III.) Kinetic Equations

Contents:

- Overview – Kinetic Equations
- Fokker-Planck Theory
- Zwanzig – Mori Theory
- Master Equation
- Special Applications: TST, Kramers, Colloidal Aggregation, Ito vs. Stratonvich, Diffusion on 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.

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

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

$f(\underline{x}_1, \underline{v}_1, \ldots \underline{x}_N, \underline{v}_N, t)$: Liouvillean

$f(\underline{x}, \underline{v}, t)$: standard distribution eqn. (phase space density)

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 (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'

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

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

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

· 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.

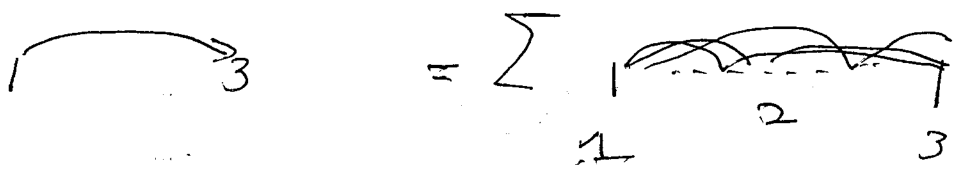
② Fokker–Planck Equation

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
to 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 $x_1, x_2, \ldots x_N$

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

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

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:

- $\underset{S}{P}(x_1, x_2, \ldots x_N) \rightarrow (x_1, \ldots x_p)$

Projection operator P_S 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

$$\underbrace{P(\underline{v},\, t+\Delta t)}_{\text{state at } t+\Delta t} = \int d(\Delta \underline{v})\, \underbrace{P(\underline{v}-\Delta\underline{v},\, t)}_{\text{state at } t}\, \underbrace{T(\Delta\underline{v},\Delta t)}_{\text{transition probability}}$$

$\Rightarrow$ 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:

- $\frac{\partial P}{\partial t} = -\underline{\nabla} \cdot \underline{\Gamma}_P$ 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

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

$\hookrightarrow$ broadband noise

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

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

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

(uncorrelated direction)

$\therefore$

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial \underline{V}} \cdot \left\{ -\beta \underline{V} P - \frac{\partial}{\partial \underline{V}} \cdot \underline{\underline{D}}_V P \right\}$$

$\rightarrow$ F.-P. Eqn. for Brownian Motion

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 $\rightarrow$ $-\dfrac{\partial}{\partial \underline{V}} \cdot \dfrac{\langle \Delta \underline{V} \Delta \underline{V} \rangle}{2\Delta t} P = -\dfrac{\partial}{\partial \underline{V}} \cdot \underline{\underline{D}}_v P$

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 ⟺ Liouville Thm.
  - no systematic bias

can show: (HW)

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

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

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

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

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

→ 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 ---

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

→ 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:

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

more generally, have shown can write:

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

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

<u>or</u>

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

<u>obviously</u> akin to deriving fluid equations from Boltzmann equation!

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

derive equations for:

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

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

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...

$$\frac{\partial P}{\partial t} = \beta\left(\frac{\partial}{\partial \underline{V}} - \frac{1}{\beta}\frac{\partial}{\partial \underline{X}}\right)\cdot\left(\underline{V}P + \frac{D_V}{\beta}\frac{\partial P}{\partial \underline{V}}\right.$$

$$\left. - \frac{q_{ext}}{\beta}P + \frac{D_V}{\beta^2}\frac{\partial P}{\partial \underline{X}}\right)$$

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

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 $\quad \dot{\underline{x}} = -\dot{\underline{v}}/\beta$

→ This annihilates term #1 !

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

so obtain :

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

- 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,

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

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

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

$\Rightarrow$ 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 } 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

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

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

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

{ $(\underline{q}, \underline{p})$ 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 $\underline{\nabla}\cdot\underline{V}_{\Gamma} = 0$

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

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

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

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

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

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

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} <u>mean</u>, physically?

In general; seek calculate aspects of general many body system

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

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

$$= LA$$

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

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

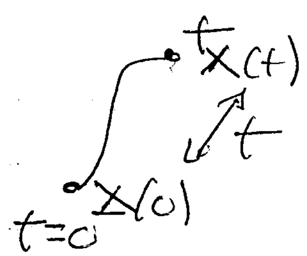
$$= \sum_{n=0}^{\infty} \frac{t^n}{n!} L^n A(x) = e^{tL} A(\underline{x})$$

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

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

$\rightsquigarrow$ moves particle along trajectory in phase space

i.e.



$\Leftrightarrow e^{tL}$

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.

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

avg. at time t

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

i.e. ala' Schrodinger $\rightarrow$ 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 $\rightarrow$ 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
$$\underbrace{\frac{d\underline{q}}{dt} = \underbrace{\underline{V}(\underline{q})}_{\text{deterministic velocity/flow}} + \underbrace{\underline{F}(t)}_{\text{noise fdctns}}}_{\text{schematic Langevin equation}}$$

→ schematic Langevin equation

Now, generically:

$$\frac{\partial f(\underline{q},t)}{\partial t} + \frac{\partial}{\partial \underline{q}} \cdot \Big(\underbrace{\big(\underline{V}(\underline{q}) + \underline{F}(t)\big) f}_{(d\underline{q}/dt)\, f} \Big) = 0$$

Can develop P.T. in noise strength

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

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

Now,

– l. o. in $\tilde{F}$

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

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

and plugging into (*) gives:

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

– 1^{st} order in F

Solving (**) ⇒

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

and plug $f(q,t)$ above into Eqn. (*)

⇒

$\Rightarrow$

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

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

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

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

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

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

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

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

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 ...