

Another Look at Fokker-Planck Theory

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- Stochastic Liouville Eqn
- Moment closure for Noise

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Next: I - Another look at Fokker-Planck Theory

II - Kinetics of Chemical Reactions

- Transition State Theory
- Kramers' Problem

- 1.) first passage time
 - 2.) reaction rate constants
 - 3.) energy diffusion
- } γ 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:

Theory of
Liouville

$$\frac{d}{dt} \frac{\partial}{\partial x_n} = \left(\frac{\partial}{\partial \underline{z}}, \frac{\partial}{\partial \underline{p}} \right); \quad \underline{v} = \underline{v}_T = \left\{ \frac{d\underline{z}}{dt}, \frac{d\underline{p}}{dt} \right\} \quad \text{operator}$$

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

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

$(\underline{z}, \underline{p})$ dimensionality
arbitrary

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

Interesting to note properties of Liouville operator, . . .

1) For $A = A(x) \rightarrow$ arbitrary function operator of/in Γ

often seek: $\int_{Vol} dx L A F$ c.e. { weighted avg/expectation of A in domain Γ }

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 $\frac{\partial \rho}{\partial t} = -\underline{\nabla} \cdot (\rho \underline{v})$)

$\int_{Vol} dx L A F = + \int_{Vol} dx \underline{\nabla} \cdot (\underline{v} A F)$ effective flow velocity
 $= - \oint d\underline{s} \cdot \underline{v} A F$ (normal \hat{n})

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

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

$L(A F) = (L A) F + A(L F)$
as L is first order diffntl operator

Now, consider $\int dx A(L F)$

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

$$\begin{aligned} \therefore \int dx A(LF) &= \int dx \{ L(AF) - (LA)F \} \\ &= \int dx \left\{ \frac{d}{dx} (LAF) - (LA)F \right\} \end{aligned}$$

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

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

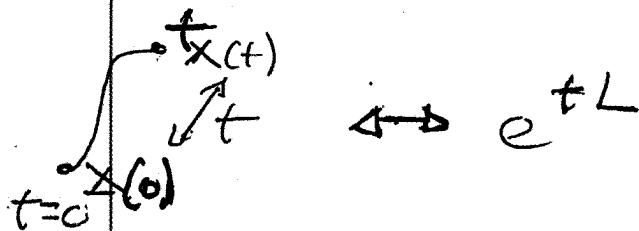
$$\text{and } \left(\left. \frac{\partial^n A}{\partial t^n} \right)_{t=0} \right) = L^n A$$

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

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

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

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

i.e. 

then rather obvious (as V_H incompressible) that

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

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.

$\sim |x|^2$ 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 $\frac{dq}{dt} = \underbrace{v(q)}_{\substack{\text{deterministic} \\ \text{velocity/flow}}} + \underbrace{F(t)}_{\substack{\text{noise} \\ \text{flucts}}} \rightarrow \text{schematic Langevin equation}$

Now, generically:

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

$$(*) \quad \frac{\partial f(q,t)}{\partial t} = - \frac{\partial}{\partial q} \cdot \left(v(q) f(q,t) + F(t) f(q,t) \right)$$

$$= -L f - \frac{\partial}{\partial q} \cdot \left(F(t) f(q,t) \right)$$

Now,

- l.o. in \tilde{F}

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

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

and plugging into (*) gives:

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

- 1st order in \tilde{F}

Solving (*) \Rightarrow

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

l.o. $\Rightarrow O(\tilde{F}^2)$

$O(\tilde{F}^2)$ - first order...

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

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\Rightarrow

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

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

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

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

"delta correlated" limit \rightarrow short τ_{av}

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

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

→ 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

$$\left\{ \begin{array}{l} \langle F(q, t) \rangle \equiv F(q, t), \text{ hereafter} \\ \underline{B} \text{ indep. } q \end{array} \right.$$

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

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

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!

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

\int
sign flip,
deriv. order
changes.

\int
diffusion is self-adjoint
(this term)

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

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

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