Physics 210B

Applications of Fokker-Planck Theory:
Kramers Problem and First Passage Time

a.) Kramers Problem

Consider
\[ \frac{\partial}{\partial t} \psi(x) \]

Particle in potential
\[ \psi(x) \ \ s/ f_{\text{detem}} = -\frac{dU}{dx} \]

- temperature \( T \)
- drag \( \zeta \)
- 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.

See: Chandrasekhar, Zwaniz.
- can imagine limits: \( B = \frac{\text{constant}}{\Gamma} \)

"viscous": \( \frac{\rho \Gamma}{\mu} \gg 1 \)

(c.f. Schmoluchofaski Equation)

"weakly viscous": \( \frac{\rho \Gamma}{\mu} \ll 1 \)

(c.f. Fokker–Planck)

- where from:
  - molecular dissociation
  - diatomic molecule

  \[ \phi(x) \xrightarrow{\text{cell}} x \rightarrow \text{"reaction coordinate"} \]

  distance between nuclei

  (need set for support, overcome restoring)

- \( E_0 = U(x_0) \rightarrow \text{dissociation energy} \)

- diffusion? \( \rightarrow \) many (collisions) kicks

  \[ \xrightarrow{\text{as } x_A \rightarrow x_C} \]

  diffusion process
So translate into particle dynamical model problem.

Kramers Problem:

1. Viscous limit

Approach: \[
\begin{align*}
\text{Calculate } & A \rightarrow B \text{ flux/current} \\
J & = \text{const.} \ ?
\end{align*}
\]

\[
\frac{dx}{dt} = v
\]

\[
-\frac{DU(x)}{m}
\]

\[
\frac{dv}{dt} = -\frac{\beta}{m} v + q_{\text{ext}}(x) + \frac{\partial^2}{\partial x^2}
\]

\[
\beta/m \approx 1/7 \text{ trans}
\]

\[
\rightarrow \text{ viscous case}
\]

So back to Schmoluchowsky Freqns:

\[
\frac{dx}{dt} = q_{\text{ext}}(x) + \frac{\partial v}{\partial x}
\]

\[
\rightarrow \text{ terminal velocity}
\]
M.D. Can write full F-x Eqn: \( f(x, y, t) \)

\[
\frac{\partial f}{\partial t} + v \frac{\partial f}{\partial x} + \rho_{\text{ext}} \frac{\partial f}{\partial v}
\]

\[
= - \frac{\partial}{\partial v} \left( \frac{f}{m} \right)
\]

\[ D_v = \frac{\beta v^2}{m}, \quad \text{as usual.} \]

Now, in viscous limit \( \rightarrow \) terminal velocity

\[
\frac{\partial n}{\partial t} = - \frac{\partial}{\partial x} \left[ \alpha_{\text{ext}}(x) n - \frac{\partial}{\partial x} D_x n \right]
\]

\[ D_x = \frac{T}{\beta} \]

as before.

\[ v_{\text{CL}} = \frac{\alpha_{\text{ext}}(x)}{\beta} \]

Of course, Schmeluchowski Equation is just a continuity equation.
\[
\frac{\partial n}{\partial t} + \frac{\partial}{\partial x} J = 0
\]

\[
J = \Gamma_n = \frac{\partial \exp(U)}{\partial \eta} \eta - \delta x \delta x \delta \eta
\]

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

Consider \( B \) empty, particles \( \sim A \) initially.

Now, can re-write:

\[
J = J_{A0}.
\]

\[
j = -\frac{\partial n}{\partial \xi} \exp \left( -\frac{\alpha U}{\beta} \right) \delta x \left( n \exp \left( \frac{\beta U}{\delta \nu} \right) \right)
\]

Check:

\[
= -\frac{\partial n}{\partial \xi} e^{-\alpha U/\beta} \left[ e^{\alpha U/\beta} \delta x \eta \right] + n \frac{\delta (\delta x \eta) e^{\alpha U/\beta}}{\delta \nu}
\]
\[
\frac{\partial}{\partial \theta} \left[ \frac{\partial^2}{\partial \theta^2} \right] \phi(x, \theta) = \nabla \cdot \nabla \left( \phi(\theta, x) \right)
\]
\[ j = \frac{1}{m} \int_{B} \exp \left[ \frac{B U}{D U} \right] dx \]

\[ = \frac{I n e^{B U / D U}}{m} \left[ \begin{array}{c} A \\ B \end{array} \right] \]

\[ j = \frac{I n e^{B U / D U}}{m} \left( \frac{A}{B} \right) \]

\[ \int_{A}^{B} \exp \left[ m U / T \right] dx \]

\[ \text{current over barrier } A \rightarrow B \]

Now, at A:

\[ U = 0 \]

\[ V = 0 \]
\[ A + B, \]
\[ n_B \ll n_A, \quad \text{so} \quad n_B \to 0 \]

\[ u = -\frac{1}{2} N_B \quad \text{(U\xrightarrow{\to} 0)} \]

\[ j = \frac{\nabla}{\beta m} \left( n_A - n_B e \right) \]

\[ \frac{B}{\int_A^{B} dx \exp\left( \frac{m U x}{T} \right)} \]

\[ \delta \]

Current

\[ P \equiv \text{rate of escape} \]

\[ P = \frac{j}{N_A} \quad \text{(dims!)} \]

\[ P \to \# \text{ near } A \]
\[ n \rightarrow \text{density} \]

\[ n \rightarrow \# \text{ near} \]

\[ dV = \rho \, dx \]

\[ dv_A = n_A \exp \left[-\frac{m \sqrt{v}}{kT}\right] \, dx \]

Now,

\[ U = \frac{\alpha}{2} \psi^2 x^2 \rightarrow \text{Parabolic approx.} \]

So,

\[ v_A = n_A \int_{-\infty}^{\infty} \exp \left[-\frac{m \psi^2 x^2}{2T}\right] \, dx \]

\[ v_A = \frac{n_A \sqrt{2\pi T/m}}{\psi_A} \]
\[
\rho = \frac{\frac{I}{m_B} \int^B_{mA} \exp[\frac{e}{m_B} \mu/T]^{-1}}{\frac{V_A^2}{w_A} (2\pi \hbar/m)^{3/2}}
\]

\[
\rho = \frac{w_A (\pi/m)^{3/2} \int^B_{mA} \exp[\frac{e}{m_B} \mu/T]^{-1}}{\hbar}
\]

For integral:
- main contribution at point / peak C.
- i.e., max. in \( U \)
- there \( U = \Phi - \frac{1}{2} m_B \left( x-x_0 \right)^2 \)

\[
\int^B_{mA} \exp[\frac{e}{m_B} \mu/T] \sim \exp[-m_B \left( x-x_0 \right)^2 / 2T]^{1/2}
\]

\[
= e^{\frac{m_B}{2T}} \left( 2\pi T m_B \right)^{1/2}
\]
Finally,

Transition Rate $A \rightarrow B$

(Probability of Transition)

\[ P = \left( \frac{\omega_s \omega_c}{2 \pi F} \right) e^{-m \phi / \Gamma} \]

N.B. $- P \sim 1 / \epsilon \sim 1 / \eta$

In various limits:

- Note $\omega_s, \omega_c$

$\omega_s \rightarrow \# \sqrt{\gamma}$

$\omega_c \rightarrow$ width of barrier (channel = easier to jump over)

# Basic Kramers Problem
(C.) Related: First Passage Time

Basic Question: old runners

What is (average) time for A→B?

More generally P(TAB)?

pdf of transit times?

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

N.B.1 First passage problems are major topic, see:
  c.f.: S. Redner monograph

N.B.2 Can phrase as “first return” time to origin of random walk.
\[ \frac{d\varrho}{dt} = -v(\varrho) + \frac{F(t)}{\varrho} \]

\text{Confining volume } V \]
\text{Surface } \partial V \to \text{absorbancy.}

\text{Time to absorption } \to \text{First Passage Time} \]
\text{(time to pass out)}

\[ T \text{ distributed due to noise} \]

\[ P(\varrho, t) \to \text{distribution of particles which have not left yet at time } t \]

\[ P(\varrho_0, 0) = \delta(\varrho - \varrho_0) \]

\[ P(\varrho, t) \]

\text{starting point}
where:

\[ \frac{\partial P}{\partial t} = \Delta P \rightarrow F - P \quad \text{Eqn.} \]

Fokker-Planck operator

\[ \mathbf{D} = -D_a \left\{ \nabla_a P - \frac{\partial}{\partial a} \cdot \nabla_a P \right\} \]

For \( D_a \sim \text{const.} \quad \text{(we no Temp gradients)} \)

\[ \mathbf{D} = -D_a \left\{ \nabla_a P - \frac{\partial}{\partial a} \cdot \nabla_a P \right\} \]

\[ \text{convenient} \quad \text{(caveat \( \rightarrow \) not general)} \]

Now for mean first passage time:

\[ P \rightarrow 0 \quad \text{as all paths leave eventually} \]

\[ t \rightarrow \infty \quad \text{and so encounter absorbing boundary.} \]
\[ S(t) = \sum_{q} p(q, t) \]

\[ \delta(t) \to 0 \quad t \to \infty \]

Then, the number of particles leaving at \( t \) (in \( dt \) interval) =

\[ \rho(t, q_0) \cdot dt = S(t, q_0) - S(t + dt, q_0) \]

\[ \rho(t, q_0) \quad \text{density of first passage (exits)} \]

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

and average time:

\[ T(q_0) = \int_{0}^{t} t \cdot \rho(t, q_0) \]
\[
\begin{aligned}
&\int_{a_1}^{b_1} f(x) \, dx = \int_{a_2}^{b_2} g(x) \, dx \\
&\gamma = f(t) + \int_{a_1}^{b_1} g(t) \, dt
\end{aligned}
\]
Now, by c.c.

\[ p(a, 0) = \delta(x_1 - a_1) \]

\[ p(a, t) = e^{t B} \delta(x_1 - a_1) \]

\[ \frac{\partial p}{\partial t} = \nabla \rho \]

\[ p(a, t) = e^{t B} \delta(x_1 - a_1) \]

\[ \mathcal{T}(a_2) = \int_0^t \int \delta(x_1 - a_1) e^{t B} \delta(x_2 - a_2) \]

Now, labeling by \( \alpha \)

\[ \mathcal{T}(\alpha) = \int_0^t \int \delta(x_1 - a_1) e^{t B} \delta(x_2 - \alpha_2) \]

\[ = \int_0^t \int \delta(x_1 - a_1) \delta(x_2 - \alpha_2) e^{t B} \]

(1) trivial
time.

\[ T(\alpha) = -1 \]

\[ \epsilon = -1 \]

\[ \int \frac{d\theta}{\sqrt{\theta^2 + a^2}} = \frac{\sinh^{-1} \left( \frac{\theta}{a} \right)}{a} + C \]

\[ \phi(\theta) = \int \frac{d\theta}{\sqrt{a^2 + \theta^2}} = \sinh^{-1} \left( \frac{\theta}{a} \right) + C \]

\[ \langle \phi | 1 \phi \rangle < 1 \]

\[ \phi \neq \text{asymptotic} \]
Then

\[
\begin{align*}
\frac{\partial}{\partial t} \left( e^{-\frac{u^2}{2}} \mathcal{N}(e^{-\frac{u^2}{2}}) \right) & = -I \\
\mathcal{N} & = 0 \text{ as } u \to \infty \\
\frac{\partial}{\partial u} \left( e^{-\frac{u^2}{2}} \right) & = 0 \text{ as } u \to \infty
\end{align*}
\]

For Kronecker:
\[
e^{-\frac{u(x)}{T}} \frac{\partial}{\partial x} e^{-\frac{u(x)}{T}} = -\int_a^x dx' \frac{e^{-\frac{u(x')}{T}}}{D}
\]

\[
\frac{\partial}{\partial x} e^{-\frac{u(x)}{T}} = e^{-\frac{u(x)}{T}} \int_a^x dx' \frac{e^{-\frac{u(x')}{T}}}{D} (-1)
\]

Fix $x(y)$:

\[
T(x) = \frac{1}{D} \int_{y}^{b} dy e^{\frac{u(y)}{T}} \int_{x}^{y} dz e^{-\frac{u(z)}{T}}
\]

\[
T(x) = \frac{1}{D} \int_{y}^{b} dy e^{\frac{u(y)}{T}} \int_{x}^{y} dz e^{-\frac{u(z)}{T}}
\]

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