Next: (I) – Another look at Fokker-Planck Theory

(II) – Kinetics of Chemical Reactions

a) Transition State Theory

b) Kramers' Problem

1.) first passage time } γ large

2.) reaction rate constants }

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

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

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

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

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

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

Interesting to note properties of Liouville operator...

1) For $A = A(\underline{x})$ → arbitrary $\begin{cases}\text{function}\\ \text{operator}\end{cases}$ of/in Γ

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

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

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

$$\int_{Vol} d\underline{x}\, L A f = + \int_{Vol} d\underline{x}\, \frac{d}{d\underline{x}}\cdot(\underline{V} A f)$$

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

so avgd 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. $L^{+} = -L$

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

as L is first order diffntl operator

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

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

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

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

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

$$= LA$$

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

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

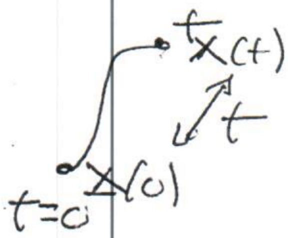
$$= \sum_{n=0}^{\infty} \frac{t^n L^n}{n!} A(x) = e^{tL} A(\underline{x})$$

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} → propagator / orbit evolution operator

→ moves particle along trajectory in phase space

i.e.



$\Leftrightarrow e^{tL}$

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

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

and

trajectory unique!

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

- 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 $\underline{x}$.

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

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 $\frac{d\underline{q}}{dt} = V(\underline{q}) + \underline{F}(t)$ → schematic Langevin equation

$V(\underline{q})$ ↳ deterministic velocity/flow

$\underline{F}(t)$ ↳ noise factors

Now, generically:

$$\frac{\partial f(\underline{q},t)}{\partial t} + \frac{\partial}{\partial \underline{q}} \cdot \left(\left(\underline{V}(q) + \underline{F}(t) \right) f \right) = 0$$

($\underline{V}(q) + \underline{F}(t)$ ↳ (dq/dt); $(dq/dt)\,f$)

{ Can develop P.T. in noise strength

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

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

Now,

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

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

and plugging into (*) gives:

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

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

Solving (**) ⇒

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

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

⇒

$\Rightarrow$

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

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

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

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

→ $\langle F \rangle = 0$, $\langle F F \rangle \neq 0$

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

"delta correlated" limit

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

↓ coarse-grained pdf

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

→ 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

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

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

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

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!

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

sign flip, deriv. order changes.

diffusion is self-adjoint (this form)

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

so expectation value defined as:

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

~ Schrodinger representation → pdf evolves.

or

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

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