III.) Kinetic Equations

Two examples:
→ Boltzmann Eqn.
→ Landau.
(B.E. for small $|\underline{Z}|$ → glancing collision)

Contents:
- → Overview – Kinetic Equations
- → Fokker-Planck Theory
- → Zwanzig – Mori Theory
- → Master Equation
- → Special Applications: TST, Kramers, Colloidal Aggregation, Ito vs. Stratonvich, Diffusion in Inhomogeneous Medium, Poisson Processes, Slow Modes, Mode Coupling

a.) Kinetic Equations – An Overview

– consider Langevin equation, for Brownian motion

$$\frac{d\underline{v}}{dt} = -\beta \underline{v} + \tilde{a}$$

i.e. $\dfrac{du}{dt} = \dfrac{q}{m} \tilde{E}$ ← stochastic E field

really seek $P(\underline{x}, \underline{v}, t) \equiv$ probability to find the particle at $(\underline{x}, \underline{v})$ in phase space at time t.

$P(\underline{x}, \underline{v}, t)$ ← object of Kinetic Equation

[Kinetic equations seek to evolve/determine $P(\underline{x}, \underline{v}, t)$ directly, rather than to solve Langevin equation and the average.]

Landau/

– Boltzmann equation is an example of a kinetic equation

$$\underbrace{f(\underline{x}_1, \underline{v}_1, \ldots \underline{x}_N, \underline{v}_N, t)}_{\text{Liouvillean}} \xrightarrow[\text{BBGKY}]{} \underbrace{f(\underline{x}, \underline{v}, t)}_{\substack{\text{standard distribution eqn.} \\ \text{(phase space density)}}} + \text{Boltzmann Eqn}$$

e.g. involves $\left\{ \begin{array}{l} \text{coarse graining} \\ \text{averaging} \end{array} \right\}$, from $\Gamma_1, \ldots \Gamma_N \to \underline{x}, \underline{v}$.

– for stochastic processes, can formulate hierarchy of equations:

① Master Equation

$P(n,t) \equiv$ probability to find system in n^{th} state

then,

$$\frac{\partial P(n,t)}{\partial t} = \underbrace{\text{in}}_{\substack{\text{transitions} \\ \text{in from} \\ \text{other states} \\ n'}}^{\text{"birth"}} - \underbrace{\text{out}}_{\substack{\text{transitions} \\ \text{out from } n \\ \text{to other states } n'}}^{\text{"death"}}$$

$n' \to n$ transition probability (rate) $\qquad$ $n \to n'$ transition probability (rate)

So $$\frac{\partial P(n,t)}{\partial t} = \sum_{n' \neq n} \left[P(n',t)\, W(n',n) - P(n,t)\, W(n,n') \right]$$

probability of state n' $\qquad$ probability of state n

here: probability in $\sim$ (P of other states) * (transition probability (rate))

probability out $\sim$ (P of n) * (transition probability (rate))

Master equation is splendid example of "garbage in, garbage out" nature of kinetic equations, in that Master Eqn. is only as good as transition probabilities used to construct it!

- Master equation tacitly "coarse-grains", in that P evolution slower than transition event rate

$t \to t+\tau \to t+2\tau \to \ldots\ldots$

then $n \to n'$ event occurs faster than τ.

② Fokker-Planck Equation

Consider system with no memory ⟷ i.e. each step on τ independent of prior history.

so can write:

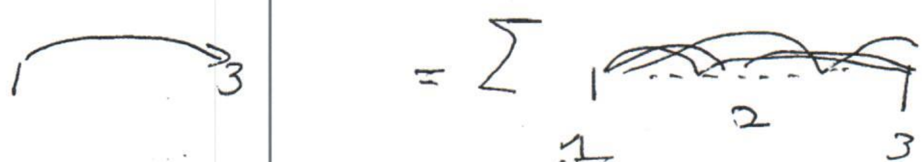
$$P(x_3, t_3 \mid x_1, t_1) = \int dx_2 \; P(x_3, t_3 / x_2, t_2) \; P(x_2, t_2 / x_1, t_1)$$

prob. of x_3 at t_3 starting from x_1 at t_1.

integration over intermediate states

$2 \to 3$ jump

$1 \to 2$ jump.



and

→ multiplicative, as independent steps

→ sum over intermediate states.

above is Chapman-Kolmogorov Equation

Now, can extend to where

transition probability, of x, of step Δx in time τ

$$P(x_2, t_2 \mid x_1, t_1) = T(x, \Delta x, \tau)$$

i.e. $t_2 - t_1$ is jump time τ
$x_2 - x_1$ is jump step Δx

then Chapman - Kolmogorov Equation becomes:

$$P(x, t+\tau) = \int d(\Delta x)\; P(x-\Delta x, t)\, T(x, \Delta x, \tau)$$

and expansion (with T indep. x) $\Rightarrow$

i.e. Δx small $\Rightarrow$ small increments

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x}\left\{ \frac{\langle \Delta x \rangle}{\tau} P - \frac{\partial}{\partial x} \frac{\langle \Delta x \Delta x \rangle}{2\tau} P \right\}$$

$$= -\frac{\partial}{\partial x} \underbrace{\Gamma_P}_{\text{probability flux}}$$

generic form of Fokker-Planck Equation (F-P. E.)

Note:

- F-P. Equation — no memory on scales $t > \tau$
- F-P. Equation — "coarse-grains" out $\begin{cases} t < \tau \\ x < \Delta x \end{cases}$

- F.-P. Equation is <u>less general</u>, but <u>more tractable</u> than Master Equation.
- intimately connected to diffusion.

③ Zwanzig - Mori Equation is

F.-P. Eqn. <u>with</u> Memory Kernel (Memory Correction).

<u>i.e.</u> variables $x_1, x_2, \cdots x_N$

for t slower than some τ, separate into 'fast' and 'slow' variables

$$\underbrace{x_1, x_2, \cdots x_p}_{\text{slow}} \Big\} \underbrace{x_{p+1} \cdots x_N}_{\text{fast}}$$

$\dot{x}_i / x_i < 1/\tau$ $\qquad\qquad$ $\dot{x}_i / x_i > 1/\tau$

Z-M theory:

- assumes <u>fast</u> variables come to ☺ equilibrium on time scales τ
- can describe evolution in terms of <u>slow</u> variables, only.

then:

- $\underset{\S}{P}(x_1, x_2, \cdots x_N) \to (x_1, \cdots x_p)$

Projection operator P, projects evolution onto reduced # degrees of freedom, the <u>slow</u> variables.

- write projected Liouville equation, for slow variables $\Rightarrow$ Z.-M. Eqn.

- not surprisingly, Z.-M. Eqn. can reduce to F.-P. Eqn.

- Z.-M. clearly coarse-grains over fast variables

- Z.-M.: projection procedure <u>part</u>, but <u>not all</u>, of R.G. procedure (Renormalization Group) theory.

8.) Fokker–Planck Theory

{ Extends basic ideas notes

- seek pdf P of Markovian, stochastic variable

- Markovian $\equiv$ stochastic process s/t $t+\Delta t$ determined by state at t, only.

$\Leftrightarrow$ no memory

so, as in Brownian Motion

$$P(\underline{v}, t+\Delta t) = \int d(\Delta \underline{v})\, P(\underline{v}-\Delta\underline{v}, t)\, T(\Delta\underline{v}, \Delta t)$$

state at $t+\Delta t$ — state at t — transition probability

$\Rightarrow$ expand

$$P(\underline{v},t) + \Delta t \frac{\partial P}{\partial t} = \int d(\Delta\underline{v}) \Big\{ P(\underline{v},t)\, T(\Delta\underline{v},\Delta t)$$

$$- \frac{\partial}{\partial \underline{v}}\left(\Delta\underline{v}\, T(\Delta\underline{v},\Delta t)\, P(\underline{v},t)\right) + \frac{1}{2}\frac{\partial^2}{\partial v^2}\left(\Delta v \Delta v\, T(\Delta\underline{v},\Delta t)\, P(\underline{v},t)\right)\Big\}$$

Now, as T is transition probability, it is normalized, so $\Rightarrow$

so $$\int d\underline{\Delta V}\; T(\underline{\Delta V}, \Delta t) = 1$$

$$\int d\underline{\Delta V}\; \underline{\Delta V}\; T(\underline{\Delta V}, \Delta t) = \langle \underline{\Delta V} \rangle$$ expectation (must exist)

$$\int d\underline{\Delta V}\; \underline{\Delta V}\; \underline{\Delta V}\; T(\underline{\Delta V}, t) = \langle \underline{\Delta V}\; \underline{\Delta V} \rangle$$ variance (must exist)

$\therefore$

$$P(\underline{v}, t) + \Delta t \frac{\partial P}{\partial t} = P(\underline{v}, t) - \frac{\partial}{\partial \underline{V}} \cdot \left(\langle \underline{\Delta V} \rangle P(\underline{v}, t) \right)$$

$$+ \frac{1}{2} \frac{\partial}{\partial \underline{V}} \cdot \left[\frac{\partial}{\partial \underline{V}} \cdot \left(\langle \underline{\Delta V}\; \underline{\Delta V} \rangle P(\underline{v}, t) \right) \right]$$

so

$$\boxed{\begin{aligned} \frac{\partial P(\underline{v}, t)}{\partial t} &= -\frac{\partial}{\partial \underline{V}} \cdot \left\{ \frac{\langle \underline{\Delta V} \rangle}{\Delta t} P(\underline{v}, t) - \frac{\partial}{\partial \underline{V}} \cdot \frac{\langle \underline{\Delta V}\; \underline{\Delta V} \rangle}{2\Delta t} P(\underline{v}, t) \right\} \\ &= -\frac{\partial}{\partial \underline{V}} \cdot \underline{\Gamma}_P \end{aligned}}$$

– Fokker-Planck Equation,

Now, can note:

- $\frac{\partial \rho}{\partial t} = -\underline{\nabla} \cdot \underline{\Gamma}_\rho$ structure assures F.-P. Eqn. conserves probability. Derivative order matters!

- Obviously, can relate F.-P. Eqn. to Master Eqn. in "small kick" limit.

- as example, for Brownian Motion:

$$\frac{\partial \underline{V}}{\partial t} = -\beta \underline{V} + \underline{\tilde{a}}(t)$$

$\hookrightarrow$ broadband noise

$$\therefore \quad \frac{\langle \Delta \underline{V} \rangle}{\Delta t} = -\beta \underline{V}$$

$$\frac{\langle \Delta \underline{V}\, \Delta \underline{V} \rangle}{2 \Delta t} = D_V \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$D_V = \tilde{a}_0^2 \tau_{ac}$

(uncorrelated direction)

$$\therefore \quad \frac{\partial \rho}{\partial t} = -\frac{\partial}{\partial \underline{V}} \cdot \left\{ -\beta \underline{V} \rho - \frac{\partial}{\partial \underline{V}} \cdot \underline{\underline{D}}_V \, \rho \right\} \rightarrow \text{F.-P. Eqn. for Brownian Motion}$$

in 1D,

$$\frac{\partial \rho}{\partial t} = +\frac{\partial}{\partial V} \left\{ \beta V \rho + D_V \frac{\partial \rho}{\partial V} \right\}$$

$D_V = \beta V_{Th}^2$

so, at equilibrium $(\partial P/\partial t = 0)$

$$P \simeq \exp\left[-\beta V^2/2D_V\right]$$

i.e. Gaussian pdf formed by balance of drag with diffusion.

In the absence of drag, with $P(V,0) = \delta(V - V_0)$

$$P(V,t) = \frac{1}{\sqrt{\pi D_V t}} \exp\left[-V^2/2D_V t\right]$$

i.e. diffusion pdf.

- F.-P. Equation structure (general):

drag/drift term $\rightarrow \frac{\langle \Delta V \rangle}{\Delta t} P = \underline{V} P$ ↳ drift velocity

diffusion term $\rightarrow -\frac{\partial}{\partial \underline{V}} \cdot \frac{\langle \Delta \underline{V} \Delta \underline{V} \rangle}{2\Delta t} P = -\frac{\partial}{\partial \underline{V}} \cdot \underline{\underline{D}}_V P$

diffusion tensor

and: $\frac{\partial P}{\partial t} + \underline{\nabla}_V \cdot (\underline{V} P) = + \underline{\nabla}_V \cdot \underline{\nabla}_V \underline{\underline{D}} P$

$$\underline{\Gamma}_V = -\underline{V} P - \underline{\nabla}_V \cdot \underline{\underline{D}}_V P$$

drift → deterministic part of motion

diffusion → random part. (noise related)

- requirements for applicability of Fokker-Planck Theory

→ stochastic motion
→ step size
  $\Delta v, \Delta x$
→ no memory $(t > \Delta t)$

and

$$\left.\begin{array}{l}\langle \Delta v \rangle < \infty \\ \langle \Delta v^2 \rangle < \infty\end{array}\right\} \rightarrow \text{convergence of lowest 2 moments}$$

a/a/ Central Limit Theorem.

if $\langle \Delta v^2 \rangle \to \infty$, need turn to Fractional Kinetics.
CTRW
→ Levy Flights, etc.

- Fokker-Planck equation ↔ Markov Process or chain, which is gradual unfolding of transition probability just as conservative dynamical system is gradual unfolding of contact transformation.

- for
  - Hamiltonian system $\leftrightarrow$ Liouville Thm.
  - no systematic bias

can show: (HW)

$$\frac{1}{2}\frac{\partial}{\partial \underline{v}}\cdot\langle \underline{\Delta v}\,\underline{\Delta v}\rangle = \langle \underline{\Delta v}\rangle$$

i.e. partial cancellation of diffusion and drag/drift

i.e.

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial \underline{v}}\cdot\left(\frac{\langle \underline{\Delta v}\rangle}{\Delta t}f - \frac{\partial}{\partial \underline{v}}\cdot\frac{\langle \underline{\Delta v}\,\underline{\Delta v}\rangle f}{2\Delta t}\right)$$

$$= -\frac{\partial}{\partial \underline{v}}\cdot\left(\left(\frac{\langle \underline{\Delta v}\rangle}{\Delta t} - \frac{\partial}{\partial \underline{v}}\cdot\frac{\langle \underline{\Delta v}\,\underline{\Delta v}\rangle}{2\Delta t}\right)f - \frac{\langle \underline{\Delta v}\,\underline{\Delta v}\rangle}{2\Delta t}\cdot\frac{\partial f}{\partial \underline{v}}\right)$$

$$= \frac{\partial}{\partial \underline{v}}\cdot\underline{\underline{D}}_v\cdot\frac{\partial f}{\partial \underline{v}}$$

$\rightarrow$ Form of diffusion equation for Hamiltonian system (note: order of derivatives!)

here $\langle \underline{\Delta V} \rangle = \frac{1}{2} \frac{\partial}{\partial \underline{V}} \cdot \langle \underline{\Delta V}\, \underline{\Delta V} \rangle$ is analogue of incompressibility of phase space flow for stochastic system.

...

→ Now, can extend Fokker-Planck theory to bivariate evolution.

i.e. consider Brownian Motion in External Force Field ...

$$\frac{\partial \underline{V}}{\partial t} = -\beta \underline{V} + \underbrace{\underline{q}_{ext}}_{\frac{f_{ext}}{m_p} = -\frac{\nabla \phi}{m_p}} + \underbrace{\tilde{\underline{q}}}_{\text{Brownian force}}$$

→ potential (i.e. spring, gravity)

$$\frac{d\underline{x}}{dt} = \underline{v}$$

so obviously, particle random walks in $\underline{x}$ and $\underline{v}$. For phase space pdf:

$$P(\underline{x}, \underline{v}, t+\Delta t) = \int d(\underline{\Delta x}) \int d\underline{\Delta v} \left\{ P(\underline{x}-\underline{\Delta x}, \underline{v}-\underline{\Delta v}, t)\, T(\underline{\Delta x}, \underline{\Delta v}, \underline{\Delta t}) \right\}$$

Furthermore, Brownian kick applied only in $\underline{v}$
so $\underline{x}$ kinematic

$\Rightarrow$

$$T(\Delta\underline{x}, \Delta\underline{v}, \Delta t) = \delta(\Delta\underline{x} - \underline{v}\,\Delta t)\, T(\Delta\underline{v}, \Delta t)$$

$\therefore$

$$P(\underline{x}, \underline{v}, t+\Delta t) = \int d(\Delta\underline{x}) \int d(\Delta\underline{v})\, P(\underline{x} - \Delta\underline{x}, \underline{v} - \Delta\underline{v}, t) \; * \; \delta(\Delta\underline{x} - \underline{v}\,\Delta t)\, T(\Delta\underline{v}, \Delta t)$$

$$= \int d(\Delta\underline{v})\, P(\underline{x} - \underline{v}\,\Delta t, \underline{v} - \Delta\underline{v}, t)\, T(\Delta\underline{v}, \Delta t)$$

so can re-write:

$$P(x + \underline{v}\,\Delta t, \underline{v}, t+\Delta t) = \int d\,\Delta\underline{v}\; P(\underline{x}, \underline{v} - \Delta\underline{v}, t)\, T(\Delta\underline{v}, \Delta t)$$

and now expand, as before:

$$\frac{\partial P}{\partial t} + \underline{v}\cdot\nabla_x P \underbrace{}_{+\, \underline{a}_{ext}\cdot\partial P/\partial\underline{v}} = -\frac{\partial}{\partial\underline{v}}\cdot\left[\frac{\langle\Delta\underline{v}\rangle}{\Delta t} P - \frac{\partial}{\partial\underline{v}}\cdot\frac{\langle\Delta\underline{v}\,\Delta\underline{v}\rangle}{2\Delta t} P\right]$$

more generally, have shown can write:

$$\left.\frac{dP}{dt}\right) = \underbrace{\text{F-P. Operator}}_{\text{randomly fluctuating orbits}} = \beta \frac{\partial}{\partial \underline{v}} \cdot (\underline{v} P) + D_v \frac{\partial^2 P}{\partial v^2}$$

deterministic orbits

where "deterministic orbits" means:

$$\frac{d\underline{x}}{dt} = \underline{v} \quad , \quad \frac{d\underline{v}}{dt} = \underline{a}_{ext}$$

→ Now $P = P(\underline{x}, \underline{v}, t)$.

Often seek only $P(\underline{x}, t)$. So ... can obtain full $P(\underline{x}, \underline{v}, t)$ and integrate over $\underline{v}$, which is laborious

or

derive moment equations of F-P. Equation in $\underline{\Gamma}$, yield "fluid equations" in $\underline{x}$!

obviously akin to deriving fluid equations from Boltzmann equation!

i.e. from F.-P. eqn. for $P(\underline{x}, \underline{v}, t)$

derive equations for:

$$n(\underline{x}, t) = \int d\underline{v}\, P(\underline{x}, \underline{v}, t) \quad \rightarrow \text{density}$$

$$V(\underline{x}, t) = \int d\underline{v}\, \underline{v}\, P(\underline{x}, \underline{v}, t) \Big/ n(\underline{x}, t) \quad \rightarrow \text{Eulerian Velocity}$$

n - equation $\leftrightarrow$ Schmoluchowski Equation

Now, have: (for Brownian Particle)

$$\frac{\partial P}{\partial t} + \underline{v} \cdot \underline{\nabla}_x P + \underline{a}_{ext} \cdot \underline{\nabla}_v P$$

$$= \beta \frac{\partial}{\partial \underline{v}} \cdot \left(\underline{v}\, P \right) + D_v \frac{\partial^2 P}{\partial v^2}$$

which can be re-written as:

in a superficially very complicated form, as...

$$\frac{\partial P}{\partial t} = \beta\left(\frac{\partial}{\partial \underline{v}} - \frac{1}{\beta}\frac{\partial}{\partial \underline{x}}\right)\cdot\left(\underline{v}P + \frac{D_v}{\beta}\frac{\partial P}{\partial \underline{v}} - \frac{q_{ext}}{\beta}P + \frac{D_v}{\beta^2}\frac{\partial P}{\partial \underline{x}}\right)$$

1

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$$+ \frac{\partial}{\partial \underline{x}}\cdot\left(\frac{D_v}{\beta}\frac{\partial P}{\partial \underline{x}} - \frac{q_{ext}}{\beta}P\right)$$

now : $n(\underline{x}, t) = \int d\underline{v}\; P(\underline{x}, \underline{v}, t)$

$$\underline{x} + \frac{\underline{v}}{\beta} = \underline{x}_0$$

i.e. integrate along line s.t. $\dot{\underline{x}} = -\dot{\underline{v}}/\beta$

→ This annihilates term #1 !

i.e. $\underline{x} + \frac{\underline{v}}{\beta} = \text{const} \Rightarrow \frac{\partial}{\partial \underline{v}} - \frac{1}{\beta}\frac{\partial}{\partial \underline{r}} = 0$

so obtain:

$$\boxed{\frac{\partial n}{\partial t}(\underline{x},t) = \frac{\partial}{\partial \underline{x}} \cdot \left(\frac{D_v}{\beta^2} \frac{\partial n}{\partial \underline{x}} - \frac{q_{ext}}{\beta} n \right)}$$

- the Schmoluchowski eqn. for $n(\underline{x},t)$ → spatial pdf!

Observe:

- can short-circuit complicated derivation by simply going to "terminal velocity" limit.

i.e. eqns of motion:

$$\frac{\partial \underline{v}}{\partial t} = -\beta \underline{v} + \underline{q}_{ext} + \tilde{q}$$

$$\frac{d\underline{x}}{dt} = \underline{v}$$

at terminal velocity,

$$\underline{v} = \frac{\underline{q}_{ext}}{\beta} + \frac{\tilde{q}}{\beta}$$

$$\frac{dx}{dt} = \underbrace{\frac{q_{ext}}{\beta}}_{\text{deterministic}} + \overbrace{\frac{\tilde{q}}{\beta}}^{\text{random}}$$

$$\therefore \begin{cases} \dfrac{\partial n}{\partial t} + \dfrac{\partial}{\partial \underline{x}} \cdot \left(\underbrace{\dfrac{d\underline{x}}{dt}}_{\text{deterministic}} n \right) = D_{xx} \dfrac{\partial^2 n}{\partial x^2} \\ D_{xx} = D_v / \beta^2 \end{cases}$$

$\Rightarrow$ Schmoluchowski Eqn.

– still conservative:

$$\frac{\partial n}{\partial t} = -\frac{\partial}{\partial \underline{x}} \cdot \underline{\Gamma}_n$$

$$\underline{\Gamma}_n = \left(\underbrace{\frac{\underline{a}_{ext}}{\beta} n}_{\text{convection velocity}} - \underbrace{\frac{D_v}{\beta^2} \frac{\partial n}{\partial \underline{x}}}_{\text{Diffn}} \right).$$