Lecture 11
7. Jump Processes

Up to this point, we have discussed how to build SM models for time dependent systems in which the phase space is continuous, rather than discrete. Often, however, events appear in systems that reflect nearly instantaneous transitions between discrete levels, e.g.

\[ \text{Alt} ]

Some examples:

1. Chemical reactions, e.g. \[ A + B \rightarrow C \]

2. Activated hopping of atoms, impurities, or defects

3. Coagulation / aggregation processes

4. Transport of localized electronic excitations (e.g. photosynthesis)
We would like to discuss how to build models for such systems. As a first step, let's examine how to build models for the transition rates (kinetic rate coefficients) that appear in such models.

A. **Kramers Theory**

Imagine that we have a Brownian particle confined to move in one dimension, and in a potential field $V(x)$ that looks like

![Potential Energy Diagram](image)

We are interested in the probability per unit time, $W$, that a particle initially in potential well $A$ traverses the barrier $C$ to arrive at $B$. This is a problem very relevant to chemical kinetics, where $x$ is the reaction coordinate between...
two molecules, and \( U(x) \) is the potential energy along that coordinate.

In the asymptotic limit of high barrier, \( \Delta E/k_BT \gg 1 \), this problem was solved by Kramers in 1940.

Consider the Chandrasekhar FP eqn in 1D:

\[
\frac{\partial f}{\partial t} + \frac{1}{m} p \frac{\partial}{\partial x} f - \frac{2}{\hbar} \frac{\partial}{\partial p} f = \frac{x}{\hbar^2} \frac{\partial}{\partial p} (p f) + \frac{\Delta E}{\hbar^2} \frac{\partial^2}{\partial p^2} f
\]

Define \( u = p/m \), \( \kappa = \pi/m \), \( x = \kappa (\Delta E/m) \)

\[
\frac{\partial f}{\partial t} + \kappa \frac{\partial f}{\partial x} - \frac{1}{\hbar} \frac{\partial}{\partial u} \frac{\partial f}{\partial u} = \kappa \frac{\partial}{\partial p} (u f) + x \frac{\partial^2}{\partial u^2} f
\]

If we waited a really long time, we expect an equilibrium solution

\[
f_{eq} (x, u) = N e^{-\beta [\frac{1}{2} m u^2 + U(x)]}
\]

However, then there will be no net flux across the barrier at \( C \). At earlier times, the particle is localized near \( A \) and there is a very small and nearly steady leakage of probability across the
barrier at C. Suppose we look for a quasi-stationary solution of the form

\[ f(x, u) = G(x, u) f_{eq}(x, u) \]

where \( G(x, u) \approx \begin{cases} 1 & x \ll x_c \\ 0 & x \gg x_c \end{cases} \)

First, we do a local analysis in the vicinity of \( x_c \).

\[ U(x) = \Delta E - \frac{1}{2} \omega_c^2 (x - x_c)^2 + \ldots \]

Then, with \( x = x - x_c \),

\[ u \frac{df}{dx} + \frac{\omega_c^2}{m} x \frac{df}{du} = \kappa \frac{\partial}{\partial u} (uf) + \chi \frac{\partial^2}{\partial u^2} f \]

Now, we substitute

\[ f(x, u) = \mathcal{N} e^{\frac{-\beta E}{\Delta E} - \frac{\beta \mu u^2 - \frac{1}{2} \omega_c^2 x^2}{\Delta E} \mathcal{G}(x, u) \mathcal{E} \mathcal{G}(x, u) \mathcal{E}} \]

\[ u \frac{2\mathcal{G}}{\partial x} + u \beta \frac{\omega_c^2}{m} x \mathcal{G} + \frac{\omega_c^2}{m} x \frac{\partial \mathcal{G}}{\partial u} + \frac{\omega_c^2}{m} x \mathcal{G} (-\beta \mu u) \]

\[ = \kappa \mathcal{G} + \kappa \mu u \frac{\partial \mathcal{G}}{\partial u} + \kappa \mu \mathcal{G} (-\beta \mu u) \]

\[ + \chi \left[ \frac{\partial^2 \mathcal{G}}{\partial u^2} + 2 \frac{\partial \mathcal{G}}{\partial u} (-\beta \mu u) + \mathcal{G} (-\beta \mu u)^2 \right] \]
So

\[ u \frac{\partial G}{\partial x} + \frac{\omega_0^2}{m} x \frac{\partial G}{\partial u} = -\kappa u \frac{\partial G}{\partial u} + \chi \frac{\partial^2 G}{\partial u^2} \]

Clearly, \( G(x, u) = \text{const} \) is the equilibrium soln to this eqn. We want a different soln satisfying

\[
G(x, u) \to 1 \quad \text{for} \quad x \to -\infty \\
G(x, u) \to 0 \quad \text{for} \quad x \to +\infty
\]

We can find this soln, by a similarity method. Let \( \xi = u - a x \), with \( a \) to be determined. Look for \( G(x, u) = G(\xi) \).

Substituting:

\[
u (a) G'(\xi) + \frac{\omega_0^2}{m} x G'(\xi) = -\kappa u G'(\xi) + \chi G''(\xi),
\]

\[-[a - \kappa (a - \kappa)] G'(\xi) = \chi G''(\xi)\]

Choose \( \frac{\omega_0^2/\kappa}{a - \kappa} = \xi \implies \]

\[-(a - \kappa) \xi G'(\xi) = \chi G''(\xi)\]

This is easily integrated to yield:
\[ G(\bar{\theta}) = G_0 \int_{-\infty}^{\bar{\theta}} dy \sqrt{-(a-N)y^2/(2x)} \]

Now the equation determining \( a \) is:

\[ a^2 - \pi a - \pi_{2/2} = 0 \]

\[ a = \frac{\pi}{2} \pm \sqrt{\frac{\pi^2 + 4\pi_{2/2}}{2}} \]

The positive root is the physical one that leads to a \( G \) satisfying the BCs.

Then

\[ a - \pi = \sqrt{\pi^2/4 + \pi_{2/2}} - \pi/2 > 0 \]

So

\[ \bar{\theta} = a - \pi x \]

\[ \bar{\theta} \to -\infty, x \to -\infty \]

\[ \bar{\theta} \to \infty, x \to 0 \]

Thus, we want to impose the BC's

\[ G \to 1, \bar{\theta} \to +\infty ; \quad G \to 0, \bar{\theta} \to -\infty \]

This is achieved by

\[ G(\bar{\theta}) = G_0 \int_{-\infty}^{\bar{\theta}} dy \sqrt{-(a-N)y^2/(2x)} \]

\[ G_0 = \left[ \frac{(a-N)/(2\pi x)}{2} \right]^{1/2} \]

We now summarize our local analysis.
leading to an approximate solution valid near \( C \):

\[
f_c(x, u) \approx N e^{-\beta \left[ \frac{1}{2} m u^2 + \frac{1}{2} \omega^2 x^2 \right]}
\]

\[
\cdot \left[ \frac{(a-x)^2}{2\pi x} \right] \int e^{-\frac{u-a}{2x} - (a-x)y^2/(2x)} dy \cdot \int e^{-\infty}
\]

\& Next, we do a similar local analysis around the basin at \( A \):

\[
U(x) = \frac{1}{2} \omega_A^2 x^2 + \ldots
\]

The PDF is nearly the equilibrium solution in this basin:

\[
f_A(x, u) = N e^{-\beta \left[ \frac{1}{2} m u^2 + \frac{1}{2} \omega_A^2 x^2 \right]}
\]

Now, under the relevant quasi-static conditions, we want to choose \( N \) so that there is exactly \( N_A = 1 \) particles in the basin at \( A \):

\[
N_A = 1 = N \int dx \int du e^{-\beta \left[ \frac{1}{2} m u^2 + \frac{1}{2} \omega_A^2 x^2 \right]}
\]

\[
= N \left( \frac{2\pi}{\beta m} \right)^{1/2} \left( \frac{2\pi}{\beta \omega_A^2} \right)^{1/2}
\]
So \( \mathcal{N} = \frac{\beta \Delta E \ c \ m^2}{2\pi} \).

Finally, we analyze the flow of particles crossing the barrier \( \mathcal{C} \):

The current of particles crossing the barrier is

\[
\mathbf{j} = \int_{\mathcal{C}} d\mathbf{u} \ u \ f_{\mathcal{C}}(0, u)
\]

so

\[
\mathbf{j} = \mathcal{N} \ e^{-\beta \Delta E} \int_{\infty}^{-\infty} du \ u \ e^{-\frac{\beta}{2\Delta E} m u^2} \left[ \frac{(\mathcal{C} - \mathcal{K})}{2\pi \mathcal{X}} \right]^{1/2} \int_{-\infty}^{\infty} d\eta \ e^{-(\mathcal{C} - \mathcal{K}) \eta^2 / (2\mathcal{X})}
\]

Write

\[
-\beta \frac{1}{2} m u^2 \quad u \ e^{-\frac{\beta}{2\Delta E} m u^2} = \frac{1}{\Delta E} \left[ e^{-\frac{\beta}{2\Delta E} m u^2} \right]^{1/2}
\]

and then integrate by parts:

\[
\mathbf{j} = \mathcal{N} \ e^{-\beta \Delta E} \left[ \frac{(\mathcal{C} - \mathcal{K})}{2\pi \mathcal{X}} \right]^{1/2} \int_{\infty}^{-\infty} du \ e^{-\beta \frac{1}{2} m u^2 - (\mathcal{C} - \mathcal{K}) \eta^2 / (2\mathcal{X})}
\]

But

\[
\frac{1}{2} \beta m + \frac{(\mathcal{C} - \mathcal{K})}{(2\mathcal{X})} = \frac{\mathcal{C}}{2\mathcal{X}}
\]
So,
\[ j = \pi e^{-\beta \Delta E} \frac{1}{\beta m} \left[ \frac{a-x}{2\pi \hbar} \right] \frac{2\pi}{\alpha/y} \]
\[ = \pi e^{-\beta \Delta E} \frac{k_B T}{m} \left[ \frac{a-x}{\alpha} \right] \]

The probability per unit time of crossing the barrier is

\[ W_{BA} = \frac{J}{\eta A} = \frac{J}{\beta \frac{a-x}{m} \cdot 2\pi} \]
\[ = e^{-\beta \Delta E} \frac{\alpha}{a} \]

\[ W_{BA} = \frac{\omega A}{2\pi \sqrt{m}} e^{-\beta \Delta E} \left[ \frac{a-x}{a} \right] \]

\[ \frac{a-x}{a} = \frac{\sqrt{\frac{\hbar^2}{4} + \omega_0^2/4m} - \omega/2}{\sqrt{\frac{\hbar^2}{4} + \omega_0^2/4m} + \omega/2} = \frac{\sqrt{\frac{\hbar^2}{4} + \omega_0^2/4m} - \omega/2}{\sqrt{\frac{\hbar^2}{4} + \omega_0^2/4m} + \omega/2} \]
\[ = \left[ \frac{\sqrt{\frac{\hbar^2}{4} + \omega_0^2/4m} - \omega/2}{\omega_0^2/4m} \right] \]

\[ W_{BA} = \frac{\omega A}{2\pi \omega_0} \left( \frac{\sqrt{\frac{\hbar^2}{4} + \omega_0^2/4m} - \omega/2}{\omega_0^2/4m} \right) e^{-\beta \Delta E} \]

This is the general Kramers rate formula.
Before examining limits of this rate expansion it is useful to identify three frequencies. Recall the Langevin eqn:

\[ m \ddot{x}(t) = -\gamma \dot{x}(t) + R(t) \quad -\nabla U(x) \]

If we balance the inertial \(-\omega_c^2 x(t)\) term with the friction or potential terms we have:

\[ \omega_p = \frac{\gamma}{m} \quad \text{viscous damping frequency} \]
\[ \omega_A = \frac{\omega_c}{\sqrt{m}} \quad \text{harmonic oscillation frequency in a bath} \]
\[ \omega_c = \frac{\omega_0}{\sqrt{m}} \quad \text{undamped barrier crossing frequency} \]

In terms of these, the general rate expansion is

\[ W_{BA} = \frac{\nu_A}{2\pi \nu_c} \left( \sqrt{\nu_p^2 + \nu_c^2} - \frac{\nu_p}{2} \right) \exp \left( -\frac{-\Delta E}{k_B T} \right) \]

In the low friction limit, \( \nu_p \ll \nu_c \):

\[ W_{BA} \sim \frac{\nu_A}{2\pi} \exp \left( -\frac{-\Delta E}{k_B T} \right) \quad \text{"Transition State Theory"} \]
This formula is familiar in texts on chemical reaction kinetics. In the absence of friction, the "attempt frequency", i.e., the pre-factor in the Arrhenius rate law is set by the undamped oscillation frequency in the starting potential basin, \( \nu_A \).

In the high friction limit, \( \nu_p \gg \nu_c \):

\[
W_{BA} \sim \frac{\nu_A \nu_c}{2\pi \nu_p} e^{-\beta \Delta E}
\]

and the "attempt frequency" is set by a non-trivial combination of all these frequencies.

A couple of comments about the Kramer's formula and analysis:

1. The derivation is asymptotic for \( \Delta E/k_B T \gg 1 \). Only in this limit is the quasi-static assumption valid since the crossing rate is exponentially small. Corrections are \( O(\gamma^{-1} e^{-\beta \Delta E}) \) for \( \beta \Delta E \to \infty \).