Physics 210B

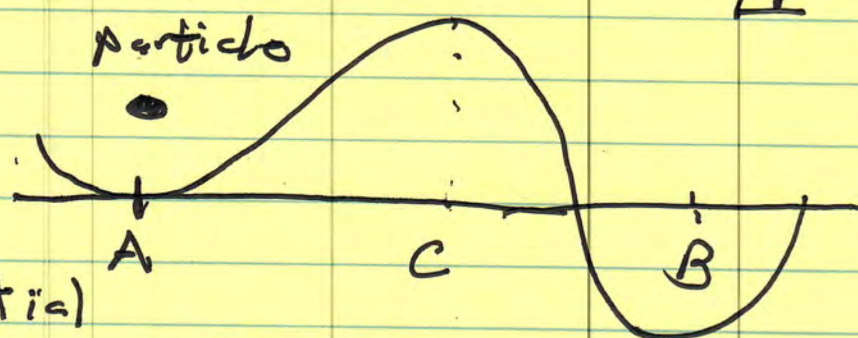
See:
Chandrasekhar
Zwanzig

Applications of Fokker-Planck Theory:

Kramers Problem and First Passage Time

a.) Kramers Problem

I



Consider
1D $U(x)$

Particle in potential
$U(x)$ s/t $f_{determ} = -dU/dx$

- temperature T, drag β
- probability / rate of escape $A \to B$.

N.B.

- Hamiltonian - if in A well $\Rightarrow$ oscillates
- noise (+ drag) $\Rightarrow$ can hop into deeper well at B.

- can imagine limits : $\beta = 6\pi \eta a$

"viscous" : $\frac{\beta}{m} \tau \gg 1$

(i.e. Schmoluchowski Equation)

"weakly viscous" : $\frac{\beta}{m} \tau \ll 1$

(i.e. Fokker - Planck)

- Where from:
  - molecular dissociation
  - diatomic molecule

x → "reaction coordinate"
distance between nuclei
(need get far apart, overcome restoring)

- $E_c = U(x_c)$ → dissociation energy
- diffusion ?? ⇔ many (collisional) kicks as $x_A \to x_c$

diffusion process

so

- translate into particle dynamics model problem.

⇒ Kramers Problem:

i.) Viscous limit

Approach: $\begin{cases} \text{Calculate } A \to B \text{ flux/current} \\ J = \text{const. ?} \end{cases}$

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

$$\frac{dV}{dt} = -\frac{\beta}{m} V + \underbrace{a_{ext}(x)}_{\text{motion in potential}}^{-\nabla U(x)/m} + \underbrace{\tilde{a}}_{\text{noise}}$$

$$\langle \tilde{a}(t_1)\tilde{a}(t_2)\rangle = a_0^2 \tilde{\tau}_{ac} \, \delta(t_2 - t_1)$$

$\beta/m > 1/\tau_{trans}$ → viscous case

so...

back to Schmoluchowski Eqns:

$$\frac{dx}{dt} = \frac{a_{ext}(x)}{\beta} + \frac{\tilde{a}}{\beta}$$ → terminal velocity

N.B. Can write full F-P Eqn: $f(x, v, t)$

$$\partial_t f + v \partial_x f + a_{ext} \partial_v f$$
$$= + \partial_v \left\{ \frac{\beta}{m} v f + \partial_v D_v f \right\}$$

$D_v = \frac{\beta}{m} v_{Th}^2$, as usual.

Now, in viscous limit $\Rightarrow$ terminal velocity

$\Rightarrow$

$$\boxed{\begin{aligned} \frac{\partial n}{\partial t} &= -\frac{\partial}{\partial x}\left[\frac{a_{ext}(x)}{\beta} n - \frac{\partial}{\partial x} D_x n\right] \\ D_x &= T/\beta \end{aligned}}$$

as before.

$$V(x) = \frac{a_{ext}(x)}{\beta}$$

of course, Schmoluchowski Equation is just a continuity equation

$$\frac{\partial n}{\partial t} + \partial_x J = 0$$

$J = \Gamma_n = \underbrace{\frac{q_{ext}(x)}{B}\, n}_{\text{drift}}\ -$ [redacted] $\underbrace{D_x\, \partial_x n}_{\text{diffusive}}$

Now, look for $J = \text{const}$ solutions.

$J = J_{A,B}$.

Consider B empty, particles $\sim A$, initially

Now, can re-write:

$$j = -\frac{D_v}{B^2} \exp\left(-\frac{B U}{D_v}\right) \partial_x \left(n \exp\left(\frac{B U}{D_v}\right)\right)$$

check

$$= -\frac{D_v}{B^2} e^{-BU/D_v} \left[e^{BU/D_v} \partial_x n + n \frac{B}{D_v} (\partial_x U) e^{BU/D_v} \right]$$

$$j = -\frac{D_v}{\beta^2}\left[\partial_x n + \frac{\beta}{D_v}\partial_x U\, n\right]$$

$$= -D_x \partial_x n + \frac{a_{ext}(x)}{\beta} n \quad \checkmark$$

so

$$\boxed{j = -\frac{D_v}{\beta^2}\exp\left(-\frac{\beta U}{D_v}\right)\partial_x\left(n\exp\left(\frac{\beta U}{D_v}\right)\right)}$$

- re-write

- now look for $j = \text{const.}$,

so

$$\int_A^B \beta j e^{\beta U/D_v} = -\int_A^B \partial_x\left(n\exp(\beta U/D_v)\right)\frac{D_v}{\beta}$$

$$= n\frac{D_v}{\beta}\exp\left[\beta U/D_v\right]$$

as $D_v/\beta = v_{th}^2$

const

$$j \int_A^B \mathcal{B} \exp\left[\mathcal{B} U / D_v\right] dx$$

$$= \frac{T}{m} n \, e^{\mathcal{B} U / D_v} \Big|_B^A$$

$\Rightarrow$

$$j = \frac{T}{m} n \, e^{\mathcal{B} U / D_v} \Big|_B^A \Big/ \int_A^B \mathcal{B} \exp\left[\mathcal{B} U / D_v\right] dx$$

current over barrier

$$j = \frac{T}{m\mathcal{B}} \left(\frac{n \quad \exp\left[m U / T\right] \Big|_B^A}{\int_A^B \exp\left[m\, U(x) / T\right] dx} \right)$$

$\equiv$ current over barrier, $A \to B$

Now, at A:

$U \cong 0$

n_A

A + B,

$n_B \ll n_A$, so $n_B \to 0$

$U = -|U_B|$ $(U \leq 0)$

$$j = \frac{\frac{T}{\beta m}\left(n_A - n_B e^{-|U_B| m/T}\right)}{\int_A^B dx\, \exp(mU/T)}$$

$$\boxed{j = \frac{T}{m\beta}\, n_A \Big/ \left(\int_A^B dx\, \exp\left(mU(x)/T\right)\right)}$$

§

current

$r \equiv$ <u>rate of escape</u>

$r_{A\to B} \simeq j / n_A$ (dims!)

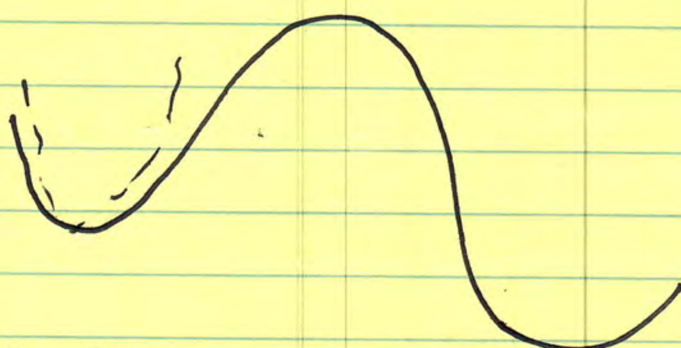
↳ # near A

$n \to$ density

$\nu \to$ # near $\qquad d\nu = \rho\, dx$

$$d\nu_A = n_A \exp\left[-mU/T\right] dx$$

Now,



$U = \frac{1}{2}\omega_A^2 x^2 \quad \to$ Parabolic approx

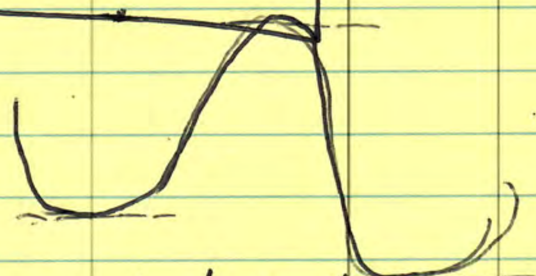
so

$$\nu_A = n_A \int_{-\infty}^{+\infty} \exp\left[-m\omega_A^2 x^2/2T\right] dx$$

$$\boxed{\nu_A = \frac{n_A}{\omega_A}\left(2\pi T/m\right)^{1/2}}$$

$$p = \frac{j}{\nu_A} = \frac{\frac{T}{mB}\, n_A \left[\int_A^B dx\, e^{mU/T}\right]^{-1}}{\frac{\cancel{n_A}}{\omega_A}\left(2\pi T/m\right)^{1/2}}$$

$$\boxed{p = \frac{\omega_A}{B}\left(T/m\right)^{1/2}\left\{\int_A^B e^{mU/T}\right\}^{-1}}$$



For integral:

- main contribution at point / peak C. i.e. max. in U
- there $U = Q - \frac{1}{2}\omega_C^2 (x-x_C)^2$

so

$$\int_A^B e^{mU/T} \cong e^{mQ/T}\int_{-\infty}^{+\infty} \exp\left[-m\omega_C^2 (x-x_C)^2/2T\right]^{1/2}$$

$$= e^{mQ/T}\left(2T/m\omega_C^2\right)^{1/2}$$

so finally,

$$\left.\begin{array}{l}\text{Transition Rate } A \to B \\ \text{(Probability of Transition)}\end{array}\right\} \to P$$

$$\boxed{P = \left(\omega_A \omega_C / 2\pi\beta\right) e^{-m\Phi/T}}$$

N.B. – $P \sim 1/\beta \sim 1/\eta$

in viscous limit.

– note ω_A, ω_C

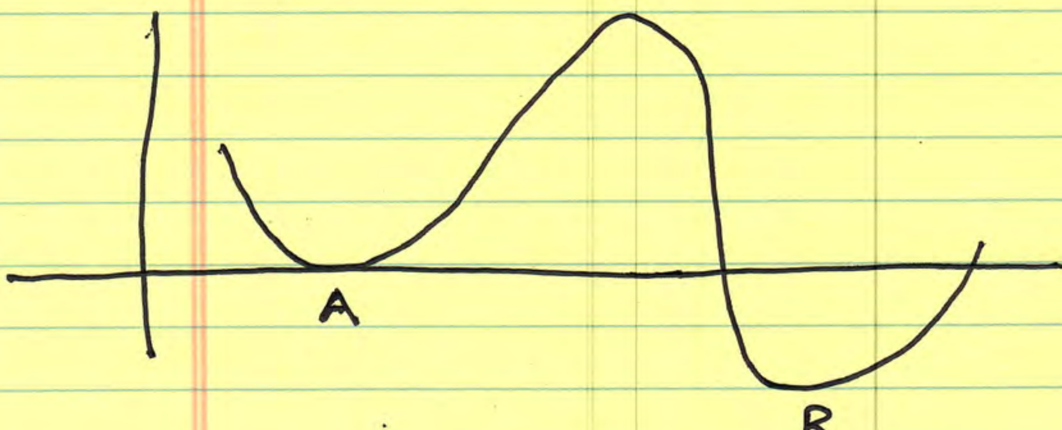
$\omega_A \to \# \ \nu$

$\omega_C \to$ width of barrier
(narrow $\to$ easier to
jump over).

$\rightsquigarrow$ Basic Kramers Problem

(D.) Related : First Passage Time

Basic Question: a la' Kramers,



What is (average) time for $A \to B$?

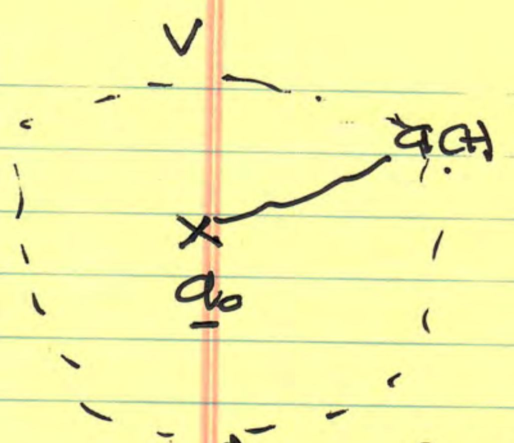
More generally $P(\tau_{AB})$?

pdf of transit times ?

More precisely, what is time for first transit (passage) from $A \to B$?

N.B.: "First passage" problems are major topic, see:
c.f.: S. Redner monograph

N.B.: Can phrase as "first return" time to origin of random walk.



velocity

$$\frac{d\underline{q}}{dt} = \underline{v}(\underline{q}) + \underline{\tilde{F}}(t)$$

$\boxed{\text{Force / Noise (Flctn.)}}$

Confining volume V

Surface ∂V → absorbing.

Time to absorption → First Passage Time
(leave V) (time to pass <u>out</u>)

T distributed due noise!

$P(\underline{q}, t)$ → distribution of (particles) points which have <u>not</u> left, at time t

$$P(\underline{q}, 0) = \delta(\underline{q} - \underline{q}_0)$$

starting point

$$P(\underline{q}, t)\Big|_{\partial V} = 0$$

where:

$$\underbrace{\frac{\partial P}{\partial t} = \mathcal{D} P}_{} \rightarrow \underline{\text{F-P Eqn.}}$$

$\mathcal{D}$: Fokker-Planck Operator

$$\mathcal{D} = -\underline{\nabla}_a \left\{ \underline{V}(a) P - \underline{\nabla}_a \cdot \underline{\underline{D}}_a P \right\}$$

For $\underline{\underline{D}}_a \sim$ const. (i.e. no Temp gradients)

$$\mathcal{D} \doteq -\underline{\nabla}_a \left\{ \underline{V}(a) P - \underline{\underline{D}}_a \cdot \underline{\nabla}_a P \right\}$$

convenient
(caveat → <u>not</u> general)

Now, for mean first passage time:

- $P \underset{t \to \infty}{\rightarrow} 0$, as all paths leave eventually and so encounter absorbing boundary.

so

– # particles still confined at t is:

$$S(t) = \int_V dq\, P(q, t)$$

$$S(t) \underset{t \to \infty}{\to} 0$$

Then # leaving at t (in dt) interval =

$$\underbrace{\rho(t, q_0)\, dt}_{\text{density of first passages (exits).}} = \underbrace{S(t, \overset{\text{i.c.}}{q_0})}_{\# \text{ in}} - \underbrace{S(t + dt, q_0)}_{\# \text{ in}}$$

so

$$-\frac{dS}{dt}(t, q_0) = \rho(t, q_0)$$

and average time:

$$T(q_0) = \int_0^t dt'\, t'\, \rho(t, q_0)$$

so $\quad T(a_0) = \int_0^t dt' \, t' \left(-\frac{dS(t', a_0)}{dt'} \right)$

$$= -t' S(t', \underline{a}_0) \Big|_0^t + \int_0^t dt' \, S(t', \underline{a}_0)$$

$$= -t S(t, \underline{a}_0) + \int_0^t dt' \, S(t', \underline{a}_0)$$

then, anticipating $S \underset{t \to \infty}{\to} 0$ (faster than $1/t$)

$S(0) = 0$ (all in)

$t \to \infty$

$$\boxed{T(a_0) = \int_0^\infty dt \, S(t, a_0)}$$

so

$\boxed{T}$[redacted]$\boxed{(\underline{a}_0) = \int_0^\infty dt \int_V d\underline{a} \, P(\underline{a}, t)}$

- avg. first passage time to ∂V
- for all points a_j within V.

Now,

$$P(\underline{q}, 0) = \overset{\text{i.c.}}{\overset{\downarrow}{\delta(\underline{q}-\underline{q}_0)}}$$

$$P(q,t) = e^{t\mathcal{D}}\delta(\underline{q}-q_0)$$

i.e. $\frac{\partial P}{\partial t} = \mathcal{D} P$

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

$\Rightarrow$

$$\boxed{T(\underline{q}_0) = \int_0^\infty dt \int d\underline{q}\, e^{t\mathcal{D}}\delta(\underline{q}-\underline{q}_0)}$$

Now, labeling by $\underline{q}$

$$T(\underline{q}) = \int_0^\infty dt \int d\underline{q}_0\, e^{t\mathcal{D}}\delta(\underline{q}-\underline{q}_0)$$

$$= \int_0^\infty dt \underbrace{\int d\underline{q}_0\, \delta(\underline{q}-\underline{q}_0)}_{\text{trivial}} e^{t\mathcal{D}^T}(1)$$

$\mathcal{D}^{T} \equiv$ adjoint of $\mathcal{D}$

$$\langle a | \mathcal{D} | b \rangle = \langle b | \mathcal{D}^{T} | a \rangle$$

$\Rightarrow$

$$T(\underline{a}) = \int_0^\infty dt \, e^{t\mathcal{D}^T} 1$$

$$\mathcal{D}^T T(a) = \int_0^\infty dt \, \mathcal{D}^T e^{t\mathcal{D}^T} 1$$

$$= \int_0^\infty dt \, \frac{d}{dt} e^{t\mathcal{D}^T} 1$$

$$= -1$$

(upper limit $\rightarrow 0$, due absorption ∂V)

$\Rightarrow$

$$\boxed{\mathcal{D}^T T(a) = -1}$$

$\rightarrow$ determines first passage time.

N.B: re-ordering derivatives in F-P Eqn. (const. T) allows $\mathcal{D}^T$.

For Kramers:

$$\frac{\partial n}{\partial t} = \mathcal{D} n$$

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

so

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

$\Rightarrow$

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

gives $\mathcal{T}(x)$.

Then

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

$$e^{-U(x)/T}\frac{\partial T}{\partial x} = -\int_a^x dx'\,\frac{e}{D}^{-U(x')/T}$$

$$\frac{\partial T}{\partial x} = e^{U(x)/T}\int_a^x dx'\,\frac{e}{D}^{-U(x')/T}(-1)$$

$\Rightarrow$ finally:

$$\boxed{T(x) = \frac{1}{D}\int_x^b dy\, e^{U(y)/T}\int_a^y dz\, e^{-U(z)/T}}$$

$$\boxed{T(x) = \frac{1}{D}\int_x^b dy\, e^{U(y)/T}\int_a^y dz\, e^{-U(z)/T}}$$

- 1D
- higher D: - path integral
  - computation.