1. Kramers' escape problem

1.1. Introduction to the Problem

As a model for a chemical reaction we study the escape from a metastable state in a double-well potential $V(x)$, where x is the reaction coordinate. Furthermore x_a refers to the metastable

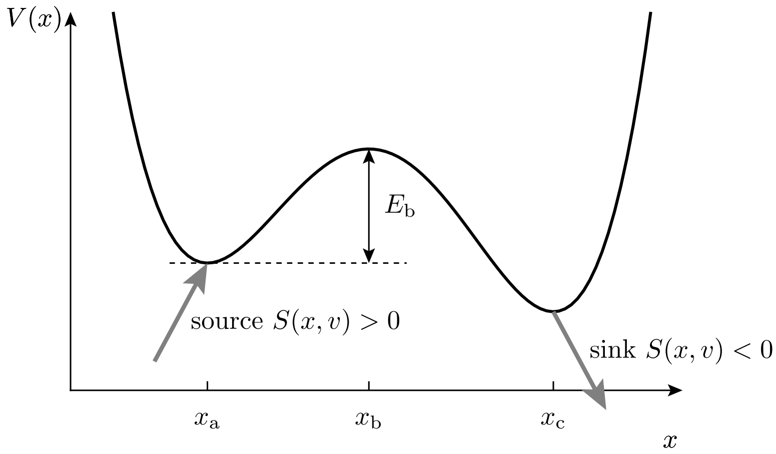

Figure 1: Double-well potential model for a chemical reaction

reactant state and x_c to the product. The transition state is denoted by x_b and the activation energy is given by $E_b = V(x_b) - V(x_a)$. In the following we try to derive an expression for the reaction rate k (per reactant).

1.2. Description of dyamics

The dynamics of this system is described by the Langevin equation

$$M\ddot{\hat{x}} = -M\gamma\dot{\hat{x}} - V'(x) - \sqrt{2k_\mathrm{B}T\gamma/M}\,\hat{\xi}(t)$$

with $\hat{\xi}(t)$ being Gaussian white noise, i.e. $\langle\hat{\xi}(t)\rangle = 0$ and $\langle\hat{\xi}(t)\hat{\xi}(t')\rangle = \delta(t-t')$.

Equivalently it can be desribed by the Klein-Kramers equation

$$\frac{\partial}{\partial t}\,p(x,v,t) + \mathrm{div}\vec{j}(x,v,t) = 0 \tag{1}$$

with the probability current density

$$\vec{j}(x,v,t) = \begin{pmatrix} v\;p(x,v,t) \\ -\left[\frac{V'(x)}{M} + \gamma v + \frac{\gamma k_\mathrm{B}T}{M}\frac{\partial}{\partial v}\right]p(x,v,t) \end{pmatrix}.$$

The stationary solution is given by the Boltzmann distribution

$$p^{\rm eq}(x,v) = Z^{-1} \exp\left\{-\frac{Mv^2/2 + V(x)}{k_{\rm B}T}\right\}.$$

Show that this ansatz indeed solves Eq. (1). Note that the equilibrium probability does not depend on γ! Does this result surprise you?

1.2.1. Separation of time scales

The nonequilibrium preparation of a "particle" around x_a will decay on a time-scale given by the inverse of the reaction rate k. For $k_{\rm B}T \ll E_b$, this time-scale $1/k$ is separated from all other time-scales of the problem, e.g. the time-scale of the damped oscillation around x_a, fluctuations around x_a, etc. Therefore we assume that the reactant state is equilibriated, i.e. sharply peaked around x_a, before the transition. Convince yourself that this assumption is valid.

2. Flux-over-population method

There are several ways to calculate the reaction rate k. One method consists in calculating the inverse of the mean-first-passage time (cf. problem set 5). Here, we will follow an alternative route and employ the so-called flux-over-population method due to Farkas and Kramers. Its main idea is to generate a current-carrying non-equilibrium solution by adding to the Fokker-Planck dynamics (1) a source term $S(x,v)$ which feeds in reactant particles around x_a and a sink term which removes the same amount of product particles around x_c. See illustration in Fig. 1.

This provides a new non-equilibrium stationary dynamics describing the decay process. Due to the separation of time scales, the specific form of the source term $S(x,v)$ is not relevant: the in-feed around x_a thermalizes before the decay and the out-take around x_c does not return to x_a anyway.

2.1. Reaction rate in the flux-over-population method

Due to the addition of the source term the Fokker-Planck equation reads

$$\frac{\partial}{\partial t}p(x,v,t) + {\rm div}\vec{j}(x,v,t) = S(x,v)$$

with stationary, current-carrying solution $p^{\rm s}(x,v)$ and $j^{\rm s}(x,v)$, which fulfill

$${\rm div} j^{\rm s}(x,v) = S(x,v).$$

In the flux-over-population method the reaction rate k is derived as the "flux over population"

$$k = \frac{\Phi}{N}$$

where the flux across x_b is given by

$$\Phi := \int_{-\infty}^{\infty} \mathrm{d}v \; j_x(x = x_b, v) = \int_{-\infty}^{\infty} \mathrm{d}v \; v \; p^{\mathrm{s}}(x_b, v)$$

and the population of the reactant state reads

$$N := \int_{-\infty}^{\infty} \mathrm{d}v \int_{-\infty}^{x_b} \mathrm{d}x \; p^{\mathrm{s}}(x, v).$$

2.2. Ansatz due to Kramers

To solve the Fokker-Planck equation we use the ansatz

$$p^{\mathrm{s}}(x, v) = p^{\mathrm{eq}}(x, v)\,\zeta(x, v),$$

where $\zeta(x, v)$ denotes the Kramers form function.

We have to take three regimes into account

(i)	$x \ll x_b$:	$p^{\mathrm{s}}(x, v) \approx p^{\mathrm{eq}}(x, v)$	$\Rightarrow \zeta(x, v) \approx 1$
(ii)	$x \approx x_b$:	no sources and sinks	$\Rightarrow \mathrm{div} j^{\mathrm{s}}(x, v) \approx 0$
(iii)	$x \gg x_b$:	$p^{\mathrm{s}}(x, v) \ll p^{\mathrm{eq}}(x, v)$	$\Rightarrow \zeta(x, v) \to 0$

Thus we do not prescribe the source term $S(x, v)$ a priori but look for a solution fulfilling conditions (i)-(iii) and then can calculate $S(x, v)$ from $\mathrm{div} j^{\mathrm{s}}(x, v)$ and verify its validity a posteriori.

2.3. Barrier region

Consider the condition (ii) in the barrier region and approximate

$$V(x) \approx V(x_b) + \frac{V''(x_b)}{2}(x - x_b)^2 = V(x_b) - \frac{1}{2} M\omega_b^2 (x - x_b)^2$$

with the barrier coefficient $\omega_b = \sqrt{|V''(x_b)|/M}$.

Condition (ii) therefore leads to the equation

$$\left\{ -\frac{\partial}{\partial x} v + \frac{\partial}{\partial v}\left[-\omega_b^2 (x - x_b) + \gamma v\right] + \frac{\gamma k_{\mathrm{B}} T}{M} \frac{\partial^2}{\partial v^2} \right\} p^{\mathrm{s}}(x, v) = 0.$$

Show that Kramers form function $\zeta(x, v)$ obeys the backwards equation

$$\left\{ -v \frac{\partial}{\partial x} + \left[-\omega_b^2 (x - x_b) - \gamma v\right] \frac{\partial}{\partial v} + \frac{\gamma k_{\mathrm{B}} T}{M} \frac{\partial^2}{\partial v^2} \right\} \zeta(x, v) = 0,$$

with the boundary conditions $\zeta(x - x_b \to -\infty, v) = 1$ and $\zeta(x - x_b \to \infty, v) = 0$.

2.4. Ansatz for $\zeta(x, v)$

Kramers suggested the ansatz for $\zeta(x, v)$

$$\zeta(x, v) = f(x - x_b + av) = f(u).$$

Show that the function $f(u)$ has to fulfill

$$-f'(u)\left[v(1 + a\gamma) + \omega_b^2(x - x_b)a\right] + \frac{\gamma k_{\mathrm{B}}T}{M} a^2 f''(u) = 0.$$

In order for this ansatz to make sense, the prefactor to $f'(u)$ has to be a function of $u = x - x_b + av$, as well. Convice yourself that this means that it is linear in u:

$$v(1 + a\gamma) + \omega_b^2(x - x_b)a = -\lambda u\,.$$

2.5. Solution for $\zeta(x, v)$

Derive the solutions

$$\lambda_\pm = -\frac{\gamma}{2} \pm \sqrt{\left(\frac{\gamma}{2}\right)^2 + \omega_b^2}\,, \quad a_\pm = -\frac{\lambda_\pm}{\omega_b^2}\,,$$

and show that λ_- can not be a solution due to the boundary conditions and thus $\zeta(x, v)$ is given by

$$\zeta(x, v) = \sqrt{\frac{M\omega_b^4}{2\pi k_{\mathrm{B}}T\gamma\lambda_+}} \int\limits_{x - x_b - \frac{\lambda_+ v}{\omega_b^2}}^{\infty} \mathrm{d}u\ \exp\left[-\frac{M\omega_b^4}{2k_{\mathrm{B}}T\gamma\lambda_+}u^2\right].$$

2.6. Solution of the reaction rate k

To calculate the population N we assume that $p^{\mathrm{s}}(x, v)$ is strongly peaked around x_a and we can thus approximate

$$V(x) = V(x_a) + \frac{V''(x_a)}{2}(x - x_a)^2 = V(x_a) + \frac{1}{2}M\omega_a^2(x - x_a)^2$$

where $\omega_a = \sqrt{V''(x_a)/M}$.

Derive the expression for the population

$$N = Z^{-1}\frac{2\pi k_{\mathrm{B}}T}{M\omega_a} \exp\left[-\frac{V(x_a)}{k_{\mathrm{B}}T}\right].$$

Similarly one can derive the result for the flux along the barrier

$$\Phi = Z^{-1}\frac{\lambda_+ k_{\mathrm{B}}T}{M\omega_b} \exp\left[-\frac{V(x_b)}{k_{\mathrm{B}}T}\right].$$

With the flux-over-population method we, thus, finally find the reaction rate

$$k = \frac{\sqrt{(\gamma/2)^2 + \omega_b^2} - \gamma/2}{\omega_b} \frac{\omega_a}{2\pi} \exp\left[-\frac{E_b}{k_{\mathrm{B}}T}\right].$$

Discuss and interpret the different factors in this result.