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Reaction rate theory: weak- to strong-friction turnover in Kramers' Fokker–Planck model

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Abstract

We present a unified treatment for both weak and strong friction – including the turnover regime – of Kramers' Fokker–Planck model for activated rate processes. *No* recourse to a specific microscopic model (à la Grabert et al.) or Langevin dynamics (à la Graham) will be made. Upon introducing some new theoretical concepts such as a *constrained* Gaussian transformation (CGT) and a *dynamical* extension of phase space (EPS), the analysis proceeds in terms of the unstable-mode energy and is systematic in a small parameter. We also introduce a nonlinear toy model for barrier recrossing for a simplified discussion of aspects like finite-barrier corrections, the boundary layer approximation, and exact solution in the absence of potential conditions.

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1. Introduction

The very existence of a nonequilibrium reaction process necessarily implies deviations from the exact Boltzmann equilibrium distribution. However, standard transition-state theory (TST, dating back to the work of Van 't Hoff [1] and Arrhenius [2] concerning chemical reactions) is a purely kinetic theory based on mere equilibrium statistical mechanics. In particular, it requires perfect thermal equilibration at the transition state (i.e., at the top of the energy barrier which separates one metastable potential well from another). Therefore, it does not permit the analysis of (i) depletion effects and (ii) recrossings at the barrier, which are due to the dynamical coupling of the reactive complex to its environment (e.g., a solvent or solid-state matrix).

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In a famous paper [4] Kramers investigated the validity of TST by means of a Fokker–Planck model for chemical reactions, describing the escape out of the well as Brownian motion along the reaction coordinate in a bistable potential $U(x)$. The fluctuations are provided by the environment (for example a thermal reservoir), so that the reaction process stops if the coupling to the heat bath vanishes (see also Refs. [5,6]).

This weak-friction limit is most easily understood in terms of energy diffusion, around a deterministic trajectory with conserved total mechanical energy of the particle. As a result the energy is a slow variable, and the attempt rate ν_a in the general expression for the escape rate

$$\Gamma = \nu_a e^{-\beta U_b} \tag{1.1}$$

becomes $\nu_a(\lambda \to 0) = 2\lambda\beta I_b \omega_0/2\pi$. The barrier height is denoted by U_b, 2λ is the friction coefficient, ω_0 is the harmonic frequency of the potential well, $\beta = 1/k_B T$, while $2\lambda I_b$ is the energy loss per round-trip through the well (at the barrier peak energy $E_p = 0$) because $I_b = \oint p\,dx$ is the classical action integral. For example, one has $I_b = 36U_b/5\omega_b$ and $I_b = 16U_b/3\omega_b$ for the cubic and quartic potential defined below (2.1), respectively, with ω_b the harmonic barrier curvature frequency.

The above result for $\nu_a(\lambda \to 0)$ is valid if $2\lambda\beta I_b \ll 1$. In this limit the reduction of the rate w.r.t. the standard TST value $\nu_a = \omega_0/2\pi$ is a consequence of the aforementioned deviations from exact equilibrium. Such depletion effects were calculated in detail by Büttiker et al. [7], and by Mel'nikov and Meshkov [8] in an elaboration of Kramers' weak-damping analysis (see also Ref. [9]). In both Refs. [7] and [8], *increasing* the friction ultimately leads to the simple TST result. This is incorrect, however, since if the coupling to the environment becomes very strong (i.e., not only $2\lambda\beta I_b \gg 1$, but also $\lambda/\omega_b \gg 1$), the reaction rate again tends to zero. Namely, in the latter case the particle coordinate (rather than the energy) becomes the slow variable and the activation process reduces to Smoluchowski diffusion [14]. This yields $\nu_a(\lambda \to \infty) = \omega_0\omega_b/2\pi\lambda$. Here the lowering of the rate relative to standard TST is a consequence of diffusive recrossing of particles at the barrier peak.

Such recrossings make the transition state imperfectly absorbing (and hence its original notion ill-defined). For this situation the Smoluchowski result generalizes to $\nu_a = \kappa\omega_0/2\pi$, where

$$\kappa = [1 + (\lambda/\omega_b)^2]^{1/2} - \lambda/\omega_b \tag{1.2}$$

is known as the Kramers correction factor for moderate-to-strong friction values. According to this result, now *decreasing* the friction ultimately leads to the simple TST value (which is also incorrect). For a review, see Ref. [17]. Clearly, Kramers' original analysis does not provide a unified description for all values of the friction (nor do its simple extensions). Such a treatment has been lacking in particular for those intermediate values of λ where the physics changes from energy diffusion (depletion) to spatial diffusion (recrossings), and where the rate Γ reaches a maximum. This is known as the Kramers turnover problem.

Several attempts were made to bridge the two Kramers limits. See, for example, Refs. [7–9,12,18,19]. All of them were based the Kramers Fokker–Planck equation, but did not involve a unified picture of the reaction dynamics, leading to considerable variation in the predictions for the turnover region [21].

On the other hand, on the basis of a microscopic model (see for example Refs. [24–27]) Pollak (Ref. [23], see also [22]) showed that $\kappa\omega_b$ is the eigen-frequency of the only unstable normal mode at the barrier peak. For an Ohmic environment this model indeed implies Kramers' Fokker–Planck process. The reverse, however, is not necessarily true.

In Refs. [28,29] a unified treatment of the Kramers turnover problem was given in an extension of Pollak's work, by introducing the energy E of the unstable barrier mode (instead of the particle energy E_p). The energy E is a collective variable mixing the particle and microscopic environmental degrees of freedom, allowing the connection of Pollak's multi-dimensional TST with the theory of Mel'nikov and Meshkov [8]. Similarly, by mixing particle and noise variables Graham [31] formulated a 'macroscopic' turnover theory a la Grabert et al. on the basis of the Langevin equation derived from the microscopic model. However, the analyses of both Refs. [29] and [31] still leave us with the challenge [9,30,31] of clarifying how one should introduce the unstable-mode energy E (which appears to play such a crucial role in the high-dimensional microscopic analysis) within the context of the low-dimensional macroscopic Fokker–Planck model itself.

This challenge will be fully met in the present paper. In Section 2 we investigate the separatrix of the particle motion near a parabolic barrier. The stable and unstable directions at the saddle point are used to define a transformation from (x, p) to (η, ζ). In Section 3, the noise along the unstable coordinate η is eliminated by means of a Gaussian integral transformation [32,33], a constraint taking care of preserving the dynamical significance of the potential $U(x)$. In Section 4 phase space is extended along a new coordinate ϑ. The dynamically stable coordinate ϑ is defined such that upon transforming from (ϑ, η, ζ) to new coordinates (u, v, w) the pair $(u, v = \dot{u})$ represents the unstable barrier mode. This mode is completely deterministic in the barrier region. Outside this region it couples to the original environment only indirectly via the w-mode. This allows the definition of the unstable-mode energy E.

In Section 5 the equilibrium distribution $R_{eq}(E)$ in extended phase space (EPS) is shown to be Boltzmannian (in terms of E). Its normalization is discussed in Appendix B.1. The existence of a quasi-equilibrium distribution like that of Kramers – but *without* recrossings – allows a calculation of the Kramers–Smoluchowski escape rate by means of TST in EPS; this is the low-dimensional version of Pollak's theory [23]. Finite-barrier corrections are considered in a systematic analysis in Appendix C, while Appendix F elucidates the physical origin of quasi-equilibrium distributions. Section 6 provides a systematic analysis of the quasi-equilibrium distribution $R(u, v, w)$ in EPS in the weak-friction regime. Using a fictitious time variable, a 'system size'-type [14] expansion of the Fokker–Planck equation for R is developed by means of

a simultaneous scaling of friction ($\lambda \sim \Omega^{-1/2} \to 0$) and temperature ($\beta \sim \Omega^{1/2} \to \infty$). The resulting leading order Green's function is a Gaussian in terms of E and obeys detailed balance with respect to $R_{\mathrm{eq}}(E)$. In Section 7 the decay rate is obtained by combining the results from Sections 5 and 6 in a unified treatment. Finally, we emphasize that the appendices form a substantial part of this article. In particular, Appendix G presents a nonlinear toy model for barrier crossing which allows us to clarify aspects as finite-barrier corrections and the boundary layer approximation, and moreover in one case has an exact solution in the absence of potential conditions.

The present analysis among other things clarifies (or, in other cases, avoids) certain intricacies involved in the microscopic formulation, such as those concerning the systematic nature of corrections to the leading result. It also (re)establishes the microscopic-model independence of activated rate theory based on Kramers' stochastic process. This article is based on a chapter from the Ph.D. thesis [34] of one of the authors, which is available on request. Part of the material has been reported previously in [35].

2. The separatrix: stable and unstable barrier modes

Kramers' process of Brownian motion in an externally applied potential $U(x)$ is uniquely defined by the Fokker–Planck equation

$$\frac{\partial P}{\partial t} = -p\frac{\partial P}{\partial x} + U'(x)\frac{\partial P}{\partial p} + 2\lambda\frac{\partial}{\partial p}\left(pP + \frac{1}{\beta}\frac{\partial P}{\partial p}\right), \tag{2.1}$$

where $P(x,p,t)$ is the probability density to find the particle (with unit mass, for convenience) at position x with momentum p at time t. In order to model an activated rate process, the potential should have (at least) one local minimum with an adjacent barrier. Typical model potentials are the cubic $U_{\mathrm{c}}(x) = -\frac{1}{2}\omega_{\mathrm{b}}^2 x^2(1+x/a)$ and the quartic $U_{\mathrm{q}}(x) = -\frac{1}{2}\omega_{\mathrm{b}}^2 x^2(1-x^2/a^2)$. In general, near the barrier peak $U(x) \approx -\frac{1}{2}\omega_{\mathrm{b}}^2 x^2$ while near the potential minimum $U(x) \approx -U_{\mathrm{b}} + \frac{1}{2}\omega_0^2(x-x_0)^2$. For the cubic potential, the relations between the parameters characterizing the well and those pertaining to the barrier read $U_{\mathrm{b}} = 2\omega_{\mathrm{b}}^2 a^2/27$, $\omega_0 = \omega_{\mathrm{b}}$, and $x_0 = -2a/3$. For the quartic potential one has $U_{\mathrm{b}} = \frac{1}{8}\omega_{\mathrm{b}}^2 a^2$, $\omega_0 = \sqrt{2}\,\omega_{\mathrm{b}}$, and $x_0 = \pm\frac{1}{2}\sqrt{2}\,a$.

At zero temperature (2.1) reduces to the Liouville equation corresponding to the deterministic dynamics $\dot{x} = p$, $\dot{p} = -2\lambda p - U'(x)$. In the harmonic barrier region the separatrix $\mathscr{S}$ [12,17,36] for these dynamics is given by $p(x|\mathscr{S}) = -(\omega_{\mathrm{b}}/\kappa)x$, where κ is Kramers' coefficient (1.2). $\mathscr{S}$ is a repeller, i.e., the barrier motion is unstable in a direction orthogonal to $\mathscr{S}$. On the other hand, the barrier motion is stable towards the attractor $\mathscr{T}$ [12], which is given by $p(x|\mathscr{T}) = \kappa\omega_{\mathrm{b}}x$. Therefore, we introduce coordinates

$$\eta = x + p/\omega_2, \qquad \zeta = x - p/\omega_1, \tag{2.2}$$

with $\omega_1 = \kappa\omega_b$ and $\omega_2 = \omega_b/\kappa$, so that the barrier motion along η is unstable and that along ζ is stable. One finds $\dot{\eta} = F_1(\eta,\zeta)$ and $\dot{\zeta} = F_2(\eta,\zeta)$, with

$$F_1(\eta,\zeta) = \omega_1\eta - U_a'(x)/\omega_2, \qquad F_2(\eta,\zeta) = -\omega_2\zeta + U_a'(x)/\omega_1 , \tag{2.3}$$

where $U_a(x) = \frac{1}{2}\omega_b^2 x^2 + U(x)$ is the anharmonic part of the barrier potential. Transforming (2.1) from (x,p) to (η,ζ) yields (cf. Appendix A)

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial\eta}(F_1 P) - \frac{\partial}{\partial\zeta}(F_2 P) + \frac{\partial^2}{\partial\eta^2}(\mathscr{D}_{11}P) + 2\frac{\partial^2}{\partial\eta\,\partial\zeta}(\mathscr{D}_{12}P) + \frac{\partial^2}{\partial\zeta^2}(\mathscr{D}_{22}P) , \tag{2.4}$$

where

$$\mathscr{D}_{11} = 2\lambda/\beta\omega_2^2 , \qquad \mathscr{D}_{12} = -2\lambda/\beta\omega_b^2 , \qquad \mathscr{D}_{22} = 2\lambda/\beta\omega_1^2 . \tag{2.5}$$

Of course, since $\omega_1\omega_2 = \omega_b^2$, the diffusion tensor $\mathbf{D} = \{\mathscr{D}_{kl}\}$ given by (2.5) is singular but nonnegative ($\det\mathbf{D} = 0$, $\mathscr{D}_{kk} > 0$).

3. The constrained Gaussian transformation

Let us now map the process $P(\eta,\zeta,t)$ onto $Q(\eta,\zeta,t)$, such that for the new process the component of the diffusion tensor in the unstable direction η will be zero. Generalizing earlier work (in the study of one-dimensional unstable systems [32,33]), we introduce the *constrained* Gaussian (integral) transformation (CGT)

$$Q(\tilde{\eta},\tilde{\zeta},t) = \frac{1}{2\kappa r}\left(\frac{K}{\pi}\right)^{1/2}\int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} d\zeta\, e^{-K(\tilde{\zeta}-\zeta)^2}\,\delta(\tilde{x}-x)\,P(\eta,\zeta,t) . \tag{3.1}$$

For the present purpose K will be time-independent. The constraint $\delta(\tilde{x}-x)$ takes care of conserving the dynamical significance of the potential $U_a(x)$. Since with $r \equiv \frac{1}{2}(\kappa+\kappa^{-1})$ one has $x = (\eta+\kappa^2\zeta)/2\kappa r$, (3.1) leads to

$$Q(\tilde{\eta},\tilde{\zeta},t) = \left(\frac{K}{\pi}\right)^{1/2}\int_{-\infty}^{+\infty} d\zeta\, e^{-K(\tilde{\zeta}-\zeta)^2} P[\tilde{\eta}+\kappa^2(\tilde{\zeta}-\zeta),\zeta,t] . \tag{3.2}$$

This CGT implies a Fokker–Planck operator transformation, such that if (2.4) is written as

$$\frac{\partial P}{\partial t} = \mathbb{F}\left[\frac{\partial}{\partial\eta},\frac{\partial}{\partial\zeta},\eta,\zeta\right]P , \tag{3.3}$$

then

$$\frac{\partial Q}{\partial t} = \mathbb{F}\left[\frac{\partial}{\partial\eta},\frac{\partial}{\partial\zeta},\eta-\frac{\kappa^2}{2K}\left(\frac{\partial}{\partial\zeta}-\kappa^2\frac{\partial}{\partial\eta}\right),\zeta+\frac{1}{2K}\left(\frac{\partial}{\partial\zeta}-\kappa^2\frac{\partial}{\partial\eta}\right)\right]Q . \tag{3.4}$$

In (3.3) $\mathbb{F}P$ is unambiguously defined with all operators $\partial/\partial\eta$ and $\partial/\partial\zeta$ ordered to the left. Generally, with $K > 0$, the CGT (3.1), (3.2) has the property of shifting noise *from* the unstable *to* the stable degree of freedom. With $K = \beta\omega_1^3/4\lambda$, the Q-flow along η becomes deterministic (in the harmonic barrier region). In that case (3.4) yields

$$\frac{\partial Q}{\partial t} = -\frac{\partial}{\partial\eta}(F_1 Q) - \frac{\partial}{\partial\zeta}(F_2 Q) + \frac{\partial^2}{\partial\eta^2}(D_{11}Q) + 2\frac{\partial^2}{\partial\eta\,\partial\zeta}(D_{12}Q) + \frac{\partial^2}{\partial\zeta^2}(D_{22}Q)\,, \tag{3.5}$$

where $F_k = F_k(\eta,\zeta)$ as defined in (2.3), and where

$$D_{11} = 0\,, \qquad D_{12} = -2\lambda r/\beta\kappa\omega_b^2\,, \qquad D_{22} = 4\lambda r/\beta\kappa\omega_1^2\,, \tag{3.6}$$

with (see also above Eq. (3.2))

$$r = [1 + (\lambda/\omega_b)^2]^{1/2}\,. \tag{3.7}$$

The diffusion tensor $\mathbf{D}$ defined by (3.6) is nonsingular but indefinite ($\det\mathbf{D} < 0$, $D_{kk} \geqslant 0$). This merely means that, while it is well-defined, Eq. (3.5) – or its extension (4.3) below – is unsuitable for studying initial value problems,[1] and indeed we shall carefully refrain from doing so (in particular in Section 6, see also Appendix D.2).

4. Dynamical phase space extension: the unstable-mode energy

The stochastic process (3.5), (3.6) is deterministic in the unstable direction η in the harmonic barrier region. Since this region suffices (apart from finite-barrier corrections; see Appendix C) for the description of the escape process in the moderate-to-strong friction regime, the Kramers–Smoluchowski rate can be calculated from (3.5), (3.6) by means of TST [31]. An analysis unifying this result with the small-friction regime will be given in terms of the unstable-mode energy E à la Grabert [28,29]. Within the framework of Kramers' Fokker–Planck equation (FPE) the definition of E is nontrivial. This problem [9,30,31] will be tackled in the present section. Its solution requires the introduction of the concept of a *dynamical extension* of phase space.

Let us embed the phase space (η,ζ) in a three-dimensional space (ϑ,η,ζ). In this extended space we define a process $R(\vartheta,\eta,\zeta,t)$, such that $Q(\eta,\zeta,t)$ is the marginal distribution

$$Q(\eta,\zeta,t) = \int_{-\infty}^{+\infty} R(\vartheta,\eta,\zeta,t)\,\mathrm{d}\vartheta \tag{4.1}$$

[1] As an illustration, in one space dimension a diffusion equation with a negative diffusion coefficient is equivalent to an equation with $D > 0$ evolving backwards in time. Thus, the Fourier coefficients of the relevant density increase without bound. This increase is fastest for the highest order coefficients, and for any initial distribution the evolution is unstable.

in the subspace (η,ζ). The extension becomes unambiguous upon imposing dynamics along ϑ. These dynamics will be defined by the deterministic flow $\dot{\vartheta} = F_0(\vartheta,\eta,\zeta)$, with

$$F_0(\vartheta,\eta,\zeta) = -\omega_1\vartheta - U_a'(x)/\omega_2 \,. \tag{4.2}$$

In view of the subsequent rotation (4.4) in the (ϑ,η)-plane, any diffusion along ϑ would add to the flow along the unstable coordinate u (and its momentum $v = \dot{u}$), thereby hampering TST. In addition, as will be shown in Section 5, with the noiseless flow (4.2) the extended process R has the correct Maxwell–Boltzmann equilibrium properties. Therefore, the extended version of (3.5), (3.6) reads

$$\frac{\partial R}{\partial t} = -\frac{\partial}{\partial\vartheta}(F_0R) - \frac{\partial}{\partial\eta}(F_1R) - \frac{\partial}{\partial\zeta}(F_2R) + 2\frac{\partial^2}{\partial\eta\,\partial\zeta}(D_{12}R) + \frac{\partial^2}{\partial\zeta^2}(D_{22}R) \,. \tag{4.3}$$

Now let

$$u = \tfrac{1}{2}(\eta - \vartheta) \,, \qquad v = \tfrac{1}{2}\omega_1(\eta + \vartheta) \,, \qquad w = \zeta + \vartheta/\kappa^2 \,. \tag{4.4}$$

Transforming (4.3) from (ϑ,η,ζ) to (u,v,w) gives

$$\begin{aligned}\frac{\partial R}{\partial t} = &-v\frac{\partial R}{\partial u} - \kappa^2[\omega_b^2 u - U_a'(x)]\frac{\partial R}{\partial v} - \frac{\partial}{\partial w}(\mathsf{F}_w R) \\ &+ 2\frac{\partial^2}{\partial u\,\partial w}(\mathsf{D}_{uw}R) + 2\frac{\partial^2}{\partial v\,\partial w}(\mathsf{D}_{vw}R) + \frac{\partial^2}{\partial w^2}(\mathsf{D}_{ww}R) \,,\end{aligned} \tag{4.5}$$

with $x = (u + \frac{1}{2}\kappa^2 w)/\kappa r$, and

$$\mathsf{F}_w(u,v,w) = -\omega_2 w - \frac{2\lambda}{\kappa^2}(u - v/\omega_1) \,, \tag{4.6}$$

$$\mathsf{D}_{uw} = -\tfrac{1}{4}\kappa^2\mathsf{D}_{ww} \,, \qquad \mathsf{D}_{vw} = -\tfrac{1}{4}\kappa^3\omega_b\mathsf{D}_{ww} \,, \qquad \mathsf{D}_{ww} = 4\lambda r/\beta\kappa\omega_1^2 \,. \tag{4.7}$$

Note that, for fixed w, the dynamics in the (u,v)-plane is deterministic and conservative. In particular, in the harmonic barrier region this flow ($\dot{u} = v$, $\dot{v} = \omega_1^2 u$) decouples from the environmental variable w and is unstable. Moreover, outside this region the pair $(u, v = \dot{u})$ keeps its mechanical significance because $\partial x/\partial v = 0$. It is not difficult to show that – up to the trivial rescaling $(u,v,w) \mapsto (c_1u, c_1v, c_2w)$ – the linear transformation (4.4) is the only one with these properties if one imposes the final condition that w should only be driven by anharmonic effects, i.e., that F_w involves u and v only as $u - v/\omega_1$, which vanishes in the harmonic region for the 'bounce' path in extended phase space (EPS). See further Section 6.

The unstable-mode energy [28,31] is now defined as

$$E = \tfrac{1}{2}(v^2 - \omega_1^2u^2) + \kappa^3 r U_a(x) \,, \tag{4.8}$$

so that for the deterministic part of the dynamics $\dot{u} = \partial E/\partial v$ and $\dot{v} = -\partial E/\partial u$. Note that $\partial E/\partial w = \frac{1}{2}\kappa^4 U_a'(x)$.

5. The equilibrium distribution and barrier recrossings: transition-state theory of the Kramers–Smoluchowski rate

Let us rewrite (4.5)–(4.7) in terms of (u, E, w) [4,7–10,37,38]. The result reads

$$\frac{\partial R}{\partial t} = -v\frac{\partial R}{\partial u} + \frac{\partial J}{\partial w} + \frac{1}{2}\kappa^4 U_a'(x)\frac{\partial J}{\partial E}\,, \tag{5.1}$$

where, to be certain, in this and the following section $\partial_u = \partial_u|_{E,w}$ and similarly for ∂_w, and where J is given by

$$J = -\frac{1}{2}\kappa^2 \mathsf{D}_{ww}\frac{\partial R}{\partial u} + \omega_2\left(wR + \frac{1}{\beta_w}\frac{\partial R}{\partial w}\right) + \frac{2\lambda}{\kappa^2}(u - v/\omega_1)\left(R + \frac{1}{\beta_E}\frac{\partial R}{\partial E}\right), \tag{5.2}$$

with $\beta_w = \omega_2/\mathsf{D}_{ww}$ and $\beta_E = \beta/\kappa^3 r$, and where $R(u, E, w)$ is still normalized according to $\int du \int dv \int dw\, R = 1$. The equilibrium distribution is defined by (i) $\partial R_{eq}/\partial t = 0$, (ii) $\partial R_{eq}/\partial u = 0$, and (iii) $J_{eq} = 0$. The process (5.1), (5.2) unambiguously yields

$$R_{eq}(E, w) = \mathcal{N} e^{-\beta_E E - \beta_w w^2/2}\,. \tag{5.3}$$

The value of $\mathcal{N}$ corresponding to normalization in the local (harmonic) minimum of the potential $U(x)$ is found by noticing that the marginal distribution $Q_{eq}(\eta, \zeta)$ as resulting from (5.3) – by means of (4.1) – should be identical to $Q_{eq}(\tilde{\eta}, \tilde{\zeta})$ as resulting from the equilibrium distribution $P_{eq}(x, p) = N_0 \exp(-\beta E_p)$ of Kramers' FPE (2.1) – by means of (3.1). Note that $E \neq E_p$, the latter representing the *particle* energy. For P_{eq} one has $N_0 = (\beta\omega_0/2\pi)\exp(-\beta U_b)$. The analysis most easily proceeds in the (harmonic) barrier region, see Appendix B.1. The result reads

$$\mathcal{N} = \kappa\frac{\beta_E\omega_0}{2\pi}\left(\frac{\beta_w}{2\pi}\right)^{1/2} e^{-\beta U_b}\,. \tag{5.4}$$

By rescaling $E/\kappa^3 r \mapsto E$ one can make $\beta_E = \beta$. In that case (which will be implicit in Section 6) the normalization constant of the marginal distribution $R_{eq}(E)$, of course, reads $\mathcal{N}_E = (\kappa\beta\omega_0/2\pi)\exp(-\beta U_b)$.

Recalling the remarks made in Section 4, let us now calculate the decay rate by means of (5.3), (5.4). In EPS the decay rate is given by (Ref. [4], see also Appendix B.2)

$$\Gamma = -\frac{\partial}{\partial t}\int_{-\infty}^{0} du \int_{-\infty}^{+\infty} dv \int_{-\infty}^{+\infty} dw\, R(u, v, w)\,, \tag{5.5}$$

where $R(u, v, w)$ is the *quasi*-equilibrium distribution (see also Appendix F) normalized according to (5.4). Using (4.5) for $\partial R/\partial t$ in (5.5), one finds

$$\Gamma = \int_{-\infty}^{+\infty} dv \int_{-\infty}^{+\infty} dw\, v R(0, v, w)\,. \tag{5.6}$$

This result hinges on the absence in (4.5) of direct diffusion along the unstable degrees of freedom (u, v). Since the (u, v)-flow decouples from the environmental degree of freedom w in the harmonic barrier region, this feature also implies the absence of barrier recrossings (apart from finite-barrier corrections $\sim 1/\beta U_b$; see Appendix C). Hence, one has $R(0, v, w) = \theta(v) R_{eq}(E, w)$, where $\theta(v)$ is the unit step function, so that (5.6) becomes

$$\Gamma = \int_0^{\infty} dE \int_{-\infty}^{+\infty} dw\, R_{eq}(E, w)\,. \tag{5.7}$$

Using (5.3), (5.4) one thus finds the escape rate (1.1) with the Kramers–Smoluchowski value $\nu_a = \kappa\omega_0/2\pi$ for the attempt rate. This establishes the validity of the EPS-version of TST in the moderate-to-strong damping regime.

6. Unstable-mode energy diffusion

In Section 5 we have met the challenge (posed by the moderate-to-strong damping theory of Pollak [23]) to formulate a low-dimensional Fokker–Planck version of multi-dimensional TST. That is, by the combination of the CGT and EPS the (stochastic) dynamics of recrossings have been projected onto the equilibrium statistics.

For very weak damping, deviations from exact equilibrium (depletion effects) invalidate the analysis of Section 5. However, in (5.1) direct diffusion along the unstable E-axis is absent in the harmonic barrier region for *all* values of the friction. This feature implies the possibility of a unified treatment like that of Grabert [28]. In what follows we present a systematic simultaneous small-friction plus low-temperature expansion (FTE) for the (quasi-)equilibrium state of (5.1).

Depletion effects are important if $2\lambda\beta I_b \ll 1$. In order to cover *all* values of $2\lambda\beta I_b$ in a single expansion, let $\lambda \mapsto \lambda\Omega^{-1/2}$ and $\beta \mapsto \beta\Omega^{1/2}$, with $\Omega \to \infty$. As a consequence, to leading order in Ω one has $\beta_w \mapsto \beta_w\Omega$ and $\mathsf{D}_{ww} \mapsto \mathsf{D}_{ww}\Omega^{-1}$. In addition, let both $w \mapsto w\Omega^{-1/2}$ and $E/\kappa^3 r \mapsto E\Omega^{-1/2}$ (so that $\beta_E = \beta$ for *all* values of the friction). Upon introducing Ω into (5.1) (with $\partial R/\partial t = 0$, and expanding $\kappa \sim \Omega^0$, $r \sim \Omega^0$, $U_a(x) \sim \Omega^0$, $v(u, E, w) \sim \Omega^0$, as well as $R = R^{(0)} + \Omega^{-1/2} R^{(1)} + \Omega^{-1} R^{(2)} + \cdots$ as power series in $\Omega^{-1/2}$), the leading terms ($\sim\Omega^0$) yield

$$\frac{\partial R}{\partial \tau} = \frac{\partial J}{\partial w} + \frac{1}{2}\mathscr{U}_a'(\tau)\frac{\partial J}{\partial E}\,, \tag{6.1}$$

with

$$J = \omega_b \left(wR + \frac{4\lambda}{\beta\omega_b^3}\frac{\partial R}{\partial w} \right) + 2\lambda(\alpha(\tau) - v(\tau)/\omega_b)\left(R + \frac{1}{\beta}\frac{\partial R}{\partial E} \right), \tag{6.2}$$

where the *fictitious* time τ (in place of u) is defined by the nonlinear mapping $u = \alpha(\tau)$, with $\dot{\alpha} = v(\tau)$, $v(\tau) = \pm[-2\mathscr{U}(\tau)]^{1/2}$ and $\mathscr{U}(\tau) = U(\alpha(\tau))$. To make sure, $\mathscr{U}_a'(\tau) = U_a'(\alpha(\tau))$. Note that $v(\tau) = v^{(0)}(u)$, that $v^{(0)}(u)\,\partial R/\partial u = \partial R/\partial\tau$, and that $\{\dot{\alpha} = v,$

$\dot{v} = -U'(u)\}$ represents the Hamiltonian motion in the original potential at the barrier peak energy ($E=0$). The trajectory $\{u(\tau), v(\tau)\}$ is a 'bounce'-type configuration [15–17] in EPS. For the cubic potential one finds $u(\tau) = -a/\cosh^2(\frac{1}{2}\omega_b\tau)$. The quartic potential yields $u(\tau) = -a/\cosh(\omega_b\tau)$.

The result (6.1), (6.2) is a two-dimensional *linear* FPE for $R(E,w,\tau)$ with τ-dependent coefficients [14]. Hence, the fundamental solution is a Gaussian. The equations of motion for its first moments $\mathscr{E}(\tau) = \langle E\rangle$ and $\mathscr{W}(\tau) = \langle w\rangle$ read

$$\dot{\mathscr{E}} = \tfrac{1}{2}\mathscr{U}_a'(\tau)\dot{\mathscr{W}}, \tag{6.3a}$$

$$\dot{\mathscr{W}} = -\omega_b\mathscr{W} - 2\lambda(u - v/\omega_b)\,. \tag{6.3b}$$

Note that the change in energy is due to the work done by the environmental mode w [31]. For the variances $\sigma_{EE}(\tau) = \langle(E-\mathscr{E})^2\rangle$, $\sigma_{wE}(\tau) = \langle(w-\mathscr{W})(E-\mathscr{E})\rangle$ and $\sigma_{ww}(\tau) = \langle(w-\mathscr{W})^2\rangle$ one obtains

$$\begin{aligned}
\dot{\sigma}_{EE} &= -\omega_b\,\mathscr{U}_a'(\tau)\left(\sigma_{wE} - \frac{2\lambda}{\beta\omega_b}(u - v/\omega_b)\right),\\
\dot{\sigma}_{wE} &= -\omega_b\left(\sigma_{wE} - \frac{2\lambda}{\beta\omega_b}(u - v/\omega_b)\right) - \frac{1}{2}\omega_b\,\mathscr{U}_a'(\tau)\left(\sigma_{ww} - \frac{4\lambda}{\beta\omega_b^3}\right),\\
\dot{\sigma}_{ww} &= -2\omega_b\left(\sigma_{ww} - \frac{4\lambda}{\beta\omega_b^3}\right).
\end{aligned} \tag{6.4}$$

With the environment in equilibrium at $\tau = -\infty$, one has $\sigma_{ww} = 4\lambda/\beta\omega_b^3$ for all τ. Hence, comparison of (6.4) and (6.3), and noticing that $\sigma_{wE}(-\infty) = \mathscr{W}(-\infty) = 0$, yields $\sigma_{wE}(\tau) = -\mathscr{W}(\tau)/\beta$ and the fluctuation–dissipation relation

$$\sigma_{EE}(\tau) = -2\Delta\mathscr{E}(\tau)/\beta\,, \tag{6.5}$$

with $\Delta\mathscr{E}(\tau) = \mathscr{E}(\tau) - \mathscr{E}(-\infty)$. It is easily shown that the energy loss per round-trip resulting from (6.3) exactly equals $-\Delta\mathscr{E}(\infty) = 2\lambda I_b$, see Appendix D.1. In view of the remark at the end of Section 3 it further is gratifying that the equilibrium condition on w leads to a positive definite covariance matrix Σ; see Appendix D.2.

For the calculation of the escape rate (5.5) one only needs the marginal distribution $R(E,\tau) = \int R(E,w,\tau)\,dw$. The marginal Green's function [8,9] is a Gaussian with its first and second cumulants related by (6.5), viz.,

$$G_\tau(E|E') = [\beta/4\pi|\Delta\mathscr{E}(\tau)|]^{1/2}\exp\left\{-\beta\frac{[E-E'-\Delta\mathscr{E}(\tau)]^2}{4|\Delta\mathscr{E}(\tau)|}\right\}, \tag{6.6}$$

and obeys detailed balance, i.e., $G(E|E')R_{eq}(E') = G(E'|E)R_{eq}(E)$ with $R_{eq}(E) = \mathscr{N}_E\exp(-\beta E)$ being the equilibrium distribution in EPS at $\beta_E = \beta$ according to Section 5.

7. Generalized transition-state theory

The Green's function (6.6) allows the problem to be rewritten in its equivalent integral form. In particular, one has

$$R(E,\infty) = \int_{-\infty}^{+\infty} W(E|E')R(E',-\infty)\,\mathrm{d}E' , \tag{7.1}$$

where the transition probability density $W(E|E') = G_\infty(E|E')$. The TST-version of (7.1) amounts to $R(E,-\infty) = \theta(-E)R(E,\infty)$, so that

$$R(E) = \int_{-\infty}^{0} W(E|E')R(E')\,\mathrm{d}E' , \tag{7.2}$$

where $R(E) = R(E,\infty)$ is the *quasi*-equilibrium distribution subject to the boundary conditions $R(E) \to R_{\mathrm{eq}}(E)$ if $E \to -\infty$, and $R(E) \to 0$ if $E \to \infty$.

The lower limit of E'-integration equals $E' = -U_{\mathrm{b}}\Omega^{-1/2} \to -\infty$ because of the Ω-scaling (see above Eq. (6.1)). Besides being technically convenient (i.e., admitting a Wiener–Hopf-type solution) the infinite interval of integration is vital for obtaining any nonzero solution. Namely, on an arbitrary finite interval $-U \leqslant E' \leqslant 0$ the function R has a finite probability norm and hence could not be invariant under the mapping (7.2) in which part of this probability escapes to $E > 0$. Mathematically, this is merely an instance of the contraction mapping theorem.[2] Physically, the infinite range $-\infty \leqslant E' \leqslant 0$ mimics a reservoir continuously supplying the escaping particles (cf. Appendix B.2).[3]

The integral equation (7.2) can be solved by the Wiener–Hopf method (Ref. [9], see also Appendix E), and according to Mel'nikov and Meshkov [8] the result for the decay rate $\Gamma = \int_0^\infty R(E)\,\mathrm{d}E$ is given by (1.1) with

$$\nu_{\mathrm{a}} = \frac{\kappa\omega_0}{2\pi} \exp\left\{ \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\mathrm{d}y}{1+y^2} \ln(1 - \mathrm{e}^{-\varepsilon(1+y^2)/4}) \right\}, \tag{7.3}$$

where $\varepsilon = \beta|\Delta\mathscr{E}(\infty)| = 2\lambda\beta I_{\mathrm{b}}$. If $\varepsilon \ll 1$, (7.3) reduces to Kramers' weak-friction result $\nu_{\mathrm{a}}(\lambda \to 0) = 2\lambda\beta I_{\mathrm{b}}\omega_0/2\pi$ as [8] $\nu_{\mathrm{a}}(\varepsilon \ll 1) \approx (\varepsilon\omega_0/2\pi)[1 - 0.82\varepsilon^{1/2}]$. On the other hand, if $\varepsilon \gg 1$, (7.3) reduces to Kramers' moderate-to-strong friction result $\nu_{\mathrm{a}} = \kappa\omega_0/2\pi$ as $\nu_{\mathrm{a}}(\varepsilon \gg 1) \approx (\kappa\omega_0/2\pi)[1 - 1.13\varepsilon^{-1/2}\mathrm{e}^{-\varepsilon/4}]$.

[2] In general, the theorem (e.g., [39]) also yields the existence of the – unique – solution; for the linear operator at hand, however, existence is trivial.

[3] This is analogous to the infinite strings in Ch. 3 of Ref. [34] (published in Physica A 226 (1996) 64), which model reservoirs continuously supplying phonons in the Kapitza boundary resistance problem.

8. Discussion

The present unified treatment of Kramers escape – in Section 7, leading to Eqs. (1.1), (7.3) for the rate Γ – is due to the possibility of (low-dimensional) transition-state theory (TST) in extended phase space (EPS) for both very weak and moderate-to-strong values of the damping. Specifically, the EPS construction (Section 4) enables one to define the unstable-mode energy E, whereas the constrained Gaussian integral transformation (Section 3) is essential for making TST in terms of E possible.

The rate (7.3) differs subtly from the results of both Mel'nikov and Meshkov [8], and of Grabert et al. [28,29] and Graham [31]. The present theory allows for a unified analysis of depletion and barrier-recrossing, because it proceeds in terms of E rather than the particle energy E_p of Ref. [8]. Therefore, the authors of the latter paper could introduce the Kramers correction factor κ in (7.3) only as an *ad hoc* prefactor (see also Refs. [9,20]). On the other hand, the work of both Grabert [28,29] (microscopy) and Graham [31] (Langevin analysis) *does* involve E.

From the present systematic expansion (Section 6), however, it is clear that the integral equation (7.2) – with a Gaussian propagator W – is only valid to leading order in the small-friction plus low-temperature expansion (FTE). This leading order is sufficient for describing Kramers turnover, since it shows (below Eq. (7.3)) the exponentially fast approach to TST in EPS, and (for a high barrier, see Appendix C) in EPS transition-state theory remains valid for *any* λ upon further increasing the friction, regardless of the applicability of the FTE. It follows that the relative energy loss of Refs. [28,29,31] differs from the ε found here (and which agrees with that of Ref. [8]) only in insignificant higher-order terms in λ/ω_b.[4] Of course, this does not necessarily exclude the possibility that – for a particular finite barrier – the much more complicated expression for the ε of Grabert et al. agrees slightly better with numerical data. For this, however, current evidence [40] is at best inconclusive.

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Appendix A. Transforming Fokker–Planck equations

Throughout the main text, we have only given the results of the various coordinate transformations that have been applied. For the convenience of the reader we here

[4] This remark should not detract from the significance of their work for escape problems with memory friction, which have not been considered in the present version of the low-dimensional theory.

derive the general formula for a (time-independent) transformation of a Fokker–Planck equation. Let $w(y,t)$ obey

$$\partial_t w = -\partial_\alpha[K^\alpha w] + \tfrac{1}{2}\partial_\alpha\partial_\beta[K^{\alpha\beta}w]\,, \tag{A.1}$$

where $K^{\alpha(\beta)} = K^{\alpha(\beta)}(y)$, where $\partial_\alpha = \partial/\partial y^\alpha$, and with summation over repeated indices. Now let $y = y(z)$, $w(y) = \tilde{w}(z)|\partial z/\partial y|$. For the derivative of a determinant depending on a parameter at a point where it is nonzero one has $|A|' = |A|\,\mathrm{Tr}(A^{-1}A')$. This can be derived by developing both sides with respect to the minors of A and comparing the prefactors of A'_{ij} (e.g., Section 5.3 of Ref. [42]); a very short proof follows by writing $A = \mathrm{e}^B$, upon which one has $|A|' = (\exp\{\mathrm{Tr}\,B\})' = \exp\{\mathrm{Tr}\,B\}\,\mathrm{Tr}\,B' = |A|\,\mathrm{Tr}(\mathrm{e}^{-B}(\mathrm{e}^B B')) = |A|\,\mathrm{Tr}(A^{-1}A')$, q.e.d. Applying this relation as

$$\left|\frac{\partial y}{\partial z}\right| \frac{\partial}{\partial y^\alpha}\left|\frac{\partial z}{\partial y}\right| = \frac{\partial}{\partial y^\alpha} + \left(\frac{\partial y^\beta}{\partial z^\gamma}\right)\frac{\partial}{\partial y^\alpha}\left(\frac{\partial z^\gamma}{\partial y^\beta}\right) = \frac{\partial}{\partial y^\alpha} + \frac{\partial}{\partial z^\gamma}\left(\frac{\partial z^\gamma}{\partial y^\alpha}\right) = \frac{\partial}{\partial z^\gamma}\frac{\partial z^\gamma}{\partial y^\alpha}\,, \tag{A.2}$$

one finds

$$\begin{aligned}\frac{\partial\tilde{w}(z)}{\partial t} &= -\left|\frac{\partial y}{\partial z}\right| \frac{\partial}{\partial y^\alpha}\left|\frac{\partial z}{\partial y}\right|[K^\alpha\tilde{w}] + \frac{1}{2}\left|\frac{\partial y}{\partial z}\right| \frac{\partial}{\partial y^\alpha}\left|\frac{\partial z}{\partial y}\right| \cdot \left|\frac{\partial y}{\partial z}\right| \frac{\partial}{\partial y^\beta}\left|\frac{\partial z}{\partial y}\right|[K^{\alpha\beta}\tilde{w}] \\ &= -\frac{\partial}{\partial z^\gamma}\left[\left(\frac{\partial z^\gamma}{\partial y^\alpha}K^\alpha + \frac{1}{2}\frac{\partial^2 z^\gamma}{\partial y^\alpha\,\partial y^\beta}K^{\alpha\beta}\right)\tilde{w}\right] + \frac{1}{2}\frac{\partial}{\partial z^\gamma}\frac{\partial}{\partial z^\delta}\left[\frac{\partial z^\gamma}{\partial y^\alpha}\frac{\partial z^\delta}{\partial y^\beta}K^{\alpha\beta}\tilde{w}\right].\end{aligned} \tag{A.3}$$

This transformation rule admits a differential geometric interpretation (see Ref. [43]; a slightly different formulation, in which the diffusion tensor itself defines the metric,[5] can be found in [38]. For a path integral formulation of diffusion in a Riemannian geometry, see [44]). Given a Riemann connection $\{\Gamma^\alpha_{\rho\sigma}\}$, one can define a contravariant drift field

$$D^\alpha = K^\alpha + \tfrac{1}{2}\Gamma^\alpha_{\rho\sigma}K^{\rho\sigma}\,. \tag{A.4}$$

Using the vector transformation $D'^\gamma = (\partial z^\gamma/\partial y^\alpha)D^\alpha$, the familiar [42,43] transformation rule for the Christoffel symbols, and noticing that $K^{\rho\sigma}$ is a contravariant tensor, the primed version of (A.4) can be solved for $K'^\gamma = (\partial z^\gamma/\partial y^\alpha)K^\alpha + \frac{1}{2}(\partial^2 z^\gamma/\partial y^\alpha\,\partial y^\beta)K^{\alpha\beta}$, i.e., the same as occurring between parentheses on the last line of Eq. (A.3).

[5] The tacit assumption that the diffusion tensor is invertible renders this latter approach inapplicable to the Kramers equation.

Appendix B. Details of the TST calculation of the escape rate

B.1. Normalization of the extended equilibrium distribution

Let the one-particle equilibrium distribution $P_{\rm eq}(x,p) = N_0 \exp(-\beta E_{\rm p})$ of (2.1) be normalized so that $N_0 = (\beta\omega_0/2\pi)\exp(-\beta U_{\rm b})$. In the harmonic barrier region the particle energy reads $E_{\rm p} = \frac{1}{2}(p^2 - \omega_{\rm b}^2 x^2)$. Note that the Jacobian of the transformation (2.2) equals $|\partial(x,p)/\partial(\eta,\zeta)| = \omega_{\rm b}/2r$, and substitute the ensuing $P_{\rm eq}(\eta,\zeta)$ into the CGT (3.1). The result reads

$$Q_{\rm eq}(\eta,\zeta) = N_Q \exp(-\tfrac{1}{2}K_{11}\eta^2 - K_{12}\eta\zeta)\,, \tag{B.1}$$

where $K_{11} = -\beta\lambda\omega_{\rm b}/r$, $K_{12} = 2\beta\kappa\omega_{\rm b}^2/r$, and $N_Q = (\kappa\omega_{\rm b}/2r)N_0$.

On the other hand, by (5.3) one has $R_{\rm eq}(E,w) = \mathcal{N}\exp(-\beta_E E - \frac{1}{2}\beta_w w^2)$. In the harmonic barrier region the unstable-mode energy becomes $E = \frac{1}{2}(v^2 - \omega_1^2 u^2)$, by (4.8). Now recall that $R_{\rm eq}(E,w)$ is normalized according to $\int {\rm d}u \int {\rm d}v \int {\rm d}w\, R = 1$, and note that the Jacobian of the transformation (4.4) equals $|\partial(u,v,w)/\partial(\vartheta,\eta,\zeta)| = \frac{1}{2}\omega_1$. Substituting the ensuing result for $R_{\rm eq}(\vartheta,\eta,\zeta)$ into the EPS condition (4.1), and comparing the upshot for $Q_{\rm eq}(\eta,\zeta)$ with (B.1), one then finds

$$\mathcal{N}/N_Q = (\omega_{\rm b}/2\pi\lambda\kappa^4 r)^{1/2}\,. \tag{B.2}$$

Use of the above value for N_Q, and of the definitions of β_E and β_w below (5.2), yields (5.4). Finite-barrier corrections in the normalization, occurring beyond the above harmonic-well approximation, will be friction independent and are, therefore, not considered here (nor in Appendix C).

B.2. Transformation of the escape rate

The escape rate is defined by

$$\Gamma = -\frac{\partial}{\partial t}\int_{-\infty}^{0} {\rm d}x \int_{-\infty}^{+\infty} {\rm d}p\, P(x,p) \tag{B.3a}$$

$$= \int_{-\infty}^{+\infty} {\rm d}p\; pP(0,p)\,, \tag{B.3b}$$

where $P(x,p)$ is the quasi-equilibrium state, and where the second line is an immediate consequence of the Fokker–Planck equation (2.1). It is often convenient [7] to assume that escaping particles are absorbed by a boundary which is well-separated from the barrier,[6] while the normalization of P is maintained by re-injecting these particles in the metastable minimum ($x = x_0$, $p = 0$). Thus one arrives at a strictly stationary

[6] For the cubic potential such a device is unnecessary since the particles escape to infinity.

distribution which is mildly singular in the metastable potential well, and for which only the definition (B.3b) of Γ is appropriate. An explicit and perhaps novel construction of such a stationary quasi-equilibrium state can be found in Appendix F.

Using the transformation (2.2), implying the Jacobian $|\partial(x,p)/\partial(\eta,\zeta)| = \omega_b/2r$ from Appendix B.1, Eq. (B.3b) can be rewritten as

$$\Gamma = -2\kappa^2 r\omega_b \int_{-\infty}^{+\infty} d\zeta\, \zeta P(-\kappa^2\zeta,\zeta)\,. \tag{B.4}$$

Since the Gaussian transformation (3.1) is not invertible, the easiest way to proceed is to define

$$\tilde{\Gamma} = -2\kappa^2 r\omega_b \int_{-\infty}^{+\infty} d\tilde{\zeta}\, \tilde{\zeta} Q(-\kappa^2\tilde{\zeta},\tilde{\zeta})\,, \tag{B.5}$$

and substitute the r.h.s. of Eq. (3.2) for Q. One finds that the function P can be taken in front of the $\tilde{\zeta}$-integral, which subsequently cancels the normalization constant in (3.2) to yield $\tilde{\Gamma} = \Gamma$. The constraint $\tilde{x} = x$, originally implemented to conserve the Fokker–Planck structure of the evolution equation, is now seen to be crucial in order to leave Γ invariant.

The next step – phase space extension – is simple. Namely, again omitting tildes, the condition (4.1) at once implies

$$-2\kappa^2 r\omega_b \int_{-\infty}^{+\infty} d\zeta\, \zeta Q(-\kappa^2\zeta,\zeta) = -2\kappa^2 r\omega_b \int_{-\infty}^{+\infty} d\zeta \int_{-\infty}^{+\infty} d\vartheta\, \zeta R(\vartheta,-\kappa^2\zeta,\zeta)\,, \tag{B.6}$$

and transformation to (u,v,w) yields

$$\Gamma = -2\kappa^2 r\omega_b \int_{-\infty}^{+\infty} dv \int_{-\infty}^{+\infty} dw \left(\frac{w}{4} - \frac{v}{2\kappa^3\omega_b}\right) R(-\tfrac{1}{2}\kappa^2 w, v, w)\,, \tag{B.7}$$

where we again used the value given in Appendix B.1 for the Jacobian.

The final step amounts to using the divergence theorem in order to rotate the plane on which the integral (B.7) is taken to the plane $u = 0$. Let us therefore write the FPE (4.5) as $\partial_t R = -\nabla \cdot \boldsymbol{J}$, the current density $\boldsymbol{J}$ (which is, of course, determined up to a curl) being given by

$$\boldsymbol{J} = \Big(v, \kappa^2[\omega_b^2 u - U_a'(x)],$$
$$-\omega_2 w - \frac{2\lambda}{\kappa^2}(u - v/\omega_1) - \mathsf{D}_{ww}\left\{\partial_w - \tfrac{1}{2}\kappa^2(\partial_u + \omega_1\partial_v)\right\}\Big)^{\mathsf{T}} R\,, \tag{B.8}$$

and parametrize the surface $S = \{u + \frac{1}{2}\kappa^2 w = 0\}$ as $\boldsymbol{r} = (-\frac{1}{2}\kappa^2 w, v, w)^{\mathsf{T}}$. The normal vector pointing outwards w.r.t. the well region becomes $\boldsymbol{n} = \partial_v \boldsymbol{r} \times \partial_w \boldsymbol{r} = (1, 0, \frac{1}{2}\kappa^2)^{\mathsf{T}}$.

The diffusion part (i.e., the part $\propto \mathsf{D}_{ww}$) of the total current $\int_S \boldsymbol{J}\cdot\hat{n}\,\mathrm{d}\sigma$ turns out to be a total derivative on the surface, the integral of which vanishes.[7] Straightforward substitution of (B.8) for $\boldsymbol{J}$ concludes the verification of $\Gamma = \int_S \boldsymbol{J}\cdot\hat{n}\,\mathrm{d}\sigma$. Since the quasi-equilibrium density R is stationary, the value of the surface integral will remain invariant under a change $S \mapsto S'$ if two conditions are satisfied:

(a) The region between S and S' does not contain any sources.

(b) The region between S and S' does not contain any currents flowing to infinity.

These conditions will be verified below for $S' = \{u = 0\}$, after which one can write $\Gamma = \int_{S'} \boldsymbol{J}\cdot\hat{n}\,\mathrm{d}\sigma = \int_{-\infty}^{+\infty}\mathrm{d}v\int_{-\infty}^{+\infty}\mathrm{d}w\, vR(0,v,w)$. This concludes the derivation of Eq. (5.6). □

It remains to verify the above two requirements, e.g., as follows:

(a) The inverse projection of the original well (see below Eq. (B.3b)) is located on the line $(u,v,w)^{\mathrm{T}} = (\frac{1}{2}x_0, \frac{1}{2}\omega_1 x_0, x_0)^{\mathrm{T}} + \vartheta(-\frac{1}{2}, \frac{1}{2}\omega_1, \kappa^{-2})^{\mathrm{T}}$, of which the part with $\vartheta > -|x_0| = x_0$ has no points in common with the region between S and S'. Locating the source in EPS on any point of this half-line thus satisfies the condition (a) and at the same time via the projection (4.1) leads to a quasi-equilibrium state in (x,p)-space such as defined below Eq. (B.3b). One can for instance take $\vartheta = |x_0| = -x_0$ (which puts the source at a point with $u = x_0$, $v = 0$) since its precise position is immaterial as long as it is not close to either S or S', the rate Γ being insensitive to this position up to exponentially small errors (cf. Ref. [7]).

(b) Escape takes place along the η-direction, i.e., along the line $v = \omega_1 u$, $w = 0$. This line does not lie between S and S'.

Appendix C. Beyond TST: finite-barrier corrections

The validity of the EPS-version of TST hinges on the fact that the unstable mode (u,v) decouples from the environmental degree of freedom (w) in the harmonic barrier region, i.e., with $U_{\mathrm{a}}(x) = 0$. In this Appendix we briefly investigate the corrections in Γ due to $U_{\mathrm{a}}(x) \neq 0$. Let us therefore following Kramers [4,21] set

$$R = \mathcal{Q}(u,v,w)R_{\mathrm{eq}}(E,w)\,, \tag{C.1}$$

where R_{eq} is given by (5.3), with E as defined in (4.8). Substitution of (C.1) into (4.3), and rewriting the resulting equation for $\mathcal{Q}$ in terms of u, $\vartheta = -u + v/\omega_1$, and $x = (u + \frac{1}{2}\kappa^2 w)/\kappa r$, yields

$$0 = \mathscr{F}_u\frac{\partial\mathcal{Q}}{\partial u} + \mathscr{F}_v\frac{\partial\mathcal{Q}}{\partial\vartheta} + \mathscr{F}_x\frac{\partial\mathcal{Q}}{\partial x} + \mathscr{D}_{ux}\frac{\partial^2\mathcal{Q}}{\partial u\,\partial x}\,, \tag{C.2}$$

[7] This is the EPS counterpart of the vanishing of current terms $\propto \lambda$ which leads to Eq. (B.3b). Besides the choice of a dividing line parallel to the p-axis in (x,p)-space, the deterministic dynamics (4.2) defined for ϑ is also involved in the present cancellation.

with $\mathscr{D}_{ux} = -\lambda/\beta\omega_b^2$, and

$$\mathscr{F}_u(u,\vartheta,x) = -\omega_1\vartheta + r\omega_b(x-2u) + \lambda U_a'(x)/\omega_b^2 ,$$
$$\mathscr{F}_v(u,\vartheta,x) = \omega_1\vartheta + U_a'(x)/\omega_2 ,$$
$$\mathscr{F}_x(u,\vartheta,x) = -\omega_b(u+\vartheta)/r . \tag{C.3}$$

Note that $\mathscr{Q}=1$ amounts to full equilibrium. On the other hand, if $U_a(x)$ is zero, (C.2), (C.3) allow for a solution $\mathscr{Q}(\vartheta)$ with $\vartheta\partial\mathscr{Q}/\partial\vartheta = 0$, i.e., $\mathscr{Q}=\theta(\vartheta)$. This corresponds to the quasi-equilibrium state pertinent to TST at the barrier peak ($u=0$). Including the anharmonic barrier terms, (C.2), (C.3) still allow for a solution with $\mathscr{Q}(-\infty)=0$ and $\mathscr{Q}(\infty)=1$. In that case, however, recrossing effects will show up in terms of the small parameter $(1/\beta U_b)^{1/2}$.

Upon introducing (C.1) into (5.6), it is convenient to write the decay rate in terms of $g=\partial\mathscr{Q}/\partial\vartheta$ by means of a partial integration. In addition, let $u=(\beta\omega_b^3/\lambda r)^{1/2}u$ and $x=(\beta\omega_b^3 r/\lambda)^{1/2}\kappa x$ and define (cf. below Eq. (G.38))

$$f(k,u,x) = \int_{-\infty}^{+\infty} d\vartheta\, e^{-ik\vartheta} g(\vartheta,u,x) , \tag{C.4}$$

so that Γ becomes an integral over k and x of $f(k,0,x)$.[8] For $\beta U_b \to \infty$, the integral over k can be performed in steepest descent around $k=0$. Differentiating (C.2) with respect to ϑ, one finds an equation for $f(k,u,x)$.

Consider the *cubic* potential $U_a(x) = -\frac{1}{2}\omega_b^2 x^3/a$; see also below Eq. (2.1). In that case, we define the small parameter $\ell = (\lambda/6\kappa^3 r^3\omega_1\beta U_b)^{1/2}$, and with $\mathscr{k} = (\lambda r/\beta\omega_b^3)^{1/2}\ell k$ the expansion ($l\geqslant 1$; $m,n\geqslant 0$)

$$f(\mathscr{k},0,x) = 1 + \sum_{lmn} c_{lmn}\mathscr{k}^l x^m \ell^n \tag{C.5}$$

leads to (1.1) with

$$\nu_a = \frac{\kappa\omega_0}{2\pi}\left[1 + a_2\ell^2 + \mathcal{O}(\ell^3)\right] , \tag{C.6a}$$

$$a_2 = \tfrac{5}{24}\kappa^2(1-\kappa^2)^2 + (\lambda/\omega_1)(c_{200} + c_{220}\kappa^2 + 3c_{240}\kappa^4 + \cdots) . \tag{C.6b}$$

Hence, to leading order in ℓ it suffices to determine f for $\ell = 0$. In that case one has

$$0 = i\mathscr{k}x^2 f + \mathscr{k}\frac{\partial f}{\partial \mathscr{k}} - \frac{1}{\kappa^2}(x - 2\kappa r u)\frac{\partial f}{\partial u} + u\frac{\partial f}{\partial x} + \frac{\partial^2 f}{\partial u\,\partial x} , \tag{C.7}$$

which can be solved systematically in powers of $\mathscr{k}$, the coefficients being polynomials in u and x, see also Eqs. (G.40), (G.41). In particular one obtains $c_{2m0}=0$ if $m\geqslant 6$, so that only the indicated terms contribute in Eq. (C.6b). The final result for a_2 reads

$$a_2 = -\frac{1}{24}\frac{\kappa^2(1-\kappa^4)(10+41\kappa^2+10\kappa^4)}{(1+2\kappa^2)(2+\kappa^2)} . \tag{C.8}$$

[8] Note that $f(0,u,x)=1$.

For the *quartic* potential $U_a(x) = \frac{1}{2}\omega_b^2 x^4/a^2$. In that case, $\ell = (\lambda/4\kappa^2 r^2 \omega_1 \beta U_b)^{1/2}$ and $\mathcal{k} = (\lambda r/\beta\omega_b^3)^{1/2}\ell^2 k$, and the result reads

$$a_2 = -\tfrac{3}{8}\kappa^2(1-\kappa^2)\,. \tag{C.9}$$

These results agree with those obtained using methods put forward recently by Pollak and Talkner [41], and by Mel'nikov [20]. In Ref. [20], however, only the quartic potential was treated *in extenso* and a factor $1/8\alpha$ in Mel'nikov's formula (167) should be corrected into $\alpha/8$.

Appendix D. Details of the FTE calculation

D.1. The energy loss

In this appendix we derive the expression for $\Delta\mathscr{E} \equiv \mathscr{E}(\tau=\infty) - \mathscr{E}(\tau=-\infty)$ used in the main text. In Eq. (6.3a) we substitute $\mathscr{W}_a'(\tau) = \omega_b^2 u - \dot{v}$ (obtained by combining the (u, v)-equation of motion given below Eq. (6.2) with the definition of U_a following Eq. (2.3)) and the solution

$$\mathscr{W}(\tau) = -2\lambda \int_{-\infty}^{\tau} \mathrm{d}\tau'\, \mathrm{e}^{\omega_b(\tau'-\tau)}\{u(\tau') - v(\tau')/\omega_b\} \tag{D.1}$$

of (6.3b) for $\mathscr{W}$. After integration over all τ one obtains

$$\frac{\Delta\mathscr{E}}{-2\lambda} = -\frac{\omega_b}{2}\int_{-\infty}^{+\infty}\mathrm{d}\tau \int_{-\infty}^{\tau}\mathrm{d}\tau'\, \mathrm{e}^{\omega_b(\tau'-\tau)}\{\omega_b^2 u(\tau) - \dot{v}(\tau)\}\{u(\tau') - v(\tau')/\omega_b\}$$

$$+\frac{1}{2}\int_{-\infty}^{+\infty}\mathrm{d}\tau\,\{\omega_b^2 u(\tau) - \dot{v}(\tau)\}\{u(\tau) - v(\tau)/\omega_b\}\,. \tag{D.2}$$

On the first line, one can change the order of integration. On the second line, the last term in the second pair of braces gives a vanishing contribution because of τ-parity, while $\int \mathrm{d}\tau\, \dot{v}(\tau)u(\tau)$ can be integrated by parts with a vanishing boundary term since $v(\pm\infty) = 0$. This leads to

$$\frac{\Delta\mathscr{E}}{-2\lambda} = -\frac{\omega_b}{2}\int_{-\infty}^{+\infty}\mathrm{d}\tau'\,\{u(\tau') - v(\tau')/\omega_b\}\int_{\tau'}^{+\infty}\mathrm{d}\tau\,\partial_\tau\left[\mathrm{e}^{\omega_b(\tau'-\tau)}\{-\omega_b u(\tau) - v(\tau)\}\right]$$

$$+\frac{1}{2}\int_{-\infty}^{+\infty}\mathrm{d}\tau\,\{\omega_b^2 u(\tau)^2 + v(\tau)^2\}\,. \tag{D.3}$$

The integral $\int d\tau\, \alpha(\tau)^2$ cancels the corresponding contribution from the double integral on the first line, and one is left with

$$\Delta\mathscr{E} = -2\lambda \int_{-\infty}^{+\infty} d\tau\, v(\tau)^2 = -2\lambda I_b\,, \tag{D.4}$$

which is what we set out to show.

D.2. Positive-definiteness of the FPE covariance matrix

The diffusion tensor pertaining to the fictitious τ-evolution resulting from the FTE can be read off from Eqs. (6.1), (6.2); its determinant reads $\det \mathbf{D} = -(\lambda/\beta\omega_b^2)^2\{\omega_b^2(\alpha - v/\omega_b) + \mathscr{W}'_a(\tau)\}^2 < 0$, and hence it is not possible to stably propagate an arbitrary initial distribution in the (E,w)-plane. However, since we are only interested in the marginal Green's function $G(E|E')$ it is sufficient to take the w-mode in equilibrium as has been done in the main text, upon which the formulas given below Eq. (6.4) lead to

$$\beta^2 \det \Sigma \equiv \beta^2(\sigma_{EE}\sigma_{ww} - \sigma_{wE}^2) = -\frac{8\lambda}{\omega_b^3}\Delta\mathscr{E}(\tau) - \dot{\mathscr{W}}(\tau)^2\,. \tag{D.5}$$

Integrating Eq. (6.3a) over $-\infty < \tau' < \tau$ and eliminating $\mathscr{W}'_a$ from the ensuing expression for $\Delta\mathscr{E}(\tau)$ by means of the relation

$$\ddot{\mathscr{W}}(\tau) + 2\omega_b\dot{\mathscr{W}}(\tau) + \omega_b^2\mathscr{W}(\tau) = -\frac{2\lambda}{\omega_b}\mathscr{W}'_a(\tau) \tag{D.6}$$

which is readily derived by differentiating Eq. (6.3b) w.r.t. τ, one obtains

$$\Delta\mathscr{E}(\tau) = -\frac{\omega_b}{8\lambda}\dot{\mathscr{W}}(\tau)^2 - \frac{\omega_b^2}{2\lambda}\int_{-\infty}^{\tau} d\tau'\, \dot{\mathscr{W}}(\tau')^2 - \frac{\omega_b^3}{8\lambda}\mathscr{W}(\tau)^2 \tag{D.7}$$

by means of a partial integration. Substitution in (D.5) finally leads to

$$\beta^2 \det \Sigma = \frac{1}{\omega_b^2}\dot{\mathscr{W}}(\tau)^2 + \frac{4}{\omega_b}\int_{-\infty}^{\tau} d\tau'\, \dot{\mathscr{W}}(\tau')^2 > 0\,. \qquad \square \tag{D.8}$$

Appendix E. Solution of the Wiener–Hopf turnover equation

In this appendix we derive the result (7.3) for ν_a from Eq. (7.2). Besides making this article self-contained, its purpose is to examine in some detail to what extent the asymptotic properties of $R(E)$ mentioned below (7.2) indeed constitute 'boundary conditions' (a term also used in Ref. [8]) that can be specified independently.

Let us define $h(s)=\beta^{-1}R(E=s/\beta)\mathrm{e}^{s/2}$, so that $\Gamma=\int_0^\infty R(E)\,\mathrm{d}E=\int_0^\infty h(s)\mathrm{e}^{-s/2}\,\mathrm{d}s$. The function h satisfies the integral equation

$$h(s)=\int_{-\infty}^{0} k(s-s')h(s')\,\mathrm{d}s'\;;\qquad k(s)=\frac{1}{4\pi\varepsilon}\,\mathrm{e}^{-s^2/4\varepsilon-\varepsilon/4}\,, \tag{E.1}$$

with ε as defined below Eq. (7.3). The general strategy for solving integral equations like (E.1) is to map them onto a matching problem for the Fourier–Laplace transforms $\eta^{\pm}(\lambda)=\int_{-\infty}^{+\infty}h^{\pm}(s)\mathrm{e}^{\mathrm{i}\lambda s}\,\mathrm{d}s$ of the functions $h^{\pm}(s)\equiv h(s)\theta(\pm s)$. A common approach (e.g., Ref. [45]) is to assume the joint existence of $\eta^{\pm}(\lambda)$ on a line $\operatorname{Im}\lambda=C$, and to pose the matching problem on this line. However, the space of solutions thus obtained will in general depend on C. Moreover, studying the integral occurring in Eq. (7.3) (which will be shown below to have a direct relation to this matching problem) is most convenient on the real axis $C=0$, where the argument of the logarithm is positive definite.

We therefore proceed slightly differently, and make only the assumption that there is one λ_0 for which the Fourier transform $\eta^-(\lambda_0)$ converges absolutely. From this one can conclude that $\eta^-(\lambda)$ is analytic for $\operatorname{Im}\lambda<\operatorname{Im}\lambda_0$ and continuous up to the boundary $\operatorname{Im}\lambda=\operatorname{Im}\lambda_0$, while $\eta^-(\lambda)\to 0$ for $\operatorname{Im}\lambda\to-\infty$. By inspecting its representation as the convolution (E.1) one sees that $h(s)$ is continuous, and that $h(s)\to 0$ for $s\to\infty$. The assumption on $\eta^-(\lambda_0)$ and the Gaussian form of k now permit the estimate

$$\begin{aligned}
\int_0^\infty |h(s)\mathrm{e}^{\mathrm{i}\lambda s}|\,\mathrm{d}s \;&=\; \int_0^\infty \mathrm{d}s\,\left|\mathrm{e}^{\mathrm{i}\lambda s}\int_{-\infty}^{0}k(s-s')h(s')\,\mathrm{d}s'\right| \\
&\leqslant \int_{-\infty}^{0}\mathrm{d}s'\,|\mathrm{e}^{\mathrm{i}\lambda_0 s'}h(s')|\int_0^\infty \mathrm{d}s\,k(s-s')|\mathrm{e}^{\mathrm{i}\lambda s-\mathrm{i}\lambda_0 s'}| \\
&= \text{const.}\int_{-\infty}^{0}\mathrm{d}s'\,|\mathrm{e}^{\mathrm{i}\lambda_0 s'}h(s')| \\
&\quad\times\int_0^\infty \mathrm{d}s\,\exp\left\{-\frac{s^2}{4\varepsilon}+\frac{ss'}{2\varepsilon}-\frac{s'^2}{4\varepsilon}-\operatorname{Im}\lambda s+\operatorname{Im}\lambda_0 s'\right\} \\
&\leqslant \text{const.}\int_{-\infty}^{0}\mathrm{d}s'\,|\mathrm{e}^{\mathrm{i}\lambda_0 s'}h(s')|\,\mathrm{e}^{-s'^2/4\varepsilon+\operatorname{Im}\lambda_0 s'}\int_0^\infty \mathrm{d}s\,\mathrm{e}^{-s^2/4\varepsilon-\operatorname{Im}\lambda s}\,,
\end{aligned} \tag{E.2}$$

where on the last line we used $ss'\leqslant 0$. The integral over s converges and $\exp\{-s'^2/4\varepsilon+\operatorname{Im}\lambda_0 s'\}$ is a bounded function of s', so $\int_0^\infty |h(s)\mathrm{e}^{\mathrm{i}\lambda s}|\,\mathrm{d}s<\infty$ for all λ, and it follows that $\eta^+(\lambda)$ is an entire function, with $\eta^+(\lambda)\to 0$ for $\operatorname{Im}\lambda\to+\infty$.

Since also $\kappa(\lambda)=\int_{-\infty}^{+\infty} k(s)e^{i\lambda s}\,ds=e^{-\varepsilon(\lambda^2+1/4)}$ is an entire function, for $\operatorname{Im}\lambda\leqslant\operatorname{Im}\lambda_0$ one can apply the convolution theorem to Eq. (E.1) in order to see that

$$\eta^+(\lambda)=[\kappa(\lambda)-1]\eta^-(\lambda)\,. \tag{E.3}$$

Using the above result on η^+, one can now use Eq. (E.3) to *define* the – unique – analytic continuation of $\eta^-(\lambda)$ to the whole λ-plane, and we shall henceforth suppose this done. The function η^- can have first order poles at

$$\lambda^2=2\pi ni/\varepsilon-\tfrac{1}{4}\quad(n\in\mathbb{Z})\,; \tag{E.4}$$

conversely, η^+ apparently has zeros for values of λ that obey this equation and for which in addition one has $\operatorname{Im}\lambda\leqslant\operatorname{Im}\lambda_0$.

Let us introduce the auxiliary function

$$f(\lambda)=\int_{-\infty}^{+\infty}\frac{d\mu}{2\pi i}\,\frac{\ln[1-e^{-\varepsilon(\mu^2+1/4)}]}{\mu-\lambda}\,. \tag{E.5}$$

Since $|e^{-\varepsilon(\mu^2+1/4)}|<1$ for all μ one can choose the real principal value of the logarithm. Because the jump in $f(\lambda)$ across the real axis is determined by the residue of the integrand at $\mu=\lambda$, one has $e^{f(\lambda+i0)}=[1-e^{-\varepsilon(\lambda^2+1/4)}]e^{f(\lambda-i0)}$ if $\lambda\in\mathbb{R}$. If one defines $\eta_0^+=e^f$ for $\operatorname{Im}\lambda>0$ and $\eta_0^-=-e^f$ for $\operatorname{Im}\lambda<0$, it follows that

(a) $\eta_0^\pm$ are analytic on their respective domain of definition.

(b) $\eta_0^\pm$ do not vanish on their domain of definition.

(c) $\lim_{|\lambda|\to\infty}\eta_0^\pm(\lambda)=\pm 1$ if the limit is taken in the upper half plane for η_0^+, and in the lower one for η_0^-.

(d) $\eta_0^\pm$ have a continuous extension to the real axis, and obey Eq. (E.3) on the real axis. The functions have no zero on this line, for $f(\lambda)$ has a regular limit as $\lambda\uparrow 0$ $(\lambda\downarrow 0)$.

Let $\eta^\pm$ satisfy the conditions derived above, and examine the functions η^+/η_0^+ for $\operatorname{Im}\lambda\geqslant 0$ and η^-/η_0^- for $\operatorname{Im}\lambda\leqslant 0$. These functions are analytic above and below the real axis, respectively, with the possible exception of a finite number of first order poles for the latter. On the real axis the functions coincide, and by a theorem due to Riemann[9] the functions η^+/η_0^+ and η^-/η_0^- in fact are parts of one single analytic function. As this function vanishes at infinity it must be rational, and the above information on its poles implies that it must be of the form

$$\frac{\eta^\pm(\lambda)}{\eta_0^\pm(\lambda)}=\sum_{l=1}^{N}\frac{a_l}{\lambda-\lambda_l}\,, \tag{E.6}$$

with $\operatorname{Im}\lambda_l<0$ for all l. From this form for η^- it can be seen that the inverse Fourier transform can indeed be performed (in the sense of a principal value, i.e., as

[9] The integral of $\eta^\pm/\eta_0^\pm$ along any closed contour (including those which cross the line $\operatorname{Im}\lambda=0$) vanishes, allowing the introduction of a differentiable – and hence analytic – primitive function. It follows that $\eta^\pm/\eta_0^\pm$ itself is analytic.

$\lim_{u\to\infty}\int_{-u+iC}^{u+iC}(d\lambda/2\pi)e^{-i\lambda s}\eta^-(\lambda))$ if $\operatorname{Im}\lambda = C < M \equiv \min \operatorname{Im}\lambda_l$; for η^+ inverse Fourier transformation is unproblematic. The inverse transforms $h^\pm(s)$ vanish for $s > 0$ and $s < 0$, respectively (as can be verified by closing the λ-contours in the appropriate half planes), and their sum $h(s) = h^+(s) + h^-(s)$ satisfies Eq. (E.1) for all $s \in \mathbb{R}$. However, if $M \neq -\frac{1}{2}$ the function $\eta^-(\lambda)$ has at least one pole on the line $\operatorname{Im}\lambda = M$ outside the imaginary axis and no pole on this axis, as follows from the expression (E.4) for the possible λ_l.[10] For *positive* $h^-(s)$ this is incompatible with the inequality

$$|\eta^-(\lambda)| \leqslant \int_{-\infty}^{0} ds\, |h^-(s)e^{i\lambda s}| = \int_{-\infty}^{0} ds\, h^-(s)e^{-M} = \eta^-(iM)\,. \tag{E.7}$$

It can be concluded that $M = -\frac{1}{2}$, and that $\eta^\pm(\lambda) = (a_1/(\lambda + i/2))\eta_0^\pm(\lambda)$ is the unique – up to a constant factor – solution of Eq. (E.3) for which the corresponding $R(E)$ has a density interpretation (see also the very end of this appendix). Since Fourier transformation is invertible for continuous functions, $h(s)$ of course is unique as well.

It remains to calculate Γ. For this we need to determine the constant a_1; apart from ruling out the possibility of having other $a_l \neq 0$ this is the only instant at which the 'boundary condition' $R(E\to-\infty) \to R_{\mathrm{eq}}(E)$ enters the calculation. This normalization determines the residue of the pole at $\lambda = -i/2$ of $\eta^-(\lambda)$, from which it follows that $a_1 = i(\kappa\omega_0/2\pi)e^{-\beta U_b - f(\lambda = -i/2)}$. Substitution in $\Gamma = \eta^+(i/2) = (a_1/i)\eta_0^+(i/2)$, use of the expression (E.5) for f, and finally a change of variable $\mu = y/2$ in the latter formula, yields Γ as given by (1.1) with (7.3) for ν_a. □

Let us in conclusion clarify one final detail. By the inequality (E.7) it has been shown that $a_{l>1} = 0$ is a necessary condition for obtaining a function h that is positive definite. To show that together with $a_1 = i$ this condition is also sufficient, let us introduce the function $\eta = \eta^+ + \eta^- = \kappa\eta^-$,[11] and examine

$$h(s) = \int_{-\infty}^{+\infty} \frac{d\tau}{2\pi} e^{(-i\tau + C)s}\eta(\tau + iC) \quad (C < -\tfrac{1}{2})\,. \tag{E.8}$$

By symmetrization of the μ-integral occurring in the definition of f (Eq. (E.5)), in terms of which η is defined through η_0^- and η^-, one can show that $\eta(-\tau + iC) = \eta(\tau + iC)^*$, so that h is real. For $s \to -\infty$ the pole in $\eta(\lambda)$ at $\lambda = -i/2$ dominates the integral in (E.8), and it follows that

$$h(s) = e^{-s/2}\exp\left\{\int_0^\infty \frac{d\mu}{2\pi}\,\frac{\ln[1 - e^{-\varepsilon(\mu^2 + 1/4)}]}{\mu^2 + 1/4}\right\} + \mathcal{O}(s^0)\,, \tag{E.9}$$

while it has already been remarked above Eq. (E.2) that $h(s) \to 0$ if $s \to \infty$. If h is nonnegative, the r.h.s. of (E.1) cannot vanish for any s unless $h \equiv 0$, since h is

[10] We here exclude the trivial possibility $\eta^\pm \equiv 0$.

[11] The rapid vanishing of $\eta(\lambda)$ as $|\operatorname{Re}\lambda| \to \infty$ of course is a direct consequence of the smoothness of $h(s)$, which – as opposed to $h^\pm(s)$ – has no jump at $s = 0$.

continuous. Combination of this fact with the stated asymptotic properties of h now shows that either h is indeed positive definite, or h has a global minimum $h(s_0) < 0$. This latter possibility, however, is ruled out by the contradiction [12]

$$h(s_0) = \int_{-\infty}^{0} k(s_0 - s')h(s')\,\mathrm{d}s' \geqslant \int_{-\infty}^{0} k(s_0 - s')h(s_0)\,\mathrm{d}s'$$

$$> h(s_0) \int_{-\infty}^{+\infty} k(s_0 - s')h(s_0)\,\mathrm{d}s' = h(s_0)\,\mathrm{e}^{-\varepsilon/4}\,, \tag{E.10}$$

implying $1 < \mathrm{e}^{-\varepsilon/4}$ while $\varepsilon > 0$. □

Appendix F. A stationary Fokker–Planck Green's function and the Kramers quasi-equilibrium state

In this appendix it will be shown how a quasi-equilibrium probability distribution can be established by a source which is continuously injecting particles at a point in phase space. While this is a notion frequently occurring in the literature (e.g., Ref. [7]; see also Section 7) most treatments are qualitative, and here we therefore present an explicit and detailed derivation.

Consider the Kramers equation in the inverted parabolic potential, for which the exact propagator can be calculated. In scaled coordinates with $\beta = \omega_b = 1$ this is the causal solution $P(x, p, t|x_0, p_0)$ of

$$\partial_t P = -p\,\partial_x P + \partial_p[-x + \gamma(p + \partial_p)]P + \delta(t)\delta(x - x_0)\delta(p - p_0)\,, \tag{F.1}$$

where the dimensionless friction coefficient γ is related to the parameter λ of Eq. (2.1) by $\gamma = 2\lambda/\omega_b$. The *stationary* Green's function, i.e., the solution $Q(x, p|x_0, p_0)$ of the equation

$$-p\,\partial_x Q + \partial_p[-x + \gamma(p + \partial_p)]Q = -\delta(x - x_0)\delta(p - p_0) \tag{F.2}$$

that is bounded at infinity, is then given by

$$Q = \int_0^{\infty} P(t)\,\mathrm{d}t. \tag{F.3}$$

While P is readily calculated (see Eq. (F.5) below) the time integral is formidable, and it can only be evaluated in an asymptotic case. Namely, we shall derive the equality

$$P_{\mathrm{q.e.}}(x, p) = \lim_{x_0 \to -\infty} \frac{Q(x, p|x_0, 0)}{2Q(0, 0|x_0, 0)} \tag{F.4}$$

[12] Note that this proof of positivity in fact is the integral form (cf. above Eq. (7.1)) of the standard one, demonstrating that the Fokker–Planck equation conserves positivity by showing that local minima cannot occur for an elliptic evolution operator.

for the quasi-equilibrium distribution (F.10) below. Moving the source to $x_0 = -\infty$ eliminates artifacts due to the vicinity of the source for all finite x and p. The denominator in Eq. (F.4) is a constant of normalization, the factor two is chosen in order to have the standard Boltzmann form for $P_{\text{q.e.}}$ if $x \ll -1$, cf. below Eq. (F.10).

Physically, the statement (F.4) is not quite trivial: particles which are injected with zero momentum at $x_0 \ll -1$ will with overwhelming probability escape to $x = -\infty$ without ever reaching the barrier at $x = 0$, and for the inverted parabola there is no metastable well in which the particles can equilibrate. The population in the vicinity of the barrier consists of particles which have diffused 'upward' immediately after injection, and it is not obvious that their distribution is quasi-equilibrium.

The demonstration proceeds by explicit calculation of Q. This is most conveniently done in the coordinates η, ζ of Eq. (2.2), in which the deterministic evolution is diagonal. Calculation of the propagator P solving Eq. (F.1) is an immediate application of the procedure given in Ref. [14] for a general linear Fokker–Planck equation. One obtains

$$P(\eta, \zeta, t|\eta_0, \zeta_0) = \frac{1}{2\pi\sqrt{|A|}} \exp\left\{-\frac{\boldsymbol{y}^{\mathrm{T}} A \boldsymbol{y}}{2|A|}\right\}, \tag{F.5}$$

with $\boldsymbol{y}^{\mathrm{T}} = (\eta - \eta_0 \mathrm{e}^{\kappa t}, \zeta - \zeta_0 \mathrm{e}^{-t/\kappa})$ and with

$$A = \begin{pmatrix} \kappa^{-1}\gamma(1 - \mathrm{e}^{-2t/\kappa}) & 2(1 - \mathrm{e}^{-\gamma t}) \\ 2(1 - \mathrm{e}^{-\gamma t}) & \kappa\gamma(\mathrm{e}^{2\kappa t} - 1) \end{pmatrix}, \tag{F.6}$$

where we recall that[13] $\gamma = \kappa^{-1} - \kappa$. To derive (F.4) we will only need the case $\eta_0 = \zeta_0 = x_0$.

Instead of giving a systematic but tedious sequence of asymptotic formulae, we will explain the steps involved in the evaluation of (F.3) for large $|x_0|$ by giving a calculation of the normalization $Q(0, 0|\eta_0 = \zeta_0 = x_0)$. For small t the integrand vanishes exponentially fast, since one has $|A| \propto t^4$ while $\boldsymbol{y}^{\mathrm{T}} A \boldsymbol{y} \propto t$. For large t, the exponent in (F.5) approaches a constant, while $|A|^{-1/2} \sim \mathrm{e}^{-\kappa t}$. A maximum is thus reached for intermediate values of t, and – noticing that $\boldsymbol{y}^{\mathrm{T}} A \boldsymbol{y} \propto x_0^2$ – one can convince oneself graphically that this maximum shifts to increasing values of t as $|x_0| \to \infty$. Physically this is gratifying, since for large times one may expect thermalization to occur so that a quasi-equilibrium will indeed be established. Thus, one can substitute the leading asymptotic behaviour for P. In the exponent on the r.h.s. of (F.5), the leading deviation from its limit for $t \to \infty$ comes from the first finite-t correction to the denominator: $|A| \sim \gamma^2 \mathrm{e}^{2\kappa t} - 4r^2$, where it is recalled that $r = \frac{1}{2}(\kappa^{-1} + \kappa)$. It follows that

$$Q(0,0) \approx \frac{\mathrm{e}^{-x_0^2/2\kappa\gamma}}{2\pi\gamma} \int_0^\infty \mathrm{d}t \, \exp\left\{-\frac{2r^2 x_0^2}{\kappa\gamma^3} \mathrm{e}^{-2\kappa t} - \kappa t\right\}, \tag{F.7}$$

[13] Incidentally, using this relation to parametrize γ as a function of κ – instead of expressing κ by means of Eq. (1.2) – avoids unnecessary square roots throughout this paper.

with the maximum of the integrand located at $t = t_0 = (2\kappa)^{-1} \ln(4r^2 x_0^2/\kappa\gamma^3)$, proving self-consistency of the large-t expansion. Making a change of variables $\kappa t = \kappa t_0 + u$ one arrives at

$$Q(0,0) \approx \frac{e^{-x_0^2/2\kappa\gamma}}{4\pi r|x_0|}\sqrt{\frac{\gamma}{\kappa}}\int_{-\infty}^{+\infty} du\, \exp\left\{-\tfrac{1}{2}e^{-2u} - u\right\}, \tag{F.8}$$

where the lower limit of integration has been set to $-\infty$ since $t_0 \gg 1$, yielding the integral as $\sqrt{\pi/2}$.

The same procedure will now be applied to $Q(\eta,\zeta)$, viz.,

$$\begin{aligned} Q(\eta,\zeta) &= \int_0^\infty dt\, P(\eta,\zeta,t) \\ &\approx \int_0^\infty dt\, \frac{e^{-\kappa t}}{2\pi\gamma}\exp\left\{-\frac{1}{2}\frac{e^{2\kappa t}[\kappa^{-1}\gamma x_0^2 + \kappa\gamma\zeta^2] - e^{\kappa t}x_0[4\zeta + 2\kappa^{-1}\gamma\eta]}{\gamma^2 e^{2\kappa t} - 4r^2}\right\} \\ &\approx \int_0^\infty dt\, \frac{e^{-\kappa t}}{2\pi\gamma}\exp\left\{-\frac{1}{2\gamma}\left[\frac{x_0^2}{\kappa} + \kappa\zeta^2\right] + e^{-\kappa t}x_0\left[\frac{2\zeta}{\gamma^2} + \frac{\eta}{\kappa\gamma}\right] - e^{-2\kappa t}\frac{2r^2x_0^2}{\kappa\gamma^3}\right\}, \end{aligned} \tag{F.9}$$

where one can restrict attention to leading terms in both t *and* x_0. The lower limit of t-integration can again be set to $-\infty$, and substitution of $e^{-\kappa t} = s$ transforms (F.9) into a Gaussian integral over a semi-infinite interval which can be expressed in terms of an error function. In the ensuing intermediate result, x_0 only occurs in a prefactor as in Eq. (F.8), which cancels when taking the ratio (F.4). Substitution of (2.2) for η and ζ (with $\omega_b \mapsto 1$) then finally yields

$$P_{\text{q.e.}}(x,p) = \frac{1}{2}\operatorname{erfc}\left\{\frac{1}{\sqrt{2\kappa\gamma}}x - \sqrt{\frac{\kappa}{2\gamma}}\,p\right\}\exp\left\{\frac{1}{2}x^2 - \frac{1}{2}p^2\right\}, \tag{F.10}$$

i.e., the famous quasi-equilibrium state first found by Kramers [4], approaching the Boltzmann distribution $P_{\text{q.e.}}(x,p) \approx \exp\{-(\frac{1}{2}p^2 - \frac{1}{2}x^2)\}$ for $x < 0$ and algebraically decaying in the η-direction for $x > 0$. It should be stressed that here this distribution has not been obtained as the solution of a certain ansatz for P, but as a result of a physically motivated limiting procedure (which is exact for all values of the friction). Therefore, corrections to $P_{\text{q.e.}}$ due to $x_0 \neq -\infty$ can now be estimated, and one can examine which distributions in p_0 (as a function of x_0) are admissible so that the result (F.10) still emerges in the limit $x_0 \to -\infty$. In the present work, however, these questions have not been pursued further.

To illustrate the difference which – despite the result (F.10) – exists between the inverted parabola problem and a quasi-equilibrium state in a system with a well, let

us calculate the escape (from the half-line $x_0 < 0$) probability [14]

$$\alpha \equiv \lim_{t\to\infty} \int_{x_1}^{\infty} \mathrm{d}x \int_{-\infty}^{+\infty} \mathrm{d}p\, P(x, p, t|x_0, p_0)\,. \tag{F.11}$$

One expects that owing to the limit $t \to \infty$ the probability α will be independent of x_1, and that α will tend to 0 and 1 if $\eta_0 \ll -1$ and $\eta_0 \gg 1$, respectively. Since one only needs the propagator P for large times, the calculation of α for arbitrary η_0 and ζ_0 is not difficult. One has

$$\alpha = \lim_{t\to\infty} \int_{-\infty}^{+\infty} \mathrm{d}\zeta \int_{\eta_1}^{\infty} \mathrm{d}\eta\, \frac{1}{2\pi\gamma} \times \exp\left\{-\frac{\mathrm{e}^{-2\kappa t}}{2\gamma^2}[\kappa\gamma \mathrm{e}^{2\kappa t}\zeta^2 + 4\zeta(\eta - \eta_0 \mathrm{e}^{\kappa t}) + \kappa^{-1}\gamma(\eta - \eta_0 \mathrm{e}^{\kappa t})^2] - \kappa t\right\}, \tag{F.12}$$

with $\eta_1 = 2\kappa r x_1 - \kappa^2\zeta$. Introducing $\tilde{\eta} = \eta \mathrm{e}^{-\kappa t} - \eta_0$, the covariance matrix occurring in Eq. (F.12) turns out to be asymptotically diagonal for large times when written in terms of $\tilde{\eta}$ and ζ, while the lower limit of $\tilde{\eta}$-integration becomes independent of ζ, leading to

$$\alpha = \int_{-\infty}^{+\infty} \mathrm{d}\zeta \int_{-\eta_0}^{\infty} \mathrm{d}\tilde{\eta}\, \frac{1}{2\pi\gamma} \exp\left\{-\frac{\kappa}{2\gamma}\zeta^2 - \frac{1}{2\kappa\gamma}\tilde{\eta}^2\right\} = \frac{1}{2}\mathrm{erfc}\left\{-\frac{\eta_0}{\sqrt{2\kappa\gamma}}\right\} \tag{F.13}$$

$$\sim \sqrt{\frac{\kappa\gamma}{2\pi}}|\eta_0|^{-1}\mathrm{e}^{-\eta_0^2/2\kappa\gamma} \quad (\eta_0 \to -\infty)\,. \tag{F.14}$$

The expectations mentioned below Eq. (F.11) are borne out, and one further observes that the exponent in Eq. (F.14) does not have the Arrhenius form $\mathrm{e}^{-x_0^2/2}$ (although by virtue of Eq. (2.2) for η_0 it approaches this form if $\gamma \to \infty$), thereby underlining the nonequilibrium character of the present barrier crossing problem (Eqs. (F.1), (F.11)). In particular one has $\alpha \to 0$ *exponentially fast* for $\gamma \to 0$, in contrast with the linear decay given below Eq. (7.3) for a problem with a well (see also the Introduction).

In closing we remark that analogous calculations are carried out for a different diffusion process in Appendices G.2 and G.4. In fact, the quantity α from the present appendix has a counterpart in the function Q studied there. The motivations are different, however. Here, the calculation of α merely serves to illustrate the nonequilibrium features of the process described by the propagator (F.5). There, the corresponding calculation introduces a less intuitive but more powerful method for the – in one case exact – determination of the escape probability Q.

[14] The present definition needs modification for potentials which tend to minus infinity so fast (for instance cubically) that the particle escapes to $x = \pm\infty$ in a finite time.

Appendix G. A nonlinear toy model for barrier recrossing

G.1. Preliminaries

In our study of Eq.(C.2) for the adjoint function $\mathcal{Q}$ we have profited from analyzing a simpler two-dimensional equation, which exhibits essentially the same behaviour. This model is defined on the (x, y)-plane by

$$[x + \varepsilon(y)]\partial_x Q - Ay\partial_y Q + v\partial_y^2 Q = 0 \,. \tag{G.1}$$

For $\varepsilon(y)=0$ one immediately sees the solution $Q(x, y) = \theta(x)$. In analogy with the situation in Appendix C, deviations from this step function are due to the nonlinear (i.e., anharmonic) term $\varepsilon(y)$. We will restrict attention mostly to

$$\varepsilon(y) = \alpha y^n \tag{G.2}$$

with $n \in \mathbb{N}_{\geqslant 2}$, and look for solutions with the same asymptotic behaviour as in the case $\varepsilon(y) = 0$, i.e., $Q(x, y) \to \theta(x)$ for $|x| \to \infty$.

It is advantageous to introduce an interpretation of the solution $Q(x, y)$ of the above boundary value problem which is different from the one in Appendix C. Namely, if a Fokker–Planck process is described by the forward equation

$$\partial_t P = -\partial_i [A_i P] + \frac{1}{2}\partial_i \partial_j [B_{ij} P] \,, \tag{G.3}$$

one can define a function $\pi(\boldsymbol{a}, \boldsymbol{x})$ which gives, for a particle starting in a point $\boldsymbol{x}$, the probability per unit area for eventually leaving a closed region in space at a point $\boldsymbol{a}$ on the – absorbing – boundary S (see, e.g., Ref. [36]). This function π is a solution of the stationary backward equation

$$A_i\, \partial_i \pi + \frac{1}{2} B_{ij}\, \partial_i \partial_j \pi = 0 \,, \quad \pi(\boldsymbol{a}, \boldsymbol{x})|_{x \in S} = \delta_S(\boldsymbol{a} - \boldsymbol{x}) \,. \tag{G.4}$$

Comparing the coefficients of this latter equation with Eq. (G.1), and integrating over all $\boldsymbol{a}$ in the region to the right (large positive x) of the deterministic separatrix (e.g., Ref. [17, Section IV.A]) given by

$$x_0(y) = -\frac{1}{A} \int_0^y \mathrm{d}y' \, \frac{\varepsilon(y')}{y'} \left| \frac{y'}{y} \right|^{1/A} \,, \tag{G.5}$$

one sees that Eq. (G.1) with the boundary condition $Q(x, y)|_S = \theta(x - x_0)$ can be interpreted as the backward equation for the *auxiliary stochastic process*

$$\partial_t P = -\partial_x [(x + \varepsilon(y))P] + \partial_y [AyP] + v\partial_y^2 P \,, \tag{G.6}$$

with Q giving the probability that a particle exits a region bounded by a curve S on a point $(x, y) \in S$ with $x > x_0(y)$. Clearly, the problem (G.6) and therefore (G.1) is well-posed physically. The emergence of a boundary layer solution for

Eq. (G.1) – i.e., deviations from $Q(x,y)=\theta(x-x_0)$ localized near the separatrix $x_0(y)$ – in the limit $v \downarrow 0$ also becomes obvious by inspection of (G.6); see further Section G.2.

In the case of even n, the auxiliary process reveals a nontrivial property of Q. For definiteness taking $\alpha > 0$, consider the Langevin equations equivalent to Eq. (G.6), i.e., [14]

$$\dot{x} = x + \alpha y^n\,, \qquad \dot{y} = -Ay + \sqrt{2v}\xi(t)\,. \tag{G.7}$$

If $x > 0$ – and with n even – one thus has $\dot{x} > 0$, regardless of y and the Gaussian white noise process ξ. Hence, in that case the particle certainly escapes to positive x, implying

$$1 - Q(x,y) \propto \theta(-x)\,. \tag{G.8}$$

For unity of method, let us pause to derive Eq. (G.8) from the Fokker–Planck equation. Specify the region in which the boundary value problem is posed as $|x| \leqslant L_x$, $|y| \leqslant L_y$, and let the prescribed boundary value be $Q(x,y)|_S = 1$ for $x \geqslant 0$. We claim that with this boundary value one actually has $Q(x,y)=1$ for *all* $0 \leqslant x \leqslant L_x$ and $|y| \leqslant L_y$. For a proof, choose $x' > 0$ and y' fixed. Let $P(x,y)$ be the solution of

$$-\partial_x[(x+\alpha y^n)P] + \partial_y[AyP] + v\partial_y^2 P = -\delta(x-x')\delta(y-y') \tag{G.9a}$$

with $P(x, \pm L_y) = 0$, satisfying

$$P(x < x', y) \equiv 0\,. \tag{G.9b}$$

Existence and uniqueness of such a solution follow since, for[15] $\frac{1}{2}x' \leqslant x < L_x$, Eq. (G.9a) is a heat equation for $(x+\alpha y^n)P$ with x as a fictitious time and positive definite diffusion coefficient $(x+\alpha y^n)^{-1}$. Standard theory [46] for such equations yields a unique retarded Green's function smoothly matching onto the null solution for P in the region $-L_x \leqslant x \leqslant \frac{1}{2}x'$. Green's theorem then shows that

$$Q(x',y') = \int_S \mathrm{d}l\, \hat{\sigma} \cdot (P(x+\alpha y^n)Q, -PAyQ - vQ\partial_y P)^{\mathrm{T}}\,, \tag{G.10}$$

where on the r.h.s. Q has the above-mentioned boundary value, that is, on the contributing part of the boundary S one has $Q=1$. The divergence theorem finally yields

$$\begin{aligned} Q(x',y') &= \int\int \mathrm{d}x\,\mathrm{d}y\, \{\partial_x[(x+\alpha y^n)P] - \partial_y[AyP] - v\partial_y^2 P\} \\ &= 1\,, \end{aligned} \tag{G.11}$$

a result which can be extended to the y-axis by continuity of Q. □

[15] The factor $\frac{1}{2}$ is chosen for definiteness, any β with $0 < \beta < 1$ will do.

G.2. Boundary layer approximation

The characteristic curves of Eq. (G.1) satisfy

$$\frac{\mathrm{d}x}{x+\varepsilon(y)}+\frac{\mathrm{d}y}{Ay}=0\,, \tag{G.12}$$

which can be integrated to yield

$$\phi = Ax|y|^{1/A}+\int_0^y \mathrm{d}y'\,\frac{\varepsilon(y')}{y'}|y'|^{1/A}=\text{const.}\,, \tag{G.13}$$

of which the deterministic separatrix (G.5) is seen to be the special case $\phi=0$. Transforming to coordinates (ϕ, y), one arrives at

$$-Ay\partial_y Q+v\left[\partial_y+\frac{x(\phi,y)+\varepsilon(y)}{y}|y|^{1/A}\partial_\phi\right]^2 Q=0\,. \tag{G.14}$$

The *boundary layer approximation* (BLA) [11] now implements the idea that, for small v, the spatial variation of Q is localized near the separatrix. This means that in Eq. (G.14) one may replace x by $x_0(y)$. Moreover, since the function Q mainly varies in a direction orthogonal to the separatrix, of the terms proportional to v only the one involving ∂_ϕ^2 is taken into account, leading to

$$-Ay\partial_y Q+vD(y)\partial_\phi^2 Q=0\,, \tag{G.15}$$

with

$$D(y)=\left[\frac{\varepsilon(y)}{y}|y|^{1/A}-\frac{1}{Ay}\int_0^y \mathrm{d}y'\,\frac{\varepsilon(y')}{y'}|y'|^{1/A}\right]^2\,. \tag{G.16}$$

At this point no further scaling assumptions on the form of Q are necessary, since its value on the ϕ-axis, $Q(\phi, y=0)=\theta(\phi)$, can be propagated in the direction of increasing $|y|$ (playing the role of fictitious time in the boundary layer problem, in contrast with the analysis following Eq. (G.9)) to yield

$$Q(\phi,y)=\frac{1}{2}\mathrm{erfc}\left\{-\frac{\phi}{2\ell(y)}\right\}\,, \tag{G.17}$$

with

$$\ell^2(y)=\int_0^y \mathrm{d}y'\,\frac{vD(y')}{Ay'}\,. \tag{G.18}$$

The 'initial value' $\ell(y=0)=0$ can be understood in the following two ways:

(a) Only if $Q(\phi, y)$ tends to $\theta(\phi)$ for fixed ϕ and $y\to 0$ does the BLA to Q satisfy the boundary condition imposed at $|x|=\infty$ as $y\to 0$ in the original coordinates (x, y).

(b) The function $D(y)$ vanishes for $y \to 0$, so that the approximation made on x below Eq. (G.14) is only justified in a ϕ-interval of length tending to zero for $y \to 0$. Hence, the 'initial value' imposed on ℓ is the only one for which the BLA is consistent.

If $\varepsilon(y)$ is of the form (G.2), one has

$$D(y) = \left(\frac{\alpha n}{n + 1/A} |y|^{n-1+1/A} \right)^2 \tag{G.19}$$

and

$$\ell(y) = \frac{\sqrt{\nu}}{\sqrt{2A(n-1+1/A)}} \frac{\alpha n}{n+1/A} |y|^{n-1+1/A}, \tag{G.20}$$

while

$$\phi(x, y) = Ax|y|^{1/A} + \frac{\alpha y^n |y|^{1/A}}{n + 1/A} \tag{G.21}$$

so that the fractional powers of y cancel in Eq. (G.17), cf. (G.37).

Let us estimate the error involved in the BLA. Throughout we take A to be a parameter of order unity.

(a) The validity of neglecting the ϕ-dependence of $D(\phi, y)$ can be assessed as follows. The relevant range in ϕ for the solution (G.17) is given by $|\phi| \lesssim \ell(y)$, on which the coefficient of ∂_ϕ in Eq. (G.14) varies by an amount $\sim \ell(y)/A|y|$, as follows from comparison with Eq. (G.18). One therefore should have $(\ell(y)/Ay)^2 \ll D(y)$, or $|y| \gg \sqrt{\nu}$. Thus, no matter how thin the boundary layer becomes in the limit $y \to 0$, it is too broad for the approximation $D = D(y)$.

(b) The neglect of y-diffusion in comparison with y-drift is valid if the former ($\nu \partial_y Q \sim \nu \ell'(y)/\ell(y) \sim \nu/y$) is much smaller than the latter ($AyQ \sim y$). The approximation again fails if $|y| \lesssim \sqrt{\nu}$.

(c) Finally, for even n the solution (G.17) is compatible with the rigorous relation (G.8) only if the boundary layer does not extend to the y-axis, i.e., if $\ell(y) \ll \phi(x = 0, y)$. One arrives at the condition $|y| \gg \sqrt{n\nu}$, in accordance with the above results.

In all three estimates, the difference between a cubic[16] ($n = 2$) and a quartic or other ($n \geqslant 3$) nonlinear term does not play an important role. Rather, the fact that diffusion at the saddle point $x = y = 0$ only takes place in a direction parallel to the separatrix causes boundary layer theory to fail within a diffusive length $\sqrt{\nu}$ near the origin, and one must resort to numerical (Section G.3) or less conventional analytic methods (Sections G.4 and G.5). The above internal consistency checks of the solution (G.17) may be supplemented by a comparison with the result of a different method; see Section G.4.

To illustrate the interplay between the forward (P) and backward (Q) equations, let us reformulate the BLA in terms of the auxiliary stochastic process. For this purpose,

[16] Terminology chosen in analogy with the main text.

transform the FPE (G.6) to coordinates (ϕ, y) (with Jacobian $\partial(\phi, y)/\partial(x, y) = A|y|^{1/A}$), and make the same approximations which lead to Eq. (G.15). One obtains

$$\partial_t P = \partial_y[AyP] + \nu D(y)\,\partial_\phi^2 P\,, \tag{G.22}$$

which leads to the Green's function

$$P(\phi, y|\phi_0, y_0) = \frac{\delta(y - y_0 e^{-At})}{2\sqrt{\pi}(\ell^2(y_0) - \ell^2(y))} \exp\left\{-\frac{(\phi - \phi_0)^2}{4(\ell^2(y_0) - \ell^2(y))}\right\}. \tag{G.23}$$

The probability of leaving the boundary layer in the direction of positive ϕ therefore is

$$\lim_{t\to\infty} \int \mathrm{d}y \int_0^\infty \mathrm{d}\phi\, P(\phi, y|\phi_0, y_0) = \frac{1}{2}\mathrm{erfc}\left\{-\frac{\phi_0}{2\ell(y_0)}\right\}. \qquad \square \tag{G.24}$$

Notice that the distribution P tends to a finite width in ϕ as $t\to\infty$, and hence to an exponentially increasing width in x (cf. Eq. (G.13)). Therefore, the Gaussian (G.23) will be a bad approximation to the exact propagator for large times since it has been obtained by setting $D(x, y) = D(x = x_0(y), y)$. We are, however, only interested in $\int_0^\infty P\,\mathrm{d}\phi$, for which the approximation remains a good one.

G.3. Numerical analysis

From here on we will analyze the model (G.1) beyond the BLA, i.e., in particular in the range $|y| \lesssim \sqrt{\nu}$. It will therefore be advantageous to introduce scaled coordinates $y' = y/\sqrt{\nu}$ and $x' = x/\alpha\nu^{n/2}$, so that $Q(x', y')$ satisfies Eq. (G.1) with $\alpha, \nu \mapsto 1$. That is, on this scale the problem does not involve a small parameter. In the following it will be assumed that this scaling has been carried out, and the primes on x and y will be omitted.

For the numerical solution of Eq. (G.1), we choose the same rectangular region as introduced below Eq. (G.8) and discretize the equation on a uniform grid. When symmetrically differencing $\partial_x Q$, the even and odd columns on the grid decouple (apart from boundary effects) and a numerical instability results. This difficulty is solved by approximating $\partial_x Q$ by either $[Q(x + \Delta x) - Q(x)]/\Delta x$ or $[Q(x) - Q(x - \Delta x)]/\Delta x$. We take the former (latter) if $x + y^n > 0$ (< 0), since in the auxiliary process the particle escapes almost always to $x = +\infty$ $(-\infty)$ for $x \gg 1$ ($\ll -1$), so that $Q(x, y)$ is predominantly influenced by its boundary value at $x = +L_x$ and $x = -L_x$, respectively (cf. Sections G.1. and G.2). This choice renders the matrix to be inverted as close as possible to the identity. Moreover, by changing from 'backward' to 'forward' differencing at a point where the prefactor of the term involved vanishes, numerical artifacts are minimized (cf. the 'upwind' differencing scheme in Ref. [3]).

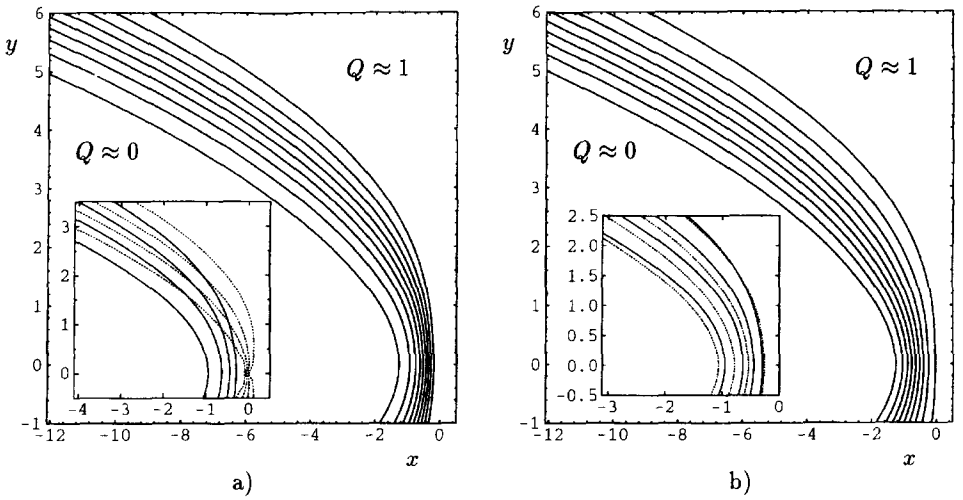

Fig. 1. Contour plots of $Q(x, y)$ for the cubic potential with $A=1$. The contours correspond to $Q=0.1, \ldots, 0.9$: (a) numerical solution, computed for $-18 < x < 0$ and $-9 < y < 9$ on a 180×180 grid and (b) Gaussian approximation according to Eqs. (G.34) and (G.35). Insets show a comparison of the numerical solution (solid lines) with (a) the BLA (dotted; the nonzero width at the origin is due to finite resolution) and (b) the Gaussian approximation (dotted), contours corresponding to $Q = 0.2, \ldots, 0.8$.

Using the above discretization, Eq. (G.1) has been solved by the relaxation method [17] [3]. Convergence is excellent, and the numerical solution for Q is determined to high accuracy on the rectangle $|x, y| \leqslant L_{x,y}$ by making the grid spacing sufficiently small. For even n, a further large gain in speed resulted from implementation of the feature that $Q(x, y)$ is even in y and constant for $x \geqslant 0$ (see Section G.1).

Results for the *cubic* potential are plotted in Fig. 1, those for the *quartic* potential in Fig. 2. For comparison, the upshot of the Gaussian approximation to be derived in Section G.4 is included in these figures.

Since our principal interest is in the solution for Q on the entire (x, y)-plane, one should investigate how Q behaves for $L_{x,y} \to \infty$. Fortunately, because in the auxiliary process (G.6) the stable y-flow dominates over y-diffusion for large $|y|$, the boundary value imposed at $y = \pm L_y$ influences the solution only in a narrow region near these boundaries, the width of this region being a decreasing function of L_y. [18] This feature is confirmed in Fig. 3, where the numerical solution for Q is plotted in a case where a pathological set of boundary values has been imposed on purpose, the jump in the boundary value from zero to one being located at $x = 0$ instead of at $x = x_0(y)$. This hardly affects the solution already at $y = 5$, i.e., one unit from the boundary. Since $Q(x, y)$ rapidly approaches its asymptotic value $Q(x, y) \sim \theta(x)$ when (G.1) is solved

[17] Overrelaxation was not used, since efficiency was less important than stability. The latter is only guaranteed by Ref. [3] for elliptic partial differential operators, while the diffusion tensors implicit in Eqs. (G.1), (G.6) have a zero eigenvalue (cf. Sections 2, 3).

[18] This holds independent from – and should not be confused with – the extent of validity of the BLA.

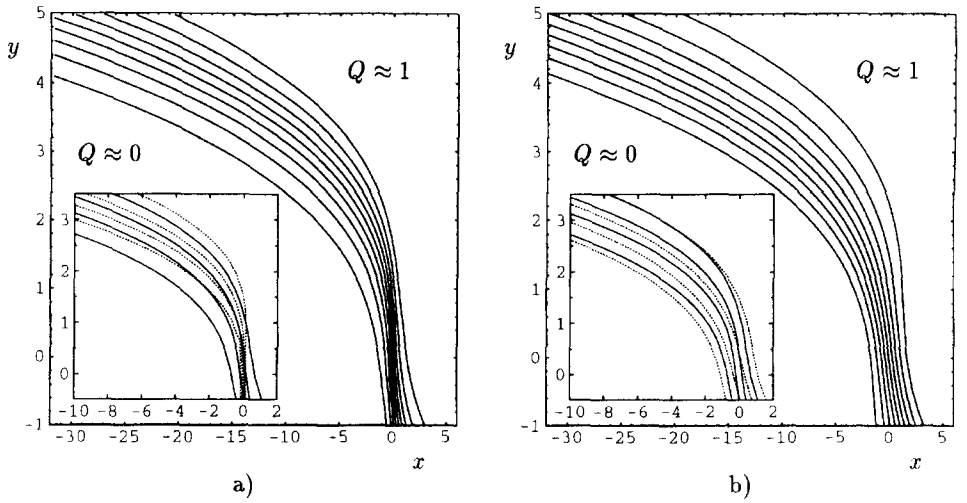

Fig. 2. Contour plots of $Q(x, y)$ for the quartic potential with $A=1$. The contours correspond to $Q=0.1, \ldots, 0.9$: (a) numerical solution, computed for $-36 < x < 36$ and $-7 < y < 7$ on a 200×200 grid and (b) Gaussian approximation according to Eqs. (G.34) and (G.36). Insets show a comparison of the numerical solution (solid lines) with (a) the BLA (dotted; the nonzero width at the origin is due to finite resolution) and (b) the Gaussian approximation (dotted), contours corresponding to $Q=0.2, \ldots, 0.8$.

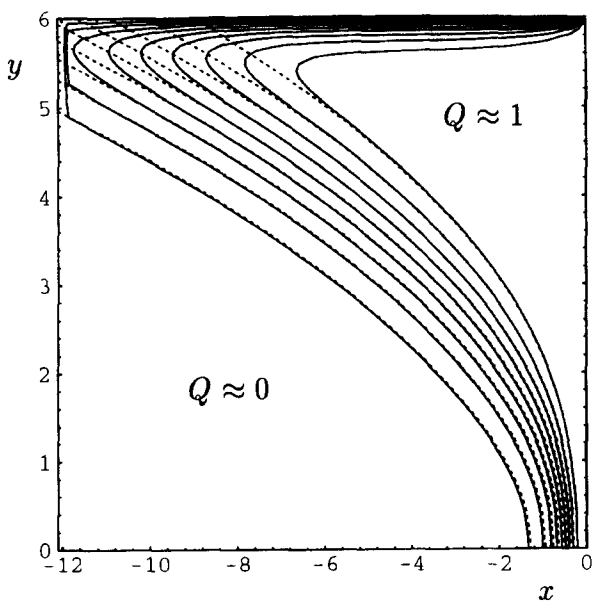

Fig. 3. Numerical solution of Q (solid lines), computed for $-12 < x < 0$ and $0 < y < 6$ on a 80×80 grid with pathological boundary values, see the main text. By exploiting the symmetry in y (see the third paragraph of Section G.3), boundary effects near the x-axis are eliminated. Dashed lines show the numerical solution of Fig. 1a, agreeing with the pathological solution except near the upper boundary. Remaining tiny deviations near the origin are due to discretization errors.

on the entire (x, y)-plane, the solution is equally insensitive to the value of L_x at which this behaviour is imposed as a boundary condition. Therefore, given any $L_0 > 0$, it is numerically feasible to choose $L_{x,y}$ in such a way (in practice only slightly larger than L_0) that the solution $Q(x, y)$ is free of finite-size effects for $|x, y| \leqslant L_0$ to any desired precision.

G.4. The moment method

For an analytical understanding of the results obtained in Section G.3, let us study the propagator from the end of Section G.2 in more detail. Starting from the full (i.e., *without* the BLA) equation (G.6), it is readily verified that this propagator obeys the symmetry

$$P(x, y, t \mid x_0, y_0) = P(x - x_0 \mathrm{e}^t, y, t \mid 0, y_0) . \tag{G.25}$$

Thus one only has to consider initial points on the y-axis, and we will henceforth omit the argument $x_0 = 0$.[19] Let us introduce the moments $P_m(y, t \mid y_0) = \mathrm{e}^{-mt} \int_{-\infty}^{+\infty} x^m \times P(x, y, t \mid y_0)\,\mathrm{d}x$, where the scaling prefactor e^{-mt} is chosen such that P_m tends to a finite limit as $t \to \infty$. The moments can be calculated from the equation

$$\partial_t P_m = \partial_y [A y P_m] + \partial_y^2 P_m + m y^n \mathrm{e}^{-t} P_{m-1} + \delta_{m0} \delta(t) \delta(y - y_0) . \tag{G.26}$$

For $m = 0$ this is an Ornstein–Uhlenbeck process, with the solution

$$P_0(y, t \mid y_0) = \sqrt{\frac{A}{2\pi(1 - \mathrm{e}^{-2At})}} \exp\left[-\frac{A(y - y_0 \mathrm{e}^{-At})^2}{2(1 - \mathrm{e}^{-2At})} \right] , \tag{G.27}$$

which can be used as a Green's function for the higher order moment equations to yield

$$P_{m \geqslant 1}(y, t \mid y_0) = m \int_0^t \mathrm{d}t' \int_{-\infty}^{+\infty} \mathrm{d}y'\, y'^n \mathrm{e}^{-t'} P_0(y, t - t' \mid y') P_{m-1}(y', t' \mid y_0) . \tag{G.28}$$

For $t \to \infty$ the inhomogeneous term in (G.26) disappears, so that P_m relaxes to equilibrium:

$$P_m(y, t \mid y_0) \to \sqrt{A/2\pi} \exp(-A y^2/2) P_m(y_0) . \tag{G.29}$$

This points at a shortcoming of Eq. (G.28) – expressing the asymptotic value of $P_m(y, t \mid y_0)$ in terms of the full time dependence of P_{m-1} – as a calculational procedure, which can be remedied as follows. Using the recurrence relation (G.28), one expresses P_m as an m-fold convolution of P_0s. Subsequently, one reverses the order of time integration (so that the time integral expressing P_1 in terms of P_0 becomes the outer

[19] For even n, the results from this section thus lead to the intriguing conclusion that, in order to determine the escape probability $Q(x, y)$ for *all* x, it suffices to determine the propagator for initial points that are certain to escape to positive x.

one) and introduces the time differences $\Delta t_i = t_i - t_{i+1}$ (such as occurring in the argument of P_0 in Eq. (G.28), and running from 0 to ∞) as new integration variables. Inspection of the resulting convolution structure yields the recurrence relation

$$P_m(y_0) = m \int_0^\infty \mathrm{d}t \int_{-\infty}^{+\infty} \mathrm{d}y\, y^n \mathrm{e}^{-mt} P_0(y,t\,|\,y_0) P_{m-1}(y) + \delta_{m0}\,, \tag{G.30}$$

where we have refrained from taking $P_{m-1}(y)$ outside the time integral since the latter can be performed in closed form only after the y-integration has been carried out.

It will now be investigated how the moments $P_m(y_0)$ can be used for the determination of Q. Substitute $z = \ln x$ on the half plane $x > 0$ to obtain

$$\partial_t P(z,y) = -\partial_z[(1 + \mathrm{e}^{-z} y^n)P] + \partial_y[AyP] + \partial_y^2 P\,. \tag{G.31}$$

Asymptotically (in z) this yields a propagator in equilibrium in the y-direction, and translating uniformly in the z-direction. Transforming back, this is seen to imply that the propagator for large times has the scaling form (on the entire (x,y)-plane)[20]

$$P(x,y,t\,|\,y_0) = \sqrt{A/2\pi}\exp(-Ay^2/2)\mathrm{e}^{-t} f(x\mathrm{e}^{-t}\,|\,y_0)\,, \tag{G.32}$$

and comparison with Eq. (G.29) shows that the P_m are precisely the moments of this scaling function, i.e., $P_m(y_0) = \int_{-\infty}^{+\infty} s^m f(s\,|\,y_0)\,\mathrm{d}s$. Combination of Eqs. (G.25) and (G.32) now yields the escape probability as

$$Q(x_0,y_0) = \lim_{t\to\infty} \int_{-\infty}^{+\infty} \mathrm{d}y \int_0^\infty \mathrm{d}x\, P(x,y,t\,|\,x_0,y_0) = \int_{-x_0}^{\infty} \mathrm{d}s\, f(s\,|\,y_0)\,. \tag{G.33}$$

Neglecting all cumulants of f of higher than second order, one arrives at the *Gaussian approximation* to Q,

$$Q_{\mathrm{Gauss}}(x,y) = \frac{1}{2}\mathrm{erfc}\left\{-\frac{x + R_1(y)}{\sqrt{2R_2(y)}}\right\}, \tag{G.34}$$

with cumulants $R_1 = P_1$, $R_2 = P_2 - P_1^2$, etc. Eq. (G.34) represents a substantial improvement over (G.17) since, while the error function shape is still an approximation – implicit in Section G.2 in the linearization leading to (G.15) – the position and width $R_{1,2}(y)$ have now been calculated exactly, as will become even clearer from the analysis following Eq. (G.38). Calculating these cumulants by (G.30) with Eq. (G.27) for P_0, one finds

$$R_1(y) = \frac{y^2 + 2}{2A + 1}, \tag{G.35a}$$

$$R_2(y) = \frac{4(y^2 + 1)}{(2A + 1)^2(A + 1)} \tag{G.35b}$$

[20] Strictly speaking, the very existence of the $P_m(y_0)$ for all m already implies the scaling form (G.32).

for $n=2$, while for $n=3$ one has

$$R_1(y) = \frac{(A+1)y^3 + 6y}{(A+1)(3A+1)}, \tag{G.36a}$$

$$R_2(y) = 9\frac{(A+1)^2y^4 + (14A+10)y^2 + 22A + 14}{(A+1)^2(3A+1)^2(2A+1)}. \tag{G.36b}$$

It is instructive to compare the Gaussian and boundary layer approximations. Using (G.20) for ℓ and (G.21) for ϕ, one finds that Eq. (G.17) is also of the form (G.34), with

$$R_1(y) = \frac{y^n}{nA+1}, \tag{G.37a}$$

$$R_2(y) = \frac{n^2y^{2n-2}}{(nA+1)^2((n-1)A+1)}. \tag{G.37b}$$

In both the cubic and the quartic case, the boundary layer approximation is seen to give the highest order term (in y) of the $R_{1,2}$ exactly, while omitting all lower order terms. This is in agreement with the error estimates below Eq. (G.21), which state that boundary layer theory is valid only if the rescaled $y \gtrsim 1$.

The Gaussian approximation to Q is plotted in Figs. 1(b) and 2(b) for the cubic and quartic potential, respectively. Compared to the BLA, agreement to the numerical result is improved significantly. However, features of the numerical solution such as the asymmetric shape at $y=0$ in Fig. 1(a) are not reproduced, cf. below Eq. (G.34).

Eq. (G.33) shows that the above-developed moment method admits a perhaps surprising reformulation. Namely, the scaling function f apparently is nothing else than the derivative $f(-x\,|\,y) = \partial_x Q(x,y)$. The fact that the moments of f can be calculated recursively implies that the equation

$$[-\mathrm{i}ky^n - k\partial_k - Ay\partial_y + \partial_y^2]\,\hat{f}(k,y) = 0 \tag{G.38}$$

for the Fourier transform $\hat{f}(k) = \int_{-\infty}^{+\infty} f(x)\mathrm{e}^{-\mathrm{i}kx}\,\mathrm{d}x$ is solved by a power series ansatz for the k-dependence of $\hat{f}$. By taking the derivative of Q we have arrived at a peaked function, the Fourier transform of which is assumed to be analytic in a strip around the real k-axis, enabling the use of series methods. Since the interest lies in the cumulants R_m rather than the moments P_m let $\hat{f} = \exp(\hat{g})$, leading to

$$-\mathrm{i}ky^n - k\partial_k\hat{g} - Ay\partial_y\hat{g} + \partial_y^2\hat{g} + (\partial_y\hat{g})^2 = 0. \tag{G.39}$$

Inserting the cumulant expansion

$$\hat{g}(k,y) = \sum_{m=1}^{\infty} \frac{(k/\mathrm{i})^m}{m!} R_m(y) \tag{G.40}$$

(where the absence of an $\mathcal{O}(k^0)$ term implements the normalization of Q), in $\mathcal{O}(k^m)$ one finds an inhomogeneous Hermite equation of negative order $-m/A$ for $R_m(y)$,

$$R_m''(y) - AyR_m'(y) - mR_m(y) + \sum_{l=1}^{m-1} \binom{m}{l} R_l'(y)R_{m-l}'(y) + \delta_{m1}y^n = 0. \tag{G.41}$$

For each $m \geqslant 1$ and $n \geqslant 2$ this equation has a unique polynomial solution,[21] so that the cumulants can be calculated recursively. In particular, one reproduces Eqs. (G.35) and (G.36).

While cumulants of higher than second order can be readily calculated from Eq. (G.41), they are of little use unless one can sum all of them, as in Section G.5. Namely, since the function $\hat{f}(k)$ is not entire (cf. below (G.46) for $n=2$), including more terms in the cumulant expansion does not necessarily lead to a better approximation of $\hat{f}(k)$ on the real k-axis. We have verified this by truncating the series (G.40) after the sixth order (the lowest order beyond the second leading to an $\hat{f}(k)$ vanishing at $k=\pm\infty$) for $n=2$ and carrying out the Fourier inversion numerically [3]. Agreement with the numerical data of Section G.3 was not improved over Q_{Gauss}.

G.5. An exactly solvable case

Inspection of the cumulants (G.35), and of the higher orders mentioned at the end of Section G.4, leads to the following ansatz for $\hat{g}$ for the case $n=2$:

$$\hat{g}(k, y) = y^2 a(z) + b(z), \tag{G.42}$$

with $z \equiv k/\mathrm{i}$. Substitution of (G.42) into Eq. (G.39) shows that the latter is satisfied as an identity, provided that the functions a and b satisfy

$$za'(z) + 2Aa(z) - 4a(z)^2 = z, \tag{G.43a}$$

$$zb'(z) = 2a(z), \tag{G.43b}$$

while the normalization of Q implies the initial conditions

$$a(0) = b(0) = 0. \tag{G.43c}$$

Eq. (G.43a) is a Ricatti equation, which can be transformed to a linear one to yield[22] [13]

$$a(z) = \frac{A}{2} - \frac{\sqrt{z}}{2}\frac{J_{2A-1}(4\sqrt{z})}{J_{2A}(4\sqrt{z})}, \tag{G.44}$$

which can be verified to satisfy Eqs. (G.43a) and (G.43c) by means of the standard recurrence relations and series expansion of the Bessel functions J, respectively. Rewriting Eq. (G.44) as

$$a(z) = \frac{A}{4} - \frac{\sqrt{z}}{2}\frac{J'_{2A}(4\sqrt{z})}{J_{2A}(4\sqrt{z})} \tag{G.45}$$

the quadrature solving (G.43b) becomes trivial.

[21] Two linearly independent (confluent hypergeometric [13]) solutions, both diverging as $R_m(y) \sim e^{Ay^2/2} y^{(m/A)-1}$, have been discarded.

[22] Notice that the r.h.s. of (G.44) is an even function of $\sqrt{z}$, so that the choice of sign for the square root is arbitrary.

Finally, recalling the definition of $\hat{f}$ in terms of $\hat{g}$ above Eq. (G.39), use of (G.44) and (G.42) gives

$$\hat{f}(k) = \frac{(2q)^A}{\sqrt{\Gamma(2A+1)J_{2A}(4q)}} \exp\left[\frac{y^2}{2}\left\{A - q\frac{J_{2A-1}(4q)}{J_{2A}(4q)}\right\}\right] \quad (q = \sqrt{k/\mathrm{i}}), \tag{G.46}$$

the inverse Fourier transform of which can be substituted into (G.33) to yield an exact closed-form solution of Eq. (G.1). The real zeros of J_{2A} lead to singularities in $\hat{f}$ on the positive imaginary axis, so that for $x < 0$ the Fourier inversion of $\hat{f}(k)$ can be carried out by closing the k-contour in the lower half plane implying $f(x<0)=0$, in accordance with Eq. (G.8).

While the properties of Eq. (G.46) have not yet been investigated in detail, we stress that it is one of the very rare instances in which a nonlinear Fokker–Planck type equation yields to exact solution in the absence of potential conditions [36], here in a case which does not correspond to complete thermal equilibrium.

G.6. Application to the Kramers problem

In this appendix, Eq. (G.1) has been primarily studied for its independent interest, but let us in conclusion briefly return to its application as a model for Eq. (C.2). In particular, the Fourier analysis following Eq. (G.38) turns out to be adaptable to three dimensions. In that case, series expansion w.r.t. the Fourier variable ℓ in each order l leads to a partial differential equation in the remaining variables u and x (cf. Eq. (C.7)), as opposed to the ordinary differential equation (G.41). However, a polynomial solution (in two variables) can still be obtained. Moreover, while termination of the cumulant expansion (G.40) is an *ad hoc* procedure, in Appendix C the analogous steps are seen to correspond to a systematic expansion of the attempt rate ν_a in the small parameter ℓ. The analysis finally yields the closed-form expressions (C.6a), (C.8), (C.9) for the leading correction to the – generalized – transition-state result $\nu_a = \kappa\omega_0/2\pi$, cf. the discussion above Eq. (1.2) and below Eq. (7.3).

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