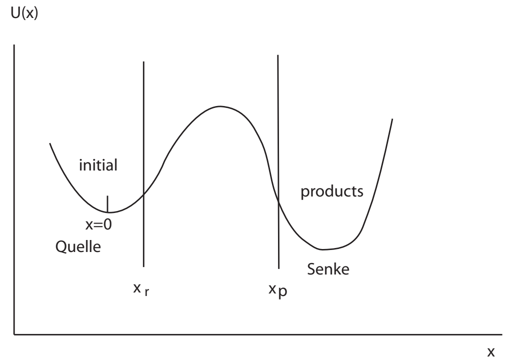
# Kramer's theory




We consider particles in a double well as shown in the figure. At the bottom of the left well there is a source of particles, at the bottom of the right well a sink. We consider the probability $P(x,t)$ to find a particle at the position $x$ at the time $t$. We first derive an equation for the current density $j$ of the particles. This will depend on the gradient of $P(x,t)$ via the diffusion equation, and there will be a second term, proportional to $P(x,t)$, representing the influence of the potential energy $U(x)$. We proceed to derive the second term. We write:

$$j = -D\frac{dP}{dx} + f(x)P(x,t) \tag{1}$$

$D$ is the diffusion coefficient, and $f(x)$ as yet an unknown function. At equilibrium, $j = 0$, $P$ is independent of time and follows a Boltzmann distribution. In this case:

$$P(x,t) \propto \exp -\frac{U(x)}{kT} \tag{2}$$

and:

$$j = 0 = D\frac{U'(x)}{kT}P(x,t) + f(x)P(x,t) \tag{3}$$

where the dash denotes differentiation. Hence:

$$f(x) = -D\frac{U'(x)}{kT} = -\beta DU'(x) \tag{4}$$

Using the identity:

$$e^{-\beta U(x)}\frac{\partial}{\partial x}\left(P(x,t)e^{\beta U(x)}\right) = \frac{\partial P}{\partial x} + \beta U'(x)P \tag{5}$$

we arrive at:

$$\frac{j}{D}e^{\beta U(x)} = -\frac{\partial}{\partial x}\left(P(x,t)e^{\beta U(x)}\right) \tag{6}$$

Our aim is to derive an equation for the rate of transfer of particles from the left to the right well. For this purpose we consider the stationary case of constant $j$ and assume that the stream of particles generated at the source at the left is annihilated at the sink at the right. In the right well, we choose a line $x = x_r$ which is so close to the source, that the density is not disturbed by the escaping particle and hence in equilibrium. At the right we choose a line $x = x_p$ which is so close to the sink that the particle density there is practically zero. We integrate eqn. (6) between $x_r$ and $x_p$:

$$\frac{j}{D} \int_{x_r}^{x_p} e^{\beta U(x)}\, dx = -P e^{\beta U(x)}\Big|_{x_r}^{x_p} = P(x_r) e^{\beta U(x_r)} \tag{7}$$

To evaluate the left hand side we note that the main contribution from the integral comes from the region near the saddle point. Therefore we approximate the potential through:

$$U(x) \approx E_a - \frac{1}{2} m\omega_b^2 (x - x_b)^2 \tag{8}$$

where $x_b$ is the position of the barrier, and $E_a$ its energy. We may extend the integration limits to infinity and obtain:

$$\int_{x_r}^{x_p} e^{\beta U(x)}\, dx \approx e^{\beta E_a} \int_{-\infty}^{\infty} e^{-\beta \frac{1}{2} m\omega_b^2 (x-x_b)^2}\, dx = e^{\beta E_a} \left( \frac{2\pi kT}{m\omega_b^2} \right)^{1/2} \tag{9}$$

To evaluate the right hand side, we note that $x_r$ has been chosen so close to the origin that $P(x_r)$ is in equilibrium. We expand the potential in the left well:

$$U(x) = \frac{1}{2} m\omega_r^2 x^2 \text{ for small } x \tag{10}$$

use eq. (2) and normalize $P(x)$, so that we obtain:

$$P(x) = \left( \frac{m\omega_r^2}{2\pi kT} \right)^{1/2} e^{-\beta U(x)} \tag{11}$$

which gives for the right hand side just:

$$\left( \frac{m\omega_r^2}{2\pi kT} \right)^{1/2} \tag{12}$$

Putting things together we obtain:

$$j = D \frac{m\omega_r \omega_b}{2\pi kT}\, e^{-\beta E_a} \tag{13}$$

Using the Einstein relation: $mD/kT = 1/\gamma$, we obtain finally:

$$j = \frac{\omega_b}{\gamma} \frac{\omega_r}{2\pi} \, e^{-\beta E_a} \tag{14}$$

which differs from the result of transition state theory by a factor of $\omega_b/\gamma$. Equation (14) is valid for high friction. For intermediate to high friction, the correction factor is:

$$\frac{1}{\omega_b} \left( \sqrt{\frac{\gamma^2}{4} + \omega^2} - \frac{\gamma}{2} \right) \tag{15}$$

In the limit of high friction, this reduces to $\omega_b/\gamma$.