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Diffusion in a Bistable Potential: A Systematic WKB Treatment

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We study 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, in the limit of constant and small diffusion coefficient. A systematic WKB analysis of the lowest eigenmodes of the equivalent Schrödinger-like equation yields the following results: the final approach to equilibrium is governed by the Kramers high-viscosity rate, which is shown to be exact in this limit; for intermediate times, we show that Suzuki's scaling statement does give the correct behavior for the transition between the one-peak and the two-peak structure for P. However, the intermediate time domain also contains a second "half," where P enters the diffusive equilibrium regions, characterized by a time scale of the same order as Suzuki's time.

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

1. INTRODUCTION

There has been recently considerable interest in the study of fluctuations in nonlinear systems. In this paper we treat the simplest model describing such a situation, namely that of a single, one-dimensional, stochastic variable x, the distribution of which, $P(x, t)$, obeys the generalized Fokker–Planck equation:

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

where $U'(x) = dU(x)/dx$ is a nonlinear function of x. More precisely, we will specialize to the case where U' derives from a bistable "potential" U (Fig. 1). Here θ is a constant (independent of x).

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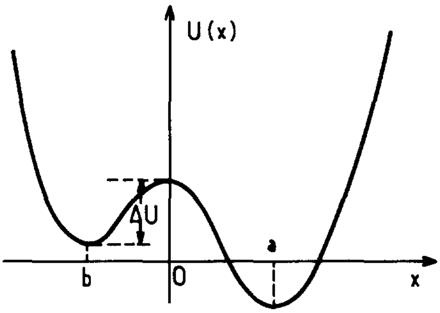

Fig. 1. A bistable potential U.

Equation (1) can be considered either as describing a Brownian motion in the presence of an external nonlinear force[1] (θ is then proportional to the temperature of the viscous medium), or, possibly, as resulting from the truncated Kramers–Moyal development of the master equation for an extensive variable[3] (θ is then proportional to the inverse volume of the system). In any case, we will make the assumption that θ is small, or, more precisely, that $\theta \ll \Delta U$, where ΔU is the height of the bump separating the valleys of U (Fig. 1).

Although this problem may be considered rather academic, it has the interest of being a first step toward the study of more realistic nonlinear problems involving several or many stochastic degrees of freedom, for example, relaxation from far from equilibrium situations or the dynamics of appearance of dissipative structures.

This model has been studied, from various points of view, in several recent articles:

1. Van Kampen[1] and Tomita *et al.*[3] have reduced the Fokker–Planck equation to a Schrödinger-like form and studied the normal mode decomposition of $P(x, t)$; van Kampen was able to distinguish qualitatively among different regimes corresponding to various time scales. In particular, these authors calculate the longest relaxation time, which describes the escape of particles from one of the potential wells to the other after local equilibrium has been established. This time corresponds to the inverse Kramers reaction rate[4] in the high-viscosity limit. We will call the corresponding time domain the Kramers regime.

2. Suzuki[5] has studied specifically the case where the system starts with an initial distribution concentrated in the vicinity of the instability point $x = 0$ (where U has its local maximum). He claims that, for small θ, one can distinguish between: (i) an initial diffusive regime, at small times, where U can be approximated by its antiharmonic development around its local

[3] We will not consider here the problem of the validity of such a procedure, which has been and still is the subject of discussion by several authors.[2]

maximum; and (ii) an intermediate "scaling" regime, where diffusion (i.e., fluctuation) effects would be negligible, for times such that

$$\tau(t) \equiv \theta(\sigma_0 + 1/|U_0''|)\exp(2t|U_0''|) \sim a^2 \tag{2a}$$

(where $\theta\sigma_0$ is the width of the initial distribution and $U_0'' \equiv U''(x = 0)$), the corresponding time

$$t_0 \simeq \frac{1}{2|U_0''|}\left|\mathrm{Log}\left\{\frac{\theta}{a^2}\left(\sigma_0 + \frac{1}{2|U_0''|}\right)\right\}\right| \tag{2b}$$

giving the order of magnitude of the time necessary for $P(x, t)$ to split into two well-separated peaks located in the wells of U. That is, t_0 would be, in this simple one-variable model, the characteristic onset time of the equilibrium (or stationary state) type of structure for P.

He claims that, in this regime, P depends on t only through the variable $\tau(t)$, i.e., $P \equiv P_{sc}(x, \tau)$, and defines P_{sc} with the help of a procedure of matching at small times.

3. Moreau[6] has used the expression for $P(x, t)$ in terms of an Onsager–Machlup functional integral,[7] which he calculates, for small θ, by a stationary phase method. This amounts to keeping only the contributions of the paths in (x, t) space that are close to the path of extremal action.

He finds a sound physical answer, with relaxation toward equilibrium, for potentials U with a single minimum. However, for bistable U, if his result does account for relaxation toward local equilibrium in each well separately, it does not describe the relaxation toward global equilibrium. His approximation should therefore be improved to describe the possibility of escape from one well to the other.

This type of problem, well-known in field theory, where it is called "tunneling between two vacuums," has been solved, in the language of functional integrals, in terms of the instanton theory.[8] It has been shown[8,9] that the same results can be obtained from the associated Schrödinger equation with the help of the WKB approximation adapted to a tunneling problem (this equivalence holds even for a many-variable system).

In order to get a systematic approximate expression for $P(x, t)$ valid for small θ, one can therefore use either of these equivalent methods: (i) the instanton theory if one starts from the Onsager–Machlup formulation; (ii) the WKB method if one uses the equivalent Fokker–Planck equation.

In this paper, we choose the second approach, which we believe, probably on the basis of previous addiction, to be slightly more transparent. This will enable us to obtain, for a general bistable potential, an explicit expression for the normal mode decomposition of $P(x, t)$ for times $t \gg (|U_0''|^{-1}, (U_a'')^{-1}, (U_b'')^{-1})$, where U_0'', U_a'', and U_b'' are the curvatures of U at its extrema. This result extends explicitly those of van Kampen and of Tomita *et al.* (for the small-θ case) into the intermediate time regime. Therefore, it provides a basis for discussing the scaling treatment of Suzuki. We show that Suzuki's time t does give some qualitative information about the time it takes for a distribution starting from the instability region to build up a two-peak structure. However, we find that there is no true time scaling, in the sense that, even in the intermediate regime, P is not a function of the single time variable τ for all x's: this is the case only far enough from the extrema of U. So, Suzuki's expression for the distribution does not describe properly the shape of the peaks when these have developed enough to approach the minima of U.

2. THE APPROXIMATE SOLUTION IN THE INTERMEDIATE AND FINAL REGIMES

Setting in Eq. (1)

$$P(x, t) = e^{-U(x)/2\theta} G(x, t) \tag{3}$$

we find that the equation of evolution of $G(x, t)$ takes the Schrödinger-like form

$$\theta\, \partial G(x, t)/\partial t = [\theta^2\, \partial^2/\partial x^2 - V(x)] G(x, t) \tag{4}$$

where

$$V(x) = \tfrac{1}{4}[U'(x)]^2 - \tfrac{1}{2}\theta U''(x) \tag{5}$$

The solution of Eqs. (3)–(4) that satisfies the initial condition

$$P(x, t = 0) = \delta(x - x_0) \tag{6}$$

is[1]

$$P(x, t|x_0) = \left\{\exp \frac{U(x_0) - U(x)}{2\theta}\right\} \sum_{n \geqslant 0} \varphi_n(x_0)\varphi_n(x) \exp \frac{-t\lambda_n}{\theta} \tag{7}$$

The φ_n are the solutions (regular for $|x| \to \infty$ and normalized) of the eigenmode equation

$$-\theta^2\, d^2\varphi_n/dx^2 + V\varphi_n = \lambda_n \varphi_n \tag{8}$$

with eigenvalue λ_n ($n = 0, 1, \ldots$). From the equilibrium solution

$$P_{\text{eq}}(x) = Ce^{-U(x)/\theta} \tag{9}$$

of Eq. (1), we immediately know the exact lowest eigenmode $\varphi_0(x) = C^{1/2} \exp[-U(x)/2\theta]$, which of course corresponds to $\lambda_0 = 0$. The other λ_n/θ ($n \geqslant 1$) give the inverse normal relaxation times of the system.

Let us first consider the structure of the potential function $V(x)$ associated with a bistable U. From definition (5) it is clear that, for small θ, ($\theta \ll \Delta U$),

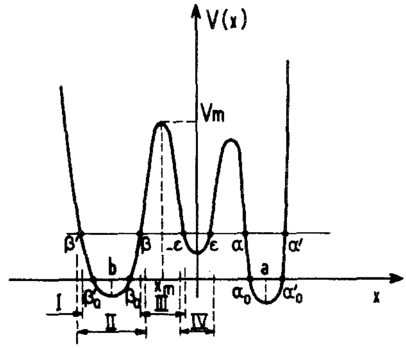

Fig. 2. The potential $V(x)$ associated with $U(x)$. Here I, II, III, IV, ... label the different ranges of definition of the eigenfunctions.

V exhibits three minima (Fig. 2) located close to the three extrema of U. More precisely, it will appear in the following that, in order to be consistent with our approximations, we only need to know each of the characteristic parameters of V at its minima (position of the minima, values of V and of its curvatures) to lowest order in θ. That is

$$V(x) \simeq -\tfrac{1}{2}\theta U_i'' + \tfrac{1}{4}(U_i'')^2(x - x_i)^2 \qquad \text{for } x \simeq x_i \tag{10}$$

with $x_i = b$, 0, or a.

In order to get an estimate of the orders of magnitude of the first of the λ_n, we calculate the "energy" levels of the three harmonic wells corresponding to the three valleys of V. From Eq. (10) we find

$$\lambda_p^{(i)} = -\tfrac{1}{2}\theta U_i'' + \theta|U_i''|(p + \tfrac{1}{2}), \qquad p = 0, 1, 2,... \tag{11}$$

The lowest of these levels are given by $i = a$ or b and $p = 0$, with $\lambda_0^{(a,b)} = 0$: there always is, even for an asymmetric U, a double degeneracy of the lowest harmonic levels in wells (a) and (b). [Quite obviously, this result would remain true to higher orders in θ, since it only expresses the fact that $\exp(-U/2\theta)$ is the exact lowest eigenfunction of Eq. (8).]

From these remarks, it is clear that one may distinguish among three different regions for the values of the λ_n, i.e., among three time regimes:

(i) The tunneling coupling between the two lowest harmonic levels will lift their degeneracy: the two resulting levels will have an exponentially small separation $\lambda_1 - \lambda_0$, controlled by some "activation factor" $\exp(-\Delta U/\theta)$. Therefore $t \gtrsim \tau_1 = (\lambda_1/\theta)^{-1}$ will define the final or Kramers regime.

(ii) The next excited levels have λ values of order $\theta|U_i''|$. They control the time variation of $P(x, t)$ in the intermediate regime defined by $|U_i''|^{-1} \lesssim t \ll \tau_1$.

(iii) The levels with λ's comparable to $V_m \sim (\Delta U/a)^2$ or larger become important in the initial regime $t \lesssim \theta(a/\Delta U)^2$. In this regime, the normal mode expansion (7) is not well suited for obtaining a simple description of P, which instead can be calculated from Eq. (1) where U is developed up to second order in the vicinity of $x = 0$. In the transition region between $|U_i''|^{-1}$ and $\theta(a/\Delta U)^2$, as shown by van Kampen,[1] no clear statement can be made.

From now on, we shall only concentrate on the intermediate and final regimes.

We want to solve Eq. (8) in the small-θ limit. This immediately suggests that we must use the WKB method (the role of $\hbar$ in the usual Schrödinger problem being played here by θ).

We are only interested in the low-lying levels, for which $|\lambda - V| \simeq \theta|U_i''|$ in the vicinity of the bottoms of the three wells of $V(x)$, where the WKB expression for the φ_n is therefore not valid. Fortunately, in these regions we may safely approximate V by harmonic potentials [Eq. (10)], for which there exist exact solutions that we want to match with the WKB solutions. The matching technique, which is equivalent to that of Miller and Good,[10] is developed in detail in Appendix A. Its principle is the following: consider, for example, the matching between regions II and III (see Fig. 2) around the turning point at $x = \beta$. Region II is defined as the quasiharmonic region around $x = b$, where V is given by Eq. (10), and region III is a WKB region, $(V(x) \gg \lambda)$. The wave function has the following form for region II:

$$\varphi(x) = A_{\mathrm{II}} D_\nu((x - b)(U_b''/\theta)^{1/2}) + B_{\mathrm{II}} D_\nu(-(x - b)(U_b''/\theta)^{1/2}) \qquad (12)$$

where $\nu = [\lambda - V(b)]/\theta U_b'' - 1/2 = \lambda/\theta U_b''$, and D_ν is a Weber function; and for region III

$$\varphi(x) = \left[\frac{\theta}{[V(x) - \lambda]^{1/2}}\right]^{1/2} \left(A_{\mathrm{III}} \exp\left\{\int_\beta^x \frac{dx'}{\theta} [V(x') - \lambda]^{1/2}\right\}\right.$$
$$\left. + B_{\mathrm{III}} \exp\left\{-\int_\beta^x \frac{dx'}{\theta} [V(x') - \lambda]^{1/2}\right\}\right) \qquad (13)$$

For small θ, regions II and III overlap in a domain where $(x - b)(U_b''/\theta)^{1/2} \gg 1$, so that one can use the asymptotic development of the D_ν, and where the phase integrals in Eq. (13) can be calculated with the quadratic expression (10) for V. As is shown in Appendix A, a comparison of the two resulting expressions for $\varphi(x)$ determines uniquely A_{III} and B_{III} in terms of A_{II} and B_{II}.

Note that, contrary to what is asserted in many textbooks, it is therefore possible, with this method, to determine, not only the coefficient A_{III} of the exponentially increasing function in the classically forbidden region III, but also that of the exponentially decreasing component. This is due to the fact that using the full asymptotic development (including exponentially small terms) of the Weber functions amounts to taking advantage of the full behavior of $\varphi(x)$ in the complex x plane around the turning point(s).[11] This matching procedure can be repeated in the vicinity of the three minima of potential V separately (since these minima are separated by "good" WKB regions). To build the wave function of an eigenstate, we start from region I, where only the increasing (for increasing x) WKB exponential is present; we perform these successive matchings and impose that the increasing WKB exponential be absent in region VII (Fig. 2). This condition, which determines the λ eigenvalues, reads

$$\frac{(2\pi)^{3/2}}{\Gamma(-\xi)\Gamma(-\nu)\Gamma(-\mu)}\left(\frac{e}{\xi+1/2}\right)^{\xi+1/2}\left(\frac{e}{\nu+1/2}\right)^{\nu+1/2}\left(\frac{e}{|\mu+1/2|}\right)^{\mu+1/2}$$
$$-\,e^{-2S_a(\lambda)}\cos\pi\xi\cos\pi\mu\,\frac{(2\pi)^{1/2}}{\Gamma(-\nu)}\left(\frac{e}{\nu+1/2}\right)^{\nu+1/2}$$
$$-\,e^{-2S_b(\lambda)}\cos\pi\nu\cos\pi\mu\,\frac{(2\pi)^{1/2}}{\Gamma(-\xi)}\left(\frac{e}{\xi+1/2}\right)^{\xi+1/2}$$
$$-\,e^{-2[S_a(\lambda)+S_b(\lambda)]}\cos\pi\xi\cos\pi\nu\sin^2\pi\mu\,\frac{\Gamma(-\mu)}{(2\pi)^{1/2}}\left(\frac{e}{|\mu+1/2|}\right)^{-(\mu+1/2)}=0 \tag{14}$$

where $\nu = \lambda/\theta U_b''$, $\mu = (\lambda/\theta|U_0''|) - 1$, $\xi = \lambda/\theta U_a''$, Γ is the Euler gamma function, and $S_b(\lambda)$ is defined by

$$S_b(\lambda) = \int_\beta^0 \frac{dx'}{\theta}\,[V(x') - \lambda]^{1/2}, \qquad \lambda < \theta|U_0''|/2$$
$$= \int_\beta^{-\epsilon} \frac{dx'}{\theta}\,[V(x') - \lambda]^{1/2}, \qquad \lambda > \theta|U_0''|/2 \tag{15}$$

where the classical turning points β and $-\epsilon$ are shown in Fig. 2, and $S_a(\lambda)$ is the corresponding quantity for the $x > 0$ part of potential V $\left(\int_\beta^0 \to \int_0^\alpha\right.$ and $\left.\int_\beta^{-\epsilon} \to \int_\epsilon^\alpha\right)$.

It is clear from Eq. (14) that, since $\exp[-2S_a(\lambda)]$ and $\exp[-2S_b(\lambda)]$ are small quantities, the solutions for λ will lie in the vicinity of the points where at least one of μ, ν, ξ is a positive integer or zero, i.e., obviously, in the vicinity of the harmonic energies given by Eq. (11).

3. KRAMER'S REGIME

As already mentioned, this regime corresponds to times $t \gg |U_i''|^{-1}$, i.e., it is determined by a knowledge of the first two levels of potential V, which result from the lifting of the degeneracy between the $(b, 0)$ and $(a, 0)$ harmonic levels due to the tunneling coupling.

Therefore they correspond, in Eq. (14), to ν and $\xi \simeq 0$ and $\mu \simeq -1$. One can first check directly that $\lambda = 0$ (i.e., $\nu = \xi = 0$, $\mu = -1$) is an exact solution of Eq. (14). That is, our approximation reproduces, as it should, the correct zero value for the lowest eigenvalue λ_0. The corresponding wavefunction φ_0, as given by our calculation, is of course the local approximation [Gaussian in the (a) and (b) wells] to the exact $\varphi_0 = C^{1/2}\exp[-U(x)/2\theta]$.

In order to calculate the eigenvalue λ_1 for the first excited level, we develop Eq. (14) up to second order in $\exp(-2S_a)$ and $\exp(-2S_b)$, which gives

$$\lambda_1 = (\theta/2\pi)[U_a'' e^{-2S_a(0)} + U_b'' e^{-2S_b(0)}] \tag{16}$$

The quantities $S_a(0)$ and $S_b(0)$ are calculated in Appendix B to be

$$S_i(0) = (\Delta U_i/2\theta) - \tfrac{1}{4}\log(|U_0''|/U_i'') \tag{17}$$

where $\Delta U_i = U(0) - U(i)$, $i = (a, b)$.

This gives for the inverse Kramers time

$$\frac{1}{\tau_1} = \frac{\lambda_1}{\theta} = \frac{1}{2\pi}[(U_a''|U_0''|)^{1/2} e^{-\Delta U_a/\theta} + (U_b''|U_0''|)^{1/2} e^{-\Delta U_b/\theta}] \tag{18}$$

Some comments about our expression for τ_1^{-1} may be useful:

(i) In the case of a symmetric bistable U, Eq. (18) reduces to

$$\frac{1}{\tau_1} = \frac{1}{\pi}(U_a''|U_0''|)^{1/2} e^{-\Delta U/\theta} \tag{19}$$

This is exactly the expression obtained using Kramers' method of resolution of his equation in the high-viscosity limit,[1,4] where it reduces to Eq. (1).

(ii) For an asymmetric U, the expression for τ_1 is completely symmetric with respect to the interchange $a \leftrightarrows b$. This is obviously related to the fact that, as appears from the general expression (7) for P, it is the single time τ_1 which characterizes, at long times, the escape of particles from well (a) to well (b) as well as the reverse process. The fact that τ_1^{-1} is the sum of two chemical activation rates for wells (a) and (b) is general: this result can be derived directly from the two phenomenological equations, valid in the Kramers regime

$$dn_a/dt = -n_a W_{a\to b} + n_b W_{b\to a}, \qquad dn_b/dt = n_a W_{a\to b} - n_b W_{b\to a} \tag{20}$$

where n_a and n_b are the numbers of particles in wells (a) and (b), and the W's are interwell transition probabilities. From Eq. (20) one gets

$$1/\tau_1 = W_{a\to b} + W_{b\to a} \tag{21}$$

which is equivalent to expression (18) is one chooses for the W's the values

$$W_{i\to j} = (1/2\pi)(U_i''|U_0''|)^{1/2} e^{-\Delta U_i/\theta} \tag{22}$$

which of course satisfy the detailed balance condition.

(iii) An analogous result for τ_1^{-1} has been obtained by Tomita *et al.*[3] However, their prefactor differs from that of Eq. (18) by a factor $2/\sqrt{\pi}$. We believe this discrepancy to result from the fact that they use the WKB form for $\varphi_1(x)$ in the quadratic region $x \simeq 0$, where it is not valid, instead of the Weber function expression.

4. THE INTERMEDIATE TIME REGIME

This regime, as has been seen in Section 2, corresponds to times $|U_i''|^{-1} \sim t \ll \tau_1$, so that it is determined by a knowledge of the excited levels (n) of potential V with λ values of order $p\theta|U_i''|$ (with, of course, $p\theta|U_i''| \ll V_m$, i.e., $p \ll \Delta U/\theta$). These states are those that derive from the approximate harmonic levels $\lambda_p^{(0)}$ with $p = 0, 1, 2,...$ and $\lambda_{p'}^{(a)}$, $\lambda_{p'}^{(b)}$ with $p' = 1, 2,...$, which energies are given by Eq. (11).

We consider here the case of a general bistable U with no particular symmetry, so that the harmonic states of interest are not systematically degenerate (we neglect the case of accidental degeneracy).

Let us call $\varphi_p^{(i)}(x)$ the eigenfunction of the state deriving from the (p, i) harmonic state. We can build $\varphi_p^{(i)}$, which has a large amplitude in well (i) only, by the same matching procedure that we used to build the fundamental and first excited states φ_0 and φ_1. The corresponding algebra is presented in Appendix C.

We are interested here in checking the scaling statement of Suzuki.[5] In order to compare our and his results, we must consider the case where the initial distribution is concentrated in the vicinity of the point of instability of U ($x_0 \simeq 0$), i.e., in the (0) well of potential V. Moreover, we will only study $P(xt|x_0)$ for $x < 0$ (the case $x > 0$ would be completely analogous).

It appears from the calculation (Appendix C) that, as expected, the λ eigenvalues corresponding to the $\varphi_p^{(i)}$ only differ from the harmonic values $\lambda_p^{(i)}$ given in Eq. (11) by exponentially small terms due to the tunneling among the three wells of V. For all levels with $\lambda_p^{(i)} \neq 0$ these differences can be neglected in the corresponding time exponentials of the development (7) of P, which can therefore be written, in this regime,

$$P(xt|x_0) = P_{\text{fin}}(xt|x_0) + \frac{\varphi_0(x)}{\varphi_0(x_0)}\left\{\sum_{p\geq 0} \varphi_p^{(0)}(x)\varphi_p^{(0)}(x_0)\exp[-(p+1)|U_0''|t] + \sum_{p\geq 1} \varphi_p^{(b)}(x)\varphi_p^{(b)}(x_0)\exp(-pU_b''t) + \sum_{p\geq 1} \varphi_p^{(a)}(x)\varphi_p^{(a)}(x_0)\exp(-pU_a''t)\right\} \quad (23)$$

The sums on p run on indices $p \ll \Delta U/\theta$ (the contribution of higher levels being negligible in this time range), and

$$P_{\text{fin}}(xt|x_0) = [\varphi_0(x)]^2 + \frac{\varphi_0(x)}{\varphi_0(x_0)} \varphi_1(x)\varphi_1(x_0)e^{-t/\tau_1} \tag{24}$$

and, since we are interested in times $t \ll \tau_1$,

$$P_{\text{fin}}(xt|x_0) \cong P_{\text{fin}}(x, t = 0|x_0) \tag{25}$$

is a time-independent quantity.

Since we consider $x_0 \simeq 0$, $x \lesssim 0$, the (a) sum on the rhs of Eq. (23) is negligible: indeed, $\varphi_p^{(a)}(x_0)$ [resp. $\varphi_p^{(a)}(x)$] is exponentially small as compared with $\varphi_p^{(0)}(x_0)$ [resp. $\varphi_p^{(0)}(x)$]. Their ratio is of order $\exp[-S_a(\lambda_p^{(a)})]$ where $i\theta S_a(\lambda_p^{(a)})$ is the classical action corresponding to the crossing of the forbidden region between wells (a) and (0).

Let us first consider the three following cases:

(*i*) *x in the* (0) *well of V:* The time dependence of P is entirely controlled by the sum corresponding to $\varphi_p^{(0)}$ states [the (b) sum in Eq. (23) is exponentially small compared with the (0) one]. In this region (see Appendix C), up to exponentially small errors,

$$\varphi_p^{(0)}(x) = (p!)^{-1/2}(|U_0''|/2\pi\theta)^{1/4}D_p(x(|U_0''|/\theta)^{1/2}), \qquad \lambda_p^{(0)} = (p+1)\theta|U_0''| \tag{26}$$

so that

$$P(xt|x_0) \cong P_{\text{fin}}(x, t = 0|x_0) + \frac{\varphi_0(x)}{\varphi_0(x_0)}\left(\frac{|U_0''|}{2\pi\theta}\right)^{1/2} \times F^{(0)}\left(x\left(\frac{|U_0''|}{\theta}\right)^{1/2}, x_0\left(\frac{|U_0''|}{\theta}\right)^{1/2}, \exp[-t|U_0''|]\right) \tag{27}$$

where

$$F^{(0)}(y, z, \exp[-t|U_0''|]) = \sum_{p\geqslant 0} \frac{1}{p!} D_p(y)D_p(z)[\exp(-t|U_0''|)]^{p+1} \tag{28}$$

Note that P_{fin} also contains a normalization factor proportional to $\theta^{-1/2}$ (since, to lowest order, both φ_0 and φ_1 are combinations of Gaussians of widths proportional to $\theta^{1/2}$).

(*ii*) *x in the* (b) *well of V:* In this region, the two (0) and (b) sums on the rhs of Eq. (23) give comparable contributions, since each term contains one exponentially small factor. The successive matching procedure (Appendix C) gives, for $x \simeq b$,

$$\varphi_p^{(0)}(x) = \Lambda_p D_{\nu(p)}[(x - b)(U_b''/\theta)^{1/2}] \tag{29}$$

where $\nu(p) = (p + 1)|U_0''|/U_b''$ is a noninteger since we exclude accidental degeneracy, and

$$\Lambda_p = (-)^p (p!)^{-1/2} \left(\frac{|U_0''|}{2\pi\theta}\right)^{1/4} \frac{\Gamma(-\nu(p))}{(2\pi)^{1/2}} \left(\frac{|U_0''|}{U_b''}\right)^{1/2} \left(\frac{U_b''(x_m - a)^2}{\theta}\right)^{\nu(p)/2} \times \left(\frac{|U_0''|x_m^2}{\theta}\right)^{(p+1)/2} \exp\left\{-\frac{\Delta U_b}{2\theta} - (p + 1)|U_0''|\delta\right\} \tag{30}$$

x_m is the point at which V reaches its local maximum V_m in the $x < 0$ region, and δ is a geometrical parameter which characterizes the local anharmonicity of potential U:

$$\delta = -\int_b^{x_m} dx \left(\frac{1}{U'(x)} - \frac{1}{(x - b)U_b''}\right) - \int_{x_m}^0 dx \left(\frac{1}{U'(x)} - \frac{1}{xU_0''}\right) \tag{31}$$

In the same way, we find, for x in the (b) quasiharmonic region, and with $\lambda_p^{(b)} = p\theta U_b''$,

$$\varphi_p^{(b)}(x \simeq b) = (p!)^{-1/2}(U_b''/2\pi\theta)^{1/4} D_p((x - b)(U_b''/\theta)^{1/2}) \tag{32}$$

which is continued, for x in the (0) quasiharmonic region, by

$$\varphi_p^{(b)}(x \simeq 0) = (p!)^{-1/2} \left(\frac{U_b''}{2\pi\theta}\right)^{1/4} \frac{\Gamma(-\mu(p))}{(2\pi)^{1/2}} \left(\frac{U_b''(x_m - b)^2}{\theta}\right)^{p/2} \left(\frac{|U_0|x_m^2}{\theta}\right)^{[\mu(p)+1]/2} \times \left\{\exp\left(-\frac{\Delta U_b}{2\theta} - pU_b''\delta\right)\right\} D_{\mu(p)}\left(x\left(\frac{|U_0''|}{\theta}\right)^{1/2}\right) \tag{33}$$

and $\mu(p) = (pU_b''/|U_0''|) - 1$.

So, finally, we can write

$$P(xt|x_0) = P_{\text{fin}}(x, t = 0|x_0) + \frac{\varphi_0(x)}{\varphi_0(x_0)} \left(\frac{U_b''}{2\pi\theta}\right)^{1/2} e^{-\Delta U_b/2\theta} \times \left\{\phi^{(0)}\left(x_0\left(\frac{|U_0''|}{\theta}\right)^{1/2}, (x - b)\left(\frac{U_b}{\theta}\right)^{1/2}, \tau_b\right) + \phi^{(b)}\left(x_0\left(\frac{|U_0''|}{\theta}\right)^{1/2}, (x - b)\left(\frac{U_b''}{\theta}\right)^{1/2}, \tau_b'\right)\right\} \tag{34}$$

where

$$\phi^{(0)}(y, z, \tau_b) = \frac{|U_0''|}{U_b''} \sum_{p \geq 0} \frac{(-)^p}{p!} \frac{\Gamma(-\nu(p))}{(2\pi)^{1/2}} D_p(y) D_{\nu(p)}(-z) \tau_b^{-(p+1)/2} \tag{35}$$

$$\phi^{(b)}(y, z, \tau_b') = \sum_{p \geq 1} \frac{1}{p!} \frac{\Gamma(-\mu(p))}{(2\pi)^{1/2}} D_{\mu(p)}(y) D_p(z) (\tau_b')^{-p/2} \tag{36}$$

and the time variables τ_b, τ_b' are defined by

$$\tau_b = \left(\frac{\theta}{|U_0''|x_m^2}\right)\left(\frac{\theta}{U_b''(x_m - b)^2}\right)^{|U_0''|/U_b''} e^{2(t+\delta)|U_0''|} \tag{37}$$

$$\tau_b' = \left(\frac{\theta}{|U_0''|x_m^2}\right)^{U_b''/|U_0''|}\left(\frac{\theta}{U_b''(x_m - b)^2}\right) e^{2(t+\delta)U_b''} = (\tau_b)^{U_b''/|U_0''|} \tag{38}$$

So, $\phi^{(0)} + \phi^{(b)}$ can be rewritten as a function $H(y, z, \tau_b)$ of the unique time variable τ_b given by Eq. (37).

(iii) x in the WKB region between wells (0) *and* (b)*:* Coming back to expression (23) for P, one can notice that the contribution $P^{(0)}$ of the $\varphi_p^{(0)}$ terms spreads everywhere between the (b) and (a) wells: indeed, the exponential decrease of $\varphi_0(x)$ when going from, e.g., well (b) to well (0) is compensated by the exponential increase of $\varphi_p^{(0)}$. Moreover, for $x_0 \simeq 0$, $\varphi_p^{(0)}(x_0)/\varphi_0(x_0) \sim \exp(\Delta U/2\theta)$, while $\varphi_p^{(0)}(x)\varphi_0(x) \sim \exp(-\Delta U/2\theta)$ (for all $b \leqslant x \leqslant a$).

On the other hand, $\varphi_p^{(b)}(x_0)/\varphi_0(x_0) \sim 1$, while $\varphi_p^{(b)}(x)\varphi_0(x)$ is of order 1 [as far as powers of $\exp(\Delta U/2\theta)$ are concerned] in the (b) well, and of order $\exp(-\Delta U/\theta)$ for $x \simeq 0$.

So, the contribution $P^{(b)}$ to P of the $\varphi_p^{(b)}$ terms is essentially concentrated, as well as P_{fin}, in the vicinity of point b. Therefore, in the WKB region,

$$P_{\text{WKB}}(xt\,|\,x_0) \simeq P^{(0)}(xt\,|\,x_0) = \frac{\varphi_0(x)}{\varphi_0(x_0)} \sum_{p \geqslant 0} \varphi_p^{(0)}(x)\varphi_p^{(0)}(x_0) \exp[-(p+1)t\,|U_0''|] \tag{39}$$

Using the technique explained in Appendix C, we find in this region

$$\varphi_p^{(0)}(x) = (-)^p c_p^{(0)} \left(\frac{|U_0''|}{4\theta}\right)^{1/4} \frac{(2\theta|U_0''x|)^{1/2}}{U'(x)} \left(\frac{x^2|U_0''|}{\theta}\right)^{(1/2)(p+1/2)} \times \exp\frac{U(x) - U(x_0)}{2\theta} \exp(-(p+1)\delta'(x)|U_0''|) \tag{40}$$

with

$$\delta'(x) = \int_x^0 dx' \left(\frac{1}{x'U_0''} - \frac{1}{U'(x')}\right) \tag{41}$$

From this, we get

$$P_{\text{WKB}}(xt\,|\,x_0) \cong \frac{|U_0''|}{(2\pi)^{1/2}U'(x)} \sum_{p \geqslant 0} \frac{(-)^p}{p!} D_p\left(x_0\left(\frac{|U_0''|}{\theta}\right)^{1/2}\right) \times \left\{\left(\frac{|U_0''|b^2}{\theta}\right)^{1/2} \exp(-t\,|U_0''|)\right\}^{p+1} \times \left\{\left|\frac{x}{b}\right| \exp[-|U_0''|\delta'(x)]\right\}^{p+1} \tag{42}$$

It is clear from this expression that, in the WKB region for x, the true time variable is the quantity

$$\tau = (\theta / U_0''|b^2) \exp(2t|U_0''|) \tag{43}$$

i.e., as shown by Suzuki,[5] in that region, where the drift effect dominates over the diffusion one, there is a true "time scaling" of P, in terms of the dimensionless time variable τ, which is exactly Suzuki's variable.

The p sum in Eq. (42) can be performed exactly (since, in the present time regime, it can be extended up to $p \to \infty$ with a negligible error). In order to simplify the resulting expression, we choose, following Suzuki, $x_0 = 0$, and get

$$P_{\text{WKB}}(xt|0) \cong \frac{\exp[-|U_0''|\delta'(x)]}{(2\pi\tau)^{1/2}} \frac{|U_0'' x|}{bU'(x)} \exp\left\{-\frac{x^2}{2b^2\tau} \exp[-2|U_0''|\delta'(x)]\right\} \tag{44}$$

In the particular case of the quartic potential $U(x) = -\frac{1}{2}\gamma x^2(1 - \frac{1}{2}x^2)$, where

$$\delta'(x) = (1/2\gamma) \log|1 - x^2| \tag{45}$$

this becomes

$$P_{\text{WKB}}^{(\text{Qu})}(xt|0) \cong \frac{1}{(2\pi\tau)^{1/2}(1 - x^2)^{3/2}} \exp - \frac{x^2}{2\tau(1 - x^2)} \tag{46}$$

i.e., exactly the "scaling distribution" found by Suzuki for this potential.

Let us, however, insist that the above results [Eqs. (42)–(46)] only hold in the region where the WKB approximation is valid (i.e., in the region where the drift force is dominant). They break down for x in the close vicinity of the extrema of U, as can be seen from both Eq. (28) and Eqs. (34)–(36).

For $x_0 = 0$ [or $|x_0| \leqslant (\theta/|U_0''|)^{1/2}$] and $|x| \leqslant (\theta/|U_0''|)^{1/2}$, P is given by Eqs. (27)–(28) with y and z of order 1, so that the characteristic time is clearly, in that region, of order $|U_0''|^{-1}$, i.e., much smaller than Suzuki's time t_0 [Eq. (2b)].

For $|x_0| \leqslant (\theta/|U_0''|)^{1/2}$ and $|x - b| \leqslant (\theta/U_b'')^{1/2}$, P is given by Eqs. (34)–(36), where, again, y and z are of order 1, and the characteristic time scale t_b is given by $\tau_b = 1$, where τ_b is given by Eq. (37), i.e., is proportional to $\theta^{1+|U_0''|/U_b''}$, while Suzuki's variable τ is proportional to θ. So, it is seen that the characteristic time t_b is always larger than t_0, although both lie in the same intermediate time domain.

Therefore, Suzuki's result will be a good approximation for P as long as the part of the distribution that lies in the vicinity of b and on the left of it $[x - b \leqslant (\theta/U_b'')^{1/2}]$ remains negligible. This can be estimated by calculating the weight of that part of the distribution lying between $x \sim 0$ and $x = b + \alpha$, where $\alpha \gtrsim (\theta/U_b'')^{1/2}$, in which region P is Suzuki's distribution (44).

Setting

$$u^2 = (x^2/2b^2\tau)\exp[-2|U_0''|\delta'(x)] \tag{47}$$

we obtain from Eq. (44)

$$P_{\text{WKB}}(xt|0)\,dx = (1/\sqrt{\pi})\exp(-u^2)\,du \tag{48}$$

i.e., one can notice that, in the Suzuki regime, the true scaling variable, in terms of which P has a universal Gaussian form, is u, and not, separately, τ and x.

On the other hand, from Eq. (41)

$$\delta'(b+\alpha) \cong -(1/U_b'')\log(b/\alpha) \tag{49}$$

so that

$$\int_{b+\alpha}^{\infty} dx\,P(xt|0) \cong \frac{1}{2} - \frac{1}{\sqrt{\pi}}\operatorname{erfc}\left[\frac{1}{(2\tau)^{1/2}}\left(\frac{b}{\alpha}\right)^{|U_0''|/U_b''}\right] \tag{50}$$

So, as long as

$$\tau \ll (b/\alpha)^{2|U_0''|/U_b''} \lessgtr (b^2U_b''/\theta)^{|U_0''|/U_b''}$$

the WKB region contains practically all the weight of P, and it can be concluded that Suzuki's statement, as generalized by Eqs. (44) and (47)–(48), is essentially exact.

This breaks down when $\tau \gtrsim (b^2U_b''/\theta)^{|U_0''|/U_b''}$, or, equivalently, when $\tau_b \simeq 1$. This corresponds, in the intermediate time regime, to the time domain where the peaks of the Suzuki distribution enter the diffusive region around the minima of U. For $\tau_b \simeq 1$, the shape of the peaks of P should therefore be calculated numerically from the full expression (34)–(36).

Note that this discrepancy with Suzuki's prediction should not show up very much in a calculation of the second moment of P around $x = 0$, $\langle x^2\rangle$, since, for $\tau_b \simeq 1$, the distribution already exhibits rather well-defined peaks around the minima. A better test would be to calculate $\langle(x-b)^2\rangle$ for the $x < 0$ part of P.

Finally, it can therefore be concluded that Suzuki's prediction correctly describes the evolution of P in the first part of the intermediate time domain, in which the distribution leaves the $x = 0$ diffusive region, with a characteristic time

$$t_0 \simeq (1/2|U_0''|)\log(|U_0''|b^2/\theta)$$

The drift region is then passed relatively rapidly; then, in the second part of the intermediate time domain, P enters a new diffusive region [$x \simeq b$ (or a)], with a characteristic time

$$t_0' \simeq (1/2U_b'')\log(U_b''b^2/\theta)$$

The total time scale t_b for obtaining peaks of width comparable with that at equilibrium around b is

$$t_b = t_0 + t_0'$$

which corresponds to $\tau_b \simeq 1$.

The order of magnitude of t_0 and t_0' is precisely the same as the time needed for a distribution starting from a finite distance [of order $(\theta/U'')^0$] from the minimum of a harmonic potential to build the equilibrium shape in the vicinity [of order $(\theta/U'')^{1/2}$] of that minimum.

APPENDIX A

We want to calculate the first two eigensolutions of the equation

$$-\theta^2\, d^2\varphi/dx^2 + V(x)\varphi(x) = \lambda\varphi(x) \tag{A1}$$

where

$$V(x) = \tfrac{1}{4}[U'(x)]^2 - \tfrac{1}{2}\theta U''(x) \tag{A2}$$

is depicted in Fig. 2. We know that the two lowest eigenvalues λ_0 and λ_1 will be exponentially close to the lowest harmonic eigenvalue: $\lambda_0^{(b)} = \lambda_0^{(a)} = 0$. So, we have $\lambda_0, \lambda_1 < V(0) = \tfrac{1}{2}\theta|U_0''|$.

In order to build $\varphi(x)$, we start from the WKB region I (see Fig. 2), where

$$\varphi_{\mathrm{I}}(x) = K_{\mathrm{I}}\left[\frac{\theta}{[V(x)-\lambda]^{1/2}}\right]^{1/2} \exp\left\{\int_{\beta'}^{x} \frac{dx'}{\theta}\, [V(x') - \lambda]^{1/2}\right\} \tag{A3}$$

β' is the turning point on the left of b, and K_{I} will be calculated from the normalization condition.

We want to match expression (A3) with the solution of (A1) in the quadratic (b) region II, which is

$$\varphi_{\mathrm{II}}(x) = K_{\mathrm{II}} D_\nu(-y_b) + K_{\mathrm{II}}' D_\nu(y_b) \tag{A4}$$

with $\nu = \lambda/\theta U_b''$ and $y_b = (x-b)(U_b''/\theta)^{1/2}$. The D_ν are Weber functions. In the matching domain, where regions I and II overlap, V is still quasiharmonic, and expression (A3) can be calculated with

$$V = -\tfrac{1}{2}\theta U_b'' + \tfrac{1}{4}(U_b'')^2(x-b)^2, \qquad (\beta' - b)^2 = (2\theta/U_b'')(2\nu + 1) \tag{A5}$$

Using

$$\frac{1}{\theta}\int_{\beta'}^{x} dx'\, [V(x') - \lambda]^{1/2} = -\frac{(x-b)^2 U_b''}{4\theta} + (\nu + \tfrac{1}{2}) \log\left|(x-b)\left(\frac{U_b''}{\theta}\right)^{1/2}\right| + \tfrac{1}{2}(\nu + \tfrac{1}{2}) \log\left(\frac{e}{\nu + \frac{1}{2}}\right) + O(\theta) \tag{A6}$$

we obtain [since $V(x) \gg \lambda$]

$$\varphi_{\mathrm{I}} \cong K_{\mathrm{I}}\left(\frac{4\theta}{U_b''}\right)^{1/4}\left(\frac{e}{\nu+\frac{1}{2}}\right)^{(1/2)(\nu+1/2)}|y_b|^{\nu}\exp\left(-\frac{y_b{}^2}{4}\right) \tag{A7}$$

In the matching region, $y_b \gg 1$, so that we can use in Eq. (A4) the complete asymptotic development of the Weber functions[10] for y real

$$\begin{aligned} D_\nu(|y|) &\cong e^{-y^2/4}|y|^\nu[1 + O(y^{-2})] \\ D_\nu(-|y|) &\cong e^{y^2/4}|y|^{-\nu-1}[(2\pi)^{1/2}/\Gamma(-\nu)][1 + O(y^{-2})] \\ &\quad + e^{-y^2/4}|y|^\nu \cos\nu\pi\,[1 + O(y^{-2})] \end{aligned} \tag{A8}$$

Inserting (A8) into (A4) and comparing with (A7), we obtain

$$K_{\mathrm{II}} = K_{\mathrm{I}}\left(\frac{4\theta}{U_b''}\right)^{1/4}\left(\frac{e}{\nu+\frac{1}{2}}\right)^{(1/2)(\nu+1/2)}, \qquad K_{\mathrm{II}}' = 0 \tag{A9}$$

We must now match $\varphi_{\mathrm{II}}(x)$ with the WKB expression

$$\begin{aligned} \varphi_{\mathrm{III}}(x) = \left[\frac{\theta}{[V(x)-\lambda]^{1/2}}\right]^{1/2}\Bigg(&K_{\mathrm{III}}\exp\left\{\int_\beta^x \frac{dx'}{\theta}[V(x')-\lambda]^{1/2}\right\} \\ &+ K_{\mathrm{III}}'\exp\left\{-\int_\beta^x \frac{dx'}{\theta}[V(x')-\lambda]^{1/2}\right\}\Bigg) \end{aligned} \tag{A10}$$

The same procedure as above [calculate the integral in (A10) in the quadratic approximation, develop φ_{II} with the help of (A8)] can be used again, and gives

$$K_{\mathrm{III}} = K_{\mathrm{I}}\frac{(2\pi)^{1/2}}{\Gamma(-\nu)}\left(\frac{e}{\nu+\frac{1}{2}}\right)^{\nu+1/2}, \qquad K_{\mathrm{III}}' = K_{\mathrm{I}}\cos\nu\pi \tag{A11}$$

We can rewrite φ_{III} as

$$\begin{aligned} \varphi_{\mathrm{III}}(x) = \left[\frac{\theta}{[V(x)-\lambda]^{1/2}}\right]^{1/2}\Bigg(&K_{\mathrm{III}}\exp[S_b(\lambda)]\exp\left\{-\int_0^x \frac{dx'}{\theta}[V(x')-\lambda]^{1/2}\right\} \\ &+ K_{\mathrm{III}}'\exp[-S_b(\lambda)]\exp\left\{\int_0^x \frac{dx'}{\theta}[V(x')-\lambda]^{1/2}\right\}\Bigg) \end{aligned} \tag{A12}$$

with

$$S_b(\lambda) = \int_\beta^0 \frac{dx'}{\theta}[V(x')-\lambda]^{1/2}, \qquad \lambda < V(0) \tag{A13}$$

This we must match with the solution in the quadratic (0) region

$$\varphi_{\mathrm{IV}}(x) = K_{\mathrm{IV}}D_\mu(-y) + K_{\mathrm{IV}}'D_\mu(y) \tag{A14}$$

where $y = x(|U_0''|/\theta)^{1/2}$, and $\mu = (\lambda/\theta|U_0''|) - 1$.

Repeating once more the matching procedure, we get

$$K_{\mathrm{IV}} = K_{\mathrm{I}}\left(\frac{4\theta}{|U_0''|}\right)^{1/4}\frac{\Gamma(-\mu)}{(2\pi)^{1/2}}\left(\frac{|\mu+\frac{1}{2}|}{e}\right)^{(1/2)(\mu+1/2)}\cos\nu\pi\, e^{-S_b(\lambda)}$$

$$K_{\mathrm{IV}}' = K_{\mathrm{I}}\left(\frac{4\theta}{|U_0''|}\right)^{1/4}\left\{\frac{(2\pi)^{1/2}}{\Gamma(-\nu)}\left(\frac{e}{\nu+\frac{1}{2}}\right)^{\nu+1/2}\left(\frac{e}{|\mu+\frac{1}{2}|}\right)^{(1/2)(\mu+1/2)}e^{S_b(\lambda)}\right. \qquad \text{(A15)}$$

$$\left. - \frac{\Gamma(-\mu)}{(2\pi)^{1/2}}\left(\frac{|\mu+\frac{1}{2}|}{e}\right)^{(1/2)(\mu+1/2)}\cos\mu\pi\cos\nu\pi\, e^{-S_b(\lambda)}\right\}$$

where we have taken into account the fact that, for the states of interest here, $\mu \simeq -1$, i.e., $\mu + 1/2 < 0$.

These matchings can be repeated until the WKB region VII on the right side of well (a), where one must impose that the coefficient of the increasing WKB solution be zero. This gives the condition which determines the eigenvalues λ as

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

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

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

$$- e^{-2[S_a(\lambda)+S_b(\lambda)]}\cos\pi\xi\cos\pi\nu\sin^2\pi\mu\frac{\Gamma(-\mu)}{(2\pi)^{1/2}}\left(\frac{|\mu+\frac{1}{2}|}{e}\right)^{\mu+1/2} = 0 \quad \text{(A16)}$$

where $\xi = \lambda/\theta U_a''$.

We look for the two solutions of (A16) with $\lambda/\theta|U_i''| \ll 1$. One can first notice by mere inspection that, since $[\Gamma(0)]^{-1} = 0$, $\lambda_0 = 0$, which corresponds to $\nu = \xi = 0$, $\mu = -1$, is an exact solution of (A16). In order to find λ_1, we develop the equation up to second order in $\exp(-2S_a)$ or $\exp(-2S_b)$ (knowing that λ_1 is of that same order of magnitude). With the help of the development $[\Gamma(-\epsilon)]^{-1} = -\epsilon + O(\epsilon^2)$, this gives

$$\lambda_1 = (\theta/2\pi)(U_a''e^{-2S_a(0)} + U_b''e^{-2S_b(0)})] \qquad \text{(A17)}$$

One easily checks that φ_0 is proportional to $\exp[-U(x)/2\theta]$, up to exponentially small errors. In order to normalize φ_0, we approximate it by

$$\varphi_{0,\mathrm{II}}(x) + \varphi_{0,\mathrm{VI}}(x) = C^{1/2}\{e^{-U(b)/2\theta}D_0(y_b) + e^{-U(a)/2\theta}D_0(y_a)\} \quad \text{(A18)}$$

where $C^{1/2}$ is related to $K_{\mathrm{I},0}$ [Eq. (A3)] by $C^{1/2} = K_{\mathrm{I},0}(8e\theta/U_b'')^{1/4}$. Expression (A18) is simply the sum of the Gaussian developments of $\exp(-U/2\theta)$ around the minima of U. This approximation is sufficient to calculate the normalization coefficient up to exponentially small errors. We get

$$C \cong (2\pi\theta)^{-1/2}[(U_b'')^{-1/2}e^{-U(b)/\theta} + (U_a'')^{-1/2}e^{-U(a)/\theta}]^{-1} \tag{A19}$$

When we calculate φ_1, we found that in region II

$$\varphi_{1,\mathrm{II}}(x) = K_{1,\mathrm{I}}(4\theta/U_b'')^{1/4}(2e)^{1/4}D_{\nu_1}(-y_b) \tag{A20}$$

with $\nu_1 = \lambda_1/\theta U_b''$, and an analogous expression involving $D_{\nu_1}(y_a)$ in well (a). In view of the divergent asymptotic behavior of $D_{\nu_1}(-y)$ for $y \gg 1$ [Eq. (A8)], it is seen that we cannot simply approximate in the whole space φ_1 by $\varphi_{1,\mathrm{II}} + \varphi_{1,\mathrm{VI}}$. However, since ν_1 is exponentially small, it can be shown that, in the quadratic (b) region II, $D_{\nu_1}(-y_b)$ is equal, up to exponentially small terms, to $D_0(-y_b)$. This can easily be checked, for $y_b \gg 1$, on the second equation (A8), where it appears that the increasing term is much smaller than the decreasing one in region II. Since φ_1 is exponentially small outside regions II and VI, we can safely calculate the normalization coefficient of φ_1 with the approximate expression

$$\varphi_1(x) \cong \alpha D_0(y_b) + \beta D_0(y_a) \tag{A21}$$

This gives

$$\alpha = C^{1/2}e^{-U(a)/2\theta}(U_b''/U_a'')^{1/4}, \qquad \beta = -C^{1/2}e^{-U(b)/2\theta}(U_a''/U_b'')^{1/4} \tag{A22}$$

that is,

$$K_{1,\mathrm{I}} = (U_b''/8e\theta)^{1/4}C^{1/2}e^{-U(a)/2\theta}(U_b''/U_a'')^{1/4} \tag{A23}$$

APPENDIX B

We want to calculate

$$S_b(0) = (1/\theta)\int_{\beta_0}^{0} dx'\, [V(x')]^{1/2} \tag{B1}$$

where $(\beta_0 - b)^2 = 2\theta/U_b''$.

Let ξ and η be two cutoffs situated in the overlap domain between regions II and III and regions III and IV, respectively, i.e., $\beta_0 < \xi < \eta < 0$. Now, ξ (resp. η) lies in the (b) [resp. (0)] quadratic region, i.e.,

$$\begin{aligned} V(x) &\cong -\tfrac{1}{2}\theta U_b'' + \tfrac{1}{4}(U_b'')^2(x-b)^2 \qquad &&\text{for} \quad \beta_0 \leqslant x \leqslant \xi \\ V(x) &\cong \tfrac{1}{2}\theta|U_0''| + \tfrac{1}{4}(U_0'')^2x^2 &&\text{for} \quad \eta \leqslant x \leqslant 0 \end{aligned} \tag{B2}$$

and

$$(U')^2 \gg \theta U'' \qquad \text{for} \quad \xi \leqslant x \leqslant \eta$$

so that

$$[V(x)]^{1/2} \cong \tfrac{1}{2}U'(x)\{1 - \theta U''(x)/[U'(x)]^2\} \tag{B3}$$

in that region.

We can split $S_b(0)$ into three integrals:

$$S_b(0) = I_1 + I_2 + I_3 \tag{B4}$$

with

$$I_1 \cong \frac{1}{\theta}\int_{\beta_0}^{\xi} dx \left\{-\frac{\theta U_b''}{2} + \frac{(U_b'')^2}{4}(x-b)^2\right\}^{1/2}$$

$$= \frac{1}{2}\left(\frac{\xi - b}{\beta_0 - b}\right)^2 - \frac{1}{4} - \frac{1}{2}\log\left|\frac{2(\xi - b)}{\beta_0 - b}\right| \tag{B5}$$

$$I_2 \cong \frac{1}{\theta}\int_{\eta}^{0} dx \left(\frac{\theta|U_0''|}{2} + \frac{(U_0'')^2}{4}x^2\right)^{1/2}$$

$$= \frac{\eta^2|U_0''|}{4\theta} + \frac{1}{4} - \frac{1}{2}\log\left|\frac{1}{2\eta}\left(\frac{2\theta}{|U_0''|}\right)^{1/2}\right| \tag{B6}$$

and

$$I_3 \cong \frac{1}{\theta}\int_{\xi}^{\eta} dx \left\{\frac{U'(x)}{2} - \frac{\theta}{2}\frac{U''(x)}{U'(x)}\right\}$$

$$= \frac{1}{2\theta}[U(\eta) - U(\xi)] - \frac{1}{2}\log\left|\frac{U'(\eta)}{U'(\xi)}\right| \tag{B7}$$

For $x \simeq \eta$ and $x \simeq \xi$, U (as well as V) may be considered as quasiquadratic:

$$U(\eta) = U(0) + \tfrac{1}{2}U_0''\eta^2 + \cdots, \qquad U(\xi) = U(b) + \tfrac{1}{2}U_b''(\xi - b)^2 + \cdots \tag{B8}$$

Inserting Eqs. (B5)–(B8) into (B4), we find

$$S_b(0) = \frac{U(0) - U(b)}{2\theta} - \frac{1}{4}\log\frac{|U_0''|}{U_b''} \tag{B9}$$

$S_a(0)$ is calculated by the same technique to be

$$S_a(0) = \frac{U(0) - U(a)}{2\theta} - \frac{1}{4}\log\frac{|U_0''|}{U_a''} \tag{B10}$$

APPENDIX C

We want to calculate here the wave functions $\varphi_p^{(0)}(x)$ ($p \geqslant 0$) and $\varphi_p^{(b)}(x)$ ($p \geqslant 1$) and the λ values of the eigenstates of potential V which derive from the approximate harmonic levels $\lambda_p^{(0)} = (p + 1)\theta|U_0''|$ and $\lambda_p^{(b)} = p\theta U_b''$. Since we only consider here the case where $\lambda_p^{(0)}$, $\lambda_{p'}^{(a)}$, and $\lambda_{p''}^{(b)}$ are nondegenerate, these states are essentially localized in wells (0) and (b). Among them, those with λ values larger than $V(0)$ have six real, classical turning points (instead of four real ones for, e.g., states φ_0 and φ_1).

We build the wave functions by the same matching method that we used in Appendix A for φ_0 and φ_1. It is found that the wave functions are always given by the same expressions as those found for $\lambda < V(0)$ [Eqs. (A3)–(A4), (A9)–(A11), and (A14)–(A15)], where now $S_b(\lambda)$ is defined by

$$S_b(\lambda) = \int_\beta^{-\epsilon} \frac{dx}{\theta}\,[V(x) - \lambda]^{1/2} \qquad \text{for} \quad \lambda > V(0)$$
$$= \int_\beta^{0} \frac{dx}{\theta}\,[V(x) - \lambda]^{1/2}. \qquad \text{for} \quad \lambda < V(0) \tag{C1}$$

The quantification condition therefore keeps the form (A16). The $\varphi_p^{(0)}$ states correspond to solutions with μ close to a positive integer or zero and noninteger ν and ξ, while the $\varphi_p^{(b)}$ states have ν close to a positive integer, μ and ξ nonintegers. The corresponding shifts of the λ values with respect to the $\lambda_p^{(i)}$ are found to be of order $\exp[-2S(\lambda_p^{(i)})]$.

From this, one easily checks that the normalization coefficient can be calculated (as explained in Appendix A in the case of φ_1) in the approximation

$$\varphi_p^{(i)}(x) \simeq K D_p(y_i) \tag{C2}$$

This finally gives, in the regions of interest for checking Suzuki's scaling statement,

$$\varphi_{p,\mathrm{II}}^{(0)}(x) = (-)^p c_p^{(0)} \left(\frac{|U_0''|}{U_b''}\right)^{1/4} \frac{\Gamma(-\nu)}{(2\pi)^{1/2}} \left(\frac{\nu+\frac{1}{2}}{e}\right)^{(1/2)(\nu+1/2)} \left(\frac{p+\frac{1}{2}}{e}\right)^{(1/2)(p+1/2)}$$
$$\times \{\exp[-S_b(\lambda_p^{(0)})]\} D_\nu(-y_b) \tag{C3}$$

$$\varphi_{p,\mathrm{III}}^{(0)}(x) = (-)^p c_p^{(0)} \left(\frac{|U_0''|}{4\theta}\right)^{1/4} \left(\frac{p+\frac{1}{2}}{e}\right)^{(1/2)(p+1/2)}$$
$$\times \{\exp[-S_b(\lambda_p^{(0)})]\} \left[\frac{\theta}{[V(x) - \lambda_p^{(0)}]^{1/2}}\right]^{1/2}$$
$$\times \left(\exp\left\{\int_\beta^x \frac{dx'}{\theta}\,[V(x') - \lambda_p^{(0)}]^{1/2}\right\} + \frac{\Gamma(-\nu)}{(2\pi)^{1/2}} \left(\frac{\nu+\frac{1}{2}}{e}\right)^{\nu+1/2} \cos \nu\pi\right.$$
$$\left.\times \exp\left\{-\int_\beta^x \frac{dx'}{\theta}\,[V(x') - \lambda_p^{(0)}]^{1/2}\right\}\right) \tag{C4}$$

$$\varphi_{p,\mathrm{IV}}^{(0)}(x) = c_p^{(0)} D_p(y) \tag{C5}$$

where $\nu \equiv \nu(p) = (p + 1)|U_0''|/U_b''$, $c_p^{(0)} = (p!)^{-1/2}(|U_0''|/2\pi\theta)^{1/4}$, and, for states localized in well (b),

$$\varphi_{p,\mathrm{II}}^{(b)}(x) = c_p^{(b)} D_p(y_b) \tag{C6}$$

$$\begin{aligned}\varphi_{p,\mathrm{III}}^{(b)}(x) = c_p^{(b)}\left(\frac{U_b''}{4\theta}\right)^{1/4}\left(\frac{p+\frac{1}{2}}{e}\right)^{(1/2)(p+1/2)}\left[\frac{\theta}{[V(x)-\lambda_p^{(b)}]^{1/2}}\right]^{1/2} \\ \times\left(\exp-\int_\beta^x \frac{dx'}{\theta}[V(x')-\lambda_p^{(b)}]^{1/2}\right\} \\ + \cos\mu\pi \exp[-2S_b(\lambda_p^{(b)})]\frac{\Gamma(-\mu)}{(2\pi)^{1/2}} \\ \times\left(\frac{|\mu+\frac{1}{2}|}{e}\right)^{\mu+1/2}\exp\left\{\int_\beta^x \frac{dx'}{\theta}[V(x')-\lambda_p^{(b)}]^{1/2}\right\}\Bigg)\end{aligned} \tag{C7}$$

$$\begin{aligned}\varphi_{p,\mathrm{IV}}^{(b)}(x) = c_p^{(b)}\left(\frac{U_b''}{|U_0''|}\right)^{1/4}\frac{\Gamma(-\mu)}{(2\pi)^{1/2}}\left(\frac{|\mu+\frac{1}{2}|}{e}\right)^{(1/2)(\mu+1/2)}\left(\frac{p+\frac{1}{2}}{e}\right)^{(1/2)(p+1/2)} \\ \times\{\exp[-S_b(\lambda_p^{(b)})]\}D_\mu(y)\end{aligned} \tag{C8}$$

where $\mu \equiv \mu(p) = (pU_b''/|U_0''|) - 1$ and $c_p^{(b)} = (p!)^{-1/2}(U_b''/2\pi\theta)^{1/4}$.

In order to calculate $S_b(\lambda)$, we proceed as in Appendix B. Let us as an example give the details of the algebra for the case $\lambda > V(0)$. We introduce again the two cutoffs ξ and η defined in Appendix B. We split $S_b(\lambda)$ into

$$S_b(\lambda) = I_1 + I_2 + I_3 \tag{C9}$$

with

$$\begin{aligned}I_1 &\cong \int_\beta^\xi \frac{dx}{\theta}\left\{\frac{(U_b'')^2}{4}(x-b)^2 - \frac{\theta U_b''}{2} - \lambda\right\}^{1/2} \\ &= (2\nu+1)\left\{\frac{(\xi-b)^2}{2(\beta-b)^2} - \frac{1}{4} - \frac{1}{2}\log\left|\frac{2(\xi-b)}{\beta-b}\right|\right\} + O(\theta)\end{aligned} \tag{C10}$$

$$\begin{aligned}I_2 &\cong \int_\eta^{-\epsilon} \frac{dx}{\theta}\left\{\frac{(U_0'')^2}{4}x^2 + \frac{\theta|U_0''|}{2} - \lambda\right\} \\ &= (2\mu+1)\left\{\frac{\eta^2}{2\epsilon^2} - \frac{1}{4} - \frac{1}{2}\log\left|\frac{2\eta}{\epsilon}\right|\right\} + O(\theta)\end{aligned} \tag{C11}$$

$$\begin{aligned}I_3 &\cong \int_\xi^\eta \frac{dx}{2\theta}\left\{U'(x) - \frac{\theta U''(x)}{U'(x)} - \frac{2\lambda}{U'(x)}\right\} \\ &= \frac{1}{2\theta}[U(\eta) - U(\xi)] + \frac{1}{2}\log\left|\frac{U'(\xi)}{U'(\eta)}\right| - \frac{\lambda}{\theta}\int_\xi^\eta \frac{dx}{U'(x)}\end{aligned} \tag{C12}$$

We split the integral on the rhs of Eq. (C12) into

$$\int_{\xi}^{\eta} \frac{dx}{U'(x)} = \int_{\xi}^{x_m} dx \left(\frac{1}{U'(x)} - \frac{1}{(x-b)U''_0}\right) + \int_{x_m}^{\eta} dx \left(\frac{1}{U'(x)} - \frac{1}{xU''_0}\right) - \frac{1}{U''_0} \log\left|\frac{x_m}{\eta}\right| - \frac{1}{U''_b} \log\left|\frac{\xi - b}{x_m - b}\right| \tag{C13}$$

The intermediate point x_m can be chosen anywhere between ξ and η. We take, for simplicity, x_m to correspond to the local maximum of V.

Noticing that

$$\int_{\eta}^{0} dx \left(\frac{1}{U'(x)} - \frac{1}{xU''_0}\right) \cong \frac{1}{2} \eta \frac{U'''_0}{(U''_0)^2} \tag{C14}$$

we see that the condition for neglecting such an integral [i.e., for extending the integrals on the rhs of Eq. (C12) to, respectively, $x = 0$ and $x = b$] is precisely that ξ and η lie in the quasiharmonic regions, which corresponds to condition (B2). So

$$I_3 \cong \frac{\Delta U_b}{2\theta} + \frac{1}{2} \log\left|\frac{(\xi - b)U''_b}{\eta U''_0}\right| + \frac{1}{2\theta}\left[\frac{U''_0\eta^2}{2} - \frac{U''_b(\xi - b)^2}{2}\right] - (\mu + 1)\log\left|\frac{x_m}{\eta}\right| + \nu \log\left|\frac{\xi - b}{x_m - b}\right| + \frac{\lambda}{\theta}\delta \tag{C15}$$

with

$$\delta = \int_{b}^{x_m} \left(\frac{1}{(x-b)U''_b} - \frac{1}{U'(x)}\right) + \int_{x_m}^{0} dx \left(\frac{1}{xU''_0} - \frac{1}{U'(x)}\right) \tag{C16}$$

From which

$$S_b(\lambda) = \frac{\Delta U_b}{2\theta} + \frac{\lambda\delta}{\theta} + \frac{1}{2}\left(\mu + \frac{1}{2}\right) \log\left(\frac{\mu + \frac{1}{2}}{e}\right) + \frac{1}{2}\left(\nu + \frac{1}{2}\right) \log \frac{\nu + \frac{1}{2}}{e} + (\mu + 1) \log\left[\frac{1}{x_m}\left(\frac{\theta}{|U''_0|}\right)^{1/2}\right] + \nu \log\left[\frac{1}{(x_m - b)}\left(\frac{\theta}{U''_b}\right)^{1/2}\right] + \frac{1}{4} \log \frac{U''_b}{|U''_0|} \tag{C17}$$

Finally, it is easily checked that, for states with four real turning points, $S_b(\lambda)$ is still given by Eq. (C17), with the simple transformation

$$\log \frac{\mu + \frac{1}{2}}{e} \to \log\left|\frac{\mu + \frac{1}{2}}{e}\right|$$

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REFERENCES

1. N. G. van Kampen, *J. Stat. Phys.* **17**:71 (1977).
2. R. Kubo, K. Matsuo, and K. Kitahara, *J. Stat. Phys.* **9**:51 (1973). N. G. van Kampen, *Can. J. Phys.* **39**:551 (1961).
3. H. Tomita, A. Itö, and H. Kidachi, *Progr. Theor. Phys.* **56**:786 (1976).
4. H. A. Kramers, *Physica* **7**:284 (1940).
5. M. Suzuki, *J. Stat. Phys.* **16**:11 (1977), and references therein.
6. M. Moreau, *Physica* **90A**:410 (1978).
7. R. Graham, in *Statistical Theory of Instabilities in Stationary Non-Equilibrium Systems* (Springer Tracts in Modern Physics No. 66), G. Höhler, ed. (Springer-Verlag, Berlin, 1973).
8. S. Coleman, Lecture at the International School of Subnuclear Physics Ettore Majorana (1977).
9. H. J. de Vega, J. L. Gervais, and B. Sakita, *Nucl. Phys. B* **139**:20 (1978).
10. S. C. Miller, Jr. and R. H. Good, Jr., *Phys. Rev.* **91**:174 (1953).
11. M. V. Berry and K. E. Mount, *Rep. Progr. Phys.* **35**:315 (1972).
12. C. D. Graham, *Metal Progr.* **71**:75 (1957).