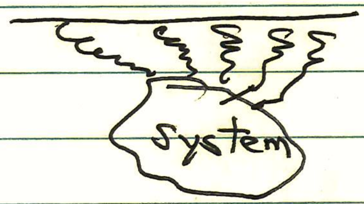
Notes 5: Non-Markovian Stochastic Processes and Zwanzig-Mori Theory

Idea: Time scale separation $\rightarrow$ bath, system.

Recall:



x, p

$U(X)$

bath $\rightarrow$ ensemble H.O.

$\omega_j^2 \gg \omega^2$

$$H_S = \frac{p^2}{2m} + U(x)$$

$$H_B = \sum_j \frac{p_j^2}{2} + \frac{\omega_j^2}{2}\left(q_j - \frac{\gamma_j x}{\omega_j^2}\right)^2$$

then can derive generalized Langevin Equation for system:

memory fctn

$$\frac{dp}{dt} = -U'(x(t)) - \int_0^t K(s)\,\frac{p(t-s)}{m} + F_p(t)$$

drag, non-Markovian

noise

$$K(t) = \sum_j \frac{\gamma_j^2}{\omega_j^2}\cos\omega_j t$$

$$F_p(t) = \sum_j \gamma_j\, p_j(0)\,\frac{\sin\omega_j t}{\omega_j} + \sum_j \gamma_j\left(q_j(0) - \frac{\gamma_j x(0)}{\omega_j^2}\right)\cos\omega_j t$$

Finite Memory Time / Kernel.
↓

(i.) Non-Markovian Stochastic Processes

→ general idea is to derive Master Eqn.
for Non-Markovian stochastic processes

a.) → but what, really, does Markovian mean?
Markovian ≡ no memory; factorizable transition probability
e.g. consider particle motion in stochastic electric field → Paradigmatic Example
Field prescribed → bath

$$\frac{dx}{dt} = v, \quad \frac{dv}{dt} = \frac{q}{m} E(x, t)$$

$$= \frac{q}{m} \sum_{k} E_k e^{i(kx - \omega_k t)}$$

$$\Rightarrow \delta v(t) = \int dt' \frac{q}{m} \sum_{\substack{k \\ \omega}} E_{\substack{k \\ \omega}} e^{i(k x(t) - \omega_k t)}$$

$x(t) \to x_0 + vt$ i.e. ballistic orbit (i.e. un-perturbed)

$\langle \delta v \, \delta v(t) \rangle$

so $\langle \delta v^2 \rangle = D_v \tau$ $\qquad \langle \delta v(0) \delta v(\tau) \rangle = D_v \tau$

$$D_v = \sum_{k, \omega} \frac{q^2}{m^2} |E_{\substack{k \\ \omega}}|^2 \pi \delta(\omega - kv)$$

$$= \sum_{k, \omega} \frac{q^2}{m^2} \frac{|E_k|^2}{|v|} \delta\left(\frac{\omega}{k} - v\right)$$

resonance condition

so $\tau_{ac}^{-1} = |\Delta k| V$ is wave-particle correlation time. (~ width density states)

Now, from viewpoint of kinetic equation Hamiltonian system ⇒ Vlasov equation $(n\lambda_D^3 \gg 1)$ ⇒

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \underline{\nabla}_{ph} \cdot [\underline{V}_{ph} f] = \frac{\partial f}{\partial t} + \underline{V}_{ph} \cdot \underline{\nabla} f = 0$$

$\underline{\nabla} \cdot \underline{V}_{ph} = 0$ ⇒ Liouville's Thm.

so
$$\frac{\partial f}{\partial t} + v\frac{\partial f}{\partial x} + \frac{q}{m} E \frac{\partial f}{\partial v} = 0$$
Vlasov, [collisionless Boltzmann]

averaging, for homogeneous, stationary process ⇒

$$\frac{\partial \langle f \rangle}{\partial t} = -\frac{q}{m}\frac{\partial}{\partial v}\langle E f \rangle$$
implicit scale sep.

simplest approach ⇒ mean-field theory (quasi-linear theory)

$$\langle \tilde{E}\tilde{f} \rangle = \sum_{\underline{k},\omega} E_{\underline{k}, -\omega}\, \tilde{f}_{\underline{k},\omega}$$

[plug in linear response ⇒ un-perturbed orbits.

$$-i(\omega - kv)\tilde{f}_{\substack{k\\ \omega}} = -\frac{q}{m}\hat{E}_{\substack{k\\ \omega}}\frac{\partial\langle f\rangle}{\partial v}$$

$P/\omega - kv$ negligible

$$-\frac{q}{m}\langle E f\rangle_{MF} = -\frac{q^2}{m^2}\sum_{\substack{k\\ \omega}}|E_{\substack{k\\ \omega}}|^2 \pi\delta(\omega - kv)\frac{\partial\langle f\rangle}{\partial v}$$

uses R.P.A.

$$= -\Gamma_v = -D\frac{\partial\langle f\rangle}{\partial v}$$

$$\Rightarrow \quad D = \sum_{k,\omega}\frac{q^2}{m^2}|E_{\substack{k\\ \omega}}|^2 \pi\delta(\omega - kv)$$

QL

i.e. mean field theory recovers Langevin result (both rest on unperturbed orbits, only and Gaussian Pdf /RPA)

Now, consider response for k, ω; seek $\dfrac{\delta f}{\delta \mathcal{N}_{ext\, k,\omega}}$

$$\frac{\partial f}{\partial t} + v\frac{\partial f}{\partial x} + \frac{q}{m}E\frac{\partial f}{\partial v} = \mathcal{N}_{ext.}$$

i.e. need response function. To calculate perturbatively, extract piece of nonlinearity phase coherent with external perturbation $\mathcal{N}_{k,\omega}$

$$N_{k,\omega} = +\frac{q}{m}\frac{\partial}{\partial v}\sum_{k',\omega'} E_{\substack{-k'\\ -\omega'}} f_{\substack{k'+k\\ \omega'+\omega}}$$

Need determine $\delta N_{k,\omega}/\delta \mathcal{N}_{k,\omega}$

Now, assume $E_{k,\omega}$ specified (acceleration problem)

$$N_{k,\omega} = \frac{q}{m}\frac{\partial}{\partial v}\sum_{k',\omega'} E_{\substack{-k'\\-\omega'}} f^{(2)}_{\substack{k'+k\\ \omega'+\omega}}$$

driven by beat-interaction of (k,ω), (k',ω') modes

$\Rightarrow$

$$\left[-i(\omega+\omega') + i(k+k')v\right] f^{(2)}_{\substack{k+k'\\ \omega+\omega'}} = -\frac{q}{m}\left[E_{\substack{k'\\ \omega'}} \frac{\partial f_{\substack{k\\ \omega}}}{\partial v} + \frac{\partial f_{k',\omega'}}{\partial v} E_{\substack{k\\ \omega}}\right]$$

$$f^{(2)}_{\substack{k+k'\\ \omega+\omega'}} = \underset{\substack{\uparrow\\ \text{response.}}}{R(\omega+\omega', (k+k')v)}\left(\frac{-q}{m}\right)\left[E_{\substack{k'\\ \omega'}} \frac{\partial f_{\substack{k\\ \omega}}}{\partial v} + \frac{\partial f_{k',\omega'}}{\partial v} E_{\substack{k\\ \omega}}\right]$$

$\Rightarrow$

$$N_{k,\omega} = -\frac{\partial}{\partial v}\sum_{k',\omega'} \frac{q^2}{m^2} |E_{\substack{k'\\ \omega'}}|^2 R(\omega'', k''v) \frac{\partial f_{k,\omega}}{\partial v}$$

$$-\frac{\partial}{\partial v}\sum_{k',\omega'} \frac{q}{m} E^{*}_{\substack{k'\\ \omega'}} \frac{\partial f_{\substack{k'\\ \omega'}}}{\partial v} R(\omega'', k''v)\, \frac{q}{m} E_{k,\omega}$$

$$= -\frac{\partial}{\partial v} D_{k,\omega} \frac{\partial}{\partial v} f_{k,\omega} - \frac{\partial}{\partial v} b_{k,\omega} \frac{q}{m} E_{k,\omega}$$

$\downarrow$ analogous to $\frac{\partial}{\partial v} D \frac{\partial}{\partial v}$

$\hookrightarrow$ background renorm. (disregard here)

Now $D_{k,\omega} = \sum_{k',\omega'} \frac{q^2}{m^2} |E_{k' \atop \omega'}|^2 \pi \delta(\omega'' - k''v)$

compare to Markovian / Mean Field result:

$$D = \sum_{k',\omega'} \frac{q^2}{m^2} |E_{k' \atop \omega'}|^2 \pi \, \delta(\omega' - k'v)$$

$\therefore \quad D = \lim_{k,\omega \to 0} D_{k,\omega} \; !$

$\rightarrow$ propagator renormalization

i.e. $+i(\omega - kv)^{-1} \rightarrow$ (linear)

$i\left(\omega - kv - \frac{\partial}{\partial v} D_{k \atop \omega} \frac{\partial}{\partial v}\right)^{-1}$

(renormalized)

$\rightarrow$ amplitude dependent

i.e. reflects "dressing" of unperturbed orbit by fluctuating field

D: Markovian limit

$D_{k,\omega}$: non-Markovian diffusivity

i.e.

$\rightarrow$ Markovian dynamics recovered in $k \ll k'$, $\omega \ll \omega'$ limit

k, ω k', ω'

i.e. { renormalization $\Leftrightarrow$ interaction of k, ω test mode with spectrum k', ω' modes

→ in $k,\omega < k',\omega'$ limit, interaction events of duration $1/|\Delta k| v$ appear as (random) kicks of vanishingly short duration ⇒ diffusion

* Non-Markovian ≡ time duration of test 'mode' interaction with scattering 'modes' comparable to time scales of test mode.

* Markovian ≡ time duration of scattering mode interaction with test mode short in comparison to time scales of test mode.

→ if $\omega = kv$ (resonance) Markovian limit recovered ⇒ plasma physics topic

→ ω dependence of $D_{k,\omega}$ implies time history! i.e.

$$\int e^{-i\omega t} L_{k,\omega} = \int e^{-i\omega t}\left[-i\omega + ikv - \frac{\partial}{\partial v} D_{k,\omega} \frac{\partial}{\partial v}\right] f_{k,\omega}$$

$$= \frac{\partial f_k}{\partial t} + ikv f_k - \int_{-\infty}^{t} \frac{\partial}{\partial v} D_{k,\tau} \frac{\partial}{\partial v} f_k(t-\tau)$$

b.) General Theory: Zwanzig - Mori Formalism

→ $\underline{\underline{N}}$ variables $\{$modes / particles$\}$ $\underset{\sim}{q} = (q_1, \ldots q_N)$

$$\dot{q}_j = h_j(\underset{\sim}{q}) \quad \Rightarrow \text{dynamical equations.}$$

→ Assume (via linear transformation), dynamical equations of form:

$$\dot{\rho}_j = -\gamma_j \rho_j + g_j(\rho) \qquad j = 1, \ldots N$$

→ if concerned with phenomena / evolution on time scale $\sim \tilde{T}$, then can divide/classify variables:

$\gamma_i \tilde{T} > 1$ → "irrelevant" / fast variables
i.e. have 'equilibrated' on time scale $\tilde{T}$ (analogous terminal velocity)

$\gamma_i \tilde{T} < 1$ → "relevant" / slow variables
i.e. evolve / not 'equilibrated' on $\tilde{T}$

idea is to describe in terms relevant variables.

For fast variables:

$$\dot{\rho}_j = -\gamma_j \rho_j + g_j(\rho) \quad , \quad j = \underline{M+1, \ldots N}$$

$$\Rightarrow \dot{\rho}_j \cong 0 \Rightarrow \rho_j = \frac{g_j}{\gamma_j}(\rho) \quad \Delta$$

so $\quad p_{fast} = \frac{q_{fast}(p)}{\gamma_f} \Rightarrow$ ['slaves' / eliminates fast variables to slow variables]

Can use to obtain dynamical equations in terms slow variables only
↓
"relevent" $\quad$ [project system onto relevent]

Now, for pdf evolution; → { seek Master Eqn. for Non-Markovian system

- variables $\begin{cases} a \to \text{slow relevent} \\ b \to \text{fast, irrelevent} \end{cases}$

- for pdf

$$\frac{\partial}{\partial t} \rho(a, b, t) = \underbrace{L}_{\text{i.e. Liouvillian}} \rho(a, b, t)$$

L → differential operator, { i.e. - Poisson bracket; - FP operator

Can define reduced pdf:

$$s(a, t) = \int db \; \rho(a, b, t)$$

↓ integrates out irrelevent, fast variables.

also, assume can decompose L as:

$$L = \underbrace{L_a}_{\text{slow}} + \underbrace{L_b}_{\text{fast}} + L_i$$

interactions (i.e. fast–slow)

Now, assume equilibrium distribution exists only for b variables, $P_{eq}(b)$

$\Rightarrow$

$$L_b P_{eq}(b) = 0$$

what is $P_{eq}(b)$?

$$\int db \, P_{eq}(b) = 1$$

$\therefore$ can define projection $\underline{\underline{P}}$ onto $\underline{\underline{a}}$ variables via:

projection

$$\underline{\underline{P}}p(a,b,t) = P_{eq}(b)\int db \; p(a,b,t) = P_{eq}(b)\,s(a,t)$$

Now, for projection, need: ("idempotency")

$$\underline{\underline{P}}\,\underline{\underline{P}}p = \underline{\underline{P}}p$$

$\therefore$

$$\underline{\underline{P}}^2 p(a,b,t) = \underline{\underline{P}}P_{eq}(b)\,s(a,t)$$

$$= P_{eq}(b)\int db\, P_{eq}(b)\,s(a,t)$$

$$= P_{eq}(b)\,s(a,t) = \underline{\underline{P}}p(a,b,t) \checkmark$$

So $\underline{\underline{P}}$ is indeed projection ✓.

Now, can define:

$$\rho_1 = \underline{\underline{P}}\, \rho(a,b,t)$$

$$\rho_2 \equiv (\underbrace{\underline{\underline{1}}}_{\text{identity}} - \underline{\underline{P}})\, \rho(a,b,t) \equiv \underline{\underline{Q}}\, \rho(a,b,t)$$

so $\frac{\partial}{\partial t} \rho = L\rho$ Liouville Eqn.

$\rho = \rho_1 + \rho_2$

$$\Rightarrow \begin{cases} \frac{\partial \rho_1}{\partial t} = PL(\rho_1 + \rho_2) \quad \text{(slow)} & \text{(oper } P\text{)} \\ \frac{\partial \rho_2}{\partial t} = QL(\rho_1 + \rho_2) \quad \text{fast} & \text{(oper } Q\text{)} \end{cases}$$

Solving ρ_2 equation $\Rightarrow$

$$\rho_2(t) = e^{QLt}\rho_2(0) + e^{QLt}\int^{t} ds\, e^{-QLs} QL\rho_1(s)$$

$$= e^{QLt}\rho_2(0) + \int_0^t e^{QLs} QL\rho_1(t-s)\, ds$$

Recall, have obtained Master Eqn. for pdf of relevant variables ρ_1:

$$\frac{\partial}{\partial t}\rho_1(t) = \mathcal{P}\mathcal{L}\mathcal{P}\rho(t) + \mathcal{P}\mathcal{L}e^{\mathcal{Q}\mathcal{L}t}\mathcal{Q}\rho(0) + \int_0^t \underbrace{\mathcal{P}\mathcal{L}e^{\mathcal{Q}\mathcal{L}s}\mathcal{Q}\mathcal{L}\mathcal{P}}_{\phi(s)\,\to\,\text{memory kernel}}\rho(t-s)\,ds$$

slow → slow; → i.c. prop.; → fast → slow

$a \to$ relevant, slow
$b \to$ irrelevant, fast

$$\begin{cases} \mathcal{P}_b \equiv \rho_{eq}(b)\int db\,\rho(a,b,t) = \rho_{eq}(b)\,S(a,t) \\ \mathcal{Q} = 1-\mathcal{P} \end{cases}$$

[similar in "Toth" prblm.]

and $\frac{\partial\rho}{\partial t} = \mathcal{L}\rho$ → Liouville operator

Salient features:

(i) memory kernel $\phi(s)$ → from elimination of fast b's in terms slow a's

has form:

$$\underbrace{\mathcal{P}\mathcal{L}e^{\mathcal{Q}\mathcal{L}s}\mathcal{Q}\mathcal{L}}_{\text{Liouville operators (2)}}\mathcal{P}$$

→ time propagator

Recall non-Markovian renormalized Vlasov equation

$$-i(\omega-kv)f_{k,\omega} - \frac{\partial}{\partial v}D_{k,\omega}\frac{\partial f_{k,\omega}}{\partial v} = -\frac{q}{m}E_{k,\omega}\frac{\partial\langle f\rangle}{\partial v}$$

→ Representions for NMSP Master Eqn.

Now, have Master Eqn.

$$\frac{\partial}{\partial t}\rho_1 = PLP\rho(t) + PLe^{QLt}Q\rho(0) + \int_0^t \phi(s)\,\rho(t-s)\,ds$$

$$L \equiv L_a + L_b + L_i$$

$$\equiv L_o + L_i$$

L_o → zeroth order/decoupled Liouvillian operator

L_i → a, b interaction Liouville operator

(Zwansig) (Mori)

Thus, akin Schroedinger → Heisenberg change of rep:

$$\rho \equiv e^{-L_o t}\rho(a, b, t)$$

$$L_o \equiv L_a + L_b$$

$$L_i(t) = e^{-L_o t} L_i e^{L_o t}$$

$$\boxed{\frac{\partial}{\partial t}\rho(t) = L_i(t)\,\rho(t)}$$

i.e. $\frac{\partial}{\partial t}\left(e^{-L_0 t}\rho(a,b,t)\right) = \left(e^{-L_0 t} L_i e^{L_0 t}\right)\left(e^{-L_0 t}\rho\right)$

$$\cancel{e^{-L_0 t}}\left(-L_0\,\rho + \frac{\partial \rho}{\partial t}\right) = \cancel{e^{-L_0 t}}\,L_i\,\rho$$

note ordering

$$\frac{\partial \rho}{\partial t} = (L_0 + L_i)\,\rho \quad \checkmark$$

Note: Understood that exponential to be calculated as

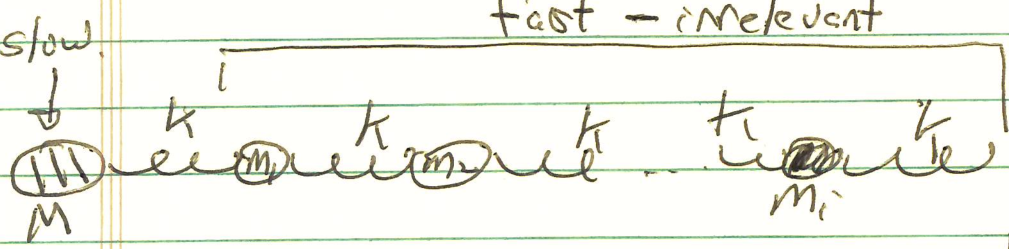
$$\overleftarrow{\exp}\left[\int_0^t A(s)\,ds\right] = 1 + \sum_{r=1}^{\infty}\frac{(-1)^r}{r!}\int_0^t ds_1\int_0^{s_1} ds_2 \cdots \int_0^{s_{r-1}} ds_r \;*$$

$$A(s_1)\cdots\cdots A(s_r).$$

→ Linear Chain: A Case Study

Consider a chain of springs with spring constant K and masses $M \gg m_1, m_2 \ldots m_i \ldots m_N$

i.e.



X X_1 X_2 X_i

V V_1 V_2 V_i

Key Point

$$\omega^2_{\text{end mass}} = \frac{k}{M} \ll \omega_i^2 = \frac{k}{m_i}$$

Application of Linear Chain Paradigm

$T \to$ thermal noise

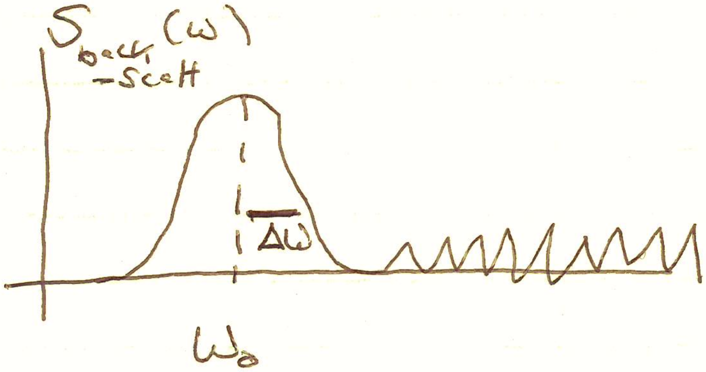
$\to$ primitive macro-molecular model (real case entropic)

$\to$ tweak ala laser

$\Rightarrow$ output is measured spectra — mode frequencies

but recall $\omega_0^2 = \dfrac{k_1}{M} \ll \omega_i^2$

$\Rightarrow$



what is $\Delta\omega_0$? $\to$ $\left\{\begin{array}{l}\text{relaxation rate of} \\ \text{low } \omega \text{ mode!!}\end{array}\right.$

but relaxation rate set by kicks due fast modes $\leftrightarrow$ background "effective noise"

$\Rightarrow$ $\left\{\begin{array}{l}\text{Z-M method useful in calculating relaxation} \\ \text{rates for slow modes in complex systems!}\end{array}\right.$

Then can immediately write down equations of motion: { i.e. coupled eqns. for each mass }

$$\dot{x} = v \qquad \left\{ \begin{array}{l} \dot{x}_1 = v_1 \\ \dot{v}_1 = -\frac{k}{m_1}(x_1 - x_2) - \frac{k_1}{m_1}(x_1 - x) \end{array} \right.$$

$$\dot{v} = -\frac{k}{M}(x - x_1)$$

$$\vdots \qquad \vdots$$

$$\left\{ \dot{x}_i = v_i \qquad \dot{v}_i = -\frac{k_i}{m_{i+1}}(x_i - x_{i-1}) - \frac{k_i}{m_{i+1}}(x_i - x_{i+1}) \right.$$

$$\vdots \qquad \vdots$$

To simplify, can define relative coordinates: (work in relative coordinates only)

$$\delta x_0 = x - x_1$$
$$\delta x_1 = x_1 - x_2 \qquad \Rightarrow \qquad \{ \text{all } k\text{'s same} \rightarrow \text{simplicity}$$
$$\delta x_i = x_i - x_{i+1}$$

$$\delta \dot{x}_0 = v \;; \quad \dot{v} = -\frac{k}{M}\delta x_0 \quad \xrightarrow{} \oplus \text{ from } -(x_1 - x)$$

$$\delta \dot{x}_1 = v - v_1 \;; \quad \dot{v}_1 = \frac{k}{m_1}\delta x_0 - \frac{k}{m_1}\delta x_1$$

$$\vdots \qquad \vdots$$

$$\delta \dot{x}_i = v_i - v_{i+1} \;; \quad \dot{v}_i = \frac{k}{m_i}\delta x_{i-1} - \frac{k}{m_i}\delta x_i$$

} eqns. motion in simplest coordinates.

Note: In reality for taking fast modes/oscillators in equilibrium, need:

a la fluctn-dissipn. { (1) stochastic forcing in each
(2) some dissipation in coupling } "define eqbrm."

Now, need construct "Liouvillian" for system: (note Hamiltonian, so far)

$$L = \frac{dx}{dt}\frac{\partial}{\partial x} + \frac{dv}{dt}\frac{\partial}{\partial v} + \sum_j \left(\frac{d\,\delta x_j}{dt}\frac{\partial}{\partial \delta x_j} + \frac{dv_j}{dt}\frac{\partial}{\partial v_j} \right)$$

Now,

$\rightarrow$ x variable absorbed into δx_0

$\rightarrow$ $\dot{v} = -\frac{k}{M}\delta x_0$

$\rightarrow$ $\frac{d}{dt}\delta x_j = (v_j - v_{j+1})$

$$\frac{dv_j}{dt} = \frac{k}{m_i}\delta x_{i-1} - \frac{k}{m_i}\delta x_i$$

So

$$L = -\frac{k}{M}\delta x_0 \frac{\partial}{\partial v} + (v - v_1)\frac{\partial}{\partial \delta x_0} + \left(\frac{k}{m_1}\delta x_0 - \frac{k}{m_1}\delta x_1\right)\frac{\partial}{\partial v_1}$$

$$+ (v_1 - v_2)\frac{\partial}{\delta x_1} + \left(\frac{k}{m_1}\delta x_1 - \frac{k}{m_1}\delta x_2\right)\frac{\partial}{\partial v_2}$$

$$+ \ldots\ldots$$

$$+ (v_i - v_{i+1})\frac{\partial}{\partial \delta x_i} + \left(\frac{k}{m_i}\delta x_{i-1} - \frac{k}{m_i}\delta x_i\right)\frac{\partial}{\partial v_{i+1}}$$

This yields Liouville equation $\Rightarrow$ continuity equation in phase space, i.e.

$$\frac{\partial}{\partial t}\rho + \nabla_{\substack{\text{phase}\\\text{space}}} \cdot \left[V_{\substack{\text{phase}\\\text{space}}} \rho \right] = 0$$

but here, $\nabla \cdot V_{\substack{\text{phase}\\\text{space}}} = 0$ (Hamiltonian system)

$$\Rightarrow \boxed{\frac{\partial \rho}{\partial t} + L\rho = 0 \quad , \qquad L \equiv \underline{V}_{\substack{\text{phase}\\\text{space}}} \cdot \nabla_{\substack{\text{phase}\\\text{space}}}}$$

given above $\mathcal{J}$.

$\rightarrow$ Now, need decompose into $\left\langle \begin{array}{l} \text{relevant (a)} \\ \text{(slow)} \\ \text{interaction (i)} \\ \text{irrelevant (b)} \\ \text{fast} \end{array} \right\}$ variables operators

- key point $\omega_0^2 = \frac{k}{M} \ll \omega_j = \frac{k}{m_j}$

<u>but</u>

- relative coordinates $\Rightarrow$ no <u>isolated</u> slow variables i.e. $\delta x_0 = x - x_i$

$$\underset{\text{slow}}{\downarrow} \quad \hookrightarrow \text{fast}$$

<u>so</u>

$\rightarrow \quad L_a = 0$

$$\rightarrow \quad L_i = -\frac{k}{M}\,\delta x_0 \frac{\partial}{\partial V} + V \frac{\partial}{\partial \delta x_0}$$

interaction Liouvillian

i.e. note here $\delta x_0 = \underset{\text{slow}}{x} - \underset{\text{fast}}{x_1}$

$\rightarrow$ irrelevant variable Liouvillian:

$$L_b = (\cancel{V}-V_1)\frac{\partial}{\partial \delta x_0} + \left(\frac{k}{m_1}\delta x_0 - \frac{k}{m_1}\delta x_1\right)\frac{\partial}{\partial V_1}$$

$$+ (V_1 - V_2)\frac{\partial}{\partial \delta x_1} + \left(\frac{k}{m_2}\delta x_1 - \frac{k}{m_2}\delta x_2\right)\frac{\partial}{\partial V_2}$$

$$\vdots \qquad\qquad \vdots$$

$$+ (V_i - V_{i+1})\frac{\partial}{\partial \delta x_i} + \left(\frac{k}{m_i}\delta x_{i-1} - \frac{k}{m_i}\delta x_i\right)\frac{\partial}{\partial V_{i+1}}$$

"slow"

To implement projection onto variables
(i.e. eliminate fast variables)

$\rightarrow$ integrate out the fast variables

but

$\leftrightarrow$ need equilibrium pdf of fast $\Rightarrow$ i.e.
$P_{eq}(b)$.

i.e. recall projection operator $P \equiv P_{eq}(b)\int db$.

Now, can conveniently write pdf for irrelevant variables as:

$$P_{eq}(\delta x_i, v_i) = M \prod_{i=1}^{N} \exp\left[-\delta x_{i-1}^2/2\Delta_{i-1}^2\right] \exp\left[-v_i^2/2\langle v_i^2\rangle\right]$$

variances

Questions:

- requirement for 'equilibrium' $\left\{ \begin{array}{l} L_b\, P_{eq}(b) = 0 \\ \text{implicit fluctuation} \\ \text{-dissipation thm.} \\ \text{(damping)} \end{array} \right.$
- origin of distribution function? (Markov's thm!)
- validity $\Rightarrow \left\{ \begin{array}{l} \text{i.c.'s} \\ \text{forcing / damping} \end{array} \right.$

Now,

$\rightarrow$ must have (a la' Chapman - Enskog expansion)

$L_b\, P_{eq}(b) = 0$ cancels interaction Liouvillian at absolute equilibrium

i.e. $+ (v - v_1)\dfrac{\delta x_0}{\Delta_0^2} + \left(\dfrac{k}{m_1}\delta x_0 - \dfrac{k}{m_1}\delta x_1\right)\dfrac{v_1}{\langle v_1^2\rangle}$

$+ (v_1 - v_2)\dfrac{\delta x_1}{\Delta_1^2} + \left(\dfrac{k}{m_2}\delta x_1 - \dfrac{k}{m_2}\delta x_2\right)\dfrac{v_2}{\langle v_2^2\rangle}$

$+ \ldots\ldots$

observe $L_b P_{eq}(b) = 0$ annihilation occurs

if :

$$(\Delta_0^2)^{-1} = \frac{k}{m_1 \langle V_1^2 \rangle} \qquad \Rightarrow m_1 \frac{\langle V_1^2 \rangle}{2} = \frac{k}{2} \Delta_0^2$$

$$\frac{1}{\Delta_1^2} = \frac{k}{m_2 \langle V_2^2 \rangle} \qquad \Rightarrow \frac{m}{2} \langle V_2^2 \rangle = \frac{k}{2} \Delta_1^2$$

$\vdots$

$$\frac{1}{\Delta_i^2} = \frac{k}{m_{i+1} \langle V_{i+1}^2 \rangle} \qquad \Rightarrow m_{j+1} \langle V_{j+1}^2 \rangle = \frac{k}{2} \Delta_j^2$$

i.e.

red : "sequential equipartition" thru chain

$$\text{i.e.} \quad \boxed{\frac{k}{2} \Delta_j^2 = \frac{m_{j+1}}{2} \langle V_{j+1}^2 \rangle} \quad \checkmark$$

$$\Rightarrow \quad k \langle \Delta_0^2 \rangle = \ldots\ldots = m_i \langle V_i^2 \rangle$$

Hence linked equipartition is necessary for Gaussian pdf of irrelevant variables.

→ also must regulate energy in chain
→ i.c.'s ⇒ chaos development

→ stochastic forces
damping

Aside: For <u>total</u> equilibrium distribution

$$\rho = M \exp\left[-\frac{V^2}{2\langle V^2\rangle}\right] \rho_{eq}(b)$$

and of course have:

$$M\langle V^2\rangle_{eq} = k\langle \Delta_0^2\rangle_{eq} = \cdots\cdots m_i\langle V_i^2\rangle_{eq}.$$

Thus, can proceed with construction of projection operator:

$$P\,\rho(V, \underline{b}, t) = \rho_{eq}(b)\int db\, \rho(V, \underline{b}, t)$$

Now, to construct Master equation:

– recall derived: $(\mathcal{L} = L)$ (in Heisenberg rep.)

$$\frac{\partial}{\partial t} \underbrace{P\rho(t)}_{\rho_{red}} = P\mathcal{L}_i(t)\, P\tilde{\rho}(t) + P\mathcal{L}_i(t)\, \overleftarrow{\exp}\left[\int_0^t ds\, Q\mathcal{L}_i(s)\right] * Q\,\tilde{\rho}(0)$$

$$(L = \mathcal{L}) \quad + \int_0^t ds\, \underbrace{P L_i(t)\, \overleftarrow{\exp}\left[\int_s^t ds_1\, Q\mathcal{L}_i(s_1)\right] Q\mathcal{L}_i(s)}_{\text{memory kernel}}\, P\tilde{\rho}(s)$$

higher order interaction effect in memory kernell

I.C. → as previous

Now

→ ignore higher order interactions implicit in exponential ⇒ exp [ ] ≈ 1

⇔ weak interaction limit

Thus, reduced pdf evolution (in Heisenberg representation) becomes:

$$\frac{\partial}{\partial t}\tilde{\rho}_1(t) = \int_0^t ds\, \mathcal{P}\, \mathcal{L}_i(t)\, \mathcal{L}_i(s)\, \tilde{\rho}_1(s)$$

$\rho_1 = \frac{\rho}{\rho_{eq}(v)}$ ⇓ must absorb $\rho_{eq}(v)$ in $\rho_{eq}(b)$ deviation counts!

→ {alternatively, correspondingly}, can truncate memory kernel for Master Eqn

$$\Phi = e^{-\mathcal{L}_0(t-s)}\,\Phi_B(t-s)$$

$$\Phi_B(t-s) = \mathcal{P}\,\mathcal{L}_i\, e^{(\cancel{\mathcal{L}_a} + \mathcal{L}_b)(t-s)}\,\mathcal{L}_i\,\mathcal{P}$$

Thus, can finally write Non-Markovian Master equation for reduced system as:

pdf of relevant variable (vel. M)

$$\frac{\partial}{\partial t}\rho(v,t) = \frac{1}{\rho_{eq}(b)}\int_0^t \Phi_B(t-s)\,\rho_{eq}(b)\,\rho(v_0,s)\,ds$$

$\rho_{eq}(b)$ → to cancel piece $\underline{P}$

$\Phi_B(t-s)$ → Memory kernel

$$\Phi_B = \underline{P}\,\mathcal{L}_i\,e^{-\mathcal{L}_b(t-s)}\,\mathcal{L}_i\,\underline{P}$$

Now, as t increases:

→ time scale for observation $\rho(v_0,t)$ evolution exceeds memory time of slow-fast interactions drastically

→ can take Markovian limit

$$\frac{\partial \rho}{\partial t} = \mathcal{L}_{eff}\,\rho \qquad \rho = \rho(v_0,t)$$

→ integration over full memory time

$$\mathcal{L}_{eff} = \frac{1}{\rho_{eq}(b)}\left(\int_0^\infty ds\,\Phi_B(s)\right)\rho_{eq}(b)$$

$$\Phi_B = \underline{P}\,\mathcal{L}_i\,e^{-\mathcal{L}_b(t-s)}\,\mathcal{L}_i\,\underline{P}$$

→ kernel

i.e. $\frac{\partial \rho}{\partial t} = -\frac{1}{\tau_{eff}}\rho \qquad \tau_{eff}^{-1} \equiv |\mathcal{L}|$

Now, to evaluate explicitly for linear chain problem, recall:

$$\to \mathcal{L}_i = -\frac{k}{M}\,\delta x_0 \frac{\partial}{\partial v} + v \frac{\partial}{\partial \delta x_0}$$

$$\to f = \rho_{eq}(b)\int db\, \rho(a, b, t)$$

where b includes $\underline{\underline{\delta x_0}}$ (relative separation!)

→ also useful to recall:

$$\rho_{eq}(b) = M \prod_{i=1}^{N} \exp\left[-\delta x_{i-1}^2 / 2\Delta_{i-1}^2\right] \exp\left[-v_{i-1}^2 / 2\langle v_{i-1}^2\rangle\right]$$

(total ρ_{eq}).

$\rho_{eq}(v)$ absorbed.

Thus, can note

$$\to \rho\, v \frac{\partial}{\partial \delta x_0} = \int dx_0\; v \frac{\partial}{\partial \delta x_0} \ldots\ldots$$

$$= 0,$$ upon integration by parts

i.e. only $\partial/\partial v$ pieces $\mathcal{L}_i$ survive

→ should recall $\partial/\partial v$ acts on $\rho_{eq}(v, b)$

i.e. ⇒ $\rho = \rho_{eq} \dfrac{\rho}{\rho_{eq}}$, calculated.

$$\mathcal{L}_i = \frac{k}{M}\delta x_0\left(\frac{\partial}{\partial V} + \frac{V}{V_T^2}\right) - V\left(\cancel{\frac{\partial}{\partial \delta x_0}} + \frac{k\,\delta x_0}{k_B T}\right)$$

(sign absorbed, as $\overset{(\text{or } \rho_{eq})}{\mathcal{L}_i^2}$).

$\underline{b}$ includes V

$\underline{\underline{\text{So}}}$ for $\mathcal{L}_{eff}$:

$$\mathcal{L}_{eff} = \frac{1}{\rho_{eq}(b)}\left(\int_0^\infty ds\, \underline{P}\,\mathcal{L}_i\, e^{-\mathcal{L}_b(t-s)}\,\mathcal{L}_i\,\underline{P}\right)\rho_{eq}(b)$$

$$= \cancel{\frac{1}{\rho_{eq}(b)}}\left(\int_0^\infty ds\, \cancel{\rho_{eq}(b)}\int db\left(\frac{k}{M}\delta x_0\left(\frac{\partial}{\partial V} + \frac{V}{V_T^2}\right) - V\frac{k\,\delta x_0}{k_B T}\right) e^{-\mathcal{L}_0(t-s)}\left(\frac{k}{M}\delta x_0\left(\frac{\partial}{\partial V} + \frac{V}{V_T^2}\right) - V\frac{k\,\delta x_0}{k_B T}\right)\right.$$

$$\left.\rho_{eq} \ast \int db \qquad \right)\rho_{eq}(b)$$

Note:

$\rightarrow$ $\langle \delta x_0 \rangle = 0$

$\rightarrow$ $P\mathcal{L}_i P = P e^{-\mathcal{L}_0 t}\mathcal{L}_i e^{\mathcal{L}_i t} P = 0$ (obv.)

cleaning it all up finally yields:

$$\mathcal{L}_{eff} = \frac{k}{M}\,\Phi(0)\left\{\langle V^2\rangle \frac{\partial^2}{\partial V^2} + \frac{\partial}{\partial V} V\right\}$$

$$\Phi(0) = \Phi(z)\Big|_{z=0}\quad , \text{ where}$$

→ normalized correln. fctn.

$$\Phi(z) = \int_0^\infty dz\, e^{-zt}\, \frac{\langle \delta X_0\, \delta X_0(t)\rangle_{eq}}{\langle \delta X_0^2\rangle_{eq}} \quad \to \quad \left\{ \frac{k}{M}\langle \delta X_0^2\rangle \sim m\langle V^2\rangle \sim T. \right.$$

and

$$\boxed{\begin{aligned} \frac{\partial}{\partial t}\rho(V,t) &= \mathcal{L}_{eff}\,\rho(V,t) \\ &= \underset{\substack{\downarrow \\ \frac{1}{T^2}}}{\frac{k}{M}}\;\underset{\substack{\text{cst} \\ T}}{\Phi(0)}\left\{\langle V^2\rangle \frac{\partial^2}{\partial V^2} + \frac{\partial}{\partial V} V\right\}\rho(V,t) \\ &\qquad\qquad \frac{L^2}{T^2} \end{aligned}}$$

Note can re-write in F.P.E. form:

$$\frac{\partial \rho}{\partial t} = \frac{\partial^2}{\partial V^2}(D\rho) - \frac{\partial}{\partial V}(\beta V \rho)$$

where, back-tracking thru calculation:

$$\begin{cases} D = \int_0^\infty \rho_{eq}^{-1}(b)\, \frac{k^2}{M^2} P\, \delta x_0\, e^{L_b(t-\tau)}\, \delta x_0\, \rho_{eq}(b)\, d(t-\tau) \\ \beta = P \int_0^\infty \rho_{eq}^{-1}(b)\, \frac{k}{M}\, \delta x_0\, e^{L_b(t-\tau)}\, \frac{\partial}{\partial \delta x_0} \rho_{eq}\, d(t-\tau) \end{cases}$$

Some observations and discussion:

→ F.P.E. recovered in

→ weak interaction limit $\exp[\;] \approx 1$

→ Markovian limit

of non-Markovian master equation.
Indicates how incorporate/treat more complex physical problem

→ physical ideas:

$\omega_0^2 = \frac{k}{M} \ll \omega_i^2$ time scale separation only

→ major assumptions

$\left.\begin{array}{l} \text{- chaos / stocasticity} \\ \text{- "thermal flucth. analogy"} \end{array}\right\} \Rightarrow$ irreversibility

→ mathematically,

$$D_{eff} = \frac{k}{M} \Phi(0) \langle v^2 \rangle$$

$$\Phi(0) = \lim_{z \to 0} \int_0^\infty dz\, e^{-zt} \frac{\langle \delta x_0 \, \delta x_0(t) \rangle_{eq}}{\langle \delta x(0)^2 \rangle_{eq}}$$

i.e. Laplace transform of correlation function determines all

⇒ essence of memory kernel formalism!

- some questions:

→ what if we keep higher order stuff?

answer: D_{eff} will be renormalized

$$\frac{k}{M} \Phi(0) = \gamma_v \Rightarrow \gamma_v + \delta\gamma_v$$

↓
friction

i.e. consider simple case

$$\Phi(t) = \frac{\langle \delta x_0 \, \delta x_0(t) \rangle}{\langle \delta x_0^2 \rangle} = e^{-\gamma_c t}$$

↓
usual assumed form

.hen: → lowest order: $\gamma_v = \dfrac{k/M}{\gamma_c}$

→ $\Delta\gamma_v = \dfrac{(k/M)^2}{\gamma_c^3}$ ⇒ impact of stronger interactions

↱ h.o. in spring const.

etc.

essence is random coupling!

→ What's left out?

- time scale separation arbitrary ⇒ scaling, etc.
- essence of Zwanzig - Mori formalism is projection of fast variables onto ρ_{eq}

i.e. $$\rho = \rho_{eq}(b) \int db$$

but slow variables can induce adiabatic variation in fast variables

i.e. suggests back-track: instead of adiabatic elimination, allow adiabatic evolution of fast scales on slow time scale such that ρ 'near' ρ_{eq}

(i.e. for fast ρ_{eq} → fluid equations)