# 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 $t$.

object of Kinetic Equation

Kinetic equations seek to evolve/determine $P(\underline{x}, \underline{v}, t)$ directly, rather than to solve Langevin equation and then average.

- $\underline{\text{Boltzmann equation}}$ is an example of a kinetic equation

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

Liouvillean

standard distribution eqn. (phase space density)

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

- 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"

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

transitions $\underline{\text{in}}$ from other states $n'$

transitions $\underline{\text{out}}$ from $n$ to other states $n'$

$n' \to n$ transition probability (rate) $\quad\quad$ $n \to n'$ transition probability (rate)

so $$\frac{\partial P(n,t)}{\partial t} = \sum_{n'} \Big[ P(n',t)\, W(n',n) - P(n,t)\, W(n,n') \Big]$$

$\neq n$ $\quad$ probability of state $n'$ $\quad\quad$ 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 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 $\tau$.

## ② Fokker–Planck Equation

Consider system with no memory → i.e. each step on $\tau$ independent of prior history.

so can write:

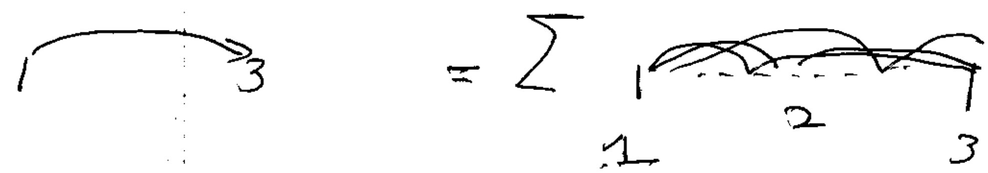
$$P(x_3, t_3 \mid x_1, t_1) = \int dx_2 \; P(x_3, t_3 / x_2, t_2) \; P(x_2, t_2 / x_1, t_1)$$

prob. of $x_3$ at $t_3$ starting from $x_1$ at $t_1$.

integration over intermediate states

2 → 3 jump

1 → 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 $\Delta X$ in time $\tau$

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

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 $T$ indep. $x$) $\Rightarrow$

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

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

$\Gamma_p$: 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. Eqn. with Memory Kernel (Memory Correction)

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

for $t$ slower than some $\tau$, separate into 'fast' and 'slow' variables

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

$\dot{x}_i / x_i < 1/\tau$ $\qquad$ $\dot{x}_i / x_i > 1/\tau$

Z-M theory:

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

- can describe evolution in terms of slow variables, only then:

- $\underset{\uparrow}{P}(x_1, x_2, \ldots x_N) \rightarrow (x_1, \ldots x_p)$
  Projection operator $P$, projects evolution onto reduced # degrees of freedom, the slow 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 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.

$\Longleftrightarrow$ no memory

So, as in Brownian Motion

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

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

$\Rightarrow$ expand

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

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

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)

$\therefore$

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

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

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

$\tilde{\underline{q}}(t) \to$ broadband noise

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

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

$D_V = \tilde{q}_0^2 \tau_{ac}$ (uncorrelated direction)

$\therefore$

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

$\to$ 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 $\rightarrow$ $\frac{\langle \Delta \underline{v} \rangle}{\Delta t} P = \underline{V} P$

$\underline{V}$ ↳ drift velocity

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

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
$\Delta v, \Delta x$
→ 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 $\langle \Delta v^2 \rangle \rightarrow \infty$, 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. $$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial \underline{v}}\cdot\left(\frac{\langle \underline{\Delta v}\rangle}{\Delta t} f - \frac{\partial}{\partial \underline{v}}\cdot\frac{\langle \underline{\Delta v}\,\underline{\Delta v}\rangle}{2\Delta t} f\right)$$

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

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

$\rightarrow$ 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 ---

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

$\underline{g}_{ext}$ ↓ $\frac{\underline{f}_{ext}}{m_p} = -\frac{\nabla \phi}{m_p}$ → potential (i.e. spring, gravity)

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

$$\frac{d\underline{x}}{dt} = \underline{v}$$

so obviously, particle random walks in $\underline{x}$ and $\underline{v}$. For phase space pdf:

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

Furthermore, Brownian kick applied only in $\underline{v}$
so $\underline{x}$ kinematic

$\Rightarrow$

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

$\therefore$

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

so can re-write:

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

and now expand, as before:

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

more generally, have shown can write:

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

deterministic orbits

where "deterministic orbits" means:

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

→ 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:

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

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

$n$ - 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...

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

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

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

$\Rightarrow$ This annihilates term # 1 !

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

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:

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

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

at terminal velocity,

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

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

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

$\Rightarrow$ 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 $\Big\}$ $\gamma$ large
3.) energy diffusion $\Big\}$ $\gamma \to 0$.
(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:

$$\frac{\partial}{\partial \underline{x}} = \frac{\partial}{\partial \underline{x}_\Gamma} = \left(\frac{\partial}{\partial \underline{q}}, \frac{\partial}{\partial \underline{p}}\right) \quad ; \quad \underline{V} = \underline{V}_\Gamma = \underbrace{\left\{\frac{d\underline{q}}{dt}, \frac{d\underline{p}}{dt}\right\}}_{\text{Theory of Liouville operator}}$$

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

as $\quad \dfrac{\partial f}{\partial t} + Lf = 0 \qquad \Big\{ (\underline{q}, \underline{p})$ dimensionality arbitrary

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

Interesting to note properties of Liouville operator...

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

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

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

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

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

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

so avg'd 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 i.e. $L^{+} = -L$

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

as $L$ is first order diff'ntl 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 $$\left.\frac{\partial A}{\partial t}\right|_{t=0} = \frac{\partial A}{\partial \underline{q}} \cdot \left.\frac{\partial q}{\partial t}\right|_{t=0} + \frac{\partial A}{\partial \underline{p}} \cdot \left.\frac{\partial p}{\partial t}\right|_{t=0}$$

$$= LA$$

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

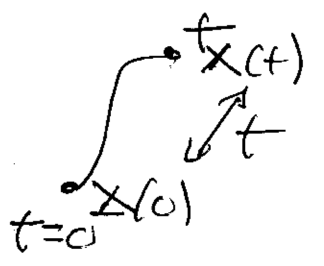
$$= \sum_{n=0}^{\infty} \frac{t^n}{n!} L^n A(\underline{x}) = e^{tL} A(\underline{x})$$

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

$\therefore$ $e^{tL}$ $\leadsto$ <u>propagator</u> / <u>orbit evolution operator</u>

$\leadsto$ 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.

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

avg. at time $t$

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

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

Now, generically:

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

{ Can develop P.T. in noise strength

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

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

Now,

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

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

and plugging into (*) gives:

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

- 1st order in $\underset{\sim}{F}$

solving (**) $\Rightarrow$

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

ii) plug $f(q, t)$ above 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, <u>average</u> over $P(F)$, assuming:

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

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

"delta correlated" limit

<u>so</u> $\langle f\rangle = \langle f(q,t)\rangle$ 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

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

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

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

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!

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

sign flip, deriv. order changes.

diffusion is self-adjoint (this form)

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

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 → $\phi$, the expectation of which is calculated, evolves ...

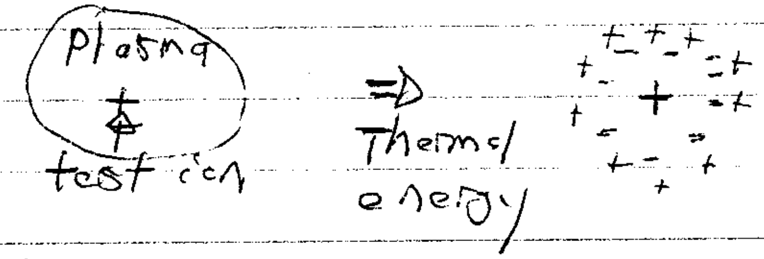
# Applications of Fokker-Planck Theory

## ⓐ Coagulation in Colloidal Suspension

general idea range

Aside: Screening and Scale Lengths in Plasmas and Electrolytic Solutions

Consider ion-electron (i.e. neutral) plasma:




electrons and other ions adjust to screen test ion potential on scale $\lambda_D$

$$\phi_{ion} = \frac{q}{r}$$

$$\phi_{ion} = \frac{q}{r} e^{-r/\lambda_D}$$

so an effective "sphere of influence" for a given test charge is established.

$R_{sphere} = \lambda_D$.

How calculate screening length?

$$\nabla^2 \phi = -4\pi\rho = -4\pi|e|(n_i - n_e)$$

Now, write $n_i = q\delta(x - \underline{x}_T) + n_i^{screen}$

$n_e = n_e^{screen}$

$\left. \begin{array}{l} n_i^{screen} \\ n_e^{screen} \end{array} \right\}$ screening ~~responses~~ of plasma to external charge.

As $t \to \infty$, can use equilibrium distribution fctns:

$T_i = T_e$

$$f_{ion} = \frac{n_0}{(\sqrt{\pi} v_{th_i})^3} e^{-(\epsilon_K^{ion} + |q| \phi)/T}$$

$$n_{ion} = n_0 e^{-q\phi/T}$$
$$n_{elec} = n_0 e^{q\phi/T}$$

Alternatively, can proceed from kinetic equation:

$$\frac{\partial f}{\partial t} + \underline{v} \cdot \nabla f + \frac{q}{m}(-\nabla \phi) \cdot \frac{\partial f}{\partial v} = C(f)$$

if $\lambda_D < l_{mfp} \Rightarrow$ ignore $C(f)$ (Vlasov Eqn.)
$\partial f / \partial t = 0$ (eqbrm.)

$$v \cdot \nabla f - \frac{q}{m} \nabla \phi \cdot \frac{\partial f}{\partial v} = 0$$

$\to$ amplitude factor

Write: $f = A(x) f_M^{(0)}$

$$\therefore \left( \underline{v} \cdot \nabla A + \frac{q}{m} \nabla \phi \cdot \frac{\underline{v}}{v_{Th}^2} \right) f_M^0 = 0$$

$\Rightarrow A = -q\phi$

$\Rightarrow$ suggests immediate extension to dynamic screening! $\epsilon(\omega, k)$

Then:

$$\nabla^2 \phi = -4\pi n_0 |e| \left( e^{-|e|\phi/T} - e^{+|e|\phi/T} \right) + 4\pi q \delta$$

$$\cong -4\pi n_0 |e| \left( 1 - \frac{|e|\phi}{T} - 1 - \frac{|e|\phi}{T} \right) + 4\pi q \delta$$

$$\therefore \nabla^2 \phi - 4\pi \left( \sum_z \frac{n_z q_z^2}{T_z} \right) \phi = 4\pi q \delta(x - x_0)$$

$$\Rightarrow \underbrace{1/\lambda_D^2}_{\text{Debye Length}} = \left( 4\pi \sum_z \frac{n_z q_z^2}{T_z} \right)$$

$\lambda_D^2 \sim T / 4\pi n_0 q^2$

$\Rightarrow$ thermal energy allows adjustment

$$\therefore \phi_{Test} = q_T e^{-r/\lambda_D} / r$$

Co-agulation problem is classic paradigm of "self-organization" in stochastic system



In electrolytic solutions: similar story, with inclusion of Stokes Drag on electrolytes. i.e. $\lambda \to$ range. Alternatively: Van-der-Waals Forces

Now, can consider co-agulation problem!

$\Rightarrow$ colloidal suspension = bunch of Brownian particles in solution

$\Rightarrow$ $t=0$ $\Rightarrow$ electrolyte added, uniformly [dusty plasma]

- each Brownian particle surrounded by sphere of influence of radius $R (\to \lambda_D)$
- when two spheres come within $R$ $\Rightarrow$ particles aggregate to form "double particle"

$\Rightarrow$ Brownian motion will result in formation of aggregates $\Rightarrow$ coagulation

$\to$ seek describe dynamics of aggregation process:

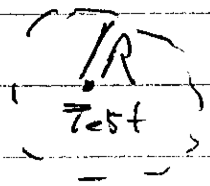
① - aggregation due BM to single, fixed particle

② - Consider ensemble of such in Brownian motion.

Plasma: $n \lambda_D^3 \gg 1$
Electrolyte: $n \lambda_D^3 \gtrsim 1$

$n_e \equiv$ background density of other particles

i.)




$\hookrightarrow$ perfectly absorbing surface

sticking # $\sim S\,\Gamma$
$\sim R^2 \frac{D}{R}$

$\therefore$ need solve:

$\hookrightarrow$ aggregate density

$$\frac{\partial n_A}{\partial t} = D \nabla^2 n_A \qquad D = T/6\pi a M$$

$$n_A = 0 \quad \text{at } r = R,\ t > 0$$

(particles at radius interaction aggregated)

$$n_A = n_0 \quad \text{at } t = 0,\ r > R$$

Can immediately exploit spherical symmetry

$$\frac{\partial}{\partial t}(r n_A) = D \frac{\partial^2}{\partial r^2}(r n_A) \qquad \frac{1}{r}\frac{\partial^2}{\partial r^2}(r n_A)$$

$$\Rightarrow n_A = n_0 \left[ 1 - \frac{R}{r} + \frac{2R}{r\sqrt{\pi}} \int_0^{(r-R)/2(Dt)^{1/2}} e^{-x^2}\, dx \right]$$

Rate of arrival at $r = R$ surface:

$\Gamma = D\,\partial n_A/\partial r$

$(\Gamma)\,4\pi r^2$ — i.e. dimensional analysis

$$\text{Rt arrival} = 4\pi D\left(r^2 \frac{\partial n_A}{\partial r}\right)_R = 4\pi D R n_0 \left(1 + \frac{R}{(\pi D t)^{1/2}}\right)$$

large guys cluster faster

i.e. $(tD) \gg R^2$ (long time)

$$\text{Rt arrival} = 4\pi D R n_0 \qquad \left(\frac{\partial n_A}{\partial r} \sim \frac{n_A}{R}\right)$$

diffn, scale, density

$\longrightarrow$ advantage

ii.) Now, allow all particles to undergo Brownian Motion

$\Rightarrow$ flux determined by
- BM thru $r=R$ sphere
- BM of $r=R$ sphere.

(i.e. consider diffn. in $r$, - coordinates)

∴ not surprised:

$$\text{Rt Arrival} = 4\pi (D_1 + D_2) R n_0 \left(1 + \frac{R}{(\pi(D_1+D_2)t)^{1/2}}\right) \; *$$

Now generally, for density of k-fold aggregates:

$$\frac{dn_k}{dt} = \left(\begin{array}{c}\text{Birth of}\\ \text{k-fold}\end{array}\right) - \left(\text{Death of k-fold}\right)$$

Birth of k-fold $\equiv \sum$ all $i, j$ aggregate combinations s/t $i+j=k$

$$\left(\frac{dn_k}{dt}\right)_{Birth} = \sum_{\substack{i,j\\ i+j=k}} n_j \left(\text{Rt Arrival } i \,\middle|\, i+j\right)$$

↳ symm. factor – avoid double counting

$$= \frac{1}{2} \sum_{\substack{i,j\\ i+j=k}} n_i n_j (4\pi) D_{ij} R_{ij}$$

$D_{ij} = D_i + D_j \qquad D = D(a)$

$R_{ij}$ = Radius influence $R_{ij}$ aggregation

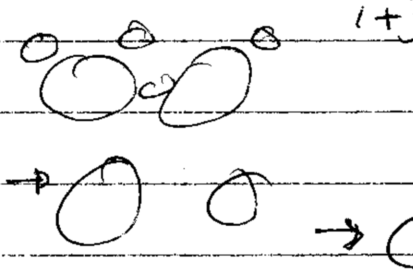
Similarly:

$\left(\frac{dn_k}{dt}\right)_{death}$ = all $k$ + something else to form higher aggregates

$$\left(\frac{dn_k}{dt}\right)_{death} = -n_k \sum_i 4\pi D_{ki} R_{ki} n_i$$

$\Rightarrow$ have 'birth-death' model of colloidal suspension:

$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{\substack{i,j \\ i+j=k}} 4\pi D_{ij} R_{ij} n_i n_j$$



$$- n_k \sum_i 4\pi D_{ki} R_{ki} n_i$$

a/a' - inverse cascade
- bubble competition

has generic form: $\to$ prod. of concen/occup.

$$dn_k/dt = \sum \frac{1}{\tau_{k/ij}} n_i n_j - \sum \frac{n_i}{\tau_{j/ik}} n_k$$

$n R D \sim \frac{1}{\tau}$ $\to$ time scale.

here.

Simplifying swindle: $D_{ij} R_{ij} = \underbrace{DR}_{}$

~ constancy of rate, up to concen

$$\frac{dn_k}{dt} = 4\pi DR\left(\frac{1}{2}\sum_{\substack{i,j\\ i+j=k}} n_i n_j - \sum_i n_k n_i\right)$$

normalize $t$ to diff n time: $\tau = 2\pi DRt$

$$\frac{dn_k}{d\tau} = \left(\sum_{i,j} n_i n_j - 2n_k \sum_i n_i\right)$$

To solve, can note:

$$\frac{d}{dt}\sum_k n_k = \left(\sum_{i,j} n_i n_j - 2\sum_{i,k} n_k n_i\right)$$

just re-label:

$$= -\left(\sum_{k=1} n_k\right)^2$$

$$\therefore \sum_k n_k = n_0 / 1 + n_0\tau \qquad \sum_k n_k \equiv n_0$$

$$\frac{dn_1}{dt} = -2 n_1 \sum_{k=1}^{\infty} n_k$$

$$= -2\, n_1 n_0 / (1 + n_0 \tau)$$

$$\Rightarrow \quad n_1 = n_0 / (1 + n_0 \tau)^2$$

in general : $\quad n_k = n_0 \left[ (n_0 \tau)^{k-1} / (1 + n_0 \tau)^{k+1} \right]$

gives basic decay law.

Message: - big guy's eat the little guys, becoming progressively bigger...

until

- one big guy eats them all..

— Kinetics and Stochastic Dynamics of Chemical Reactions.

→ Chemical reaction ↔ [transition
evolution in state space
birth + death process]

i.e.

(dies) $H_2O$ + energy → 2H + O (born)

↳ progression

→ often characterized by rate constant

$A + B \rightarrow AB$

↳ the answer

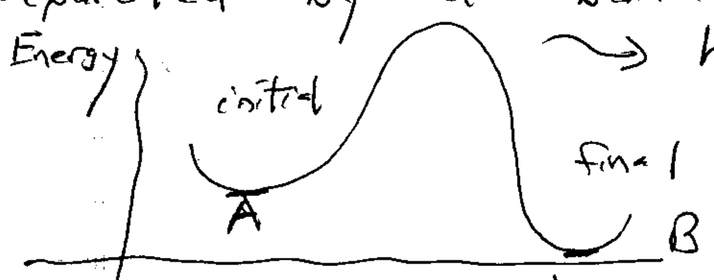
$k_1 = [AB] / [A][B]$

rate constant, at equilibrium.

→ often/usually associated with transition between two states ("attractors") separated by a barrier

→ hill, barrier

i.e.




"reaction coordinate" →

begs questions:

- how does reaction progress over the barrier? → noise, thermal fluctuations
  - temperature $T$
- what is rate of progression, at $T$?

i.e. might expect:

$$(\text{rate}) \sim \underbrace{(D, \gamma, \text{etc.})}_{\substack{\text{characteristic}\\\text{parameters of}\\\text{fluctuation}}} \exp\Big[-\underbrace{(E_A - E_B)/T}_{\substack{\text{equilibrium}\\\text{factor.}}}\Big]$$

∴ two topics:

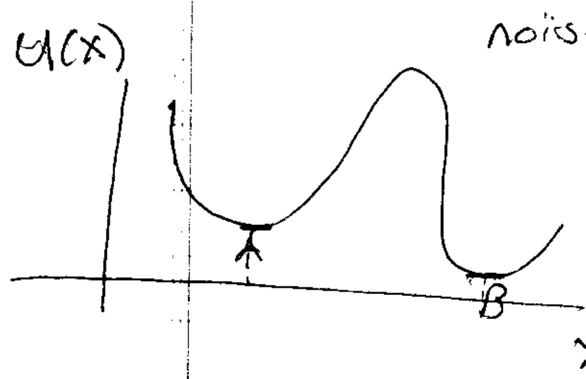
a) transition state theory (Wigner, '32)

→ simple theory of relating rate constants to microscopics

→ reaction as phase space flow.

D.) Kramers Problem (Kramers, '40)

"reaction" → particle in potential
+
noise




I

→ $J_{AB}$ → current / flow rate from A to B ?

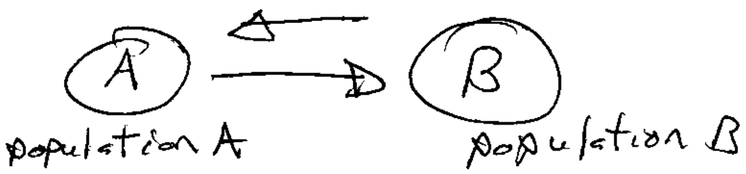
→ $T_{AB}$ → time of first passage ?
→ mean "confinement time" of particle in well at A

i.e. mean time after which noise will cause escape to B.

$J_{AB}$, $T_{AB}$ ↔ related to "rate constants" for $A \to B$ reaction / evolution.

## 9a) Transition State Theory (TST)

reaction ⟶ macroscopically; birth/death

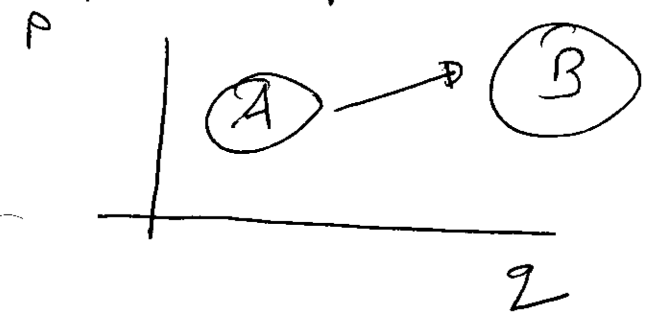



$$\frac{dP_A}{dt} = -\underbrace{k_{BA}\,P_A(t)}_{\substack{\text{outflow from}\\ A \text{ to } B\\ \text{(death)}}} + \underbrace{k_{AB}\,P_B(t)}_{\substack{\text{inflow from } B\\ \text{to } A\\ \text{(birth)}}}$$

$$\frac{dP_B}{dt} = -k_{AB}\,P_B(t) + k_{BA}\,P_A(t)$$

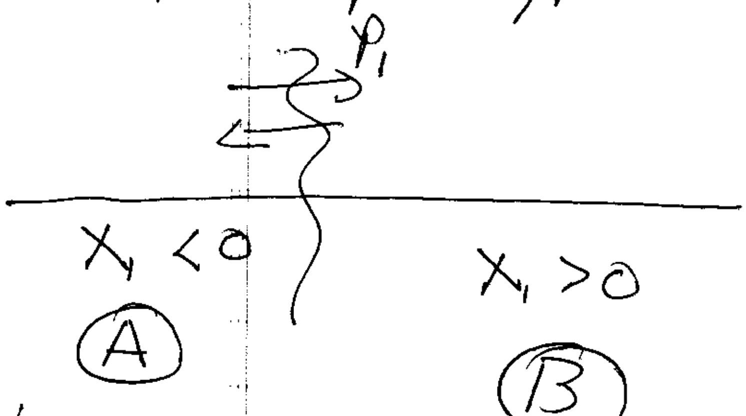
How represent dynamics of $N \gg 1$ degree of freedom system (i.e. "moles")?

⟹ phase space flow




i.e. associate A, B with regions of phase space then calculate flux.

simplest prototype:




$N \gg 1$ degrees freedom
$x_1 \to$ reaction

$$\boxed{f = f(\underbrace{x_1}_{\substack{\text{reaction}\\ \text{coordinate}}},\ \underbrace{p_1}_{\substack{\text{momentum}\\ \text{conjugate to}\\ \text{reaction coordinate}}},\ \underline{X},\ t)}$$

$\underline{X} \to$ all other degrees of freedom

then can define populations $P_{\substack{B\\A}}(t) \to$ population of $B$ at time $t$

relative populations $\leftrightarrow$ relative probabilities

$$\therefore \quad \boxed{P_{\substack{B\\A}} = \iiint dx_1\, dp_1\, d\underline{X} \begin{Bmatrix} \Theta(x_1) \\ \Theta(-x_1) \end{Bmatrix} f}$$

Now, seek <u>rates</u> of reaction, i.e. $\frac{dP_A}{dt}$, $\frac{dP_B}{dt}$.

Now, $\frac{d}{dt} = \underset{\text{Liouville operator}}{L}$

so

$$\frac{dP_B}{dt} = \int dx_1 \int dp_1 \int d\underline{X} \; \frac{d\theta(x_1)}{dt} \, f$$

as $df/dt = 0$ (Liouville's Thm.)

but $\frac{d\theta(x_1)}{dt} = L\theta(x_1)$

$\Rightarrow$

$$\frac{dP_B}{dt} = \int dp_1 \int d\underline{X} \int dx_1 \, f \, L\theta(x_1)$$

but: $L = \sum_i \left( \frac{dq_i}{dt} \frac{\partial}{\partial q_i} + \frac{dp_i}{dt} \frac{\partial}{\partial p_i} \right)$

$$= \underbrace{\frac{p_1}{m} \frac{\partial}{\partial x_1} + \frac{dp_1}{dt} \frac{\partial}{\partial p_1}}_{\text{reaction coordinate piece of Liouvillian}} + \underset{\text{everything else}}{L_{\underline{X}}}$$

so $\quad L\,\theta(x_1) = \dfrac{p_1}{m}\dfrac{\partial}{\partial x_1}\theta(x_1)$

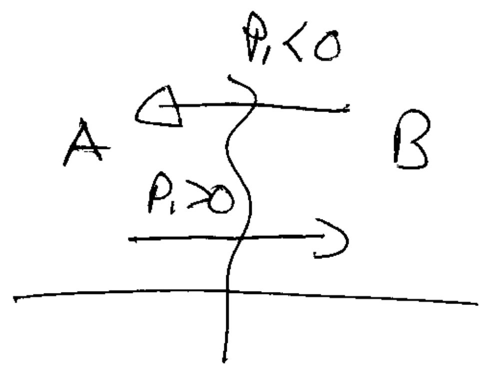
$$= \frac{p_1}{m}\,\delta(x_1)$$

$\Rightarrow$

$$\frac{dP_B}{dt} = \int dx_1 \int dp_1 \int d\underline{X}\; \frac{p_1}{m}\,\delta(x_1)\, f(p_1, x_1, \underline{X}, t)$$

so for outflow, take $p_1 < 0$
$\downarrow$
from B

inflow, take $p_1 > 0$
$\downarrow$
to B




$$\boxed{\begin{aligned} \frac{d}{dt} P_{B\,\,B\to A} &= \int_{-\infty}^{0} dp_1 \int d\underline{X}\; \frac{p_1}{m_1}\, f(p_1, 0, \underline{X}, t) \quad (*) \\ \frac{d}{dt} P_{B\,\,A\to B} &= \int_{0}^{\infty} dp_1 \int d\underline{X}\; \frac{p_1}{m_1}\, f(p_1, 0, \underline{X}, t) \end{aligned}}$$

$\rightarrow$ relate macro-rates to $f$.

Note:

→ $f\big|_{x_1=0}$ is crucial quantity ⇒ value at boundary (or separatrix) between A, B. → "hence transition state"

→ nice, but what is f ? ? ← the question

$$\boxed{\text{Key Assumption: } f = f_{eq}, \text{ in } A, B}$$

- i.e. equilibrium maintained in A, B

↓

- $\tau_{\text{relax to equilibrium}} < \tau_{A\to B}$ etc. ⇒ severe restriction

i.e. reaction → heating, cooling → deviation from equilibrium, etc.

∴

TST only valid for slow reactions, in general...

so $$f \cong f_{eq} = \frac{e^{-H/T}}{Q}$$

where: $$H = \sum_{j=1}^{N}\left\{\frac{p_j^2}{2m} + u(x_1, x_2 \cdots x_N)\right\}$$

$$Q = Q_A + Q_B = \iiint dx_1\, dp_1\, d\underline{X}\, e^{-H/T}$$

obviously, $$\left.\begin{aligned} Q_A &= \int_{x_1>0} dx_1 \iiint dp_1\, d\underline{X}\, e^{-H/T} \\ Q_B &= \int_{x_1<0} dx_1 \quad \text{''} \qquad \text{''} \end{aligned}\right\}$$ partition sums

$$\therefore \quad \left.\begin{aligned} P_{eq}(A) &= Q_A/Q \\ P_{eq}(B) &= Q_B/Q \end{aligned}\right\}$$ probabilities of being in A, B

so $$\boxed{\underbrace{f_B}_{\text{local}} = \frac{P_B(t)}{P_{B,eq}}\, f_{eq}}$$

dist in B

equilibrium distribution fctn.

weighting factor (allows slow deviation from eqbrm.)

so inserting into $\left.d\rho_B(t)\right)_{B\to A}$ expression (*)

$\Rightarrow$

$$\left.\frac{d\rho_B(t)}{dt}\right)_{B\to A} = \int_{-\infty}^{0} dp_1 \int d\underline{X}\, \frac{p_1}{m} f_{eq}(p_1, 0, \underline{X})\, \frac{\rho_B(t)}{\rho_B(eq)}$$

$\therefore$ can extract (modulo approximation) rate constant ($-p_1 \to +p_1$ flip)

$$k_{AB} = \int_0^{\infty} dp_1 \int d\underline{X}\, \frac{p_1}{m_1} f_{eq}(p_1, 0, \underline{X}) \Big/ \rho_B(eq)$$

and similarly:

$$k_{BA} = \int_0^{\infty} dp_1 \int d\underline{X}\, \frac{p_1}{m_1} f_{eq}(p_1, 0, \underline{X}) \Big/ \rho_A(eq)$$

and can write rate equations in form:

$$\frac{d\rho_A}{dt}(t) = -k_{BA}\,\rho_A(t) + k_{AB}\,\rho_B(t)$$

$$\frac{d}{dt}\rho_B(t) = -k_{AB}\,\rho_B(t) + k_{BA}\,\rho_A(t)$$

Now, useful to define:

$$Q^* = \int d\underline{X} \left( e^{-H^*/T} \right) \Big|_{\substack{p_1 = 0 \\ x_1 = 0}}$$

i.e. – $H^*$ is "$\underline{X}$-part" of $H$
– $Q^*$ is partition sum associated

i.e. $$H^* = \sum_{j=2}^{N} \frac{p_j^2}{2m} + U(0, x_2, \ldots x_N)$$

$$H\Big|_{x_1=0} = \frac{p_1^2}{2m} + H^*$$

then $$K_{AB} = \int_0^{\infty} dp_1 \int d\underline{X} \, \frac{p_1}{m_1} \, e^{-\frac{p_1^2}{2mT}} e^{-H^*/T}$$

$$= k_b T \left( Q^* / Q_B \right)$$

$\therefore$ $$K_{AB} = k_b T \left( Q^* / Q_B \right)$$

$\Downarrow$

TST rate constant is ratio of two partition functions, obviously by construction.

Note:

- crucial to keep in mind two key assumptions of transition state theory

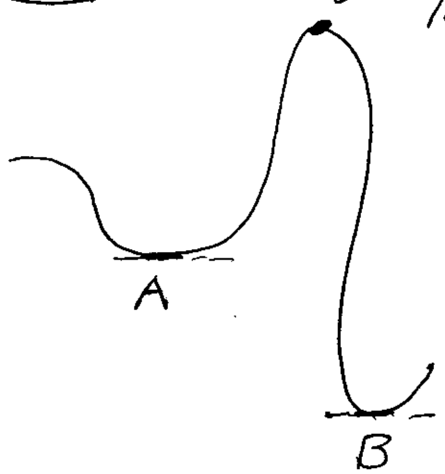
  → well defined boundary, i.e. "$x_1 = 0$" border between A, B unambiguous

  → $f \to f_{eq}$ in A, B i.e. A, B regions equilibrate faster than $\tau_{AB}$

Typical Application

"saddle pt." local maximum at origin

potential $U$




minimum at $(b_1, b_2, \ldots b_N)$

barrier is "high" →
- why ?
- for gas, how guesstimate "how high" ?!

so
, near b. s/t minimum

$$U \cong U_0 + \frac{1}{2} \sum_i m_i \omega_i^2 (x_i - b_i)^2$$

→ near origin (saddle point):

$$U \cong U_S - \tfrac{1}{2} a_{1,1} X_1^2 + \tfrac{1}{2}\sum_{j=2} m_i \omega_i^2 X_i^2$$

local max. "along" $X_1$ direction

other directions

so, to calculate $Q_B$, use expansion near potential minimum, i.e.:

$$\boxed{Q_B \cong (2\pi k_b T)^N e^{-\beta U_0} \Big/ \prod_{i=1}^{N} \omega_i}$$

i.e. $\begin{cases} 2\,(k_bT/2) \text{ per degree freedom} \\ \omega_i \Leftrightarrow i\text{th spring const.} \end{cases}$

$$\iint e^{-\frac{1}{2}[m\omega_1^2(x-b_1)^2 + m\omega_2^2(x-b_2)^2 + \cdots]/T} = \prod_{i=1}^{N} \int dx_i\, e^{-\frac{1}{2} m \frac{\omega_i^2}{T}(x_i-b_i)^2}$$

and, to calculate $Q^*$, use expansion near $X_1 = 0$

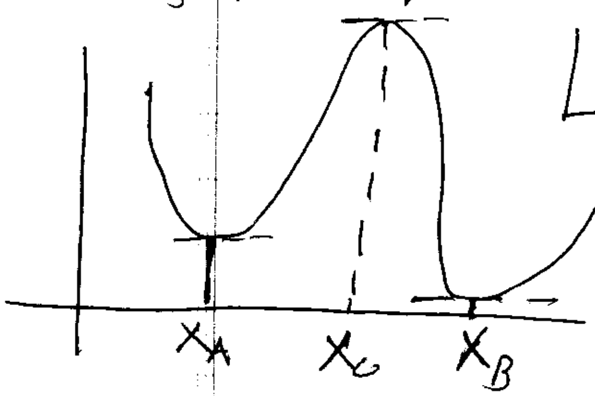
$$\boxed{Q^* = (2\pi k_b T)^{N-1} e^{-\beta U_S} \Big/ \left(\prod_{i=2}^{N} \omega_i\right)}$$

$$\cong \quad k_{AB} = k_b T \left( Q^* / Q_B \right)$$

$$\cong \underbrace{\frac{\omega_1}{2\pi}}_{\substack{\text{(at minimum)} \\ \text{vibration} \\ \text{frequency}}} \; \underbrace{e^{-(U_s - U_0)/T}}_{\substack{\text{Arrenhius} \\ \text{factor}}}$$

b.) Kramers' Problem ref. { Chandrasekhar or Review. Zwanzig "NonEquilibrium Statistical Mechanics" }

Now, go beyond rate ~~constants~~ to consider kinetics, phase space flow, etc. of reaction, i.e.:




$T, \beta$ → thermal noise, damping

seek $A \to B$ transition rate

Now:

a.) relax TST assumption of absolute equilibrium locally in A, B ↔ "hill" at $C$ need not be so high.

b.) consider both $\beta$ large ↔ "viscous" and $\beta$ small — "energy diffusion" cases

i.e.

$$\dot{\underline{x}} = \underline{v}$$

$$\dot{\underline{v}} = -\beta \underline{v} - \frac{\partial U}{m \partial \underline{x}} + \underset{\mapsto \text{noise}}{\tilde{\underline{a}}}$$

$$\underline{f} = -\underline{\nabla} U \rightarrow \text{deterministic force}$$

paradigm useful for:

1.) particle motion
2.) chemical reaction
3.) flip-flop devices — tunnel diode

a) $\beta$-large case

So, convert immediately to Schmoluchowski equation (scattering in $\underline{x}$) $\Rightarrow$

$$\underline{v} = \frac{1}{\beta}\left(-\frac{\partial U}{\partial \underline{x}} + \tilde{\underline{q}}\right)$$

so

$$\left\{\begin{array}{l} \dfrac{\partial n}{\partial t} + \underline{\nabla}\cdot\left(\dfrac{-1}{m\beta}\dfrac{\partial U}{\partial \underline{x}}\, n\right) = \dfrac{\partial^2}{\partial \underline{x}^2}\left(D_x n\right) \\ \dfrac{\partial n}{\partial t} = -\underline{\nabla}\cdot\left(\dfrac{-1}{m\beta}\dfrac{\partial U}{\partial \underline{x}}\, n - \dfrac{\partial}{\partial \underline{x}} D_x n\right) = -\underline{\nabla}\cdot\underbrace{\underline{J}}_{\text{reaction flux/current}} \end{array}\right.$$

$$D_x = D_v/\beta^2 = T/m\beta$$

Now, - hereafter in 1D

- seek # particles making $A \to B$ jump / reaction per second

so

$$\underbrace{-r}_{\text{rate const}} = K_{AB} = J/\underbrace{\bar{n}_A}_{\text{\# reacting particles "near" } A} \equiv \text{\# jumping/sec.} \Big/ \text{\# available to react.}$$

i.e. usually


$n_A >> n_B$

so, seek J!

$$J = -\frac{1}{m\beta}\frac{\partial U}{\partial x} n - D_x \frac{\partial n}{\partial x}$$

= const, for steady flow.

so $$J = -\frac{T}{m\beta}\frac{\partial}{\partial x}\left(\left(U/T\right) n\right) - D_x \frac{\partial n}{\partial x}$$

$$= -D_x e^{-U/T} \frac{\partial}{\partial x}\left(n e^{U/T}\right)$$

now J = const (assumed) so

$$\int_A^B J e^{U/T} dx = -D_x \int_A^B dx \frac{\partial}{\partial x}\left(n e^{U/T}\right)$$

$$= -D_x \, n e^{U(x)/T} \Big|_{x_A}^{x_B}$$

∴, finally have reaction current

$$\boxed{J = -D_x\, n\, e^{U(x)/T}\Big|_{x_A}^{x_B} \Big/ \int_{x_A}^{x_B} e^{U(x)/T}\,dx}$$

Let $\begin{cases} n(x_B)/n(x_A) \to 0, \text{ i.e. "nearly all" reactants in attractor } A. \text{ Few 'make it' over barrier} \\ A \to B \text{ path dominated by point } C. \end{cases}$

$$J = -D_x\left(n_B e^{U(x_B)/T} - n_A e^{U(x_A)/T}\right) \Big/ \int_{x_A}^{x_B} e^{U(x)/T}\,dx$$

$$\cong D_x\, n_A\, e^{U(x_A)/T} \Big/ \int_{x_A}^{x_B} dx\, e^{U(x)/T}$$

Now, near $x \sim x_A$;

$$U(x) \cong U(x_A) + \frac{1}{2}(2\pi\omega_A)^2(x-x_A)^2$$

to determine $n_A$

near $x \sim x_C$ (peak)

$$U(x) \cong U(x_C) - \frac{1}{2}(2\pi\omega_C)^2(x-x_C)^2$$

$\bar{n}_A = $ # particles $\left\{ \begin{matrix} \text{in} \\ \text{near} \end{matrix} \right\}$ well at $x_A$ (near)

↳ integral

so

$$\bar{n}_A = n_A \int_{x_A-}^{x_A+} dx\, e^{-\left[U(x_A) + \frac{1}{2}(2\pi\omega_A)^2(x-x_A)^2\right]/T}$$

$$\boxed{n(x) \equiv n_A e^{-U(x)/T}}$$

{partition sum approximated

$$= n_A e^{-U(x_A)/T} \frac{1}{\omega_A} \sqrt{T/2\pi}$$

then

$$r = J/\bar{n}_A = \left(D_x \omega_A \sqrt{2\pi/T}\, e^{+U_A/T}\right) \Big/ \int_A^B e^{U(x)/T} dx$$

Now $\displaystyle\int_A^B e^{U(x)/T} dx \cong \int_{x_c-}^{x_c+} \exp\left[\frac{U(x_c)}{T} - \frac{\omega_c^2}{T}(2\pi)^2(x-x_c)\right] dx$

(dominated by c)

$$\cong \frac{e^{+U(x_c)/T}}{\omega_c} \sqrt{T/2\pi}$$

Putting it all together:

$$r = \left(\Delta x\, \omega_A \sqrt{2\pi/T}\, e^{+U_A/T}\right) \Big/ \frac{e^{U(x_c)/T}}{\omega_c}\left(\sqrt{T/2\pi}\right)$$

$$\boxed{r \cong \frac{2\pi\omega_A\,\omega_c}{\beta} \exp\left[-\left(U(x_c) - U(x_A)\right)/T\right]}$$

- reaction constant

$$\left(\Delta x = \frac{T}{\beta}\right)$$

$$r = \left(\frac{\omega_c}{\beta}\right) \underbrace{2\pi\omega_A \underbrace{\exp\left[-\left(U(x_c) - U(x_A)\right)/T\right]}_{\text{Arrhenius factor}}}_{\text{TST}}$$

$(\omega_c \Leftrightarrow \omega_{\text{saddle}})$

$$\boxed{r = \frac{\omega_c}{\beta} k_{TST} < k_{TST}}$$

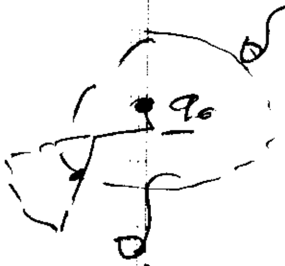
as $\beta$ large limit!

$$\boxed{r = \frac{\omega_c}{\beta} 2\pi\omega_A \exp\left[-\left(U(x_c) - U(x_A)\right)/T\right]}$$

rate const.

$\omega_c \equiv$ maximum frequency

b.) related: Consider well-known "first passage time" problem




$T(\underline{q_0})$ is time to cross boundary $\partial V$, starting from $\underline{q_0}$.

Noise $\Rightarrow$ distribution of crossing times, so need probabilistic approach.

So Classic Problem

(*)

- seek mean first crossing time $\leftrightarrow$ time to $\partial V$,

$\rightarrow$ to remove paths on V which cross $\partial V$ (i.e. undergo first passage), impose absorbing boundary conditions on $\partial V$.

So pdf $P$ of what is left off obeys:

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

Fokker-Planck operator

$P(\underline{q}, 0) = \delta(\underline{q} - \underline{q_0}) \rightarrow$ i.c.

$P(q, t) = 0$ on $\partial W \rightarrow$ absorption so

$$P(\underline{q}, t) = e^{\mathcal{D}t} P(\underline{q}_0, 0) = e^{\mathcal{D}t} \delta(\underline{q} - \underline{q}_0)$$

(symbolic solution)

Now,

$$\int_V d\underline{q}\, P(\underline{q}, t) = \#\text{ paths, particles in } V \text{ at } t$$

$$= S(t, q_0) \Rightarrow \#\text{ surviving at } t.$$

depends on start point

$$S(t, \underline{q}_0) = \int_V d\underline{q}\, P(\underline{q}, t) \qquad (\#\text{ survivors})$$

$$\to 0, \text{ as } t \to \infty \qquad (\text{due absorbing b. c.'s})$$

so

$S(t) - S(t+dt)$ = # initial points which have not left prior $t$ but do leave during $t+dt$ interval.

$S(t)$

# survivors drop - - -

so $S(t, \underline{q}_0) - S(t+dt, \underline{q}_0) = \rho(t, \underline{q}_0)\, dt$

pdf of first passage times

$p(t, q_0) = -dS/dt$

pdf of first passage time (i.e. passage out of attractor $A \Leftrightarrow$ confinement time)

so $T(\underline{q_0})$ from:

$\hookrightarrow$ mean first passage time, starting from point $\underline{q_0}$.

$$T(\underline{q_0}) = \int_0^t dt\, t\, p(t, \underline{q_0})$$

$$= \int_0^t dt\, t\left(-\frac{dS}{dt}\right)$$

$$= \int_0^t dt\, S - tS\Big|_0^t$$

$t \to \infty \Rightarrow$

$$\boxed{T(\underline{q_0}) = \int_0^\infty dt\, S}$$

$\rightarrow$ integral for first passage.

but, can formulate in more simple way

i.e. $P(\underline{q}, \underline{q}_0, t) = P(\underline{q}, t)$ st $q_0$ at $t=0$ and <u>with</u> absorbing b.c. on $\partial V$.

so

$$\boxed{T(\underline{q}_0) = \int_0^\infty dt \int d\underline{q}\; P(\underline{q}, \underline{q}_0, t)}$$

but $P(\underline{q}, \underline{q}_0, t) = e^{t\mathcal{D}}\delta(\underline{q} - \underline{q}_0)$

$\mathcal{D}$: F-P operator

then $\mathcal{D}^+ \equiv$ adjoint to $\mathcal{D}$ $\Rightarrow$

$$T(\underline{q}_0) = \int_0^\infty dt \int d\underline{q}\; \delta(\underline{q} - \underline{q}_0)\left(e^{t\mathcal{D}^+} 1\right)$$

(i.e. Left mult by operator $\Leftrightarrow$ right multiply by adjoint)

so $T(\underline{q}) = \int_0^\infty dt \left(e^{t\mathcal{D}^+} 1\right)$ ($\underline{q}, \underline{q}_0$ just relabeled)

$$\boxed{T(q) = \int_0^\infty dt \left(e^{t\mathcal{D}^+} 1\right)}$$

Note: study of formal structure of Fokker–Planck equation of utility here!

$$T(q) = \int_0^\infty dt\, e^{tD^+}(1)$$

operate on both sides

$$D^+ T(q) = \int_0^\infty dt\, D^+ e^{tD^+}(1)$$

$$= \int_0^\infty dt\, \frac{d}{dt} e^{(tD^+)} 1$$

$$= -1$$

(absorbing b.c. ensure no contribution from $t \to \infty$).

so

$$\boxed{\begin{aligned} D^+ T(q) &= -1 \\ T(q) &= 0 \text{ on } \partial V \end{aligned}}$$

is simplified equation, solution of which is first passage.

Now, $D = -\frac{\partial}{\partial \underline{q}} \cdot \left( \underline{V}(q) \quad \right) + \frac{\partial}{\partial \underline{q}} \cdot \left( \underline{\underline{\beta}} \cdot \frac{\partial}{\partial \underline{q}} \quad \right)$

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

Now, specializing to 1D Schmoluchowski Equation formulation of Kramers' Problem:

i.e. for $P$:

$$\frac{\partial P}{\partial t} = D\frac{\partial}{\partial x}\left\{-\frac{U'}{T}P + \frac{\partial P}{\partial x}\right\} \quad \to \text{Schmoluchowski}$$

$$= -\frac{\partial}{\partial x}\left\{\frac{U'P}{\beta} - D\frac{\partial P}{\partial x}\right\} \qquad \left\{\frac{\partial P}{\partial t} = D\frac{\partial}{\partial x}e^{-U(x)/T}\frac{\partial}{\partial x}e^{U/T}P\right.$$

$$\mathcal{D} = -\frac{\partial}{\partial x}\frac{U'}{\beta} + D\frac{\partial^2}{\partial x^2} = -\frac{\partial}{\partial x}\left(\frac{U'}{\beta} - \frac{\partial}{\partial x}D\right)$$

$$\mathcal{D}^{+} = \frac{\partial}{\partial x}\frac{U'}{\beta} + D\frac{\partial^2}{\partial x^2} = \frac{\partial}{\partial x}\left(\frac{U'}{\beta} + \frac{\partial}{\partial x}D\right)$$

$\mathcal{D}^{+}T = -1$ is F-P eqn. for first passage time.

$$\Rightarrow \boxed{D e^{U/T}\frac{\partial}{\partial x}e^{-U/T}\frac{\partial}{\partial x}T(x) = -1}$$

First Passage time F-P Eqn.

i.e. note contrast:

Note: On Hermiticity

Consider F-P eqn. for Hamiltonian system:

$$\underbrace{\frac{df}{dt}}_{\text{deter.}} = \frac{\partial f}{\partial t} + \underline{v}\cdot\frac{\partial f}{\partial x} + \underline{a}\cdot\frac{\partial f}{\partial v} = \underbrace{\frac{\partial}{\partial \tilde{v}} D \frac{\partial f}{\partial \tilde{v}}}_{\text{stochastic}}$$

so

$$\tilde{\mathcal{F}} = \frac{\partial}{\partial t} + v\cdot\frac{\partial}{\partial x} + a\cdot\frac{\partial}{\partial v} - \frac{\partial}{\partial \tilde{v}} D \frac{\partial}{\partial \tilde{v}}$$

as $\frac{\partial}{\partial \underline{x}}\cdot\underline{v} + \frac{\partial}{\partial \underline{v}}\cdot\underline{a} = 0$ here

$$(a, \tilde{\mathcal{F}} b) = -(b, \tilde{\mathcal{F}} a)_{\text{deterministic}} + (b, \tilde{\mathcal{F}} a)_{\text{stoch}}$$

i.e. - as $L$ is anti-Hermitian, deterministic part of F-P eqn. is anti-Hermitian

- stochastic part is hermitian.
- overall, no symmetry

- Schmoluchowski:

$$\frac{\partial \rho}{\partial t} = D \frac{\partial}{\partial x}\left(e^{-u(x)/T} \frac{\partial}{\partial x}\left(e^{u(x)/T}\rho\right)\right)$$

$$\ominus \qquad\qquad \oplus$$

- adjoint:

$$D e^{+u/T} \frac{\partial}{\partial x}\left(e^{-u/T} \frac{\partial T(x)}{\partial x}\right) = -1$$

$$\oplus \qquad\qquad \ominus$$

and outside derivative.

To solve for $T(x)$:

- $x$ is starting point
- $b$ is absorbing barrier
- assume reflecting barrier at $a$.

to kill e.p. contrib

$a < x < b$

$$\frac{\partial}{\partial x}\left(e^{-u(x)/T} \frac{\partial T(x)}{\partial x}\right) = -\frac{e^{-u(x)/T}}{D}$$

$$-\int_a^x dy \, \frac{e^{-u(y)/T}}{D} = e^{-u(x)} \frac{\partial T}{\partial x}\Big|_a^x$$

reflecting

$$\frac{\partial T}{\partial x} - \cancel{\left.\frac{\partial T}{\partial x}\right|_a} = -e^{U(x)/T}\int_a^x dy\,\frac{e^{-U(y)/T}}{D}$$

$$\int_x^b \frac{\partial T}{\partial x} = -\int_x^b dz\, e^{U(z)/T}\int_a^z dy\,\frac{e^{-U(y)/T}}{D}$$

absorbing

$$T(x) - \cancel{T(b)} = +\int_x^b dz\, e^{U(z)/T}\int_a^z dy\,\frac{e^{-U(y)/T}}{D}$$

so finally, have first passage time:

$$\boxed{T(x) = \int_x^b dz\, e^{U(z)/T}\int_a^z dy\,\frac{e^{-U(y)/T}}{D}}$$

⇒ closed form expression for first passage time, in 1D!

⇒ concrete case that formal structure simplifies the problem .....

b.) Weak Damping $\leftrightarrow$ Energy Diffusion

$\Rightarrow$ till now, have been concerned with large friction, large $\beta$ limit

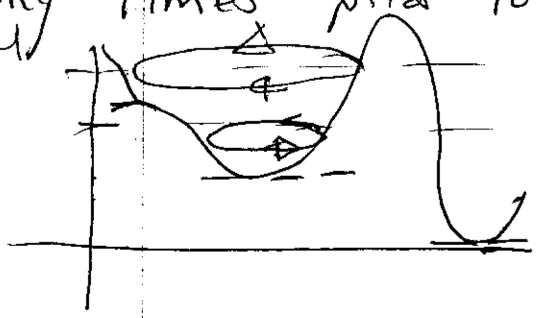
$\Rightarrow$ now consider weak friction limit

$\therefore$

- full evolution in $x, v, t$ must be tracked.

- if scattering weak, particle oscillates in well many times prior to kick

i.e.



i.e. $\omega_{kick} \ll \omega_{osc.}$

- so, can expect particle scattering in $v$ $\Rightarrow$ stochastic acceleration i.e. particle will

oscillate, eventually achieving high enough energy to escape from well.

- useful to think of scattering in energy, hence energy diffusion.

→ Convenient to work with $f(x, v, t)$ → distribution of phase space variable....

Now,

$$\frac{\partial f}{\partial t} = -L_0 f + \beta T \frac{\partial}{\partial p} f_{eq} \frac{\partial}{\partial p} \frac{f}{f_{eq}}$$

$$L_0 = \frac{p}{m}\frac{\partial}{\partial x} + F(x)\frac{\partial}{\partial p}$$ → Liouville operator

$$f_{eq} = (\#) e^{-H/T}, \quad H = p^2/2m + U$$
$$F = -dU/dx$$

and distribution of energy $g(E)$ from:

$$g(E, t) = \int dx \int dp \, \underbrace{\delta(H(x,p) - E)}_{\text{selects pts on energy surface}} f(x, p, t)$$

Now, consider:

$$\int dx \int dp \, \delta(H(p,x) - E)\left(\frac{\partial f}{\partial t} + L_0 f - \beta T \frac{\partial}{\partial p} f_{eq} \frac{\partial}{\partial p}\frac{f}{f_{eq}}\right) = 0$$

i.e. energy surface integrated Liouvillian, so....

now: $LH = 0$

$\{L, H\} = 0$

so

$$\boxed{\frac{\partial}{\partial t} g(E,t) = \beta T \int dx \int dp\, \delta(H-E)\, \frac{\partial}{\partial p} f_{eq} \frac{\partial}{\partial p} \frac{f}{f_{eq}}}$$

evolution F-P eqn. for energy distribution.

Now, <u>key</u> <u>approximation</u>:

- replace actual distribution function $f(x,p,t)$ on RHS by $\phi(H,t)$. $\phi$ <u>must</u> yield correct energy distribution

$$-\int dx \int dp\, \delta(H-E)\, f(x,p,t) = \int dx \int dp\, \delta(H-E)\, \phi(H,t)$$

$$= g(E,t)$$

$$= \phi(E,t) \int dx \int dp\, \delta(H-E)$$

now $\underbrace{\Omega(E) = \int dx \int dp\, \delta(H-E)}_{\text{microcanonical partition function}}$

so

$$\boxed{\phi(E,t) = g(E,t)/\Omega(E)}$$

Now,

$$f(x,p,t)\,/\,f_{eq}(x,p) = \frac{g(H,t)}{g_{eq}(H)}$$

$$\frac{\partial}{\partial p}\left(\frac{f}{f_{eq}}\right) \cong \frac{p}{m}\frac{\partial}{\partial H}\frac{g(H,t)}{g_{eq}(H)}$$

so

$$\frac{\partial g(E,t)}{\partial t} \cong \beta T \int dx \int dp\, \delta(H-E)\, \frac{\partial}{\partial p} f_{eq}\, \frac{p}{m}\frac{\partial}{\partial H}\frac{g(H,t)}{g_{eq}(H)}$$

ibp $\quad \int dp\, \delta(H-E)\frac{\partial}{\partial p} \to -\int dp\, \frac{\partial}{\partial p}(H-E)$

$$\to \frac{\partial}{\partial E}\int dp\, \frac{p}{m}\,\delta(H-E)$$

so, equation for $g(E,t)$ becomes:

$$\frac{\partial g}{\partial t}(E,t) \cong \beta T \frac{\partial}{\partial E}\int dx \int dp \left(\frac{p}{m}\right)^2 \delta(H-E)\, f_{eq}(E)\, \frac{\partial}{\partial E}\frac{g(E,t)}{g_{eq}(E)}$$

and if define:

$$D(E) = \beta T \frac{\int dx \int dp \, (p/m)^2 \delta(H-E)}{\int dx \int dp \, \delta(H-E)}$$ → energy diffusion

where;

now $\int dp \, f(p) \, \delta(p^2 - a^2) = \frac{f(a)}{2a}$ , $a > 0$

$$\therefore \quad D(E) = 2 \frac{\beta}{m} T \frac{\int dx \sqrt{E - U(x)}}{\int dx \, 1/\sqrt{E-U(x)}}$$

$$= 2 \frac{\beta}{m} T \frac{I(E)}{\left(\omega(E)/2\pi\right)^{-1}}$$

$I(E)$ = action $= \oint dx \, p(x)$

$p(x) = \left(2m(E - U(x))\right)^{1/2}$ i.e. $\omega_{osc.} \ll \omega_{esc.}$

$\left(\partial I/\partial E\right)^{-1} = \frac{\omega(E)}{2\pi}$ → angular frequency.

i.e. consider scattering of closed orbits $I$, $\theta$!

then:

$$\frac{\partial g(E,t)}{\partial t} \cong \frac{\partial}{\partial E} D(E)\, g_{eq}(E) \frac{\partial}{\partial E} \frac{g(E,t)}{g_{eq}(E)}$$

or, in action variables:

$$\boxed{\frac{\partial g}{\partial t}(E,t) \cong \frac{\partial}{\partial E}\left(\frac{\beta I(E)}{m}\left[1 + T\frac{\partial}{\partial E}\right]\frac{\omega(E)}{2\pi} g(E,t)\right)}$$

drag → effect $f(E)$

diffn in energy

- energy diffusion equation:
- resembles Schmoluchowski equation.
- $x \to E$

  $e^{-U/T} \to \Omega(E)\, e^{-E/T}$
- $x, p$ phase space replaced by $X, P$ in Hamiltonian.

Now can proceed as before to calculate first passage time for escape over barrier.

i.e. → near minimum at $x = x_A$,

$$U(x) = \frac{m\omega_0^2}{2} x^2$$

→ absorbing b.c. at $E = E_b$.

so, ala' calculation for high $\beta$ case, have mean first passage time:

$$\boxed{\tau(E) = \int_E^{E_b} dE' \frac{1}{D(E') g_{eq}(E')} \int_0^{E'} dE'' g(E'')}$$

by correspondence.

Exercise: Show this!

plugging in:

$$g_{eq}(E) = \Omega(E) e^{-E/T}$$

$$D(E) = 2\beta \frac{T}{m} I(E) \frac{\omega(E)}{2\pi}$$

⇒

$$\tau(E) = \frac{2m}{\beta T} \int_E^{E_b} dE' \frac{e^{+E'/T}}{I(E')} \int_0^{E'} dE'' \Omega(E'') e^{-E''/T}$$

near well, $I(E) \cong \dfrac{2mE}{\omega_0}$

$\Omega(E) = \pi/\omega_0$

$\Rightarrow$

$$\boxed{\tau \approx \frac{2\pi m T}{\beta} \frac{1}{\omega_0 I(E_b)} e^{E_b/T}}$$ Ex: show this!

$\therefore \begin{cases} \text{low friction } 1/\tau \sim \beta \\ \text{high friction } 1/\tau \sim \beta^{-1} \end{cases}$