

Diffusion in a Bistable Potential: The Functional Integral Approach¹

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We study, with the help of the Onsager–Machlup functional integral approach, the distribution P of a single stochastic variable, the evolution of which is described by a Fokker–Planck equation with a first moment deriving from a bistable potential. We set up the approximation scheme appropriate, in this approach, to the limit of constant and small diffusion coefficient. Two regimes are to be distinguished: Very long times (Kramers regime) are treated within the frame of a free-instanton–molecule gas approximation, and at intermediate times (Suzuki regime) a standard semiclassical calculation is legitimate. We thus rederive exactly the results obtained from the mode expansion and WKB method.

KEY WORDS: Path integral; instanton; nonlinear Fokker–Planck equation; instability; diffusion.

1. INTRODUCTION

Diffusion in bistable systems has attracted considerable attention in the past few years, in connection with the growing interest about dissipative structures and self-organization. Much work has been done, in particular, about diffusion in bistable macrosystems described by a single one-dimensional stochastic variable, physical examples of which are provided by, e.g., the one-mode laser⁽¹⁾ or one-dimensional motion of a Brownian particle in the high-friction limit.⁽²⁾ The dynamical behavior of such one-variable systems has been completely analyzed in the limit of small diffusion coefficient, where the dynamics of both metastability^(2–5) and

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instability^(5,6) are now understood. This small diffusion coefficient analysis has been extended to multivariable systems for which the drift force derives from a potential such that the two points of locally stable equilibrium are connected by a narrow valley.⁽⁷⁾ However, to our knowledge, there exists no such general treatment for multivariable systems in which the drift force does not derive from a potential, i.e., open systems which may exhibit dissipative structures. Another very important class is that of bistable systems described by fields, i.e., having a quasi-infinite number of degrees of freedom (e.g., magnetic systems, nonhomogenized reacting chemical systems, alloys presenting spinodal decomposition . . .). Much progress has been made recently^(8,9) towards understanding their dynamics of instability, but many questions about fluctuation effects still remain open.

These diffusion problems are usually formulated in terms of Fokker-Planck equations (or of the equivalent Langevin equations). As is well known, a probability distribution satisfying a Fokker-Planck equation can be equivalently expressed, with the help of the generalized Onsager-Machlup formalism, as a path integral. This parallels the equivalent Schrödinger and Feynman formalisms for quantum mechanical systems, for which the functional integral approach has proved very useful to treat systems with many degrees of freedom, in particular field problems and critical fluctuations. One can therefore hope, analogously, that the Onsager-Machlup formalism will provide a useful tool to study diffusion in multivariable systems.

Surprisingly, if the formalism itself has been established in detail, it has not received much practical application. Our aim in this paper is to establish a well-defined approximate treatment of the Onsager-Machlup path integral providing a coherent and explicit description of relaxation towards equilibrium in a bistable system.

As is known from what has been done in field theory about instanton effects^(10,11) and perturbation developments at large orders,^(12,13) bistability gives rise, in the functional integral approach, to specific mathematical difficulties which can best be clarified by first treating the problem in a case which has already been solved by the Fokker-Planck equation approach. We choose here the one-variable bistable case, in the small- θ limit (where θ is the diffusion coefficient) which has already received a complete WKB treatment.⁽⁵⁾

We shall not derive here any new result, but will rederive the solution of this problem, and, thus, will establish the prescriptions to be used in path integral calculations appropriate to more complex systems.

Our derivation makes extensive use of the methods first introduced by Langer,⁽⁹⁾ and developed in the context of the instanton problem by field theorists,^(10,13) the principle of which we will recall briefly in Section 2.

2. THE PATH INTEGRAL IN THE SMALL-DIFFUSION-COEFFICIENT LIMIT

We want to calculate the long-time behavior of the probability distribution $P(x_1 t | x_i, t_i)$ of the stochastic variable x_1 , the evolution of which is described by the Fokker–Planck equation:

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x_1} [U'(x_1)P] + \theta \frac{\partial^2 P}{\partial x_1^2} \quad (1)$$

with the initial value at $t = t_i$

$$P(x_1, t = t_i | x_i, t_i) = \delta(x_1 - x_i) \quad (2)$$

$U'(x) = dU/dx$ is a nonlinear function of x . More precisely, we will specialize to the case where U' derives from a bistable “potential” $U(x)$ (Fig. 1). θ is assumed to be constant and small: $\theta \ll \Delta U$, where ΔU is the height of the bump separating the wells of U .

The solution of Eqs. (1) and (2) can be written⁽¹⁴⁾ as

$$P(x_1, t | x_i, t_i) = \int_{x_i}^{x_1} \mathcal{D}x(\tau) \exp \left[-\frac{1}{\theta} \int_{t_i}^t d\tau O(\dot{x}(\tau), x(\tau)) \right] \quad (3)$$

where the path integral sums the contributions of all trajectories $x(\tau)$ satisfying the boundary conditions

$$x(t_i) = x_i, \quad x(t) = x_1 \quad (4)$$

and the integration measure is $(4\pi\theta\Delta t)^{-1/2}$. O is the Onsager–Machlup functional:

$$O(\dot{x}, x) = \frac{\dot{x}^2}{4} + V(x) + \frac{\dot{x}}{2} U'(x) \quad (5)$$

and the “effective” potential is

$$V(x) = \frac{[U'(x)]^2}{4} - \frac{\theta}{2} U''(x) \quad (6)$$

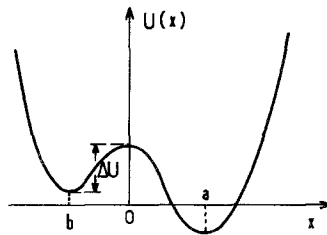


Fig. 1. A bistable potential $U(x)$.

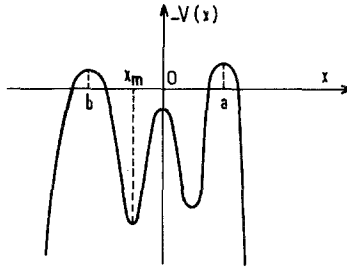


Fig. 2. The potential $(-V(x))$ associated with $U(x)$.

Noticing that $\dot{x}U'(x) = dU/d\tau$, one can immediately rewrite

$$P(x_1, t | x_i, t_i) = \exp \left[- \frac{U(x_1) - U(x_i)}{2\theta} \right] K(x_1, t | x_i, t_i) \quad (7a)$$

$$K(x_1, t | x_i, t_i) = \int_{x_i}^{x_1} \mathcal{D}x(\tau) \exp \left[- \frac{1}{\theta} \int_{t_i}^t d\tau L(\dot{x}, x) \right] \quad (7b)$$

$$L(\dot{x}, x) = \frac{\dot{x}^2}{4} + V(x) \quad (7c)$$

That is, L can be considered as the Lagrangian of a particle of mass $1/2$ in the potential $-V(x)$, represented in Fig. 2.

Expressions (7b, c) are similar to Feynman's expression of the propagator for motion in the potential $-V$,⁽¹⁵⁾ θ being here the analog of \hbar in the quantum mechanical problem.

We want to study the small- θ case, i.e., the equivalent of the semiclassical limit. In that limit, the main contribution to the path integral (7b) comes from trajectories close to the classical one, $x_{cl}(\tau)$, which extremalizes the action $S = \int_{t_i}^t L d\tau$, and is defined by the classical equation of motion

$$\begin{aligned} \ddot{x}_{cl/2} &= \left. \frac{dV}{dx} \right|_{x=x_{cl}} \\ x_{cl}(t_i) &= x_i, \quad x_{cl}(t) = x_1 \end{aligned} \quad (8)$$

We develop the action around this trajectory, retaining only variations up to second order in $y(\tau) = x(\tau) - x_{cl}(\tau)$. This gives

$$\begin{aligned} K(x_1, t | x_i, t_i) &\cong \exp \left[- \frac{1}{\theta} S_{cl}(x_1, t | x_i, t_i) \right] \\ &\times \int_{y(t_i)=0}^{y(t)=0} \mathcal{D}y(\tau) \exp \left\{ - \frac{1}{\theta} \int_{t_i}^t d\tau \right. \\ &\quad \left. \times \left[\frac{\dot{y}^2(\tau)}{4} + \frac{y^2(\tau)}{2} V''(x_{cl}(\tau)) \right] \right\} \quad (9) \end{aligned}$$

The fluctuation contribution δS to the action can be rewritten

$$\delta S = \frac{1}{2} \int_{t_i}^t d\tau y(\tau) \left[-\frac{1}{2} \frac{d^2}{d\tau^2} + V''(x_{cl}(\tau)) \right] y(\tau) \quad (10)$$

Following, for example, Coleman,⁽¹⁰⁾ we expand $y(\tau)$ on the appropriate normalized eigenmodes $y_n(\tau)$ of the fluctuation operator:

$$y(\tau) = x(\tau) - x_{cl}(\tau) = \sum_n c_n y_n(\tau) \quad (11a)$$

$$\left[-\frac{1}{2} \frac{d^2}{d\tau^2} + V''(x_{cl}(\tau)) \right] y_n = \lambda_n y_n \quad (11b)$$

$$y_n(t_i) = y_n(t) = 0, \quad \int_{t_i}^t y_n(\tau) y_m(\tau) d\tau = \delta_{nm} \quad (11c)$$

This gives⁴

$$K(x_1, t | x_i, t_i) \cong N \left(\prod_n \lambda_n \right)^{-1/2} \exp \left[-\frac{1}{\theta} S_{cl}(x_1 t | x_i t_i) \right] \quad (12)$$

where N is a constant, to be determined at the end of the calculation, either by fitting with the well-known solution for the harmonic problem,⁽¹⁵⁾ or with the help of the normalization condition on P .

Coleman has shown that Eq. (12) can be rewritten as

$$K(x_1, t | x_i, t_i) \cong [4\pi\theta\psi(t)]^{-1/2} \exp \left(-\frac{1}{\theta} S_{cl} \right) \quad (13)$$

where $\psi(\tau)$ is the solution of

$$-\frac{1}{2} \frac{d^2\psi}{d\tau^2} + V''(x_{cl}(\tau))\psi = 0 \quad (14)$$

such that

$$\psi(t_i) = 0, \quad d\psi/d\tau|_{t=t_i} = 1 \quad (15)$$

Clearly, the condition for expression (13) to be valid is that the range of important values of the c_n 's, $\Delta c_n \sim (\theta/\lambda_n)^{1/2}$, be small enough for $\delta x(\tau)$ to be small compared with the range of space variations of potential V . This is realized, for $S_{cl} \gg \theta$, provided that all eigenvalues λ_n remain finite.

For monostable potentials, this is the case. However, a problem arises in the case of bistable potentials V with degenerate (or, as we shall see later, quasidegenerate) minima. Let us consider such a potential (Fig. 3), with the maxima of $(-V)$ at $x = \pm a$ and $V(\pm a) = 0$, and concentrate for instance

⁴ This expression is completely equivalent to the standard Van Vleck one⁽¹⁶⁾:

$$K(x_1, t | x_i, t_i) = \frac{1}{(2\pi\theta)^{1/2}} \left[-\frac{\partial^2 S_{cl}(x_1 t | x_i t_i)}{\partial x_i \partial x_1} \right]^{1/2} \exp \left(-\frac{1}{\theta} S_{cl} \right)$$

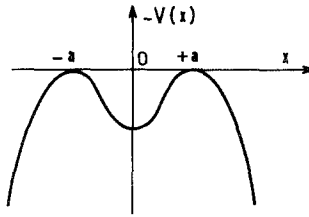


Fig. 3. A symmetric degenerate bistable ($-V$) potential.

on $P(a, t/2 | -a, -t/2)$ in the limit of very large t . For simplicity, we assume for the moment V to be symmetric around $x = 0$.

One easily checks that the classical trajectory connecting $(-a, -t/2)$ and $(a, t/2)$ has the shape shown on Fig. 4: it corresponds to an exponentially small energy ($E = \dot{x}^2/4 - V \simeq 2V_a'' a^2 \exp[-t(2V_a'')^{1/2}]$); it spends a finite time Δt in the region $x \simeq 0$, and a quasiinfinite time $(t - \Delta t)/2$ in each of the harmonic regions close to $(-a)$ and (a) , where it has an exponentially small velocity.

Such a trajectory $x_I(\tau)$ is usually referred to as an instanton (a soliton in the time variable) or a pseudoparticle.

Since the classical equation of motion (8) is invariant under time translation, $x_I(\tau - t_1)$ is a solution of this equation for all values of t_1 . Moreover, as long as $t/2 - |t_1| \gg \Delta t$, for $\tau = \pm t/2$, $x_I(\tau - t_1)$ still satisfies the same boundary conditions as the classical solution $x_I(\tau)$, up to an exponentially small error ($\sim \exp[-t(2V_a'')^{1/2}]$). This entails that there is a quasidegeneracy of the action for this family of solutions—called translated instantons. This means that the quadratic development around the classical trajectory [Eq. (9)] becomes questionable at very long times for such a bistable potential.

Mathematically, this is seen when one notices that $\dot{x}_{cl}(\tau)$ is always a solution of Eq. (11b) with eigenvalue zero. In the situation corresponding to

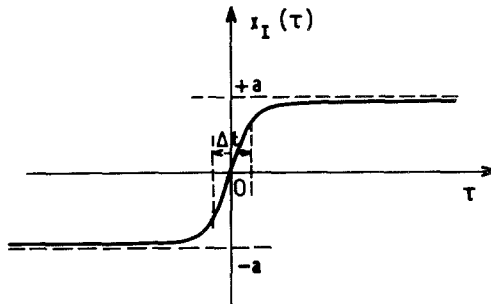


Fig. 4. The instanton trajectory associated with the potential of Fig. 3.

Figs. 3 and 4, $x_{\text{cl}}(\pm t/2)$ is exponentially small, so that $\dot{x}_{\text{cl}}(\tau)$ almost satisfies the boundary conditions (11c) and it is clear that, by continuity, in this case, the smallest eigenvalue λ_0 of the fluctuation equation is exponentially small, the range of important values of the corresponding c_0 becomes accordingly large, and the Gaussian approximation breaks down for this particular fluctuation mode, which must therefore be treated separately from the others, by means of explicit integration on the position t_1 of the instanton center. Coleman shows that $K(a, t/2 | -a, -t/2)$ can then be written (up to terms of order $\Delta t/t$)

$$K(a, t/2 | -a, -t/2) = \left[\frac{\lambda_0(t)}{4\pi\theta\psi(t/2)} \right]^{1/2} \int_{-t/2}^{t/2} dt_1 \left\{ \frac{S[x_I(\tau - t_1)]}{4\pi\theta} \right\}^{1/2} \times \exp \left\{ -\frac{1}{\theta} S[x_I(\tau - t_1)] \right\} \quad (16)$$

Up to exponentially small terms, $S[x_I(\tau - t_1)] = \lim_{t \rightarrow \infty} S[x_I(\tau)] = S_0$, and

$$K(a, t/2 | -a, -t/2) = \left[\frac{\lambda_0(t)}{4\pi\theta\psi(t/2)} \right]^{1/2} \left(\frac{S_0}{4\pi\theta} \right)^{1/2} t e^{-S_0/\theta} \quad (17)$$

So, the instanton degeneracy introduces a contribution to K linear in t .

One notices, moreover, that $x_I(-\tau)$, called ‘‘anti-instanton,’’ is the classical trajectory for propagation between $(a, -t/2)$ and $(-a, t/2)$, and that it is quasidegenerate with its time-translated associates $x_I(-\tau + t/2)$. It is then clear that any trajectory $(-a, -t/2; a, t/2)$ made of a succession of any number $(2n + 1)$ of instantons and antiinstantons is also quasidegenerate with $x_I(\tau)$ (neglecting, again, terms of order $\Delta t/t$), and that the contributions of all such paths must be added to (17), giving rise to a power series in t , which resumes simply into an exponential.^(10,11) This, in the equivalent quantum mechanical problem, amounts to calculating the splitting of the degenerate lower levels of the separate minima of V induced by the tunneling coupling.

We shall not enter into further details about the solution for a degenerate bistable V since, in the present problem, although we deal with a bistable (in general nonsymmetric) physical potential U , Eqs. (6) and (7) show that we must solve the path integral problem in the effective potential $V(x)$ of Fig. 2, which has three nondegenerate minima.

3. VERY-LONG-TIME BEHAVIOR OF THE DISTRIBUTION: KRAMERS REGIME

Consider the effective potential $-V$ associated with our diffusion problem (Fig. 2). As in the WKB treatment of Ref. 5, in order to be

consistent with our approximation (which will calculate the small- θ development of the action up to terms of order $\log \theta$) we only need to know the characteristic parameters of V at its minima (position of the minima, values of V and of its curvatures) to lowest order in θ . For small θ , $-V$ has three maxima at $x = b, 0, a$, of respective heights $\theta U_i''/2$ ($i = b, 0, a$), with U_a'' and $U_b'' > 0$, $U_0'' < 0$. So, even if U is symmetric, the 0 maximum of $-V$ is not degenerate with the a and b ones.

We are interested here in the behavior of P at very long times, when local relaxation in each well of U separately is already completed, and when its evolution simply corresponds to an exchange of populations between the two wells. This happens on the scale of Kramers time^(2,5) $\tau_K \propto \exp(\Delta U/\theta)$, and the corresponding regime is known to be controlled by the tunneling coupling between the wells of U .

This means that, in the path integral (7), trajectories connecting the various maxima of $-V$ will have an important weight.

Let us for example concentrate on the path integral expression of

$$P(b, t | b, 0) = P\left(b, \frac{t}{2} | b, -\frac{t}{2}\right) = K\left(b, \frac{t}{2} | b, -\frac{t}{2}\right) \quad (18)$$

in the small- θ limit, and in the case where $U_b'' > U_a''$. Following the semiclassical method [Eqs. (7)–(9)], we are led to look for the classical trajectory in potential $-V$ connecting $(b, -t/2)$ and $(b, t/2)$: this trajectory is given by the trivial solution $x_{cl}(\tau) = b$. The corresponding contribution $K^{(0)}$ to $K(b, t/2 | b, -t/2)$ can be calculated by replacing V by its local harmonic approximation, valid for $x \simeq b$, and is therefore⁽¹⁵⁾

$$K^{(0)}\left(b, \frac{t}{2} | b, -\frac{t}{2}\right) = \left(\frac{U_b''}{2\pi\theta}\right)^{1/2} [1 - \exp(-2U_b''t)]^{-1/2} \quad (19)$$

which, in the long time limit ($t \gg U_b''^{-1}$) reduces to

$$K^{(0)}\left(b, \frac{t}{2} | b, -\frac{t}{2}\right) \cong \left(\frac{U_b''}{2\pi\theta}\right)^{1/2} \quad (20)$$

Since $-V(b)$ is the absolute maximum of $-V$, no classical trajectory connecting b to itself with one or more turning points is allowed. However, $V(0) - V(b)$ and $V(a) - V(b)$ are very small quantities, of order θ , which leads us to suspect that, in analogy to the instanton problem of Section 2, trajectories going from b to b via the 0 or a region are important, even though they are not exact classical paths.

We must therefore adapt and extend the dilute instanton gas theory to this more complicated problem; for the sake of clarity, we will first describe the method of approximation—which follows closely a technique developed by Brézin, Parisi, and Zinn-Justin⁽¹³⁾—on the case where $-V$ only has two quasidegenerate maxima at $x = b, 0$ [with $V(0) - V(b) = 0(\theta)$].

3.1. Instanton–Anti-instanton Pair in the Quasidegenerate Case

Consider the potential represented in Fig. 5, for which we want to calculate the contribution $K^{(1)}(b, t/2 | b, -t/2)$ due to trajectories of the type $b \rightarrow (0)$ region $\rightarrow b$. Following Ref. 13, we define a zero-order potential $V^{(0)}$ (see Fig. 5)

$$V^{(0)}(x) = V(x) - \delta V(x) \quad (21a)$$

$$\begin{aligned} \delta V(x) &= 0, & x < x_m \\ &= V_0 - V_b, & x > x_m \end{aligned} \quad (21b)$$

The precise shape of δV is in fact irrelevant, provided that it satisfies $V^{(0)}(0) = V^{(0)}(b)$, and $\delta V = 0(\theta)$. We choose for x_m the position of the minimum of $-V$. However, it can be shown that our results are independent of its precise location in that region.

We define as $x_I(\tau - t_0)$ the family of classical trajectories, in the potential $-V^{(0)}$, which leave $x = b$ at time $(-\infty)$ and reach $x = 0$ at time $(+\infty)$. Note that, since they correspond to the limit $t \rightarrow \infty$, they are all exact solutions of the classical equation of motion with the same energy $E = -V_b$ and the same classical action S_{b0} .

We now define the instanton–anti-instanton pair family of trajectories by

$$x_{IA}(\tau, t_0, t_1) = \begin{cases} x_I(\tau - t_0), & \tau < \frac{1}{2}(t_0 + t_1) \\ x_I(t_1 - \tau), & \tau > \frac{1}{2}(t_0 + t_1) \end{cases} \quad (22)$$

Such a trajectory is shown in Fig. 6. Then, as in the degenerate case, we develop the action in Eq. (7b) around $x_{IA}(\tau, t_0, t_1)$ up to second order in the fluctuation amplitude $\delta x(\tau)$.

The zeroth-order term is

$$\begin{aligned} S_{IA}(t, t_0, t_1) &\cong (V_0 - V_b)(t_1 - t_0) + V_b t + 2S_{b0} \\ &\quad - 2 \int_{(t_1+t_0)/2}^{\infty} d\tau \frac{[\dot{x}_I(\tau - b_0)]^2}{2} \end{aligned} \quad (23)$$

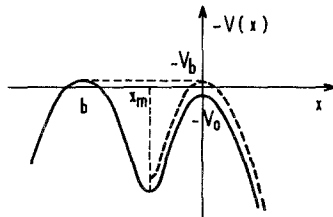


Fig. 5. A quasidegenerate potential $(-V(x))$ (full line) and the associated zeroth-order degenerate potential $(-V^{(0)}(x))$ (dashed line). $V_0 - V_b$.

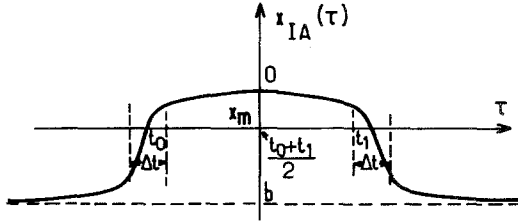


Fig. 6. An instanton antiinstanton pair trajectory in the potential $(-V^{(0)}(x))$ of Fig. 5.

where

$$S_{b0} = \int_b^0 dx [V^{(0)}(x) - V_b]^{1/2} \quad (24)$$

In Eq. (23) we neglect the correction to S_{b0} due to the fact that t is large, but finite: this term, which describes “edge” effects (i.e., situations where the instanton or anti-instanton comes close to the edges of the time interval) are of order $\Delta t/t$, and negligible in the long time limit.⁽¹⁰⁾ As we shall see later, the important trajectories correspond to $t_1 - t_0 \gg \Delta t$. Then, using for $\dot{x}_I(\tau)$ the large time asymptotic expansion derived in Appendix B, one finds

$$S_{IA}(t, t_0, t_1) = (V_0 - V_b)(t_1 - t_0) + V_b t + 2S_{b0} - \frac{x_m^2 (V_0'')^{1/2}}{\sqrt{2}} \exp[(2V_0'')^{1/2}(2\Delta_{m0} - t_1 + t_0)] \quad (25)$$

where $V_0'' = d^2V/dx^2|_{x=0}$, and

$$\Delta_{m0} = \frac{1}{2} \int_{x_m}^0 dx \left\{ \frac{1}{[V^{(0)}(x) - V_b]^{1/2}} - \frac{1}{[V_h^{(0)}(x) - V_b]^{1/2}} \right\} \quad (26)$$

$V_h^{(0)}$ is the local harmonic approximation to $V^{(0)}$:

$$V_h^{(0)}(x) = \begin{cases} V_b + \frac{V_0''}{2} x^2, & x > x_m \\ V_b + \frac{V_b''}{2} (x - b)^2, & x < x_m \end{cases} \quad (27)$$

Since $x_{IA}(\tau, t_0, t_1)$ is not an exact classical solution in potential V , the development of the action around it contains, besides the term $\delta S^{(2)}$ quadratic in $\delta x(\tau)$ [Eq. (9)], a linear contribution $\delta S^{(1)}$ proportional to δV .

In the spirit of the method described in Section 2, the path integral is then rewritten as an integral on the amplitudes ξ_n of the eigenmodes of the fluctuation equation—except for the two lowest ones: these correspond to

the modes of translation of t_0 and t_1 , i.e., to the global translation of x_{IA} and to a “breathing” mode (variation of $t_1 - t_0$). These modes, which correspond to very slow variations of the action, have large amplitude, and are thus taken into account by explicit integration on t_0 and t_1 .

It is shown in Appendix A that (i) because $V_0 - V_b = 0(\theta)$, $\delta S^{(1)}$ is negligible, and (ii) for the large values of $t_1 - t_0$ of interest (a) up to exponentially small factors, the integration measure for the variables t_0, t_1 is simply $S_{b0}/2\pi\theta$, and (b) the contribution to the path integral of the small fluctuations around x_{IA} is (up to a normalization constant) the product of the fluctuation terms around the instanton and anti-instanton separately.

Using these results, one may rewrite

$$K^{(1)}\left(b, \frac{t}{2} \mid b, -\frac{t}{2}\right) = \int_{-t/2}^{t/2} dt_0 \int_{t_0}^{t/2} dt_1 \frac{S_{b0}}{2\pi\theta} \left(\frac{\lambda_0}{4\pi\theta\psi} \right)_I^{1/2} \left(\frac{\lambda_0}{4\pi\theta\psi} \right)_A^{1/2} \times \left[\frac{2\pi\theta}{(2V_0'')^{1/2}} \right]^{1/2} \exp\left[-\frac{1}{\theta} S_{IA}(t, t_0, t_1)\right] \quad (28)$$

$(\lambda_0)_I$ [respectively, $(\lambda_0)_A$] is the lowest eigenvalue of the fluctuation equation (11b, c) for $x_{cl}(\tau) \equiv x_I(\tau - t_0)$ [respectively, $x_I(t_1 - \tau)$] on the time interval $(-t/2, (t_0 + t_1)/2)$ [respectively, $((t_0 + t_1)/2, t/2)$]. ψ_I (respectively, ψ_A) is the value at $\tau = (t_0 + t_1)/2$ (respectively, $\tau = t/2$) of the corresponding solution of Eqs. (14) and (15), with $t_i = -t/2$ [respectively, $(t_0 + t_1)/2$].

These quantities are calculated in Appendix B. Then, with the help of Eq. (25), one obtains

$$K^{(1)}\left(b, \frac{t}{2} \mid b, -\frac{t}{2}\right) = \left[\frac{2\pi\theta}{(2V_0'')^{1/2}} \right]^{1/2} \frac{(x_m - b)|x_m|V_0''V_b''}{2\pi^2\theta^2} \exp[-\epsilon_0^{(b)}t/\theta] \times \exp\left[-\frac{2S_{b0}}{\theta} + \Delta_{bm}(2V_b'')^{1/2} + \Delta_{m0}(2V_0'')^{1/2}\right] \times \int_{-t/2}^{t/2} dt_0 \int_{t_0}^{t/2} dt_1 \exp\left\{-\frac{\epsilon_0^{(0)} - \epsilon_0^{(b)}}{\theta}(t_1 - t_0) + \frac{C}{\theta} \exp[-(2V_0'')^{1/2}(t_1 - t_0)]\right\} \quad (29)$$

where

$$\epsilon_0^{(i)} = V_i + \theta(V_i''/2)^{1/2} \quad (30)$$

is precisely the lowest eigenvalue of the Schrödinger equation associated with the diffusion equation (1),⁽⁵⁾ in the local harmonic approximation to

potential V in well (i), and

$$C = x_m^2 \left(\frac{V_0''}{2} \right)^{1/2} \exp[2(2V_0'')^{1/2} \Delta_{m0}] \quad (31)$$

and

$$\Delta_{ij} = \frac{1}{2} \int_{x_i}^{x_j} dx \left\{ \frac{1}{[V^{(0)}(x) - V_b]^{1/2}} - \frac{1}{[V_h^{(0)}(x) - V_b]^{1/2}} \right\} \quad (32)$$

At this point, it is necessary to consider more closely the variation of the integrand in expression (29) with the separation $(t_1 - t_0)$ between the instanton and the anti-instanton. Since the constant C is positive, the important region in the t_1 integration corresponds to $(t_1 - t_0) \ll 1/(2V_0'')^{1/2} \sim \Delta t$, where the integrand is of order $\exp(C/\theta)$. That is, the most important configurations would be those where the instanton and the anti-instanton are very close to each other. This is clearly unphysical: such trajectories are very far from a quasisolution of the classical equation of motion, they must therefore have a negligible weight in the large time limit. As we will now see, this deficiency must be cured by extending the integration contour for variable $(t_1 - t_0)$ into the complex plane.⁽¹⁷⁾ It should be pointed out that this same problem arises in the perturbation expansion at large orders for quasidegenerate bistable potentials,⁽¹³⁾ in which case it results in a nontrivial choice of the integration contour in the space of the coupling constant.

In order to discuss the prescription to be used in the evaluation of (29) and its physical meaning, we shall now come back to our specific problem, where V is given by Eq. (6). Equation (29) then gives the contribution to K of trajectories going from b to b with only one excursion into the (0) region.

3.2. Evaluation of $K^{(1)}(b, t/2 | b, -t/2)$

We now have $V_{b,0} = -(\theta U_{b,0}'')/2$ and $V_i'' = U_i''/2$. The calculation of S_{b0} is sketched briefly in Appendix C, and one gets

$$S_{b0} = \frac{U_0 - U_b}{2} + \frac{\theta}{2} \log \left| \frac{U_b''(x_m - b)}{U_0'' x_m} \right| + \frac{\theta}{2} (U_b'' \Delta_{bm} + U_0'' \Delta_{m0}) \quad (33)$$

Equation (29) then reads

$$K^{(1)}\left(b, \frac{t}{2} | b, -\frac{t}{2}\right) = \frac{U_b'' |U_0''| x_m^2}{2} \left(\frac{|U_0''|}{2\pi\theta} \right)^{3/2} I(t) \\ \times \exp\left(-\frac{U_0 - U_b}{\theta} + 2\Delta_{m0} |U_0''|\right) \quad (34a)$$

$$I(t) = \int_{-t/2}^{t/2} dt_0 \int_{(c)} dz \exp\left[-|U_0''|z + \frac{C}{\theta} \exp(-|U_0''|z)\right] \quad (34b)$$

In the absence of a general theory of analytic continuation for functional integrals, it is not possible to provide a direct complete mathematical proof of the prescription to be used to define the proper integration path (C) in the plane of the complex variable $z = (t_1 - t_0)$. As is usually done in such situations, we derive this prescription on the basis of a physically plausible argument, and will show that it is indeed correct by proving that the distribution P thus obtained reproduces the correct Kramers behavior derived in Ref. 5 with the help of the mode decomposition and of the WKB method. One thus finds that (C) must be defined as

$$\text{Im } z = \pi/|U_0''|, \quad 0 \leq \text{Re } z \leq t/2 - t_0 \quad (35)$$

Intuitively, one can interpret this result in the following way: as long as τ remains real, $x_{IA}(\tau, t_0, t_1)$ is not a solution of the classical equation of motion; this appears, in the absence of a real turning point in the (0) region, as an exponentially small, but finite, discontinuity of \dot{x}_{IA} in the vicinity of $x = 0$. On the contrary, if one allows τ to become complex, $x_{IA}(\tau, t_0, t_1)$ can be considered as a classical trajectory with a continuous velocity even in the vicinity of $x = 0$.⁽¹⁸⁾ This trajectory is real and identical to x_{IA} until time $(t_0 + t_1)/2$, where τ starts moving along the imaginary axis. It then reaches an imaginary turning point where it reverses its velocity. It is found that $i\pi/|U_0''|$ is precisely the "time" necessary for the extended trajectory to come back to $\{\text{Re } x = x_{IA}((t_0 + t_1)/2); \text{Im } x = 0\}$, from where it can proceed along the real x axis according to Fig. 6 (with $\text{Im } \tau = \text{Im } t_1 = \pi/|U_0''|$). It can then be treated on the same footing as any classical trajectory in a path integral calculation.

With the above prescription, (34) reduces (up to exponentially small corrections⁵) to

$$K^{(1)}\left(b, \frac{t}{2} | b, -\frac{t}{2}\right) = -t \left(\frac{U_b''}{2\pi\theta}\right)^{1/2} \frac{(|U_0''| U_b'')^{1/2}}{2\pi} \exp\left(-\frac{U_0 - U_b}{\theta}\right) \quad (36)$$

The minus sign appearing in this expression is related with the presence of a turning point on the trajectory. The appearance of such factors associated with turning points is well known in path integral calculations.⁽¹⁹⁾ In fact, this (-1) factor can be traced back to the term $\exp(-|U_0''|z)$ in (34) and, from there, to the fluctuation term $(\lambda_0/\psi)_I^{1/2} \times (\lambda_0/\psi)_A^{1/2}$ [Eq. (28)]. As is well known (see Appendix A and Ref. 17), each factor $(\lambda_0/\psi)^{1/2}$ is proportional to $[\dot{x}(t_i)\dot{x}(t_f)]^{1/2}$, where $\dot{x}(t_i)$, $\dot{x}(t_f)$ are the velocities at the end points of the classical trajectory with which ψ is associated. On x_I , \dot{x} is positive, i.e., $\arg \dot{x} = 0$, $(\lambda_0/\psi)_I^{1/2} > 0$. By continuity, on the anti-instanton

⁵ These corrections are of order $\exp(-t/t_S)$, where Suzuki's time t_S is given by⁽⁶⁾ $t_S = |U_0''|^{-1} \log(2b^2|U_0''|/\theta)$. They are negligible in Kramers regime where $t \sim \tau_K \gg t_S$.

part of the path, $\arg \dot{x} = \pi$, so that $(\lambda_0/\psi)_A^{1/2} = -|(\lambda_0/\psi)_A^{1/2}|$. So, it is seen that, in order to be absolutely correct, one must rewrite equation (34b) as

$$I(t) = - \int_{-t/2}^{t/2} dt_0 \int_{\mathcal{C}} dz \exp \left[-|U_0''| \operatorname{Re} z + \frac{C}{\theta} \exp(-|U_0''|z) \right] \quad (37)$$

where, again, the minus sign results from the velocity reversal.

Finally, coming back to Eq. (36), it should be noted that $K^{(1)}(b, t/2|b, -t/2)$ is proportional to t and that, consequently, the $(b0b)$ instanton-anti-instanton pair behaves like a standard *single composite pseudoparticle* [see Eq. (17)]. The calculation of the contribution to $P(b, t/2|b, -t/2)$ of any number of such $(b0b)$ "pseudomolecules" can then proceed in complete analogy with the dilute instanton gas theory.

Besides these contributions, we must of course consider trajectories which explore, not only the (0) region, but also the (a) well.

3.3. Calculation of $K_{ba}^{(2)}(b, t/2|b, -t/2)$.

$K_{ba}^{(2)}$ is defined as the contribution to K of trajectories of the type $(b) \rightarrow (0) \rightarrow (a) \rightarrow (0) \rightarrow (b)$, which therefore explore region (a) only once.

We extend the definition of the zeroth-order potential $V^{(0)} = V - \delta V$ into the (a) region, by

$$\delta V(x) = \begin{cases} 0, & x < x_m \\ V_0 - V_b, & x_m < x < x_p \\ V_a - V_b, & x > x_p \end{cases} \quad (38)$$

where x_p is a point in the region of the right-hand minimum of $(-V)$, to be defined more precisely later.

We then define the $(0a)$ instanton family of paths, $\tilde{x}_I(\tau - t_1)$, as the classical trajectories in potential $(-V^{(0)})$, centered at $x = x_p$, which leave $x = 0$ at time $(-\infty)$ and reach $x = a$ at time $(+\infty)$.

We consider the 4-pseudoparticle family (see Fig. 7)

$$x_{IIAA}(\tau, t_0, t_1, t_2, t_3) = \begin{cases} x_I(\tau - t_0), & \tau < \frac{1}{2}(t_0 + t_1) \\ \tilde{x}_I(\tau - t_1), & \frac{t_0 + t_1}{2} < \tau < \frac{t_1 + t_2}{2} \\ \tilde{x}_I(t_2 - \tau), & \frac{t_1 + t_2}{2} < \tau < \frac{t_2 + t_3}{2} \\ x_I(t_3 - \tau), & \tau > \frac{t_2 + t_3}{2} \end{cases} \quad (39)$$

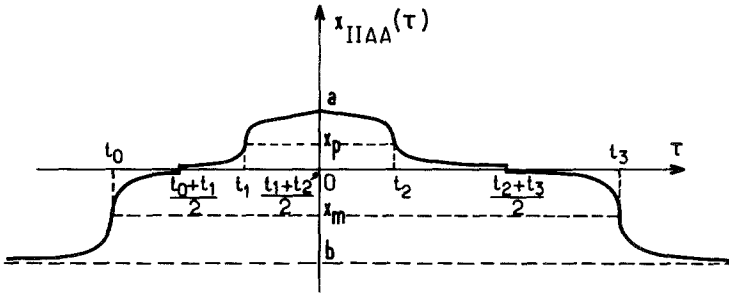


Fig. 7. A 4-pseudoparticle trajectory in the potential $(-V^{(0)}(x))$ associated with the physical potential of Fig. 2.

In fact, again, these trajectories are not continuous: at $t = (t_1 + t_2)/2$, as in the pair case, they exhibit an (exponentially small at large separation) discontinuity in the velocity, while, at $(t_0 + t_1)/2$ and $(t_2 + t_3)/2$, both x_{IIAA} and \dot{x}_{IIAA} are slightly discontinuous.

As we have seen in Section 3.2, this deficiency must be cured by a proper extension of the trajectories into the complex time plane. This results into defining for the variables $z_1 = t_1 - t_0$, $z_2 = t_2 - t_1$, $z_3 = t_3 - t_2$, three integration contours

$$\begin{aligned}
 (\mathcal{C}_1) \quad \text{Im } z_1 &= \pi/|U_0''|, & 0 \leq \text{Re } z_1 &\leq t/2 - t_0 \\
 (\mathcal{C}_2) \quad \text{Im } z_2 &= \pi/U_a'', & 0 \leq \text{Re } z_2 &\leq \text{Re}(t/2 - t_1) \\
 (\mathcal{C}_3) \quad \text{Im } z_3 &= \pi/|U_0''|, & 0 \leq \text{Re } z_3 &\leq \text{Re}(t/2 - t_2)
 \end{aligned}
 \tag{40}$$

Contour (\mathcal{C}_2) describes the same type of extended trajectory as the one defined in Section 3.2 (with a complex turning point allowing for the velocity reversal). Contours (\mathcal{C}_1) and (\mathcal{C}_3) are devised in order to recover continuity of x_{IIAA} in the (0) region: the corresponding extended trajectories can be considered as the limit, for energy $E \rightarrow -V_b (E < -V_b)$ of paths tunneling through the harmonic potential $V_h^{(0)}$ [Eq. (27)] in the (0) region.⁽¹⁸⁾ On such a path (Fig. 8) the particle reaches the left “turning point” $x = -\epsilon$ at time τ_0 , the tunneling part corresponds to an excursion

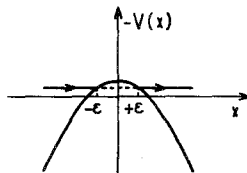


Fig. 8. A path tunneling through the harmonic potential $V_h^{(0)}$ in the (0) region.

towards imaginary times (with $\text{Re } \tau = \tau_0$), it emerges onto the real x axis at the symmetric turning point $x = \epsilon$, with $\dot{x}(\epsilon) = \dot{x}(-\epsilon)$, at time $\tau_0 + (i\pi/|U_0''|)$. So, in order for this procedure to make x_{IIAA} continuous at $t = (t_0 + t_1)/2$, we must choose the center x_p of the $(0a)$ instanton so that

$$x_I \left(\text{Re} \left(\frac{t_1 - t_0}{2} \right) \right) = -\tilde{x}_I \left(\text{Re} \left(\frac{t_0 - t_1}{2} \right) \right) \quad (41)$$

This implies (for large $t_1 - t_0$) that

$$x_p \exp(|U_0''|\Delta_{0p}) = |x_m| \exp(|U_0''|\Delta_{m0}) \quad (42)$$

The calculation of the fluctuation contribution to $K^{(2)}$ follows exactly the lines sketched out above for $K^{(1)}$, and one obtains

$$\begin{aligned} K_{ba}^{(2)} \left(b, \frac{t}{2} \mid b, -\frac{t}{2} \right) &= \left(\frac{2\pi\theta}{U_a''} \right)^{1/2} \frac{U_b'' U_a'' U_0''^2}{4} x_m^2 x_p^2 \frac{|U_0''|^3}{(2\pi\theta)^3} \\ &\times \exp \left[-\frac{2U_0 - U_a - U_b}{\theta} + 2|U_0''|(\Delta_{m0} + \Delta_{0p}) \right] \\ &\times \int_{-t/2}^{t/2} dt_0 \int_{(\mathcal{C}_1)} dz_1 \int_{(\mathcal{C}_2)} dz_2 \int_{(\mathcal{C}_3)} dz_3 \\ &\times \exp [F(z_1) + G(z_2) + F(z_3)] \end{aligned} \quad (43)$$

where

$$F(z) = \frac{C_0}{\theta} \exp(-|U_0''|z) - |U_0''| \text{Re } z \quad (44a)$$

$$G(z) = \frac{C_a}{\theta} \exp(-U_a'' z) \quad (44b)$$

and

$$C_0 = \frac{x_m^2 |U_0''|}{2} \exp(2|U_0''|\Delta_{m0}) \quad (44c)$$

$$C_a = \frac{(a - x_p)^2 U_a''}{2} \exp(2U_a''\Delta_{pa}) \quad (44d)$$

The overall (+) sign in Eq. (43) results, as discussed in Section 3.2, from the fact that x_{IIAA} contains two anti-instantons, each of which introduces a (-) sign.

Neglecting, as usual, edge effects, the z_3 integration simply results in the constant $\theta/C_0|U_0''|$. The z_2 integration only involves $G(z_2)$, which does not contain a term $\propto \text{Re } z_2$. This, as can be seen from Eq. (29), is a direct consequence of the degeneracy of the first local harmonic levels of the true effective potential V in wells (a) and (b): these two levels both have zero

energy, for all physical potentials U , which results from the specific structure of the Fokker–Planck equation.

$G(z_2)$ is very close to 1 as soon as $\text{Re } z_2 \gg t_S^{(a)} \simeq U_a''^{-1} \log(C_a/\theta)$, where Suzuki's time for region (a) $t_S^{(a)} \ll t \sim \tau_K$. So (up, again, to negligible edge effects),

$$\int_{(c_2)} G(z_2) dz_2 \simeq t/2 \quad (45)$$

Repeating the same procedure for z_1 and t_0 , one finally gets

$$K_{ba}^{(2)}\left(b, \frac{t}{2} \mid b, -\frac{t}{2}\right) = \frac{t^2}{2!} \left(\frac{U_b''}{2\pi\theta}\right)^{1/2} \frac{(|U_0''|U_a'')^{1/2}}{2\pi} \\ \times \frac{(|U_0''|U_b'')^{1/2}}{2\pi} \exp\left(-\frac{2U_0 - U_a - U_b}{\theta}\right) \quad (46)$$

So, while $K^{(1)} \propto t$, $K^{(2)} \propto t^2$. That is, owing to the above-mentioned degeneracy between wells (a) and (b), the trajectory x_{IIAA} is in fact made of two *independent* pseudomolecules ($b0a$) and ($a0b$). The $t^2/2!$ factor in (46) results from the fact that the center of each of these undistinguishable molecules can explore independently the whole “volume” t in time-space.

It is the nondegeneracy between the first (0) and (a, b) harmonic levels which gives rise to the binding of pairs of pseudoparticles [i.e., limits, for example, $\text{Re}(t_3 - t_2)$ to finite values].

3.4. The Complete P : Resummation of Instanton Terms

We can now proceed to the complete calculation of $P(b, t/2 \mid b, -t/2)$, which appears as the sum of the contributions of trajectories corresponding to any number of independent pseudomolecules of four species [($b0b$), ($b0a$), ($a0b$), ($a0a$)], arranged in configurations such that the paths effectively start from b and return to it.

It is easy to see that, to each pseudomolecule, one must associate the factors

$$\left. \begin{array}{l} (b0b) \leftrightarrow -\alpha_b \\ (b0a) \leftrightarrow \alpha_b \\ (a0b) \leftrightarrow \alpha_a \\ (a0a) \leftrightarrow -\alpha_a \end{array} \right\} \alpha_i = \frac{(|U_0''|U_i'')^{1/2}}{2\pi} \exp\left(-\frac{U_0 - U_i}{\theta}\right) \quad (47)$$

Noticing that a ($b \rightarrow b$) path contains the same number p of ($b0a$)'s and ($a0b$)'s one obtains, for the contribution of one particular path with n ($b0b$)

and m ($a0a$)

$$(-)^{n+m} \frac{t^{n+m+2p}}{(n+m+2p)!} \alpha_b^{n+p} \alpha_a^{p+m} \left(\frac{U_b''}{2\pi\theta} \right)^{1/2} \quad (48)$$

After proper counting of the number of paths giving the same contribution (48) one finally finds

$$\begin{aligned} P\left(b, \frac{t}{2} | b, -\frac{t}{2}\right) &= \left(\frac{U_b''}{2\pi\theta} \right)^{1/2} \left[1 + \alpha_b \sum_{q=1}^{\infty} (-)^q \frac{t^q}{q!} (\alpha_b + \alpha_a)^{q-1} \right] \\ &= \left(\frac{U_b''}{2\pi\theta} \right)^{1/2} (\alpha_b + \alpha_a)^{-1} \{ \alpha_a + \alpha_b \exp[-t(\alpha_a + \alpha_b)] \} \end{aligned} \quad (49)$$

This result is identical with the one obtained with the help of the WKB mode development.⁽⁵⁾ In particular, the time scale which appears in Eq. (49) is precisely Kramers time τ_K :

$$\begin{aligned} \tau_K^{-1} = \alpha_a + \alpha_b &= \frac{(|U_0''|U_b'')^{1/2}}{2\pi} \exp[-(U_0 - U_b)/\theta] \\ &+ \frac{(|U_0''|U_a'')^{1/2}}{2\pi} \exp[-(U_0 - U_a)/\theta] \end{aligned} \quad (50)$$

An analogous procedure, applied to the calculation of, e.g., $P(a, t/2 | b, -t/2)$, yields

$$P\left(a, \frac{t}{2} | b, -\frac{t}{2}\right) = \left(\frac{U_a''}{2\pi\theta} \right)^{1/2} \frac{\alpha_b}{\alpha_a + \alpha_b} \{ 1 - \exp[-t(\alpha_a + \alpha_b)] \} \quad (51)$$

which, again, reproduces the long time mode expansion result.

Finally, with the same method, one easily rederives the long time limit⁽⁵⁾ of $P(x, t/2 | x_0, -t/2)$ for all values of x, x_0 . We will simply give here its expression for x_0 and x both belonging to either of the harmonic (a) and (b) regions [note that it is only in these regions that $P(x)$ is important at long times].

Consider, for example, the case where x_0 belongs to region (b) and x to region (a). The first important path connecting x_0 and x is the direct one. Clearly, its contribution to $K(x, t/2 | x_0, -t/2)$ is of order $\exp[-(S_{b0} + S_{0a})/\theta]$. On the other hand, since $x_0 \neq b$ and/or $x \neq a$, the corresponding classical trajectory has at least one end with a nonexponentially small slope. For this reason, there is no longer a quasidegeneracy of the action with respect to translation of the instanton centers, and no factor proportional to the time appears in this term. For the same reason, the two trajectories connecting x_0 and x with one single quasireflection at either a or b give a contribution of comparable order.

On the other hand, the term corresponding to the trajectory with two quasireflections ($x_0 \rightarrow b \rightarrow a \rightarrow x$) has a different behavior. Indeed, with the help of the technique used in Appendix A to factorize fluctuations, one immediately shows that, in the very long time regime, the corresponding $K^{(1)}(x, t/2 | x_0, -t/2)$ can be factorized into

$$K^{(1)}\left(x, \frac{t}{2} | x_0, -\frac{t}{2}\right) = K_{\text{harm}}\left(x, \frac{t}{2} | a, t'\right) \left(\frac{2\pi\theta}{U_a''}\right)^{1/2} K^{(1)}(a, t' | b, t'') \\ \times \left(\frac{2\pi\theta}{U_b''}\right)^{1/2} K_{\text{harm}}\left(b, t'' | x_0, -\frac{t}{2}\right) \quad (52)$$

where Eq. (52) is valid and independent of t' and t'' provided that $t/2 - t'$ and $t'' + t/2$ are large compared with Suzuki's time t_s but small compared with τ_K (see Appendix A).

Then

$$K_{\text{harm}}\left(x, \frac{t}{2} | a, t'\right) \cong \left(\frac{U_a''}{2\pi\theta}\right)^{1/2} \exp\left[-\frac{U(x) - U_a}{2\theta}\right] \quad (53)$$

Moreover,

$$K^{(1)}(a, t' | b, t'') \cong K^{(1)}\left(a, \frac{t}{2} | b, -\frac{t}{2}\right) \quad (54)$$

Finally, it is clear that all significant contributions to $K^{(1)}(x, t/2 | x_0, -t/2)$ are obtained by replacing in expression (52) $K^{(1)}(a, t/2 | b, -t/2)$ by the full $K(a, t/2 | b, -t/2)$, and we obtain

$$P\left(x, \frac{t}{2} | x_0, -\frac{t}{2}\right) = \exp\{-[U(x) - U_a]/\theta\} P\left(a, \frac{t}{2} | b, -\frac{t}{2}\right) \quad (55)$$

where $P(a, t/2 | b, -t/2)$ is given by Eq. (51). An analogous calculation shows that, if x and x_0 both belong to the harmonic (b) region,

$$P\left(x, \frac{t}{2} | x_0, -\frac{t}{2}\right) = \exp\left[-\frac{U(x) - U_b}{\theta}\right] P\left(b, \frac{t}{2} | b, -\frac{t}{2}\right) \quad (56)$$

Again, expressions (55) and (56) are identical with the expression derived from the mode development.

4. INTERMEDIATE TIME BEHAVIOR: SUZUKI REGIME

Let us now concentrate on the behavior of the distribution $P(x, t | x_0, 0)$ in the intermediate time regime first analyzed by Suzuki,⁽⁶⁾ where t is of order

$$t_s = |U_0''|^{-1} \log\left(\frac{2a^2 |U_0''|}{\theta}\right) \quad (57)$$

As is now well known, the most interesting effects, in this regime, correspond to the case where the initial distribution is concentrated in the region of instability. That is, we now choose $x_0 = 0$ (the generalization to finite values of x_0 is trivial).

Since we are interested in times $t \sim t_S \ll \tau_K$, it is clear that effects due to instanton translation are negligible [$t \exp(-S_{b0}/\theta) \ll 1$].⁶ The small- θ approximation to P thus reduces to the standard semiclassical evaluation of the path integral (7), by second-order expansion of the action around the classical path(s) between x_0 and x .

We choose x in the "WKB region"⁽⁵⁾ between (0) and (a), i.e., outside the harmonic (0) and (a) regions. In this case, the only important contribution is that of the direct path: indeed, even if there exists a path with one real reflection in the (a) region connecting x_0 and x in time t , its classical action is much larger than that of the direct path $S_{cl}(x, t | 0, 0)$. We thus obtain for P the standard expression (for a particle of mass 1/2)

$$P(x, t | 0, 0) \cong \frac{1}{(2\pi\theta)^{1/2}} \left[- \frac{\partial^2 S_{cl}(x, t | x_0, 0)}{\partial x \partial x_0} \Big|_{x_0=0} \right]^{1/2} \times \exp \left\{ - \frac{U(x) - U_0}{2\theta} - \frac{1}{\theta} S_{cl}(x, t | 0, 0) \right\} \quad (58)$$

where

$$\frac{\partial^2 S_{cl}(x, t | x_0, 0)}{\partial x \partial x_0} = \frac{1}{4} [E + V(x_0)]^{-1/2} [E + V(x)]^{-1/2} \frac{dE}{dt} \quad (59)$$

E is the energy associated with the classical trajectory:

$$t = \int_0^x \frac{du}{2[E + V(u)]^{1/2}} = \int_0^x \frac{du}{2[E + V_h(u)]^{1/2}} + \int_0^x \frac{du}{2} \left\{ \frac{1}{[E + V(u)]^{1/2}} - \frac{1}{[E + V_h(u)]^{1/2}} \right\} \quad (60a)$$

$$V_h(x) = \frac{U_0''^2 x^2}{4} - \frac{\theta U_0''}{2} \quad (60b)$$

For $t \sim t_S$, one can check on the result of integration (60a) that $E - V(0) = 0(\theta)$. Then, neglecting terms of order θ in the second integral on the

⁶ This corresponds to the fact that, in the mode development approach and in Suzuki's regime, one can neglect the shift of the mode energies due to the tunneling coupling between the wells of V .

right-hand side of (60a) we get

$$t \cong \frac{1}{2|U_0''|} \log \left| \frac{U_0'' x^2}{E - \theta U_0''/2} \right| - \delta(x) \quad (61a)$$

$$\delta(x) = \int_0^x du \left[\frac{1}{U'(u)} - \frac{1}{U_0'' u} \right] \quad (61b)$$

$S_{cl}(x, t | 0, 0)$ can then be calculated, up to terms of order θ , by the method explained in Appendix C of Ref. 5, and one obtains finally, for x in the WKB region,

$$P_{\text{WKB}}(x, t | 0, 0) \cong \frac{\exp[-|U_0''|\delta(x)]}{(2\pi\tau)^{1/2}} \frac{|U_0'' x|}{a|U'(x)|} \times \exp \left\{ -\frac{x^2}{2a^2\tau} \exp[-2|U_0''|\delta(x)] \right\} \quad (62)$$

$$\tau = \frac{\theta}{|U_0''|a^2} \exp(2t|U_0''|) \quad (63)$$

which is exactly the “scaling distribution” found by Suzuki⁽⁶⁾ and also derived from the mode expansion,⁽⁵⁾ which describes the splitting of P into two peaks in the (a) and (b) wells.

Note, finally, that one could use the same simple semiclassical procedure to calculate P , in the intermediate time regime, for values of x in the (a) [or, equivalently, (b)] diffusive region. However, the corresponding calculation is in practice more complicated. Indeed, (i) for $x \lesssim b$, depending on the values of x and t , there may be two classical paths [with energies, respectively, very close to $-V(0)$ and $-V(a)$], and (ii) since the path(s) now explore(s) two harmonic regions, the relation between time and energy analogous to (61) now contains two logarithmic terms with different coefficients, so that it can in general not be inverted analytically, and one cannot derive a simple analytic expression of P that would extend (62). (This parallels the fact that, in this case, the mode expansion cannot be resummed simply.) Note, however, that the present approach is particularly well suited to perform a numerical estimate of P .

In conclusion, it appears that the path integral approach, as developed above, is able to reproduce *exactly* the results obtained, for one-dimensional systems, from the mode expansion and WKB approximation—in contradistinction with the results obtained by the method of Weiss and Haffner,⁽²⁰⁾ which, in our opinion, makes use of an unnecessary variational approximation. Our approximation scheme generalizes Moreau's⁽²¹⁾ treatment of the path integral, which could not describe Kramers regime, owing to its neglect of the instanton effect. It may be worthy to point out that the present approach provides a particularly short and simple method for

rederiving Suzuki's results about the dynamics of instability. Finally, the prescriptions which we have been able to derive in the simple one-dimensional case seem to be clear enough to be extended to more complex—and more interesting—systems with more degrees of freedom.

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APPENDIX A

We consider here the contribution to $K(x_1, t | x_i, t_i)$ [Eq. (7b)] of the paths lying—in configuration space—in the vicinity of the quasistationary path $x_{IA}(\tau, t_0, t_1)$ [Eq. (22)], which describes one instanton–anti-instanton pair (with centers at t_0, t_1). Following the one instanton calculation (Section 2), we define eigenfunctions $y_n(\tau, t_0, t_1)$ of the equation of fluctuations around $x_{IA}(\tau, t_0, t_1)$ in the approximate potential $V^{(0)}$. n runs from 3 to N , N being the (quasi-infinite) number of degrees of freedom corresponding to the path integration:

$$\left\{ -\frac{1}{2} \frac{d^2}{d\tau^2} + V^{(0)''}[x_{IA}(\tau, t_0, t_1)] \right\} y_n(\tau, t_0, t_1) = \lambda_n y_n(\tau, t_0, t_1) \quad (\text{A1})$$

The y_n must satisfy the boundary conditions

$$y_n(\tau = t_i) = y_n(\tau = t) = 0 \quad (\text{A2})$$

and are orthonormal

$$\int_{t_i}^t d\tau y_n(\tau, t_0, t_1) y_m(\tau, t_0, t_1) = \delta_{nm} \quad (\text{A3})$$

We set

$$x(\tau) = x_{IA}(\tau, t_0, t_1) + \sum_{n=3}^N \xi_n y_n(\tau, t_0, t_1) \quad (\text{A4})$$

The eigenfunctions y_n defined above do not contain the two collective modes $y_1 \propto \partial x_{IA}/\partial t_0$ and $y_2 \propto \partial x_{IA}/\partial t_1$ which describe the separate translation of the instanton and anti-instanton, to which the y_n 's are orthogonal.

We want to express the functional integral (7b) in terms of variables $t_0, t_1, \{\xi_n\}$. We thus need the Jacobian of the transformation

$$J = \frac{\mathcal{D}\{x(\tau_1), \dots, x(\tau_N)\}}{\mathcal{D}\{t_0, t_1, \{\xi_n\}\}} \tag{A5}$$

We use the relation

$$J = [\text{Det}\{\Delta^+ \Delta\}]^{1/2} \tag{A6}$$

where

$$\Delta = \begin{vmatrix} \frac{\partial x(\tau_1)}{\partial t_0} & \frac{\partial x(\tau_1)}{\partial t_1} & \frac{\partial x(\tau_1)}{\partial \xi_1} & \dots \\ \frac{\partial x(\tau_2)}{\partial t_0} & \frac{\partial x(\tau_2)}{\partial t_1} & \frac{\partial x(\tau_2)}{\partial \xi_1} & \dots \\ \frac{\partial x(\tau_3)}{\partial t_0} & \dots & & \\ \vdots & & & \end{vmatrix} \tag{A7}$$

Then, assuming that the relevant values of the ξ_n 's are $\lesssim 0(\theta^{1/2})$ (which can be checked at the end of the calculation), and taking advantage of the orthonormality relations, J can be calculated to zeroth order in the ξ_n , and reduces to

$$J = \Lambda \left\{ \text{Det} \begin{vmatrix} \int_{t_i}^t \left(\frac{\partial x_{IA}}{\partial t_0} \right)^2 d\tau & \int_{t_i}^t d\tau \frac{\partial x_{IA}}{\partial t_0} \frac{\partial x_{IA}}{\partial t_1} \\ \int_{t_i}^t d\tau \frac{\partial x_{IA}}{\partial t_0} \frac{\partial x_{IA}}{\partial t_1} & \int_{t_i}^t d\tau \left(\frac{\partial x_{IA}}{\partial t_1} \right)^2 \end{vmatrix} \right\}^{1/2} \tag{A8}$$

where the constant Λ is, as usual, determined at the end of the calculation by fitting with the solution of the harmonic problem. $\partial x_{IA}/\partial t_0$ and $\partial x_{IA}/\partial t_1$ are functions of width Δt centered, respectively, at t_0 and t_1 . For the large $t_1 - t_0$ of interest, their overlap integral is exponentially small. Moreover, using Eq. (22), one gets

$$\int_{t_i}^t \left(\frac{\partial x_{IA}}{\partial t_{0,1}} \right)^2 d\tau \cong 2S_{b0} \tag{A9}$$

where S_{b0} is defined by Eq. (24). So, one obtains

$$K^{(1)}\left(b, \frac{t}{2} \mid b, -\frac{t}{2}\right) = \int_{-t/2}^{t/2} \frac{dt_0}{(4\pi\theta)^{1/2}} \int_{t_0}^{t/2} \frac{dt_1}{(4\pi\theta)^{1/2}} 2S_{b0}\Lambda \\ \times \prod_n \int d\xi_n \exp\left[-\frac{1}{\theta} S\left\{x_{IA} + \sum_n \xi_n y_n\right\}\right] \quad (\text{A10})$$

We now develop S up to second order in the ξ_n 's:

$$S\left\{x_{IA} + \sum_n \xi_n y_n\right\} \cong S_{IA}(t, t_0, t_1) + \delta S^{(1)} + \delta S^{(2)} \quad (\text{A11})$$

with

$$S_{IA}(t, t_0, t_1) = \int_{-t/2}^{t/2} \left[\frac{(\dot{x}_{IA})^2}{4} + V(x_{IA}) \right] d\tau \\ = \int_{-t/2}^{t/2} d\tau \delta V(x_{IA}) + \int_{-t/2}^{t/2} \left[\frac{(\dot{x}_{IA})^2}{2} + V_b \right] d\tau \\ = (V_0 - V_b)(t_1 - t_0) + V_b t + 2 \int_{-t/2}^{(t_0+t_1)/2} d\tau \frac{[\dot{x}_I(\tau - t_0)]^2}{2} \quad (\text{A12})$$

The term linear in the ξ_n is given (up to exponentially small terms in $t_1 - t_0$) by

$$\delta S^{(1)} = \sum_n \xi_n \int_{-t/2}^{t/2} d\tau y_n(\tau, t_0, t_1) \delta V'(x_{IA}) \quad (\text{A13})$$

$[\delta V' \equiv d(\delta V)/dx]$. With the choice of δV given by Eq. (21)

$$|\delta S^{(1)}| \cong \sum_n \xi_n y_n(\tau(x_m)) \frac{V_0 - V_b}{[V(x_m)]^{1/2}} \equiv \sum_n \xi_n \mu_n \quad (\text{A14})$$

y_n is normalized on the interval t . For large n 's, the y_n 's extend in the whole interval, so $|y_n| \sim 1/\sqrt{t}$. For the first n 's, they may be more localized, but their time range is at least of the order of the finite instanton width Δt , so that $|y_n| \gtrsim 1/\sqrt{\Delta t}$.

On the other hand, the y_n 's are chosen so that $\delta S^{(2)}$ is simply (up to terms of order $\delta V = 0(\theta)$ which are negligible at the order at which we are working)

$$\delta S^{(2)} = \sum_n \lambda_n \xi_n^2 \quad (\text{A15})$$

and

$$\delta S^{(1)} + \delta S^{(2)} \cong \sum_n \left[\lambda_n \left(\xi_n + \frac{\mu_n}{2\lambda_n} \right)^2 - \frac{\mu_n^2}{4\lambda_n} \right] \quad (\text{A16})$$

That is, $\delta S^{(1)}$ results in (i) a shift of the average ξ_n 's, of order μ_n/λ_n . Since $\mu_n \propto (V_0 - V_b) \propto \theta$, this shift is negligible with respect to the effective range, of order $\theta^{1/2}$, of the ξ_n integration; and (ii) a correction to the action, of order $\mu_n^2 \propto \theta^2$, which is therefore negligible.

Finally, $\delta S^{(1)}$ can be completely neglected, and one is left with the standard fluctuation integral in potential $V^{(0)}$, around the path x_{IA} . We will now show that the fluctuation contribution factorizes (up to terms exponentially small in $(t_1 - t_0)$) into the fluctuation terms associated with the separate instanton and anti-instanton parts of the trajectory.

Let us define two times t_u and t_v such that

$$t_0 \ll t_u \ll \frac{t_0 + t_1}{2} \ll t_v \ll t_1 \quad (\text{A17})$$

The contribution $K_{IA}^{(1)}$ to $K^{(1)}$ of paths close to a given x_{IA} can be rewritten approximately as⁽¹⁵⁾

$$\begin{aligned} K_{IA}^{(1)} \left(b, \frac{t}{2} \mid b, -\frac{t}{2} \right) &\cong \int du dv K_I \left(b, \frac{t}{2} \mid v, t_v \right) \\ &\times K_{\text{harm}}(v, t_v \mid u, t_u) K_A \left(u, t_u \mid b, -\frac{t}{2} \right) \end{aligned} \quad (\text{A18})$$

where K_I (respectively, K_A) sums the contributions of paths in the vicinity of the x_I (respectively, x_A) part of x_{IA} . Since t_u and t_v obey condition (A17), the important values of u and v lie in the (0) harmonic region, so that $K_{\text{harm}}(v, t_v; u, t_u)$ is the propagator for the harmonic problem in that region.⁽¹⁵⁾ Provided that

$$t_v - t_u \gg t_S \propto \log(\theta^{-1})$$

one can replace K_{harm} by its large-time expression:

$$\begin{aligned} K_{\text{harm}}(v, t_v \mid u, t_u) &= \left(\frac{|U_0''|}{2\pi\theta} \right)^{1/2} \exp \left\{ \frac{|U_0''|}{4\theta} (v^2 + u^2) + \frac{(U_b'' - |U_0''|)}{2} (t_v - t_u) \right\} \\ &= \left(\frac{2\pi\theta}{|U_0''|} \right)^{1/2} K_{\text{harm}} \left(v, t_v \mid 0, \frac{t_0 + t_1}{2} \right) K_{\text{harm}} \left(0, \frac{t_0 + t_1}{2} \mid u, t_u \right) \end{aligned} \quad (\text{A19})$$

Inserting (A19) into (A18), one gets

$$K^{(1)}\left(b, \frac{t}{2} \mid b, -\frac{t}{2}\right) \cong \left(\frac{2\pi\theta}{|U_0''|}\right)^{1/2} K_I\left(b, \frac{t}{2} \mid 0, \frac{t_0 + t_1}{2}\right) K_A\left(0, \frac{t_0 + t_1}{2} \mid b, -\frac{t}{2}\right) \quad (\text{A20})$$

from which one immediately obtains⁽¹⁰⁾ Eq. (28).

APPENDIX B

We want to calculate explicitly, here, the shape of the instanton solution $x_I(\tau - t_0)$ in potential $(-V^{(0)})$ [Eq. (21) and Fig. 5], which leaves $x = b$ at time $-\infty$, and reaches $x = 0$ at time $+\infty$. It corresponds to energy $(-V_b)$. We define the instanton center t_0 as the time at which $x = x_m$. The equation of the trajectory is

$$\begin{aligned} \tau - t_0 &= \int_{x_m}^{x_I} \frac{dx}{2[V^{(0)}(x) - V_b]^{1/2}} \\ &= \int_{x_m}^{x_I} \frac{dx}{2} \left\{ \frac{1}{[V^{(0)}(x) - V_b]^{1/2}} - \frac{1}{[V_h^{(0)}(x) - V_b]^{1/2}} \right\} \\ &\quad + \int_{x_m}^{x_I} \frac{dx}{2[V_h^{(0)}(x) - V_b]^{1/2}} \end{aligned} \quad (\text{B1})$$

$V_h^{(0)}$ is defined by Eq. (27).

For $x_I \simeq 0$, i.e., $\tau \gg t_0$,

$$\tau - t_0 \cong \Delta_{m0} + \frac{1}{(2V_0'')^{1/2}} \log\left(\frac{x_m}{x_I}\right) \quad (\text{B2})$$

where Δ_{ij} is defined by Eq. (32).

From Eq. (B2), one gets the large-time asymptotic expression of $\dot{x}_I(\tau - t_0)$:

$$\dot{x}_I(\tau - t_0) \underset{\tau \gg t_0}{\sim} |x_m|(2V_0'')^{1/2} \exp\left[-(2V_0'')^{1/2}(\tau - t_0 - \Delta_{m0})\right] \quad (\text{B3})$$

Analogously, one finds

$$\dot{x}_I(\tau - t_0) \underset{\tau \ll t_0}{\sim} (x_m - b)(2V_b'')^{1/2} \exp\left[(2V_b'')^{1/2}(\tau - t_0 + \Delta_{bm})\right] \quad (\text{B4})$$

Following Coleman,⁽¹⁰⁾ we define the instanton translation eigenfunction, normalized on the time interval of interest $(-t/2, t')$ (with $-t/2 \ll t_0$, $t' \gg t_0$):

$$x_1(\tau - t_0) = \mathcal{N}^{1/2} \dot{x}_I(\tau - t_0) \quad (\text{B5})$$

Up to exponentially small terms

$$\mathcal{N} = (2S_{b0})^{-1} \quad (\text{B6})$$

and x_1 has the asymptotic expressions:

$$x_1(\tau - t_0) \underset{\tau \gg t_0}{\sim} A_0 \exp\left[-(2V_0'')^{1/2}(\tau - t_0)\right] \quad (\text{B7a})$$

$$x_1(\tau - t_0) \underset{\tau \ll t_0}{\sim} A_b \exp\left[(2V_b'')^{1/2}(\tau - t_0)\right] \quad (\text{B7b})$$

and

$$A_0 = |x_m|(V_0''/S_{b0})^{1/2} \exp\left[(2V_0'')^{1/2}\Delta_{m0}\right] \quad (\text{B8a})$$

$$A_b = (x_m - b)(V_b''/S_{b0})^{1/2} \exp\left[(2V_b'')^{1/2}\Delta_{bm}\right] \quad (\text{B8b})$$

$x_1(\tau - t_0)$ is a solution of the fluctuation Eq. (11b) in potential $(-V^{(0)})$ with eigenvalue $\lambda = 0$. Note that it is exponentially small, but nonzero, at the edges of the interval $(-t/2, t')$.

Let us call y_1 a solution of the fluctuation equation (11b) for $\lambda = 0$, and which satisfies

$$x_1 \frac{dy_1}{d\tau} - y_1 \frac{dx_1}{d\tau} = W \quad (\text{B9})$$

where W is an arbitrary constant. Equations (B9) and (B7)–(B8) entail

$$y_1(\tau - t_0) \underset{\tau \gg t_0}{\sim} W \left[2A_0(2V_0'')^{1/2}\right]^{-1} \exp\left[(2V_0'')^{1/2}(\tau - t_0)\right] \quad (\text{B10a})$$

$$y_1(\tau - t_0) \underset{\tau \ll t_0}{\sim} -W \left[2A_b(2V_b'')^{1/2}\right]^{-1} \exp\left[-(2V_b'')^{1/2}(\tau - t_0)\right] \quad (\text{B10b})$$

The function ψ satisfying Eqs. (14) and (15) can be written

$$\psi(\tau) = \alpha x_1(\tau - t_0) + \beta y_1(\tau - t_0) \quad (\text{B11})$$

with

$$\alpha = \left[2A_b(2V_b'')^{1/2}\right]^{-1} \exp\left[-(2V_b'')^{1/2}\left(-\frac{t}{2} - t_0\right)\right] \quad (\text{B12a})$$

$$\beta = \frac{A_b}{W} \exp\left[(2V_b'')^{1/2}\left(-\frac{t}{2} - t_0\right)\right] \quad (\text{B12b})$$

We now want to calculate the first eigenvalue λ_0 of Eq. (11b) with boundary conditions (11c). Let ψ_{λ_0} be the corresponding eigenfunction. Transforming (11b) into the integral equation

$$\psi_{\lambda_0}(\tau) = \psi(\tau) - \frac{2\lambda_0}{W} \int_{-t/2}^{\tau} d\tau' \left[y_1(\tau)x_1(\tau') - x_1(\tau)y_1(\tau') \right] \psi_{\lambda_0}(\tau') \quad (\text{B13})$$

where ψ_{λ_0} satisfies $\psi_{\lambda_0}(-t/2) = 0$. The value of λ_0 is obtained by solving

(B13) by iteration and imposing $\psi_{\lambda_0}(t') = 0$. This gives

$$\frac{\lambda_0}{\psi(t')} = \frac{W}{2} \left\{ \int_{-t/2}^{t'} d\tau [y_1(t')x_1(\tau) - x_1(t')y_1(\tau)] [\alpha x_1(\tau) + \beta y_1(\tau)] \right\}^{-1} \quad (\text{B14})$$

A straightforward but slightly heavy⁽²²⁾ analysis of the time variations of functions x_1 and y_1 shows that the integral in Eq. (B14) reduces to the term

$$\alpha y_1(t') \int_{-t/2}^{t'} d\tau x_1^2(\tau) = \alpha y_1(t')$$

so that, for the time interval $(-t/2, t')$, the factor associated with fluctuations around the instanton centered at t_0 is

$$\left(\frac{\lambda}{\psi} \right)_I = \left\{ 2A_b(V_b'')^{1/2} \exp \left[(2V_b'')^{1/2} \left(-\frac{t}{2} - t_0 \right) \right] \right\} \\ \times \left\{ 2A_0(V_0'')^{1/2} \exp \left[-(2V_0'')^{1/2} (t' - t_0) \right] \right\} \quad (\text{B15})$$

which can be rewritten, with the help of Eqs. (B3) and (B4):

$$\left(\frac{\lambda}{\psi} \right)_I = \frac{2(V_0'' V_b'')^{1/2}}{S_{b0}} \dot{x}_I(t') \dot{x}_I \left(-\frac{t}{2} \right) \quad (\text{B16})$$

APPENDIX C

We calculate here the action S_{b0} in potential $V^{(0)}$ and at energy $(-V_b)$

$$S_{b0} = \int_b^0 dx [V^{(0)}(x) - V_b]^{1/2} \\ = \int_b^{x_m} dx \left(\frac{U^2}{4} - \frac{\theta U''}{2} + \frac{\theta U_b''}{2} \right)^{1/2} + \int_{x_m}^0 dx \left(\frac{U^2}{4} - \frac{\theta U''}{2} + \frac{\theta U_0''}{2} \right)^{1/2} \quad (\text{C1})$$

In order to calculate the integrals (C1), one introduces two cutoffs ξ (respectively, η) located in the domains of overlap between the (b) [respectively, (0)] quadratic regions and the "WKB region" [$V^{(0)}(x) \gg V_b$]. Following exactly all the steps of the calculation developed in Appendix C of Ref. 5, we obtain (up to terms of order θ)

$$S_{b0} = \frac{U_0 - U_b}{2} + \frac{\theta}{2} \log \left| \frac{U_b''(x_m - b)}{U_0'' x_m} \right| + \frac{\theta}{2} (U_b'' \Delta_{bm} + U_0'' \Delta_{m0}) \quad (\text{C2})$$

NOTE ADDED IN PROOF

We would like to mention that the problem of the continuity of the instanton-antiinstanton trajectories, treated here in Section 3.3, has been solved by E. B. Bogomolny (*Phys. Lett.* **91B**:431, (1980)), who uses truly continuous quasitrajectories. The analytic continuation into the time plane is then unnecessary, but is replaced by corrections to the classical action S_{IA} , leading to equivalent results. We are indebted to Dr. U. Weiss for pointing out to us Bogomolny's article.

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