III.) Kinetic Equations

Contents:

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

a.) Kinetic Equations – An Overview

– consider Langevin equation, for Brownian motion

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

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.

- Boltzmann equation is an example of a kinetic equation

$$f(\underline{x}_1, \underline{v}_1, \dots \underline{x}_N, \underline{v}_N, t) \xrightarrow[\text{BBGKY}]{} f(\underline{x}, \underline{v}, t) + \text{Boltzmann Eqn}$$

Liouvillean

standard distribution eqn. (phase space density)

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

- for stochastic processes, can formulate hierarchy of equations

① Master Equation (c.f. homework)

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

then, "birth" "death"

$$\frac{\partial P(n,t)}{\partial t} = \text{in} - \text{out}$$

in: transitions in from other states n'

out: transitions out from n to other states n'

so
$$\frac{\partial P(n,t)}{\partial t} = \sum_{\substack{n' \\ \neq n}} \Big[\underbrace{P(n',t)}_{\substack{\text{probability} \\ \text{of state } n'}} \overbrace{W(n',n)}^{\substack{n' \to n \text{ transition} \\ \text{probability} \\ \text{(rate)}}} - \underbrace{P(n,t)}_{\substack{\text{probability} \\ \text{of state } n}} \overbrace{W(n,n')}^{\substack{n \to n' \text{ transition} \\ \text{probability} \\ \text{(rate)}}} \Big]$$

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

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

<u>Master equation</u> 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:

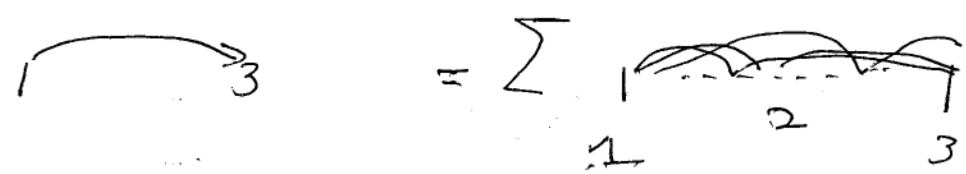
$$P(x_3, t_3 \mid x_1, t_1) = \int dx_2 \; P(x_3, t_3 / x_2, t_2) \; P(x_2, t_2 / x_1, t_1)$$

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) $\Rightarrow$

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

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

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 less general, but more tractable than Master Equation.

③ Zwanzig-Mori Equation is

F.-P. Eqn. with Memory Kernel (memory correction)

i.e. variables $x_1, x_2, \dots x_N$

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

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

slow: $\dot{x}_i / x_i < 1/\tau$

fast: $\dot{x}_i / x_i > 1/\tau$

Z-M theory:

- assumes fast variables come to ☺ equilibrium on time scales τ

- can describe evolution in terms of slow variables, only.

then:

- $\underset{\wr}{\underline{P}}(x_1, x_2, \dots x_N) \rightarrow (x_1, \dots x_p)$

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

- 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

$$\underset{\substack{\uparrow \\ \text{state at} \\ t+\Delta t}}{P(\underline{v}, t+\Delta t)} = \int d(\Delta \underline{v})\, \underset{\substack{\uparrow \\ \text{state at} \\ t}}{P(\underline{v}-\Delta \underline{v}, t)}\; \underset{\substack{\uparrow \\ \text{transition} \\ \text{probability}}}{T(\Delta \underline{v}, \Delta t)}$$

$\Rightarrow$ expand

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

$$- \frac{\partial}{\partial \underline{v}} \Big(\Delta \underline{v}\, T(\Delta \underline{v}, \Delta t)\, P(\underline{v}, t) \Big) + \frac{1}{2} \frac{\partial^3}{\partial v^2} \Big(\Delta v \Delta v\, T(\Delta \underline{v}, \Delta t)\, P(\underline{v}, t) \Big) \Big\}$$

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

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

— Fokker-Planck Equation,

Now, can note:

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

- Obviously, can relate F.-P. Eqn. to Master Eqn. in "small" kick" limit. (see Pblm. 3 of HW 1).

- as example, for Brownian Motion

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

$\tilde{q}(t)$ → broad band noise

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

$$\frac{\langle \underline{\Delta V}\,\underline{\Delta V}\rangle}{2\Delta t} = D_V \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \qquad D_V = \tilde{q}_0^2\,\tau_{ac}$$

(uncorrelated direction)

$\therefore$

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

in 1D,
$$\frac{\partial p}{\partial t} = +\frac{\partial}{\partial v}\left\{ \beta v\,p + D_V\frac{\partial p}{\partial v} \right\}$$

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 $\rightarrow$ $\dfrac{\langle \Delta \underline{V} \rangle}{\Delta t} P = \underline{V} P$ ↳ drift velocity

diffusion term $\rightarrow$ $-\dfrac{\partial}{\partial \underline{V}} \cdot \underbrace{\dfrac{\langle \Delta \underline{V} \Delta \underline{V} \rangle}{2\Delta t}}_{\text{diffusion tensor}} P = -\dfrac{\partial}{\partial \underline{V}} \cdot \underline{\underline{D}}_v P$

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

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

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

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

here $\langle \Delta \underline{V} \rangle = \frac{1}{2} \frac{\partial}{\partial \underline{V}} \cdot \langle \Delta \underline{V} \Delta \underline{V} \rangle$ 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 ---

$$\frac{\partial \underline{V}}{\partial t} = -\beta \underline{V} + \underline{g}_{ext} + \tilde{\underline{g}}$$

$\tilde{\underline{g}}$ → Brownian force

$$\underline{g}_{ext} = \frac{\underline{f}_{ext}}{m_p} = -\frac{\nabla \phi}{m_p}$$

ϕ → 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:

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

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!

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

more generally, have shown can write:

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

deterministic orbits

where "deterministic orbits" means:

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

→ 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 Γ, 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...

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

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

now : $n(\underline{x}, t) = \int d\underline{v}\ \rho(\underline{x}, \underline{v}, t)$
$\underline{x} + \frac{\underline{v}}{\beta} = \underline{x}_0$

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

→ This annihilates term #1 !

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

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 $n(\underline{x}, t) \rightarrow$ 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,

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

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

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

$\Rightarrow$ Schmoluchowski Eqn.

— still conservative:

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

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

Next: (I) – Another look at Fokker-Planck Theory
(II) – Kinetics of Chemical Reactions
a) Transition State Theory
b) Kramers' Problem
1.) first passage time
2.) reaction rate constants $\Big\}$ γ large
3.) energy diffusion $\}$ $\gamma \to 0$
(III.) Colloidal Aggregation

(I) Another Look at Fokker-Planck Theory

ref. R. Zwanzig, "Nonequilibrium Statistical Mechanics"

For dynamics which preserves phase space volume (i.e. incompressible $\underline{V}_\Gamma$), can write:

Theory of Liouville operator

$$\frac{\partial}{\partial \underline{x}} = \frac{\partial}{\partial \underline{x}_\Gamma} = \left(\frac{\partial}{\partial \underline{q}}, \frac{\partial}{\partial \underline{p}}\right) \quad ; \quad \underline{V} = \underline{V}_\Gamma = \left\{\frac{dq}{dt}, \frac{dp}{dt}\right\}$$

so
$$f(\underline{x},t) = e^{-tL} f(\underline{x},0)$$

as
$$\frac{\partial f}{\partial t} + Lf = 0$$

$\Big\{$ $(\underline{q}, \underline{p})$ dimensionality arbitrary

$$L = \frac{\partial H}{\partial \underline{p}} \cdot \frac{\partial}{\partial \underline{q}} - \frac{\partial H}{\partial \underline{q}} \cdot \frac{\partial}{\partial \underline{p}} \rightsquigarrow \text{Liouville operator}$$

Interesting to note properties of Liouville operator...

1) For $A = A(\underline{x})$ → arbitrary $\left\{\begin{array}{l}\text{function}\\ \text{operator}\end{array}\right.$ of/in Γ

often seek: $\int_{Vol} d\underline{x}\; L A f$ i.e. $\left\{\begin{array}{l}\text{weighted avg/expectation}\\ \text{of } A \text{ in domain } \Gamma\end{array}\right.$

now: $L = \underline{V}\cdot\underline{\nabla} = \underline{\nabla}\cdot(\underline{V}\quad)$, as $\nabla\cdot\underline{V}_\Gamma = 0$

$\frac{\partial}{\partial t} + L = 0$, $\left(\text{and } \frac{\partial\rho}{\partial t} = -\nabla\cdot(\rho\underline{V})\right)$

effective flow velocity

$$\int_{Vol} d\underline{x}\; LAf = + \int_{Vol} d\underline{x}\; \frac{d}{d\underline{x}}\cdot(\underline{V}Af)$$

$$= -\oint d\underline{s}\cdot\underline{V}Af \qquad \text{(normal in)}$$

so avg'd evolution A entirely determined by values of: $\underline{V}$ ↔ phase space flow velocity and f on boundary of averaging region

2) L is anti-self adjoint i.e. $L^\dagger = -L$

$$L(Af) = (LA)f + A(Lf)$$

as L is first order diff'ntl operator

Now, consider $\int d\underline{x}\, A(Lf)$

but $\qquad L(Af) = (LA)f + A(Lf)$

$$\therefore \quad \int d\underline{x}\, A(Lf) = \int d\underline{x} \left\{ L(Af) - (LA)f \right\}$$

$$= \int d\underline{x} \left\{ \frac{d}{d\underline{x}} \cdot (\underline{V}Af) - (LA)f \right\}$$

and for $f \to 0$ at $\underline{x} \to \infty$ (normalizability) $\Rightarrow$

$$\boxed{\int d\underline{x}\, A(Lf) = -\int d\underline{x}\, (LA)f}$$

What does L, e^{Lt} mean, physically ?

In general; seek calculate aspects of general many body system

$A(\underline{x}) \equiv$ generic dynamical variable

then $$\left.\frac{\partial A}{\partial t}\right|_{t=0} = \frac{\partial A}{\partial \underline{q}} \cdot \left.\frac{\partial \underline{q}}{\partial t}\right|_{t=0} + \frac{\partial A}{\partial \underline{p}} \cdot \left.\frac{\partial \underline{p}}{\partial t}\right|_{t=0}$$

$$= LA$$

and $$\left(\frac{\partial^n}{\partial t^n} A\right)_{t=0} = L^n A$$

so $$A(\underline{x},t) = \sum_{n=0}^{\infty} \frac{t^n}{n!} \left.\frac{\partial^n A}{\partial t^n}\right|_{t=0}$$ i.e. Taylor series

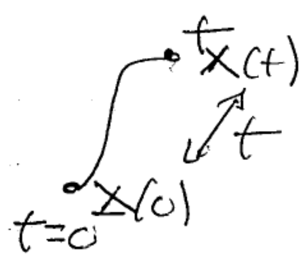
$$= \sum_{n=0}^{\infty} \frac{t^n}{n!} L^n A(x) = e^{tL} A(\underline{x})$$

thus $$\begin{cases} \dfrac{\partial A}{\partial t}(\underline{x},t) = L A(\underline{x},t) \Rightarrow A(\underline{x},t) = e^{tL} A(\underline{x}) \\ A(\underline{x},0) = A(\underline{x}) \end{cases}$$

$\therefore$ e^{tL} $\rightsquigarrow$ propagator / orbit evolution operator

$\rightsquigarrow$ moves particle along trajectory in phase space

i.e.



$\Longleftrightarrow e^{tL}$

then rather obvious (as $\underline{V}_\Gamma$ incompressible) that:

$$e^{tL} A(\underline{x}) = A(e^{tL}\underline{x})$$

trajectory unique!

and

$$e^{tL}\left(A(\underline{x})\, B(\underline{x})\right) = \left(e^{tL}A(\underline{x})\right)\left(e^{tL}B(\underline{x})\right)$$
$$= A(e^{tL}\underline{x})\, B(e^{tL}\underline{x})$$

- Now, can formulate phase space averages of A (ala' expectation in QM). Point is that can approach either ala' Schrodinger or Heisenberg, i.e.

$$\langle A, t\rangle = \int d\underline{x}\; A(\underline{x})\, f(\underline{x}, t)$$

avg. at time t

$$= \int d\underline{x}\; A(\underline{x})\, e^{-tL} f(\underline{x}, 0)$$

$$\frac{\partial f}{\partial t} + Lf = 0$$

i.e. ala' Schrodinger → f evolves

~ $|\psi|^2$ weighting pdf

equivalently

value of A at t, from initial state $\underline{x}$.

$$\langle A, t\rangle = \int dx\; A(\underline{x}, t)\, f(\underline{x}, 0)$$
$$= \int d\underline{x}\left(e^{tL}A(\underline{x}, 0)\right) f(\underline{x}, 0)$$

L anti-self-adjoint

i.e. ala' Heisenberg → A evolves

~ ala' operator.

→ which brings us to Fokker–Planck theory, again . . . . .

Point of F–P. theory:

- convert stochastic orbit equation (i.e. Langevin equation) into 'well-behaved' equation for pdf [HARD, in general]

- consider 'simplest' case → "zero memory" limit → Markovian approximation

now
$$\underbrace{\frac{dq}{dt} = \underbrace{V(\underline{q})}_{\substack{\text{deterministic}\\\text{velocity/flow}}} + \underbrace{\underline{F}(t)}_{\substack{\text{noise}\\\text{fluctns}}}}$$
→ schematic Langevin equation

Now, generically:
$$\frac{\partial f(q,t)}{\partial t} + \frac{\partial}{\partial \underline{q}} \cdot \Big(\underbrace{\big(\underline{V}(q) + \underline{F}(t)\big) f}_{(dq/dt)\, f} \Big) = 0$$
Can develop P.T. in noise strength

(*)
$$\frac{\partial f(q,t)}{\partial t} = -\frac{\partial}{\partial \underline{q}} \cdot \Big(\underline{V}(q) f(q,t) + \underline{F}(t) f(q,t) \Big)$$

$$= -Lf - \frac{\partial}{\partial \underline{q}} \cdot \Big(\underline{F}(t) f(\underline{q},t) \Big)$$

Now,

$-$ l.o. in $\tilde{F}$ $\quad \frac{\partial f}{\partial t} + Lf = 0$

$$f(\underline{q},t) = e^{-tL} f(\underline{q},0)$$

and plugging into (*) gives:

$$\frac{\partial f(\underline{q},t)}{\partial t} = -Lf - \frac{\partial}{\partial \underline{q}} \cdot \left(\underline{F}(t) f(\underline{q},t) \right) \qquad (**)$$

$-$ $\underline{1^{st} \text{ order}}$ in $\tilde{F}$

Solving (**) $\Rightarrow$

$$f(\underline{q},t) = \underbrace{e^{-tL} f(\underline{q},0)}_{\text{l.o.} \to O(F^{(0)})} - \int_0^t ds\, e^{-(t-s)L} \underbrace{\frac{\partial}{\partial \underline{q}} \cdot \left(\underline{F}(s) f(\underline{q},s) \right)}_{O(F^{(1)}) - \text{first order....}}$$

and $\underline{\text{plug}}$ $f(\underline{q},t)$ $\underline{\text{above}}$ $\underline{\underline{\text{into}}}$ Eqn (*)

$\Rightarrow$

$\Rightarrow$

$$\frac{\partial f(\underline{q},t)}{\partial t} = -Lf - \frac{\partial}{\partial \underline{q}} \cdot \left(\underline{F}(t) \left\{ e^{-tL} f(\underline{q},0) - \int_0^t ds\, e^{-(t-s)L} \frac{\partial}{\partial \underline{q}} \cdot \left(\underline{F}(s) f(\underline{q},s) \right) \right\} \right)$$

$$= -Lf - \frac{\partial}{\partial \underline{q}} \cdot \underline{F}(t)\, e^{-tL} f(\underline{q},0)$$

$$+ \frac{\partial}{\partial \underline{q}} \cdot \underline{F}(t) \int_0^t ds\, e^{-(t-s)L} \frac{\partial}{\partial \underline{q}} \cdot \left(\underline{F}(s) f(\underline{q},s) \right)$$

Now, average over $P(F)$, assuming:

$\rightarrow \langle F \rangle = 0, \quad \langle F F \rangle \neq 0$

$\rightarrow \langle F(t) F(s) \rangle = F_0^2 \tau_{ac} \delta(t-s)$

"delta correlated" limit

so $\langle f \rangle = \langle f(q,t) \rangle$ evolves according to:

coarse-grained pdf

$$\boxed{\frac{\partial \langle f \rangle}{\partial t} = -\frac{\partial}{\partial \underline{q}} \cdot \left(\underline{V}(q) \langle f \rangle - \frac{\partial}{\partial \underline{q}} \cdot \underline{\underline{B}} \langle f \rangle \right)}$$

→ Fokker-Planck Eqn.
(again ...)

the lesson:

→ F.-P. Eqn. emerges from Liouville equation for stochastic phase space evolution, i.e. Langevin eqn. = orbit eqn. + noise.

→ F.-P. Eqn. requires: delta correlated forcing (Markovianization), symmetric pdf forcing, $\langle \tilde{F}^2 \rangle < \infty$

→ Can develop F.-P. equation as series expansion in $\tilde{F}$.

→ Properties of Fokker–Planck Operator

$$\begin{cases} \langle f(\underline{q},t)\rangle \equiv f(q,t) \ , & \text{hereafter} \\ \underline{B} \text{ indep. } \underline{q} \end{cases}$$

$$\frac{\partial f(q,t)}{\partial t} = \mathcal{D} f(q,t)$$

$$\mathcal{D} f = -\frac{\partial}{\partial \underline{q}} \cdot \left(\underline{V}(q)\, f\right) + \frac{\partial}{\partial \underline{q}} : \underline{\underline{B}} \cdot \frac{\partial f}{\partial \underline{q}}$$

Now, easy to define/derive adjoint operator to $\mathcal{D}$.

$$\int d\underline{q}\ \varphi(\underline{q})\, \mathcal{D}\, \Psi(\underline{q}) = \int d\underline{q}\ \Psi(\underline{q})\, \mathcal{D}^{+} \varphi(\underline{q})$$

Exercise: Show this!

$$\mathcal{D}^{+} = \underline{V}(q) \cdot \frac{\partial}{\partial \underline{q}} + \frac{\partial}{\partial \underline{q}} \cdot \underline{\underline{B}} \cdot \frac{\partial}{\partial \underline{q}}$$

sign flip, deriv. order changes.

diffusion is self-adjoint (this form)

Now, $$f(\underset{\sim}{q},t) = e^{\mathcal{D}t} f(\underset{\sim}{q},0)$$

so expectation value defined as:

$$\langle \phi, t \rangle = \int d\underline{q}\ \varphi(\underline{q})\, f(\underline{q},t)$$
$$= \int d\underline{q}\ \varphi(\underline{q})\, e^{\mathcal{D}t} f(\underline{q},0)$$

~ Schrodinger representation → pdf evolves

or

$$\langle \phi, t \rangle = \int d\underline{q}\ f(\underline{q},0)\, e^{\mathcal{D}^{+}t} \varphi(\underline{q})$$

~ Heisenberg representation → ϕ, the expectation of which is calculated, evolves ...