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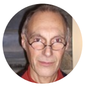

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THERMAL ACTIVATION: KRAMERS' THEORY REVISITED

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The Brownian motion model of classical noise-induced escape from a metastable potential well is reconsidered, in particular for the friction dependence of the decay rate. Kramers' Fokker–Planck equation is reformulated in terms of the particle's energy and the action variable near the peak of the barrier. The ensuing probability density $\rho(s, \epsilon)$ – and, hence, the decay rate Γ – is uniquely determined (i) by means of a spectral analysis and (ii) upon specifying the energy distribution of incoming particles. If such particles are taken to be absent, the decay rate goes to zero in the low friction limit according to Kramers' original formula, while for increasing friction it approaches the transition state value. The significance of diffusively re-entering particles for obtaining the correct high friction Kramers–Smoluchovski result is discussed. A problem with the underlying density is pointed out. The nature of the intermediate friction – the so-called turnover – regime is critically examined and a comparison is made with related recent work by Büttiker, Harris and Landauer, Mel'nikov and Meshkov, and Grabert.

1. Introduction

Let us consider the problem of a particle that moves in an externally applied potential field of force and which is – in addition – subject to Brownian fluctuations (at temperature T). Moreover, let the potential be such that the particle can be prepared in a locally stable minimum (with harmonic frequency ω_0) from which it can escape in the course of time by noise-activated passage over a potential energy barrier (of height U_b). An obviously interesting quantity to be calculated then is the mean lifetime of the local oscillator state, or – alternatively – the mean rate of escape Γ.

On January 29th 1940 the Editor of Physica received a manuscript from H.A. Kramers [1] in which the author proposed to study the above diffusion model in order to elucidate some aspects in the theory of chemical reactions. In this manner Kramers provided for the first time a dynamical framework for the earlier concepts of Arrhenius, where one essentially models the escape process as ballistic motion of thermally equilibrated particles across the barrier peak (the transition state). However, the very existence of the decay in fact contradicts the assumption of perfect equilibrium. Kramers in particular aimed at clarifying the significance of transition state theory (TST).

If the barrier is sufficiently high (i.e. $U_b/k_BT \gg 1$), the time scale set by the decay becomes very large and completely separates from all the local relaxation times, which are relatively short. In that generic case the escape rate is given by the general formula

$$\Gamma = (\omega_a/2\pi)\exp(-U_b/\vartheta)\,, \tag{1.1}$$

where $\vartheta = k_BT$ and where the attempt frequency $\omega_a < \omega_0$. Since the simple TST-value amounts to $\omega_a = \omega_0$, Kramers found that the intrinsic nonequilibrium effects reduce the rate, in any case in the two limiting cases of large and small viscosity (i.e. frictional damping) for which he was able to obtain exact results. In the weak damping limit the decay rate is suppressed because of an insufficiently rapid replenishment of the population at energies near the barrier peak, which is depleted as a consequence of the escape current. In the high damping limit the rate is lowered as a result of spatial diffusion which causes Brownian re-enterings of escaping particles, while several arguments have been advanced (e.g. by Dekker [2] and by Grabert [3]) in order to explain why this effectively still amounts to ballistic – but essentially (i) unstable and (ii) dissipative – motion, namely along a special trajectory (or mode).

In retrospect it appears quite remarkable that Kramers original (and only) paper on this subject – and in particular his insight in the weak damping limit – did not immediately attract all that much attention. With the apparent exception of Chandrasekhar's review paper [4], Brinkman's two 1956-papers [5] and an article by Landauer and Swanson [6], it took another four decades until the present flood of pertinent papers began appearing (see e.g. refs. [7–12] and references contained therein). In fact, many of the current literature on these matters is a mere elaboration on Kramers' work, in particular concerning (i) the details of the crossover from weak to strong damping and (ii) the extension into the low temperature quantum regime. In what follows, quantum effects will be absent.

It is – historically – worth mentioning that R. Landauer and coworkers have been among the most persistent recognizers of Kramers' work, especially of the weak damping treatment. In 1982 Büttiker, Harris and Landauer (BHL) [13] submitted their interesting remold of the low-damping Kramers theory, in which it was shown that a more careful balancing of an effectively upward (vertical) energy diffusion current – inside the potential hole – with the outward (horizontal) flux – at the peak of the barrier – implied a smooth connection with TST upon approaching the strong damping limit. The approach to the pertinent value of the decay rate Γ – i.e. (1.1) with attempt frequency $\omega_a = \omega_0$ – was found to be (inverse) powerlike in terms of the variable $\varepsilon = 2\lambda I_b/\vartheta$, 2λ being the classical (ohmic) friction coefficient and $I_b = \oint p\,dx$ representing the classical action integral evaluated at the barrier peak energy $E = U_b$. This appears to be in line – at least, qualitatively – with findings directly from the original Fokker–Planck equation [8, 9]. A recent attempt by Dekker [2, 14] to further connect the BHL theory with the correct strong damping Smoluchovsky limit – with $\omega_a = \omega_0\omega_b/2\lambda$, ω_b being the harmonic curvature frequency of the barrier peak region – invokes the earlier mentioned analysis of the outward current as an unstable free flight along a dissipative attractor in phase space. A more detailed description seems to require the possibility of discriminating between incoming and outgoing particles, a feature that is not available in the BHL formulation as – in fact – it implicitly only involves an averaged phase space density $\bar{\rho}(E)$, although from the very beginning Landauer et al. realized the underlying nonuniformity by setting $\rho_{out} - \rho_{in} = \alpha\bar{\rho}$ with α being a – within their theory undetermined – correction parameter.

The parameter α can only be determined by solving the original two-dimensional phase space problem. In principle it should be expected to be a somewhat complicated function not only of the friction coefficient λ, but also of the temperature ϑ and the energy E. In fact, an explicit analytic expression for $\alpha(\lambda, \vartheta, E)$ has been obtained by Dekker [15] on the basis of the boundary layer solution for $\rho(x, E)$ – see e.g. ref. [7] or Risken's work [16] – which after energy averaging gives an $\alpha(\varepsilon)$ where the only remaining argument is the earlier defined variable $\varepsilon = 2\lambda I_b/\vartheta$. It appears that $\alpha(0) = \frac{3}{2}$ while $\alpha(\infty) = 1$, in good agreement with numerical values from Risken and Voigtlaender (namely [17]: $\alpha(0) = 1.47$) and Mel'nikov and Meshkov (i.e. [18]: $\alpha(0) = 1.49$), and with expectations, respectively. Indeed, since the involved boundary layer density implied $\rho_{in} = 0$, the latter value of unity in the strong damping limit had to be anticipated.

The same assumption – i.e. the perfect absence of incoming classical particles – is equally implicit in the integral formulation of Kramers' problem by Mel'nikov [19], and Mel'nikov and Meshkov [18]. As an immediate consequence their result for the decay rate approaches the TST value if $\varepsilon \gg 1$, instead of the correct Kramers–Smoluchovsky limit. The latter could only be obtained by means of an a posteriori *ad hoc* multiplication by Kramers' dissipative correction factor

$$\kappa = \sqrt{1 + \lambda^2/\omega_b^2} - \lambda/\omega_b\,. \tag{1.2}$$

Furthermore, the approach to the pertinent Γ value was found to be exponentially fast (i.e. in terms of $e^{-\varepsilon/4}$) rather than in inverse powers of ε. Nevertheless – somewhat contrary to the impression that emerges from Grabert's recent analysis [3], namely that one has to resort necessarily to a more microscopic modeling – , all ingredients for the description of the classical Kramers turnover problem are fully contained in the original two-dimensional Kramers Fokker–Planck equation which is completely specified in terms of the particle's mechanical degrees of freedom. Within its context it is unclear how one should properly introduce the unstable mode energy (*not* purely a particle variable), which appears to play such a crucial role in the analysis of ref. [3].

Let us therefore reconsider the original two-dimensional diffusion model,

$$\frac{\partial \rho}{\partial t} = -p\,\frac{\partial \rho}{\partial x} + U'\,\frac{\partial \rho}{\partial p} + 2\lambda\,\frac{\partial}{\partial p}\left(p\rho + \vartheta\,\frac{\partial \rho}{\partial p}\right), \tag{1.3}$$

with particular emphasis on the nature of the crossover between weak and strong damping. For that purpose let us evaluate (1.3) such as to obtain the two-dimensional differential form of Mel'nikov's integral equation. Instead of applying the Wiener–Hopf method to the latter [3, 19], the subsequent analysis will presently be done directly on this partial differential equation – in fact by means of a rather conventional technique, namely Fourier analysis.

2. The model

The Kramers Fokker–Planck equation (1.3) can be rewritten in terms of the position x and the energy E as new variables, without any loss of generality. The detailed mathematics can be found e.g. in Risken's [16] or Stratonovich's [20] work. The result reads

$$\frac{\partial \rho}{\partial t} = p(x,E)\left\{-\,\frac{\partial \rho}{\partial x} + 2\lambda\,\frac{\partial}{\partial E}\left[p(x,E)\left(\rho + \vartheta\,\frac{\partial \rho}{\partial E}\right)\right]\right\}, \tag{2.1}$$

where

$$p(x,E) = \pm\sqrt{2[E - U(x)]}\,, \tag{2.2}$$

and where the density ρ is still normalized as $\int \mathrm{d}x \int \mathrm{d}p\; \rho = 1$, i.e.

$$\int \mathrm{d}E \oint \frac{\mathrm{d}x}{p(x,E)}\;\rho(x,E) = 1\,, \tag{2.3}$$

so that the equilibrium Boltzmann distribution for the local oscillator – in the omnipresent harmonic well approximation – reads

$$\rho_{\rm eq}(E) = (\omega_0/2\pi\vartheta)\, e^{-E/\vartheta} . \tag{2.4}$$

In the strong damping limit the principal consequence of the energy diffusion terms in (2.1) will be to enforce the local equilibrium distribution (2.4) with increasing precision. On the other hand, their main role in the weak damping limit is to provide the correct particle flux for the escape process. Since – in particular in the latter limit – the significant contributions to the escape rate come from particles within an extremely narrow energy range near $E = U_{\rm b}$, one then expands the momentum $p(x, E)$ in the diffusion terms in (2.1) in powers of $\epsilon = E - U_{\rm b}$. It is common practice to keep only the leading term $p(x, U_{\rm b})$. For instance, this approximation is implicit in the work of Büttiker, Harris and Landauer [13] and of Mel'nikov [18, 19]. Although the accuracy of this approximation is somewhat difficult to access, it will be adopted in the sequel based on the following argument.

While the pertinent energy range near $E = U_{\rm b}$ varies typically from $\langle\epsilon\rangle \approx \varepsilon^{1/2}\vartheta$ if $\varepsilon \ll 1$ (weak damping) to $\langle\epsilon\rangle \approx \vartheta$ if $\varepsilon \gg 1$ (moderate to strong damping), the relevant momenta determining the phase space density $\rho(x, E)$ are essentially those belonging to the main portion of trajectories through the well, i.e. near $U(x) = 0$ where $p(U_{\rm b}) \approx (2U_{\rm b})^{1/2}$. This argument is corroborated by the subsequent analysis for $\rho(x, E)$ wherein its Fourier coefficients are determined by integrals through the well at barrier peak energies. As $p(x, E) \approx p(U_{\rm b}) + \epsilon/p(U_{\rm b})$, one then estimates the relative error $\epsilon/U_{\rm b}$ introduced by this approximation to vary from the order of magnitude of $[(\lambda/\omega_{\rm b})(\vartheta/U_{\rm b})]^{1/2}$ if $\lambda/\omega_{\rm b} \ll 1$ to $\vartheta/U_{\rm b} \ll 1$ if $\lambda/\omega_{\rm b}$ becomes of the order of unity. Such tiny terms are disregarded throughout anyway. See section 4.3 for further considerations.

Now (2.1) becomes

$$\frac{\partial \rho}{\partial t} = p(x, E)\left[-\frac{\partial \rho}{\partial x} + 2\lambda p(x, U_{\rm b})\,\frac{\partial}{\partial E}\left(\rho + \vartheta\,\frac{\partial \rho}{\partial E}\right)\right], \tag{2.5}$$

which in the steady state, and upon introducing the local action variable

$$s(x) = 2\lambda \int_0^x p(x', U_{\rm b})\,{\rm d}x' , \tag{2.6}$$

reduces to

$$\frac{\partial \rho}{\partial s} = \frac{\partial}{\partial \epsilon}\left(\rho + \vartheta\,\frac{\partial \rho}{\partial \epsilon}\right). \tag{2.7}$$

Mathematically speaking, this parabolic diffusion-type equation (with s playing the role of time) requires Dirichlet conditions at an open boundary (open towards increasing s) in order to yield a unique, stable solution. Physically this implies that we should be able to find a unique solution for $\rho(s, \epsilon)$, given an "initial" distribution $\rho(0, \epsilon)$ – i.e. the energy distribution of incoming particles. Of course, our principal interest then is in the energy distribution of outgoing particles – i.e. $\rho(s_b, \epsilon)$ with $s_b = 2\lambda I_b$, $I_b = \oint p(x, U_b)\,dx$ being the classical round trip action at the barrier peak energy. For example, for the cubic barrier model $I_b = \frac{36}{5} U_b/\omega_b$ while for the quartic case $I_b = \frac{16}{3} U_b/\omega_b$.

With the density being normalized to one particle in the well, the escape rate is fundamentally defined by

$$\Gamma = -\int dE \oint \frac{dx}{p(x, E)} \frac{\partial}{\partial t} \rho(x, E) . \tag{2.8}$$

Hence, using (2.5) one has

$$\Gamma = \int_0^\infty [\rho(s_b, \epsilon) - \rho(0, \epsilon)]\, d\epsilon . \tag{2.9}$$

Before proceeding with the analysis in order to calculate Γ according to (2.9), let us briefly point out the connection with the earlier work of (i) Mel'nikov [18, 19] and of (ii) Büttiker, Harris and Landauer [13] – and related articles [2, 14].

The Green's function for (2.7) reads

$$G(\epsilon, s|\epsilon', s') = [4\pi\vartheta(s - s')]^{-1/2} \exp\left(-\frac{(\epsilon - \epsilon' + s - s')^2}{4\vartheta(s - s')}\right) , \tag{2.10}$$

and allows (2.7) to be written in its equivalent integral form

$$\rho(s, \epsilon) = \int_{\infty}^{\infty} G(\epsilon, s|\epsilon', s')\, \rho(s', \epsilon')\, d\epsilon' . \tag{2.11}$$

Letting $s' = 0$ and $s = s_b$, and defining a transition probability density $W(\epsilon|\epsilon')$ through

$$W(\epsilon|\epsilon') = G(\epsilon, s_b|\epsilon', 0) , \tag{2.12}$$

one obtains

$$\rho(s_b, \epsilon) = \int_{\infty}^{\infty} W(\epsilon|\epsilon')\, \rho(0, \epsilon')\, d\epsilon' \tag{2.13}$$

as a special case of (2.11). Notice that the conditional density (2.12) obeys detailed balance,

$$W(\epsilon|\epsilon')\,\mathrm{e}^{-\epsilon'/\vartheta} = W(\epsilon'|\epsilon)\,\mathrm{e}^{-\epsilon/\vartheta}\,, \tag{2.14}$$

and that the equilibrium distribution $\rho = a_0 \exp(-\epsilon/\vartheta)$ is a fixed point solution of (2.13). If one further – ad hoc – assumes that there are no particles entering (or re-entering) the potential well, to the effect that $\rho(0,\epsilon) = 0$ if $\epsilon > 0$, and moreover accounts for the uniqueness condition $\rho(s_b, \epsilon) = \rho(0, \epsilon)$ – which defines a $\rho(\epsilon)$ – if $\epsilon < 0$, (2.13) reduces to

$$\rho(\epsilon) = \int_{-\infty}^{0} W(\epsilon|\epsilon')\rho(\epsilon')\,\mathrm{d}\epsilon'\,. \tag{2.15}$$

Mel'nikov tackled this Fredholm integral equation (homogeneous and of the second kind) by means of the method of Wiener and Hopf (see e.g. Morse & Feshbach [21]). On the other hand – returning to the differential form of the problem – , integrating (2.7) on both sides from $s = 0$ to $s = s_b$ and setting

$$\rho(s_b, \epsilon) - \rho(0, \epsilon) = \alpha\theta(\epsilon)\,\bar{\rho}(\epsilon)\,, \tag{2.16}$$

where

$$\bar{\rho}(\epsilon) = (1/s_b)\int_{0}^{s_b} \rho(s, \epsilon)\,\mathrm{d}s \tag{2.17}$$

is the average density on $s \in (0, s_b)$ and where $\theta(\epsilon)$ is the unit step function, one arrives at

$$\alpha\theta(\epsilon)\,\bar{\rho}(\epsilon) = 2\lambda I_b \frac{\partial}{\partial\epsilon}\left(\bar{\rho} + \vartheta\,\frac{\partial\bar{\rho}}{\partial\epsilon}\right), \tag{2.18}$$

while the escape rate is then given by $\Gamma = \int_0^\infty \alpha\bar{\rho}(\epsilon)\,\mathrm{d}\epsilon$. This precisely constitutes the original BHL model [13]. As noted before, the ad hoc parameter α can only be determined by solving the full two-dimensional problem. The preceding considerations thus clearly show how the BHL theory is contained in (2.7) and provide a precise definition – namely (2.16) – for the parameter $\alpha(\epsilon)$. Finally, observe that the classical decay rate can always be written as

$$\Gamma = -2\lambda I_b\left(\bar{\rho} + \vartheta\,\frac{\partial\bar{\rho}}{\partial\epsilon}\right)_{\epsilon=0}, \tag{2.19}$$

which manifests the intrinsic connection between nonequilibrium effects at barrier peak energies and the very existence of the escape process. The quantum generalization of (2.19) has been given recently in refs. [2, 14].

3. The general solution

Let us now proceed with solving (2.7). In order not to mathematically overspecify the problem the boundary in the (s, ϵ)-plane must be open and the boundary conditions must be of the Dirichlet type. In particular, the boundary should be open towards increasing values of s (the "time" variable). Consequently, the relevant boundary is specified by (i) the line $s = 0$ and (ii) the lines $\epsilon = -U_b$ (i.e. $\epsilon \to -\infty$) and $\epsilon = \infty$. The boundary conditions on the latter two borders are simply given by

$$\rho(s, \epsilon) \to \rho_{eq}(\epsilon) \qquad \text{if } \epsilon \to -\infty\,, \tag{3.1}$$

$$\rho(s, \epsilon) \to 0 \qquad \text{if } \epsilon \to +\infty\,, \tag{3.2}$$

for all pertinent values of s. On the line $s = 0$ – i.e. following (2.6) at the location $x = 0$ of the barrier peak – the physical boundary condition is different for energies below or above the barrier peak $\epsilon = 0$. If $\epsilon < 0$, there is a classical turning point at $s = 0, s_b, 2s_b, \ldots$ (i.e. at $x = 0$). Hence, in that case $\rho(s, \epsilon)$ should be periodic on s_b. On the other hand, if $\epsilon > 0$ no classical turning point exists at $x = 0$ and we will require an explicit "initial" distribution $\rho(0, \epsilon)$ of (re-)entering particles.

3.1. *Below the barrier: $\epsilon < 0$*

The general form of a function $\rho(s, \epsilon)$ which is periodic in s with period $s_b = 2\lambda I_b$ reads

$$\rho(s, \epsilon) = \sum_{n=-\infty}^{+\infty} \rho_n(\epsilon)\, e^{2\pi i n s / s_b}\,. \tag{3.3}$$

Inserting this expression into (2.7) one finds

$$\vartheta \rho_n''(\epsilon) + \rho_n'(\epsilon) - (2\pi i n / s_b)\rho_n(\epsilon) = 0\,, \tag{3.4}$$

where the primes on ρ_n denote differentiation with respect to ϵ. The general solution of (3.4) is given by

$$\rho_n(\epsilon) = a_n \exp[-(1 + \mu_n)\epsilon / 2\vartheta] + b_n \exp[-(1 - \mu_n)\epsilon / 2\vartheta]\,, \tag{3.5}$$

where

$$\mu_n = \sqrt{1 + 8\pi i n\vartheta/s_b}\ . \tag{3.6}$$

In view of the equilibrium boundary condition (3.1), if $\epsilon \to -\infty$ the fastest growing exponential in (3.5) should tend to $\exp(-\epsilon/\vartheta)$. Since it is not difficult to show that the real part of μ_n fulfils the inequality $\mathrm{Re}\,\mu_n \geq 1$, one readily concludes that all a_n – with the exception of a_0, of course – must be excluded from the solution. Therefore

$$\rho(s, \epsilon < 0) = \mathrm{e}^{-\epsilon/\vartheta}\left[a_0 + \sum_{n=-\infty}^{+\infty} b_n\, \mathrm{e}^{2\pi i n s/s_b + (1+\mu_n)\epsilon/2\vartheta}\right], \tag{3.7}$$

where – disregarding exponentially small contributions, relatively of the order of $\exp(-U_b/\vartheta)$ – one has $a_0 = (\omega_0/2\pi\vartheta)\exp(-U_b/\vartheta)$, in view of (2.4).

3.2. *Above the barrier: $\epsilon > 0$*

On the domain $\epsilon > 0$ there also exist solutions that are periodic in s with period s_b, as an immediate consequence of the periodic nature of the current supplying particles from below the barrier. However, above the barrier particles are allowed to enter (at $s = 0$) and to escape (at $s = s_b$), so that – in addition to this periodic steady state solution – one should include here the existence of a transient disturbance (see e.g. Carlslaw and Jaeger [22], esp. ch. 2.6). The general solution may then appropriately be written as

$$\rho(s, \epsilon > 0) = \rho_p(s, \epsilon) + \int_0^\infty \mathrm{d}\epsilon'\, G(\epsilon - \epsilon', s)\,[\rho(0, \epsilon') - \rho_p(0, \epsilon')]\,, \tag{3.8}$$

where $G(\epsilon - \epsilon', s) = G(\epsilon, s|\epsilon', 0)$ is the Green's function (2.10) and where

$$\rho_p(s, \epsilon) = \sum_{n=-\infty}^{+\infty} c_n\, \mathrm{e}^{2\pi i n s/s_b - (1+\mu_n)\epsilon/2\vartheta} \tag{3.9}$$

represents the above-barrier periodic solution. The transient propagation of $\rho_p(0, \epsilon')$ in (3.8) only involves an elementary Gaussian integration which is easily evaluated in terms of an error function. Upon combining this contribution with $\rho_p(s, \epsilon)$ itself, (3.8) leads to

$$\rho(s, \epsilon > 0) = \sum_{n=-\infty}^{+\infty} c_n\, \mathrm{e}^{2\pi i n s/s_b - (1+\mu_n)\epsilon/2\vartheta}\, \mathrm{erfc}\!\left(-\tfrac{1}{2}\mu_n\sqrt{s/\vartheta} + \tfrac{1}{2}\epsilon/\sqrt{s\vartheta}\right)$$
$$+ \int_0^\infty \mathrm{d}\epsilon'\, G(\epsilon - \epsilon', s)\, \rho(0, \epsilon')\,, \tag{3.10}$$

where $\mathrm{erfc}(x) = (2/\sqrt{\pi}) \int_x^\infty \mathrm{d}y \exp(-y^2)$ represents the standard complementary error function. In view of the property $\mathrm{erfc}(\infty) = 0$ one readily verifies that (3.10) neatly satisfies the initial condition $\rho(s \to 0, \epsilon > 0) \to \rho(0, \epsilon)$.

3.3. *Matching at $\epsilon = 0$*

The phase space density $\rho(s, \epsilon)$ has thus been expressed in terms of the as yet unknown Fourier coefficients b_n and c_n, separately for $\epsilon < 0$ – in (3.7) – and for $\epsilon > 0$ – in (3.10). At $\epsilon = 0$ these expressions simplify to

$$\rho(s, -0) = a_0 + \sum_{n=-\infty}^{+\infty} b_n \, \mathrm{e}^{2\pi i n s / s_\mathrm{b}} \tag{3.11}$$

and

$$\rho(s, +0) = \sum_{n=-\infty}^{+\infty} c_n \, \mathrm{e}^{2\pi i n s / s_\mathrm{b}} \, \mathrm{erfc}(-\tfrac{1}{2}\mu_n \sqrt{s/\vartheta}) + \int_0^\infty \mathrm{d}\epsilon \; G(-\epsilon, s) \, \rho(0, \epsilon) \,, \tag{3.12}$$

while for the energy derivatives $\rho'(s, \epsilon) = \partial\rho/\partial\epsilon$ one obtains

$$\rho'(s, -0) = -\frac{1}{\vartheta}\left(a_0 + \tfrac{1}{2} \sum_{n=-\infty}^{+\infty} (1 - \mu_n) b_n \, \mathrm{e}^{2\pi i n s / s_\mathrm{b}}\right) \tag{3.13}$$

and

$$\begin{aligned}
\rho'(s, +0) = &- \frac{1}{2\vartheta} \sum_{n=-\infty}^{+\infty} c_n \, \mathrm{e}^{2\pi i n s / s_\mathrm{b}} \Big[(1 + \mu_n) \, \mathrm{erfc}(-\tfrac{1}{2}\mu_n \sqrt{s/\vartheta}) \\
&+ 2\sqrt{\frac{\vartheta}{\pi s}} \exp(-\tfrac{1}{4}\mu_n^2 s/\vartheta) \Big] \\
&- \int_0^\infty \mathrm{d}\epsilon \; \rho(0, \epsilon) \frac{\partial}{\partial\epsilon} G(-\epsilon, s) \,.
\end{aligned} \tag{3.14}$$

Equating (3.11) and (3.12), multiplying on either side of the equality by $\mathrm{e}^{-2\pi i m s / s_\mathrm{b}}$ and integrating over the fundamental period $s \in (0, s_\mathrm{b})$, then yields

$$b_n - \sum_{m=-\infty}^{+\infty} \mathscr{A}_{nm} c_m = -a_0 \delta_{n0} + \mathscr{I}_n \,, \tag{3.15}$$

where

$$\mathscr{A}_{nm} = \int_0^1 \mathrm{d}x \, \mathrm{e}^{-2\pi i (n-m) x} \, \mathrm{erfc}(-\tfrac{1}{2}\mu_m \sqrt{\varepsilon x}) \,, \tag{3.16}$$

while $\mathscr{I}_n$ is given by

$$\mathscr{I}_n = (1/s_b) \int_0^\infty d\epsilon\, \mathscr{G}_n(-\epsilon, s_b)\, \rho(0, \epsilon)\,, \tag{3.17}$$

with

$$\mathscr{G}_n(\epsilon, s) = \int_0^s ds'\, G(\epsilon, s')\, e^{-2\pi i n s'/s_b}\,, \tag{3.18}$$

and where – as before – $\varepsilon = s_b/\vartheta$ (recalling that $s_b = 2\lambda I_b$). Using (2.10) for the Green's function, it then is a somewhat laborious though essentially straightforward matter to evaluate (3.18) as

$$\begin{aligned}\mathscr{G}_n(\epsilon, s) = (1/2\mu_n)\, e^{-\epsilon/2\vartheta}[&e^{-\mu_n|\epsilon|/2\vartheta} \operatorname{erfc}(-\tfrac{1}{2}\mu_n\sqrt{s/\vartheta} + \tfrac{1}{2}|\epsilon|/\sqrt{s\vartheta}) \\ &- e^{+\mu_n|\epsilon|/2\vartheta} \operatorname{erfc}(\tfrac{1}{2}\mu_n\sqrt{s/\vartheta} + \tfrac{1}{2}|\epsilon|/\sqrt{s\vartheta})]\,.\end{aligned} \tag{3.19}$$

Similarly, equating (3.13) and (3.14) – and once exploiting the equality of (3.11) and (3.12) for an obvious simplification of the formula – thus leads to

$$\mu_n b_n + \sum_{m=-\infty}^{+\infty} (\mathscr{A}_{nm}\mu_m + \mathscr{B}_n) c_m = a_0 \delta_{n0} + \mathscr{I}_n + \mathscr{I}'_n\,, \tag{3.20}$$

where

$$\mathscr{B}_n = \sqrt{4/\pi\varepsilon} \int_0^1 dx\, x^{-1/2}\, e^{-2\pi i n x} \exp(-\tfrac{1}{4}\varepsilon x)\,, \tag{3.21}$$

while $\mathscr{I}'_n$ is defined as

$$\mathscr{I}'_n = -(2\vartheta/s_b) \int_0^\infty d\epsilon\, \rho(0, \epsilon)\, \frac{\partial}{\partial \epsilon}\, \mathscr{G}_n(-\epsilon, s)\,. \tag{3.22}$$

From (3.19) one easily obtains $\mathscr{G}'_n(\epsilon, s) = 2\vartheta\, \partial \mathscr{G}_n(\epsilon, s)/\partial\epsilon$ as

$$\begin{aligned}\mathscr{G}'_n(\epsilon, s) = &- \mathscr{G}_n(\epsilon, s) \\ &- \tfrac{1}{2}\, \frac{\epsilon}{|\epsilon|}\, e^{-\epsilon/2\vartheta}[e^{-\mu_n|\epsilon|/2\vartheta} \operatorname{erfc}(-\tfrac{1}{2}\mu_n\sqrt{s/\vartheta} + \tfrac{1}{2}|\epsilon|/\sqrt{s\vartheta}) \\ &+ e^{+\mu_n|\epsilon|/2\vartheta} \operatorname{erfc}(\tfrac{1}{2}\mu_n\sqrt{s/\vartheta} + \tfrac{1}{2}|\epsilon|/\sqrt{s\vartheta})]\,.\end{aligned} \tag{3.23}$$

Let there be $N \to \infty$ modes available in Fourier space, i.e. let there be $2N+1$ coefficients b_n and the same number of c_n's. Then (3.15) plus (3.20) represent $4N+2$ equations in $4N+2$ unknown variables. Since a_0 is known – see below (3.7) – , this set of equations can be solved for the b_n and the c_n upon specifying the energy distribution $\rho(0, \epsilon)$ of (re-)entering particles at the top of the barrier.

In view of the relatively simple structure of (3.15) and (3.20) regarding the b_n – as they appear only diagonally – it is a simple matter to eliminate them and thus to obtain a separate set of equations for the c_n along. Namely, subtracting μ_n times (3.15) from (3.20) yields

$$\sum_{m=-\infty}^{+\infty} [\mathcal{A}_{nm}(\mu_n + \mu_m) + \mathcal{B}_n]c_m = (1+\mu_n)a_0\delta_{n0} + (1-\mu_n)\mathcal{I}_n + \mathcal{I}'_n . \quad (3.24)$$

A further evaluation of the matrix featuring on the left-hand side of (3.24) will be given in the next section. Having determined the c_n from (3.24), one calculates the b_n from either (3.15) or (3.20), or – of course – any linear combination of them. For instance, in some cases it may be profitable to add μ_n times (3.15) to (3.20), which leads to

$$2\mu_n b_n - \sum_{m=-\infty}^{+\infty} [\mathcal{A}_{nm}(\mu_n - \mu_m) - \mathcal{B}_n]c_m = (1+\mu_n)\mathcal{I}_n + \mathcal{I}'_n , \quad (3.25)$$

where it has been noted that $(1-\mu_n)a_0\delta_{n0} = 0$ for all n.

4. The decay rate

Although the above formulation of the Kramers' problem – culminating in matrix equation (3.24) – in principle yields all c_n and, hence, all the b_n simultaneously, in some limiting cases it will be possible to extract more direct information merely concerning the decay rate Γ. Invoking (2.17) for $\bar{\rho}(\epsilon)$, the expression (2.19) for Γ becomes

$$\Gamma = -\int_0^{s_b} ds \left(\rho + \vartheta \frac{\partial \rho}{\partial \epsilon}\right)_{\epsilon=0} . \quad (4.1)$$

In view of the equality of the zero mode (i.e. $n=0$) projection of the vertical flux at $\epsilon = 0$ – contained in (3.15) and (3.20) – the value of Γ in (4.1) is indeed unambiguously defined, i.e. it is properly independent of whether it is evaluated slightly above (at $\epsilon = +0$) or slightly below (at $\epsilon = -0$) the barrier peak energy. It is therefore a matter of mere convenience to choose $\epsilon = -0$. Using the below-barrier solution (3.7) – in particular (3.11) plus ϑ times (3.13) – one then immediately obtains

$$\left(\rho + \vartheta \frac{\partial \rho}{\partial \epsilon}\right)_{\epsilon=-0} = -\frac{1}{2} \sum_{n=-\infty}^{+\infty} (1+\mu_n) b_n \, e^{2\pi i n s / s_b} , \tag{4.2}$$

so that – upon inserting (4.2) into (4.1) – the only remaining, nonzero contribution arises from $n = 0$. Since $\mu_0 = 1$, the result thus simply reads

$$\Gamma = -s_b b_0 . \tag{4.3}$$

In view of (3.7), this upshot means physically that the escape rate is basically determined by the leading functional deviation from perfect local equilibrium (deep in the potential hole). In that sense there is, therefore, in fact little difference between the classical case and the quantum case (see ref. [2]).

4.1. Preliminaries

In the limiting case of very low friction the equations determining the b_n and the c_n (i.e. (3.15) and (3.20), or (3.24) and (3.25)) can be simplified – at least for the case of a single metastable well – by setting $\rho(0, \epsilon) = 0$ for $\epsilon > 0$. In that case the only remaining parameter is $\varepsilon \ll 1$. Notice that $\mu_m = (1 + 8\pi i m/\varepsilon)^{1/2}$, so that the case $m = 0$ does not commute with the limit $\varepsilon \to 0$.

Let us first evaluate the pertinent matrix elements $\mathscr{A}_{nm}$ and $\mathscr{B}_{nm} = \mathscr{B}_n$ – and their relevant combinations – explicitly in more detail in the general case. From the definition (3.16), only once performing a partial integration, one directly finds

$$\mathscr{A}_{n \neq m} = \frac{1}{2\pi i(m-n)} \left(\mathrm{erf}(\tfrac{1}{2}\mu_m \sqrt{\varepsilon}) - \frac{\mu_m}{\mu_n} \mathrm{erf}(\tfrac{1}{2}\mu_n \sqrt{\varepsilon}) \right) , \tag{4.4}$$

where use has been made of the relations $\mathrm{erfc}(-x) - \mathrm{erfc}(x) = 2\mathrm{erf}(x)$ and $\mathrm{erfc}(-x) + \mathrm{erfc}(x) = 2$, with $\mathrm{erf}(x) = (2/\sqrt{\pi}) \int_0^x \mathrm{d}y \exp(-y^2)$ being the usual error function. Realizing that $2\pi i(m-n) = (\mu_m^2 - \mu_n^2)\varepsilon/4$, the result (4.4) is comfortably rewritten as

$$\mathscr{A}_{n \neq m} = \frac{4}{\varepsilon \mu_n} \frac{1}{\mu_n + \mu_m} \left(-1 + \frac{\mu_n \, \mathrm{erfc}(\tfrac{1}{2}\mu_m \sqrt{\varepsilon}) - \mu_m \, \mathrm{erfc}(\tfrac{1}{2}\mu_n \sqrt{\varepsilon})}{\mu_n - \mu_m} \right) . \tag{4.5}$$

Further, carefully evaluating the diagonal elements one obtains

$$\mathscr{A}_{nn} = -\frac{2}{\varepsilon \mu_n^2} \mathrm{erf}(\tfrac{1}{2}\mu_n \sqrt{\varepsilon}) + \frac{2}{\mu_n} \sqrt{\frac{1}{\pi \varepsilon}} \exp(-\tfrac{1}{4}\varepsilon) + \mathrm{erfc}(-\tfrac{1}{2}\mu_n \sqrt{\varepsilon}) , \tag{4.6}$$

while (3.21) is easily seen to yield

$$\mathscr{B}_n = \frac{4}{\varepsilon\mu_n} \operatorname{erf}(\tfrac{1}{2}\mu_n\sqrt{\varepsilon}) . \tag{4.7}$$

Upon combining (4.5) and (4.7) – in view of (3.24) – one now finds that

$$\mathscr{A}_{n\neq m}(\mu_n + \mu_m) + \mathscr{B}_n = -\frac{4}{\varepsilon}\left(\frac{\operatorname{erfc}(\frac{1}{2}\mu_n\sqrt{\varepsilon}) - \operatorname{erfc}(\frac{1}{2}\mu_m\sqrt{\varepsilon})}{\mu_n - \mu_m}\right), \tag{4.8}$$

while

$$2\mu_n\mathscr{A}_{nn} + \mathscr{B}_n = 4\sqrt{\frac{1}{\pi\varepsilon}}\exp(-\tfrac{1}{4}\varepsilon) + 2\mu_n \operatorname{erfc}(-\tfrac{1}{2}\mu_n\sqrt{\varepsilon}) . \tag{4.9}$$

Recognizing the first term on the right-hand side of (4.9) as the direct limiting value of (4.8) when $m \to n$, we may represent (3.24) in the form

$$\begin{aligned} &2\mu_n c_n \operatorname{erfc}(-\tfrac{1}{2}\mu_n\sqrt{\varepsilon}) - \frac{4}{\varepsilon}\sum_{m=-\infty}^{+\infty} c_m\left(\frac{\operatorname{erfc}(\frac{1}{2}\mu_n\sqrt{\varepsilon}) - \operatorname{erfc}(\frac{1}{2}\mu_m\sqrt{\varepsilon})}{\mu_n - \mu_m}\right) \\ &\quad = (1+\mu_n)a_0\delta_{n0} + (1-\mu_n)\mathscr{I}_n + \mathscr{I}'_n . \end{aligned} \tag{4.10}$$

Similarly, in view of (3.25) one also combines (4.5) and (4.7) so as to obtain

$$\mathscr{A}_{nm}(\mu_n - \mu_m) - \mathscr{B}_n = -\frac{4}{\varepsilon}\left(\frac{\operatorname{erf}(\frac{1}{2}\mu_n\sqrt{\varepsilon}) + \operatorname{erf}(\frac{1}{2}\mu_m\sqrt{\varepsilon})}{\mu_n + \mu_m}\right), \tag{4.11}$$

which obviously also holds if $m = n$. Hence, (3.25) can be rewritten in the form

$$2\mu_n b_n + \frac{4}{\varepsilon}\sum_{m=-\infty}^{+\infty} c_m\left(\frac{\operatorname{erf}(\frac{1}{2}\mu_n\sqrt{\varepsilon}) + \operatorname{erf}(\frac{1}{2}\mu_m\sqrt{\varepsilon})}{\mu_n + \mu_m}\right) = (1+\mu_n)\mathscr{I}_n + \mathscr{I}'_n . \tag{4.12}$$

4.2. Weak damping

In the limit $\varepsilon \to 0$ – disregarding diffusive barrier recrossings or otherwise entering particles – expanding all coefficients into a power series in terms of ε, (4.10) becomes

$$c_0 + \sum_{m\neq 0} c_m \operatorname{erf}(\sqrt{2\pi i m})/\sqrt{8 i m} = \tfrac{1}{2}a_0\sqrt{\pi\varepsilon}\,[1 + \mathcal{O}(\varepsilon^{1/2})] , \tag{4.13}$$

for $n = 0$, while if $n \neq 0$ one has

$$[1 + \tfrac{1}{2}\pi\sqrt{8\mathrm{i}n}\,\mathrm{erfc}(-\sqrt{2\pi\mathrm{i}n}]c_{n\neq 0} - \sum_{m\neq 0,n} c_m \frac{\mathrm{erfc}(\sqrt{2\pi\mathrm{i}n}) - \mathrm{erfc}(\sqrt{2\pi\mathrm{i}m})}{\sqrt{8\mathrm{i}n} - \sqrt{8\mathrm{i}m}}$$
$$= - c_0\,\mathrm{erf}(\sqrt{2\pi\mathrm{i}n})/\sqrt{8\mathrm{i}n}\,[1 + \mathcal{O}(\varepsilon^{1/2})]\,. \tag{4.14}$$

Since in view of (4.3) our particular interest lies in b_0, we also evaluate (4.12) for $n = 0$, in the same manner. This gives

$$b_0[1 + \mathcal{O}(\varepsilon)] = -2\sqrt{\frac{1}{\pi\varepsilon}}\left[c_0 + \sum_{m\neq 0} c_m\,\mathrm{erf}(\sqrt{2\pi\mathrm{i}m})/\sqrt{8\mathrm{i}m}\right]$$
$$-\frac{2}{\pi}\sum_{m\neq 0} c_m \frac{1 - \mathrm{erf}(\sqrt{2\pi\mathrm{i}m})/\sqrt{8\mathrm{i}m}}{\sqrt{8\mathrm{i}m}}\,. \tag{4.15}$$

The singular term of order $\varepsilon^{-1/2}$ on the right-hand side of (4.15) vanishes in view of (4.13), and the leading term becomes of order one. Obviously, the last sum in (4.15) will be of order $\varepsilon^{1/2}$, so that keeping it while eliminating the quantity in square brackets by means of (4.13) one should carry the contributions $\mathcal{O}(\varepsilon^{1/2})$ – not shown there explicitly – along. Doing so, the result reads

$$b_0[1 + \mathcal{O}(\varepsilon)] = -a_0 + c_0 - \frac{4}{\pi}\sum_{m\neq 0} c_m \frac{1 - \mathrm{erf}(\sqrt{2\pi\mathrm{i}m})/\sqrt{8\mathrm{i}m}}{\sqrt{8\mathrm{i}m}}\,, \tag{4.16}$$

which of course agrees with what would have been found for instance from the original (3.15). Next setting

$$\begin{aligned} b_n &= b_n^{(0)} + \varepsilon^{1/2} b_n^{(1)} + \mathcal{O}(\varepsilon)\,, \\ c_n &= c_n^{(0)} + \varepsilon^{1/2} c_n^{(1)} + \mathcal{O}(\varepsilon) \end{aligned} \tag{4.17}$$

into (4.13), (4.14) and (4.16) and collecting the contributions in terms of powers of $\varepsilon^{1/2}$, one finds to begin with that $c_n^{(0)} = 0$ for all n. Hence, by (4.16) $b_0^{(0)} = -a_0$. With this value the decay rate (4.3) becomes

$$\Gamma = (\varepsilon\omega_0/2\pi)\exp(-U_b/\vartheta)\,, \tag{4.18}$$

recalling that $\varepsilon = 2\lambda I_b/\vartheta$. This expression completely agrees with Kramers' [1] original weak damping result, and with the weak damping limit formula of Büttiker, Harris and Landauer [12, 13], and of Mel'nikov and Meshkov [18] (See also Risken [17, 16] and ref. [2]). It is further not difficult to show that $b_{n\neq 0}^{(0)} = 0$.

The first order correction to (4.18) follows from solving (4.13) and (4.14) for $c_n^{(1)}$, with $b_0^{(1)}$ then in view of (4.16) being given by

$$b_0^{(1)} = c_0^{(1)} - \frac{4}{\pi} \sum_{n \neq 0} c_n^{(1)} \frac{1 - \mathrm{erf}(\sqrt{2\pi i n})/\sqrt{8in}}{\sqrt{8in}} . \tag{4.19}$$

While this shows that a correction term $b_0^{(1)} \neq 0$ indeed exists, it is still nontrivial to extract an explicit result. Although in the present paper no attempt is made at an acurate numerical evaluation of (4.19) – perhaps one should in that case rather spend the effort on the original nonperturbative set of equations – an approximate numerical value for $b_0^{(1)}$ can be obtained within the context of Jacobi's diagonal approximation (see e.g. Pearson's Handbook [23]), where it is legitimate to introduce the following useful simplification. Namely, with the argument $x = \sqrt{2\pi i n}$ the error function $\mathrm{erf}(x)$ fairly rapidly approaches the value one for increasing $|n| = 1, 2, \ldots$. In what follows we throughout set the value of all occurring erf-functions (with $n \neq 0$) equal to unity, which implies that all erfc-functions with positive argument vanish. Actually taking into account one correction term in the prefactor of $c_{n\neq 0}$ in (4.14), a consistent leading approximation to that equation is simply given by

$$c_{n\neq 0}^{(1)} = c_0^{(1)}/8\pi i n , \tag{4.20}$$

while in the same numerical approximation (4.13) reduces to

$$c_0^{(1)} + \sum_{n \neq 0} c_n^{(1)}/\sqrt{8in} = \tfrac{1}{2} a_0 \sqrt{\pi} . \tag{4.21}$$

Substituting (4.20) for $c_{n\neq 0}^{(1)}$ into (4.21), one obtains

$$c_0^{(1)} = \tfrac{1}{2} a_0 \sqrt{\pi} / [1 + \zeta(\tfrac{3}{2})/16\pi] , \tag{4.22}$$

where $\zeta(\frac{3}{2}) = 2.612\ldots$ represents a Riemann zeta function (see e.g. ref. [24], p. 264) and which thus completely solves the problem for all $c_n^{(1)}$. Next substituting these coefficients into (4.19) with the error function consistently set equal to one, the upshot for $b_0^{(1)}$ is readily found to be

$$b_0^{(1)} = \frac{1 - \zeta(\frac{3}{2})/4\pi^2 + \zeta(2)/8\pi^2}{1 + \zeta(\frac{3}{2})/16\pi} \tfrac{1}{2} a_0 \sqrt{\pi} . \tag{4.23}$$

With the earlier mentioned value (taken from Reichl's book on Statistical Physics, p. 264) for $\zeta(\frac{3}{2})$ and using $\zeta(2) = \pi^2/6$, the numerical value of (4.23) becomes $b_0^{(1)} = 0.454 a_0 \sqrt{\pi}$.

According to the above analysis the weak damping formula (4.18) needs correction in the sense that

$$\Gamma = (\varepsilon \omega_0 / 2\pi)[1 - (\varepsilon/\bar{\alpha})^{1/2} + \mathcal{O}(\varepsilon)] \exp(-U_b/\vartheta) . \tag{4.24}$$

In fact, the first order correction term is precisely as predicted originally by Büttiker, Harris and Landauer [13] on the basis of the simplified, one-dimensional model equation (2.18). Strictly speaking, $\bar{\alpha} = \alpha$ only if α is taken to be an energy independent parameter. Within the realm of the one-dimensional model the constant α had to be introduced in an ad hoc manner and remains undetermined, as explained earlier. However, having solved the two-dimensional problem (2.7), it should now be possible to identify $\alpha(E)$. Presently we confine ourselves to the effective $\bar{\alpha}$. From the preceding analysis it follows that

$$\bar{\alpha} = [a_0/b_0^{(1)}]^2 , \tag{4.25}$$

so that following the approximate numerical evaluation leading to (4.23) for $b_0^{(1)}$, we obtain the value $\bar{\alpha} = 1/\pi(0.454)^2 = 1.54\ldots$ Given the uncertainties involved in (4.23), this result is remarkably close to some earlier known values, mentioned in the introduction (Dekker [15]: $\bar{\alpha} = \frac{3}{2}$; Risken and Voigtlaender [17]: $\bar{\alpha} = 1.47$; Mel'nikov and Meshkov [18]: $\bar{\alpha} = 1.49$).

4.3. *Intermediate damping*

The moderate damping regime is defined by $\varepsilon \gg 1$ while still $\lambda/\omega_0 \ll 1$. This latter condition implies that we may still neglect the occurrence of diffusively recrossing particles. That is, for the initial distribution we take again $\rho(0, \epsilon) = 0$ so that in the general matrix equations (4.10) and (4.11) still $\mathscr{I}_n = 0$ and $\mathscr{I}_n' = 0$. Recalling that $\mu_n\sqrt{\varepsilon} = (\varepsilon + 8\pi i n)^{1/2}$, and invoking the appropriate asymptotic expansions for the error functions in the limit $\varepsilon \to \infty$, (4.10) then at once yields

$$4\mu_n c_n[1 + \mathcal{O}(\mathrm{e}^{-\varepsilon/4})] = (1 + \mu_n)a_0\delta_{n0} + \mathcal{O}(\mathrm{e}^{-\varepsilon/4}) . \tag{4.26}$$

That is, disregarding relatively exponentially small terms one has $c_0 = \frac{1}{2}a_0$ while all other $c_{n\neq 0} = 0$. Substituting (4.26) for the c_n into (4.12) for the b_n, one thus finds in this case that

$$b_n = -a_0/\varepsilon\mu_n + \mathcal{O}(\mathrm{e}^{-\varepsilon/4}) . \tag{4.27}$$

Hence, following (4.3) the intermediate damping decay rate becomes $\Gamma = a_0 s_b/\varepsilon$ plus exponentially small corrections. Recalling that $\varepsilon = s_b/\vartheta$ and that a_0 has been specified below (3.7), one concludes that the present analysis predicts the decay rate – upon entering the intermediate damping regime by increasing the friction – to approach the well-known TST value

$$\Gamma = (\omega_0/2\pi)\exp(-U_b/\vartheta) \tag{4.28}$$

exponentially fast. This finding (i) corroborates earlier results – based on the same model (2.7) – obtained by Mel'nikov and Meshkov [18, 19], using the Wiener–Hopf technique as mentioned earlier in sections 1 and 2, but (ii) is at variance with conclusions by Dekker [8, 9] – based on the original Kramers equation rather than on (2.7) – as well as by Büttiker, Harris and Landauer [12, 13]. The latter disagreement is somewhat remarkable since the one-dimensional BHL model – which is only in the energy variable – is contained in (i.e. it can be derived from) the two-dimensional model equation (2.7), as shown in section 2. Actually, the arguments given in section 2 suggest that this feature arises as a consequence of the crucially simplifying assumption that the BHL correction factor α is independent of the energy.

While this indicates that these *non*exponential correction terms to (4.28) may have no quantitative significance, it does not really settle the question whether the exponential approach is genuine – i.e. is intrinsic to the original Kramers model (1.3) – or that it is an artifact of (2.7). For that matter, it may be worth recalling that – according to the analysis preceding (2.5)–(2.7) – these approximate equations involve errors which in the moderate damping regime (where still $\lambda/\omega_0 \ll 1$) may be of the order of magnitude of $[(\lambda/\omega_b)(\vartheta/U_b)]^{1/2}$, whereas in the strong damping regime they would saturate at the order of ϑ/U_b. While that error analysis does not seem to point to any serious defects in the model (2.7) – as an approximation to (1.3) – it is, however, well known that the TST value is quite wrong in the heavily overdamped regime $\lambda/\omega_0 \gg 1$ (where the decay rate goes to zero inversely proportional to λ; see the next section). Let us therefore take a more careful look at the nature of the approximations involved in (2.7).

The crucial feature in going from (2.1) – which is still exactly equivalent to the original Kramers equation – to (2.5) and, hence, in the steady state to (2.7), is the replacement of the momentum $p(x, E)$ in the energy diffusion terms by $p_b = p(s, U_b)$. This obviously implies the neglect of contributions of the nature of ϵ/p_b, i.e. in the equation of contributions with relative magnitude

$$\mathscr{R} = \left(\frac{1}{p_b}\right)^2 \left| \frac{\partial}{\partial \epsilon}\left[\epsilon\left(\rho + \vartheta\,\frac{\partial \rho}{\partial \epsilon}\right)\right] \Big/ \frac{\partial}{\partial \epsilon}\left(\rho + \vartheta\,\frac{\partial \rho}{\partial \epsilon}\right)\right| . \tag{4.29}$$

As before, crudely speaking $\mathscr{R}$ will be of the order of the ratio $|\epsilon|/p_b^2$. However, unlike before we should now not be content with a mere estimate of this ratio due to the momenta $p_b \approx U_b^{1/2}$ in the potential hole as there exist functionally different contributions arising from the momenta in the barrier peak region. A unified treatment of both cases becomes possible if we consider a perfect parabolic barrier [2] so that $U(x) = U_b - \frac{1}{2}\omega_b^2 x^2$. One then easily finds the momentum $p_b = \omega_b x$ and the action variable $s = \lambda\omega_b x^2$, so that $p_b^2 = (\omega_b/\lambda)s$. Consequently, $\mathscr{R} \approx (\lambda/\omega_b)|\epsilon|/s$.

(i) The "*hole corrections*": far away from the barrier peak the action variable settles for a value $s \approx \lambda I_b$ and $I_b \approx U_b/\omega_b$, so that one recovers the earlier treated case $\mathcal{R} \approx |\epsilon|/U_b$. That is, upon increasing the friction these relative errors go from $\mathcal{R} \approx \varepsilon^{1/2}\vartheta/U_b$ to $\mathcal{R} \approx \vartheta/U_b\ \mathcal{O}(\varepsilon^{-1})$. While through the neglect of such terms the significance of the exponentially fast approach – which involves small terms of the order of $\exp(-U_b/\vartheta)$ – of the escape rate to the value (4.28) becomes practically nihil, that value itself might still seem to be the correct moderate-to-strong friction result – which, however, we know it is not.

(ii) The "*barrier corrections*": for the usual high barrier $\vartheta/U_b \ll 1$, and the harmonic barrier region is sufficiently specified by $\frac{1}{2}\omega_b^2 x^2 \approx \vartheta$ so that $s \approx (\lambda/\omega_b)\vartheta$. Hence, $\mathcal{R} \approx |\epsilon|/\vartheta$ in this case. Clearly, these errors are larger than the preceding ones. For weak damping one again has $|\epsilon| \approx (\vartheta s)^{1/2}$, which presently leads to $\mathcal{R} \approx (\lambda/\omega_b)^{1/2}$. Alternatively one may write this as $\mathcal{R} \approx (\varepsilon\vartheta/U_b)^{1/2}$, which shows – in view of for instance (4.24) and the high barrier assumption – that these errors are fortunately still negligible in the pertinent regime. However, in the strong damping regime one now obtains $\mathcal{R}\ \mathcal{O}(1)$. Indeed, if $\lambda/\omega_b\ \mathcal{O}(1)$ the decay rate (4.28) misses the correct Karmers–Smoluchovski value by a factor of the order of one.

Having thus identified the source of the breakdown of (2.7) as a suitable approximation to the Kramers problem in the strong damping regime (in terms of the neglect of energy diffusion contributions which are significant to the barrier dynamics), it remains to be investigated – in particular in view of recent work by Grabert [3] – to what extent the situation can be improved by properly accounting for diffusive barrier re-crossings.

4.4. Strong damping

Diffusive barrier re-crossings can be incorporated into the present treatment through a specification of the appropriate "initial" energy distribution of incoming particles, i.e. $\rho(s=0, \epsilon>0)$. Let us then return to the original equation (3.24) determining the c_n-coefficients. As is most easily seen from its equivalent form (4.10), in the strong damping regime – where $\lambda/\omega_0\ \mathcal{O}(1)$ – one finds that it reduces to

$$4\mu_n c_n[1+\mathcal{O}(\mathrm{e}^{-\varepsilon/4})] = (1+\mu_n)a_0\delta_{n0} + (1-\mu_n)\mathcal{I}_n + \mathcal{I}'_n + \mathcal{O}(\mathrm{e}^{-\varepsilon/4}), \quad (4.30)$$

which is the more general version of (4.26) – to which it reduces if one neglects the incoming particles so that $\mathcal{I}'_n = \mathcal{I}_n = 0$. It should be recalled that $\mathcal{I}_n$ and $\mathcal{I}'_n$ have been specified in (3.17) and (3.22), respectively. In view of $\mathcal{I}_n$ we therefore consider $\mathcal{G}_n(-\epsilon, s_b)$. From (3.19) – remembering that $\varepsilon = s_b/\vartheta$ – one obtains

$$\mathscr{G}_n(-\epsilon, s_b) = (1/2\mu_n)\, e^{\epsilon/2\vartheta}[e^{-\mu_n|\epsilon|/2\vartheta} \operatorname{erfc}(-\tfrac{1}{2}\mu_n\sqrt{\varepsilon} + \tfrac{1}{2}|\epsilon|/\vartheta\sqrt{\varepsilon}) - e^{-\mu_n|\epsilon|/2\vartheta} \operatorname{erfc}(\tfrac{1}{2}\mu_n\sqrt{\varepsilon} + \tfrac{1}{2}|\epsilon|/\vartheta\sqrt{\varepsilon})] . \tag{4.31}$$

As a consequence of the asymptotic behaviour of the complementary error function, it is immediately clear that the second contribution in the square brackets in (4.31) becomes exponentially small – for all n and all values of ϵ – if $\varepsilon \gg 1$. Hence,

$$\mathscr{G}_n(-\epsilon, s_b) = (1/2\mu_n)\, e^{\epsilon/2\vartheta}[e^{-\mu_n|\epsilon|/2\vartheta} \operatorname{erfc}(-\tfrac{1}{2}\mu_n\sqrt{\varepsilon} + \tfrac{1}{2}|\epsilon|/\vartheta\sqrt{\varepsilon}) + \mathscr{O}(e^{-\varepsilon/4})] . \tag{4.32}$$

In view of $\mathscr{I}_n'$ we also consider $\mathscr{G}_n'(-\epsilon, s_b)$, which by means of (3.23) now similarly becomes

$$\mathscr{G}_n'(-\epsilon, s_b) = -(1 - \mu_n\epsilon/|\epsilon|)\mathscr{G}_n(-\epsilon, s_b) + \mathscr{O}(e^{-\varepsilon/4}) . \tag{4.33}$$

Consequently, if $\epsilon > 0$ then

$$(1 - \mu_n)\mathscr{G}_n(-\epsilon, s_b) + \mathscr{G}_n'(-\epsilon, s_b) = \mathscr{O}(e^{-\varepsilon/4}) , \tag{4.34}$$

such that

$$(1 - \mu_n)\mathscr{I}_n + \mathscr{I}_n' = \mathscr{O}(e^{-\varepsilon/4}) . \tag{4.35}$$

One thus arrives at the conclusion that (4.30) again reduces to (4.26), even if one allows for the existence of incoming particles. That is, in both the intermediate *and* the strong damping regime one obtains

$$c_n = \tfrac{1}{2} a_0 \delta_{n0} + \mathscr{O}(e^{-\varepsilon/4}) . \tag{4.36}$$

Substituting this result once more into (4.12), but presently keeping the "input" terms on the right-hand side, yields

$$b_n = -a_0/\varepsilon\mu_n + [(1 + \mu_n)\mathscr{I}_n + \mathscr{I}_n']/2\mu_n + \mathscr{O}(e^{-\varepsilon/4}) . \tag{4.37}$$

Upon invoking (4.35) in order to eliminate $\mathscr{I}_n'$ in favour of $\mathscr{I}_n$, this expression for b_n is easily rewritten as

$$b_n = -a_0/\varepsilon\mu_n + \mathscr{I}_n + \mathscr{O}(e^{-\varepsilon/4}) , \tag{4.38}$$

so that the remaining problem boils down to calculating $\mathscr{I}_n$.

From an independent analysis of the original Kramers equation in the moderate-to-strong friction regime [1, 2] it is known that – disregarding exponentially small corrections of the order of $\exp(-U_b/\vartheta)$ – the pertinent density, which is valid throughout the entire phase space, reads

$$\rho(x, p)/\rho(0,0) = e^{-\epsilon/\vartheta} \operatorname{erfc}[\tfrac{1}{2}(\alpha x - p)\sqrt{\kappa\omega_b/\lambda\vartheta}] , \tag{4.39}$$

where κ is Kramers' dissipative correction factor (1.2) while $\alpha = \kappa\omega_b - 2\lambda$. It will be useful to note that $\alpha\kappa = \omega_b$. As is seen by letting $x \to \infty$, (4.39) applies to the case of a single metastable well at the left-hand side of the barrier – as it presently should. At $x = 0$ (i.e. $s = 0$ or s_b) one has $p = \pm\sqrt{2\epsilon}$ with $\epsilon > 0$, where the minus sign, of course, applies to the incoming particles (i.e. at $s = 0$). The pertinent value of $\rho(0,0)$ may be obtained by applying the above-barrier solution (3.10) at $\epsilon = 0$, and letting $s \to 0$ so that the erfc $\to 1$ while the energy integral picks up only one-half the delta function $G(-\epsilon', 0) = \delta(\epsilon')$, with the result that $\rho(0,0) = 2c_0 = a_0$. As a consequence (4.39) yields

$$\rho(s = 0, \epsilon > 0) = a_0 \, e^{-\epsilon/\vartheta} \operatorname{erfc}(\sqrt{\epsilon\kappa\omega_b/2\lambda\vartheta}) \tag{4.40}$$

as the distribution of re-entering particles. Notice that while this distribution has a cusp at $\epsilon = 0$, it is of course perfectly integrable. Substituting now (4.40) for $\rho(0, \epsilon)$ into (3.17) for $\mathcal{I}_n$ and invoking (4.32) for $\mathcal{G}_n(-\epsilon, s_b)$, one has

$$\mathcal{I}_n = \frac{a_0}{2\mu_n s_b} \int_0^\infty d\epsilon \, e^{-(1+\mu_n)\epsilon/2\vartheta} \operatorname{erfc}(-\tfrac{1}{2}\mu_n\sqrt{\varepsilon} + \tfrac{1}{2}\epsilon/\vartheta\sqrt{\varepsilon}) \operatorname{erfc}(\sqrt{\epsilon\kappa\omega_b/2\lambda\vartheta})$$
$$+ \mathcal{O}(e^{-\varepsilon/4}) . \tag{4.41}$$

With $\varepsilon \to \infty$ the first complementary error function in the integral has the value two for practically all ϵ, say $\epsilon\, \mathcal{O}(\varepsilon^0)$, the corrections to this value again being of the order of $e^{-\varepsilon/4}$. Only for extremely large energy values $\epsilon\, \mathcal{O}(\varepsilon)$ will the argument of the pertinent error function change its sign from negative to positive with ensuing deviations of order one in its value. However, in that case the remaining factors in the integral do the job of suppressing the integrand to exponentially small values. Therefore, (4.41) may be simplified to

$$\mathcal{I}_n = \frac{a_0}{\varepsilon\mu_n\vartheta} \int_0^\infty d\epsilon \, e^{-(1+\mu_n)\epsilon/2\vartheta} \operatorname{erfc}(\sqrt{\epsilon\kappa\omega_b/2\lambda\vartheta}) + \mathcal{O}(e^{-\varepsilon/4}) . \tag{4.42}$$

By means of one partial integration this integral is readily found to yield

$$\mathscr{I}_n = \frac{2a}{\varepsilon\mu_n(1+\mu_n)}\left(1 - \kappa\sqrt{\frac{1}{1+(1-\mu_n)\kappa\lambda/\omega_b}}\right) + \mathscr{O}(e^{-\varepsilon/4}) , \tag{4.43}$$

so that by (4.38) one obtains

$$b_n = \frac{2a_0}{\varepsilon\mu_n(1+\mu_n)}\left(\tfrac{1}{2}(1-\mu_n) - \kappa\sqrt{\frac{1}{1+(1-\mu_n)\kappa\lambda/\omega_b}}\right) + \mathscr{O}(e^{-\varepsilon/4}) , \tag{4.44}$$

which neatly reduces to (4.27) in the moderate damping regime (where still $\varepsilon \gg 1$, but where $\lambda/\omega_0 \ll 1$ so that $\kappa \approx 1$). In particular, for $n = 0$ one has

$$b_0 = -(\kappa/\varepsilon)a_0 + \mathscr{O}(e^{-\varepsilon/4}) , \tag{4.45}$$

in view of (4.3) leading to

$$\Gamma = (\kappa\omega_0/2\pi)[1 + \mathscr{O}(e^{-\varepsilon/4})]\exp(-U_b/\vartheta) , \tag{4.46}$$

which is nothing less than the correct Kramers modification of the TST result (4.28).

4.5. *Discussion*

The above analysis thus shows how by taking account of the existence of diffusive barrier re-crossings – through specifying the above-barrier entering particles' energy distribution as an "initial" value for the solution of the approximate model equation (2.7) – one obtains the correct escape rate Γ for all values of the friction (i.e. from $\lambda = 0$ to $\lambda = \infty$). It should be emphasized that the present formulation of the escape problem incorporates the so-called Kramers turnover regime (i) entirely within the original model (1.3) and (ii) in a dynamically unified manner. In that sense our treatment differs from that of Grabert [3] and of Mel'nikov and Meshkov [18], respectively. The latter obtained the correct moderate-to-large damping value for the decay rate only by an *ad hoc* multiplication of the TST result with the Kramers–Smoluchovsky correction factor κ. On the other hand, Grabert's formulation of the problem – in terms of the energy diffusion of the by-now well-known unstable normal mode in the barrier dynamics of a more microscopic model – suggests that a treatment of Kramers' turnover problem is not feasible in terms of the *particle* energy. Nevertheless, the pertinent microscopic model [25] – with ohmic dissipation – implies the original Kramers equation (1.3) in the classical limit, and in that case the remaining degrees of freedom pertain to the particle only. Of course, the Kramers turnover problem is fully contained in the classical Kramers model and we therefore suggest that our present results for the ohmic case are essentially equivalent to those of Grabert.

While (4.43) apparently gives the correct value for the decay rate in the intermediate and strong friction regimes, it seems in place to critically examine the underlying phase space densities. For example, from (4.39) we know not only the distribution of incoming particles in the Kramers–Smoluchovski regime, but that of the outgoing ones as well. Namely, similarly to (4.40) one also has

$$\rho(s_b, \epsilon > 0) = a_0\, e^{-\epsilon/\vartheta}\, \mathrm{erfc}(-\sqrt{\epsilon\kappa\omega_b/2\lambda\vartheta})\,, \tag{4.47}$$

and if our dynamics – generated by (2.7) – is correct, then this "output" density should be reproduced if (4.40) is taken as the "input" density in (3.10).

In the pertinent friction range – at $s = s_b$ and in view of (4.36) – (3.10) immediately simplifies to

$$\rho(s_b, \epsilon > 0) = a_0\, e^{-\epsilon/\vartheta} + \int_0^\infty d\epsilon'\, G(\epsilon - \epsilon', s_b)\, \rho(0, \epsilon')\,. \tag{4.48}$$

Using (4.40) for $\rho(0, \epsilon')$ and (2.10) for the Green's function, one then easily proves – e.g. by incorporating the equilibrium factor $\exp(-\epsilon'/\vartheta)$ into the Green's function and realizing that the occurring erfc < 1 on $\epsilon' > 0$ – that the integral only contributes terms of relative order $e^{-\varepsilon/4}$. That is, (4.48) yields

$$\rho(s_b, \epsilon > 0) = a_0\, e^{-\epsilon/\vartheta}[1 + o(e^{-\varepsilon/4})]\,, \tag{4.49}$$

which is clearly *not* in agreement with (4.47). Nevertheless, (4.40) and (4.49) seem to form a self-consistent set of densities at the barrier peak, for upon substituting them into expression (2.9) for the decay rate one has

$$\Gamma = a_0 \int_0^\infty e^{-\epsilon/\vartheta}\, \mathrm{erf}(\sqrt{\epsilon\kappa\omega_b/2\lambda\vartheta})\, d\epsilon\,, \tag{4.50}$$

which again yields the correct result (4.46). However, while according to (4.40) and (4.49) the strong damping deviations from equilibrium at the barrier – and, consequently, of the modifications of the simple TST value for Γ – are accounted for entirely by the incoming (re-crossing) particles, following (4.40) and (4.47) – which are both contained in (4.39) – these deviations are equally shared by both incoming and outgoing particles. Indeed, if we compute the decay rate following (2.9) by means of (4.39) – i.e. by means of (4.40) and (4.47) – the result again is (4.50) and, hence, (4.46) – but only if we let $\rho(0,0)=\frac{1}{2}a_0$ in lieu of twice this value. In conclusion, although the present treatment based on (2.7) yields the correct upshot for the escape rate even in the strong damping Kramers–Smoluchovski regime, the involved "input" density (4.40) is – unfortunately – twice as high as it should be.

4.6. *Modified BHL model*

Before closing this section on the strong damping regime, let us add some remarks concerning a recent modification [2] of the BHL model (2.18). As already mentioned in the introduction, this modification connects the Büttiker–Harris–Landauer theory [13] with (i) the quantum mechanical regime and (ii) the correct Smoluchovsky limit. In the classical regime the original argument involved the barrier dynamics as unstable free flight along a *dissipative* attracting trajectory in phase space. Presently – in the light of the preceding analysis – a different point of view will be taken. Namely, rather than considering the motion of the particles in the barrier region as dissipative free flight, it will here be treated as purely diffusive. As emphasized previously [2], the equivalence of the two methods is due to the underlying linearity of the stochastics in consequence of the presumed perfect harmonicity of the barrier peak region.

If one re-inserts (2.16) into (2.18), one has

$$\rho(s_b,\epsilon)-\rho(0,\epsilon)=2\lambda I_b\,\frac{\partial}{\partial\epsilon}\left(\bar{\rho}+\vartheta\,\frac{\partial\bar{\rho}}{\partial\epsilon}\right). \tag{4.51}$$

According to the above discussion the correct strong damping $\rho(s_b,\epsilon)$ and $\rho(0,\epsilon)$ are given by (4.47) and (4.40), respectively, but with a_0 replaced by $\frac{1}{2}a_0$. Using once more the standard property $\operatorname{erfc}(-x)-\operatorname{erfc}(x)=2\operatorname{erf}(x)$, we then set more generally

$$\rho(s_b,\epsilon)-\rho(0,\epsilon)=\operatorname{erf}(\sqrt{\epsilon\kappa\omega_b/2\lambda\vartheta})\,f_0(\epsilon)\,\rho_{eq}(\epsilon)\,, \tag{4.52}$$

where $\rho_{eq}(\epsilon)=a_0\exp(-\epsilon/\vartheta)$ – in line with (2.4) – and where $f_0(\epsilon)$ accounts for the depletion effects at barrier peak energies, which are typical of the zero friction limit. Upon redefining $f_0(\epsilon)$ in terms of a correction factor $\alpha(\epsilon)$ according to

$$f_0(\epsilon)=\alpha(\epsilon)\,\bar{\rho}(\epsilon)/\rho_{eq}(\epsilon)\,, \tag{4.53}$$

with $\bar{\rho}(\epsilon)$ as before representing the action-averaged density defined in (2.17), and – like in the original BHL formulation – replacing the actual $\alpha(\epsilon)$ by its typical energy independent mean value $\bar{\alpha}$, (4.52) becomes

$$\rho(s_b, \epsilon) - \rho(0, \epsilon) = \bar{\alpha}\ \mathrm{erf}(\sqrt{\epsilon\kappa\omega_b/2\lambda\vartheta})\ \bar{\rho}(\epsilon)\,. \tag{4.54}$$

Notice that in the weak damping limit – i.e. $\lambda \to 0$ – the error function in (4.54) tends to the value one for all $\epsilon > 0$, so that in that case one immediately identifies $\bar{\alpha} = \alpha_{\mathrm{BHL}}$ [13]. As a final simplification also replacing the strong damping correction factor – i.e. the error function in (4.54) – by the effective energy independent mean value

$$\overline{\mathrm{erf}} = \frac{1}{\vartheta}\int_0^\infty \mathrm{e}^{-\epsilon/\vartheta}\ \mathrm{erf}(\sqrt{\epsilon\kappa\omega_b/2\lambda\vartheta})\ \mathrm{d}\epsilon\,, \tag{4.55}$$

which simply yields $\overline{\mathrm{erf}} = \kappa$, and re-inserting (4.54) into the left-hand side of (4.51), one obtains

$$\bar{\alpha}\kappa\theta(\epsilon)\ \bar{\rho}(\epsilon) = 2\lambda I_b\ \frac{\partial}{\partial\epsilon}\left(\bar{\rho} + \vartheta\ \frac{\partial\bar{\rho}}{\partial\epsilon}\right), \tag{4.56}$$

which indeed completely agrees with the strong friction modification of (2.18) as given in ref. [2] – in the classical regime.

5. Final remarks

5.1. A simple formula

The utmost simplification of the results from the present formulation of Kramers' escape problem would be a single approximate expression for the decay rate Γ, interpolating between the correct weak and strong damping limits. It can be found as follows. Disregarding all $c_{n\neq 0}$, recalling (4.35) for the strong and intermediate damping regimes and taking $\mathcal{J}_n = \mathcal{J}'_n = 0$ in the weak damping regime, one finds from (4.10) for $n = 0$ that

$$c_0 \approx a_0 \bigg/ \left[\mathrm{erfc}(-\tfrac{1}{2}\sqrt{\varepsilon}) + 2\sqrt{\frac{1}{\pi\varepsilon}}\ \mathrm{e}^{-\varepsilon/4}\right]. \tag{5.1}$$

Substituting this result for $c_n = c_0\delta_{n0}$ into (4.12) for $n = 0$, once more recalling (4.35) and using (4.43) for $\mathcal{J}_n$, leads to an expression for b_0 that – in view of the widely separated friction scales pertinent to the weak and strong damping regimes – is practically indistinguishable from

$$b_0 \approx -\frac{2}{\varepsilon}\,\kappa a_0\,\mathrm{erf}(\tfrac{1}{2}\sqrt{\varepsilon})\Big/\left(\mathrm{erfc}(-\tfrac{1}{2}\sqrt{\varepsilon}) + 2\sqrt{\frac{1}{\pi\varepsilon}}\,\mathrm{e}^{-\varepsilon/4}\right). \tag{5.2}$$

With this result for b_0 the escape rate according to (4.3) becomes

$$\Gamma \approx \frac{\omega_0}{2\pi}\,\frac{2\kappa\,\mathrm{erf}(\tfrac{1}{2}\sqrt{\varepsilon})}{\mathrm{erfc}(-\tfrac{1}{2}\sqrt{\varepsilon}) + 2\sqrt{\frac{1}{\pi\varepsilon}}\,\mathrm{e}^{-\varepsilon/4}}\,\exp(-U_\mathrm{b}/\vartheta)\,. \tag{5.3}$$

One easily checks that in the zero fiction limit (i.e. $\varepsilon \to 0$ and $\kappa = 1$) the expression (5.3) indeed reproduces the correct value (4.18), while in the moderate-to-strong friction regime (i.e. $\varepsilon \to \infty$) it tends exponentially fast to the appropriate value (4.46). The significance of this exponential approach, however, has been criticized in section 4.

5.2. *Conclusions*

Let us now conclude by summarizing our findings. In this article Kramers' Brownian motion model (1.3) for escape from a metastable potential hole has been reconsidered for the following reasons.

First, to correct the Mel'nikov–Meshkov [18, 19] treatment in the strong damping regime (where it failed) in a *dynamically meaningful* sense.

Second, to elucidate certain features of recent work by Grabert [3], where the escape problem is discussed *not* in terms of the *particle energy* but in terms of the energy of the *unstable barrier mode* – a quantity which can be recognized in an underlying microscopic model, but which as such does not occur in the original Kramers model.

Third, to shed further light on the nature of the one-dimensional model proposed by Büttiker, Harris and Landauer [13], and its strong damping generalization of ref. [2].

Fourth, to investigate the so-called Kramers turnover regime in between weak and strong damping – in particular the nature of the approach of the Kramers–Smoluchovsky value of the escape rate – about which various authors have expressed different opinions.

The analysis essentially rests on (2.7), which also forms the basis of the treatment of Mel'nikov and Meshkov [18]. However, while these authors apply the Wiener–Hopf integral method at $x = 0$ (i.e. $s = 0$ and s_b), we make a complete spectral analysis (along the action coordinate s) of the phase space density. The unique, stable solution of (2.7) requires the separate specification of the energy distribution of incoming particles. While – for a single metastable well – such particles are practically absent in the weak damping regime, in the strong damping regime there will be many particles diffusively recrossing the barrier. In that manner the net outgoing flux is effectively lowered. Therefore, in this latter regime we have incorporated the incoming particle density as obtained from (1.3) into the general solution of (2.7). As a consequence one indeed precisely recovers the correct strong damping Kramers–Smoluchovski value for the escape rate Γ, thus (i) improving the original Mel'nikov–Meshkov theory and (ii) demonstrating the possibility of doing the calculations entirely within the context of (1.3), i.e. in terms of the particle energy only.

Further, a careful consideration of the approximations involved in the analysis has lead to the conclusion that *neither* the exponentially small corrections of order $e^{-\varepsilon/4}$ – arising in the solution of the two-dimensional model and emphasized in refs. [3, 18] – *nor* the powerlike correction terms of order ε^{-1} – emerging from the one-dimensional BHL-model (2.18) or (4.56) – have any quantitative significance. Nevertheless, powerlike corrections exist according to an analysis [8] directly from (1.3), albeit of the order of $(\omega_b/\lambda)(\vartheta/U_b)^{1/2} \approx (\varepsilon\lambda/\omega_b)^{-1/2}$ rather than ε^{-1}.

Finally, a problem has been pinpointed by looking into the energy distributions themselves that underly the result for the decay rate (which is usually the only quantity which is calculated explicitly). Namely, while the theory based on (2.7) yields the correct moderate-to-strong damping value (4.46) for the decay rate, we have come to the conclusion that the underlying densities for the incoming as well as the outgoing particles are incorrect. They do not equally share the necessary deviations from equilibrium, as they should. The reason for this failure is that the Green's function of (2.7) is incapable of propagating such deviations through the potential hole.

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