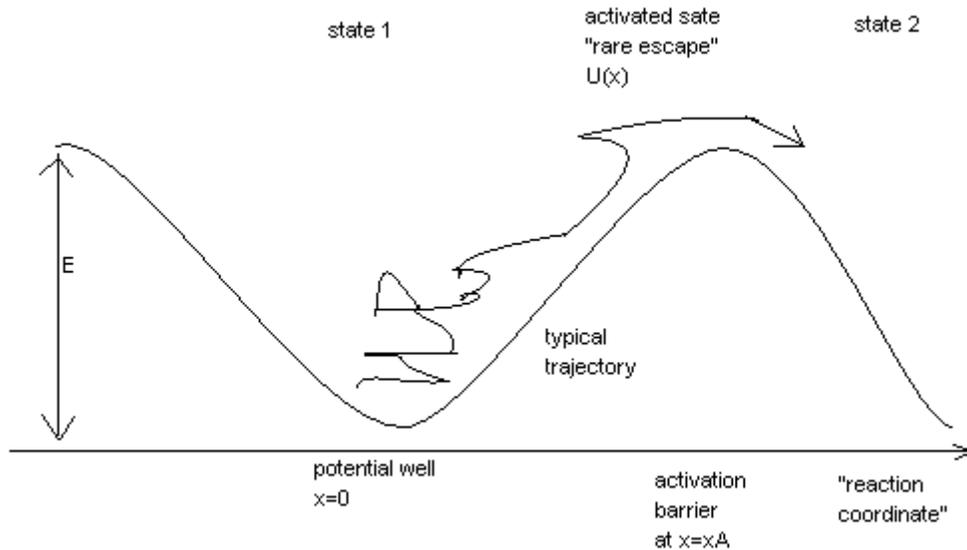


Lecture 10. Stochastic Theory of Reaction Rates

Notes by MIT Student (and MZB)

10.95 lecture on 2/25/09

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:

$$\frac{\partial P}{\partial t} + \nabla \cdot (\overline{D_1} P) = \nabla^2 (D_2 P)$$

where $D_2 =$ Diffusivity

$\overline{D_1} =$ drift velocity = mobility * force = $-\nabla U$

and let $D_2 = D =$ cons.

$$D \approx \frac{l^2 kT}{h} \text{ describes thermal noise}$$

In equilibrium in state 1 (no escape, $E \gg kT$):

$$\begin{aligned} \overrightarrow{D_1 P} &= D \nabla P + \text{cons.} (= 0) \\ \Rightarrow -M P \nabla U(x) &= D \nabla P \\ \Rightarrow -\frac{M}{D} \nabla U(x) &= \nabla \ln P \\ \Rightarrow P &= P_0 e^{-\frac{MU}{D}} = P_0 e^{-\frac{U(x)}{kT}} \end{aligned}$$

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:

$$\tilde{x} = \frac{x}{x_A}, \tilde{t} = \frac{t}{x_A^2/D}, \tilde{U} = \frac{U}{kT}$$

$$\frac{\partial P}{\partial \tilde{t}} = \frac{\partial^2 P}{\partial \tilde{x}^2} + \frac{\partial}{\partial \tilde{x}} (\tilde{U}'(x) P)$$

drop $\tilde{}$ 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 $\langle T \rangle =$ mean first passage time starting from the potential well = 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” $S(t) =$ Probability the process has not hit the target set (here, the activation barrier) at $x=x_A$ 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 solve (1) with initial condition localized on the starting point (2) subject to the boundary condition $P=0$ on the target set. This describes an “absorbing boundary” that “eats” stochastic trajectories as soon as they reach it, leaving behind only trajectories that have “survived” and not yet hit the set. For the 1d Kramers problem:

$$\text{"absorbing boundary" that "eats" trajectories } P(x = \pm x_A, t) = P(\tilde{x} = \pm 1, \tilde{t}) = 0 \quad (3)$$

So we get:

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

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

$$\langle \tilde{t}^n \rangle = \int_0^\infty \tilde{t}^n f(\tilde{t}) d\tilde{t}$$

$$\text{and } \sigma_t = \sqrt{\langle \tilde{t}^2 \rangle - \langle \tilde{t} \rangle^2}$$

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

$$\frac{\partial P}{\partial t} = L_x P = \frac{\partial^2 P}{\partial x^2} + \frac{\partial}{\partial x} (U'(x)P)$$

$$\Rightarrow \frac{\partial P}{\partial t} = L_x P = \frac{\partial}{\partial x} (e^{-U(x)} \frac{\partial}{\partial x} (e^{U(x)} P))$$

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

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10.626 Electrochemical Energy Systems
Spring 2014

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