Physics 210B

→ Kinetics and Kinetic Equations

Classical Mechanics - Hamiltonian
  (includes others)

Liouville Equation → [Kubo Formalism]

Stochastic Transport

Chapman-Enskog

Master Equation (Aggregation)

[*]

Fokker-Planck → [Levy]

Central Limit Thm (Dist)

Brownian Motion (FDT)

Brownian Motion Appl.

Sedimentation

Kinematic Problem (Hoc)

Resonant MF Quasilinear

Quasilinear Mean Field
Master Equation

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

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

\[
\begin{align*}
\frac{dp}{dt} &= \text{in} - \text{out} \\
&= \sum_{y} p(x) \mathbb{P}(x \to y) - \sum_{y} p(y) \mathbb{P}(y \to x) \\
&= \sum_{y} \left( w(x | y') \mathbb{P}(x | y') - w(y' | y) \mathbb{P}(y | y') \right)
\end{align*}
\]

(specific)

(by definition)

(input)

(loss)
Can write in discrete form:

$$\frac{dP_n(t)}{dt} = \sum_n \left[ \frac{\Delta n}{n!} \right] \left[ W_{n' n}(t) - W_{n n}(t) \right]$$

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

- Quantum compatible: i.e.

$$W_{n' n} = \frac{2\pi \hbar}{\hbar^2} \frac{n!}{n'!} \langle \mathcal{E} \rangle$$

(e.g. Fermi's Golden rule)

- All content is in transition probabilities

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

- by: Nordsieck, Lamb, Uhlenbeck '40

- Key point:

- Forster-Planck is small increment (state variable time) of Master Eqn.
Master equation is more general than Fokker-Planck.

**Derivation**

- Recall Chapman-Kolmogorov:
  \[ P(y_2, t_2 | y_1, t_1) = \int dy_3 P(y_2, t_2 | y_3, t_2) \cdot P(y_3, t_2 | y_1, t_1) \]
  (understood times ordered)

- For stationary Markov processes:
  \[ P(y_2, t_2 | y_1, t_1) = T_r(y_2 | y_1) \quad r = t_2 - t_1 \]

So G-h eqn:

\[ T_{r + r_1} = \int dy_2 T_r(y_3 | y_2) T_{r_1}(y_2 | y_1) \]

d e. matrix product

\[ T_{r + r_1} = T_r \cdot T_{r_1} \]

then consider small \( r_1 \):
system fixed, already at $3$

$$T_{x_1}(y_3|y_2) = (\text{Prob. no transition}) \delta(y_3 - y_1)$$

$$+ \tau^i W(y_3|y_2)$$

*Short time expression*

Now: $\text{Prob. (no transition)}$

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

$$\text{Prob. (transition)} = \tau^0 a_0$$

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

so plugging into $G$: $C$-$h$

$$T_{x_1} = \int dy_2 \left[ (1 - a_0 \tau^i) \delta(y_3 - y_2) T_{x_1}(y_3|y_1) ight.$$ 

$$+ \tau^i \int dy_2 W(y_3|y_2) T_{x_1}(y_3|y_1) \right]$$

$$= (1 - a_0 \tau^i) T_{x_1}(y_3|y_1)$$

$$+ \tau^i \int dy_2 W(y_3|y_2) T_{x_1}(y_3|y_1)$$

$$a_0 = a_0 (y_3)$$
Expand:

\[
\begin{align*}
T_\infty + \frac{d}{dt} T_{i0} &= T_{\infty}(y_2, y_1) \\
&+ \int \delta y_2 \, w(y_2, y_3) \, T_{\infty}(y_2, y_1) \\
&- \int \delta y_2 \, w(y_2, y_3) \, T_{\infty}(y_3, y_1) \\
\end{align*}
\]

\[
\frac{d}{dt} T_{i0} = \int \delta y_2 \left[ w(y_2, y_3) \, T_{\infty}(y_2, y_1) \\
- w(y_2, y_3) \, T_{\infty}(y_3, y_1) \right]
\]

- in - out

Clearer to write as:

\[
T_{\infty}(y_2, y_1) = P(y_2)
\]

Prob of \( y = y_2 \), starts from \( y \)

\[
\begin{align*}
& P(y) = \int \delta y_2 \left[ w(y, y_1) \, P(y, y_1) \\
&- w(y, y_1) \, P(y, y_1) \right]
\end{align*}
\]
so have Master Equation:

\[
\frac{\partial}{\partial t} P(x, t) = \int dy' \left[ \lambda(y') P(y', t) 
- w(y|y') P(y, t) \right]
\]

and can have discrete version, as well:

\[
\frac{\partial}{\partial t} \bar{P}(n, t) = \sum_{n'} \lambda(n, n') \bar{P}(n, t) - \sum_{n'} \lambda(n', n) \bar{P}(n', t)
\]

→ Master of general equation.
Small step time \( \tau \), but arbitrary step size.

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

\[
w(y|y') = w(y', n) \sim \text{Pert of starting point } y
\]

\[
r = \frac{y - y'}{|y - y'|} \quad \text{"small"
}
\]

\[y_1 = y - n \quad \text{ if step away} \]
Then,

\[ \phi_{y}(x, t) = \sum \left[ w(y - s, r) \right] \rho_{y}(s, t) - \rho_{y}(x) \sum w(y, r) \right] \]

\[ w(y, y) \]

d.e. small jumps

And, expand:  

(φ smooth)  

(Roughness \Rightarrow Levy)

\[ \phi_{x}(x, t) = \sum \left[ w(y, r) \right] \rho_{y}(y, t) - \int \rho_{y}(y, t) \frac{\partial}{\partial y} \left[ w(y, r) \right] \phi_{y}(x, t) \]

\[ + \frac{1}{2} \int \rho_{y}(y, t) \frac{\partial^{2}}{\partial y^{2}} \left[ w(y, r) \right] \phi_{y}(x, t) \]

\[ - \rho_{y}(y, t) \int w(y, r) \phi_{y}(x, t) \, dr \]

\[ = - \rho_{y}(y, t) \left[ \int \left( \sum w(y, r) \right) \phi_{y}(x, t) \right] \]

\[ + \frac{3}{2} \frac{\partial^{3}}{\partial y^{3}} \left[ \int \rho_{y} \frac{1}{2} w(y, r) \phi_{y}(x, t) \right] \]
\[
\frac{d}{dt} P(x,t) = \frac{d}{dy} \left[ \varphi(y) P(x,t) - \int_{-\infty}^{\infty} \frac{1}{\sigma} \varphi(y) P(x,t) dy \right]
\]

\[
\varphi(y) = \int_{-\infty}^{\infty} \delta(x) w(x,y) dx
\]

\[
\sigma(y) = \int_{-\infty}^{\infty} \frac{r^2}{2} w(x,y) dx
\]

→ recovering Fokker-Planck Eqn. From limiting form of Master Eqn.

Example:

→ Easy: Radioactive Decay

All known 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 $P(n, t)$, the time evolution of the PDF of emitters.

Now, Master Eqn.

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

Decay → lose emitters progressively

$$T_{n'}(n'/n) = \text{prob. jump } n' \rightarrow n \text{ in } \Delta t$$

$$= n' \times \Delta t, \quad n = n' - 1$$

$$= 0, \quad n > n'$$

(no gain)

$$= 0 (\Delta t^2), \quad n < n' - 1$$

(more than 1 step)

$$W_{n, n'} = s_{n, n'-1} \times n'!$$
Then
\[ P_n = cn \text{ out} \]
\[ = \gamma (n+1) P_{n+1} \text{ in} - \gamma n P_n \text{ out} \]
\[ \text{cn from n+1 out to n}\]
\[ \sim \text{ Master Equation} \]
\[ P_n (t) = \sum_{j=0}^{n} n_j n_0 \]
\[ \dot{P}_n = \gamma (n+1) P_{n+1} (t) - \gamma n P_n (t) \]

Can write solution:
\[ w(t) = e^{-x} \text{ of a emitter} \rightarrow \text{probability to survive at } t \]
\[ \mathcal{P}(n, t) = \frac{n!}{n^0} w^{n-n} e^{-w} \]
\[ \text{binomial coeff.} \]
For mean (i.e. familiar formula):

\[ \langle N \rangle = \sum_{n=0}^{\infty} n \rho_n \]

So \( N \times \) Master equation and sum:

\[ \sum_{n=0}^{\infty} n \dot{\rho}_n = \sum_{n=0}^{\infty} \gamma n (n+1) \rho_{n+1} \]

\[ = \gamma \sum_{n=0}^{\infty} (n+1) n \rho_n \]

\[ = \gamma \sum_{n=0}^{\infty} n^2 \rho_n \]

\[ = -\gamma \sum_{n=0}^{\infty} n \rho_n \]

\[ \frac{d}{dt} \langle N \rangle = -\gamma \langle N \rangle \]

Exponential decay of mean.
Easy: Random Walk on Lattice

\[ j \rightarrow j+1 \]

\[ W \in \text{step probability} / \Delta t \]

\[
\frac{dP_j}{dt} = \text{in} - \text{out} \\
= w (P_{j+1} + P_{j-1}) - 2w P_j + \text{out to } j+1 - \text{out to } j-1 \\
= w \left[ P_{j+1} - 2P_j + P_{j-1} \right] \\
= w \Delta^2 P \\
\text{i.e. diffusion} \]

To solve: transform

\[ g(\theta_{t+1}) = \sum_j P_j (\theta_t e^{i\theta_j}) \]

\[
\frac{d}{dt} g(\theta_{t+1}) = -2w (1 - \cos \theta) g(\theta_{t+1})
\]
\[ g(\theta,t) = \exp \left[ -2\omega t \mu(\cos \theta) \right] g(\theta,0) \]

Now \( p_j(\bar{\theta}) = c_{j,0} \Rightarrow g(\bar{\theta},0) = 1 \)

\[ p_j(\bar{\theta}) = \frac{1}{2\pi} \int_{-\pi}^{\pi} g(\bar{\theta},\bar{\theta}) e^{-i\bar{\theta} \bar{\tau}} \, d\bar{\theta} \]  

(circular)

\[ p_j(\bar{\theta}) = e^{-2\omega t} \int_{-\pi}^{\pi} g_j(2\omega t) \, d\bar{\theta} \]

\[ I_j = \frac{i}{2\pi} \int_{-\pi}^{\pi} \exp \left[ 2i \cos \theta \right] e^{-i\bar{\theta} \bar{\tau}} \, d\bar{\theta} \]

Bernoulli Eqn.

3) Medium: Kinetics of Bimolecular Reaction

\[ A + B \rightarrow A + A \]

\[ k_1, k_2 \, \text{rate constants for reaction, each way.} \]
Counting

\[ A - m \text{ molecules} \]
\[ B - n \text{ molecules} \]

Reaction \[ \rightarrow A + B \rightarrow A + A \quad \text{i.e.} \quad B \rightarrow A \]
\[ A + A \rightarrow A + B \quad \text{i.e.} \quad A \rightarrow B \]

So \[ n + m = N, \text{ const.} \]

State \[ [m, n] \]

Transitions

Transitions are to nearest neighbors only, so:

\[ [m, n] \rightarrow [m+1, n-1] \quad \text{at} \quad k_1 \]

with

\[ W(m, n \rightarrow m+1, n-1) = k \frac{m! n!}{V} \]

(B becomes A)

& volume avg

\[ \sim k_1 m \text{ C(n)} \]

& concentration
and reverse:

\[ W(m, n \rightarrow m-1, n+1) = k_2 \frac{m}{v} m \]

(A becomes B) \[ = k_2 m \cdot \text{C(m)} \]

as always:

\[ \frac{dP_m}{dt} = \text{in} - \text{out} \]

(from adjoining) (to adjoining)

\[ = B \rightarrow A \quad \text{(from } m-1 \text{ A}) \]

\[ A \rightarrow B \quad \text{(from } m+1 \text{ A)} \]

\[ = A \text{ becomes } B \quad \text{(from } A+B) \Rightarrow MA \cap B \]

\[ = A \text{ becomes } B \quad \text{(from } 2A) \Rightarrow m+1 A \]

\[ \frac{dP_m}{dt} = \frac{k_1 (m-1) (N-(m-1)) P_{m-1}}{v} + \frac{k_2 (m+1)^2 P_{m+1}}{v} \]

\[ - \frac{k_1 m (m^2-m)}{v} P_m - \frac{k_2 m m P_m}{v} \]
\[
\frac{\partial P_m}{\partial t} = \frac{4}{V} (m-1) (N+1-m) P_{m-1} - \frac{4}{V} m (N-m) P_m \\
+ \frac{4}{V} (m+1)^2 P_{m+1} - \frac{4}{V} m^2 P_m
\]

\text{in from } M+1.

\text{out from } M.

\text{Express as concentration...}

\[C = \frac{m}{V}\]

\[C_0 = \frac{N}{V}\]

\[P_m(t) = P(C_0 t)\]

\[\text{pdf of } C\]

And consider \(V \) large (so noise small)

\[P_m(t) \to P_m + \frac{1}{V} \frac{\partial}{\partial C}\]
Where is this going?

Fokker-Planck Equation of Concentration

\[ \frac{\partial p}{\partial t} = \frac{\partial}{\partial c} \left[ D(C) \frac{\partial p}{\partial c} \right] - \frac{\partial}{\partial c} \left( \frac{1}{2V} \frac{\partial^2 p}{\partial c^2} \right) \]

\[ \frac{\partial p}{\partial t} = -\frac{\partial}{\partial c} \left[ V(C) \left( \frac{\partial p}{\partial c} + \frac{1}{2V} \frac{\partial^2 p}{\partial c^2} \right) \right] \]

\[ V(C) = k_1 c (c_0 - c) - k_2 c^2 \]

\[ D(C) = k_1 c (c_0 - c) + k_2 c^2 \]

\[ \text{similar to multiphase flow} \]
Now, for $V \to \infty$, noise (diffusion)

vanishes, $\Xi$

\[
\frac{\partial}{\partial t} \rho + \frac{\partial}{\partial c} \left( \nu(c) \rho \right) = 0
\]

so, for $\langle c \rangle$

\[
\langle c \rangle = \int d\rho \, \rho(c) \, c
\]

\[
\frac{d}{dt} \langle c \rangle = \nu \langle c \rangle
\]

For $j$, $\bar{c}^2 \to 0$

\[
\nu(c) = \kappa_1 c (c_0 - c) - \kappa_2 c^2
\]

\[
\langle c \rangle = \frac{\kappa_1 c_0}{(\kappa_1 + \kappa_2)}
\]

and linearize for stability, $d$.

Broadened by diffusion.