Physics 210B

→ Kinetics and Kinetic Equations

Classical Mechanics – Hamiltonian (includes chaos)

↓

Liouville Equation → { Kubo Formalism ↓ Transport

stochastic

BBGKY (diluteness)

↓

Boltzmann Eqn – H Thm

↓

Transport Coeff

↓

Hydrodynamics (lmfp short)

↓

[ Flux-Gradient Rel'n.
Onsager Symmetry

↓

Vlasov Eqn. (lmfp long)

↓

Landau Problem

↓

Quasilinear Mean Field

Chapman-Kolmogorov

↓

* $\boxed{\text{Master Equation (Aggregation)}}$ *

↓

[ Fokker-Planck ↔ { Levy Dist
Central Limit Thm
Brownian Motion (FDT)

↓

[ Brownian Motion Appl.
Sedimentation
Kramers Problem (tbc)
Resonant MF Quasilinear

→ Master Equation

→ van Kampen: "The Master equation is an equivalent form of the Chapman-Kolmogorov equation for Markov processes (i.e. stochastic process with $\tau_{mem} \to 0$), but it is easier to handle and more directly related to physical concepts."

→ Differential form of Chapman-Kolmogorov Eqn., valid for stationary Markov process

$$\frac{\partial P}{\partial t} = \underbrace{\text{in}}_{\text{sum}} - \text{out} \qquad P = \underset{\text{prob. at } y \text{ at } t}{P(y,t)}$$

$$= \int dy' \Big\{ \underbrace{\underbrace{W(y|y')}_{\substack{\text{transition prob} \\ y' \to y}} \underbrace{P(y',t)}_{\text{prob } y'}}_{\text{input}} - \underbrace{\underbrace{W(y'|y)}_{\substack{\text{transition prob.} \\ y \to y'}} \underbrace{P(y,t)}_{\text{prob } y}}_{\text{loss.}} \Big\}$$

(self-evident)

Can write in discrete form:

$$\frac{dP_n(t)}{dt} = \sum_{n'} \left[ W_{n,n'} P_{n'}(t) - W_{n',n} P_n(t) \right]$$

"The Master equation is a gain-loss equation for the probability of each step $n$."

- quantum compatible: i.e.

$$W_{n,n'} = \frac{2\pi}{\hbar} |\tilde{H}_{I\,n,n'}|^2 \rho(E_n)$$

(c.f. Fermi Golden rule)

- all content is in transition probabilities

- $W_{n,n'} \geq 0$.

- by: Nordsieck, Lamb, Uhlenbeck '40

→ Key point:

- Fokker-Planck is small increment (state variable, time) of Master Eqn.

- Master equation is more general than Fokker-Planck.

→ <u>Derivation</u>

- Recall Chapman-Kolmogorov:

$$P(y_3, t_3 | y_1, t_1) = \int dy_2 \, P(y_3, t_3 | y_2, t_2) \, P(y_2, t_2 | y_1, t_1)$$

(understood times <u>ordered</u>)

- For <u>stationary</u> Markov processes:

$$P(y_2, t_2 | y_1, t_1) = T_\tau(y_2 | y_1) \qquad \tau = t_2 - t_1$$

so C-K eqn:

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

i.e. matrix product

$$T_{\tau+\tau'} = T_{\tau'} T_\tau$$

then consider small $\tau'$:

system fixed, already at 3

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

short time expansion

Now: Prob. (no transition)

$$= 1 - \text{Prob. (transition)}$$

$$\text{Prob. (transition)} = \tau' a_0$$

$$a_0 = \int dy_2\, W(y_3|y_2)$$

So plugging into C-K:

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

$$= (1 - a_0 \tau')\, T_\tau(y_3|y_1)$$
$$+ \tau' \int dy_2\, W(y_3|y_2)\, T_\tau(y_2|y_1)$$

$$a_0 = a_0(y_3)$$

Expand:

$$\cancel{T_\tau} + \lambda^{-1}\frac{\partial T}{\partial t} = \overset{(1)}{\cancel{T_\tau(y_3|y_1)}}$$
$$+ \lambda^{-1}\int dy_2\, W(y_3|y_2)\, T_\tau(y_2|y_1)$$
$$- \lambda^{-1}\int dy_2\, W(y_2|y_3)\, T_\tau(y_3|y_1)$$

$$\frac{\partial T}{\partial t} = \int dy_2 \Big[ W(y_3|y_2)\, T_\tau(y_2|y_1) - W(y_2|y_3)\, T_\tau(y_3|y_1) \Big]$$

~ in − out

Clearer to write as:

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

prob of $y = y_2$, starting from $y_1$

$\Rightarrow$

$$\frac{\partial}{\partial t}\underbrace{P(y)}_{P(y,t)} = \int dy' \Big[ \overset{\text{in}}{W(y|y')\, P(y',t)} - \underset{\text{out}}{W(y'|y)\, P(y,t)} \Big]$$

so have Master Equation:

$$\boxed{\partial_t P(y,t) = \int dy' \left[ W(y|y') P(y',t) - W(y'|y) P(y,t) \right]}$$

and can have discrete version, as well:

$$\boxed{\frac{\partial}{\partial t} P_n(t) = \sum_{n'} W_{n,n'} P_{n'}(t) - W_{n',n} P_n(t)}$$

→ Master is general equation.
Small step time $\tau$, but arbitrary step size

→ to reduce to Fokker-Planck, consider Master in limit of small jumps:

i.e.

$$W(y|y') = W(y', r) \sim$$ fctn of starting point $y'$ and step $r$

$$\underbrace{r = y - y'}_{\text{"small"}}$$

$$y' = y - r$$ ⇒ 1 step away

then,

$$\frac{\partial P(y,t)}{\partial t} = \int dr \Big[ \overset{W(y|y')}{\overset{\downarrow}{W(y-r,r)}} P(y-r,t) - P(y,t) \int dr \underset{W(y'|y)}{\underset{\Downarrow}{W(y,-r)}} \Big]$$

in

out

i.e. small jumps

And, expand: ($P$ smooth) (Roughness → Levy)

$$\frac{\partial P(y,t)}{\partial t} = \int dr\, W(y,r)\, P(y,t)$$

$$- \int r\, dr\, \frac{\partial}{\partial y}\left[W(y,r)\, P(y,t)\right]$$

$$+ \frac{1}{2}\int r^2 dr\, \frac{\partial^2}{\partial y^2}\left[W(y,r)\, P(y,t)\right]$$

$$- P(y,t) \int W(y,-r)\, dr$$

$$= -\frac{\partial}{\partial y}\left[\left(\int dr\, r\, W(y,r)\right) P(y,t)\right]$$

$$+ \frac{\partial^2}{\partial y^2}\left[\left[\int dr\, \frac{r^2}{2}\, W(y,r)\right] P(y,t)\right]$$

then;

$$\frac{\partial}{\partial t} P(y,t) = -\frac{\partial}{\partial y}\left[\underbrace{V(y)\, P(y,t)}_{\text{drift}} - \frac{\partial}{\partial y}\underbrace{D(y)\, P(y,t)}_{\text{Diffusion}}\right]$$

$$\boxed{\begin{aligned} V(y) &= \int dr\; r\, W(y,r) \\ D(y) &= \int dr\; \frac{r^2}{2}\, W(y,r) \end{aligned}}$$

→ recovers Fokker-Planck Eqn. from limiting form of Master Eqn.

Examples

→ Easy : Radioactive Decay

All know for $N \gg 1$ emitters (i.e. $N \gg 1$, $N \sim \langle N \rangle$), then

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

$$\langle N(t)\rangle = N_0 \exp(-\gamma t)$$

Calculate $P(n,t) \equiv$ time evolution of pdf of emitters ?!

Now, Master Eqn. $\Rightarrow$

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

Decay $\rightarrow$ lose emitters progressively

$T_{\Delta t}(n'|n) \equiv$ prob. jump $n' \rightarrow n$ in $\Delta t$

$= n' \gamma \Delta t$ , $n = n'-1$

$= 0$ $n > n'$ (no gaining)

$= O(\Delta t^2)$ , $n < n'-1$ (more than 1 $\rightarrow$ more than 1 step)

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

Then,

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

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

$\rightsquigarrow$ Master Equation

$$P_n(0) = \delta_{n,n_0}$$

$$\boxed{\dot{P}_n = \gamma(n+1)\, P_{n+1}(t) - \gamma n\, P_n(t)}$$

Can write solution:

$w(t) = e^{-\gamma t}$ → probability of 1 emitter to survive at $t$

$$\boxed{P(n,t) = \underbrace{\binom{n_0}{n}}_{\text{binomial coeff.}} w^n (1-w)^{n_0-n}}$$

For mean (i.e. familiar formula):

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

so $n$ * Master equation and sum:

$$\sum_{n=0}^{\infty} n \dot{P}_n = \sum_{n=0}^{\infty} \gamma\, n(n+1)\, P_{n+1} - \gamma \sum_n n^2 P_n$$

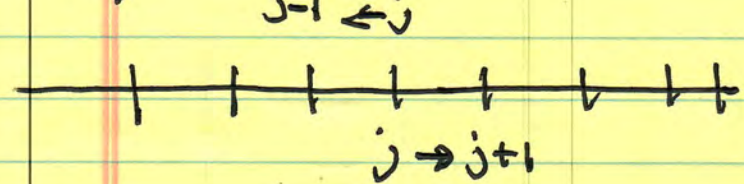
$$= \gamma \sum_{n=0}^{\infty} (n-1) n\, P_n - \gamma \sum_n n^2 P_n$$

$$= -\gamma \sum_n n P_n$$

so $$\boxed{\frac{d}{dt}\langle N \rangle = -\gamma \langle N \rangle}$$

exponential decay of mean.

→ Easy: Random Walk on Lattice




$$W \equiv \text{step probability} / \Delta t$$

$$\frac{\partial P_j}{\partial t} = \text{in} - \text{out}$$

$$= \underbrace{w\left(P_{j+1} + P_{j-1}\right)}_{\text{in}} - 2wP_j \quad \begin{cases} \text{out to } j-1 \\ \text{out to } j+1 \end{cases}$$

$$= w\left[P_{j+1} - 2P_j + P_{j-1}\right]$$

$$= w\nabla^2 P \qquad \text{i.e. diffusion!}$$

To solve: transform;

$$g(\theta,t) \equiv \sum_j P_j(t)\, e^{i\theta j} \qquad \text{subst,}$$

⇒

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

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

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

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

(inversion)

$\Rightarrow$

$$P_j(t) = e^{-2wt}\, I_j(2wt)$$

$$I_j = \frac{1}{2\pi}\int_{-\pi}^{\pi} d\theta\, \exp\left[z\cos\theta\right] e^{-i\theta j}$$

Bessel Fctn.

3) Medium: Kinetics of Bimolecular Reaction.

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

$k_1, k_2$ rate constants for reaction, each way.

→ Counting

A – m molecules
B – n molecules

Reaction → $A+B \to A+A$ i.e. $B \to A$
$A+A \to A+B$ i.e. $A \to B$

so $n+m = N$, const.

state $[m, n]$

→ Transitions

Transitions are to nearest neighbors, only, so:

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

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

(B becomes A)

↳ volume avg

$\sim k\, m\, c(n)$

↓

concentration

and reverse:

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

(A becomes B)

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

as always:

$$\frac{dP_m}{dt} = \underset{\text{(from adjoining)}}{\text{in}} \quad \underset{\text{(to adjoining)}}{-\text{out}}$$

= B to A ① (from m-1 A)
A to B ② (from m+1 A)

− A becomes B ③ (from A+B) → m A, n B

− A becomes B ④ (from 2 A) → m+1 A

so

$$\frac{dP_m}{dt} = \overset{①}{k_1 (m-1) \frac{(N-(m-1))}{V} P_{m-1}} + \overset{②}{k_2 \frac{(m+1)^2}{V} P_{m+1}}$$

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

so

$$\boxed{\begin{aligned}\frac{dP_m}{dt} &= \frac{k_1}{V}(m-1)(N+1-m)P_{m-1} - \frac{k_1}{V}m(N-m)P_m \\ &+ \frac{k_2}{V}(m+1)^2 P_{m+1} - \frac{k_2}{V}m^2 P_m\end{aligned}}$$

in from $m \pm 1$.

Master Eqn.

out from $m$.

→ Express as concentration...

$c = m/V$
$c_0 = N/V$

$P_m(t) = \rho(c, t)$
↳ pdf of $c$

And consider $V$ large (~~to~~ noise small)

i.e. $P_{m+1} \to P_m + \frac{1}{V}\frac{\partial \rho}{\partial c}$

→ Where is this going?

→ Fokker-Planck Equation in Concentration

i.e. expand $P_{m+1}$, $P_{m-1}$

drop $1/V^2$

→ crank: index V – drift / Flow

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial c}\Big( \big(k_1 c (c_0 - c) - k_2 c^2\big) P$$

$$+ \frac{1}{2V} \frac{\partial^2}{\partial c^2} \underbrace{\big(k_1 c (c_0 - c) + k_2 c^2\big)}_{>0} P \Big)$$

Diffusion (>0)

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

↳ diffusion vanishes as $V \to \infty$

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

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

[similar to multiplicative noise

→ Now, for $V \to \infty$, noise (diffusion) vanishes, so

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

so, for $\langle c \rangle$

$$\langle c \rangle = \int dc\, \rho(c)\, c$$

⇒

$$\frac{d\langle c \rangle}{dt} = v(\langle c \rangle) \qquad \text{for, } \tilde{\sigma}^2 \to 0$$

$$v(c) = k_1 c\,(c_0 - c) - k_2 c^2$$

$$\langle c \rangle \Big|_{\substack{\text{fixed} \\ \text{pt}}} = k_1 c_0 / (k_1 + k_2)$$

and linearize for stability, etc.

→ Broadened by diffusion.....