

Lecture 12 – Reactions as Rare Events

3/02/2009

Notes by MIT Student (and MZB)

1. Introduction

In this lecture, we'll tackle the general problem of reaction rates involving particles jumping over barriers in energy landscapes. Next time, we will extend our analysis to tackle *free energy* landscapes. Along the way, we'll learn a useful and neat math tool called *asymptotic expansion of integrals*.

Recall from the last lecture our expression for the mean first passage time, τ , for a particle trapped in an energy well defined by the (symmetric) energy landscape $U(x)$:

$$\tau = \frac{1}{D} \int_0^{x_A} e^{-\alpha \tilde{U}(x)} \int_x^{x_A} e^{\alpha \tilde{U}(y)} dy dx$$

In this expression, we had defined:

$$\tilde{U}(x) = \frac{U(x)}{E}, \alpha = \frac{E}{kT}$$

Finally, we note that x_A was the location of the barrier, and E was the energy barrier at that location (see Figure 1).

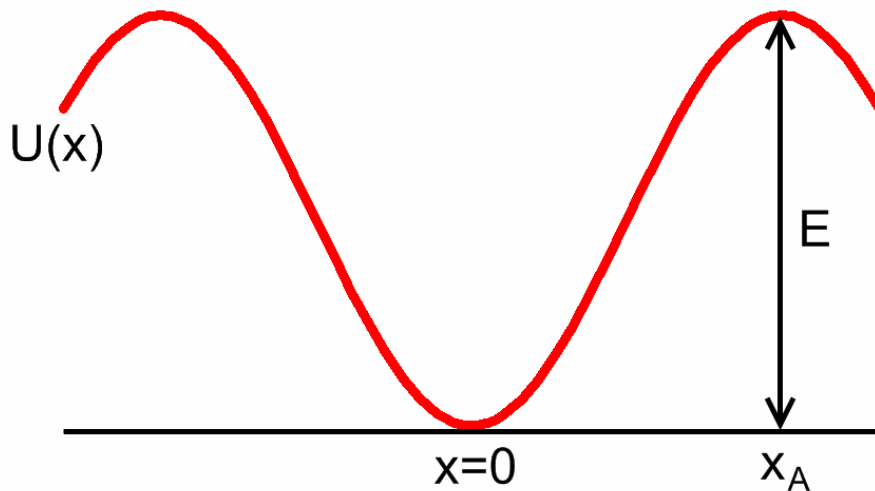


Figure 1: Symmetric potential well

We will now proceed in approximating the integral for the mean first passage time, τ . Note that for $\alpha \ll 1$, corresponding to very small energy barriers, we could simply Taylor expand the exponentials in the above expression and integrate. However, we are interested in the case $\alpha \gg 1$, corresponding to large energy barriers and rare hopping events. In this scenario, we will find that the expansion we use and the final result won't depend on many of the intermediate details of the $U(x)$ function, but only on its extreme values.

Our strategy in this lecture will be as follows:

1. First describe the general technique of asymptotic expansion of integrals.
2. Then apply asymptotic expansion of integrals to evaluating the integral for mean first passage time.

2. Asymptotic Expansion of Integrals

Note: More about this technique can be found in the 18.366 notes, in and around Lecture 6, 2005. Bender & Orszag also cover this technique.

Consider the general integral:

$$I(\alpha) = \int f(x, \alpha) dx$$

As the parameter a gets large or small, it may be the case that $f(x, a)$ is negligible except in only a certain region of the integral. Then, it would not be necessary to evaluate the entire integral; rather, a very good approximation of the integral could be determined by simply evaluating the important region.

To get the flavor of how this could happen, let's draw an arbitrary function $\psi(x)$, shown below in Figure 2:

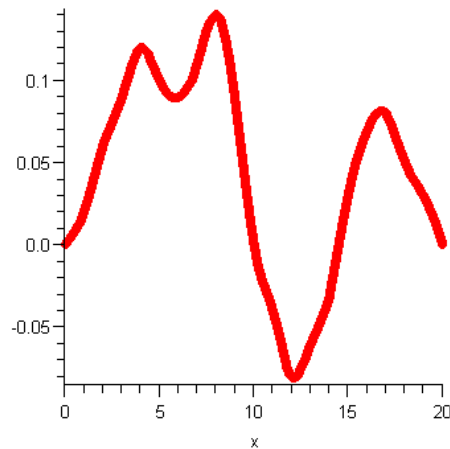


Figure 2: The arbitrary function $\psi(x)$.

Now, let's consider the function $f(x, a)$ to be $e^{a\psi(x)}$. We can start to think about what would happen if a became very large. First, any negative component in $\psi(x)$ would become a very small positive number inside the exponential, and approach zero. Second, the positive components would start to scale, with the largest components stretching more than the smaller components. As a result of this 'stretching', the function $f(x, a)$ will be dominated by the region around its maximum. This is illustrated in Figure 3.

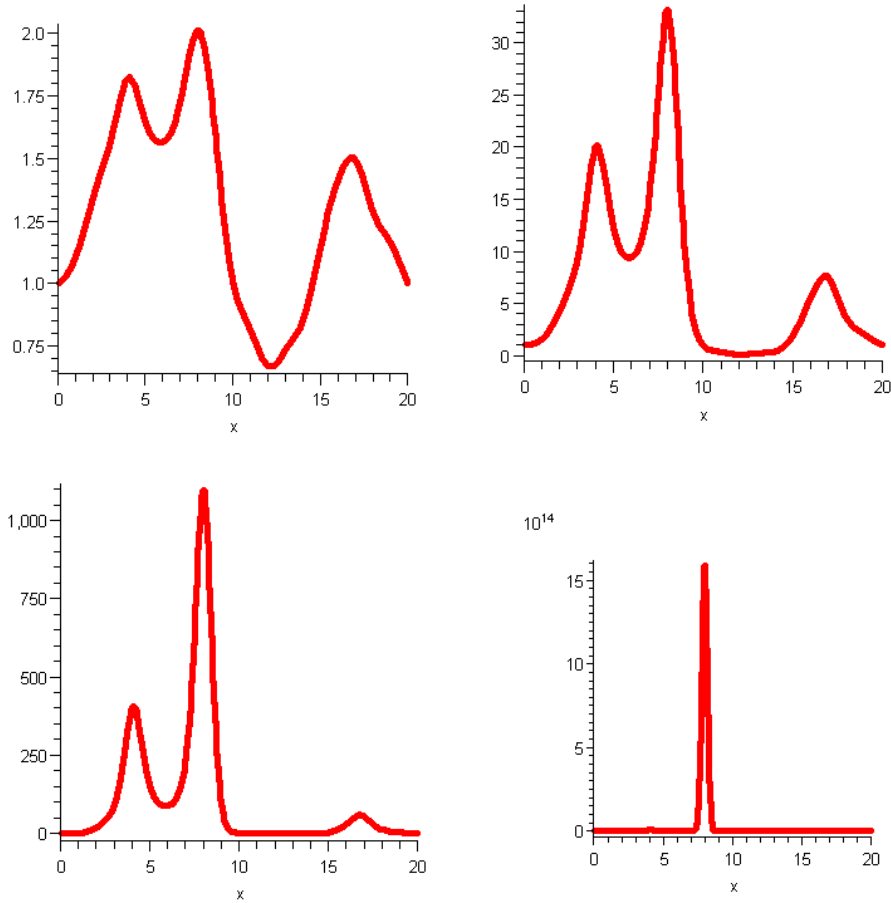


Figure 3: The function $e^{a\psi(x)}$ for $a=5$ (top-left), $a=25$ (top-right), $a=50$ (bottom-left), $a=250$ (bottom-right). As we increase a , the function becomes dominated by the region around its maximum value at $x=8$. Thus, taking an integral around this region provides a good approximation of the overall integral.

Thus, what we have shown is that we can should be able to approximate the integral of the function $f(x,a)$ by taking an integral only around its maximum. More, formally, we express:

$$I(\alpha) = \int f(x, \alpha) dx \sim \int_{x_{\max} - \varepsilon}^{x_{\max} + \varepsilon} e^{\alpha\psi(x)} dx + O(e^{-\alpha})$$

where $O(e^{-\alpha})$ represents the order of the error in our approximation, and ε is a small distance.

Next, we will proceed by approximating the function $\psi(x)$ at its maximum via a Taylor series. Note that we will be exploiting the fact that at the maximum, the first derivative of $\psi(x)$ is zero. Thus, as $x \rightarrow x_{\max}$ or equivalently as $\varepsilon \rightarrow 0$, we have:

$$\psi(x) \sim \psi_{\max} - \frac{C_2}{2}(x - x_{\max})^2$$

where C_2 is the *negative* of the second derivative of ψ with respect to x . Since we are at a maximum, C_2 will be positive. We note that though this analysis assumes a smooth function, it can be generalized to unsmooth functions as well. In addition, we are free to carry over

more terms in the Taylor series for $\psi(x)$ at its maximum. Let's in fact do this as we continue our progress towards evaluating the integral $I(a)$. Using our Taylor expansion for $\psi(x)$ (with added terms) along with our previous equation, we arrive at:

$$I(\alpha) \sim e^{\alpha\psi_{\max}} \int_{x_{\max}-\varepsilon}^{x_{\max}+\varepsilon} e^{-\alpha\left[\frac{C_2}{2}(x-x_{\max})^2 + \sum_{n=3}^{\infty} \frac{C_n}{n!}(x-x_{\max})^n\right]} dx$$

Next, we will perform a transformation to make this integral look like a standard Gaussian integral, which we know how to integrate. To do this, we define the variable y and rewrite our equation for $I(a)$ above:

$$I(\alpha) \sim e^{\alpha\psi_{\max}} \int_{-\varepsilon\sqrt{\alpha C_2}}^{+\varepsilon\sqrt{\alpha C_2}} e^{-\frac{y^2}{2}} * e^{\sum_{n=3}^{\infty} \frac{C_n}{n!} \left(\frac{\alpha y}{\sqrt{\alpha C_2}}\right)^n} \frac{dy}{\sqrt{\alpha C_2}}$$

The first exponential in our integral is a standard Gaussian function. To rid ourselves of the second exponential, we again invoke a Taylor expansion. We can do this because the second exponential goes as $a^{-n/2+1}$ for $n>3$, and we are considering the limit as a goes to infinity and thus the exponential going to zero. This gives us:

$$I(\alpha) \sim \frac{e^{\alpha\psi_{\max}}}{\sqrt{\alpha C_2}} \int_{-\varepsilon\sqrt{\alpha C_2}}^{+\varepsilon\sqrt{\alpha C_2}} e^{-\frac{y^2}{2}} \left[1 + \sum_{n=3}^{\infty} \frac{C_n}{n!} \left(\frac{\alpha y}{\sqrt{\alpha C_2}}\right)^n\right] dy$$

As final steps, we do three things:

- 1) Note that $\varepsilon(\alpha C_2)^{1/2}$ goes to infinity for large a , because ε is finite (though small). This allows us to redefine the bounds of our integral as $-\infty$ to $+\infty$.
- 2) Invoke the standard Gaussian integral, $\int_{-\infty}^{\infty} e^{-\frac{y^2}{2}} dy = \sqrt{2\pi}$. The Appendix describes how to derive this integral.
- 3) Use only the first term of our Taylor expansion, grouping all the other terms into error bounds.

This gives our final expression for $I(a)$!

$$I(\alpha) \sim \sqrt{\frac{2\pi}{\alpha C_2}} e^{\alpha\psi_{\max}} \left[1 + O\left(\sqrt{\frac{1}{\alpha}}\right) + O\left(\frac{1}{\alpha}\right) + O\left(\frac{1}{\alpha^{3/2}}\right) + \dots\right]$$

where the $O(a)$ represent error bounds. Neglecting these errors, we arrive at:

$$I(\alpha) \sim \sqrt{\frac{2\pi}{\alpha C_2}} e^{\alpha\psi_{\max}}$$

Thus, we have shown what we have set out to prove. As we go to large values of a , the integral $I(a)$ does not depend on the details of $\psi(x)$, but rather only its maximum value and the curvature at that maximum.

In the Appendix, we show how this technique can be used to derive Stirling's approximation.

2. Asymptotic Expansion of Integrals Applied to Kramer's Escape Problem

Let's use our new approximation technique to evaluate our integral for the mean first passage time:

$$\tau = \frac{1}{D} \int_0^{x_A} e^{-\alpha \tilde{U}(x)} \int_x^{x_A} e^{\alpha \tilde{U}(y)} dy dx$$

First, we evaluate the integral on the right hand side. The term in the exponential will peak at $x=x_A$. The maximum of $\tilde{U}(x)$ is by definition equal to 1. We note that we are only evaluating half a Gaussian since we do not consider the "other side" of the energy hill, and thus will add a factor of $1/2$ to our integral. This gives us:

$$\tau \sim \frac{1}{2D} \int_0^{x_A} e^{-\alpha \tilde{U}(x)} \sqrt{\frac{2\pi}{\alpha |\tilde{U}''(x_A)|}} e^{\alpha} dx$$

Rearranging:

$$\tau \sim \frac{1}{2D} \sqrt{\frac{2\pi}{\alpha |\tilde{U}''(x_A)|}} e^{\alpha} \int_0^{x_A} e^{-\alpha \tilde{U}(x)} dx$$

All that is left now is to evaluate the remaining integral. We can use the same method as before to evaluate this integral, but since we looking at the negative of $U(y)$ in the exponential, the peak will occur at $x=0$. Again, we need to add a factor of $1/2$ since we are only evaluating half a Gaussian. Putting this all together:

$$\tau \sim \frac{e^{\alpha}}{2D} \sqrt{\frac{2\pi}{\alpha |\tilde{U}''(x_A)|}} \left(\frac{1}{2} \sqrt{\frac{2\pi}{\alpha |\tilde{U}''(0)|}} \right)$$

Rearranging gives:

$$\tau \sim \frac{\pi e^{\alpha}}{2\alpha D \sqrt{|\tilde{U}''(x_A)| |\tilde{U}''(0)|}}$$

Thus, we have finished our derivation for the mean passage time. Given the mean passage time, we can find an expression for the escape rate, R . We define R to be $1/\tau$. Note that although R needs to be scaled by $1/2$ to account for the fact that a particle reaching the maximum can fall back into the well, it also needs to be scaled by a factor of 2 because a particle in the minimum can escape either to the left or to the right. Thus these scaling factors cancel and $R=1/\tau$, giving us:

$$R \sim \frac{e^{-\alpha} 2\alpha D \sqrt{|\tilde{U}''(x_A)| |\tilde{U}''(0)|}}{\pi}$$

Next, let's try to get some sort of an intuition for the second derivative factors that occur in the expression for R above. We can in fact approximate these second derivatives by looking at the width of the energy landscape at a distance kT from the maximum and minimum of our potential, as shown in Figure 4:

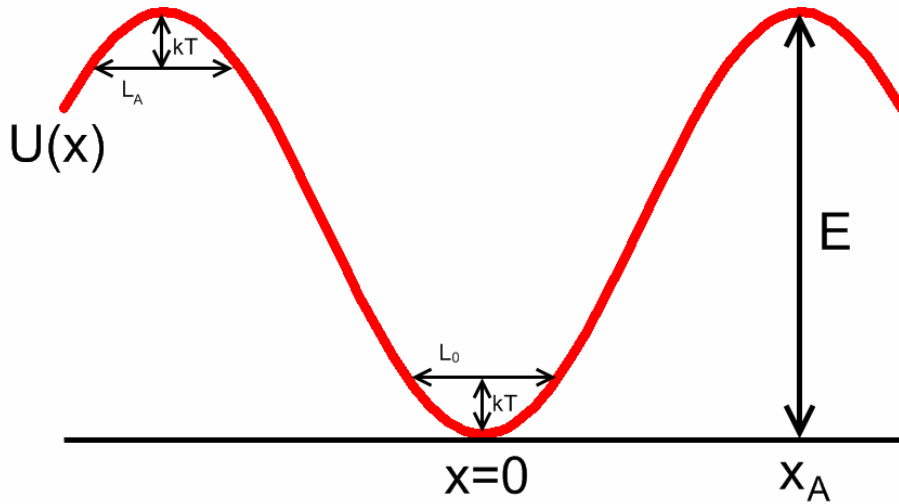


Figure 4: The distance kT from the minimum and maximum, and corresponding lengths L_0 and L_A .

Using these definitions, we can approximate our curvature as:

$$|\tilde{U}''(x_A)| \sim \frac{kT}{EL_A^2}$$

$$|\tilde{U}''(x_0)| \sim \frac{kT}{EL_0^2}$$

which allows us (along with our expression for $\alpha=E/kT$) rewrite our expression for R as:

$$R \sim \frac{2D}{\pi \sqrt{L_0^2 L_A^2}} e^{-\frac{E}{kT}}$$

Finally, we note that our diffusivity D can be modeled by an atomic length scale times an atomic frequency:

$$D \sim \frac{L^2}{\tau_0} \quad \tau_0 \sim \frac{h}{kT}$$

where h is Planck's constant, and L represents an atomic spacing.

$$R \sim \frac{2}{\pi\tau_0} \frac{L}{L_0} \frac{L}{L_A} e^{-\frac{E}{kT}}$$

Let's see what we can learn from this analysis. First, we note that our prefactor won't affect the final rate very much, but a difference in E/kT will cause huge variations in rates due to its presence in the exponential. Next, we see the effect of a wide or shallow well. For example, if we had a wide well with a large L_0 and large L_A , our overall rate R would go down. This makes intuitive sense, as in this case much time would be wasted fluttering around valleys and flat peaks in the energy landscape, rather than 'climbing' the potential well.

This lecture concludes by noting that transition state theory is very general, and not restricted to Kramer's escape problem. If we keep higher order terms in our escape rate expression, we'd arrive at something of the form:

$$R \sim R_0 [1 + \beta_1 \sqrt{\frac{kT}{E}} + \beta_2 \left(\frac{kT}{E}\right) + \dots]$$

where R_0 is now the escape rate R we calculated previously. These corrections could be put back into the Butler-Volmer equation.

Appendix

1. Integration of Gaussian

To arrive at the integral I of the Gaussian:

$$I \equiv \int_{-\infty}^{\infty} e^{-x^2} dx$$

We first square the integral:

$$I^2 \equiv \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-(x^2+y^2)} dx dy$$

And then transform to polar coordinates:

$$I^2 \equiv \int_0^{2\pi} \int_0^{\infty} e^{-r^2} r dr d\theta$$

This integral is easily evaluated as π , and so we can find I to be $\sqrt{\pi}$.

2. Stirling's Approximation

Stirling's approximation can also be derived via the asymptotic expansion of integrals technique. We start with the integral definition of the factorial¹:

¹ Weisstein, Eric W. "Stirling's Approximation." From MathWorld--A Wolfram Web Resource. <http://mathworld.wolfram.com/StirlingsApproximation.html>

$$n! \equiv I(n) = \int_0^{\infty} e^{-t} t^n dt$$

which can be rewritten as:

$$n! \equiv I(n) = \int_0^{\infty} e^{-n\psi(x,n)} dt \text{ where } \psi = \ln(t) - \frac{t}{n}$$

The function ψ reaches its maximum at $t=n$. Thus:

$$\psi_{\max} = \ln(n) - 1$$

As we go to large n , we can use our definition of asymptotic expansion of integrals:

$$I(n) \sim \sqrt{\frac{2\pi}{nC_2}} e^{n\psi_{\max}}$$

$$I(n) \sim \sqrt{\frac{2\pi}{nC_2}} e^{[n\ln(n)-n]}$$

$$I(n) \sim \sqrt{\frac{2\pi}{nC_2}} e^{-n} (n)^n$$

Next, C_2 is the second derivative of ψ evaluated at $n-1$, or $C_2=1/n^2$. This gives:

$$I(n) \sim \sqrt{2\pi n} e^{-n} n^n = \sqrt{2\pi} e^{-n} n^{n+\frac{1}{2}}$$

At this point, we are almost finished. We just need to take the log of both sides of the equation:

$$\ln(I(n)) = \ln(n!) \sim \left(n + \frac{1}{2}\right) \ln(n) - n - \frac{1}{2} \ln(2\pi)$$

As we go to large n , we recover Stirling's approximation, as we desired:

$$\ln(n!) \sim (n) \ln(n) - n$$

MIT OpenCourseWare
<http://ocw.mit.edu>

10.626 Electrochemical Energy Systems
Spring 2014

For information about citing these materials or our Terms of Use, visit: <http://ocw.mit.edu/terms>.