Lecture 10. Stochastic Theory of Reaction Rates

Model problem (1-D): reactants (at x=0) in state 1 randomly walk until they go over activation barrier (x=x_A), then it goes directly to state 2 and the reaction happens. (Kramers Problem)

In the limit of a continuous stochastic process, the probability density function \( P(x,t) \) (which is proportional to the concentration of non-interacting particles independently following the same stochastic dynamics) satisfies the Fokker-Planck Equation:

\[
\frac{\partial P}{\partial t} + \nabla \cdot (D \nabla P) = \nabla^2 (D \nabla P)
\]

where \( D \) = Diffusivity

\( \overrightarrow{D_1} = \text{drift velocity} = \text{mobility} \times \text{force} = -\nabla U \)

and let \( D_2 = D = \text{const.} \)

\[
D = \frac{\hbar^2 kT}{h} \text{ describes thermal noise}
\]

In equilibrium in state 1 (no escape, \( E \gg kT \)): 
\[ \frac{D_t P}{D_t} = D \nabla P + \text{cons.} (= 0) \]
\[ \Rightarrow -MP \nabla U(x) = D \nabla P \]
\[ \Rightarrow - \frac{M}{D} \nabla U(x) = \nabla \ln P \]
\[ \Rightarrow P = P_0 e^{\frac{MU}{D} = P_0 e^{\frac{U(x)}{kT}}} \]

where Einstein Relation \( M = \frac{D}{kT} \) is derived equating the equilibrium distribution with a Boltzmann distribution.

(Note that a Boltzmann distribution must describe the equilibrium state of zero flux, since the particles are assumed to be non-interacting point particles.) For \( P(x,t) \), we can almost guess it would be as below:

For the 1d Kramers Problem, we consider the following initial value problem

\[ P(x,t) = \delta(x) \quad (2) \]

\[ \frac{1}{D} \frac{\partial P}{\partial t} = \frac{\partial^2 P}{\partial x^2} + \frac{\partial}{\partial x} \left( \frac{U'(x)}{kT} P \right) \quad (1) \]

which describes a particle released from the origin at \( t=0 \) and diffusing in the energy landscape \( U(x) \). To calculate conveniently, we put them into Dimensionless form:

\[ \tilde{x} = \frac{x}{x_A}, \tilde{t} = \frac{t}{x_A^2 \frac{x_A}{D}}, \tilde{U} = \frac{U}{kT} \]

\[ \frac{\partial P}{\partial \tilde{t}} = \frac{\partial^2 P}{\partial \tilde{x}^2} + \frac{\partial}{\partial \tilde{x}} \left( \tilde{U}'(x) P \right) \]

\[ \text{drop} \tilde{\text{below}} \]

Recall that the probability density function \( P \) can be interpreted as the concentration (mean number) of non-interacting random walkers starting at \( x=0 \) at \( t=0 \) and arriving at \( x \pm \Delta x, t \pm \Delta t \)

The “first passage time” \( T \) is a random variable, whose value is the time when the stochastic process first achieves a certain condition, such as hitting a target set. In Kramers problem, this target is the activation barrier, and \( \langle T \rangle = \text{mean first passage time starting from the potential well} = \text{inverse of the mean reaction rate} \). If we want complete information about fluctuations in the reaction rate (not just its mean), we need to solve for PDF (probability density function) \( f(t) \) for \( T \). This can be conveniently calculated from the “survival probability” \( S(t) = \text{Probability the process has not hit the target set (here, the activation barrier) at } x=x_A \text{ up to time } t \).
\[ S(t) = \int_{t}^{\infty} f(t) dt = \text{Probability (Escape Time > t)} \]

To obtain \( S(t) \) for a general stochastic process, we solve the Fokker-Planck equation \( f(t) = \partial_x \left( \frac{\partial^2 P}{\partial x^2} + \frac{\partial}{\partial x} \left( U'(x) P \right) \right) \Rightarrow \frac{\partial P}{\partial t} = L_x P = \frac{\partial}{\partial x} \left( e^{-U(x)} \frac{\partial}{\partial x} \left( e^{U(x)} P \right) \right) \)

So we get:

\[ S(\tilde{t}) = \int_{-1}^{1} P(\tilde{x}, \tilde{t}) d\tilde{x} \]

\[ f(\tilde{t}) = -S'(\tilde{t}) \]

\[ <\tilde{t}^n> = \int_{0}^{\infty} \tilde{t}^n f(\tilde{t}) d\tilde{t} \]

and \( \sigma_t = \sqrt{<\tilde{t}^2> - <\tilde{t}>^2} \)

Consider (1)'s dimensionless form into another form for next step:

We will solve this problem in more general form and apply it to Kramers problem in the next lecture.