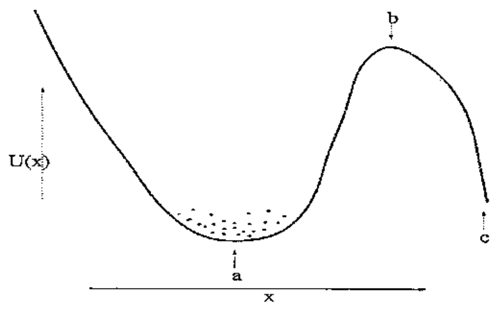
Kramer's escape rate across a barrier

Consider a collection of independent Brownian particles in a potential $U(x)$ which has the shape shown in the figure below. Let us assume that the well is very deep and initially the particles are within the well. Physically we expect that the particles will reach a close-to-equilibrium state but will leak out slowly across the barrier. What is the rate at which this escape takes place ? This is the Kramer's escape rate problem.



Let us first write the Langevin equation for the particles. We will work in the overdamped limit where it is ok to drop the inertial term $m\dot{v}$. Thus we have the equation:

$$\gamma\dot{x} = -\frac{\partial U(x)}{\partial x} + \eta. \tag{1}$$

The corresponding Fokker-Planck equation for the probability density $P(x,t)$ is given by

$$\begin{aligned} \frac{\partial P(x,t)}{\partial t} &= \frac{\partial}{\partial x}[\frac{1}{\gamma}\frac{\partial U}{\partial x}P(x,t)] + D\frac{\partial^2 P(x,t)}{\partial x^2} \\ &= \frac{\partial}{\partial x}[\frac{1}{\gamma}\frac{\partial U}{\partial x}P(x,t) + D\frac{\partial P(x,t)}{\partial x}] = -\frac{\partial J}{\partial x} \qquad (2) \\ \text{where } J &= -\frac{1}{\gamma}\frac{\partial U}{\partial x}P(x,t) - D\frac{\partial P(x,t)}{\partial x} \quad \text{and} \quad D\gamma = k_BT \qquad (3) \end{aligned}$$

We can rewrite the current in the following form:

$$J = -De^{-\frac{U(x)}{k_BT}}\frac{\partial}{\partial x}(e^{\frac{U(x)}{k_BT}}P) \tag{4}$$

If the system was completely in equilibrium there would be no currents $J = 0$ and we would therefore get

$$P(x) = e^{-\frac{U(x)}{k_BT}}P_0 \tag{5}$$

where W_0 can be determined from normalization. This is the expected equilibrium distribution. However with the given form of $U(x)$ the system cannot be exactly in equilibrium (WHY!!!). Let us thus assume that the particles are approximately in equilibrium at the bottom of the well and there is a small current J across the barrier. With $\partial P/\partial t \approx 0$, the current J will be independent of x and from Eq. 4 we get

$$\frac{\partial}{\partial x}(e^{\frac{U(x)}{k_BT}}P) = -\frac{J}{D}e^{\frac{U(x)}{k_BT}} \tag{6}$$

Integrating this between the points a and c gives

$$e^{\frac{U(x)}{k_BT}}P|_a^c = -\frac{J}{D}\int_a^c e^{\frac{U(x')}{k_BT}}dx' \tag{7}$$

But $P(x)$ is very small at c. Hence we get

$$-e^{\frac{U(a)}{k_BT}}P(x=a) = -\frac{J}{D}\int_a^c e^{\frac{U(x')}{k_BT}}dx'$$

$$\Rightarrow J = \frac{De^{\frac{U(a)}{k_BT}}P(a)}{\int_a^c e^{\frac{U(x')}{k_BT}}dx'} \tag{8}$$

The escape rate r can now be obtained by noting that this gives the *conditional* probability of escape per unit time, given that the particle is initially inside the well near $x = a$. Thus if we define p as the probability of the particle being inside the well then $J = pr$. To evaluate p we first note that if the barrier is high then we have (approximately) the equilibrium relation:

$$P(x) = P(a)e^{-\frac{U(x)-U(a)}{k_BT}} \tag{9}$$

The probability of finding a particle in the well is thus

$$p = \int_{a-\Delta}^{a+\Delta}P(x)dx = P(a)e^{\frac{U(a)}{k_BT}}\int_{a-\Delta}^{a+\Delta}e^{-\frac{U(x)}{k_BT}} \tag{10}$$

where Δ is of the order of the size of the well. Again the integrand is peaked about the point $x = a$ and expanding about it gives

$$p = P(a)(\frac{2\pi k_BT}{|U''(a)|})^{1/2} \tag{11}$$

In Eq. 8 the integrand in the denominator is peaked about the point $x = b$. Expanding about this point then gives

$$\int_a^c e^{\frac{U(x')}{k_BT}}dx' = \int_a^c e^{[U(b)+U''(b)(x-b)^2/2+..]/(k_BT)}dx' \approx e^{\frac{U(b)}{k_BT}}\int_{-\infty}^{\infty}e^{-\frac{|U''(b)|(x-b)^2}{2k_BT}}dx' = (\frac{2\pi k_BT}{|U''(b)|})^{1/2}e^{\frac{U(b)}{k_BT}}. \tag{12}$$

Using this and Eq. 11 we finally get, from $r = J/p$, the Kramer's escape rate formula:

$$r = \frac{D}{2\pi k_BT}[U''(a)|U''(b)|]^{1/2}e^{-\frac{E_b}{k_BT}} \tag{13}$$

where $E_b = U(b) - U(a)$ is the barrier height. Thus the escape rate falls exponentially with the barrier height. It also depends on how flat the potential is at the points $x = a$ and $x = b$. As expected the escape rate increases with increasing temperature ($D/k_BT = 1/\gamma$) depends weakly on temperature). Also note that the formula can only be applied for $E_b >> k_BT$ because the assumptions that have been made while deriving it hold only in this regime.

REFERENCES:

(1) H. Risken, The Fokker-Planck equation.
(2) Van Kampen, Stochastic processes in physics and chemistry.
(3) S. Chandrashekhar, Rev. Mod. Phys. 15, 1 (1943)[page 63].