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A WKB Treatment of Diffusion in a Multidimensional Bistable Potential[1]

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We extend to the case of a finite set of stochastic variables whose distribution P obeys a nonlinear Fokker–Planck equation our previous treatment of diffusion in a bistable potential U, in the limit of small, constant diffusion coefficient. This is done with the help of an extended WKB approximation due to Gervais and Sakita. The treatment is valid if there exists a well-defined most probable path connecting the minima of U, and if the valley of U along that path has a slowly varying width, and weak curvature and twisting. We find that: (i) the final approach to equilibrium is governed by Eyring's generalization of the Kramers high-viscosity rate, which we rederive; (ii) for intermediate times, if the initial distribution is concentrated in the region of instability (close vicinity of the saddle point of U), P has, along the most probable path, the behavior described by Suzuki's scaling statement for a one-dimensional system. In a second part of this time domain, P enters the diffusive regions around the minima of U and relaxes toward local longitudinal equilibrium on a time comparable with Suzuki's time scale. The time for relaxation toward transverse local equilibrium may, depending on the initial conditions, compete with these longitudinal times.

KEY WORDS: Nonlinear Fokker–Planck equation; instability; diffusion.

1. INTRODUCTION

In a previous paper[(1)] (hereafter referred to as I), we have studied the time-dependent solution of the one-dimensional Fokker–Planck equation

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x}[U'(x)P] + \theta\frac{\partial^2 P}{\partial x^2} \tag{1}$$

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in the small-θ limit and for a bistable "potential" $U(x)$. We have shown that, in this limit, Eq. (1) can be solved with the help of a WKB approximation. This gives $P(x, t)$ in the long-time (Kramers[2]) regime, which corresponds to the escape of particles from one of the potential wells to the other after local equilibrium has been established, and in the intermediate (Suzuki[3]) regime, which corresponds, in particular, to the splitting between the two wells of a distribution starting from the vicinity of the local maximum of U.

The one-dimensional model (1) applies as such—at least to our knowledge—only to the case of the laser. The Fokker–Planck equation (1) can be considered as describing diffusion or chemical reactions in the high-friction limit (θ is then proportional to the temperature), or as resulting from the truncated Kramers–Moyal development of the master equation for an extensive variable (θ is then proportional to the inverse volume of the system).

However, it is clear that, in the latter case, a realistic model would imply that Eq. (1) be extended to describe a stochastic variable with a quasiinfinite number of components (describing, e.g., a space-dependent magnetization).

The former (diffusive) case corresponds, in practice, to a finite, but larger than one, number of stochastic variables: these are the three space coordinates in the case of atomic diffusion. In the chemical reaction case, the choice of the variables is fixed by the shape of the free energy hypersurface.

In this paper we will only consider this diffusive case; that is, we will study the time-dependent solution of the N-dimensional equation

$$\frac{\partial}{\partial t} P(\mathbf{r}, t) = \nabla \cdot [P(\mathbf{r}, t)\, \nabla U(\mathbf{r})] + \theta^2\, \nabla^2 P(\mathbf{r}, t) \tag{2}$$

with $\mathbf{r} = \{x_1, x_2, \ldots, x_N\}$, where N is a finite number.

We will solve this equation in the small-θ limit, with the help of an extended WKB approximation recently developed by field theorists[4,5] to solve the multidimensional instanton problem.

This will enable us to rederive the semiphenomenological Eyring generalized expression[6] of the Kramers reaction rate. This method has the advantage that it clarifies the conditions of validity of the Eyring absolute rate formula. The corresponding long-time limit of $P(\mathbf{r}, t)$ is explicitly obtained. Moreover, the WKB method, as in the one-dimensional case, provides a systematic way to evaluate $P(\mathbf{r}, t)$ in the intermediate-time range and to analyze the characteristic times that govern its evolution.

2. PRINCIPLE OF THE WKB TREATMENT

With the help of the well-known transformation

$$P(\mathbf{r}, t) = \exp[-U(\mathbf{r})/2\theta]\, G(\mathbf{r}, t) \tag{3}$$

one obtains for the distribution $P(\mathbf{r}, t|r_0)$ which satisfies the initial condition

$$P(\mathbf{r}, t = 0) = \delta(\mathbf{r} - \mathbf{r}_0) \tag{4}$$

the expression

$$P(\mathbf{r}t|\mathbf{r}_0) = \exp\left(\frac{U(\mathbf{r}_0) - U(\mathbf{r})}{2\theta}\right) \sum_{k \geqslant 0} \varphi_k(\mathbf{r}_0)\varphi_k(\mathbf{r}) \exp\left(-\frac{t\lambda_k}{\theta}\right) \tag{5}$$

where the φ_k are the solutions (regular for $|\mathbf{r}| \to \infty$ and normalized) of the Schrödinger-like eigenmode equation (where the role of $\hbar$ is played by $\theta\sqrt{2}$):

$$-\theta^2 \nabla^2 \varphi_k + \mathscr{V}(\mathbf{r})\varphi_k = \lambda_k \varphi_k \tag{6}$$

and

$$\mathscr{V}(\mathbf{r}) = \tfrac{1}{4}[\nabla U(\mathbf{r})]^2 - \tfrac{1}{2}\theta \nabla^2 U(\mathbf{r}) \tag{7}$$

In order to make the following algebra clearer, we will now explain the multidimensional WKB technique in the case of a two-dimensional system ($x_1, x_2 \equiv x, y$). The N-dimensional generalization is given in Appendix A.

We follow here the method of Gervais and Sakita,[5] whose results we will now recall, referring the reader to their article for more details.

We assume the physical potential $U(\mathbf{r})$ to be of the type shown in Fig. 1, i.e., $U(x, y)$ has two minima separated by a saddle point. For small θ ($\theta \ll \Delta U$; see Fig. 1), the corresponding $\mathscr{V}(x, y)$ (Fig. 2) exhibits three minima, located close to the three extrema of U.

Let us consider the eigenmode equation:

$$\left[-\theta^2\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + \mathscr{V}(x, y)\right]\varphi(x, y) = \lambda\varphi(x, y) \tag{8}$$

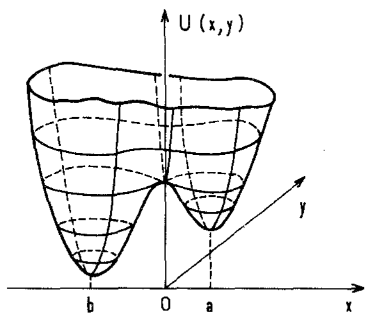

Fig. 1. A two-dimensional bistable potential $U(x, y)$.

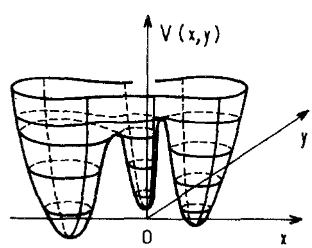

Fig. 2. The $V(x, y)$ potential associated with $U(x, y)$.

The long- and intermediate-time behavior of $P(\mathbf{r}, t)$ are controlled, as seen from Eq. (5), by the lowest eigenstates of Eq. (8), which are, obviously, essentially concentrated in the bottoms of the three wells of $\mathscr{V}$. The effects associated with the bistable character of U correspond to the tunneling coupling between the three wells of $\mathscr{V}$. We are thus led, as in the instanton problem,[4,5] to define a most probable escape path (MPEP) joining the different wells of $\mathscr{V}(x, y)$, defined as the path that minimizes the generalized classical action $\int ds\,(\mathscr{V} - \lambda)^{1/2}$ between the wells.

The spirit of the extended WKB approximation consists in noticing that, for small θ, and far from the turning points, the wave functions are essentially confined within narrow tubes (of radius $\sim \theta^{1/2}$) along the MPEP.

We assume for simplicity that, in our case, the MPEP is unique. Moreover, we also assume it to be a straight line that we choose to be the x axis (this implies, obviously, that the three extrema of U lie in the $y = 0$ plane). The method can be extended to the case of more than one MPEP, provided that the corresponding tubes do not overlap in the WKB regions. MPEPs with small curvatures can also be treated.[4]

Following the above qualitative arguments, we are led to define two types of regions in which $\varphi(x, y)$ has a nonnegligible amplitude:

(i) Quadratic regions, around the minima of $\mathscr{V}$, where, for the low-lying states of interest to us, the WKB approximation is not valid ($|\mathscr{V} - \lambda| \sim \theta$). In these regions, however, $\mathscr{V}$ can be approximated by its quadratic developments, so that Eq. (8) is exactly soluble.

(ii) WKB tubes, where $|y| \leqslant \theta^{1/2}$, and where the usual one-dimensional WKB condition is satisfied in the x direction. Here, these tubes are located in classically forbidden regions (note that, of course, for small θ, the quadratic regions and the WKB tubes overlap).

In these tubes, we approximate $\mathscr{V}$ by

$$\mathscr{V}(x, y) = V(x) + \tfrac{1}{2} y^2 W(x) \tag{9}$$

where

$$V(x) \equiv \mathscr{V}(x, 0), \qquad W(z) \equiv \partial^2 \mathscr{V}(x, y)/\partial y^2|_{y=0} \tag{10}$$

The absence of a term linear in y in this small-y development of $\mathscr{V}$ is a consequence of the fact that the $y = 0$ line is the MPEP. Indeed, the condition of extremalization of the generalized classical action is the Euler–Lagrange equation, which simply reads in the present case

$$\partial \mathscr{V}/\partial y = 0 \qquad \text{along the MPEP} \tag{11}$$

Following Ref. 5, we set

$$\lambda = \lambda_0 + \lambda_1 \tag{12}$$

where

$$\lambda_0 = O(\theta^0) \tag{13}$$

$$\lambda_1 = O(\theta) \tag{14}$$

and

$$\varphi^{\pm}(x, y) = e^{\pm S_0}(dS_0/dx)^{-1/2}\chi^{\pm}(x, y) \tag{15}$$

where

$$S_0(x) = (1/\theta)\int^x dx'\,[V(x') - \lambda_0]^{1/2} \tag{16}$$

Gervais and Sakita[5] have shown that the functions $\chi^{\pm}$ [Eq. (15)] are completely determined if one knows two independent solutions α^+ and α^- of the equation governing the small, transverse classical fluctuations around any point of the MPEP:

$$d^2\alpha^{\pm}/d\tau^2 = W[x(\tau)]\alpha^{\pm}(\tau) \tag{17}$$

where the relationship between the coordinate x along the MPEP and τ is given by the solution of the instanton equation of motion:

$$-\tfrac{1}{2}(dx/d\tau)^2 + V(x) = \lambda_0 \tag{18}$$

τ can therefore be interpreted as an imaginary time associated with "classical" propagation along the MPEP in the classically forbidden region.

Then,[5] the solutions for the χ's are given by

$$\chi_n^{\pm}(x, y) = [A^{(\pm)\dagger}]^n\chi_0^{\pm}(x, y) \tag{19}$$

where

$$A^{(\pm)\dagger} = e^{\pm\rho\tau}\left(\theta\sqrt{2}\,\alpha^{\pm}\frac{\partial}{\partial y} \mp \frac{d\alpha^{\pm}}{d\tau}\,y\right) \tag{20}$$

are effective creation operators for local transverse fluctuations. χ_0^+ and χ_0^-, defined by $A^{(\pm)}\chi_0^{\pm} = 0$, are given by

$$\chi_0^{\pm}(x, y) = [\alpha^{\pm}(\tau)]^{-1/2}\exp\left(\mp\frac{\lambda_1\tau}{\theta\sqrt{2}}\right)\exp\left(-\frac{\Omega^{\pm}(\tau)}{2\theta\sqrt{2}}\,y^2\right) \tag{21}$$

$$\Omega^{\pm}(\tau) = \mp\frac{1}{\alpha^{\pm}}\frac{d\alpha^{\pm}}{d\tau} \tag{22}$$

where we have made the choice of sign:] $dx/d\tau = \theta\sqrt{2}\,(dS_0/dx)$.

The values of the parameter ρ (Eq. (21) are determined by the boundary conditions. At this stage, the question arises of defining, among the infinite number of solutions of Eq. (18), the proper α^+ and α^- functions. This choice is obviously determined by the condition that, for both χ_0^+ and χ_0^-, the corresponding Ω's be positive.

The fact that one can find Ω's that keep a definite sign along the MPEP is by no means obvious for a general $\mathscr{V}(x, y)$. However, we must restrict ourselves to this case: a change of sign of Ω would imply the existence of regions where the radius of the propagation tube would become much larger than $O(\theta^{1/2})$, which would entail a breakdown of the whole approximation scheme.

We will now show that the condition $\Omega^{\pm} > 0$ can be satisfied, provided that $W(x)$ is a slowly varying function. Indeed, in this limit, Eq. (18) for the α's admits the two independent WKB-like solutions:

$$\alpha^{\pm}(\tau) = [W(x(\tau))]^{-1/4} \exp\left\{ \mp \int^{\tau} d\tau' \, \{W[x(\tau')]\}^{1/2} \right\} \tag{23}$$

The condition of validity of Eq. (23) is that

$$|dW/d\tau| \ll |W|^{3/2} \tag{24}$$

which can be rewritten, with the help of Eq. (18), as

$$\left| \frac{1}{W} \frac{dW}{dx} \right| \ll \left(\left| \frac{W}{V} \right| \right)^{1/2} \tag{25}$$

Calling l_x the typical range of space variations of $W(x)$ (i.e., of the transverse curvature of $\mathscr{V}$ along the MPEP), and l_y the typical transverse width of $\mathscr{V}$ $(l_y^{-2} = \mathscr{V}^{-1} \, \partial^2 \mathscr{V}/\partial y^2|_{y=0})$, we have that condition (25) reduces to

$$l_x \gg l_y \tag{26}$$

The Ω's corresponding to expression (23), which read

$$\Omega^{\pm}(\tau) = [W(\tau)]^{1/2} \pm \frac{1}{4} \frac{1}{W(\tau)} \frac{dW}{d\tau} \tag{27}$$

are thus seen to be positive, as is needed.

Finally, the solutions of Eq. (8) are

$$\varphi_n^{\pm}(x, y) = [A^{(\pm)\dagger}]^n \varphi_0(x, y) \tag{28}$$

with

$$\varphi_0^{\pm} = \left(\frac{dS_0}{dx} \right)^{-1/2} (\alpha^{\pm})^{-1/2} \exp\left\{ \pm S_0(x) \mp \frac{\lambda_1 \tau(x)}{\theta\sqrt{2}} - \frac{\Omega^{\pm}(\tau(x)) y^2}{2\theta\sqrt{2}} \right\} \tag{29}$$

We shall now write expression (29) for $\varphi_0^{\pm}$ under another form, which is equivalent to (29) to the order where the WKB approximation is valid. This is

$$\varphi_0^{\pm} = \left(\frac{dS_0}{dx} \right)^{-1/2} \exp\left\{ -\frac{\Omega^{\pm}[\tau(x)] y^2}{2\theta\sqrt{2}} \right\}$$
$$\times \exp\left\{ \pm \frac{1}{\theta} \int_{x_0}^{x} \left[V(x') - \lambda + \frac{\theta}{\sqrt{2}} \Omega^{\pm}(\tau(x')) \right]^{1/2} dx' \right\} \tag{30}$$

where $\lambda = \lambda_0 + \lambda_1$ [eq. (12)] is the total "energy."

Indeed, in the WKB regions, $V \gg \lambda - \theta\Omega^{\pm}/\sqrt{2}$, and the square root in the action integral in Eq. (30) can be developed to first order in $(\lambda_1 - \theta\Omega^{\pm}/\sqrt{2})$, which corresponds precisely, as will appear in the next section (see also I), to the highest significant order in powers of θ in the calculation of the WKB action integrals.

Using Eqs. (18) and (22), one then immediately checks that expressions (30) and (29) are equivalent, up to the multiplicative constant $[\alpha^{\pm}(x_0)]^{1/2}$. Note also that, once $\varphi_0^{\pm}$ is written in the form (30), one can move the lower limit x_0 of the action integral to any point of the x axis, which only multiplies $\varphi_0^{\pm}$ by a constant factor. As usual in the WKB method, it will be convenient to choose for x_0 the turning points that limit the various forbidden regions.

The above expressions for $\varphi_0^{\pm}$ and the $\varphi_n^{\pm}$ have a simple physical interpretation: when the one-dimensional WKB condition is satisfied on the MPEP, and when the transverse curvature of $\mathscr{V}$ is slowly varying along that path, the wavefunctions are "locally separable" in the WKB tubes:

(a) The transverse motion in the plane of abscissa x is that of a harmonic oscillator at the local frequency $\Omega^{\pm}(x)$.

(b) The longitudinal motion, along the MPEP, is the standard quasi-classical one, at the "longitudinal energy" $[\lambda - \theta\sqrt{2}(n + 1/2)\Omega^{\pm}]$, where n [Eq. (28)] is the quantum number for the transverse motion.

That is, when the transverse motion is fast with respect to the longitudinal one and to the variations of width of the allowed tube(s), the tranverse part of the wave functions exhibits an adiabatic adaptation to the x motion. This is reminiscent of the structure of waves in a waveguide with a slowly varying section.

Finally, it is shown in Appendix A that this result can be generalized to a system with several transverse variables y_i under the following condition: the quadratic development (9) of $\mathscr{V}$ in the WKB tubes becomes

$$\mathscr{V}(x, \{y_i\}) = V(x) + \frac{1}{2}\sum_{ij} y_i y_j W_{ij}(x) \tag{31}$$

For a given value of x, one can define the principal transverse axes of $\mathscr{V}$, in which the $\{W_{ij}\}$ matrix becomes diagonal. For a general $\mathscr{V}$, the orientation of these axes rotates when one moves along the MPEP.

It is found that the wave functions remain "locally separable" provided that this orientation is a slowly varying function of x.

As can be shown from the work of Banks and Bender,[4] the separability result also holds for a curved MPEP, provided that its radius of curvature remains large compared with the transverse width of $\mathscr{V}$, l_y.

Finally, one can say that the above extended WKB approximation is valid only if the valley of $\mathscr{V}$ along the MPEP is reasonably smooth, i.e., if all its geometrical characteristics vary slowly along that path.

3. WKB SOLUTION OF THE FOKKER–PLANCK EQUATION

In order to apply the above method to the study of the solution of the Fokker–Planck equation, let us first consider in more detail the shape of the potential $\mathscr{V}(x, y)$ associated with a two-dimensional bistable physical potential $U(x, y)$ (Figs. 1 and 2).

We assume that the two minima and the saddle point of U all lie on the x axis, at $x = b$, a, and 0, respectively. For small θ [$\theta \ll \Delta U = \min\{U(0) - U(a), U(0) - U(b)\}$], $\mathscr{V}$ has three minima located at the same points as the extrema of U, separated by saddle points at heights of order $(\Delta U/a)^2$.

With the help of Eq. (7), one obtains for the quantities $V(x)$ and $W(x)$ which describe the potential $\mathscr{V}$ in the vicinity of the MPEP [Eq. (9)]

$$\begin{aligned} V(x) &= \tfrac{1}{4}[u'(x)]^2 - \tfrac{1}{2}\theta[u''(x) + w(x)] \\ W(x) &= \tfrac{1}{2}[u'(x)w'(x) + w^2(x)] - \tfrac{1}{2}\theta w''(x) \end{aligned} \tag{32}$$

where

$$u(x) = U(x, 0), \qquad w(x) = \partial^2 U(x, y)/\partial y^2|_{y=0} \tag{33}$$

describe the physical potential U along the MPEP:

$$U(x, y) \simeq u(x) + \tfrac{1}{2}y^2 w(x) \tag{34}$$

In the harmonic regions around the minima of $\mathscr{V}$ ($x \simeq x_i = b, 0, a$), $\mathscr{V}$ can be approximated by its quadratic developments:

$$\mathscr{V}(x, y) \simeq \mathscr{V}^{(i)}(x, y) = -\tfrac{1}{2}\theta[u_i'' + w_i] + \tfrac{1}{4}(u_i'')^2(x - x_i)^2 + \tfrac{1}{4}w_i^2 y^2 \tag{35}$$

where $u_i'' = u''(x_i)$, $w_i = w(x_i)$.

To get an estimate of the orders of magnitude of the first of the λ_k [Eq. (5)] which govern the long-time behavior of P, let us calculate the "energy" levels of the three harmonic (i) wells [Eq. (35)]:

$$\lambda_k^{(i)} \equiv \lambda_{n,p}^{(i)} = -\tfrac{1}{2}\theta(u_i'' + w_i) + \theta|u_i''|(p + \tfrac{1}{2}) + \theta w_i(n + \tfrac{1}{2}), \qquad n, p = 0, 1, 2,... \tag{36}$$

The lowest of these levels are given by $i = a$ or b, and $n = p = 0$, with $\lambda_{0,0}^{(a,b)} = 0$. There always is, even for an asymmetric U, a double degeneracy of the lowest harmonic (a) and (b) levels, which is lifted by the tunneling coupling, thus giving rise to two levels. The lowest of these must correspond to the equilibrium distribution $P_{eq} \propto \exp[-U(x, y)/\theta]$ [$\lambda_{0,0} = 0$, $\varphi_{0,0} = C_{0,0}\exp(U/2\theta)$]. The other one corresponds to an exponentially small eigenvalue $\lambda_{0,1} \equiv \lambda_K$, of order $\exp(-\Delta U/\theta)$.

The next excited levels, which derive from the harmonic levels (36) with $(n + p) \geqslant 1$, have λ values of order θ.

The corresponding states can therefore be determined with the help of the WKB method developed in Section 2.

As in the one-dimensional case,[1] one may then distinguish among three time regimes:

(i) The Kramers–Eyring (long-time) regime $t \gtrsim \tau_K = \theta/\lambda_K$, controlled by the two lowest eigenstates.

(ii) The intermediate-time regime: $\max[(u_i'')^{-1}, (w_i)^{-1}] \lesssim t \ll \tau_K$, controlled by the eigenstates with λ values of order θ.

(iii) The short-time regime, $t \lesssim \max[(u_i'')^{-1}, (w_i)^{-1}]$, where a large number of states—including those with $\lambda > (\Delta U/a)^2$—contribute, and which we do not consider here.

3.1. The Kramers–Eyring Regime

The eigenstates of interest here, which correspond to the lowest ($n = 0$) level of the local transverse harmonic oscillator, are described in the WKB tubes by linear combinations of the wave functions $\varphi_0^{\pm}(x, y)$ of Eq. (30).

Since, for $x \to x_i$, $\Omega^{\pm}(x) \to \sqrt{W_i} = w_i/\sqrt{2}$, it is seen in Eq. (30) that the y part of the wave functions matches automatically with that of the $n = 0$ solutions in the harmonic wells.

To calculate the eigenvalues and eigenfunctions, one is thus simply left with a one-dimensional matching problem in the x direction. This leads to a calculation formally identical to the one performed in I for the one-dimensional FP equation. Namely, the wave function is built up by the same technique as that developed in Appendix A of I, except for the following modification: in the one-dimensional case, we were led to define the two generalized classical actions $S_a(\lambda)$ and $S_b(\lambda)$, connecting wells (b) and (0), and (0) and (a), respectively,

$$S_a(\lambda) = \int_0^{\alpha} \frac{dx'}{\theta} [V(x') - \lambda]^{1/2}, \qquad S_b(\lambda) = \int_{\beta}^{0} \frac{dx'}{\theta} [V(x') - \lambda]^{1/2} \quad (37)$$

where β and α are the classical turning points at energy λ, respectively, close to b and a.

These should now be replaced in the matching calculation for the φ's by, respectively, $S_i^{(+)}$ ($i = a, b$) for the φ_0^{+} components of the WKB solutions, and $S_i^{(-)}$ for the φ_0^{-} ones, where, for example,

$$S_b^{(\pm)}(\lambda) = \int_{\beta}^{0} \frac{dx'}{\theta} \left\{ V(x') - \lambda + \frac{\theta}{\sqrt{2}} \Omega^{\pm}(\tau(x')) \right\}^{1/2} \quad (38)$$

where β is now the turning point of the longitudinal motion. (Note that, since Ω^{+} and Ω^{-} have the same limits in the quadratic regions, the matching procedure in the overlap regions is not modified.) Defining

$$\nu = \lambda/\theta u_b'', \qquad \mu = \lambda/\theta|u_0''| - 1, \qquad \xi = \lambda/\theta u_a'' \quad (39)$$

we obtain for the eigenvalue equation [see Eq. (14) of I]

$$\frac{(2\pi)^{3/2}}{\Gamma(-\xi)\Gamma(-\nu)\Gamma(-\mu)}\left(\frac{e}{\xi+\frac{1}{2}}\right)^{\xi+1/2}\left(\frac{e}{\nu+\frac{1}{2}}\right)^{\nu+1/2}\left(\frac{e}{|\mu+\frac{1}{2}|}\right)^{\mu+1/2}$$

$$- e^{-\Sigma_a(\lambda)}\cos\pi\xi\cos\pi\mu\,\frac{(2\pi)^{1/2}}{\Gamma(-\nu)}\left(\frac{e}{\nu+\frac{1}{2}}\right)^{\nu+1/2} - e^{-\Sigma_b(\lambda)}\cos\pi\nu\cos\pi\mu$$

$$\times\frac{(2\pi)^{1/2}}{\Gamma(-\xi)}\left(\frac{e}{\xi+\frac{1}{2}}\right)^{\xi+1/2} - e^{-[\Sigma_a(\lambda)+\Sigma_b(\lambda)]}\cos\pi\xi\cos\pi\nu\sin^2\pi\mu$$

$$\times\frac{\Gamma(-\mu)}{(2\pi)^{1/2}}\left(\frac{e}{|\mu+\frac{1}{2}|}\right)^{-(\mu+1/2)} = 0 \tag{40}$$

where

$$\textstyle\sum_i(\lambda) = S_i^{(+)}(\lambda) + S_i^{(-)}(\lambda), \qquad i = a, b \tag{41}$$

and Γ is the Euler gamma function.

One immediately checks that, as in the one-dimensional problem, $\lambda = 0$ ($\nu = \xi = 0$, $\mu = -1$) is an exact solution of Eq. (40), as is needed to describe the relaxation of P toward its equilibrium value. The corresponding wave function $\varphi_{0,0}$ is the local approximation, in the WKB tubes and around the extrema of U, of the exact $\varphi_{0,0} = C_{0,0}^{1/2}\exp[-U(x, y)/2\theta]$.

Following I, we find for the eigenvalue of the first (Kramers–Eyring) eigenstate

$$\lambda_K = (\theta/2\pi)[u_a'' e^{-\Sigma_a(0)} + u_b'' e^{-\Sigma_b(0)}] \tag{42}$$

The quantities $\sum_{a,b}(0)$ are calculated in Appendix B. We find that

$$\textstyle\sum_i(0) = (1/\theta)\,\Delta U_i + \frac{1}{2}\,\mathrm{Log}|u_i''/u_0''| + \frac{1}{2}\,\mathrm{Log}[w(0)/w(i)] \tag{43}$$

where $\Delta U_i = u_0 - u_i$ is the difference of altitude between the saddle point and minimum (i), i.e., the activation energy. So, finally,

$$\frac{1}{\tau_K} = \frac{\lambda_K}{\theta} = \frac{1}{2\pi}\left[(u_a|u_0''|)^{1/2}\left(\frac{w(a)}{w(0)}\right)^{1/2} e^{-\Delta U_a/\theta} + (u_b''|u_0''|)^{1/2}\left(\frac{w(b)}{w(0)}\right)^{1/2} e^{-\Delta U_b/\theta}\right] \tag{44}$$

which can be rewritten, in terms of the partition functions Z_i and Z_0 for transverse vibrations at the minima and at the saddle point [$Z_{i,0} \propto (w_{i,0})^{-1/2}$] as

$$\frac{1}{\tau_K} = \frac{1}{2\pi}\left[(u_a''|u_0''|)^{1/2}\left(\frac{Z_0}{Z_a}\right)^{1/2} e^{-\Delta U_a/\theta} + (u_b''|u_0''|)^{1/2}\left(\frac{Z_0}{Z_b}\right)^{1/2} e^{-\Delta U_b/\theta}\right] \tag{45}$$

It is shown in Appendix A that formula (45) also holds for an N-dimensional system with a smooth valley.

This is precisely Eyring's[6] generalization to a multidimensional system of the Kramers reaction rate formula[2] for the high friction limit. Thus, our calculation shows that this expression is valid only under the same restrictions as the extended WKB method: (a) the wells of U must be deep ($\Delta U \gg \theta$); (b) the wells must be connected by a well-defined, i.e., steep, valley, which should also be smooth, i.e., its width should be small with respect to its radius of curvature and to the characteristic distances on which its cross section and the orientation of its principal axes vary.

These condition ensure that, as is physically reasonable, the part of the distribution associated with the transverse vibrations may adapt adiabatically to the longitudinal motion.

3.2. Intermediate Time Regime

This regime corresponds to times $\{\max(|u_i''|^{-1},\ w_i^{-1})\} \leqslant t \ll \tau_K$, and is controlled by the eigenstates of $\mathscr{V}$ deriving from harmonic states with $n + p \geqslant 1$. For a general asymmetric U, these states are not systematically degenerate, and one can, as in the one-dimensional case, distinguish among states $\varphi_k^{(i)}$ with $i = 0, b$, or a, which are essentially localized in the corresponding harmonic wells. Their energies differ from the harmonic values $\lambda_{n,p}^{(i)}$ [Eq. (36)] by exponentially small terms (which are negligible since the corresponding $\lambda_{n,p}^{(i)} \neq 0$).

Let us call $\varphi_{n,p}^{(i)}(x, y)$ the corresponding wave functions. The distribution function can be written [see Eqs. (23)–(24) of I] in this regime

$$P(\mathbf{r}t|\mathbf{r}_0) = P_{\text{fin}}(\mathbf{r}t|\mathbf{r}_0) + \frac{\varphi_{0,0}(x, y)}{\varphi_{0,0}(x_0, y_0)} \sum_{\substack{npi \\ n+p\geqslant 1}} \varphi_{n,p}^{(i)}(x, y)\varphi_{n,p}^{(i)}(x_0, y_0) \exp -\left(\frac{\lambda_{n,p}^{(i)}t}{\theta}\right) \tag{46}$$

where the sum runs on states with $\lambda_{n,p}^{(i)} \ll (\Delta U/a)^2$, and for $t \ll \tau_K$,

$$\begin{aligned} P_{\text{fin}}(\mathbf{r}t|\mathbf{r}_0) &= P_{\text{eq}}(\mathbf{r}) + \frac{\varphi_{0,0}(\mathbf{r})}{\varphi_{0,0}(\mathbf{r}_0)} \varphi_{0,1}(\mathbf{r})\varphi_{0,1}(\mathbf{r}_0)e^{-t/\tau_K} \\ &\simeq P_{\text{fin}}(\mathbf{r}, t = 0|\mathbf{r}_0) \end{aligned} \tag{47}$$

Note that expression (46) for P holds only for $\mathbf{r}$ and $\mathbf{r}_0$ in the WKB tubes or the harmonic regions.

The functions $\varphi_{n,p}^{(i)}$ can be calculated explicitly with the help of the results of Section 2, and are given in Appendix C, together with the explicit expressions of P. In view of the heaviness of the corresponding algebraic expressions, we will only give here a qualitative analysis of these results:

(i) If $|y_0| \leqslant (\theta/w_0)^{1/2}$ and $|x_0| \leqslant (\theta/|u_0''|)^{1/2}$, P factorizes into the local transverse equilibrium distribution (which is reached for $t > w^{-1}$) and a longitudinal part, describing its flow along the MPEP, which is exactly the distribution $Q(xt|x_0)$ for the one-dimensional problem with potential $u(x)$ (see I):

$$P(\mathbf{r}t|\mathbf{r}_0) = \left(\frac{w(x)}{2\pi\theta}\right)^{1/2} \exp\left(-\frac{y^2 w(x)}{2\theta}\right) Q(xt|x_0) \tag{48}$$

In the intermediate-time regime, as discussed in I, P thus evolves along the MPEP with two different behaviors: on a time of order

$$t_0 = \frac{1}{2|u_0''|} \operatorname{Log} \frac{|u_0''|b^2}{\theta} \tag{49}$$

it spreads out of the (0) diffusive region, then flows on a short time through the WKB region and grows two peaks close to the minima of U, which move toward these minima while their amplitudes increase. It exhibits Suzuki's[3] scaling property as long as most of the weight of P remains in the WKB tubes, and can be cast into the universal form

$$P_{\mathrm{WKB}}(\mathbf{r}t|\mathbf{r}_0)\, dx\, dy = (1/\pi) \exp[-(u^2 + v^2)]\, du\, dv \tag{50}$$

with

$$u^2 = \frac{1}{2}\left\{x_0\left(\frac{|u_0''|}{\theta}\right)^{1/2} - \frac{x}{b\sqrt{\tau}} \exp[-|u_0''|\, \delta'(x)]\right\}^2 \tag{51}$$

$$v^2 = \frac{1}{2}\left[y\left(\frac{w(x)}{\theta}\right)^{1/2}\right]^2 \tag{52}$$

$\delta'(x)$ is a geometrical factor, characteristic of the anharmonicity of U, independent of θ, defined in Appendix C [Eq. (C5)], and τ is Suzuki's variable

$$\tau = (\theta/|u_0''|b^2) \exp(2t|u_0''|) \tag{53}$$

Then, when an important part of the weight of P enters the (b) diffusive region $[x - b \lesssim (\theta/u_b'')^{1/2}]$ Suzuki's scaling statement is no longer valid. In this region P is given in Appendix C. It takes a time

$$t_b = \frac{1}{2u_b''} \operatorname{Log} \frac{u_b'' b^2}{\theta} \tag{54}$$

for the distribution to build the local equilibrium shape (of width $\sim \theta^{1/2}$) around the minima of U. The Kramers–Eyring regime is reached for $t \gg t_0 + t_b$. Note that t_0 and t_b have comparable orders of magnitude.

(ii) If $|x_0|$ is in the WKB region ($|x_0| \sim \theta^0$) and $|y_0 \leqslant (\theta/w_0)^{1/2}$, the only difference with case (i) is that the delay time t_0 disappears: P has a drift-controlled x motion in the WKB tubes on a time of order $(u'')^{-1}$, of the same order as the transverse equilibration time, after which its peak comes close to b, it then takes a time of order t_b for it to take the shape corresponding to local equilibrium in the wells of U.

(iii) If $|y_0|$ is finite ($\sim \theta^0$) but in the harmonic vicinity of the MPEP, the evolution is more complex: indeed, it takes a time $t_{tr} \sim (2w)^{-1} \operatorname{Log}(l_y^2 w/\theta)$ (where l_y is the transverse width of the valley of U) for P to come back to transverse equilibrium. However, in the WKB region, P still factorizes into a local transverse term and a longitudinal one, which is again $Q(xt|x_0)$. So, there still is a Suzuki phenomenon in the longitudinal direction, now superimposed on a transverse relaxation which takes place on a time t_{tr} comparable to the time t_0 of peak growth. Again P is given by Eq. (50), where now

$$v^2 = \frac{1}{2}\left\{y\left(\frac{w(x)}{\theta}\right)^{1/2} - y_0\left(\frac{w_0}{\theta}\right)^{1/2}\frac{w(x)}{w_0}\exp[-tw_0 - \delta''(x)]\right\}^2 \tag{55}$$

The θ-independent geometrical factor $\delta''(x)$ is defined in Appendix C [Eq. (C6)]. In general, since $t_{tr} \sim t_0$, P enters the ($x \simeq b$) diffusive region before complete transverse relaxation, so that it no longer factorizes, in that region, into a longitudinal and a transverse term [see Eqs. (C19)–C20)]. The Kramers–Eyring regime is reached for $t \gg \max\{t_0 + t_b, t_{tr}\}$.

Thus, it can be concluded that Suzuki's description[3] of the evolution of P from a region of instability can be extended to an N-dimensional system under the following conditions:

(a) There exists in the potential U a well-defined most probable path connecting the saddle point and the minima of U. The valley along that path must be smooth (slowly varying width, weak curvature and twisting).

(b) If the above conditions are satisfied, P has the scaling form given by Eqs. (50) and (51)–(55) for times $\lesssim t_0$, i.e., as long as its lateral peaks have not entered the diffusive regions around the minima of U.

The growth time of the lateral peaks therefore remains, as in the one-dimensional case, of order t_0,[3] but it takes a time of order $\max\{t_{tr}, t_0 + t_b\}$ for the distribution to reach the final Kramers–Eyring regime.

APPENDIX A. GENERALIZATION OF THE EXTENDED WKB TREATMENT TO N DIMENSIONS ($N > 2$)

The N-dimensional treatment, which has been set up by Gervais and Sakita,[5] follows closely the two-dimensional one. So we give here only its main lines.

Let us call x the coordinate along the MPEP (which we still assume to be a straight line; the extension to a curved MPEP can be inferred from Ref. 4) and $\mathbf{y} = (y_1,..., y_{N-1})$ the $N - 1$ transverse orthonormal coordinates.

Equation (8) generalizes obviously into

$$\left[-\theta^2\left(\frac{\partial^2}{\partial x^2} + \sum_i \frac{\partial^2}{\partial y_i^2}\right) + \mathscr{V}(x, \mathbf{y})\right]\varphi(x, \mathbf{y}) = \lambda\varphi(x, \mathbf{y}) \tag{A1}$$

In the vicinity of the MPEP, $\mathscr{V}(x, \mathbf{y})$ is approximated by

$$\mathscr{V}(x, \mathbf{y}) = V(x) + \tfrac{1}{2}\mathbf{y}\overline{\overline{W}}(x)\mathbf{y} \tag{A2}$$

where

$$V(x) \equiv \mathscr{V}(x, \mathbf{o}) \tag{A3}$$

and the $(N - 1) \times (N - 1)$ matrix $\overline{\overline{W}}$ is defined by

$$W_{ij}(x) = \left.\frac{\partial^2 \mathscr{V}}{\partial y_i\, \partial y_j}\right|_{x,\mathbf{0}} \tag{A4}$$

The equation governing the small transverse fluctuations around any point $x(\tau)$ of the MPEP [where τ is the "instanton time," Eq. (17)] is now

$$d^2\boldsymbol{\alpha}^{\pm}/d\tau^2 = \overline{\overline{W}}[x(\tau)]\boldsymbol{\alpha}^{\pm}(\tau) \tag{A5}$$

But, now, $\overline{\overline{W}}[x(\tau)]$ is, in general, nondiagonal in the fixed $\{x, y_i\}$ frame. Let $\{a_l[x(\tau)]\}$ be the unit vectors defining a local set of orthonormal transverse coordinates attached to point $x(\tau)$ of the MPEP ($l = 1,\ldots, N - 1$), which will be defined more precisely below. In this new frame, Eq. (A5) can be rewritten

$$\sum_m D_{lm}(\tau)\alpha_m^{\pm}(\tau) = \sum_m W_{lm}(\tau)\alpha_m^{\pm}(\tau) \tag{A6}$$

where

$$D_{lm}(\tau) = \left\langle a_l \middle| \frac{d^2 a_m}{d\tau^2} \right\rangle + 2\left\langle a_l \middle| \frac{da_m}{d\tau} \right\rangle \frac{d}{d\tau} + \delta_{lm}\frac{d^2}{d\tau^2} \tag{A7}$$

We now choose the local coordinates y_l defined by the unit vectors $\{a_l[x(\tau)]\}$ so that they diagonalize the matrix $\overline{\overline{W}}'$ such that

$$W'_{lm} = W_{lm} - \left\langle a_l \middle| \frac{d^2 a_m}{d\tau^2} \right\rangle \tag{A8}$$

Equation (A6) then gives

$$\frac{d^2\alpha_l^{\pm}}{d\tau^2} + 2\sum_m \left\langle a_l \middle| \frac{da_m}{d\tau} \right\rangle \frac{d\alpha_m^{\pm}}{d\tau} = W_l'(\tau)\alpha_l^{\pm}(\tau) \tag{A9}$$

Note that $\langle a_l | da_l/d\tau\rangle$ is zero ($\mathbf{a}_l^2 = 1$), while the $\langle a_l | da_m/d\tau\rangle$ for $l \neq m$ characterize the rate of rotation of the local frame along the MPEP, i.e., the rate of twist of the valley of U.

There is, to our knowledge, no general solution of the system of coupled equations (A9). However, if

$$\left|\left\langle a_l \middle| \frac{da_m}{d\tau} \right\rangle\right| \ll \left(\sqrt{|W_l'|}, \sqrt{W_m'}\right) \tag{A10}$$

the second term on the l.h.s. can be neglected, and Eqs. (A9) decouple. Moreover, if condition (A10) is satisfied, $\langle a_l | d^2 a_m / d\tau^2 \rangle$ can also be neglected in (A8), $\overline{\overline{W}}'$ reduces to $\overline{\overline{W}}$, and $(x, \{y_l\})$ is simply the set of local normal coordinates associated to the potential $\mathscr{V}$ along the MPEP. Thus, assuming that condition (A10) is satisfied, we define the creation operator for the local transverse fluctuations along $\mathbf{a}_l$ as

$$A_l^{(\pm)\dagger} = e^{\pm \rho_l \tau} \left(\theta\sqrt{2}\, \alpha_l{}^{\pm} \frac{\partial}{\partial y_l} \mp \frac{d\alpha_l{}^{\pm}}{d\tau} y_l \right) \tag{A11}$$

Then,

$$\varphi^{\pm}_{n_l, n_m, \ldots}(x, \mathbf{y}) = (A_l^{(\pm)\dagger})^{n_l} (A_m^{(\pm)\dagger})^{n_m} \cdots \varphi_0{}^{\pm}(x, \mathbf{y}) \tag{A12}$$

and

$$\varphi_0{}^{\pm}(x, \mathbf{y}) = \left(\frac{dS_0}{dx} \right)^{-1/2} \left(\prod_l \alpha_l{}^{\pm} \right)^{-1/2} \exp\left(\pm S_0(x) \mp \frac{\lambda_1 \tau(x)}{\theta\sqrt{2}} - \frac{\mathbf{y} \cdot \overline{\overline{\Omega}} \cdot \mathbf{y}}{2\theta\sqrt{2}} \right) \tag{A13}$$

where the $(N - 1) \times (N - 1)$ matrix $\overline{\overline{\Omega}}{}^{\pm}$ is defined by

$$\Omega^{\pm}_{lm}[\tau(x)] = \frac{1}{\alpha_l{}^{\pm}(\tau)} \frac{d\alpha_l{}^{\pm}(\tau)}{d\tau} \delta_{lm} \tag{A14}$$

APPENDIX B

We want to calculate here the quantity

$$\Sigma_b(0) = S_b^{(+)}(0) + S_b^{(-)}(0) \tag{B1}$$

where

$$S_b^{(\pm)}(0) = \int_{\beta_0}^{0} \frac{dx'}{\theta} \left[V(x') + \frac{\theta}{\sqrt{2}} \Omega^{\pm}(\tau(x')) \right]^{1/2} \tag{B2}$$

β_0 is the turning point of the longitudinal motion, defined by

$$\beta_0 - b = (2\theta / u_b'')^{1/2}$$

The calculation of $S_b^{(\pm)}(0)$ follows the same lines as that of $S_b(0)$ for the one-dimensional case (Appendix B of I): we define two cutoffs ξ and η located in the overlap domains between the WKB tube and the (b) and (0) quadratic regions, i.e., $\beta_0 < \xi < \eta < 0$, and:

$$\text{(i)}\quad V(x) + \frac{\theta}{\sqrt{2}} \Omega^{\pm}(\tau(x)) \cong -\frac{\theta}{2} u_b'' + \frac{(u_b'')^2}{4} (x - b)^2 \qquad \text{for } \beta_0 \leqslant x \leqslant \xi \tag{B3a}$$

$$\text{(ii)}\ V(x) + \frac{\theta}{\sqrt{2}}\,\Omega^{\pm}(\tau(x)) \cong \frac{\theta}{2}\,|u_0''| + \frac{(u_0'')^2}{4}\,x^2 \qquad \text{for } \eta \leqslant x \leqslant 0 \quad \text{(B3b)}$$

(iii) Since $\frac{1}{4}(u')^2 \gg \frac{1}{2}\theta(u'' + w - \Omega^{\pm}\sqrt{2})$ for $\xi \leqslant x \leqslant \eta$, in that region

$$\left[V(x) + \frac{\theta}{\sqrt{2}}\,\Omega^{\pm}(\tau(x))\right]^{1/2} \cong \frac{|u'(x)|}{2}\left\{1 - \frac{\theta}{[u'(x)]^2}\left[u''(x) + w(x) - \Omega^{\pm}(\tau(x))\right]\right\} \qquad \text{(B3c)}$$

Splitting the interval $(\beta_0, 0)$ in Eq. (B2) into the three intervals (β_0, ξ), (ξ, η), and $(\eta, 0)$, we get

$$S_b^{(\pm)}(0) = I_1^{\pm} + I_2^{\pm} + I_3^{\pm} \qquad \text{(B4)}$$

where

$$I_1^{\pm} \cong \frac{1}{2}\left(\frac{\xi - b}{\beta_0 - b}\right)^2 - \frac{1}{4} - \frac{1}{2}\,\mathrm{Log}\left|\frac{2(\xi - b)}{\beta_0 - b}\right| \qquad \text{(B5)}$$

$$I_2^{\pm} \cong \frac{\eta^2|u_0''|}{4\theta} + \frac{1}{4} - \frac{1}{2}\,\mathrm{Log}\left|\frac{1}{2\eta}\left(\frac{2\theta}{|u_0''|}\right)^{1/2}\right| \qquad \text{(B6)}$$

$$I_3^{\pm} = \frac{u(\eta) - u(\xi)}{2\theta} - \frac{1}{2}\,\mathrm{Log}\left|\frac{u'(\eta)}{u'(\xi)}\right| - \frac{1}{2}\int_{\xi}^{\eta} dx'\,\frac{w(x') - \sqrt{2}\Omega^{\pm}(x')}{u'(x')} \qquad \text{(B7)}$$

Using Eqs. (27) and (18), we get

$$\Omega^{\pm} = \sqrt{W} \pm \frac{(2V)^{1/2}}{4W}\frac{dW}{dx} \qquad \text{(B8)}$$

Moreover, with the help of Eq. (32), condition (25) can be rewritten as $u'w' \ll w^2$, so that, developing $W^{1/2}$ to first order, we obtain

$$\Omega^{\pm}\sqrt{2} \cong \left(w + \frac{u'w'}{2w}\right) \pm \frac{u'w'}{2w} \qquad \text{(B9)}$$

from which

$$I_3^{+} = \frac{u(\eta) - u(\xi)}{2\theta} - \tfrac{1}{2}\,\mathrm{Log}\left|\frac{u'(\eta)w(\xi)}{u'(\xi)w(\eta)}\right| \qquad \text{(B10)}$$

$$I_3^{-} = \frac{u(\eta) - u(\xi)}{2\theta} - \tfrac{1}{2}\,\mathrm{Log}\left|\frac{u'(\eta)}{u'(\xi)}\right| \qquad \text{(B11)}$$

and, finally, using quadratic developments for $u(\eta)$ and $u(\xi)$, we get

$$\Sigma_b(0) = \frac{u_0 - u_b}{\theta} + \tfrac{1}{2}\,\mathrm{Log}\left|\frac{u_b''}{u_0''}\right| + \tfrac{1}{2}\,\mathrm{Log}\,\frac{w(0)}{w(b)} \qquad \text{(B12)}$$

APPENDIX C

The general form of the wave functions $\varphi_{n,p}^{(i)}$ for the eigenstates deriving from the (np, i) harmonic states is given by Eqs. (19), (21), (30). Their y part is simply the wave function of the nth excited state of the local harmonic oscillator. Their x part is calculated with the help of a WKB matching procedure which follows completely the lines depicted in Appendices A and C of I. Choosing $\mathbf{r}_0$ in the quadratic vicinity of the saddle point of U, we obtain the following results.

C.1. r in the (o) Harmonic Region

In this region, the contribution $P^{(0)}$ of the (0) sum in Eq. (46) gives the only important contribution to P ($P^{(a)}$ and $P^{(b)}$ are exponentially small compared with it), and

$$\varphi_{n,p}^{(0)}(\mathbf{r}) = \left(\frac{|u_0''|w_0}{4\pi^2\theta^2}\right)^{1/4}(p!\,n!)^{-1/2}D_n\left(y\left(\frac{w_0}{\theta}\right)^{1/2}\right)D_p\left(x\left(\frac{|u_0''|}{\theta}\right)^{1/2}\right) \tag{C1}$$

with $\lambda_{n,p}^{(0)} = \theta|u_0''|(p+1) + \theta w_0 n$. The D_n are the Weber parabolic cylinder functions.

The sum on p and n can be, in the time domain considered here, extended to infinity with only exponentially small errors. Using the well-known formula[7]

$$\sum_{n=0}^{\infty}\frac{1}{n!}z^n D_n(x)D_n(y) = \frac{1}{(1-z^2)^{1/2}}\exp\frac{xyz - \frac{1}{4}(x^2+y^2)(1+z^2)}{1-z^2} \tag{C2}$$

we find

$$\begin{aligned} P(\mathbf{r}t|\mathbf{r}_0) = {} & \left(\frac{w_0}{2\pi\theta}\right)^{1/2}[1-\exp(-2w_0t)]^{-1/2} \\ & \times \exp\left[-\frac{w_0[y - y_0\exp(-tw_0)]^2}{2\theta[1-\exp(-2tw_0)]}\right] \\ & \times \left(\frac{|u_0''|}{2\pi\theta}\right)^{1/2}[1-\exp(-2t|u_0''|)]^{-1/2}\exp(-t|u_0''|) \\ & \times \exp\left\{-\frac{[x(|u_0''|/\theta)^{1/2}\exp(-t|u_0''|) - x_0(|u_0''|/\theta)^{1/2}]^2}{2[1-\exp(-2t|u_0''|)]}\right\} \end{aligned} \tag{C3}$$

C.2. r in the WKB Tube

Here again, $P \simeq P^{(0)}$. In this region, one finds

$$\varphi_{n,p}^{(0)}(\mathbf{r}) = (-)^p(p!\,n!)^{-1/2}\left(\frac{|u_0''|^2 w_0}{16\pi^2\theta^3}\right)^{1/4}\frac{(2\theta|u_0''x|)^{1/2}}{u'(x)}$$
$$\times\left(\frac{x^2|u_0''|}{\theta}\right)^{(p+1/2)/2}\exp[-(p+1)|u_0''|\,\delta'(x)]$$
$$\times\left(\frac{w(x)}{w_0}\right)^{n+1/2}\exp[-n\,\delta''(x)]D_n\left(y\left(\frac{w(x)}{\theta}\right)^{1/2}\right)\exp\frac{u(x)-u(0)}{2\theta} \quad \text{(C4)}$$

where the θ-independent geometrical parameters

$$\delta'(x) = \int_x^0\left(\frac{1}{u_0''\xi} - \frac{1}{u'(\xi)}\right)d\xi \quad \text{(C5)}$$

$$\delta''(x) = \int_x^0 \frac{w(\xi)-w_0}{u'(\xi)}\,d\xi \quad \text{(C6)}$$

characterize the integrated anharmonicity of U along the MPEP, measured on $(u')^{-1}$ and (w/u'). Again, for the times of interest, the n and p sums in $P^{(0)}$ can be extended to infinity, and we find

$$P_{\text{WKB}}(\mathbf{r}t|\mathbf{r}_0) = \left(\frac{w(x)}{2\pi\theta}\right)^{1/2}(1-\sigma^2)^{-1/2}$$
$$\times\exp\left\{-\frac{\{y[w(x)]^{1/2} - \sigma y_0(w_0)^{1/2}\}^2}{2\theta(1-\sigma^2)}\right\}Q_{\text{WKB}}(xt|x_0) \quad \text{(C7)}$$

where

$$\sigma = \frac{w(x)}{w_0}\exp[-tw_0 - \delta''(x)] \quad \text{(C8)}$$

and

$$Q_{\text{WKB}}(xt|x_0) = \frac{\exp[-|u_0''|\,\delta'(x)]}{(2\pi\tau)^{1/2}}\frac{|u_0''x|}{bu'(x)}$$
$$\times\exp\left\{-\frac{1}{2}\left[\frac{x}{b\sqrt{\tau}}\exp[-|u_0''|\,\delta'(x)] - x_0\left(\frac{|u_0''|}{\theta}\right)^{1/2}\right]^2\right\} \quad \text{(C9)}$$

is precisely the one-dimensional distribution in the WKB region [see Eq. (44) of I], which depends on time only via Suzuki's variable:

$$\tau = (\theta/|u_0''|b^2)\exp(2t|u_0''|) \quad \text{(C10)}$$

C.3. r in the (b) Harmonic Well

In this region, P_{fin} and $P^{(b)}$ are no longer negligible with respect to $P^{(0)}$. In order to get the full expression of P, we need to know the values of $\varphi_{n,p}^{(0)}(\mathbf{r})$, $\varphi_{n,p}^{(b)}(\mathbf{r})$ for $\mathbf{r}$ in the close vicinity of the b minimum, and of $\varphi_{n,p}^{(b)}(\mathbf{r}_0)$. These are found to be

$$\begin{aligned}\varphi_{n,p}^{(0)}(\mathbf{r}) = {} & (-)^p\left(\frac{w_0|u_0''|}{4\pi^2\theta^2}\right)^{1/4}(n!\,p!)^{-1/2}\frac{\Gamma(-\nu)}{(2\pi)^{1/2}}\left|\frac{u_0''}{u_b''}\right|^{1/2}\left(\frac{w_b}{w_0}\right)^{n+1/2} \\ & \times\left(\frac{u_b''(x_m-b)^2}{\theta}\right)^{\nu/2}\left(\frac{|u_0''|x_m{}^2}{\theta}\right)^{(p+1)/2} \\ & \times\exp\left(\frac{U(b)-U(0)}{2\theta}-\frac{\lambda_{n,p}\,\delta_0}{\theta}+n\delta_1\right) \\ & \times D_n\left(y\left(\frac{w_b}{\theta}\right)^{1/2}\right)D_\nu\left(-(x-b)\left(\frac{u_b''}{\theta}\right)^{1/2}\right)\end{aligned} \tag{C11}$$

where

$$\begin{aligned}\nu &= \frac{|u_0''|}{u_b''}(p+1)+\frac{w_0-w_b}{u_b''}n \\ \lambda_{n,p}^{(0)} &= \theta|u_0''|(p+1)+\theta w_0 n\end{aligned} \tag{C12}$$

and

$$\delta_0 = \int_b^{x_m} dx\left[\frac{1}{(x-b)u_b''}-\frac{1}{u'(x)}\right]+\int_{x_m}^0 dx\left[\frac{1}{xu_0''}-\frac{1}{u'(x)}\right] \tag{C13}$$

$$\delta_1 = \int_b^{x_m} dx\left[\frac{w_b}{(x-b)u_b''}-\frac{w(x)}{u'(x)}\right]+\int_{x_m}^0 dx\left[\frac{w_0}{xu_0''}-\frac{w(x)}{u'(x)}\right] \tag{C14}$$

The intermediate point x_m can be chosen anywhere between $x = 0$ and $x = b$. We can take, for simplicity, x_m to correspond to the local maximum of $V(x)$, i.e., to the inflection point of $u(x)$:

$$\varphi_{n,p}^{(b)}(\mathbf{r}) = \left(\frac{w_b u_b''}{4\pi^2\theta^2}\right)^{1/4}(p!\,n!)^{-1/2}D_n\left(y\left(\frac{w_b}{\theta}\right)^{1/2}\right)D_p\left((x-b)\left(\frac{u_b''}{\theta}\right)^{1/2}\right) \tag{C15}$$

$$\begin{aligned}\varphi_{n,p}^{(b)}(\mathbf{r}_0) = {} & \left(\frac{w_b u_b''}{4\pi^2\theta^2}\right)^{1/4}(p!\,n!)^{-1/2}\frac{\Gamma(-\mu)}{(2\pi)^{1/2}}\left(\frac{|u_0''|x_m{}^2}{\theta}\right)^{(\mu+1)/2}\left(\frac{u_b''(x_m-b)^2}{\theta}\right)^{p/2} \\ & \times\exp\left(\frac{U(b)-U(0)}{2\theta}-\frac{\lambda_{n,p}^{(b)}\,\delta_0}{\theta}+n\,\delta_1\right) \\ & \times D_n\left(y_0\left(\frac{w_0}{\theta}\right)^{1/2}\right)D_\mu\left(x_0\left(\frac{|u_0''|}{\theta}\right)^{1/2}\right)\end{aligned} \tag{C16}$$

with

$$\mu + 1 = \frac{u_b''}{|u_0''|}\, p + \frac{w_b - w_0}{|u_0''|}\, n \tag{C17}$$

and

$$\lambda_{n,p}^{(b)} = \theta u_b'' p + \theta w_b n$$

From which we obtain, for $\mathbf{r}$ in the (b) quadratic region,

$$P(\mathbf{r}t\,|\,\mathbf{r}_0) = P_{\text{fin}}(\mathbf{r}, t = 0\,|\,\mathbf{r}_0) + P^{(0)}(\mathbf{r}t\,|\,\mathbf{r}_0) + P^{(b)}(\mathbf{r}_0) \tag{C18}$$

$$\begin{aligned} P^{(0)}(\mathbf{r}t\,|\,\mathbf{r}_0) &= \exp\left(-\frac{U(x, y) - U(b, 0)}{2\theta}\right) \frac{(w_b u_b'')^{1/2}}{2\pi\theta} \left|\frac{u_0''}{u_b''}\right| \\ &\times \sum_{p=0, n=0}^{\infty} \frac{(-)^p}{n!\,p!} \frac{\Gamma(-\nu)}{(2\pi)^{1/2}} D_n\left(y_0\left(\frac{w_0}{\theta}\right)^{1/2}\right) D_n\left(y\left(\frac{w_b}{\theta}\right)^{1/2}\right) \\ &\times D_p\left(x_0\left(\frac{|u_0''|}{\theta}\right)^{1/2}\right) D_\nu\left(-(x - b)\left(\frac{u_b''}{\theta}\right)^{1/2}\right) (\tau_{b\perp}^{(0)})^{-n/2}\, \tau_{b\|}^{-(p+1)/2} \end{aligned} \tag{C19}$$

$$\begin{aligned} P^{(b)}(\mathbf{r}t\,|\,\mathbf{r}_0) &= \exp\left(-\frac{U(x, y) - U(b, 0)}{2\theta}\right) \frac{(w_b u_b'')^{1/2}}{2\pi\theta} \\ &\times \sum_{p=1, n=0}^{\infty} \frac{1}{n!\,p!} \frac{\Gamma(-\mu)}{(2\pi)^{1/2}} D_n\left(y_0\left(\frac{w_0}{\theta}\right)^{1/2}\right) \\ &\times D_n\left(y\left(\frac{w_b}{\theta}\right)^{1/2}\right) D_\mu\left(x_0\left(\frac{|u_0''|}{\theta}\right)^{1/2}\right) D_p\left((x - b)\left(\frac{u_b''}{\theta}\right)^{1/2}\right) \\ &\times (\tau_{b\perp}^{(b)})^{-n/2}\, \tau_{b\|}^{-pu_b''/2|u_0''|} \end{aligned} \tag{C20}$$

with

$$\tau_{b\|} = \frac{\theta}{x_m^2 |u_0''|} \left(\frac{\theta}{u_b''(x_m - b)^2}\right)^{|u_0''|/u_b''} e^{2(t+\delta_0)|u_0''|} \tag{C21}$$

$$\tau_{b\perp}^{(0)} = \left(\frac{w_0}{w_b}\right)^2 \left(\frac{\theta}{u_b''(x_m - b)^2}\right)^{(w_0 - w_b)/u_b''} e^{2w_0(t+\delta_0)+2\delta_1} \tag{C22}$$

$$\tau_{b\perp}^{(b)} = \left(\frac{\theta}{x_m^2 |u_0''|}\right)^{(w_b - w_0)/|u_0''|} e^{2w_b(t+\delta_0)+2\delta_1} \tag{C23}$$

In order to estimate the characteristic time for the evolution of P, it is important to know explicitly what powers of θ appear in the sums (C19) and (C20). If one of the quantities (x_0, $(x - b)$, y_0, y) is of order θ^0, one can replace the corresponding D function by its asymptotic development. If, for example, $(x - b) \sim \theta^0$, this gives exactly the WKB result of Eq. (C7).

We will only treat here the case where these four quantities are of order $\theta^{1/2}$, so that the true θ factors in sums (C19)–(C20) only come from the τ factors. For example, in Eq. (C19), these can be rewritten as

$$(\tau_{b\perp}^{(0)})^{-n/2}(\tau_{b11})^{-(p+1)/2} = K_{np} \exp[-\nu u_b''(t - t_0 - t_b)] \times \exp\{-n[w_b t + (w_0 - w_b)t_0]\} \qquad \text{(C24)}$$

where the constant

$$K_{np} = \left(\frac{w_b}{w_0}\right)^n \left|\frac{x_m}{b}\right|^{p+1} \left|\frac{x_m - b}{b}\right|^{\nu} \exp\left(-\frac{\lambda_{n,p}^{(0)}\,\delta_0}{\theta} - n\,\delta_1\right) \qquad \text{(C25)}$$

is θ independent;

$$t_0 = \frac{1}{2|u_0''|} \operatorname{Log} \frac{|u_0''|b^2}{\theta}$$

is the characteristic time necessary for a significant part of P to leave the central diffusive region; and

$$t_b = \frac{1}{2u_b''} \operatorname{Log} \frac{u_b b^2}{\theta}$$

is, analogously, the time for a distribution starting from a finite distance [of order $(\theta/u_b'')^0$] from the b minimum to build the equilibrium shape in the vicinity [of order $(\theta/u_b'')^{1/2}$] of that minimum.

As discussed in Section 3.2, the distribution reaches the (b) vicinity considered here only for times $t > t_0$. If $t \gg t_0 + t_b$, it is clear that $P^{(0)} + P^{(b)}$ becomes negligible, and $P \simeq P_{\text{fin}}$. So, $t_0 + t_b$ is the characteristic time for getting into the Kramers–Eyring regime. Let us therefore consider the domain $t_0 \ll t \leqslant t_0 + t_b$ where P is essentially concentrated in the (b) region and given by Eqs. (C19)–(C20). In order of magnitude, $|w_0 - w_b| \sim w_b$, and using Eq. (C24), it is seen that the $n \neq 0$ contributions to $P^{(0)}$ are negligible. One easily shows that the same result holds for $P^{(b)}$. This means that the distribution remains locally equilibrated in the transverse direction, and

$$P(\mathbf{r}t\,|\,\mathbf{0}) = (w_b/2\pi\theta)^{1/2}[\exp(-y^2 w_b/4\theta)]Q(xt\,|\,0) \qquad \text{(C26)}$$

where $Q(xt\,|\,0)$ is the distribution in the considered space ($x \simeq b$) and time domain for the one-dimensional problem with potential $u(x)$ [Eq. (34) of I]. For $|x - b| \leqslant (\theta/u_b'')^{1/2}$, Q evolves with the characteristic time $t_0 + t_b$, which corresponds to $\tau_{b\|} = 1$.

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