Notes 4

Master Equation

Models

→ Boltzmann Eqn.

- f, distribution fctn, for short range interaction in Hamiltonian system
- Transport Coeffs

→ Fluid Eqns.

- Moments of Boltzmann Eqns.
- Conservation Laws.

→ Langevin Eqn.

- Noisey mechanics, τ_c short

→ Fokker-Planck

- Markov Process ⇒ local scattering
- to pdf.

→ Master Equation

- General Transition in-out evolution of ρ
- Most general!

$\boxed{\text{F-P [illegible] Master}}$

→ Foundations of Master Eqn.

Recall C-K:

$$T_{\tau'+\tau}(y_3|y_1) = \int dy_2\, T_{\tau'}(y_3|y_2)\, T_\tau(y_2|y_1)\, dy_2$$

transition prob in $\tau'+\tau$

For small τ':

$$T_{\tau'}(y_3|y_2) = (\text{Prob. no transition})\, \delta(y_3-y_2)$$

$$+\ \tau' W(y_3|y_2)$$

Prob. $y_2 \to y_3$

obv. $W \geq 0$

Prob. (no transition) = 1 − Prob. (transition)

$$= 1 - \tau a_0$$

$$a_0 = \int dy_3\, W(y_3|y_2)$$

so, inserting into C-K Eqn.:

$$T_{\tau'+\tau}(y_3|y_1) = \left[1 - a_0(y_3)\tau'\right] T_\tau(y_3|y_1) + \tau' \int dy_2\, W(y_3|y_2)\, T_\tau(y_2|y_1)$$

expanding ; divide τ':

$$\cancel{T_\tau(y_3|y_1)} + \frac{\partial T_{\tau+\tau'}}{\partial t} = \cancel{T_\tau(y_3|y_1)} + \int dy_2\, W(y_3|y_2)\, T_\tau(y_2|y_1) - \int dy_2\, W(y_2|y_3)\, T_\tau(y_3|y_1)$$

$$\boxed{\frac{\partial T_{\tau+\tau'}}{\partial t} = \int dy_2 \left[W(y_3|y_2)\, T_\tau(y_2|y_1) - W(y_2|y_3)\, T_\tau(y_3|y_1) \right]}$$

→ Master Eqn !

~ <u>in</u> − <u>out</u>

Clearer to write with:

$$T_\tau(y_2|y_1) = P_1(y_2),$$

prob. of y_2 (started y_1)

so

$$\boxed{\frac{\partial}{\partial t} P(y,t) = \int dy' \left[\overset{①}{W(y|y') P(y',t)} - \underset{②}{W(y'|y) P(y,t)} \right]}$$

① → transitions in

② → transitions out

$P(y,0)$ — start at y at $t=0$

Can write in discrete form:

$$\frac{\partial p_n(t)}{\partial t} = \sum_{n'} \left[W_{nn'} P_{n'}(t) - W_{n'n} P_n(t) \right]$$

→ N.B.: $y' = y \pm \Delta y$ and expand $P(y', t)$ → F-P.

Master Eqn. is most general.

Simple example: Radioactive decay.

If γ is decay rate: then for N of emitters (really avg)

$$\frac{d}{dt} \langle N(t) \rangle = -\gamma \langle N(t) \rangle$$

$$\langle N(t) \rangle = N_0\, e^{-\gamma t}$$

Now, for Master Eqn. (micro-state n)

$$T_{\Delta t}(n|n') = n'\gamma\,\Delta t \quad , \quad n = n'-1$$

$$= 0 \quad , \quad n > n' \quad \text{(no gain)}$$

$$= o(\Delta t)^2 , \quad n < n'-1 \quad \text{(more than 1)}$$

so

$$W_{nn'} = \delta_{n,n'-1}\, \gamma n'$$

so

$$\dot{P}_n = \text{in} - \text{out}$$

$$= \underbrace{\gamma (n+1) P_{n+1}(t)}_{\text{in from } n+1} - \underbrace{\gamma n P_n(t)}_{\text{out, to } n-1}$$

→ Master Eqn.

→ $P_n(0) = \delta_{n,n_0}$

As for aggregation,

- consider total mass: (avg.)

$$\langle N \rangle = \sum_{n=0}^{\infty} n\, p_n$$

here N decays.

- now:

$$\sum_{n=0}^{\infty} n\, \dot{p}_n = \gamma \sum_{n=0}^{\infty} n(n+1)\, p_{n+1}$$

$$- \gamma \sum_{n=0}^{\infty} n^2 p_n$$

<u>shift</u>

$$= \gamma \sum_{n=0}^{\infty} (n-1) n\, p_n - \gamma \sum_n n^2 p_n$$

$$= -\gamma \sum_{n=0}^{\infty} n\, p_n$$

$$\frac{d}{dt} \langle N \rangle = -\gamma \langle N \rangle \qquad \text{etc.}$$

Some points:

- $W(y|y') = u(y)\,u(y')$ → Kangaroo process

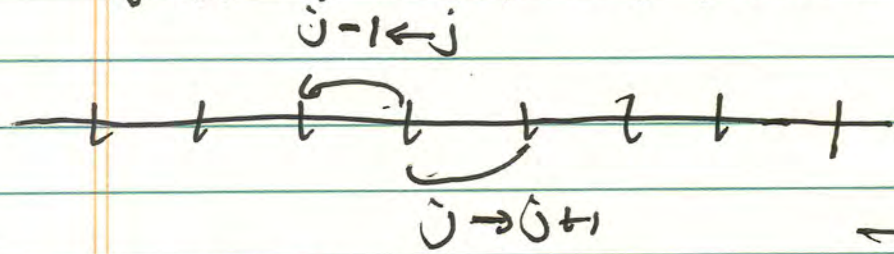
- $u(y) = \text{const}$ → Kubo-Anderson process,

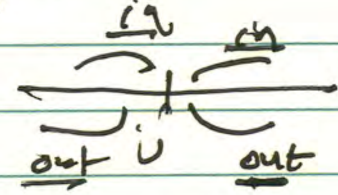
- expand $P(y, t)$ → F-P eqn.

etc.

More applications:

① - Random walk on lattice





so prob at j

$$\frac{d}{dt} P_j = \text{in} - \text{out}$$

$$= W\left(P_{j+1} - P_j\right) + W\left(P_{j-1} - P_j\right)$$

$$= W\left[\underbrace{P_{j+1}}_{\text{in from } j+1} + \underbrace{P_{j-1}}_{\text{in from } j-1}\right] - 2W\left[P_j\right]$$

out to $j-1$

out to $j+1$

so

$$\frac{d}{dt} P_j = w\left[P_{j+1} - P_j\right] + w\left[P_{j-1} - P_j\right]$$

$$\rightarrow \quad w \nabla^2 P$$

To solve:

- walker $t=0$ at $j=0$

prob j

F-T

- $g(\theta, t) = \sum_j P_j(t)\, e^{i\theta j}$

so

$$\frac{d}{dt} g(\theta, t) = -2w\,(1-\cos\theta)\, g(\theta, t)$$

so

$$g(\theta, t) = \exp\left[-2wt\,(1-\cos\theta)\right] g(\theta, 0)$$

$P_j(0) = \delta_{j,0} \rightarrow g(\theta, 0) = 1$

$$P_j(t) = \frac{1}{2\pi}\int_{-\pi}^{\pi} d\theta\, g(\theta, t)\, e^{-i\theta j}$$

(inversion)

Crank:

$$\begin{cases} P_j(t) = e^{-2\omega t} I_j(2\omega t) \\ I_j = \frac{1}{2\pi}\int_{-\pi}^{+\pi} d\theta \, \exp[z\cos\theta]\, e^{-i\theta j} \\ \Downarrow \\ \text{Bessel.} \end{cases}$$

② Kinetics → Bimolecular Reaction

$$A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} A + A$$

A — m molecules
B — n " "

- reaction ~~xxx~~ $A \to B$, $B \to A$

$$\begin{cases} n + m = N \\ \text{\# players conserved.} \end{cases}$$

- state $[m, n]$

transactions to nearest neighbors, only, so i.e.

$[m, n] \to [m+1, n-1]$ at k_1

$W(m, n \to m+1, n-1) = k_1 \, m \, \frac{n}{V}$

(B becomes A).

V → volume

$\sim k_1 \, m \, C(n)$

other way.

$W(m, n \to m-1, n+1) = k_2 \, m \, \frac{m}{V}$

(A becomes B)

$= k_2 \, m \, C(m)$

as always

$\frac{dP_m}{dt}$ = in from (adjoining) − out to adjoining

① = B to A (from m−1 A)

② A to B (from m+1 A)

③ − A becomes B (from A+B) — m A, n B

④ − A becomes B (from 2A) — m+1 A

$$\frac{dP_m}{dt} = \overset{(1)}{k_1 (m-1) \frac{(N-(m-1))}{V} P_{m-1}}$$

$$\overset{(2)}{+ k_2 \left(\frac{m+1}{V}\right)^2 P_{m+1}}$$

$$\overset{(3)}{- k_1 m \frac{(N-m)}{V} P_m} \quad \overset{(4)}{- k_2 m \frac{m}{V} P_m}$$

$$= \frac{k_1}{V} (m-1)(N+1-m) P_{m-1} - \frac{k_1 m}{V} (N-m) P_m$$

$$+ \frac{k_2}{V} (m+1)^2 P_{m+1} - \frac{k_2}{V} m^2 P_m$$

- Now, use concentration:

$$c = \frac{m}{V}, \qquad c_0 = \frac{N}{V}$$

$$P_m(t) = \underbrace{\rho}_{\to\ \mathrm{pdf}(c)}(c,t)$$

- Consider V large; expand

$$P_{m+1} \to P_m + \frac{1}{V} \frac{\partial \rho}{\partial c} \quad \Rightarrow \text{expand in } 1/V$$

→ heading to F-P → small fluctn.
Master Eqn.

Cranking (expand ρ_{m-1}, ρ_{m+1}) (drop $O(1/V)$ rel $O(1)$)

$$\frac{\partial \rho}{\partial t} = -\frac{\partial}{\partial c}\left(k_1 c(c_0 - c) - k_2 c^2\right)\rho$$

$$+ \frac{1}{2V}\frac{\partial^2}{\partial c^2}\left(k_1 c(c_0 - c) + k_2 c^2\right)\rho + \cdots$$

→ F-P!

$$\boxed{\frac{\partial \rho}{\partial t} = -\frac{\partial}{\partial c}\left\{ V(c)\rho - \frac{1}{2V}\frac{\partial}{\partial c} D(c)\rho \right\}}$$

$$V(c) = k_1 c(c_0 - c) - k_2 c^2$$

$$D(c) = k_1 c(c_0 - c) + k_2 c^2$$

if $V \to \infty$, noise (diffn) vanishes:

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial c}\left(V(c)\rho\right) = 0$$

so, for $\langle c \rangle$

$$\langle c \rangle = \int dc\, \mathcal{P}(c)\, c$$

$$\rightarrow \boxed{\frac{d\langle c\rangle}{dt} = V(c(t))}$$ ← concen. evol^n.

$$V(c) = k_1 c (c_0 - c) - k_2 c^2$$

$V=0$ $\quad k_1 \cancel{c} c_0 = (k_1+k_2)\, c^{\cancel{2}}$

$$c = (k_1+k_2)^{-1} k_1 c_0$$ fixed pt.

stability → linearize ✓.

– $\langle c \rangle$ broadened by finite V →
Diff^n enters.

→ Quantum Connection (recall FDT)

Master Eqn is 'naturally' amenable
to QM → discrete states.!

→ Pauli Master Eqn.:

Gain - Loss eqn. for probability of occupation of a state

$$\frac{d}{dt} P_m(t) = \underbrace{\sum_n W_{m,n} P_n(t)}_{\text{in from } n} - \underbrace{\sum_n W_{m,n} P_m(t)}_{\text{out from } m}$$

$$W_{m,n} = \frac{2\pi}{\hbar} \lambda^2 |V_{m,n}|^2 \delta(E_n - E_m)$$ → trans. probability

where: $H = H_0 + \lambda V$

$H_0 |m\rangle = E_m |m\rangle$

- $W_{m,n} = W_{n,m}$ (symmetry)

- transitions only for states $E_n \sim E_m$
~ (microcanonical character)

microscopic reversibility

→ What of Canonical? → weakly Couple system to a Heat Bath
~ (weakly).

→ relevant case for stat-mech.

Seek describe system coupled to bath
What is heat bath? — physically?

→ Heat Bath Master Equation

$$H = H_s + H_b + \lambda V$$

H_s ↓ system, H_b ↓ bath

[transitions in microstate of bath coupled to those in system

$H_s |m\rangle = E_m |m\rangle$ system

$H_b |\alpha\rangle = \epsilon_\alpha |\alpha\rangle$ bath

state → $|m\alpha\rangle$ — {state of system, bath

$$(H_s + H_b)|m\alpha\rangle = (E_m + \epsilon_\alpha)|m\alpha\rangle$$

∴, (microcanonical) Master Eqn:

$$\frac{d}{dt} P_{m\alpha} = \underbrace{\sum_{n,\beta} W_{m\alpha,n\beta} P_{n\beta}}_{\text{in}} - \underbrace{\sum_{n,\beta} W_{n\beta,m\alpha} P_{m\alpha}}_{\text{out}}$$

$$W_{m\alpha,n\beta} = \frac{2\pi}{\hbar} \lambda^2 |\langle m\alpha| V |n\beta\rangle|^2 \delta(E_n + \epsilon_\beta - E_m - \epsilon_\alpha)$$

Now, assume bath stays in thermal eqbrm at T, regardless of transitions

→ Factorize $P_{m\alpha}(t)$ → {statistical independence bath, system

$P_{m\alpha}(t) \cong P_m(t)\, \rho_\alpha$ (as for FDT)

→ subst.; $\sum_\alpha$

$$\sum_\alpha \frac{d}{dt} P_m(t)\, \rho_\alpha = \frac{d}{dt} P_m(t) =$$

$$= \sum_n \sum_\alpha \sum_\beta W_{m\alpha, n\beta}\, \rho_\beta\, P_n - \sum_n \sum_\alpha \sum_\beta W_{n\beta, m\alpha}\, \rho_\alpha\, P_m$$

$$\boxed{\frac{dP_m}{dt} = \sum_n w_{mn} P_n - \sum_n w_{nm} P_m}$$

where:

$$w_{mn} = \sum_\alpha \sum_\beta W_{m\alpha, n\beta}\, \rho_\beta$$

$$w_{nm} = \sum_\alpha \sum_\beta W_{n\beta, m\alpha}\, \rho_\alpha$$

system transition weights.

$\rightarrow$ describes relaxation $\overset{P_m(t)}{\uparrow}$ to eqbrm to P_m (eq) at T_{bath}

$\rightarrow$ $W_{m,n} \neq W_{n,m}$

$w_\alpha \rho_\alpha = W_{m,n} e^{-\frac{E_\alpha}{T}}$

$w_\beta \rho_\beta = W_{n,m} e^{-\frac{E_\beta}{T}}$

$\rightarrow$ $\rho_\alpha \sim \exp[-\epsilon_\alpha / T]$

$\epsilon_\alpha - \epsilon_\beta = E_m - E_n$

so using $E_n + \epsilon_\beta = E_m + \epsilon_\alpha$

$$W_{m,n} \exp[-E_n / T] = W_{n,m} \exp[-E_m / T]$$

$\rightarrow$ detailed balance:

$\left(\underset{\text{trans. prob}}{\text{Forward}}\right)\left(\underset{\text{weighting}}{\text{prob initial}}\right) = \left(\text{Backward}\right)\left(\text{prob. final}\right)$

trans

back

weighting

→ Illustrative Example re: Heat Bath Master Eqn.

Consider: $\lambda V = F(\text{system})\,G(\text{bath})$

i.e. interaction factorizes

then

$$V_{m\alpha,n\beta} = F_{mn}\,G_{\alpha\beta}$$

so

sum over bath states

$$W_{m,n} = \frac{2\pi}{\hbar}\,|F_{mn}|^2 \sum_\alpha \sum_\beta \delta(E_m - E_n + \epsilon_\alpha - \epsilon_\beta)\,*\,|G_{\alpha,\beta}|^2 \rho_\beta$$

thermally avgd transition rate

recall FDT

Can re-write, using integral rep. of delta fctn:

energy dif ~ $E_m - E_n$

$$W_{m,n} = \frac{1}{\hbar^2}\,|F_{m,n}|^2 \int_{-\infty}^{+\infty} dt\; e^{i\omega_{mn}t}\; *$$

$$\sum_\alpha \sum_\beta e^{\frac{it}{\hbar}\epsilon_\alpha} G_{\alpha,\beta}\, e^{-\frac{it}{\hbar}\epsilon_\beta}\, G_{\beta,\alpha}\, \rho_\beta$$

then, Heisenberg ⇒

$$\left(G(t)\right)_{\alpha,\beta} = \exp\left[\frac{it}{\hbar} E_\alpha\right] G_{\alpha,\beta} \exp\left[\frac{-it}{\hbar} E_\beta\right]$$

comm.

$$\boxed{w_{m,n} = \left|\frac{F_{m,n}}{\hbar^2}\right|^2 \int_{-\infty}^{+\infty} dt\, e^{i\omega_{mn} t} \langle G(0)\, G(t)\rangle_{eq}}$$

i.e. $\sum_\alpha \rightarrow \left[G(0)\, G(t)\right]_{\beta\beta}$

$\sum_\beta$, with $\rho_\beta \rightarrow \langle \quad \rangle$.

transition probability ~ F.T. of Correlation.

Specific example:

Consider now: Harmonic oscillator heat bath

[recover Langevin eqn. ?]

what is it?

→ system: x, p

→ bath: bunch h.o. $\{p_j\}$, $\{q_j\}$

system   bath

So $\Rightarrow H = H_S + H_B$

bath → many d.o.f.

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

$$H_B = \sum_j \frac{p_j^2}{2} + \frac{1}{2}\omega_j^2\left(q_j - \frac{\gamma_j}{\omega_j^2}x\right)^2$$

coupling to system

$$= \sum_j \left(\frac{p_j^2}{2} + \frac{1}{2}\omega_j^2 q_j^2\right) - x\sum_j \frac{\gamma_j \cancel{\omega_j^2}}{\cancel{\omega_j^2}} q_j$$

osc.   bilinear coupling

$$+ \left(\sum_j \frac{\gamma_j^2}{2\omega_j^2}\right)x^2$$

add to $U(x)$.

TBC.

Now, for EOM's:

N.B. Heat bath → thermal noise.
So heat bath should yield a Langevin Eqn.

$$\frac{dx}{dt} = \frac{p}{m}$$

$$\frac{dp}{dt} = -\frac{dU}{dx} + \sum_j \gamma_j \left(q_j - \frac{\gamma_j}{\omega_j^2} x \right)$$

$$\frac{dq_j}{dt} = p_j$$

$$\frac{dp_j}{dt} = -\omega_j^2 q_j + \gamma_j x$$

Now (tacitly taking x as adiabatic)
so solving for q_j in terms x:

$$\frac{d^2 q_j}{dt^2} = \dot{p}_j = -\omega_j^2 q_j + \gamma_j \dot{x}$$

$$\frac{d^2 q_j}{dt^2} + \omega_j^2 q_j = \gamma_j \dot{x}$$

$\Rightarrow$ usual ...

$$q_j(t) = q_j(0) \cos \omega_j t + p_j(0) \frac{\sin \omega_j (t)}{\omega_j}$$
$$+ \gamma_j \int_0^t ds \, x(s) \frac{\sin \omega_j (t-s)}{\omega_j}$$

so, for x, p : i.e.,

$$q_j(t) - \frac{\gamma_j}{\omega_j^2} x(t) = \left(q_j(0) - \frac{\gamma_j}{\omega_j^2} x(0)\right) \cos\omega_j t$$

$$+ p_j(0) \frac{\sin\omega_j t}{\omega_j} - \gamma_j \int_0^t ds \, \frac{p(s)}{m} \, \frac{\cos\omega_j (t-s)}{\omega_j^2}$$

now

$$\frac{dp}{dt} = -U'(x) + \sum_j \gamma_j \left(q_j - \frac{\gamma_j}{\omega_j^2} x\right)$$

$\Rightarrow$

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

noise

memory fctn (drag, but depends on time history)

where,

$$K(t) = \cancel{[illegible]}$$

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

$$F_p(t) = \sum_j \gamma_j \, p_j(0) \, \frac{\sin \omega_j t}{\omega_j}$$

noise

$$+ \sum_j \gamma_j \left(q_j(0) - \frac{\gamma_j}{\omega_j^2} X(0) \right) \cos \omega_j t$$

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

$$\frac{dp}{dt} = -U' - \gamma p + \tilde{F}$$

Now, can reduce/simplify memory fctn:

- continuous spectrum, $\sum_j \to \int d\omega \, g(\omega)$

density states

- $\gamma = \gamma(\omega)$

$$K(t) = \int_0^\infty d\omega \, g(\omega) \, \frac{\gamma(\omega)^2}{\omega^2} \cos \omega t$$

N.B. $g \sim \omega^2$, $\gamma \sim$ const.

$K(t) = \delta(t)$

$\to$ ok! Stokes

Note:

$$K(t) = \int_0^\infty d\omega\, g(\omega) \frac{\gamma^2(\omega)}{\omega^2} \cos\omega t$$

width $g(\omega) \to$ memory time

$$g(\omega) = \frac{g_0}{\omega_0^{2\alpha}} \Big/ \left[(\omega-\omega_0)^2 + (\Delta\omega)^2\right]^\alpha$$

$K(t) \sim e^{-\Delta\omega |t|}$ $\Rightarrow$ bandwidth of oscillator bath sets memory time.

For noise F_p:

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

~ sum many modes

~ treat by Central Limit thm.

→ simple stat. properties.

$$f_{eq}(p, q) = \exp(-H_B/T)$$

$$\left\langle \left(q_j(0) - \frac{\gamma_j}{\omega_j^2} x(0) \right)^2 \right\rangle = \frac{T}{\omega_j^2}$$

$$\langle p_j(0)^2 \rangle = T$$

and can show:

$$\langle F_p(t) F_p(t') \rangle = T K(t-t')$$

Now, returning to heat bath issue:

Recall: $V = F G$

$$H_B = \sum_j \left[\frac{p_j^2}{2} + \frac{1}{2} \omega_j^2 \left(q_j - \frac{\gamma}{\omega_j^2} x \right)^2 \right]$$

$$F = x$$

$$G = -\sum_j \gamma_j q_j$$

$\underline{\text{so}}$

$$\langle G(0)G(t)\rangle_{eq} = \sum_j \gamma_j^2 \cos(\omega_j t)\, \langle q_j^2\rangle_{eq} + \sum_j \frac{\gamma_j^2}{\omega_j} \sin(\omega_j t)\, \langle p_j q_j\rangle_{eq}.$$

For classical bath

$$\langle G(0)\, G(t)\rangle_{eq} = T \sum_j \frac{\gamma_j^2}{\omega_j^2} \cos \omega_j (t)$$

$$= T\, K(t)$$

memory.

For $K(t) = 2\gamma\,\delta(t)$

$$W_{m,n} = \frac{|F_{m,n}|^2}{\hbar^2} \int_{-\infty}^{+\infty} dt\, \exp(i\omega_{mn} t)\, \langle G(0) G(t)\rangle_{eq}$$

$$= \frac{T\gamma}{\hbar^2} |F_{m,n}|^2$$