t) V(0) \rangle$$

$\Rightarrow$

$$\mu(\omega) = \sigma_{V,M}(\omega) = \int_0^\infty dt\, e^{-i\omega t} \beta q \langle V(t) V(0) \rangle$$

For equilibrium of uncharged Brownian motion, we know all too well that:

$$\langle v(t)\, v(0)\rangle_{eq} = \frac{T}{m}\, e^{-\gamma t/m} \qquad \text{(for white noise)}$$

friction decay!

$$= v_{Th}^2\, e^{-\gamma t/m}$$

so

$$\mu(\omega) = \int_0^\infty dt\, e^{-i\omega t}\, \beta q \frac{T}{m}\, e^{-\gamma t/m}$$

$\beta T = 1$

$$= q/i\omega m + \gamma$$

$$\boxed{\mu(\omega) = q/i\omega m + \gamma}$$ susceptibility / mobility

$\mu(0) = q/\gamma$ → static limit

Note:

→ $\mu(\omega)$ structure generic for exponentially decaying correlation functions

→ could measure response V_ω to E_ω, determine μ and deduce γ, if unknown

- One use of Kubo formalism is compatibility with experiments / experimental data
<u>i.e.</u> theory cast in terms measureables...

2.) Magnetic Susceptibility

Generic → Specific

$E(t) \longrightarrow \underline{B}(t)$

external field → external magnetic field

$M \longrightarrow \underline{M}$

system state → magnetic moment of system

$A \longrightarrow \underline{M}/V = \underline{m}$

variable (expectation needed) → Magnetization → moment per volume

Now, $\chi_{AM} = \int_0^\infty dt\, \phi_{AM}(t)$ → general susceptibility

$$\phi_{AM}(t) = \beta \langle A(t)\dot{M}(0)\rangle_{eq}$$

and

$$\sigma_{AM}(\omega) = \int_0^\infty dt\, e^{-i\omega t}\phi_{AM}(t)$$

so here

$$\sigma_{m,M}(\omega) = \int_0^\infty dt\, e^{-i\omega t}\beta\langle \underline{m}(t)\cdot\dot{\underline{M}}(0)\rangle_{eq}$$

$$= \int_0^\infty dt\, e^{-i\omega t}\beta\left\langle \underline{m}(t)\cdot \left.\frac{d\underline{M}}{dt}\right|_0 \right\rangle$$

c.b.p.

$$\sigma_{m,M}(\omega) = \beta \langle \underline{M}(0)\cdot\underline{M}(0)\rangle + i\omega\int_0^\infty dt\, e^{-i\omega t}\,\beta\,\langle \underline{m}(t)\cdot\underline{M}(0)\rangle$$

$$= \frac{\beta}{V}\left[\langle \underline{M}\cdot\underline{M}\rangle_{eq} + i\omega\int_0^\infty dt\, e^{-i\omega t}\langle \underline{M}(t)\cdot\underline{M}(0)\rangle_{eq}\right]$$

$$\chi(\omega) = \sigma_{m,M}(\omega) \quad , \text{ as } \quad \underline{m} = \underline{M}/V$$

and if write;

$$\langle \underline{M}(t)\cdot\underline{M}(0)\rangle_{eq} = \langle \underline{M}(0)\cdot\underline{M}(0)\rangle_{eq}\, e^{-t/\tau}$$

$$\equiv M_0^2\, e^{-t/\tau}$$

$$\chi(\omega) = \frac{\beta M_0^2}{V}\left[1 + i\omega\int_0^\infty dt\, e^{-i\omega t} e^{-t/\tau}\right]$$

$$= \frac{\beta M_0^2}{V}\left[1 - \frac{i\omega\tau}{1+i\omega\tau}\right]$$

$$\frac{-i\omega\tau}{1+i\omega\tau} = \frac{-(i\omega\tau + 1 - 1)}{1+i\omega\tau} = -1 \; \frac{+1}{1+i\omega\tau}$$

so

$$\chi(\omega) = \frac{\beta M_0^2}{V}\left[1/(1+i\omega\tau)\right]$$

→ generic form

→ note more complex spectral information reveals more complex correlation function behavior, with more info!.

b) Zwanzig - Mori Theory

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

a.) partition the dynamics into relevant (i.e. usually slow) and irrelevant (i.e. usually fast) variables
b.) project the $\begin{pmatrix}\text{irrelevant}\\ \text{fast}\end{pmatrix}$ variables onto the $\begin{pmatrix}\text{relevant}\\ \text{slow}\end{pmatrix}$ variables, thereby reducing the effective # of degrees of freedom
c.) describe the relevant variables in terms of a
1.) memory function
2.) effective noise

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

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

↳ dynamical variable

Now, $\varphi_j(x) \equiv$ basis functions for Hilbert space of all functions of X $\begin{pmatrix}\text{i.e. states,}\\ \text{modes}\end{pmatrix}$

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:

$$\underbrace{b_j(t)}_{\text{projection on } \varphi_j} = \int dX\, \varphi_j(X)\, f(X,t)$$

so

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

Matrix Liouville Equation

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

Now, consider case of 2 states/modes:

$$q_1(t), \quad q_2(t)$$

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. $\left\{\begin{array}{l}\text{eliminate } q_2 \\ \text{in favor } q_1.\end{array}\right.$

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

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

$$\frac{\partial}{\partial t}\left(q_2^{(0)} + q_2^{(1)} + \cdots\right)$$
$$= L_{3,1} q_1(t) + L_{3,2}\left(q_2^{(0)} + q_2^{(1)} + \cdots\right)$$

l.o. $L_{3,2} q_2^{(0)} = 0$ as $\tau_{3,2} < \tau_{1,1}, \tau_{1,2}, \tau_{3,1}$

$$\Rightarrow q_2^{(0)} = q_{2,eq}$$

1st order: $\cancel{\frac{\partial}{\partial t} q_2^{(0)}}^{\,0} + \frac{\partial}{\partial t} q_2^{(1)} = L_{3,1} q_1(t) + \cancel{L_{3,2} q_2^{(0)}} + L_{3,2} q_2^{(1)}$

then if take $\omega \tau_{3,2} << 1$

$$\Rightarrow L_{3,2} q_2^{(1)} = -L_{3,1} q_1(t)$$
$$q_2^{(1)} = -L_{3,2}^{-1} L_{3,1} q_1(t)$$

and,

$$\frac{\partial q_1(t)}{\partial t} = \underset{\text{bare}}{L_{1,1}} q_1(t) + L_{1,2}\left(q_{3,eq} - L_{3,2}^{-1} L_{3,1} q_1(t)\right)$$

$$\frac{\partial q_1(t)}{\partial t} - L_{1,1} q_1(t) + \underbrace{L_{1,2} L_{3,2}^{-1} L_{3,1} q_1(t)}_{\text{memory kernel}}$$
$$= \underbrace{L_{1,2} q_{2,eq}}_{\text{effective noise}} \quad \text{c.f.} \; -\int_0^t k(t-s)\, q_1(s)$$

so now have for $q_1(t)$:

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

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

① - propagator, with memory function

② - effective noise.

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

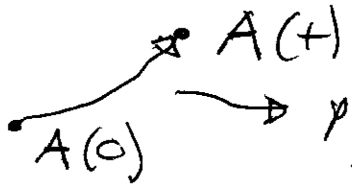
consider q_2 equation:

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

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 ⇒

$$\frac{\partial}{\partial t} q_1(t) = L_{1,1} q_1(t) + L_{1,2} \int_0^t ds \, \underbrace{\exp\left[L_{2,2}(t-s)\right] L_{2,1} q_1(s)}_{\text{memory term}}$$
$$+ \underbrace{L_{1,2} \exp\left[L_{2,2} t\right] q_2(0)}_{\text{i.c. term}}$$

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

→ Could generalize and formalize via <u>Projection</u> <u>Operator</u> <u>Theory</u>

<u>i.e.</u> Consider N variables
$n < N$ relevant variables

then can <u>projection</u> <u>operator</u> <u>matrix</u>:

where: $$\underline{\underline{P}} = \begin{pmatrix} \overset{1}{\mathbb{1}}, & \overset{2}{0} \\ \overset{3}{0}, & \overset{4}{0} \end{pmatrix}$$ is block matrix

1 → $n \otimes n$ identity matrix

2 → $n \otimes (N-n)$ zero matrix

3 → $(N-n) \otimes n$ zero matrix

4 → $(N-n) \otimes N-n$ zero matrix

obviously: $\underline{\underline{P}} \cdot \underline{\underline{P}} = \underline{\underline{P}}$ $\qquad$ $\underline{\underline{P}}$ is idempotent

Now, can write Liouville equation as:

$$\frac{\partial \underline{q}}{\partial t} = \underline{\underline{L}} \cdot \underline{q}$$

so relevant variable vector $\qquad \underline{q}_1 = \underline{\underline{P}} \cdot \underline{q}$ $\qquad$ (has $N-n$ zeroes)

irrelevant variable vector $\qquad \underline{q}_2 = (\underline{\underline{\mathbb{1}}} - \underline{\underline{P}}) \cdot \underline{q}$ $\qquad$ (has n zeroes) and for components of Liouvillian operator matrix:

$$\underline{\underline{L}}_{1,1} = \underline{\underline{P}} \cdot \underline{\underline{L}} \cdot \underline{\underline{P}}$$

$$\underline{\underline{L}}_{22} = (\underline{\underline{1}} - \underline{\underline{P}}) \cdot \underline{\underline{L}} \cdot (\underline{\underline{1}} - \underline{\underline{P}})$$

$$\underline{\underline{L}}_{1,2} = \underline{\underline{P}} \cdot \underline{\underline{L}} \cdot (\underline{\underline{1}} - \underline{\underline{P}})$$

$$\underline{\underline{L}}_{31} = (\underline{\underline{1}} - \underline{\underline{P}}) \cdot \underline{\underline{L}} \cdot \underline{\underline{P}}$$

Now, can summarize all this abstractly, i.e.

- given any set $\{A\}$
- the projection of B onto A is given by:

$$\underline{\underline{P}}\, B = (B, A) \cdot (A, A)^{-1} \cdot A$$

or

$$\underline{\underline{P}}\, B = \sum_j \sum_k (B, A_j) \left((A, A)^{-1}\right)_{jk} A_k$$

note: if $\{A\}$ orthonormal, (A, A) is identity

→ Having developed projection operator formalism, now construct:

<u>Generalized</u> <u>Langevin</u> <u>Equation</u>

i.e. write Liouville equation in form:

$$\boxed{\frac{da(t)}{dt} = i\Omega a(t) - \int_0^t ds\, \underset{\substack{\downarrow \\ \text{memory kernel}}}{K(s)}\, a(t-s) + \underset{\substack{\downarrow \\ \text{noise}}}{F(t)}}$$

where a is relevant variable. This generalizes simple example discussed above.

(H. Mori, '65
J.T. Hynes, J.M. Deutch, '75)

Now, to show; use:

$$L = \underline{P}L + \underline{(1-P)}L \qquad = \text{dropped hereafter}$$

and operator identity:

$$\boxed{e^{tL} = e^{t(1-P)L} + \int_0^t ds\, e^{(t-s)L}\, PL\, e^{s(1-P)L}}$$

$$= e^{t(1-P)L} + \int_0^t ds\, e^{(t-s)L} (P \underbrace{-1+1}) L e^{s(1-P)L}$$

$$= e^{t(1-P)L} + \int_0^t ds \left\{ e^{(t-s)L} \left(-\frac{d}{ds} e^{s(1-P)L} + L e^{s(1-P)L} \right) \right\}$$

$$e^{tL} = e^{t(1-P)L} - \int_0^t ds\, e^{(t-s)L} \frac{d}{ds}\left(e^{s(1-P)L}\right)$$

$$+ \int_0^t ds\; e^{(t-s)L} L e^{s(1-P)L}$$

$$= e^{t(1-P)L} - e^{(t-s)L} e^{s(1-P)L} \Big|_0^t$$

$$+ \int_0^t ds\; e^{(t-s)} \cancel{(-L)} e^{s(1-P)L}$$

$$+ \int_0^t ds\; e^{(t-s)L} \cancel{(L)} e^{s(1-P)L}$$

$$= \cancel{e^{t(1-P)L}} - \cancel{e^{t(1-P)L}} + e^{tL}$$

so have shown:

$$e^{tL} = e^{t(1-P)L} + \int_0^t ds\, e^{(t-s)L} P L e^{s(1-P)L}$$

Now, operate (from right) on both sides of identity with $(1-P)LA$, i.e.

$$e^{tL}(1-P)LA = \int_0^t ds\, e^{(t-s)L} PL e^{s(1-P)L}(1-P)LA$$

LHS: $\quad e^{tL}(1-P)LA = e^{tL}LA - e^{tL}PLA$

$$= \frac{\partial}{\partial t} e^{tL}A - e^{tL}(LA, A)\cdot(A,A)^{-1}\cdot A$$

$$= \frac{\partial A(t)}{\partial t} - (LA, A)\cdot(A,A)^{-1}\cdot A(t)$$

where $A(t) = e^{tL}A$

RHS: $\quad$ define $\quad F(t) = e^{t(1-P)L}(1-P)LA$

so dbp $\Rightarrow$

$$RHS = F(t) + \int_0^t ds\, e^{(t-s)L}(LF(s), A)\cdot(A,A)^{-1}\cdot A$$

$$= F(t) + \int_0^t ds\, (LF(s), A)\cdot(A,A)^{-1}\cdot A(t-s)$$

Now, if define:

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

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

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

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

thus have:

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

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

→ 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

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

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.

Now, $\frac{\partial A}{\partial t} = L A(t)$

where $L \sim O(\epsilon)$

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

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

$$F(t) = e^{t(\underline{\underline{1}}-P)L} (\underline{\underline{1}} - P) LA$$

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

so $i\Omega \sim O(\epsilon)$

$K \sim O(\epsilon^2)$

$F \sim O(\epsilon)$

Now, as $K \sim O(\epsilon^2)$, argue non-Markovian character of memory kernel is weak, so

$$\int_0^t ds \rightarrow \int_0^\infty ds$$

(irrelevant modes will "thermalize" prior to orbit scattering) so $$\frac{d}{dt} A(t) \cong i\Omega \cdot A(t) - \int_0^{\infty} ds\, K(s) \cdot A(t) + F(t)$$

and can simplify further,

Recall, $$e^{tL} = e^{t(1-P)L} + \int_0^t ds\, e^{(t-s)L} PL\, e^{s(1-P)L}$$

and

$$\underline{P}L B = (LB, A) \cdot (A,A)^{-1} \cdot A$$
$$= -(B, \underbrace{LA}_{O(\epsilon)}) \cdot (A,A)^{-1} \cdot A \qquad (L \text{ anti-Hermitian})$$

so $$\underline{P} L B \sim O(\epsilon)$$

so $$e^{tL} = e^{t(1-P)L} + O(\epsilon)$$

$\therefore$ replace $e^{t(1-P)L}$ with e^{tL} in $\underline{K}$.

Furthermore, can insert $1-P$ in LA in $\underline{T}$, as operated on by $e^{t(1-P)L}$ so

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

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

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

so Z-M eqn has form:

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

which is simple!

→ Important Application of Z-M Theory for Slow Variables → Hydrodynamics

a.) Self-Diffusion

- seek evolution of $c(x,t)$ ↔ 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

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

$$= e^{-iqR}$$

R ↳ position of tagged particle

so

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

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

$$\equiv -iqV$$

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

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

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

Note: 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:

$$\rho_q = \sum_j m_j e^{iq\cdot R_j} \qquad \text{— density}$$

$$J_q = \sum_j p_j e^{iq\cdot R_j} \qquad \text{— current / flow}$$

$$E_q = \sum_j \epsilon_j e^{iq\cdot R_j} \qquad \text{— energy}$$

$$\sum_j = \sum_{j=1}^{N} \text{, } N \text{ not small} \ldots$$

All hydrovariables can be similarly constructed.

For any time derivative, $\partial A/\partial t = LA$
where

$$LA = L\sum_j A_j e^{iq\cdot R_j}$$

and on large scale (low q)

$$\cong L\left(\sum_j A_j\right) + L\sum_j iq\cdot R_j A_j + \text{h.o.t}$$

$$= iq \cdot \sum_j L(R_j A_j)$$

momentum of   momentum of i-th molecule where first term vanishes (for no outflow) via conservation

$$\frac{\partial}{\partial t} \sum \begin{pmatrix} \text{mass} \\ \text{current/momentum} \\ \text{energy} \end{pmatrix} = 0.$$

so

$$L\Big(\sum_j A_j e^{i\underline{q}\cdot R_j}\Big) = \frac{\partial A_q}{\partial t} \cong i\underline{q} \cdot \sum_j L(R_j A_j)$$

e.g. shear flow → seek viscosity

$$\underline{V} = v(y, t)\, \hat{x}$$

then viscosity → momentum flux

$$\underbrace{(\rho v_x)_q}_{\text{momentum of } q^{th} \text{ mode}} = \sum_j \underbrace{p_{jx}}_{\text{momentum of } j^{th} \text{ molecule}} e^{iq \overbrace{y_j}^{j^{th} \text{ molecule location}}}$$

$$\frac{\partial}{\partial t}(\rho v_x)_q = iq \sum_j L(p_{jx}\, y_j)$$

$$= iq \sum_j \Big(p_{jx} \frac{dy_j}{dt} + \frac{dp_j}{dt} x\, y_j\Big)$$

$$\Rightarrow \quad \frac{\partial}{\partial t}(\rho v)_q = iq \sum_j \left(P_{jx} \frac{P_{jy}}{m} + F_{jy} Y_j \right)$$

in the absence of molecular force,

$$\frac{\partial}{\partial t}(\rho v)_q = iq \sum_j \left(\frac{P_x P_y}{m}\right)_j = iq \cdot \underline{S}_{x,y}$$

stress tensor

so

$$\boxed{\eta = \frac{1}{VT} \int_0^\infty ds \, \langle S_{x,y}(t) \, S_{x,y}(0) \rangle}$$

viscosity

This leads us next to mode-mode coupling and long-time tails.

N. B.: Point is that large scale $\Rightarrow$ low $q \Rightarrow$ effective linearization ("qR" is "small parameter") $\rightarrow$ yet another incarnation of Kubo theory structure.

→ More on Mori-Zwanzig ...

Recall, last time discussed Z.-M. theory. Z.-M. theory
a.) partioned variables $\nearrow$ relevant, $\searrow$ irrelevant (i.e. time scales)

b.) projected irrelevant variables onto relevant variables (i.e. via $\underline{\underline{P}}$, projection operator)

c.) described relevant dynamics in terms of non-Markovian Z-M. equation

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

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

set by irrelevant variables
$$\begin{cases} \underline{\underline{K}}(t) = -(LF(t), A) \cdot (A, A)^{-1} \\ F(t) = e^{t(1-P)L}(1-P)LA \end{cases}$$

considerable simplifaction for the case of slow modes is possible.

This ~~b~~egs the question:

"The Z-M. theory is clearly constructed to make the relevant variable equation 'look' like a Langevin equation. But --- does it actually <u>have</u> the properties of a Langevin equation ?"

In particular:

1) → does $F(t)$ actually behave like noise ?

2) · is there a fluctuation-dissipation relation ?

Easier to tackle # 2 first.

2)

Recall
$$K(t) = -(LF(t), A) \cdot (A,A)^{-1}$$
$$= (F(t), LA) \cdot (A,A)^{-1}$$
L anti-hermitian
$$= (F(t), (1-P)LA) \cdot (A,A)^{-1}$$

; inner product with F, $(1-P)$ redundant

but $\quad F(0) = (1-P)LA$

so

$$K(t) = (F(t), F(0)) \cdot (A, A)^{-1}$$

Memory function — noise

i.e. generalized dissipation

(sets time response)

essence of F.-D. thm is:

$$\langle \tilde{x}^2 \rangle_\omega \cong 2\frac{T}{\omega}\, \mathrm{Im}\, \alpha(\omega)$$

fluctuation level — effective memory

{ classical form

So, yes → F.-D. structure persists in Z-M theory.

N.B. from the Cynic: Z.-M. fans never entertain the possibility that $K < 0$ → i.e. inverse cascades, negative viscosity, etc. Then route off the hook is deviation from standard 'stationarity'.

1.) for $F(t)$ to behave like noise, it should have the property that

$$\langle F \rangle = 0$$

where $\langle\ \rangle$ is an average over an initial non-equilibrium state.

key issue is how to define the state?

Best to recall maximum entropy argument, i.e.

- start with Boltzmann entropy

$$S = \int dx\ f(x) \ln f(x)$$

with constraints: $\int dx\ f(x) = 1$ → normalization

$\int dx\ H(x) f(x) = E$ → energy

$$\delta S = 0 \Rightarrow \quad f(x) = \exp[-\alpha - \beta H(x)]$$

and normalization ⇒

$$e^{\alpha} = Q(\beta) = \int dx\, e^{-\beta H(x)}$$

and

$$E = -\partial \ln Z / \partial \beta$$

Now, -- add additional constraint, that

$\langle M \rangle = m$

M: dynamical variable

m: some value, assigned

then repeating maximum entropy calculation $\Rightarrow$

$$\underbrace{f(x)}_{\text{maximum entropy}} = \exp\left[-\alpha - \beta H(x) + \underbrace{\beta E}_{} M(x)\right]$$

βE is Lagrange multiplier for M
(E is external field --)

and as before:

$$\exp(\alpha) = Q(\beta, E) = \int dx \, \exp\left(-\beta H(x) + \beta E M(x)\right)$$

$$\underbrace{U}_{\text{energy}} = -\frac{\partial \ln Q}{\partial \beta}, \qquad m = \frac{\partial \ln Q}{\partial \beta E}$$

Now, <u>if</u> M is C.O.M., then procedure yields good $f(x)$

<u>if not</u>, $f(x)$ is not stationary in time (i.e. non-equilibrium state).

→ Throwing caution to the winds, then, we can use entropy maximization to specify initial distribution

→ Can think of constructing this state via applying external field E (hence notation).

Now, can generalize this approach. Obvious strategy for Z-M. theory is to associate dynamical variables with constraints, i.e.

A_j; $j = 1, 2 \ldots$ dynamical variables

a_j; $j = 1, 2, \ldots$ assigned average values (constraint)

then,

Lagrange multipliers

$$f = f_{eq}\left\{ 1 + \sum_{j=1}^{N} \gamma_j A_j^* + \ldots \right\}$$

variable

where then

$$a_j = \sum_k \langle A_j A_k^* \rangle_{eq} \gamma_k + o(\gamma^2)$$

Now, define : $M_{jk} = \langle A_j A_k^* \rangle_{eq} \equiv \underline{\underline{M}}$

so $\quad \gamma = \underline{\underline{M}}^{-1} \cdot \underline{a}$

γ solves for Lagrange multipliers

and for time dependent averages,

$$\langle A(t) \rangle = \langle A, t \rangle = \langle A(t) A^* \rangle \cdot \underline{\underline{M}}^{-1} \underline{a} .$$

Now, ... can proceed to consider averages of noise, i.e.:

can write $\quad f(x, 0) = f_{eq}(x) \left\{ 1 + \sum_j \gamma_j A_j^*(x) + \cdots \right\}$

here $\quad \langle A; 0 \rangle = \langle A A^* \rangle_{eq} \cdot \underline{\gamma}$

$\Rightarrow$

$$\boxed{\gamma = \langle A A^* \rangle_{eq}^{-1} \cdot \langle A; 0 \rangle}$$

specifies initial ensemble, to average over.

Now, can average Langevin eqn. (Z.-M. eqn):

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

where:

$$\langle F(t) \rangle = \int dx \, F(t) \, f_{eq}(x) \left\{ \overset{①}{1} + \overset{②}{\underline{\gamma} \cdot A^*(x)} + \overset{③}{\cdots} \right\}$$

Now,

- ① vanishes, as γ independent.

Follows from $\langle A; 0\rangle = \langle A\rangle_{eq} = 0$, so initial eqbrm stays so, thus all $\langle A\rangle$ terms in avg. Z-M. vanish

$\therefore$ ① $\to 0$.

- ② $\Rightarrow$ for this to vanish, need arrange:

$$\int dx\, f_{eq}(X)\, F(t)\, A^*(X) = 0$$

This can be arranged $\Rightarrow$ choose inner product as before, s/t:

$$(A, B) = \int dx\, f_{eq}(X)\, A(X)\, B^+(X)$$

Now, then $(F(t), A) = 0$

by construction!

$\therefore$ ② $\to 0$

$\therefore$ $\langle F\rangle$ must be $O(\gamma^2)$ ✓.

$\Rightarrow$ Z-M theory has requisite properties.

→ Mode Coupling and Long Time Tails

For this last topic, we consider anomalous properties of transport coefficients.

cf (Zwanzig; 2001
Kadanoff + Swift; Phys. Rev. '68)

Anomalous properties related to:

→ phase transitions:
i.e. (slow / soft) modes near criticality → large scale convection

? Mode ?

$$F = \int d^3x \left\{ \frac{D(\nabla\eta)^2}{2} + \frac{a(T-T_c)}{2}\eta^2 + \frac{b\eta^4}{4} \right\}$$

$$\frac{\partial\eta}{\partial t} = -\frac{\delta F}{\delta\eta} = -\left(a(T-T_c)\eta + b\eta^3 - D\nabla^2\eta\right)$$

so linearizing; $\eta \sim \eta_\omega e^{-i\omega t}$

$$\gamma_{\underline{k}} = -\left(a(T-T_c) + Dk^2\right)$$

$a \to 0$
$T \to T_c$ so $\gamma_{\underline{k}} \to 0$ as $\begin{cases} T \to T_c & \text{(criticality)} \\ k \to 0 & \text{(large scale)} \end{cases}$

→ "relaxation mode softens"...

→ mechanism same as divergence of fluctuation spectra.

→ dimensional anomalies

Alder & Wainwright[1] (1968) molecular dynamics studies of hard sphere/disk fluid in 3D, 2D

Noted: $D(t) = \frac{1}{d}\langle v(t)\cdot v\rangle \sim t^{-d/2} \mp \text{const}$

$D = \int_0^\infty dt\, D(t)$

power law decay set by dimension.
d = 2 ?? – Does D exist?

<u>Why</u>??

suspect slow modes (i.e. $q \to 0$ phenomena).
related to transport

→ how does energy get into slow modes? →

! from beats/nonlinear interaction of not-so-slow modes!

<u>i.e.</u>

$$D = \int_0^\infty dt\, D(t)$$

$$D(t) = \frac{1}{d}\langle \underline{V}(t)\cdot \underline{V}\rangle$$

$$= \frac{1}{d}\,\mathrm{tr}\sum_{j,k}(V,\varphi_j)(e^{tL}\varphi_j,\varphi_k)(\varphi_k,V)$$

Point is to project flows producing diffusion onto basis of states. Use inner product:

$$(\varphi_j, \varphi_k) = \int dX \, \varphi_j(X) \, \varphi_k^*(X) \, f_{eq}(X) = \delta_{j,k}$$

$\therefore$ Keys to problem are:

- calculating $(e^{tL}\varphi_j, \varphi_k) \rightarrow$ nontrivial...

one strategy is $L = \underbrace{L_0}_{\text{known deterministic piece}} + \underbrace{\tilde{L}}_{\text{stochastic piece (i.e. from model)}}$

$$\left(\frac{df}{dt} = \left.\frac{df}{dt}\right|_{\text{determ}} - \frac{\partial}{\partial v} D \frac{\partial f}{\partial v} \right)$$

then average over ensemble $\tilde{L}$, i.e.

$$\left(e^{t(L_0+\tilde{L})}\varphi_j, \varphi_k\right) \rightarrow \left(\left\langle e^{t(L_0+\tilde{L})}\varphi_j, \varphi_k\right\rangle_{\tilde{L}}\right) \text{ked.}$$

$$\cong \left(e^{tL_0} \underbrace{\left\langle e^{t\tilde{L}} \right\rangle}_{\substack{\text{propagator correction} \\ \Rightarrow \text{diffusive}}} \varphi_j, \varphi_k\right)$$

- determining $(\bar{V}, \varphi_j)$

i.e. $\bar{V}$ here is ~ homogeneous, large scale flow → survives averaging

$\underline{q} \simeq 0$ → contributes to diffusion coefficient

φ_j → state with eigenfunction of wave vector q. $(\bar{V}, \varphi) \neq 0$ only for $\underline{q} \to 0$

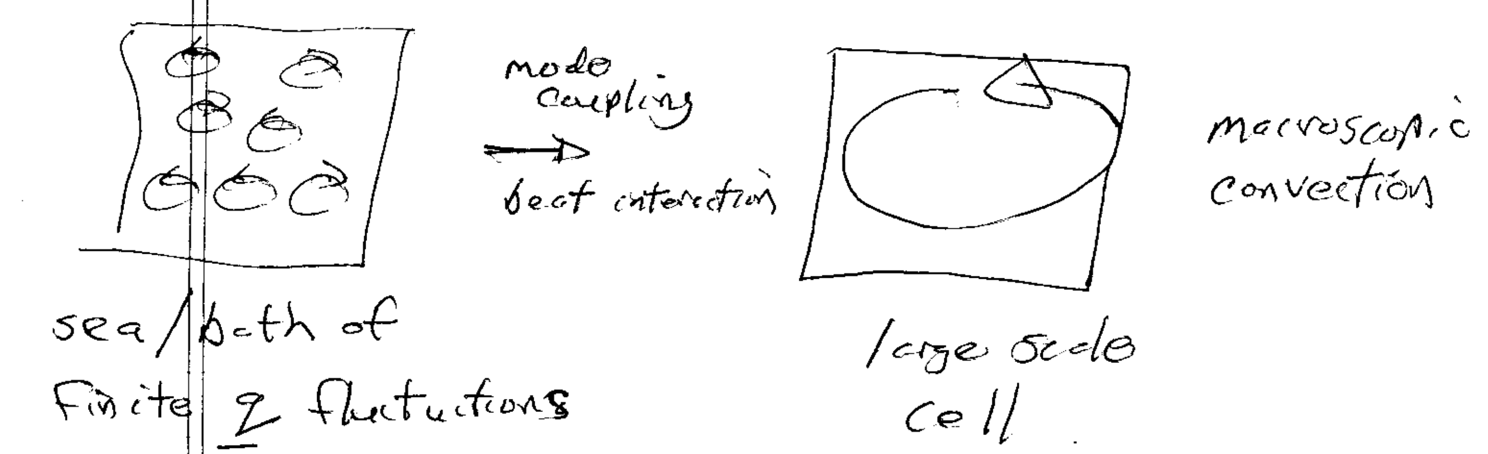
∴ generate $\bar{V}$ via nonlinear interaction of $\varphi_j(\underline{q})$

i.e.

$$\underbrace{\underline{q} + \underline{q}'}_{\text{(wavelengths)}^{-1}\text{ of base state}} \to \underbrace{0}_{\text{macro flow.}}$$

hence "mode coupling theory" of transport coefficients...

- physical idea:



→ Now, seek calculate mode coupling induced transport...

Recall for "self-diffusion":

$$\frac{\partial c(\underline{x},t)}{\partial t} = D\nabla^2 c(\underline{x},t)$$

where $c(\underline{x},t) = \sum_{\underline{q}} c_{\underline{q}}(t)\, e^{i\underline{q}\cdot\underline{x}}$

$c_{\underline{q}} = e^{-i\underline{q}\cdot\underline{R}_0}$ for $c(\underline{r},t) = \delta(\underline{R_0}-\underline{r})$

$$\frac{\partial c_{\underline{q}}}{\partial t} = -Dq^2 c_{\underline{q}} + \cancel{\text{noise}}$$

so if no noise, $c_{\underline{q}}(t) = e^{-Dq^2 t} c_{\underline{q}}$
(why? → $\cong e^{tL} c_{\underline{q}}$
$q \to 0$, and long times)

Now, possible that diffusive transport modified by convection due fluctuations in fluid velocity

$$\frac{\partial c(\underline{x},t)}{\partial t} + \underline{\tilde{v}}\cdot\nabla c(\underline{x},t) = D\nabla^2 c(\underline{x},t)$$

$\tilde{v} \neq V$

and for $\underline{\nabla}\cdot\underline{\tilde{V}} = 0$

$$\underbrace{\frac{\partial C}{\partial t} + \underline{\nabla}\cdot(\underline{\tilde{V}}\,C)}_{\text{convection by velocity flctns}} = \underbrace{D\nabla^2 C}_{\text{diffusion}}$$

→ intrinsically $\underline{\underline{\text{slow}}}$

i.e. $\underline{\nabla} \sim i\underline{q}$

$\underline{\underline{\text{so net}}}$ $\left\} \underbrace{\underline{V} \Leftrightarrow \dot{R}}_{\text{particle velocity}}\right.$, $\underline{\tilde{V}} \rightarrow \tilde{C}\tilde{V}$ beat

↳ convection pattern velocity

trick here is to 'assemble' $\underline{V}\,C$ from basis states ⟷ $\underline{\text{mode coupling}}$ ⟺ $\begin{pmatrix}\text{beat}\\\text{product}\end{pmatrix}$ states from $\underline{q} \neq 0$ mode basis.

as $\overline{V}$ is hydro $(\underline{q} \to 0)$ need couple $\tilde{V}_{\underline{q}}$ and $\tilde{C}_{\underline{q}}$ to project onto $\overline{V}$, i.e.

$$(\overline{V}, \tilde{V}_{\underline{p}}\tilde{C}_{\underline{r}}) \neq 0 \quad \text{for} \quad \underline{p} + \underline{r} = 0$$

i.e. $\underline{p} = +\underline{q}$

$\underline{r} = -\underline{q}$

$\underline{\text{i.e.}}$

$$(\overline{V}, \underbrace{\tilde{V}_{\underline{q}}\tilde{C}_{-\underline{q}}}_{\substack{\text{virtual modes has}\\ \text{finite projection on } \overline{V}}}) \neq 0$$

(other pairs → noise, but $q \to 0$ for $\overline{V}$ and time avg) strictly speaking:

$$(\underline{V}, \tilde{v}_q \tilde{C}_{-q}) = \left\langle \underline{V} \cdot \sum_j \frac{p_j}{m} e^{i\underline{q}\cdot \underline{R}_j} e^{-i\underline{q}\cdot \underline{R}_0} \right\rangle$$

$\underline{V} = \frac{p}{m}$ defn.

$$= \left\langle \underline{V} \cdot \frac{p_0}{m} e^{i(\cancel{R_0 - R_0})\cdot q} \right\rangle = \frac{T}{m} \underline{\underline{I}}$$

for normalization:

$$(\tilde{V}_q \tilde{C}_{-q}, \tilde{V}_q \tilde{C}_{-q}) = \langle \tilde{V}_q \tilde{V}_{-q} \rangle \langle \tilde{C}_{-q} \tilde{C}_q \rangle = \frac{NT}{m} \underline{\underline{I}}$$

∴ normalized $\begin{pmatrix}\text{beat}\\ \text{product}\end{pmatrix}$ state is:

$$\boxed{\varphi_{q\to 0} = (m/NT)^{1/2} \tilde{V}_q \tilde{C}_{-q}} \rightarrow$$ construct, from basis state of system, beat modes

Now, can proceed as before:

$$D(t) = \frac{1}{d} D_{fast}(t) + \frac{1}{d} \mathrm{tr} \sum_q (\underline{V}, \varphi_q) (e^{tL} \varphi_q, \varphi_q) * (\varphi_q, V$$

diffn. from fast modes, if any

$$D = \int_0^\infty dt\, D(t)$$

so, dropping D_{fast}

$$\underset{\text{M.C.}}{\underset{\wr}{D(t)}} = \frac{1}{d}\, \mathrm{tr} \sum_{\underline{q}} \left(e^{tL} \tilde{V}_{\underline{q}} \tilde{C}_{-\underline{q}} ,\, V_{\underline{q}} \tilde{C}_{\underline{q}} \right)$$

as e^{tL} propagator distributes

$$= \frac{1}{d}\, \mathrm{tr} \sum_{\underline{q}} \left\langle \left(e^{tL} \tilde{v}_{\underline{q}}\right) \left(e^{tL} \tilde{C}_{-\underline{q}}\right) ;\; v_{\underline{q}} \tilde{C}_{\underline{q}} \right)$$

$$\cong \frac{1}{d}\, \mathrm{tr} \sum_{\underline{q}} \left(\left(e^{tL} \tilde{V}_{\underline{q}}\right) e^{-q^2 D t} C_{-\underline{q}} ,\; \tilde{v}_{\underline{q}} \tilde{C}_{-\underline{q}} \right)$$

Now, $\underline{\nabla} \cdot \underline{V} = 0$ and $\underline{V}$ satisfies:

$$\rho \frac{\partial \underline{V}}{\partial t} = -\underline{\nabla} p + \eta \nabla^2 \underline{V} + \text{noise} \ldots$$

$$\left(+ \nabla^2 p = \nabla \cdot (\eta \nabla^2 V) \right)$$

$$\frac{\partial}{\partial t} V_{\underline{q}\perp} = -\underset{\underset{\eta/\rho}{\wr}}{\nu} q^2 \underline{V}_{\underline{q}} + \text{noise} \ldots$$

$$V_{\perp \underline{q}}(t) = e^{tL} \tilde{V}_{\underline{q}\perp} \cong e^{-\nu q^2 t} \tilde{V}_{\underline{q}\perp}$$

so, as only transverse $\underline{v}$ contributes)
$\hookrightarrow \underline{q}\cdot\underline{v}=0$

$$(e^{tL}\underline{v}_{q\perp}, \underline{v}_{q\perp}) \cong e^{-\nu q^2 t}(\tilde{v}_{q\perp}, \tilde{v}_{q\perp})$$

$$= \frac{N}{m}T\left(\underline{\underline{I}} - \frac{\underline{q}\underline{q}}{q^2}\right)e^{-\nu q^2 t}$$

$\rightarrow$ from distributivity e^{Lt}

so

$$D(t)_{mc} = \frac{1}{d}\,\mathrm{tr}\,\frac{T}{mN}\sum_{q} e^{-(D+\nu)q^2 t}\left(\underline{\underline{I}} - \frac{\underline{q}\underline{q}}{q^2}\right)$$

$\rightarrow 0$ in 1D

$$= \frac{d-1}{d}\left(\frac{T}{mN}\right)\sum_{q} e^{-(D+\nu)q^2 t}$$

Now, $$\sum_{q} = \left(\frac{L}{2\pi}\right)^d \int d^d q$$

$$\rho = mN/L^d$$

$$\Rightarrow \boxed{D(t)_{mc} = \frac{d-1}{d}\,\frac{kT}{\rho}\left(1\Big/\left[4\pi(D+\nu)t\right]^{d/2}\right)}$$

- n.b. small times, need large q cut-off
$\rightarrow$ removes $t \to 0$ singularity.

obviously, $d = 2 \rightarrow D \sim 1/t$

$d = 3 \rightarrow D \sim 1/t^{3/2}$

note: $d=2$, $D(t) \sim 1/t$
$D \to \infty \rightarrow$ anomaly
$d=3$, $D(t) \sim 1/t^{3/2}$ — long time tails.
$D_{Hc} \sim 1/t^{1/2} \to 0 \rightarrow$ no anomaly D_{Hc} negligible.

$\Rightarrow D = \int_0^\infty D(t)$ does not exist in 2D

(long-time divergence).

$\therefore$ no self-diffusion in 2D!

Note: dimension matters! tail decays faster as d increases. $d_{crit} = 2$ here for divergence.

Recall Stokes Paradox: In 2D, hydrodynamic friction on a particle in 2D does not exist.
i.e. ln divergence in Stokes drag, i.e. $\ln(L_{sys}/\varepsilon)$

point is that in 2D, solutions of Poisson's eqn. not localized $\Rightarrow$ i.e. $\ln(\underline{x}-\underline{x}_0)$

$-\nu \nabla^2 \underline{V} = -\underline{\nabla} P$, $\underline{\nabla} \cdot \underline{V} = 0$ for Stokes flow

etc.