

### III.) Kinetic Equations

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- a) Kinetic Equations - An Overview

- consider Langevin equation, for Brownian motion

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

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

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

$\downarrow$   $\downarrow$   
 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  $n^{\text{th}}$  state

then, "birth" "death"

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

so

$$\frac{\partial P(n,t)}{\partial t} = \sum_{n'} \left[ \overset{\substack{n' \rightarrow n \text{ transition} \\ \text{probability} \\ \downarrow \\ \text{(rate)}}}{P(n',t) W(n',n)} - \overset{\substack{n \rightarrow n' \text{ transition} \\ \text{probability} \\ \downarrow \\ \text{(rate)}}}{P(n,t) W(n,n')} \right]$$

$\uparrow$  probability of state  $n'$                        $\uparrow$  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 Egn. 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

$$t \rightarrow t + \tau \rightarrow t + 2\tau \rightarrow \dots$$

then  $n \rightarrow n'$  event occurs faster than  $\tau$ .

② Fokker-Planck Equation

Consider system with no memory i.e. each step on  $\mathcal{T}$  independent of prior history.

so can write:

$$P(x_3, t_3 | x_1, t_1) = \int dx_2 P(x_3, t_3 | x_2, t_2) P(x_2, t_2 | x_1, t_1)$$

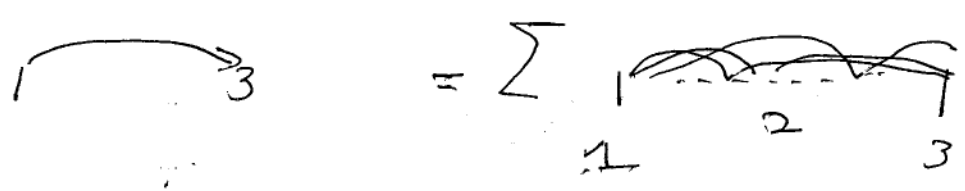
↓
↓
↓
↓

prob. of  $x_3$  at  $t_3$ 
integration
2 → 3
1 → 2 jump

starting from  $x_1$ 
over
jump
jump

at  $t_1$ 
intermediate
jump
jump

states



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  $\Delta x$  in time  $\tau$

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

i.e.  $t_2 - t_1$  is jump time  $\tau$   
 $x_2 - x_1$  is jump step  $\Delta x$

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  $\tau$  indep.  $x$ )  $\Rightarrow$

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

$$= - \frac{\partial}{\partial x} \Gamma_p$$

↓  
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  $\begin{cases} t < \tau \\ x < \Delta x \end{cases}$

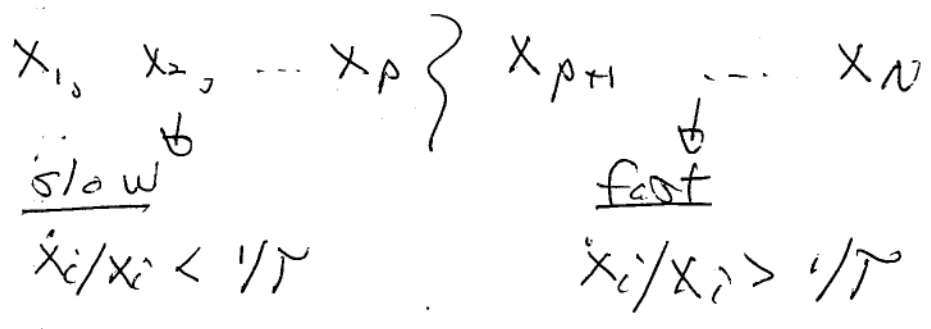
- F-P Equation is less general, but more tractable than Master Equation.

③ Zwanzig - Mori Equation is

F-P Egn. with Memory kernel (Memory correction)

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

for  $\tau$  slower than some  $\tau_i$ , separate into 'fast' and 'slow' variables



Z-M theory:

- assumes fast variables come to  $\odot$  equilibrium on time scales  $\tau$

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

then:

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

↓  
 Projection operator  $\underline{P}$ , projects evolution onto reduced # degrees of freedom, the slow variables.

- write projected Liouville equation, for slow variables  $\Rightarrow Z-M$  Egn.
- not surprisingly,  $Z-M$  Egn. can reduce to  $F-P$  Egn.
- $Z-M$ , clearly coarse-grains over fast variables
- $Z-M$ : projection procedure part, but not all, 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

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

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

$\Rightarrow$  expand

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

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

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



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

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

expectation  
(must exist)

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

variance  
(must exist)

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

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

so

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

- Fokker-Planck Equation,

Now, can note:

- $\frac{\partial P}{\partial t} = -\underline{D} \cdot \underline{\nabla} P$  structure assures F-P Egn.  
conserves probability. Derivative order matters!
- Obviously, can relate F-P Egn. to Master Egn. in "small kick" limit. (See Prob/m. 3 of HW 1).
- as example, for Brownian Motion

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

$\uparrow$   
 broadband noise

$$\infty \quad \frac{\langle \Delta \underline{v} \rangle}{\Delta t} = -\beta \underline{v}$$

$$\frac{\langle \Delta \underline{v} \Delta \underline{v} \rangle}{2\Delta t} = D_v \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$$D_v = \frac{\tilde{q}_0^2 \tau_c}{2}$$

(uncorrelated directions)

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial \underline{v}} \cdot \left\{ -\beta \underline{v} P - \frac{\partial \cdot D_v}{\partial \underline{v}} P \right\} \rightarrow \left\{ \begin{array}{l} \text{F-P Egn.} \\ \text{for} \\ \text{Brownian} \\ \text{Motion} \end{array} \right.$$

$$\tilde{\sim} 1D, \quad \frac{\partial P}{\partial t} = +\frac{\partial}{\partial v} \left\{ \beta v P + D \frac{\partial P}{\partial v} \right\}$$

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

$$\rho \approx \exp\left[-\beta V^2 / 2D_v\right]$$

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

In the absence of drag, with  $\rho(v, 0) = \delta(v - v_0)$

$$\rho(v, t) = \frac{1}{\sqrt{\pi D_v t}} \exp\left[-v^2 / 2D_v t\right]$$

i.e. diffusion  
pdf.

- Fokker-Planck Equation structure (general):

$$\text{drag/drift term} \rightarrow \frac{\langle \Delta v \rangle}{\Delta t} \rho = \underline{v} \rho \quad \hookrightarrow \text{drift velocity}$$

$$\text{diffusion term} \rightarrow - \frac{\partial}{\partial v} \cdot \frac{\langle \Delta v \Delta v \rangle}{2 \Delta t} \rho = - \frac{\partial}{\partial v} \cdot \underline{D}_v \rho$$

↓  
diffusion tensor

$$\text{and: } \frac{\partial \rho}{\partial t} + \frac{\partial}{\partial v} \cdot (\underline{v} \rho) = + \underline{D}_v \cdot \underline{\nabla}_v \rho$$

$$\underline{\Gamma}_v = - \underline{v} \rho \quad \leftarrow \underline{D}_v \cdot \underline{\nabla}_v \rho$$

drift  $\rightarrow$  deterministic part of motion

diffusion  $\rightarrow$  random part. (noise related)

- requirements for applicability of  
Fokker-Planck Theory

$\rightarrow$  stochastic motion

$\rightarrow$  step size

$\Delta V, \Delta x$

$\rightarrow$  no memory ( $t > \Delta t$ )

and

$$\langle \Delta V \rangle < \infty$$

$$\langle \Delta V^2 \rangle < \infty$$

$\rightarrow$  convergence of lowest  
2 moments

aka Central Limit Theorem.

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

- Fokker-Planck equation  $\leftrightarrow$  Markov process or  
chain, which is gradual unfolding of  
transition probability just as

conservative dynamical system is produced  
unfolding of contact transformation.

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

can show: (HW)

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

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

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

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

$$- \frac{\langle \underline{\Delta V} \underline{\Delta V} \rangle}{2 \Delta t} \cdot \frac{\partial \rho}{\partial V}$$

$$= \frac{\partial}{\partial V} \cdot \rho \cdot \frac{\partial \rho}{\partial V}$$

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

Here  $\langle \underline{A} \rangle = \frac{1}{2} \frac{\partial}{\partial \underline{v}}$ ,  $\langle \underline{A} \underline{A} \rangle$  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 ----

$$\frac{\partial \underline{v}}{\partial t} = -\beta \underline{v} + \frac{q_{\text{ext}}}{m_p} + \underline{q}$$

$\downarrow$  ↪ Brownian force  
 $\frac{f_{\text{ext}}}{m_p} = -\frac{d\phi}{m_p}$  ↪ 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  $v$   
so  $x$  kinematic

$\Rightarrow$

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

∴

$$\begin{aligned} P(\underline{x}, \underline{v}, t + \Delta t) &= \int d(\underline{\Delta x}) \int d(\underline{\Delta v}) P(\underline{x} - \underline{\Delta x}, \underline{v} - \underline{\Delta v}, t) * \\ &\quad \delta(\underline{\Delta x} - \underline{v} \Delta t) T(\underline{\Delta v}, \Delta t) \\ &= \int d(\underline{\Delta v}) P(\underline{x} - \underline{v} \Delta t, \underline{v} - \underline{\Delta v}, t) T(\underline{\Delta v}, \Delta t) \end{aligned}$$

so can re-write:

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

and now expand, as before!

$$+ \underline{a}_{\text{ext}} \cdot \frac{\partial P}{\partial \underline{v}}$$

$$\frac{\partial P}{\partial t} + \underline{v} \cdot \nabla_x P \Big|_t = - \frac{\partial}{\partial \underline{v}} \cdot \left[ \frac{\langle \underline{\Delta v} \rangle}{\Delta t} P - \frac{\partial}{\partial \underline{v}} \cdot \frac{\langle \underline{\Delta v} \underline{\Delta v} \rangle}{2 \Delta t} P \right]$$

more generally, have shown can write:

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

deterministic orbits
randomly fluctuating orbits

where "deterministic orbits" means:

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

→ 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:

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

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

$\Lambda$ -equation  $\Leftrightarrow$  Schmalchowski Equation

Now, have: (for Brownian Particle)

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

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

which can be re-written as:

↓  
in a superficially very  
complicated form, as...

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

$$\text{now: } n(x, t) = \int dv \rho(x, v, t)$$

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

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

→ This annihilates term # (1)!

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

so obtain:

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

- the Schmoluchowski eqn. for  $n(x, t) \rightarrow$   
spatial pdf

Observe:

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

i.e. eqns of motion:

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

$$\frac{dx}{dt} = v$$

at terminal velocity,

$$v = \frac{q_{\text{ext}}}{\beta} + \frac{\tilde{q}}{\beta}$$

$\rightarrow$  random.

$$\frac{dx}{dt} = \frac{q_{\text{ext}}}{\beta} + \frac{\tilde{q}}{\beta}$$

$\rightarrow$  deterministic

$$\therefore \left\{ \begin{array}{l} \frac{\partial n}{\partial t} + \frac{\partial}{\partial x} \left( \frac{dx}{dt} n \right) = D_{xx} \frac{\partial^2 n}{\partial x^2} \\ D_{xx} = D_v / \beta^2 \end{array} \right. \quad \text{deterministic}$$

$\Rightarrow$  Schmoluchowski Egn.

- still conservative!

$$\frac{\partial n}{\partial t} = - \frac{\partial}{\partial x} \Gamma_n$$

$$\Gamma_n = \left( \frac{q_{ext}}{\beta} n - \frac{D_v}{\beta^2} \frac{\partial n}{\partial x} \right)$$

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
  - 3.) energy diffusion
- }  $\gamma$  large  
}  $\gamma \rightarrow 0$

**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  $\underline{v}$ , can write:

$$\frac{\partial}{\partial t} = \frac{\partial}{\partial \underline{x}} \cdot \underline{v} = \left( \frac{\partial}{\partial \underline{q}}, \frac{\partial}{\partial \underline{p}} \right) ; \quad \underline{v} = \underline{v}(\underline{q}, \underline{p}) = \left\{ \frac{d\underline{q}}{dt}, \frac{d\underline{p}}{dt} \right\} \quad \text{Theory of Liouville operator}$$

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

$$\text{as } \frac{\partial f}{\partial t} + Lf = 0 \quad \left\{ \begin{array}{l} (\underline{q}, \underline{p}) \text{ dimensionality} \\ \text{arbitrary} \end{array} \right.$$

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

Interesting to note properties of Liouville operator...

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

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

now:  $L = \underline{v} \cdot \underline{\nabla} = \underline{\nabla} \cdot (\underline{v} \quad)$  , as  $\underline{\nabla} \cdot \underline{v} = 0$   
 $\frac{\partial}{\partial t} + L = 0$  , (and  $\frac{\partial \rho}{\partial t} = -\underline{\nabla} \cdot (\rho \underline{v})$ )

$$\int_{Vol} d\underline{x} L A F = + \int_{Vol} d\underline{x} \frac{d}{d\underline{x}} \cdot (\underline{v} A F)$$

effective flow velocity

$$= - \oint d\underline{s} \cdot \underline{v} A F \quad (\text{normal } \underline{e}_n)$$

so avgd evolution  $A$  entirely determined by values of:  $\underline{v} \leftrightarrow$  phase space flow velocity and  $F$  on boundary of averaging region

2)  $L$  is anti-self adjoint c.f.  $L^\dagger = -L$

$$L(AF) = (LA)F + A(LF)$$

as  $L$  is first order diffntl operator

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

but  $L(AF) = (LA)F + A(LF)$

$$\therefore \int dx A(LF) = \int dx \left\{ L(AF) - (LA)F \right\}$$

$$= \int dx \left\{ \frac{d}{dx} (AF) - (LA)F \right\}$$

and for  $f \rightarrow 0$  at  $x \rightarrow \infty$  (normalizability)  $\Rightarrow$

$$\boxed{\int dx A(LF) = - \int dx (LA)F}$$

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

In general; seek calculate aspects of general many body system

$A(x) \equiv$  generic dynamical variable

$$\begin{aligned} \text{then } \left. \frac{\partial A}{\partial t} \right|_{t=0} &= \frac{\partial A}{\partial \underline{z}} \cdot \left. \frac{\partial \underline{z}}{\partial t} \right|_{t=0} + \frac{\partial A}{\partial p} \cdot \left. \frac{\partial p}{\partial t} \right|_{t=0} \\ &= LA \end{aligned}$$

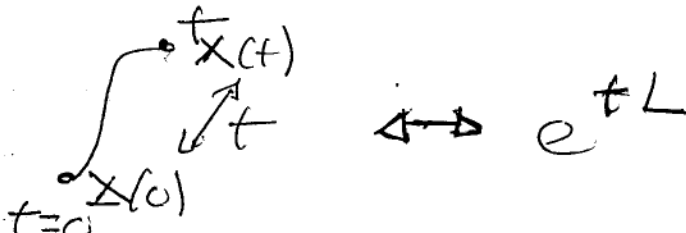
$$\text{and } \left( \left. \frac{\partial^n A}{\partial t^n} \right)_{t=0} \right) = L^n A$$

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

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

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

$\therefore e^{tL} \rightarrow$  propagator / orbit evolution operator  
 $\rightarrow$  moves particle along trajectory in phase space

i.e. 

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



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

and

trajectory unique!

$$\begin{aligned} e^{tL} (A(x) B(x)) &= (e^{tL} A(x)) (e^{tL} B(x)) \\ &= A(e^{tL} x) B(e^{tL} x) \end{aligned}$$

- Now can formulate phase space averages of  $A$  (classical expectation, in  $\mathcal{Q}M$ ). Point is that can approach either classically Schrodinger or Heisenberg, i.e.

$$\begin{aligned} \langle A, t \rangle &= \int dx A(x) F(x, t) \\ \text{avg. at} \downarrow \text{time } t &= \int dx A(x) e^{-tL} F(x, 0) \end{aligned} \quad \frac{\partial F}{\partial t} + LF = 0$$

i.e. classically Schrodinger  $\rightarrow F$  evolves.

$\downarrow$   
 $\sim |F|^2$  weighting pdf

equivalently

value of  $A$  at  $t$ , from initial state  $X$ .

$$\begin{aligned} \langle A, t \rangle &= \int dx A(x, t) F(x, 0) \\ &= \int dx (e^{tL} A(x, 0)) F(x, 0) \end{aligned}$$

$L$  anti-self-adjoint

i.e. classically Heisenberg  $\rightarrow A$  evolves

$\sim$  classically 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 
$$\frac{d\underline{q}}{dt} = \underbrace{V(\underline{q})}_{\substack{\text{deterministic} \\ \text{velocity/flow}}} + \underbrace{F(t)}_{\substack{\text{noise} \\ \text{flucts}}} \rightarrow \text{schematic Langevin equation}$$

Now, generically: 
$$\frac{\partial f(\underline{q}, t)}{\partial t} + \frac{\partial}{\partial \underline{q}} \cdot \left( \underbrace{V(\underline{q})}_{\text{deterministic}} + \underbrace{F(t)}_{\text{noise}} \right) f = 0 \quad \left\{ \begin{array}{l} \text{Can develop} \\ \text{P.T. in noise} \\ \text{strength} \end{array} \right.$$

$$\begin{aligned} (*) \quad \frac{\partial f(\underline{q}, t)}{\partial t} &= - \frac{\partial}{\partial \underline{q}} \cdot \left( V(\underline{q}) f(\underline{q}, t) + F(t) f(\underline{q}, t) \right) \\ &= -L f - \frac{\partial}{\partial \underline{q}} \cdot \left( F(t) f(\underline{q}, t) \right) \end{aligned}$$

Now,

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

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

and plugging into (\*) gives:

$$\frac{\partial f(q, t)}{\partial t} = -Lf - \frac{\partial}{\partial q} \cdot (E(t) f(q, t)) \quad (**)$$

- 1st order in  $\tilde{F}$

solving (\*\*)  $\Rightarrow$

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

l.o.  $\Rightarrow O(\tilde{F}^{(1)})$

$O(\tilde{F}^{(1)})$  - first order

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

$\Rightarrow$

⇒

$$\begin{aligned} \frac{\partial f(q, t)}{\partial t} &= -L f - \frac{\partial}{\partial q} \cdot \left( F(t) \left\{ e^{-tL} f(q, 0) \right. \right. \\ &\quad \left. \left. - \int_0^t ds e^{-(t-s)L} \frac{\partial}{\partial q} \cdot (F(s) f(q, s)) \right\} \right) \\ &= -L f - \frac{\partial}{\partial q} \cdot F(t) e^{-tL} f(q, 0) \\ &\quad + \frac{\partial}{\partial q} \cdot F(t) \int_0^t ds e^{-(t-s)L} \frac{\partial}{\partial q} \cdot (F(s) f(q, s)) \end{aligned}$$

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

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

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

"delta correlated" limit

so  $\langle f \rangle = \langle F(q, t) \rangle$  evolves according to:  
 $\downarrow$   $\downarrow$   
 coarse-grained  $f$

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

→ 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,  
 $\langle F^2 \rangle < \infty$

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

→ Properties of Fokker-Planck Operator

$$\langle F(q, t) \rangle \equiv F(q, t), \text{ hereafter}$$

$$\left\{ \begin{array}{l} \underline{B} \text{ indep } q \end{array} \right.$$

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

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

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

$$\int dq \psi(q) \mathcal{D} \chi(q) = \int dq \chi(q) \mathcal{D}^+ \psi(q)$$

Exercise: Show this!

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

↓  
sign flip,  
deriv. order  
changes.

↓  
diffusion is self-adjoint  
(this form)

Now,  $f(q, t) = e^{Dt} f(q, 0)$

so expectation value defined as:

$$\begin{aligned} \langle \phi, t \rangle &= \int dq \psi(q) f(q, t) \\ &= \int dq \psi(q) e^{Dt} f(q, 0) \end{aligned}$$

~ Schrodinger representation  $\rightarrow$  pdf evolves.

$$\stackrel{\text{or}}{=} \langle \phi, t \rangle = \int dq f(q, 0) e^{Dt} \psi(q)$$

~ Heisenberg representation  $\rightarrow$   $\phi$ , the expectation of which is calculated, evolves...