Low-dimensional turnover theory of thermal activation

H. Dekker
Institute for Theoretical Physics, University of Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands and TNO Physics and Electronics Laboratory, P.O. Box 96864, 2509 JG Den Haag, The Netherlands

A. Maassen van den Brink
Institute for Theoretical Physics, University of Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands
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Kramers' Fokker-Planck model for activated rate processes (noise-induced escape over a potential-energy barrier) is solved *without* recourse to any microscopic theory (Grabert [Phys. Rev. Lett. **61**, 1683 (1988)]) or associated Langevin equations (Graham [J. Stat. Phys. **60**, 675 (1990)]). The independence of the microscopy of Grabert's original result for the escape rate is thereby definitely proven and clarified. Throughout, the analysis is systematic in a small parameter and provides a unified treatment of both weak and strong friction, including the turnover regime. *Inter alia* we introduce some novel theoretical concepts, such as a *constrained* Gaussian transformation and a *dynamical* extension of phase space. Finite-barrier corrections are also investigated.

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I. INTRODUCTION

The notion of noise-activated rate processes dates back to the work of van't Hoff [1] and Arrhenius [2] concerning chemical reactions. A most important feature in these early calculations of reaction rates was the assumption of perfect thermal equilibrium at the transition state (i.e., at the top of the energy barrier which separates one metastable chemical complex from another). However, the very existence of a nonequilibrium reaction process *ipso facto* implies deviations from the exact Boltzmann distribution. A second pivotal element in the early theory was the assumption of the absence of transition-state (or barrier) recrossings. Both assumptions taken together provide the framework for standard transition-state theory (TST) [3].

Standard TST is a purely kinetic theory. Its basic ingredient is mere equilibrium statistical mechanics. As such it does not allow evaluation of barrier recrossings, which are due to the dynamical coupling of the reactive complex to its environment (e.g., a solvent, or solid-state matrix). In a classic paper [4] Kramers investigated the significance of TST by modeling the escape over the barrier as the dynamics of a Brownian "particle." The particle moves along the reaction coordinate in a bistable potential $U(x)$. The fluctuations arise from the coupling to a thermal environment (or heat bath). Indeed, Kramers showed that the activated reaction process should stop if the coupling to the heat bath goes to zero. Remarkably, this result was not widely appreciated until recently [5,6].

Since in the zero-coupling limit the total mechanical energy of the particle becomes a conserved (i.e., slow) quantity, this case is most easily understood in terms of energy diffusion (around a deterministic trajectory). As a result the exponential prefactor (or attempt rate ν_a) in the general expression for the escape rate

$$\Gamma = \nu_a \exp(-\beta U_b) , \tag{1.1}$$

takes on the particular value $\nu_a(\lambda \to 0) = 2\lambda\beta I_b \omega_0/2\pi$. Here U_b is the barrier height, $I_b = \oint p\, dx$ is the action integral of classical mechanics (for a round trip through the well at the barrier peak energy $E=0$), 2λ is the friction coefficient, ω_0 is the harmonic frequency at the potential minimum, and $\beta = 1/k_B T$. Notice that $2\lambda I_b$ represents the energy loss per round trip. For the cubic and quartic model potentials [see below (2.1)], one has $I_b = 36U_b/5\omega_b$ and $I_b = 16U_b/3\omega_b$, respectively, where ω_b is the harmonic (curvature) frequency at the barrier. The above result for ν_a requires that $2\lambda\beta I_b \ll 1$. In this regime the suppression of the rate relative to the standard TST value $\nu_a = \omega_0/2\pi$ is due to the deviations mentioned earlier (depletion at $E=0$) from the exact Boltzmann equilibrium distribution.

Elaborating on Kramers' weak-damping analysis, depletion effects were calculated in detail by Büttiker, Harris, and Landauer [7], and by Mel'nikov and Meshkov [8]. The latter two-dimensional theory contains the former as a one-dimensional approximation [9]. In both cases, the rate monotonically tends to the simple TST result upon *increasing* the friction (which is incorrect, as will be discussed below). Extensions along these lines in order to include quantum-mechanical tunneling effects have been given, for example, in Refs. [10–13].

If the coupling to the heat bath 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. In this case the motion of the particle itself becomes slow, and the activation process reduces to Smoluchovsky diffusion along the reaction coordinate [14]. This leads to the relation $\nu_a(\lambda \to \infty) = \omega_0\omega_b/2\pi\lambda$. Here the reduction of the rate relative to the standard TST value is caused by diffusive

returns of particles across the barrier peak, which makes the original transition state imperfectly absorbing (and, hence, its notion moot). Kramers showed that for lower (i.e., moderate-to-strong) friction values, the Smoluchovsky result generalizes to $\nu_a = \kappa\omega_0/2\pi$, where

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

Note that this rate monotonically tends to the simple transition-state value upon *decreasing* the friction (which is incorrect, as has been discussed above). As with the weak-damping result, generalizations of Kramers' result for moderate-to-strong damping in order to include quantum-mechanical tunneling effects have been discussed, e.g., in Refs. [12,15,16]. For a review, see Ref. [17].

Clearly, Kramers' original analysis and its simple extensions do not provide a single, unified description for all values of the friction. This is so in particular for those intermediate values where the actual rate reaches a maximum, i.e., where the physics changes from energy diffusion (depletion) to spatial diffusion (recrossings). This is known as the Kramers turnover problem. During the last decade several attempts have been made to provide formulas bridging the two Kramers limits (see, for example, Refs. [7–9,12,18,19]). On the one hand, these approaches were all based on Kramers' classical stochastic process. On the other hand, however, none of them—apart from Ref. [9] and a recent article by Mel'nikov [20]—involved a unified picture of the reaction dynamics. As a consequence, the predictions for the turnover region varied considerably [21].

Meanwhile [22,23] the dynamical significance of the factor κ as given in (1.2) had been pointed out (in the context of generalizing Kramers' strong-coupling theory to include memory friction). In particular, Pollak [23] showed that $\kappa\omega_b$ is the eigenfrequency of the only unstable normal mode of the Zwanzig Hamiltonian [24] near the barrier peak (see also, for example, Refs. [25–27]). This Hamiltonian models the motion of a particle which is bilinearly coupled (via an interaction term $x\sum_k c_k x_k$) to a harmonic environment (with degrees of freedom x_k and frequencies ω_k). For an Ohmic environment this microscopic model indeed implies Kramers' stochastic process. However, the reverse statement does not hold.

Elaborating on Pollak's work, Grabert [28] pioneered a unified treatment of Kramers turnover problem on the basis of the Zwanzig Hamiltonian (see also Ref. [29]). The connection of the multidimensional TST of Pollak (leading to a spatial-diffusion-limited rate) with the weak-coupling theory of Mel'nikov and Meshkov [8] is possible upon introducing the energy E of the unstable barrier mode (in lieu of the particle energy E_p). Of course, the energy E is a collective variable involving both the particle *and* the microscopic environmental degrees of freedom.

The theory of Pollak, Grabert, and Hänggi [29] clearly leaves us with a challenge [9,30,31]. Namely, from the work of Refs. [28,29] the impression emerges that—in order to solve the turnover problem—one has to resort necessarily to a microscopic model. However, all ingredients for the description of the original stochastic process are fully contained in Kramers' two-dimensional Fokker-Planck equation [4], which is completely specified in terms of the particle's mechanical degrees of freedom (i.e., x and $p = m\dot{x}$). So far it has remained unclear 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 *per se*.

The Zwanzig model Hamiltonian defines a Langevin dynamics in the particle subspace [25,27,29]. The Langevin noise arises from the environmental degrees of freedom. Recalling that the unstable mode is a mixture of particle and bath variables, Graham formulated a theory of activated decay (including the turnover region) on the basis of the Langevin equation associated with Kramers' Fokker-Planck equation, by mixing particle and noise variables [31]. Obviously, Graham's theory only partially meets the challenge formulated above.

In the present article the challenge will be fully met. A turnover theory similar to Grabert's will be given, based solely on Kramers' Fokker-Planck equation for the phase-space density $P(x,p)$. *No* recourse to a microscopic model or Langevin dynamics will be made. Apart from the unstable-mode energy, the analysis requires the introduction of some new theoretical concepts (such as a constrained Gaussian transformation and a dynamical extension of phase space).

In Sec. II the separatrix of the particle motion near a parabolic barrier is investigated. The stable and unstable direction at the saddle point are used to define a transformation from (x,p) to (η,ζ). Generalizing an earlier idea [32,33], the noise along the unstable coordinate η is eliminated in Sec. III by means of a Gaussian integral transformation. A constraint takes care of preserving the dynamical significance of the potential $U(x)$ under this mapping. In Sec. IV phase space is extended by a new coordinate ϑ. The (stable) dynamics along 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 in an indirect manner (via the w mode), which allows the definition of the unstable-mode energy E. The full equilibrium distribution in extended phase space is shown to be Boltzmannian (in terms of E) in Sec. V. Its normalization is discussed in Appendix A. The existence of a quasiequilibrium (metastable) distribution like that of Kramers—but now *without* barrier recrossings—is also shown, which allows a calculation of the Kramers-Smoluchowsky escape rate by means of TST (which constitutes the low-dimensional version of Pollak's theory for moderate-to-strong friction [23]). Finite-barrier corrections are considered in a systematic analysis in Appendix B. Section VI contains a systematic analysis of the quasiequilibrium state $R(u,v,w)$ in extended phase space in the weak-friction regime. Introducing a fictitious time variable, a "system-size"-type [14] expansion of the Fokker-Planck equation for $R(u,v,w)$ 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 Green's function is Gaussian (in terms of E). Finally, in Sec. VII the formula for the decay rate is obtained by combining the (leading-order) results from Secs. V and VI in a unified treatment.

The present analysis (re)establishes the microscopic-model independence of Kramers' stochastic process (which in that sense is universal). *Inter alia* it also clarifies (or, in other cases, circumvents) certain intricacies involved in the microscopic-model formulation, such as those concerning the systematic nature of corrections to the leading result. An exhaustive account of the theory will be available upon request [34].

II. 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

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

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 $U(x)=-\frac{1}{2}\omega_b^2x^2(1+x/a)$ and the quartic $U(x)=-\frac{1}{2}\omega_b^2x^2(1-x^2/a^2)$. In general, near the barrier peak $U(x)\approx-\frac{1}{2}\omega_b^2x^2$ while near the potential minimum $U(x)\approx-U_b+\frac{1}{2}\omega_0^2(x-x_0)^2$.

For 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 $\mathcal{S}$ [12,17,35] for these dynamics is given by $p(x|\mathcal{S})=-(\omega_b/\kappa)x$, where κ is Kramers' coefficient (1.2). $\mathcal{S}$ is a repeller, i.e., the barrier motion is unstable in a direction orthogonal to $\mathcal{S}$. On the other hand, the barrier motion is stable towards the attractor $\mathcal{T}$ [12], which is given by $p(x|\mathcal{T})=\kappa\omega_b x$. Therefore, we introduce coordinates

$$\begin{aligned}\eta&=x+p/\omega_2\ ,\\ \zeta&=x-p/\omega_1\ ,\end{aligned} \tag{2.2}$$

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

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

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

$$\frac{\partial P}{\partial t}=-\frac{\partial}{\partial\eta}(F_1P)-\frac{\partial}{\partial\zeta}(F_2P)+\frac{\partial^2}{\partial\eta^2}(\mathcal{D}_{11}P)+\frac{\partial^2}{\partial\eta\,\partial\zeta}(2\mathcal{D}_{12}P)+\frac{\partial^2}{\partial\zeta^2}(\mathcal{D}_{22}P)\ , \tag{2.4}$$

where

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

Of course, since $\omega_1\omega_2=\omega_b^2$, the diffusion tensor $\mathbf{D}=\{\mathcal{D}_{kl}\}$ given by (2.5) is non-negative but singular ($\mathcal{D}_{kk}>0$, $\mathrm{Det}\mathbf{D}=0$).

III. 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)

$$Q(\bar{\eta},\bar{\xi},t)=N\int_{-\infty}^{\infty}d\eta\int_{-\infty}^{\infty}d\zeta\,e^{-K(\bar{\xi}-\zeta)^2}\times\delta(\bar{x}-x)P(\eta,\zeta,t)\ . \tag{3.1}$$

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

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

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

$$\frac{\partial Q}{\partial t}=-\frac{\partial}{\partial\eta}(F_1Q)-\frac{\partial}{\partial\zeta}(F_2Q)+\frac{\partial^2}{\partial\eta^2}(D_{11}Q)+\frac{\partial^2}{\partial\eta\,\partial\zeta}(2D_{12}Q)+\frac{\partial^2}{\partial\zeta^2}(D_{22}Q)\ , \tag{3.5}$$

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

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

with

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

The diffusion tensor $\mathbf{D}$ defined by (3.6) is indefinite but non-singular ($D_{kk}\geq 0$, $\mathrm{Det}\mathbf{D}<0$).

IV. 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 B) for the description of the escape process in the moderate-to-strong-friction regime, the Kramers-Smoluchovsky rate can be calculated from (3.5), (3.6) by means of TST [31,34]. An elegant analysis unifying this result with the small-friction regime will be given in terms of an unstable-mode energy E (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

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

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 Sec. V, 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

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

Now let

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

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

$$\frac{\partial R}{\partial t}=-v\frac{\partial R}{\partial u}-\kappa^2[\omega_b^2u-U_a'(x)]\frac{\partial R}{\partial v}-\frac{\partial}{\partial w}(F_wR)+\frac{\partial^2}{\partial u\,\partial w}(2D_{uw}R)+\frac{\partial^2}{\partial v\,\partial w}(2D_{vw}R)+\frac{\partial^2}{\partial w^2}(D_{ww}R)\ , \tag{4.5}$$

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

$$F_w(u,v,w)=-\omega_2w-\frac{2\lambda}{\kappa^2}(u-v/\omega_1)\ , \tag{4.6}$$

$$D_{uw}=-\tfrac{1}{4}\kappa^2D_{ww},\quad D_{vw}=-\tfrac{1}{4}\kappa^3\omega_bD_{ww}\ ,\qquad D_{ww}=4\lambda\varkappa/\beta\kappa\omega_1^2\ . \tag{4.7}$$

Note that, for fixed w, the dynamics in the (u,v) plane is conservative. In particular, in the harmonic barrier region this flow ($\dot u=v$, $\dot v=\omega_1^2u$) decouples from the environmental variable w and is unstable. The unstable-mode energy [28,31] is now defined as

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

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

V. THE EQUILIBRIUM DISTRIBUTION AND BARRIER RECROSSINGS: TRANSITION-STATE THEORY OF THE KRAMERS-SMOLUCHOVSKY RATE

Let us rewrite (4.5)–(4.7) in terms of (u,E,w) [4,7–10,36,37]. The result reads

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

where the current J is given by

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

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

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

The value of $\mathcal{N}$ corresponding to normalization in the local (harmonic) minimum of the potential $U(x)$ is found by noting that the marginal distribution $Q_{\mathrm{eq}}(\eta,\zeta)$, resulting from (5.3) by means of (4.1), should be identical to $Q_{\mathrm{eq}}(\tilde\eta,\tilde\zeta)$, resulting from the equilibrium distribution $P_{\mathrm{eq}}(x,p)=N_0\exp(-\beta E_p)$ 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

A). 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 $E/\kappa^3\varkappa\to E$ one can make $\beta_E=\beta$. In that case (which will be implicit in Sec. VI), the normalization constant of the marginal distribution $R_{\rm eq}(E)$, of course, reads $\mathcal{N}_E=(\kappa\beta\omega_0/2\pi)\exp(-\beta U_b)$.

Recalling the remarks made in Sec. IV, let us now calculate the decay rate by means of (5.3) and (5.4). In extended phase space (EPS) the decay rate is given by [4,34]

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

where $R(u,v,w)$ is the *quasiequilibrium* distribution normalized according to (5.4). Using (4.5) for $\partial R/\partial t$ in (5.5), one finds

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

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 B). Hence, one has $R(0,v,w)=\Theta(v)R_{\rm eq}(E,w)$ where $\Theta(v)$ is the unit step function, so that (5.6) becomes

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

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

VI. UNSTABLE-MODE ENERGY DIFFUSION

In Sec. V we have met the challenge (posed by the moderate-to-strong-damping theory of Pollak [23]) of formulating a low-dimensional Fokker-Planck version of multidimensional TST. That is, by the combination of 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 Sec. V. 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–low-temperature expansion 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 $\lambda\to\lambda\Omega^{-1/2}$ and $\beta\to\beta\Omega^{1/2}$, with $\Omega\to\infty$. As a consequence, to leading order in Ω one has $\beta_w\to\beta_w\Omega$ and $D_{ww}\to D_{ww}\Omega^{-1}$. In addition, let both $w\to w\Omega^{-1/2}$ and $E/\kappa^3\varkappa\to E\Omega^{-1/2}$ (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 $\kappa\sim\Omega^0$, $\varkappa\sim\Omega^0$, $U_a(x)\sim\Omega^0$, $v(u,E,w)\sim\Omega^0$, 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

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

with

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

where the *fictitious* time τ (in place of u) is defined by the nonlinear mapping $u=\alpha(\tau)$, with $\dot\alpha=v(\tau)$, $v(\tau)=\pm[-2\mathcal{U}(\tau)]^{1/2}$, and $\mathcal{U}(\tau)=U(\alpha(\tau))$. To make sure, $\mathcal{U}_a'(\tau)=U_a'(\alpha(\tau))$. Note that $v(\tau)=v^{(0)}(u)$, that $v^{(0)}(u)\partial R/\partial u=\partial R/\partial\tau$, and that $\{\dot\alpha=v,\dot v=-U'(\alpha)\}$ represents the Hamiltonian motion in the original potential at the barrier peak energy ($E=0$). The trajectory $\{\alpha(\tau),v(\tau)\}$ is a "bounce"-type configuration [15–17] in EPS. For the cubic potential one finds $\alpha(\tau)=-a/\cosh^2(\frac{1}{2}\omega_b\tau)$. The quartic potential yields $\alpha(\tau)=-a/\cosh(\omega_b\tau)$.

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 $\mathcal{E}(\tau)=\langle E\rangle$ and $\mathcal{W}(\tau)=\langle w\rangle$ read

$$\dot{\mathcal{E}}=\tfrac{1}{2}\mathcal{U}_a'(\tau)\dot{\mathcal{W}},\quad \dot{\mathcal{W}}=-\omega_b\mathcal{W}-2\lambda(\alpha-v/\omega_b)\ . \tag{6.3}$$

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

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

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), noting that $\sigma_{wE}(-\infty)=\mathcal{W}(-\infty)=0$, yields $\sigma_{wE}(\tau)=-\mathcal{W}(\tau)/\beta$ and

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

with $\Delta\mathcal{E}(\tau)=\mathcal{E}(\tau)-\mathcal{E}(-\infty)$. It is easily shown that the energy loss per round trip resulting from (6.3) exactly amounts to $\Delta\mathcal{E}(\infty)=2\lambda I_b$ [34].

For 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 reads [8,9]

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

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

VII. 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

$$R(E,\infty)=\int_{-\infty}^{\infty}W(E|E')R(E',-\infty)dE', \quad (7.1)$$

where the transition probability density $W(E|E')=G_\infty(E|E')$. The TST version of (7.1) follows by letting $R(E,-\infty)=\Theta(-E)R(E,\infty)$, so that

$$R(E)=\int_{-\infty}^{0}W(E|E')R(E')dE', \quad (7.2)$$

where $R(E)=R(E,\infty)$ is the *quasiequilibrium* distribution subject to the boundary conditions $R(E)\to R_{\rm eq}(E)$ if $E\to-\infty$, and $R(E)\to0$ if $E\to\infty$. This Fredholm equation can be solved by the Wiener-Hopf method [38] (see also Ref. [9]), and according to Mel'nikov and Meshkov [8] the result for the decay rate $\Gamma=\int_0^\infty R(E)dE$ is given by (1.1) with

$$\nu_a=\left[\frac{\kappa\omega_0}{2\pi}\right]\exp\left[\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{dy}{1+y^2}\ln(1-e^{-\varepsilon(1+y^2)/4})\right], \quad (7.3)$$

where $\varepsilon=\beta\Delta\mathscr{E}(\infty)$ with $\Delta\mathscr{E}(\infty)=2\lambda I_b$. If $\varepsilon\ll1$, (7.3) reduces to Kramers' weak-friction result $\nu_a(\lambda\to0)=2\lambda\beta I_b\omega_0/2\pi$ as [8] $\nu_a(\varepsilon\ll1)\approx(\varepsilon\omega_0/2\pi)[1-0.82\varepsilon^{1/2}]$. On the other hand, if $\varepsilon\gg1$, (7.3) reduces to Kramers' moderate-to-strong-friction result $\nu_a=\kappa\omega_0/2\pi$ as $\nu_a(\varepsilon\gg1)\approx(\kappa\omega_0/2\pi)[1-1.13\varepsilon^{-1/2}e^{-\varepsilon/4}]$.

VIII. FINAL REMARKS

The present article meets the challenge [9,30,31] of solving Kramers' Fokker-Planck equation for activated rate processes (escape over a potential-energy barrier [4]) in a unified treatment (i.e., including the frictional turnover region) *without* recourse to any microscopic model (as in Refs. [28,29]) or associated Langevin equations (as in Ref. [31]). The unified FPE theory hinges on the definition of the unstable-mode energy E [28], which allows for a generalized version of (low-dimensional) transition-state theory. The definition of E within the FPE context requires some new theoretical concepts. The analysis proceeds as follows.

First (Sec. II), one investigates the harmonic barrier dynamics, in Kramers' FPE phase space (x,p), in order to identify the unstable (and stable) barrier mode η (and ζ), and to transform to the rotated coordinate system (η,ζ).

Second (Sec. III), one defines a constrained Gaussian integral transformation in order to shift the noise *from* the unstable *to* the stable degree of freedom. As a consequence, the barrier dynamics in the unstable direction becomes deterministic. The constraint takes care of preserving the dynamical significance of the potential $U(x)$.

Third (Sec. IV), one extends the two-dimensional phase space (η,ζ) in a direction ϑ. The stochastic process in this extended phase space is uniquely determined by imposing dynamics along ϑ, such that it (i) allows for the definition of E and (ii) allows for TST in EPS (Secs. V and VII). The present theory yields the exact Boltzmann distribution $R_{\rm eq}(E)$ without further ado (in lieu of, e.g., Ref. [31]).

Fourth (Sec. VI), one performs a systematic small-friction–low-temperature expansion in EPS. The irreducible part of this expansion is the "linear noise approximation" [14] in E. The ensuing Gaussian transition probability $W(E|E')$ obeys detailed balance with respect to $R_{\rm eq}(E)$ and defines a generalized TST integral equation like that of Mel'nikov and Meshkov [8].

The final result for the escape rate Γ is given by (1.1) with (7.3) for the attempt rate ν_a. The present unified treatment (Sec. VII) is due to the possibility of TST in EPS for both very weak and moderate-to-strong values of the coupling to the environment. In particular, it is the notion of EPS (Sec. IV) which allows the definition of the unstable-mode energy E, while it is the concept of CGT (Sec. III) which is crucial for allowing TST in terms of E.

The rate (7.3) differs in a subtle but significant manner from the results of Mel'nikov and Meshkov [8], and of Grabert and co-workers [28,29] and Graham [31]. The present theory proceeds in terms of E (rather than the particle energy E_p as in Ref. [8]), which allows for the unified treatment of depletion and barrier-recrossing effects. Therefore, in Ref. [8] the Kramers-Smoluchovsky coefficient κ in (7.3) could only be introduced as an *ad hoc* multiplication factor (see also Refs. [9,20]). On the other hand, both the microscopic theory of Grabert and coworkers [28,29] and the theory of Graham based on the associated Langevin equation [31] *do* involve E. However, from the present systematic expansion (Sec. VI) it follows that the relative energy loss ε is that of Ref. [8] rather than that of Refs. [28,29,31].

The present macroscopic theory (re)establishes the independence of the microscopic details of Kramers' stochastic process for activated rate processes. An exhaustive account will be available upon request [34].

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APPENDIX A: NORMALIZATION OF THE EXTENDED EQUILIBRIUM DISTRIBUTION

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

$$Q_{eq}(\eta,\zeta)=N_Q\exp(-\tfrac{1}{2}K_{11}\eta^2-K_{12}\eta\zeta)\ , \tag{A1}$$

where $K_{11}=-\beta\lambda\omega_b/\pi$, $K_{12}=2\beta\kappa\omega_b^2/\pi$, and $N_Q=(\kappa\omega_b/2\pi)N_0$.

On the other hand, by (5.3) $R_{eq}(E,w)=\mathcal{N}\exp(-\beta_E E-\frac{1}{2}\beta_{ww}w^2)$. In the harmonic barrier region $E=\frac{1}{2}(v^2-\omega_1^2u^2)$, by (4.8). Recall that $R_{eq}(E,w)$ is normalized as $\int du\int dv\int dw\,R=1$, and note that the Jacobian of the transformation (4.4) equals $|\partial(u,v,w)/\partial(\vartheta,\eta,\zeta)|=\omega_1/2$. Substituting the ensuing result for $R_{eq}(\vartheta,\eta,\zeta)$ into the EPS condition (4.1), and comparing the upshot for $Q_{eq}(\eta,\zeta)$ with (A1), one finds

$$\mathcal{N}/N_Q=(\omega_b/2\pi\lambda\kappa^4\pi)^{1/2}\ . \tag{A2}$$

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 B).

APPENDIX B: BEYOND TRANSITION-STATE THEORY: 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 $U_a(x)=0$. In this Appendix we briefly investigate the corrections in Γ due to $U_a(x)\neq 0$. Let us therefore following Kramers [4,21] set

$$R=\mathcal{Q}(u,v,w)R_{eq}(E,w)\ , \tag{B1}$$

where R_{eq} is given by (5.3), with E as defined in (4.8). Substitution of (B1) into (4.3), and rewriting the resulting equation for $\mathcal{Q}$ in terms of u, $\vartheta=-u+v/\omega_1$, and $x=(u+\frac{1}{2}\kappa^2w)/\kappa\pi$, yields

$$0=\mathcal{F}_u\frac{\partial\mathcal{Q}}{\partial u}+\mathcal{F}_v\frac{\partial\mathcal{Q}}{\partial\vartheta}+\mathcal{F}_x\frac{\partial\mathcal{Q}}{\partial x}+\mathcal{D}_{ux}\frac{\partial^2\mathcal{Q}}{\partial u\,\partial x}\ , \tag{B2}$$

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

$$\begin{aligned}\mathcal{F}_u(u,\vartheta,x)&=-\omega_1\vartheta+\pi\omega_b(x-2u)+\lambda U_a'(x)/\omega_b^2\ ,\\ \mathcal{F}_v(u,\vartheta,x)&=\omega_1\vartheta+U_a'(x)/\omega_2\ ,\\ \mathcal{F}_x(u,\vartheta,x)&=-\omega_b(u+\vartheta)/\pi\ .\end{aligned} \tag{B3}$$

Note that $\mathcal{Q}=1$ amounts to full equilibrium. On the other hand, if $U_a(x)$ is zero, (B2) and (B3) allow for a solution $\mathcal{Q}(\vartheta)$ with $\vartheta\partial\mathcal{Q}/\partial\vartheta=0$, i.e., $\mathcal{Q}=\Theta(\vartheta)$. This corresponds to the quasiequilibrium state pertinent to TST at the barrier peak $(u=0)$. Including the anharmonic barrier terms, (B2) and (B3) still allow for a solution with $\mathcal{Q}(-\infty)=0$ and $\mathcal{Q}(\infty)=1$. In that case, however, recrossing effects will show up in terms of the small parameter $(1/\beta U_b)^{1/2}$.

Upon introducing (B1) into (5.6), it is convenient to write the decay rate in terms of $\mathcal{P}=\partial\mathcal{Q}/\partial\vartheta$ by means of a partial integration. In addition, let $\mathcal{u}=(\beta\omega_b^3/\lambda\pi)^{1/2}u$ and $\mathcal{x}=(\beta\omega_b^3\pi/\lambda)^{1/2}\kappa x$ and define

$$\mathcal{f}(k,\mathcal{u},\mathcal{x})=\int_{-\infty}^{\infty}d\vartheta\,e^{-ik\vartheta}\mathcal{P}(\vartheta,\mathcal{u},\mathcal{x})\ , \tag{B4}$$

so that Γ becomes an integral over k and $\mathcal{x}$ of $\mathcal{f}(k,0,\mathcal{x})$. Note that $\mathcal{f}(0,\mathcal{u},\mathcal{x})=1$. Differentiating (B2) with respect to ϑ, one finds an equation for $\mathcal{f}(k,\mathcal{u},\mathcal{x})$.

Consider the *cubic* potential $U_a(x)=-\frac{1}{2}\omega_b^2x^3/a$, with $U_b=2\omega_b^2a^2/27$. In that case, the small parameter $\mathcal{l}=(\lambda/6\kappa^3\pi^3\omega_1\beta U_b)^{1/2}$ and with $\mathcal{k}=(\lambda\pi/\beta\omega_b^3)^{1/2}\mathcal{l}k$ the expansion $(l\geq 1;m,n\geq 0)$

$$\mathcal{f}(\mathcal{k},0,\mathcal{x})=1+\sum_{lmn}c_{lmn}\mathcal{k}^l\mathcal{x}^m\mathcal{l}^n \tag{B5}$$

leads to (1.1) with

$$\begin{aligned}\nu_a&=\frac{\kappa\omega_0}{2\pi}[1+a_2\mathcal{l}^2+O(\mathcal{l}^3)]\ ,\\ a_2&=\tfrac{5}{24}\kappa^2(1-\kappa^2)^2\\ &\quad+(\lambda/\omega_1)(c_{200}+c_{220}\kappa^2+3c_{240}\kappa^4+\cdots)\ .\end{aligned} \tag{B6}$$

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

$$0=i\mathcal{k}\mathcal{x}^2\mathcal{f}+\mathcal{k}\frac{\partial\mathcal{f}}{\partial\mathcal{k}}-\frac{1}{\kappa^2}(\mathcal{x}-2\kappa\pi\mathcal{u})\frac{\partial\mathcal{f}}{\partial\mathcal{u}}+\mathcal{u}\frac{\partial\mathcal{f}}{\partial\mathcal{x}}+\frac{\partial^2\mathcal{f}}{\partial\mathcal{u}\,\partial\mathcal{x}}\ , \tag{B7}$$

which can be solved systematically in powers of $\mathcal{k}$ with the coefficients being polynomials in $\mathcal{u}$ and $\mathcal{x}$. The final result for a_2 reads

$$a_2=-\frac{1}{24}\frac{\kappa^2(1-\kappa^4)(10+41\kappa^2+10\kappa^4)}{(1+2\kappa^2)(2+\kappa^2)}\ . \tag{B8}$$

For the *quartic* potential $U_a(x)=\frac{1}{2}\omega_b^2x^4/a^2$, with $U_b=\frac{1}{8}\omega_b^2a^2$. In that case, $\mathcal{l}=(\lambda/4\kappa^2\pi^2\omega_1\beta U_b)^{1/2}$ and $\mathcal{k}=(\lambda\pi/\beta\omega_b^3)^{1/2}\mathcal{l}^2k$, and the result reads

$$a_2=-\tfrac{3}{8}\kappa^2(1-\kappa^2)\ . \tag{B9}$$

These results agree with those obtained using methods put forward recently by Pollak and Talkner [39], 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 $\alpha/8$.

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