# Transient solution of the Kramers problem in the weak noise limit

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The one-dimensional escape problem for both overdamped and underdamped cases is treated using a combination of matched asymptotic and Laplace transformation techniques. It is shown that the shape of transient curves for the probability flux at the top of the barrier is insensitive to the specific shape of the potential, but is determined only by the ratio of the characteristic time scales at the points of stable and unstable equilibria. For the overdamped case this results in a relatively small number of possible types of transient behavior for various potentials (examples of quartic, slanted sinusoidal, cubic, and nonanalytic potentials are considered). In the underdamped situation the transient curve is identical for any shape of potential. [S1063-651X(97)06411-8]

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## I. INTRODUCTION

In his celebrated paper [1] Kramers considered Brownian diffusion of a classical particle in a nonuniform field of force described by a metastable potential $W(x)$, $x$ being the ''reaction coordinate.'' The Kramers problem (KP) can be cast in terms of a Langevin equation

$$\ddot{x}+\gamma\dot{x}+W'(x)=\zeta(t), \quad \langle\zeta(t)\zeta(t')\rangle=(2\gamma/\beta)\,\delta(t-t'), \tag{1}$$

with $\gamma$ describing dissipation and $\zeta$ the random Gaussian force; $\beta^{-1}\equiv k_BT$ is the thermal noise, with $k_B$ being the Boltzmann constant. Although originally intended to describe chemical reactions, the problem turned to a much broader applicability due to the universality of the activation decay mechanisms. As an example, one could mention the nucleation problem, which could be treated in the spirit of the Kramers approach [2]; diverse, more recent developments can be found in Refs. [3–5].

In the problems of activation decay, typically of interest is the mean exit time $\tau_K$ for a particle to escape the metastable well or, equivalently, the quasi-steady-state probability flux over the barrier $I_K\sim 1/\tau_K$. This means that one is discussing time scales when the transformation is already bound towards completion, and in a large system the number of product molecules is comparable to the one that originally entered the reaction. On the other hand, a different question can be asked: How quickly is the flux $I_K$ established? The latter can be of interest when minor amounts of the product are important and/or can be detected experimentally and will be discussed in the present work.

Since in a general case it is impossible to treat exactly Eq. (1) or its counterpart, the two-dimensional Fokker-Planck (Kramers) equation, attention is being turned to asymptotic methods for weak thermal noise. Such methods are especially effective in the strong damping limit when Eq. (1) can be mapped to a one-dimensional Fokker-Planck (Smoluchowski) equation [6–8]. Specifically, for equations describing a forced diffusion in a nonuniform potential one could mention the WKB [9] or path-integral approaches [10], operator methods [11], matched asymptotic technique [12], etc. The weak noise ideas also turned out to be very effective for the escape problems in more complicated situations where additional dimensions are added [5,13–15], the systems lacks detailed balance [16,17], or the potential $W(x)$ fluctuates [18] or changes with time periodically [19] or monotonically [15,20], etc. (The field is too broad and only representative references are given.) For the Kramers problem with arbitrary damping the weak noise (singular perturbation) methods proved very effective too [21–23]. Nevertheless, even for weak noise the general problem is not yet fully solved and there does not seem to be a straightforward way to treat analytically the two-dimensional Fokker-Planck counterpart of Eq. (1). Otherwise, numerically oriented methods [24,25] are being introduced and damping is often imitated by a contact with an oscillator bath [5]. Thus, in the present work the limits of large and small $\gamma$ will be treated separately for the transient case; the crossover problem, which is much more elaborate even in the mean first-passage time and related formulations (see, e.g., Refs. [5, 26–28]), will not be discussed.

In the treatment of the corresponding Fokker-Planck equations we will mostly rely on a combination of matched asymptotic and Laplace transformation techniques that was introduced in a simpler (nucleation) context in Ref. [29] (see also Refs. [12, 30]). Section II deals with the overdamped case and Sec. III with the underdamped case. In Sec. IV several specific examples of the potential $W(x)$ will be discussed, although our main intent is the general treatment as well as the exploration of the ''universality'' [weak sensitivity to $W(x)$] that arises in the weak noise limit. The nucleation problem also will be discussed as an example in somewhat more detail in Sec. IV; it will be shown that despite certain technical differences, this problem exhibits a very similar transient behavior to the Kramers escape problem, albeit with a nonanalytic potential. Experimental conditions where the transient effects in the KP may be of importance also will be clarified in the course of the comparison with the nucleation problem. A summary of our main findings is given in Sec. V.

## II. OVERDAMPED CASE

Let $\omega_s$ and $\omega_*$ denote the stable and unstable frequencies, i.e.,

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$$\omega_{s,*}^2 = \pm \left. \frac{d^2W}{dx^2} \right|_{x=x_s,x_*} . \tag{2}$$

Here $x_s$ and $x_* > x_s$ are, respectively, the stable and unstable points of the potential $W(x)$. In the overdamped case with $\gamma \gg \omega_s, \omega_*$, Eq. (1) can be reduced to a Smoluchowski equation for the probability density $P(x,t)$ (see, e.g., Refs. [31–33] and references therein),

$$\frac{\partial P}{\partial t} = -\frac{\partial j}{\partial x}, \quad j = -D(x)\,\frac{\partial P}{\partial x} + v(x)P. \tag{3}$$

Here

$$v(x) = -\beta D(x) dW/dx \tag{4}$$

is the deterministic rate, with $D(x)$ being the diffusion coefficient. For the KP the latter is constant, $D = 1/\beta\gamma$, but we indicate the possible $x$ dependence for potential generalizations.

Formally, one can introduce a (quasi)equilibrium density

$$P_{\rm eq}(x) = \frac{1}{\Delta_s \sqrt{\pi}} \exp\{-\beta[W(x) - W(x_s)]\},$$

$$\Delta_s \equiv \omega_s^{-1} \sqrt{2/\beta}, \tag{5}$$

which corresponds to a zero flux $j$ in Eq. (3). The reduced density $w(x,t) \equiv P(x,t)/P_{\rm eq}$ obeys an equation

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial x}\, D(x)\, \frac{\partial w}{\partial x} + v(x)\, \frac{\partial w}{\partial x}. \tag{6}$$

In the (quasi-)steady-state case Eq. (6) can be solved exactly. More instructive, however, is the singular perturbation solution. The ''outer solution'' is $w(x) = 1$ at $x < x_*$. In the vicinity of $x_*$ there is a boundary layer with a width $\Delta_* = \omega_* \sqrt{2/\beta}$; the stretched (inner) variable is given by $z_* = (x - x_*)/\Delta_*$. For a natural boundary condition (absorbing boundary placed at $z_* \to \infty$) the inner solution is $w(z_*) = \frac{1}{2}\ {\rm erfc}(z_*)$. The Kramers flux is thus given by

$$I_K = \frac{D(x_*)}{\Delta_* \sqrt{\pi}}\, P_{\rm eq}(x_*) = \frac{\omega_s \omega_*}{2\gamma\pi}\, \exp(-\beta W_*), \tag{7}$$

with $W_* \equiv W(x_*) - W(x_s)$. This is a well-known result; the corresponding flux would be doubled if an absorbing boundary were placed directly at the top of the barrier; otherwise, the description remains unchanged. Note that it is the presence of an absorbing boundary that selects the steady-state distribution with a nonzero flux (see also Ref. [5]).

We now proceed to our main concern: the evaluation of the reduced transient flux $j_*(t)/I_K$.

### A. Laplace transform

Let us switch to

$$V(x,p) = \int_0^\infty dt\ e^{-pt} w(x,t),$$

which is the Laplace transform of $w(x,t)$. The function $V(x,p)$ obeys an *ordinary* differential equation

$$pV - w(x,0) = \frac{d}{dx}\, D(x)\, \frac{dV}{dx} + v(x)\, \frac{dV}{dx}. \tag{8}$$

In the limit of weak noise, $\beta \to \infty$, this equation can be treated using the standard matched asymptotic technique (see, e.g., Ref. [34] for a general introduction). A $\delta$-function initial condition for $w(x,0)$ will be assumed, i.e., the particle is placed at the bottom of the metastable well at $t = 0$.

In the vicinity of the stable point we switch to a stretched variable $z_s = (x - x_s)/\Delta_s$. Together with the normalization condition $\int_{-\infty}^{\infty} V(z,p) P_{\rm eq}(z)\, dz = 1/p$, this leads to the inner solution

$$V(z_s,p) = \tau_s \sqrt{\pi}\, \Gamma(m_s) \exp(z_s^2)\, 2^n i^n\ {\rm erfc}(|z_s|). \tag{9}$$

Here $\Gamma$ denotes the gamma function and $i^n{\rm erfc}$ is the repeated error integral [35]. The index $n$ is given by $n = 2m_s - 1$ with $m_s = p\tau_s$ and $\tau_s^{-1} = -2v_x'$ at $x = x_s$ (so that for the KP one has $\tau_s = \gamma/2\omega_s^2$).

The outer solution at $x_s < x < x_*$ is given by

$$V(x,p) \propto \exp\left( -p \int dx/v(x) \right). \tag{10}$$

The proportionality coefficient can be determined from matching the asymptote of Eq. (10) for $x \to 0$ with the one of Eq. (9) for $z_s \to \infty$.

Similarly, near the unstable point $x_*$, one can switch to a stretched variable $z_*$. The solutions of the resulting equation that decays as $z_* \to \infty$ can be expressed through a similar repeated error integral $i^n{\rm erfc}(z_*)$, although with a different index $n$. The proportionality coefficient can be deduced from matching with Eq. (10). The Laplace transform of the flux is further obtained as $I(x,p) = -DP_{\rm eq} dV/dx$. At $x = x_*$ one ends up with the expression

$$I_*(p) = I_K p\, \frac{\tau^2}{\alpha}\, \Gamma(m)\Gamma(m/\alpha) \exp(-pt_i). \tag{11}$$

Here, in order to symmetrize the notations with respect to $x_s$ and $x_*$ we introduced

$$\tau = \max(\tau_s, \tau_*), \quad \alpha = \tau/\min(\tau_s, \tau_*) \geqslant 1, \tag{12}$$

with $\tau_*^{-1} = 2v_x'$ at $x = x_*$ and $m = p\tau$. The parameter $t_i$, the ''incubation time,'' is defined as

$$t_i = \int_{x_s+\Delta_*}^{x_*-\Delta_*} \frac{dx}{v(x)} = 2\tau_s \ln \frac{x_* - x_s}{\Delta_s} + 2\tau_* \ln \frac{x_* - x_s}{\Delta_*} + \tau C, \tag{13a}$$

$$C = \frac{1}{\tau} \int_{x_s}^{x_*} dx \left\{ \frac{1}{v(x)} - \frac{1}{v'(x_s)(x - x_s)} - \frac{1}{v'(x_*)(x - x_*)} \right\}. \tag{13b}$$

Here only the constant $C$ is sensitive to the specific shape of the potential $W(x)$.

### B. Time dependence of the flux

Equation (11) does not satisfy the formal requirements for a Laplace transform due to a rapid growth of the $\Gamma$ functions for $m\to\infty$. This is due to the asymptotic treatment of the problem: In the application of the matched asymptotic technique it is implicitly assumed that the dimensionless Laplace index $m$ is finite. Thus one does not expect the resulting transient flux to be accurate for very small times. Nevertheless, the error is present only during an initial time interval, which is asymptotically small compared to the incubation time $t_i$. Since the flux during this interval is negligibly small compared to $I_K$, the error remains practically unobservable. This situation is typical for asymptotic methods, which often do not distinguish between exact and asymptotic zeros (see, e.g., the discussion of the WKB approach in Ref. [36]).

Since Eq. (11) is accurate in any *finite* part of the complex $p$ plane, we apply the following expression to evaluate the time dependence of the flux [29,30]:

$$j_*(t)=\sum{}' \ \mathrm{Res} I_*(p)e^{pt}. \tag{14}$$

The prime indicates that only residues at finite $p$ are to be considered. The summation over finite residues of the $\Gamma$ function leads to a double-exponential time dependence [29]

$$\sum{}' \ \mathrm{Res}\Gamma(m)e^{mu}=\exp\{-\exp(-u)\}\equiv\phi_0(u), \tag{15}$$

with

$$u\equiv(t-t_i)/\tau. \tag{16}$$

When several $\Gamma$ functions are present in the Laplace transform, the convolution theorem can be applied (although certain caution is required due to the asymptotic nature of the problem [12]). In application to Eq. (11) one needs a convolution of two double-exponential functions. After some straightforward transformations this leads to

$$j_*(t)=I_K\int_0^\infty dy\ \exp\left\{-y-\left(\frac{e^{-u}}{y}\right)^\alpha\right\}, \tag{17}$$

which is the main result of this part of the study. Note an asymptotic rather than an exact zero at $t=0$, which corresponds to large negative $u$. Otherwise, Eq. (17) is expected to be asymptotically accurate for the entire transient region when $j_*(t)$ changes from negligibly small values to $I_K$. Again, one can note the insensitivity of the transient expression to the specifics of the potential $W(x)$ that enters the result only through the parameter $\alpha$, which is the ratio of corresponding frequencies near the equilibrium points.

The probability for a particle to exit the well

$$P_B=\int_{x_*}^\infty dx\ P(x,t)$$

is given by integration of Eq. (17) over time. One has with asymptotic accuracy

$$P_B(t)=\tau I_K\frac{1}{\alpha}\int_0^\infty dy\ e^{-y}E_1\left\{\left(\frac{e^{-u}}{y}\right)^\alpha\right\}, \tag{18}$$

where $E_1$ is the first exponential integral. At large times $u\gg1$ one has the correction to the Kramers-type expression $P_B^K\sim tI_K$:

$$P_B=I_K\{t-t_{\mathrm{ind}}+\tau O(e^{-u})\}. \tag{19}$$

Here

$$t_{\mathrm{ind}}=\lim_{p\to0}\left\{\frac{1}{p}-\frac{I_*(p)}{I_K}\right\}=t_i+\mathbf{C}\tau\left(1+\frac{1}{\alpha}\right) \tag{20}$$

is the ''induction time'' (in nucleation terminology) with $\mathbf{C}=0.5772...$ being Euler's constant. Obviously, the induction time can be deduced directly from the large-time asymptote of Eq. (18), which leads to the same result as given by Eq. (20) and testifies to the correctness of the inversion of the Laplace transform. For $\alpha\to\infty$ the functional form of Eqs. (17), (18), and (20) coincides with the corresponding nucleation expressions [29,37]. This correspondence is rooted in certain similarities between the nucleation and the KP and will be examined in Sec. IV.

## III. UNDERDAMPED LIMIT

In the limit $\gamma\ll\omega_s,\omega_*$ the slow variable for a Brownian particle described by Eq. (1) is the action $J$ or, equivalently, the total energy $E(J)$. Biased diffusion along the $J$ axis can be described by the equation [1] (see also the review [5] and references therein)

$$\frac{\partial}{\partial t}P(J,t)=\gamma\frac{\partial}{\partial J}\left\{\frac{J}{\omega}\left(\beta^{-1}\frac{\partial P}{\partial J}+\omega P\right)\right\}. \tag{21}$$

Here $\omega$, the angular frequency, is given by $dE/dJ$; the factor $2\pi$ (see, e.g., [5]) can be included in the definition of the action, $J$. For small $J\to0$ one has $\omega\to\omega_s$. For large $J\to J_*$ with $J_*$ corresponding to the value on the separatrix, $\omega$ goes to zero as $(\pi/\sqrt{2})\omega_*\{-\ln(J_*-J)\}^{-1}$. Equation (21) is applicable for $\omega\gg\gamma$, which is satisfied unless $J$ is exponentially close to $J_*$. Note, however, that the deterministic rate of the decay of the action $v(J)$ in the leading order in $\beta$ has no singularities as $J\to J_*$ and, in contrast to the overdamped case, remains finite near the exit point (see below). The latter belittles the role of the weak (logarithmic) singularity in $1/\omega$, at least for the time scales considered. Divergence of $1/\omega$ near $J=J_*$, rather, serves as the remainder of the limited applicability of Eq. (21).

Similarly to the overdamped case, one can introduce a formal equilibrium probability density

$$P_{\mathrm{eq}}(J)=\beta\omega_s\ \exp\{-\beta E(J)\} \tag{22}$$

and rewrite Eq. (21) in terms of $w(J,t)=P(J,t)/P_{\mathrm{eq}}$ as

$$\frac{\partial w}{\partial t}=\frac{\partial}{\partial J}D(J)\frac{\partial w}{\partial J}+v(J)\frac{\partial w}{\partial J}. \tag{23}$$

This equation may look identical to Eq. (6) with $x$ replaced by $J$, but the size dependence of the coefficients is now different:

$$D(J)=\frac{\gamma J}{\omega\beta}, \quad v(J)=-\gamma J. \tag{24}$$

An absorbing boundary is assumed at $J=J_*$. Due to logarithmic divergence of $\omega^{-1}$, the corresponding boundary layer has a rather complicated structure. A detailed study of this layer may be further hindered by the fact that Eq. (21) loses its applicability in the immediate vicinity of $J_*$, as discussed above. To bypass this boundary layer in the steady-state situation one can either consider the exact solution of Eq. (23) or shift the absorbing boundary to some $J<J_*$ and take the limit $J\to J_*$ after the flux is evaluated. The latter represents the most natural approach in view of the time-dependent generalizations. In the steady-state case it leads to the well-known result of Kramers for the underdamped flux

$$I_K^{\rm under}=\gamma J_* P_{\rm eq}(J_*). \tag{25}$$

Again, the problem is an evaluation of the transient behavior $j_*(t)$.

### A. Laplace transform

Let us temporarily switch to a dimensionless ''time'' $\gamma t$. Similarly to the overdamped case, one can introduce a Laplace transform $V(J,p)$ of the reduced probability density $w(J,t)$. The function $V(J,p)$ obeys an equation similar to Eq. (8), with the coefficients defined in Eq. (24). In the vicinity of $J=0$ this function obeys the equation

$$zV''_{zz}+(1-z)V'_z-pV=-w(z,0), \tag{26}$$

with $z=J\beta\omega_s$ being the inner variable.

The homogeneous part of Eq. (26) has two linearly independent solutions: Kummer's functions $M(p,1,z)$ and $U(p,1,z)$, with a Wronskian $W\{M,U\}=-e^z/z\Gamma(p)$ [35]. Taking into account the behavior of Kummer's functions at $z\to 0$ and $z\to\infty$, one can write the solution to Eq. (26) as

$$V(z,p)=\Gamma(p)\left\{U(p,1,z)\int_0^z dy\ M(p,1,y)e^{-y}w(y,0) + M(p,1,z)\int_z^\infty dy\ U(p,1,y)e^{-y}w(y,0)\right\}. \tag{27}$$

This expression can be inverted, giving a Green's function of Eq. (21) near $J=0$ (see the Appendix). It is easier to postpone the inversion, however, until the Laplace transform of the flux at $J=J_*$ is obtained.

The outer solution is similar to Eq. (10) with $v(J)$ from Eq. (24). This gives $V(J,p)\propto J^{-p}$. The proportionality coefficient is obtained from matching with Eq. (27). For a $\delta$-function initial distribution one has $V(z,p)\to z^{-p}\Gamma(p)$ for $z\to\infty$, so that the outer solution is given by

$$V(J,p)=(J\beta\omega_s)^{-p}\Gamma(p). \tag{28}$$

The above expression does not satisfy the right-hand boundary condition where an absorbing boundary is assumed. Placing this boundary at any $J<J_*$, however, leads only to a minor modification of the nonsingular equation (28) inside a simple boundary layer. One can show in a general situation [12] that the modified solution in the vicinity of the boundary leads to a flux $I=|v|P_{\rm eq}V$, with $V$ being a ''free-boundary'' outer solution, similar to Eq. (28). Thus one obtains

$$I(J,p)=\gamma JV(J,p)P_{\rm eq}(J) \tag{29}$$

for the flux near the absorbing boundary placed at arbitrary $J$. An important point is that this expression does not exhibit any singularities as $J\to J_*$. Thus the boundary can be ''pushed'' towards $J_*$ and Eq. (29) can be used to evaluate the Laplace transform of the flux. Otherwise, an elaborate investigation of the aforementioned logarithmic boundary layer near $J_*$ would be required. (Anyway, one can expect that the latter will affect the Laplace transform only at very large $p\sim\beta E_*$, which correspond to times so small that the flux is yet unobservable on the scale of $I_K$.) From Eqs. (25) and (29) one obtains for $I_*(p)\equiv I(J_*,p)$

$$I_*(p)=I_K^{\rm under}(J_*\beta\omega_s)^{-p}\Gamma(p). \tag{30}$$

### B. Time dependence of the flux

Applying to $I_*(p)$, the asymptotic inversion technique described in Sec. II, one ends up with the transient flux

$$j_*(t)=\sum{}' \ {\rm Res}I_*(p)e^{pt}=I_K^{\rm under}\phi_0(u), \quad u\equiv\gamma(t-t_i), \tag{31}$$

with $\phi_0(u)$ being the same double-exponential function as defined by Eq. (15) and

$$t_i=\tau\ \ln(\beta J_*\omega_s), \quad \tau\equiv\gamma^{-1}. \tag{32}$$

Formally, this expression follows from Eq. (17) in the limit $\alpha\to\infty$ (note, however, a different definition of $\tau$). In the underdamped case transient behavior originates solely from equilibration near the stable point, which gives a leading term $\tau\ \ln(\beta\omega_s)$ in the incubation time. At higher energies equilibration is fast on the scale of $t_i$. This leads only to a finite shift (of the order of $\tau$) in the incubation time and does not alter the double-exponential shape of the transient curve. In principle, similar effects can be observed in the overdamped case as well if the deterministic rate $v(x)$ does not go to zero at one of the extrema of $W(x)$. This will be discussed in the next section.

## IV. EXAMPLES

We are going to consider several frequently discussed shapes of the potential $W(x)$ for the overdamped KP. A specific shape of $W(x)$ affects the general result, Eqs. (17) and (18), via the the parameter $\alpha$, which describes the asymmetry of kinetics near the stable and unstable equilibrium points, respectively. The relation to the nucleation problem also will be examined, which might provide additional analytical and experimental insight into the KP. On the other hand, at this point one already can add little to the underdamped KP,

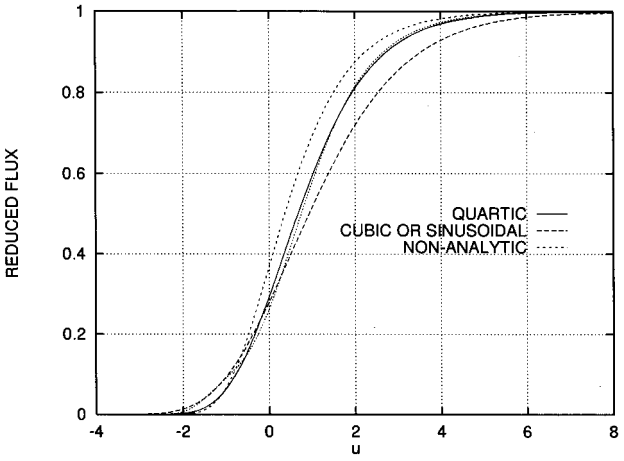


FIG. 1. Transient overdamped flux $j(t)/I_K$ for various potentials $W(x)$ as a function of dimensionless shifted time $u=(t-t_i)/\tau$. Analytical dependences used to plot the curves are listed in Table I. The dotted line shows the ''large-$\alpha$'' approximation for the quartic potential (37) with $\alpha=2$. The underdamped flux has the same shape as the nonanalytic curve (although with different parameters $\tau$ and $t_i$) and is given by Eq. (31).

which, according to Eq. (31), is completely insensitive to the shape of $W(x)$, and this problem will be invoked only occasionally.

### A. Analytic $W(x)$

Consider the escape problem in a quartic bistable potential

$$W(x)=W_*\{-2(x/x_s)^2+(x/x_s)^4\} \tag{33}$$

with stable points at $x=\pm x_s$ and a barrier at $x=x_*=0$. This potential is often discussed in connection with the Ginzburg-Landau–type description of phase separation. Transient flux is now given by Eq. (17) with $\alpha=2$. The integral cannot be evaluated in a closed form, and the results of numerical integration are shown in Fig. 1 together with an elementary approximation based on a large-$\alpha$ expansion.

The cubic potential

$$W(x)=W_*\{3(x/x_*)^2-2(x/x_*)^3\} \tag{34}$$

often arises in connection with the formation of nuclei. In such cases the cubic and quadratic terms correspond to volume and surface contributions, respectively. The parameter $\alpha$ equals 1, which allows one to express the integrals in Eqs. (17) and (18) through modified Bessel functions $K_1$ and $K_0$; see Table I. The ''real-life'' nucleation problem, however, has a different transient behavior due to the size dependence of $D(x)$ in Eq. (3) and will be discussed separately.

The slanted sinusoidal (''washboard'') potential

$$W(x)=\tfrac{1}{2}W_*\{\sin x_*-x_*\cos x_*\}^{-1}(\sin x-x\ \cos x_*),$$
$$x_*<\pi/2, \tag{35}$$

is encountered in problems of ionic conductivity or in connection with Josephson junctions. This potential has the same value of $\alpha=1$ as the cubic potential. Thus it is described by the same transient curve, which turns independently either of the barrier $W_*$ or of the ''driving force'' $x_*$. The latter affects only the constant $C$ in the expression for the incubation time; see Table I. (Naturally, we limit the discussion to a moderate driving force with $x_*<\pi/2$ so that metastable states still exist.)

### B. Nonanalytic $W(x)$ and the limit $\alpha\to\infty$

Consider a situation where the rate $v(x)$ does not go to zero (has a discontinuity of first or second order) at one of the extreme of $W(x)$. For a constant diffusion coefficient this is possible for a potential that is nonanalytic either near $x_s$ or near $x_*$. Such a behavior arises, say, for a piecewise linear potential where the transient problem can be solved exactly [38]. Formally, nonanalytic $W(x)$ also brings the situation closer to the underdamped KP as well as to the nucleation problem (see below).

The outer solution given by Eq. (10), which is not affected (up to a factor) by the equilibrium points, is still valid for a nonanalytic $W(x)$. In the latter case, however, this solution does not exhibit a singularity at a point with $v(x)\neq 0$, which simplifies the problem. In particular, there remains only a single time scale $\tau$ and the constant $C$ in the expression for the incubation time is now given by

$$C=\frac{1}{\tau}\int_{x_s}^{x_*}dx\left\{\frac{1}{v(x)}-\frac{1}{v'(x^i)(x-x^i)}\right\}. \tag{36}$$

Here $x^i$ is the equilibrium point where $v(x)$ does go to zero. The asymmetry parameter $\alpha$ goes to infinity. The transient flux has a double-exponential dependence of type (31) (note, however, different $\tau$ and $I_K$) and is shown in Fig. 1. Again, we note the universality of $j_*(t),P_B(t)$ for any particular shape of nonanalytic $W(x)$ as long as the constant $C$ defined by Eq. (36) is finite.

Since the nonanalytic situation should follow from the general equation (17) in the limit $\alpha\to\infty$, one could wish to examine the general result for large $\alpha$. Integrating Eq. (17)

TABLE I. Typical parameters and shapes of the solution with $u=(t-t_i)/\tau$.

| Potential | $v(x)$ | $\alpha$ | $C$ | $j_*(t)/I_K$ | $P_B(t)/\tau I_K$ |
|---|---|---|---|---|---|
| general | Eq. (4) | Eq. (12) | Eq. (13b) | | |
| biquadratic, Eq. (33) | $x(x^2-x_s^2)$ | 2 | $2\ln 2$ | Eq. (17) | Eq. (18) |
| cubic, Eq. (34) | $x(x-x_*)$ | 1 | 0 | | |
| slanted sinusoidal, Eq. (35) | $\cos x_*-\cos x$ | 1 | $4\ln(x_*/\sin x_*)$ | $2e^{-u/2}K_1(e^{-u/2})$ | $2K_0(e^{-u/2})$ |
| nonanalytic | discontinuous at $x_s$ or $x_*$ | $\infty$ | Eq. (36) | $\exp\{-e^{-u}\}$ | $E_1(e^{-u})$ |

by parts, switching to a new integration variable $w=[y\exp(u)]^{-\alpha}$, and expanding the resulting integral in powers of $1/\alpha$, one obtains

$$j_*(t)=I_K\phi_0(u)\left[1-\frac{e^{-u}}{\alpha}\,\mathbf{C}-\frac{e^{-u}(1-e^{-u})}{2\alpha^2}\times(\mathbf{C}^2+\pi^2/6)+\cdots\right]. \tag{37}$$

Here, again, $u$ is defined by Eq. (16), $\phi_0(u)=\exp[-\exp(-u)]$, and $\mathbf{C}$ is Euler's constant. Similarly, one has for the escape probability

$$P_B(t)=\tau I_K\{E_1(e^{-u})-\phi_0(u)0.577/\alpha+\phi_0'(u)0.989/\alpha^2+\cdots\}, \tag{38}$$

with $\phi_0'(u)=\exp[-u-\exp(-u)]$. As seen from Fig. 1, the expansion works quite well even for a moderate $\alpha=2$; a certain loss of accuracy for negative $u$ comes from the limitation $\alpha\gg\max(1,e^{-u})$, which is required in order to validate Eq. (37).

Comparing various curves shown in Fig. 1 for different values of the asymmetry parameter $\alpha$, one can note their relatively small difference from each other. This ''weak'' universality should be kept in mind when analyzing experimental (and possibly even numerical) data. In such situations it might be hard to distinguish between different dependences even for a minor amount of inevitable scatter.

Finally, since the functional form of the transient solution is determined exclusively by the equilibrium points, the results may hold even if the Fokker-Planck description is invalid in the intermediate region $x_s<x<x_*$. This can happen when the discrete version of Eq. (3) is to be considered [29,30,39]. The functions listed in Table I will remain unchanged and only the constants $C$ will be altered in such cases.

An interesting point is that transition from analytical to nonanalytical $W(x)$ goes more smoothly in the time-dependent case compared to the steady-state one. The latter, obviously, does not allow for a limiting transition $\omega_*\to\infty$ in Eq. (7) and an alternative treatment is required for a cusped-shaped potential [1,5]. In the time-dependent case, on the other hand, one deals already with a reduced flux $j_*(t)/I_K$, which tends to unity as $t\to\infty$ for any potential, so that transition to nonanalytic $W(x)$ is not so dramatic. Similarly, for the underdamped case, one does not have to expect that modification of the prefactor in Eq. (25), which is observed for certain exotic barriers [5], will necessarily affect the transient behavior, Eq. (31), at least for the time scales considered.

### C. Nucleation and the possibility of experimental observation

The classical picture of nucleation [2,40] is a random walk of a nucleus along the axis of its sizes due to gain and loss of monomers. The loss and gain kinetic coefficients are related to the minimal work $W(x)$ required to form a nucleus of a given radius $x$ by the detailed balance condition. This work has a form given by Eq. (34). In the simplest case [2] the nucleation problem can be described by a one-dimensional Fokker-Planck equation of type (3), although with an $x$-dependent diffusion coefficient; the probability density is usually replaced by a distribution function $f(x,t)$ of nuclei over their sizes. Apart from different normalization, similarities to the KP are obvious and the activation flux over the barrier determines the ''nucleation rate.''

A technical difference in the nucleation problem comes from the left-hand boundary condition: It is assumed that at the smallest (molecular) size, the distribution $f(x,t)$ is determined by the amount of monomers $f_1$. Generally speaking, the nucleation process is nonlinear due to the $f_1$ dependence of $x_*$ and $W_*$ [41]. However, variation in these parameters can be neglected during an exponentially long time interval, as long as the depletion of monomers by growing nuclei is minor. During that interval, which is much larger than the transient period, there is a strong similarity to the KP. In particular, the (quasi-)steady-state nucleation flux is given by [2]

$$I_n=D_*\omega_*\sqrt{\beta/2\pi}f_{\rm eq}(x_*), \tag{39}$$

in complete analogy with the Kramers expression. In the nucleation normalization the escape probability $P_B(t)$ corresponds to the number of nucleated particles $N(t)$ and is given by an equation that is functionally identical to the first term in Eq. (38) [37].

Another difference in the nucleation and the Kramers problems is that the deterministic rate $v(x)$ in the nucleation case must satisfy the requirement $\int dx/v(x)\to\infty$ for $x\to\infty$ since a nucleus cannot grow to an infinite size during a finite time interval. With a cubic shape of $W(x)$ this is achieved due to an $x$-dependent diffusion coefficient in Eq. (4). A typical dependence is $D(x)\propto x^{-\nu}$, with the power index $\nu\geqslant 1$ determined by the type of mass exchange between the nucleus and the surrounding. Note that $v(x)$ is nonzero at $x=0$.

Finally, a difference from the KP comes from the fact that in the nucleation context one is usually interested in the overcritical flux at $x>x_*$, where all the measurements are performed [42,43]. The solution technique remains basically the same as described in Sec. II, but one has to match the right-hand asymptote of the inner solution (9) with the corresponding outer solution at $x>x_*$. The result [29], formally, is given by the same double-exponential function as for the nonanalytic KP [the first term in Eq. (37)], although with a different $\tau$ and a with size-dependent incubation time $t_i(x)$. The values of $t_i(x)$ for different types of diffusion coefficient $D(x)$ are listed in Ref. [37].

To summarize, the nucleation problems bears strong similarities to the KP with a nonanalytic potential. This is due to rapid decay of small nuclei, which leads to a zero relaxation time $\tau_s$ or, equivalently, to an infinite asymmetry parameter $\alpha$. The nucleation situation also shows that certain care should be taken for stiff potentials $W(x)$, which are often discussed in the KP. It is unphysical for a particle to reach infinity (or to come from infinity) during a finite time interval, in which case one has to be ready for mathematical complications, up to the loss of uniqueness of the solution.

Nucleation provides an example of experimental observation of transient effects in activation decay [42,43]. With all the specifics of nucleation in glasses considered in the afore-

mentioned works, one could mention some general features that might be useful for the KP as well. In the studies in [42,43] the number of nuclei $N$ was much smaller than the number of monomers $f_1$ in the system under investigation, but $N$ was still be large enough in order to be detected. Further, a relatively short intrusion into the region of low $W_*$ was performed through temporal lowering of temperature, while the nuclei where actually counted at a later stage when nucleation became impossible. In terms of the KP, observation of the transient behavior would require the detection of small escape probabilities $P_B(t) \ll 1$. Using the nucleation analogy, one can imagine the following situation: A large number of molecules $f_1$ enters the reaction, but one is able to detect already individual (or minor amounts of) product molecules. In cases where $f_1$ is larger than the Kramers exponential $\exp(\beta W_*)$ (say $f_1$ is of the order of the Avogadro number) transient effects may have direct experimental implications. More specifically, a short pulse that temporarily reduces the metastable barrier could provide the required conditions (corresponding techniques are developed in connection with femptochemistry; see, e.g., Ref. [44]). The duration of the pulse must be much smaller than $\tau \exp(\beta W_*)$ in order to observe transient effects, but the latter condition can be quite realistic.

## V. CONCLUSION

We considered transient escape of a Brownian particle from a one-dimensional metastable well described by a potential $W(x)$ in the overdamped and underdamped limits. The term ''transient'' implies time scales that exceed the largest relaxation or increment time $\tau$ near the equilibrium points but are smaller than the Kramers time $1/I_K$. During the time scale considered, the flux that starts from negligibly small values at small $t$ achieves the (quasi-)steady-state value $I_K$ (see Fig. 1).

The main results are given by Eqs. (17) and (31) for the overdamped and underdamped cases, respectively. In the weak noise limit considered, these results turned out to be practically insensitive to the details of the potential $W(x)$. In the overdamped case the potential affects the shape of the transient curve only through a single parameter $\alpha$, which describes the asymmetry between the relaxation and the increment times. In the underdamped situation the shape of the transient curve is completely insensitive to $W(x)$.

Experimentally, results can be of importance for large systems with the number of molecules taking part in the reaction comparable to $\exp(\beta W_*)$ if one is able to detect even minor amounts of the product molecules. Similarities between the Kramers and the nucleation problems where transient effects have been studied experimentally in great detail [42,43] can be very useful in establishing limitations for each specific system under consideration.

## APPENDIX: THE GREEN'S FUNCTION OF THE UNDERDAMPED PROBLEM NEAR $J=0$

Let us define the Green's function of Eq. (21) for small values of the outer variable $J$ (or for arbitrary values of the inner variable $z=J\beta\omega_s$) in such a way that

$$w(z,t)=\int_0^\infty dy\ G(z,t;y)w(y,0). \tag{A1}$$

It is known that for a harmonic potential a two-dimensional Fokker-Planck analog of Eq. (1) can be solved exactly. In principle, the exact solution would allow one to calculate $G(x,t;y)$ directly. This might be useful when arbitrary damping is considered. For the present, more modest purposes, it is sufficient and more instructive to evaluate the Green's function from the already obtained Laplace transform. Expressing the Kummer functions $M(p,1,z)$ and $U(p,1,y)$ in Eq. (27) through the Whittaker functions $M_{p-1/2,0}(-z)$ and $W_{1/2-p,0}(y)$, respectively [35], and using standard tables of Laplace transformations [45], one ends up with

$$G(z,t;y)=\frac{1}{1-e^{-t}}\exp\left\{\frac{y+z}{2}\left(1-\coth\frac{t}{2}\right)\right\}I_0\left(\frac{\sqrt{yz}}{\sinh(t/2)}\right). \tag{A2}$$

Here $I_0$ is the modified Bessel function and to simplify notations we set $\tau=1$.

One can consider an asymptote of Eq. (A2) for $z,t\to\infty$ with $ze^{-t}\sim$const and $y\to 0$ (the latter corresponds to a localized initial condition). This gives $G\sim\exp(-ze^{-t})$, which with a size-dependent incubation time $t_i=\ln z$ is the same type of dependence as described by Eq. (31).


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