Finite barrier corrections for the Kramers rate problem in the spatial diffusion regime

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Finite barrier height corrections for the rate of thermally activated escape of a particle over a barrier out of a metastable well are determined within the framework of Fokker–Planck processes in the spatial diffusion regime. Different existing concepts to obtain the rate are extended and compared to each other. The central role that is played by Kramers' stationary current carrying probability density is demonstrated. An improvement of this function by means of a perturbation theory allows one to calculate corrections to the rate by means of the flux over population expression, the Rayleigh quotient and the mean first passage time to the stochastic separatrix. The Rayleigh quotient is in a sense superior as it allows one to obtain from the same stationary current carrying Kramers function higher order corrections than by means of the other methods. Explicit results are obtained for the case of a cubic and a quartic potential and compared with existing results.

1. Introduction

Kramers' seminal paper about a diffusional model of chemical reactions [1] has found various generalizations [#1] for example to higher dimensional problems [3] and cases with memory friction [4]. In most of these investigations the barrier height V^{*} measured in units of thermal energy $k_{\mathrm{B}}T$ is assumed to be sufficiently large not only in order that a rate description is meaningful at all but, additionally, that on the thermal length scale at the barrier any nonlinear force can safely be neglected. The latter condition, however, is not always met in experimental situations or in numerical calculations, independently of whether it is molecular dynamics simulations [5] or calculations of lowest eigenvalues of a Fokker–Planck operator [6].

Only very recently, a systematic approach to this problem has been put forward [7,8] that gives the leading nonvanishing correction of the rate in terms of the inverse barrier height. Within this approach the dynamics of the reaction coordinate is of the type of a generalized Langevin equation and, hence, as a special case contains the Markovian Brownian motion originally considered by Kramers [1]. The theory of ref. [7] is based on the transformation of the original stochastic and dissipative dynamics to an equivalent infinite dimensional Hamiltonian system [9,10]. Within the Hamiltonian formulation the rate is determined by means of the reactive flux [11] through an optimized planar dividing surface [12]. In the special case of Markovian dynamics in which the stochastic process of the reaction coordinate and its velocity is described by a Fokker–Planck equation only few and partly contradicting results can be found in the literature [13–15] except for the limiting case of large damping where the Smoluchowski equation can be used [16].

It is the main purpose of the present work to develop a perturbation theory entirely based on the Fokker–Planck equation which allows one to recover the results of refs. [7,8] for the Markovian case. This goal can be reached by the same methods that have already been used to derive the leading order Kramers rate, as there are: the flux over population method [1], the Rayleigh quotient for the eigenvalue of the Fokker–Planck operator

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[#1] For a recent review see ref. [2].

with smallest nonvanishing modulus [13,15] and the mean first passage time [17,18]. Whereas it is straightforward to use the flux over population method the two other methods need some more care. Since the Fokker–Planck operator is not self-adjoint it is not completely obvious how a Rayleigh quotient has to be defined; indeed, two different versions can be found in the literature [13,15]. We demonstrate below that the definition of ref. [15] is more effective. Concerning the mean first passage time, the deterministic separatrix is no longer the proper location in phase space to register its first crossing times but has rather to be replaced by the stochastic separatrix [14,19,20].

The paper is organized as follows. In the next section the Kramers problem is briefly reviewed and a perturbation theory for the Kramers function is developed. In section 3 the flux over population expression for the rate is evaluated using the perturbed Kramers function. In section 4 the rate being the lowest eigenvalue of the Fokker–Planck operator is determined from the Rayleigh quotient defined in ref. [15]. The connections between the Kramers function, the splitting probability [19–21] and the stochastic separatrix are outlined and utilized for the calculation of the mean first passage time in section 5. In section 6 the concepts that have so far been developed are applied to a cubic and a quartic potential. The results of the different methods are found to agree with each other and in particular with those of refs. [7,8]. For a comparison with numerical results the reader is refered to ref. [8]. For the quartic potential the second order corrections are also determined. The paper ends with a summary.

2. The Kramers form function

The diffusional model of a chemical reaction established by Kramers [1] consists of a particle with mass weighted reaction coordinate x and according velocity v. It moves in a potential $U(x)$ which has a minimum $x_0<0$ corresponding to reactants and a maximum at $x=0$ corresponding to the transition state. For positive values of x there may or may not be another minimum of the potential describing products. The solvent influences the reaction coordinate by a velocity-proportional damping force and a fluctuating force which is Gaussian and uncorrelated on the time scales set by the potential and the damping force. Under these assumptions a Markovian diffusional motion in the phase space of the reaction coordinate takes place. The time evolution of the probability density $p(x, v, t)$ in phase space is then governed by the Klein–Kramers equation

$$\dot{p}(x,v,t)=Lp(x,v,t)\,, \tag{2.1}$$

where L denotes the Fokker–Planck operator

$$L=-\frac{\partial}{\partial x}v+\frac{\partial}{\partial v}\left[U'(x)+\gamma v\right]+\gamma k_{\mathrm{B}}T\frac{\partial^2}{\partial v^2}\,. \tag{2.2}$$

The damping constant γ describes the effective coupling of the reactive coordinate to the solvent and T denotes the solvent's temperature.

In order to calculate the rate at which the initial reactants go over to the final products, Kramers constructed a current carrying stationary probability density $p(x, v)$ which smoothly matches the equilibrium distribution $p_{\mathrm{eq}}(x, v)$ in the reactant well and vanishes on the product side. Consequently, the two stationary densities are related by a form function $\zeta(x, v)$ (henceforth referred to as Kramers function) that smoothly changes from unity in the reactant well to zero on the product side:

$$p(x,v)=\zeta(x,v)p_{\mathrm{eq}}(x,v)\,, \tag{2.3}$$

$$\begin{aligned}\zeta(x,v)&=1\quad\text{on reactants}\,,\\&=0\quad\text{on products}\,,\end{aligned} \tag{2.4}$$

where

$$p_{\mathrm{eq}}(x, v) = Z^{-1} \exp\left(-\frac{\frac{1}{2}v^2 + U(x)}{k_{\mathrm{B}} T} \right), \tag{2.5}$$

with partition function Z. In order to maintain a stationary probability current there must be sources on the reactant side and sinks on the product side. However, the barrier region must be free of sources and sinks. Therefore, in the barrier region $p(x, v)$ satisfies the stationary Fokker–Planck equation. With eq. (2.3) this leads to an equation for the Kramers function

$$L^* \zeta(x, v) = 0 \quad (x, v) \text{ in the barrier region}, \tag{2.6}$$

where L^* is a linear operator defined in terms of the original Fokker–Planck operator L and the equilibrium density:

$$L^* = p_{\mathrm{eq}}^{-1} L p_{\mathrm{eq}}. \tag{2.7}$$

As the Klein–Kramers equation obeys detailed balance [6], L^* coincides with the time reversed backward operator,

$$L^* = -v \frac{\partial}{\partial x} + [((U'(x) - \gamma v] \frac{\partial}{\partial v} + \gamma k_{\mathrm{B}} T \frac{\partial^2}{\partial v^2}. \tag{2.8}$$

The final assumption Kramers made in his derivation of the rate consists in the parabolic approximation of the full potential $U(x) = -\frac{1}{2}\omega_{\mathrm{b}}^2 x^2 + V(x)$ entering the operator L^*, i.e. the nonlinear part $V(x)$ which vanishes faster than the parabolic part $-\frac{1}{2}\omega_{\mathrm{b}}^2 x^2$ is neglected:

$$L^* \approx L^*_{\mathrm{pb}} = -v \frac{\partial}{\partial x} - (\omega_{\mathrm{b}}^2 x + \gamma v) \frac{\partial}{\partial v} + \gamma k_{\mathrm{B}} T \frac{\partial^2}{\partial v^2}, \tag{2.9}$$

where ω_{b} denotes the barrier frequency,

$$\omega_{\mathrm{b}}^2 = -\frac{\mathrm{d}^2 U}{\mathrm{d}x^2}(0). \tag{2.10}$$

Within this approximation the solution of eq. (2.6) with (2.4) as asymptotic boundary conditions reads [1]

$$\zeta_{\mathrm{pb}}(x, v) = \left(\frac{\omega_{\mathrm{b}}^2}{2\pi k_{\mathrm{B}} T} \right)^{1/2} \int\limits_{(\mu\gamma^*)^{-1/2}[x - (\mu/\omega_{\mathrm{b}})v]}^{\infty} \exp\left(-\frac{\omega_{\mathrm{b}}^2 z^2}{2k_{\mathrm{B}} T} \right) \mathrm{d}z \tag{2.11}$$

where

$$\gamma^* = \frac{\gamma}{\omega_{\mathrm{b}}} \tag{2.12}$$

and

$$\mu = -\frac{\gamma^*}{2} + \sqrt{\left(\frac{\gamma^*}{2}\right)^2 + 1}. \tag{2.13}$$

The main purpose of this work is to derive corrections for the Kramers rate from an improved Kramers function that follows from a perturbational solution of eq. (2.6). To this end the full operator L^* is split into the barrier part (2.9) and a rest L^*_1,

$$L^* = L^*_{\mathrm{pb}} + L^*_1, \tag{2.14}$$

where

$$L_1^* = V'(x)\,\frac{\partial}{\partial v}\,, \tag{2.15}$$

with $V(x)$ being the nonlinear part of the potential. Since eq. (2.6) is supposed to hold in the barrier region only, $V(x)$ is small compared to the parabolic part of the potential and consequently L_1^* may be considered as a small perturbation. Neglecting L_1^* completely leads to the unperturbed Kramers function (2.11). A perturbation series for the Kramers function reads

$$\zeta(x, v) = \zeta_{\mathrm{pb}}(x, v) + \zeta_1(x, v) + \zeta_2(x, v) + \dots\,, \tag{2.16}$$

where $\zeta_1(x, v)$, $\zeta_2(x, v)$ and all higher contributions successively follow from the following hierarchy of inhomogeneous equations [20]:

$$L_{\mathrm{pb}}^*\zeta_1(x, v) = -L_1^*\zeta_{\mathrm{pb}}(x, v)\,, \tag{2.17a}$$

$$L_{\mathrm{pb}}^*\zeta_2(x, v) = -L_1^*\zeta_1(x, v)\,, \tag{2.17b}$$

and generally

$$L_{\mathrm{pb}}^*\zeta_{k+1}(x, v) = -L_1^*\zeta_k(x, v)\,. \tag{2.17c}$$

Since the zeroth order contribution $\zeta_{\mathrm{pb}}(x, v)$ already fulfills the boundary conditions of the full Kramers function (2.6), the corrections $\zeta_k(x, v)$, $k \geqslant 1$, must vanish for both large positive and negative x. With the explicit expressions (2.11) and (2.15) for $\zeta_{\mathrm{pb}}(x, v)$ and L_1^*, respectively, the inhomogeneity in eq. (2.17a) is readily found to read

$$-L_1^*\zeta_{\mathrm{pb}}(x, v) = -\left(\frac{\mu}{2\pi\gamma^* k_{\mathrm{B}} T}\right)^{1/2} V'(x) \exp\left[-\frac{\omega_{\mathrm{b}}^2}{2\gamma^*\mu k_{\mathrm{B}} T}\left(x - \frac{\mu}{\omega_{\mathrm{b}}} v\right)^2\right]. \tag{2.18}$$

It is convenient to split off a Gaussian function from $\zeta_1(x, v)$:

$$\zeta_1(x, v) = \left(\frac{\mu}{2\pi\gamma^* k_{\mathrm{B}} T}\right)^{1/2} P_1(x, v) \exp\left[-\frac{\omega_{\mathrm{b}}^2}{2\gamma^*\mu k_{\mathrm{B}} T}\left(x - \frac{\mu}{\omega_{\mathrm{b}}} v\right)^2\right]. \tag{2.19}$$

For the function $P_1(x, v)$ the following equation is then obtained:

$$\left[-v\frac{\partial}{\partial x} + \left(\omega_{\mathrm{b}}^2 x - \frac{1+\mu^2}{\mu}\omega_{\mathrm{b}} v\right)\frac{\partial}{\partial v} - \mu\omega_{\mathrm{b}} + \gamma k_{\mathrm{B}} T\frac{\partial^2}{\partial v^2}\right] P_1(x, v) = -V'(x)\,. \tag{2.20}$$

Analogously one obtains for the higher order corrections

$$\begin{aligned}
&\left[-v\frac{\partial}{\partial x} + \left(\omega_{\mathrm{b}}^2 x - \frac{1+\mu^2}{\mu}\omega_{\mathrm{b}} v\right)\frac{\partial}{\partial v} - \mu\omega_{\mathrm{b}} + \gamma k_{\mathrm{B}} T\frac{\partial^2}{\partial v^2}\right] P_{k+1}(x, v) \\
&\quad = -V'(x)\left[\frac{\partial P_k(x, v)}{\partial v} + \frac{\omega_{\mathrm{b}}}{\gamma^* k_{\mathrm{B}} T}\left(x - \frac{\mu}{\omega_{\mathrm{b}}} v\right) P_k(x, v)\right],
\end{aligned} \tag{2.21}$$

where $\zeta_k(x, v)$ and $P_k(x, v)$ are related by

$$\zeta_k(x, v) = \left(\frac{\mu}{2\pi\gamma^* k_{\mathrm{B}} T}\right)^{1/2} P_k(x, v) \exp\left[-\frac{\omega_{\mathrm{b}}^2}{2\mu\gamma^* k_{\mathrm{B}} T}\left(x - \frac{\mu}{\omega_{\mathrm{b}}} v\right)^2\right]. \tag{2.22}$$

In principle, one can construct the Green function of the operator acting on the left hand side of eq. (2.20) then solve for $P_1(x, v)$, and continue to higher k. In section 6, we construct $P_1(x, v)$ directly from eq. (2.20) for some particular nonlinear potentials $V(x)$.

At this point we assume the functions $P_k(x, v)$ to be known up to some order $k=N$, and due to eqs. (2.16) and (2.22) an improved approximation of the Kramers function. Several methods can then be applied to determine improved rate constants. We first use the flux over population method that was also employed by Kramers.

3. Flux over population

The rate may be expressed as the total flux of particles over the barrier at $x=0$ divided by the population of the reactant well [1]. Since both particle- and probability density and particle- and probability flux are proportional to each other with the same constant of proportionality, the rate Γ may be expressed as

$$\Gamma=\frac{\int_{-\infty}^{\infty}\mathrm{d}v\,v p(0, v)}{\int_{-\infty}^{0}\mathrm{d}x\int_{-\infty}^{\infty}\mathrm{d}v\,p(x, v)}\,. \tag{3.1}$$

For $p(x, v)$ we use the current carrying probability density (2.3) with the improved Kramers function (2.16) constructed from (2.17), or equivalently, (2.18)–(2.22). The integral in the denominator, for short the population, is dominated by the neighborhood of the reactant state at $x=x_0$ and $v=0$. There, the Kramers function is unity up to exponentially small corrections that can be neglected. Consequently, in the denominator the current carrying probability density, $p(x, v)$, can be replaced by the equilibrium probability density, $p_{\mathrm{eq}}(x, v)$. The population can then be calculated with the desired accuracy and will be denoted by n:

$$n=\int_{-\infty}^{0}\mathrm{d}x\int_{-\infty}^{\infty}\mathrm{d}v\,p_{\mathrm{eq}}(x, v)\,. \tag{3.2}$$

The integral in the numerator of the rate expression (3.1) gets different contributions from the different terms of the perturbation expansion of the Kramers function. The leading term stems from the parabolic-barrier Kramers function and is given by

$$\int_{-\infty}^{\infty}\mathrm{d}v\,v\zeta_{\mathrm{pb}}(0, v)p_{\mathrm{eq}}(0, v)=\mu j_{\mathrm{TST}}\,, \tag{3.3}$$

where μ is defined by eq. (2.13) and j_{TST} denotes the flux calculated by transition state theory

$$j_{\mathrm{TST}}=\int_{0}^{\infty}\mathrm{d}v\,v p_{\mathrm{eq}}(0, v)=Z^{-1}k_{\mathrm{B}}T\,. \tag{3.4}$$

From eqs. (3.1)–(3.4), in the lowest order, one just obtains Kramers' result for the rate,

$$\Gamma_{\mathrm{pb}}=\mu\Gamma_{\mathrm{TST}}\,, \tag{3.5}$$

where Γ_{TST} denotes the rate within transition state theory

$$\Gamma_{\mathrm{TST}}=\frac{k_{\mathrm{B}}T}{Zn}\,. \tag{3.6}$$

The improved Kramers rate follows from eqs. (3.1)–(3.6), (2.16) and (2.22). It reads:

$$\Gamma=\Gamma_{\mathrm{pb}}(1+\gamma_1+\gamma_2+...)\,, \tag{3.7}$$

with

$$\gamma_k = (1-\mu^2)\left\langle \frac{\partial P_k(0, v)}{\partial v} \right\rangle, \quad k=1, 2, \ldots \tag{3.8}$$

where $\langle\ \rangle$ denotes a Gaussian average over the velocity with zero mean and second moment given by

$$\langle v^2 \rangle = (1-\mu^2) k_{\mathrm{B}} T . \tag{3.9}$$

Because of the recursive type of eqs. (2.21) $P_k(x, v)$ is of kth order in the nonlinearity $V'(x)$, so is γ_k, and consequently eq. (3.7) is a series representation of the rate in powers of the nonlinear part of the force near the barrier. We further evaluate this result for a cubic and quartic potential in section 6.

4. Rayleigh quotient

The separation of time scales which is typical in barrier crossing processes shows itself in a large gap in the spectrum of the Fokker–Planck operator separating one small negative nonzero eigenvalue from the rest of the spectrum [6]. In the case where there is a locally stable product state the Fokker–Planck operator with natural boundary conditions still has a zero eigenvalue and the smallest nonzero eigenvalue is given by minus the sum of forward and backward rates. In the case of a potential with a single metastable well there is no zero eigenvalue and the small separated eigenvalue just coincides with minus the decay rate of the metastable state. The latter situation can always be enforced by introducing absorbing boundary conditions at the product state. This means that the equation

$$L\rho(x, v) = -\Gamma \rho(x, v) \tag{4.1}$$

has a nontrivial solution where $\rho(x, v)$ vanishes sufficiently fast beyond the barrier, either due to a natural absorbing boundary at infinity or an artificially introduced one at the product state. As in the case of the current carrying stationary probability density one can split off the equilibrium probability density $p_{\mathrm{eq}}(x, v)$ (2.5) from $\rho(x, v)$:

$$\rho(x, v) = h(x, v) p_{\mathrm{eq}}(x, v) . \tag{4.2}$$

With eq. (2.7) one finds from eq. (4.1) that $-\Gamma$ also is an eigenvalue of the operator L^* defined in eq. (2.8) with corresponding eigenfunction $h(x, v)$:

$$L^* h(x, v) = -\Gamma h(x, v) . \tag{4.3}$$

We already mentioned that L^* is the backward operator of the time reversed process. Therefore, the backward operator of the original process L^+ again has the same eigenvalue $-\Gamma$ with a corresponding eigenfunction $\tilde{h}(x, v)$:

$$L^+ \tilde{h}(x, v) = -\Gamma \tilde{h}(x, v) , \tag{4.4}$$

where

$$L^+ = v \frac{\partial}{\partial x} - [U'(x) + \gamma v] \frac{\partial}{\partial v} + \gamma k_{\mathrm{B}} T \frac{\partial^2}{\partial v^2} \tag{4.5}$$

and where $\tilde{h}(x, v)$ is the time reversed function of $h(x, v)$:

$$\tilde{h}(x, v) = h(x, -v) . \tag{4.6}$$

Note that for nonself-adjoint operators, as e.g., the Fokker–Planck operator L, it is not necessarily true that the operator and its adjoint have the same eigenvalues. But if this special property is met, one can split off a projection operator on the eigenfunction times the eigenvalue of the operator. In the particular case of the Fokker–Planck operator one may write

$$L^{*}=-\Gamma\frac{|h)(\tilde{h}|}{(\tilde{h},h)}+R^{*}\,, \tag{47}$$

where we introduced a scalar product having $p_{\mathrm{eq}}(x,v)$ as a weight:

$$(g,f)=\int \mathrm{d}x\,\mathrm{d}v\,g(x,v)f(x,v)p_{\mathrm{eq}}(x,v)\,, \tag{4.8}$$

with corresponding bras and kets $(g|$, $|f)$, respectively, and where the operator R^{*} and its adjoint R^{+} annihilate $h(x,v)$ and $\tilde{h}(x,v)$, respectively. This allows one to express the rate Γ as a Rayleigh quotient in terms of $h(x,v)$, $\tilde{h}(x,v)$ and L^{*}:

$$\Gamma=-\frac{(\tilde{h},L^{*}h)}{(\tilde{h},h)}\,. \tag{4.9}$$

The same formal expression was found for the plateau value of the reactive flux [15]. As already mentioned there, it differs from other Rayleigh quotients given in the literature [13] where the diagonal matrix element of L^{*} with $h(x,v)$ enters. These different definitions coincide only for a Smoluchowski operator, since there the time reversal operation reduces to the identical transformation.

Since $h(x,v)$ and $\tilde{h}(x,v)$ are not known exactly one has to look for approximate eigenfunctions of L^{*} and L^{+}, respectively. Because the eigenvalue that is to be calculated is an exponentially small quantity in $V^{\neq}/k_{\mathrm{B}}T$, one can neglect the right hand side of eq. (4.3) completely and consequently one obtains the same equation as for the Kramers function $\zeta(x,v)$, see eq. (2.6). Since the Kramers function vanishes in the product region and has a finite normalization $(\tilde{\zeta},\zeta)$, it may be used as a test function h in the Rayleigh quotient for the rate Γ, eq. (4.9),

$$\Gamma=-\frac{(\tilde{\zeta},L^{*}\zeta)}{(\tilde{\zeta},\zeta)}\,. \tag{4.10}$$

In the denominator of this expression the Kramers function and its time reversed completely suppress the product region. The remaining integral is therefore dominated by the reactant region where ζ and $\tilde{\zeta}$ equal unity. Consequently, the denominator is given by the population n (see eq. (3.2)) besides exponentially small corrections:

$$(\tilde{\zeta},\zeta)=n\,. \tag{4.11}$$

Using only the lowest order approximation of the Kramers function $\zeta_{\mathrm{pb}}(x,v)$ the numerator of the Rayleigh quotient simplifies to

$$(\tilde{\zeta}_{\mathrm{pb}},L^{*}\zeta_{\mathrm{pb}})=(\tilde{\zeta}_{\mathrm{pb}},L_{1}^{*}\zeta_{\mathrm{pb}}) \tag{4.12}$$

since the operator L_{pb}^{*} vanishes on ζ_{pb}. With eqs. (2.11), (2.15), (4.6) and (4.8) one then finds from eq. (4.12)

$$(\tilde{\zeta}_{\mathrm{pb}},L^{*}\zeta_{\mathrm{pb}})=\frac{\omega_{\mathrm{b}}}{2\pi k_{\mathrm{B}}T}\left(\frac{\mu}{\gamma^{*}}\right)^{1/2}\int\limits_{-\infty}^{\infty}\mathrm{d}x\int\limits_{-\infty}^{\infty}\mathrm{d}v\exp\left(-\frac{(v-\mu\omega_{\mathrm{b}}x)^{2}}{2(1-\mu^{2})k_{\mathrm{B}}T}\right)V'(x)$$

$$\times\exp\left(-\frac{V(x)}{k_{\mathrm{B}}T}\right)\int\limits_{(\mu\gamma^{*})^{-1/2}[x+(\mu/\omega_{\mathrm{b}})v]}^{\infty}\exp\left(-\frac{\omega_{\mathrm{b}}^{2}z^{2}}{2k_{\mathrm{B}}T}\right)\mathrm{d}z\,, \tag{4.13}$$

where we have performed the derivative with respect to v that is part of the operator L_{1}^{*} and collected quadratic terms in x and v in the exponent. After replacing v by the new variable $v-\mu\omega_b x$ one may get rid of the z-integral by a partial integration over x. This results in

$$(\tilde{\zeta}_{\mathrm{pb}}, L_1^* \zeta_{\mathrm{pb}}) = -\mu k_{\mathrm{B}} T Z^{-1} \langle\!\langle \exp[-V(x)/k_{\mathrm{B}}T] \rangle\!\rangle \,, \tag{4.14}$$

where $\langle\!\langle\ \rangle\!\rangle$ denotes a Gaussian average over x and v with vanishing means $\langle\!\langle x \rangle\!\rangle = \langle\!\langle v \rangle\!\rangle = 0$ and second moments

$$\langle\!\langle x^2 \rangle\!\rangle = \frac{1-\mu^2}{1+\mu^2} \frac{k_{\mathrm{B}}T}{\omega_b^2} \,, \tag{4.15a}$$

$$\langle\!\langle xv \rangle\!\rangle = 0 \,, \tag{4.15b}$$

$$\langle\!\langle v^2 \rangle\!\rangle = \frac{1-\mu^2}{1+\mu^2} k_{\mathrm{B}}T \,. \tag{4.15c}$$

Within the perturbation theory with respect to the nonlinear potential $V(x)$, the expectation of $\exp[-V(x)/k_{\mathrm{B}}T]$ may be expressed in terms of the moments of $V(x)$; consequently we find for the rate from the Rayleigh quotient Γ_0 (4.10) with the parabolic barrier Kramers function (4.14)

$$\Gamma_0 = \Gamma_{\mathrm{pb}} \left(1 - \frac{\langle\!\langle V(x) \rangle\!\rangle}{k_{\mathrm{B}}T} + \frac{\langle\!\langle V^2(x) \rangle\!\rangle}{2!(k_{\mathrm{B}}T)^2} - \dots \right) , \tag{4.16}$$

where we used (4.11), (3.5) and (3.6).

Further corrections to the rate are obtained from the Rayleigh quotient when one uses the Kramers function including the first correction:

$$\begin{aligned} \Gamma_1 &= -\frac{(\tilde{\zeta}_{\mathrm{pb}} + \tilde{\zeta}_1, L^*(\zeta_{\mathrm{pb}} + \zeta_1))}{n} \\ &= \Gamma_0 - \frac{(L_1^+ \tilde{\zeta}_{\mathrm{pb}}, \zeta_1)}{n} - \frac{(\tilde{\zeta}_1, L_1^* \zeta_1)}{n} \,, \end{aligned} \tag{4.17}$$

where we have used $L_{\mathrm{pb}}^* \zeta_{\mathrm{pb}} = 0$ and the defining eq. (2.17a) for ζ_1. In the following we will not go beyond second order in the perturbation V_1. Since the third term on the left hand side of eq. (4.17) is already of third order we may neglect it here. The second term contains corrections of second and still higher order. Neglecting the higher orders it reads

$$\frac{(L_1^+ \tilde{\zeta}_{\mathrm{pb}}, \zeta_1)}{n} = \Gamma_{\mathrm{pb}} \frac{\mu}{1+\mu^2} \frac{1}{\omega_b} \langle\!\langle V'(x) P_1(x,v) \rangle\!\rangle \,, \tag{4.18}$$

where we used eqs. (2.11), (2.15), (2.19) and (4.15). Formal expressions for higher order corrections may easily be obtained but will not be given here. Explicit results will be given for the cubic and quartic potential in section 6.

5. Mean first passage time

The mean first passage time gives yet another method that has frequently been applied for the calculation of rates [17,18,22]. By this method the mean time is determined that it takes to leave a certain domain of phase space when trajectories are started at the reactant state. If this domain consist of a complete phase space except a little "hole" surrounding the product state, the corresponding mean first passage time and the rate are the inverses of each other. We shall discuss elsewhere how this mean first passage time may be calculated directly. The traditional approach, however, is to determine the mean first passage time to the deterministic separatrix that is defined as the boundary of the domain of attraction of the reactants if the fluctuations are neglected.

Then it is assumed that the probabilities to go in either direction of reactants and products are equal for trajectories that start from the deterministic separatrix. Consequently, the rate is then given by the inverse of twice this mean first passage time.

However, it was noticed recently [13,19,20] that the property of the deterministic separatrix of letting trajectories go to both sides with equal probability only holds asymptotically, if the noise is sufficiently small. If the system is characterized by still other small quantities than the noise strength ($k_B T$ in the present case) the above assumption may fail grossly as e.g. at weak damping [14] and in higher dimensional systems with strongly anisotropic friction [20,23].

In this section we first relate the Kramers function to the splitting probability [21] that assigns to each point the frequency from there to visit the reactants before going to products. The points with splitting probability one half form the stochastic separatrix. Obviously, the rate is the inverse of twice the mean first passage time to the stochastic separatrix. In a second part of this section this mean first passage time is determined.

5.1. Splitting probability and stochastic separatrix

The probability $\pi(x, v)$ that a trajectory starting in the phase space point x, v first visits the reactant state before becoming a product is the solution of the backward equation [21]

$$L^+\pi(x, v) = 0 , \tag{5.1}$$

with boundary conditions

$$\pi(x, v) = 1 , \quad x, v = \text{reactant state} , \tag{5.2a}$$

$$\pi(x, v) = 0 , \quad x, v = \text{product state} . \tag{5.2b}$$

Strictly speaking one has to cut out holes around the reactant and product states and demand the respective conditions (5.2) on the boundaries of these holes, see refs. [19,20]. Since L^+ and L^* are related to each other by a time reversal transformation and since the boundary conditions for the time reversed Kramers function and the splitting probability coincide these two functions are identical:

$$\pi(x, v) = \zeta(x, -v) . \tag{5.3}$$

Hence, in first order perturbation theory the splitting probability reads, see eqs. (2.11), (2.16) and (2.19):

$$\pi(x, v) = \left(\frac{\omega_b^2}{2\pi k_B T}\right)^{1/2} \int\limits_{(\mu\gamma^*)^{-1/2}[x+(\mu/\omega_b)v]}^{\infty} \exp\left(-\frac{\omega_b^2 z^2}{2k_B T}\right) dz$$

$$+\left(\frac{\mu}{2\pi\gamma^* k_B T}\right)^{1/2} P_1(x, -v) \exp\left(-\frac{\omega_b^2[x+(\mu/\omega_b)v]^2}{2\mu\gamma^* k_B T}\right) . \tag{5.4}$$

If the contribution $P_1(x, v)$ of nonlinearities at the barrier is neglected the splitting probability equals one half on the tangent to the deterministic separatrix through the saddle point, $x = -(\mu/\omega_b)v$, and rapidly approaches zero or unity if one moves towards products or reactants, respectively. The second term in (5.4) leaves this qualitative behavior unchanged, only the location of points where $\pi(x, v) = \frac{1}{2}$ slightly alters. Hence, in presence of a nonlinear correction at the barrier the stochastic and deterministic separatrix no longer coincide. Its precise location is given by

$$x = -\frac{\mu}{\omega_b} v + \frac{\mu}{\omega_b} \xi(v) \tag{5.5}$$

where $\xi(v)$ follows from $\pi(x, v) = \frac{1}{2}$ with (5.4) in first order to read

$$\xi(v) = P_1\left(-\frac{\mu}{\omega_b} v, -v\right) . \tag{5.6}$$

It is straightforward to derive higher order corrections systematically, but we shall not do this here.

5.2. Mean first passage time to the stochastic separatrix

By definition of the stochastic separatrix the rate constant is given by the inverse of twice the mean first passage time to the stochastic separatrix. This time $t(x, v)$ obeys as a function of the starting point the following inhomogeneous backward equation [22]

$$L^{+}t(x, v) = -1 ,$$

with zero boundary conditions on the stochastic separatrix:

$$t(x, v) = 0 , \quad x, v \text{ on the stochastic separatrix} . \tag{5.7}$$

From $t(x, v)$ one may split off its maximal value T which it assumes on the reactants; see ref. [17] or ch. VII-D of ref. [2] for a description of this method in a more general context and for further references to the original literature:

$$t(x, v) = Tf(x, v) , \tag{5.8}$$

where $f(x, v)$ is a form function which becomes unity at reactants and zero at the stochastic separatrix and otherwise obeys the backward equation

$$L^{+}f(x, v) = 0 , \tag{5.9}$$

$$\begin{aligned} f(x, v) &= 1 \quad \text{on reactants} , \\ &= 0 \quad \text{on the stochastic separatrix} . \end{aligned} \tag{5.10}$$

The exponentially small inhomogeneity T^{-1} has been neglected. In passing we note that $f(x, v)$ coincides with the splitting probability to reach the reactant state before the stochastic separatrix if one starts from a phase space point (x, v) (compare eqs. (5.9), (5.10) with (5.1), (5.2)). Therefore eq. (5.8) expresses the mean first passage time from a point x, v as the probability to reach reactants multiplied by the time it takes from there to the stochastic separatrix. All other times as e.g. the one it takes for a direct exit from (x, v), if possible at all, or the time to reach reactants from x, v are neglected. These assumptions are of course based on the separation of time scales and inherent in any rate description.

Performing on eq. (5.9) a time reversal transformation, we find identical equations for the form function $\tilde{f}(x, v) = f(x, -v)$ and the Kramers function $\zeta(x, v)$, however, with different boundary conditions. But since the zeros of $f(x, v)$ are just points where $\tilde{\zeta}(x, v)$ assumes the value $\frac{1}{2}$, the function $2\tilde{\zeta}(x, v) - 1$ fulfills both the boundary conditions for $f(x, v)$ and eq. (5.9). The latter holds, because it is a linear, homogeneous equation and the operator L^{+} vanishes on constant functions. Therefore, the Kramers function determines the form function of the mean first passage time to the stochastic separatrix in the following way:

$$f(x, v) = 2\tilde{\zeta}(x, v) - 1 . \tag{5.11}$$

The mean first passage time T from reactants can be expressed by means of the ratio of the population of the reactant well and an integral along the stochastic separatrix in which the gradient of the form function f enters; see ref. [17] or chapter VII-D of ref. [2]:

$$T = -\frac{n}{\gamma k_B T \int_{\text{stochastic separatrix}} \mathrm{d}S_v \, p_{\text{eq}} \, \partial f / \partial v} , \tag{5.12}$$

where dS_v denotes the v-component of the oriented line element on the stochastic separatrix.

Using (5.11) and $\Gamma = (2T)^{-1}$ we obtain for the rate

$$\Gamma = \frac{\gamma k_B T}{n} \frac{\mu}{\omega_b} \int_{-\infty}^{\infty} dv \left(1 - \frac{d\xi}{dv}(v)\right) p_{eq}\left(x = -\frac{\mu}{\omega_b}(v - \xi(v)), v\right) \frac{\partial \zeta}{\partial v}\left(x = -\frac{\mu}{\omega_b}(v - \xi(v)), -v\right), \tag{5.13}$$

where we expressed dS_v and the integrand by means of the first order approximation of the stochastic separatrix (5.5), (5.6) in terms of v and dv. It is understood that in eq. (5.13) ζ is first differentiated with respect to v with x being kept fixed and after that x is taken at the stochastic separatrix.

Keeping always only first order corrections in the nonlinearity at the barrier one obtains from (5.13) with (2.5), (2.11), (2.19)

$$\Gamma = \Gamma_{pb}\left[1 - \frac{1}{1-\mu^2} \prec \frac{d}{dv} P_1\left(-\frac{\mu}{\omega_b} v, -v\right) \succ - \prec \frac{\partial}{\partial v} P_1\left(x = -\frac{\mu}{\omega_b} v, -v\right) \succ - \prec V\left(-\frac{\mu}{\omega_b} v\right) \succ \right], \tag{5.14}$$

where $\prec\ \succ$ denotes a Gaussian average over velocity with zero mean and

$$\prec v^2 \succ = \frac{k_B T}{1-\mu^2}, \tag{5.15}$$

and where d/dv denotes the derivative with respect to any v-dependence, whereas $\partial/\partial v$ is meant as described above.

Of course, it is possible to determine higher order corrections here, too, although the same corrections can be obtained with less algebraic effort by means of the flux over population method.

6. Explicit expressions for cubic and quartic potentials

Up to now we have derived several different looking expressions for the corrections of the rate caused by a nonlinearity at the barrier. In this section we shall demonstrate that these expressions indeed yield identical results and coincide with previously obtained results for a cubic and a quartic potential [7,8]. It turns out that up to second order perturbation theory the contributions of the potential that are even and odd with respect to an inversion about the barrier do not interact with each other. It is therefore meaningful to treat them separately.

6.1. Quartic potential

As a most simple symmetric case we treat the quartic potential

$$U(x) = -\tfrac{1}{2}\omega_b^2 x^2 + \frac{U^{IV}}{4!} x^4 \tag{6.1}$$

with the nonlinearity

$$V(x) = \frac{U^{IV}}{4!} x^4, \tag{6.2}$$

where U^{IV} denotes the fourth derivative at the barrier top $x=0$.

The first order correction, eq. (2.19), to the Kramers function, eq. (2.16), is determined through the function $P_1(x, v)$ that satisfies the partial differential equation (2.20). When acting on a polynomial in x and v the differential operator on the right hand side of eq. (2.20) either reduces the degree of the polynomial by two or keeps it constant. Hence, a polynomial ansatz of the same degree as $V'(x)$ and further contributions with orders diminished in steps of two satisfies eq. (2.20). In the particular case of a quartic potential one is hence led to write

$$P_1(x,v)=Ax+Bv+Cx^3+Dx^2v+Exv^2+Fv^3\,, \tag{6.3}$$

where the constants follow from eq. (2.20) by comparing coefficients of equal powers of x and v. With some straightforward algebra one obtains

$$A=-\frac{\gamma^* k_{\rm B}T}{1+\mu^2}\frac{8\mu^4+7\mu^2+3}{\mu^2}\omega_{\rm b}F\,, \tag{6.4a}$$

$$B=\frac{\gamma^* k_{\rm B}T}{1+\mu^2}\frac{7\mu^2+3}{\mu}F\,, \tag{6.4b}$$

$$C=-\frac{4\mu^2(3+4\mu^2)+(1+2\mu^2)[3\mu^2+(2+3\mu^2)(3+4\mu^2)]}{6\mu^3}\omega_{\rm b}^3F\,, \tag{6.4c}$$

$$D=\frac{3\mu^2+(2+3\mu^2)(3+4\mu^2)}{2\mu^2}\omega_{\rm b}^2F\,, \tag{6.4d}$$

$$E=-\frac{3+4\mu^2}{\mu}\omega_{\rm b}F\,, \tag{6.4e}$$

$$F=-\frac{\mu^2U^{\rm IV}}{8\omega_{\rm b}^4(3\mu^6+13\mu^4+13\mu^2+3)}\,, \tag{6.4f}$$

where μ is defined by eq. (2.13). With this particular solution one can evaluate the flux over population expression of the rate, see eqs. (3.7)–(3.9) and find

$$\Gamma=\Gamma_{\rm pb}\left[1-\frac{U^{\rm IV}k_{\rm B}T}{8\omega_{\rm b}^4}\left(\frac{1-\mu^2}{1+\mu^2}\right)^2+\dots\right]. \tag{6.5}$$

This coincides with the result of refs. [7,8] in the case of Ohmic dissipation. In leading order in $U^{\rm IV}k_{\rm B}T/8\omega_{\rm b}^4$ the same result is obtained from the Rayleigh quotient Γ_0 (4.16) with the parabolic Kramers function (2.11) as test function. Additional corrections that are contained in Γ_0, see eq. (4.14), are identical to those found in ref. [12] by means of variational transition state theory with a planar dividing surface. Further corrections of second and higher order in $U^{\rm IV}k_{\rm B}T/\omega_{\rm b}^4$ result from the Rayleigh quotient Γ, see eqs. (4.17) and (4.18). After some algebra one finds with eqs. (6.3) and (6.4) for Γ_1

$$\Gamma_1=\Gamma_{\rm pb}\left\{1-\frac{U^{\rm IV}k_{\rm B}T}{8\omega_{\rm b}^4}\left(\frac{1-\mu^2}{1+\mu^2}\right)^2+\frac{1}{384}\left(\frac{U^{\rm IV}k_{\rm B}T}{\omega_{\rm b}^4}\right)^2\left(\frac{1-\mu^2}{1+\mu^2}\right)^4\right.$$
$$\left.\times\left[35-\frac{16}{1-\mu^2}\frac{30\mu^6+103\mu^4+70\mu^2+12}{3\mu^6+13\mu^4+13\mu^2+3}\right]+\dots\right\}. \tag{6.6}$$

It contains all contributions to the rate up to second order in $U^{\rm IV}k_{\rm B}T/\omega_{\rm b}^4$. In particular for $\gamma\to\infty$, i.e. $\mu\to 0$, one regains the known Smoluchowski limit [16].

As we already explained, the stochastic separatrix, see eqs. (5.5), (5.6), is in lowest order i.e. for a purely parabolic barrier given by a straight line through the saddle point that coincides with the deterministic separatrix. A quartic nonlinearity changes the inclination at the saddle and slightly curves the stochastic separatrix away from the saddle. Putting the explicit expression (6.3) and (6.4) into eqs. (5.5) and (5.6) yields

$$x=-\frac{\mu}{\omega_{\rm b}}\left(1+\frac{1-\mu^2}{1+\mu^2}\frac{U^{\rm IV}k_{\rm B}T}{\omega_{\rm b}^4}\frac{\mu^4}{3\mu^6+13\mu^4+13\mu^2+3}\right)v-\frac{U^{\rm IV}\mu^5}{2\omega_{\rm b}^5(\mu^2+3)}v^3\,. \tag{6.7}$$

As a result, relatively to the deterministic separatrix the stochastic separatrix is shifted towards the reactant well for negative velocities and towards the product well for positive velocities. Eq. (6.7) is just the beginning of an asymptotic power series expansion of the stochastic separatrix about the saddle point. Higher powers in v may systematically be obtained from the higher corrections of the Kramers function.

After some straightforward algebra one finds that the mean first passage time to the stochastic separatrix yields the same rate (6.5) found from the flux over population expression. Corrections for the mean first passage time to the deterministic separatrix have been calculated in ref. [14]. They differ considerably from those for the mean first passage time to the stochastic separatrix.

6.2. Cubic potential

As a potential with asymmetric nonlinearity about the barrier we treat

$$U(x)=-\tfrac{1}{2}\omega_b^2x^2+\frac{U^{\mathrm{III}}}{3!}x^3\,. \tag{6.8}$$

The nonlinearity then reads

$$V(x)=\frac{U^{\mathrm{III}}}{3!}x^3\,, \tag{6.9}$$

where $U^{\mathrm{III}}<0$ in order that reactants are at negative x. The first order correction to the Kramers function is found from eqs. (2.19) and (2.20). By the same arguments as for the quartic potential we obtain in the present case again a polynomial function $P_1(x, v)$ determining the correction $\zeta_1(x, v)$ that now contains a constant term and quadratic terms:

$$P_1(x, v)=a+bx^2+cxv+dv^2\,, \tag{6.10}$$

where the constants a–d are found to be

$$a=2\frac{1-\mu^2}{\mu^2}k_BTd\,, \tag{6.11a}$$

$$b=\frac{6\mu^4+9\mu^2+2}{2\mu^2}\omega_b^2d\,, \tag{6.11b}$$

$$c=-\frac{3\mu^2+2}{\mu}\omega_bd\,, \tag{6.11c}$$

$$d=\frac{U^{\mathrm{III}}\mu}{3\omega_b^3(2\mu^4+5\mu^2+2)}\,. \tag{6.11d}$$

For the rate one finds from the flux over population expression (3.7) and (3.8) and the fact that $P_1(0, v)$ is an even function of v that the first order correction in the parameter $U^{\mathrm{III}}(k_bT)^{1/2}/\omega_b^3$ vanishes. The same result emerges from the mean first passage time to the stochastic separatrix; see eq. (5.14). One way to obtain higher order nonvanishing corrections would be to calculate the second order contribution to the Kramers function. This is determined by the function $P_2(x, v)$, see eqs. (2.21), (2.22), which turns out to consist of a sum of monomials in x and v of order five, three and one. The algebra needed to calculate the twelve coefficients of these monomials is straightforward but quite lengthy. It will not be performed here. Apart from the flux over population expression and the mean first passage time to the stochastic separatrix which both require the knowledge of $P_2(x, v)$, there is still the Rayleigh quotient which yields the leading nonvanishing corrections to the rate already from $\zeta_1(x, v)$. From eqs. (4.15)–(4.18) and (6.10), (6.11) one obtains for the cubic barrier

$$\Gamma_{\mathrm{l}}=\Gamma_{\mathrm{pb}}\left[1-\frac{1}{24}\left(\frac{U^{\mathrm{III}}}{\omega_{\mathrm{b}}^{3}}\right)^{2}k_{\mathrm{B}}T\left(\frac{\mu^{2}-1}{\mu^{2}+1}\right)^{2}\frac{10\mu^{4}+41\mu^{2}+10}{2\mu^{4}+5\mu^{2}+2}\right], \tag{6.12}$$

where contributions of order $\mathrm{O}((U^{\mathrm{III}}/\omega_{\mathrm{b}}^{3})^{4}(k_{\mathrm{B}}T)^{2})$ have been neglected. The rate expression (6.12) is identical to the one obtained in ref. [7].

Finally we will discuss the qualitative behavior of the stochastic separatrix. Although the first order correction in the Kramers function gives a vanishing contribution to the mean first passage time, the main qualitative behavior of the stochastic separatrix may be obtained already in this order. Eqs. (5.5), (5.6) combined with (6.10) and (6.11) yield for the stochastic separatrix

$$x=2\frac{U^{\mathrm{III}}k_{\mathrm{B}}T}{3\omega_{\mathrm{b}}^{4}}\frac{1-\mu^{2}}{2\mu^{4}+5\mu^{2}+2}-\frac{\mu}{\omega_{\mathrm{b}}}v+\frac{U^{\mathrm{III}}\mu^{3}}{2\omega_{\mathrm{b}}^{3}(\mu^{2}+2)}v^{2}\,. \tag{6.13}$$

Hence, in presence of a cubic nonlinearity because of the constant term in eq. (6.13) the stochastic separatrix no longer passes through the saddle point but is shifted towards the reactant well. The quadratic part bends the stochastic separatrix further towards reactants. The next corrections (of order $(U^{\mathrm{III}})^{2}$) will slightly change the coefficient of the linear part and introduce third and fifth order terms but will not change the relevant features of the first order contributions.

7. Conclusions

In this paper we calculated corrections to the Kramers rate caused by nonparabolic contributions to the potential in the vicinity of the barrier top by means of three different methods. For all methods the knowledge of an improved Kramers function is crucial. It is constructed from a perturbation theory that gives the original Kramers function as zeroth order solution. We showed that for a cubic and a quartic barrier the results of the different methods agree with each other and with the findings of refs. [7,8] in the case of Ohmic dissipation. It turned out that the flux over population method is more direct and simpler to use than the mean first passage time to the stochastic separatrix, though the latter method gives some additional insight. Since the Rayleigh quotient is a bilinear expression in the test function it allows one to gain higher order corrections from the same Kramers function than by means of the flux over population method.

In the present paper we dealt with the original Kramers model i.e. with a Brownian particle with Ohmic dissipation moving in one dimension. The theory presented here can be immediately generalized to Fokker–Planck processes with detailed balance in arbitrary dimensions. In this way, e.g. exponential memory [24,25] can be incorporated. Further, the influence of state dependent friction [26] can be studied by means of the same methods. We note that the improved Kramers function could also be used in the generalized reactive flux method [27] leading to a lower generalized transition state theory rate being the starting point for further numerical improvements of the rate. In this way one may obtain further rigorous bounds for the rate [15] and validity criteria for approximate rates [28] in terms of the sources and sinks that render Kramers' current carrying probability density stationary. Finally we note that finite barrier height corrections for the rate in the energy diffusion regime and for the crossover region to spatial diffusion [25] remain an open problem.

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Note added in proof

In a recent paper by Melnikov [29], finite barrier corrections are given in the whole friction range. However, in the spatial diffusion regime Melnikov's corrections do not agree with those derived in ref. [7] and the present paper.

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