Non-Markovian theory of activated rate processes. I. Formalism

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The escape of a particle from a potential well is treated using a generalized Langevin equation (GLE) in the low friction limit. The friction is represented by a memory kernel and the random noise is characterized by a finite correlation time. This non-Markovian stochastic equation is reduced to a Smoluchowski diffusion equation for the action variable of the particle and explicit expressions are obtained for the drift and diffusion terms in this equation in terms of the Fourier coefficients of the deterministic trajectory (associated with the motion without coupling to the heat bath) and of the Fourier transform of the friction kernel. The latter (frequency dependent friction) determines the rate of energy exchange with the heat bath. The resulting energy (or action) diffusion equation is used to determine the rate of achieving the critical (escape) energy. Explicit expressions are obtained for a Morse potential. These results for the escape rate agree with those from stochastic trajectories based on the original GLE. Non-Markovian effects are shown to have large effects on the rate of energy accumulation and relaxation within the well.

I. INTRODUCTION

The dynamics of activated rate processes has been a subject of renewed interest during recent years. Following Kramers,[1] many studies use a model of a particle moving in a one dimensional potential well under the effect of thermal noise and damping, the objective being to calculate the rate of escape out of the well (Fig. 1). This model has played a central role in many areas of physics and chemistry such as chemical reactions in condensed phases,[2] surface desorption,[3] diffusion of atoms or ions in solids,[4] dynamics of Josephson junctions,[5] etc.

The starting point in the Kramers model is the Langevin equation

$$\ddot{x} = -(1/M)\,\partial V(x)/\partial x - \gamma\dot{x} + (1/M)R(t)\ , \tag{1}$$

where x is the coordinate of the particle of mass M, moving in the potential $V(x)$, where γ and R are the damping rate and the (stationary Gaussian) fluctuating force associated with the coupling to the thermal bath. The fluctuation dissipation theorem relates γ and R,

$$\langle R(0)R(t)\rangle = 2\gamma M kT\,\delta(t)\ , \tag{2}$$

where k is the Boltzmann constant and T is the temperature. Kramers proceeds to solve Eq. (1) for two limiting cases:

(a) The high viscosity limit ($\gamma \gg \omega$, where ω is the well frequency). In this case Eq. (1) is reduced to the Smoluchowski diffusion equation

$$\frac{\partial \rho(x,t)}{\partial t} = \frac{1}{\gamma M}\frac{\partial}{\partial x}\left\{\left[\frac{\partial V(x)}{\partial x} + kT\frac{\partial}{\partial x}\right]\rho(x,t)\right\}\ , \tag{3}$$

where $\rho(x,t)$ is the probability to find the particle at position x at time t.

(b) In the low viscosity limit, $\gamma \ll \omega$, Eq. (1) is reduced to a Smoluchowski-type equation for the probability $P(J)$ to find the particle with a particular action $J[\omega = \omega(J)$ is in general a function of J, and the energy $E(J)$ is given by $E(J) = \int^J \omega(J')\,dJ']$

$$\frac{\partial P(J,t)}{\partial t} = \gamma\frac{\partial}{\partial J}\left\{\frac{J}{\omega(J)}\left[\omega(J) + kT\frac{\partial}{\partial J}\right]\rho(J,t)\right\}\ . \tag{4}$$

Both Eqs. (3) and (4) may be used to obtain the rate associated with the diffusion process that they describe. This may be done by either considering the steady state flux associated with these equations (the escape rate is taken to be this flux divided by the population in the well) or equivalently by considering the mean first passage time to attain a threshold position [from Eq. (3)] x_B in Fig. 1, or a threshold energy [from Eq. (4)] E_B in Fig. 1 (the escape rate is taken to be the inverse mean first passage time in the steady state). The results obtained by Kramers under the additional assumption $E_B \gg kT$ are

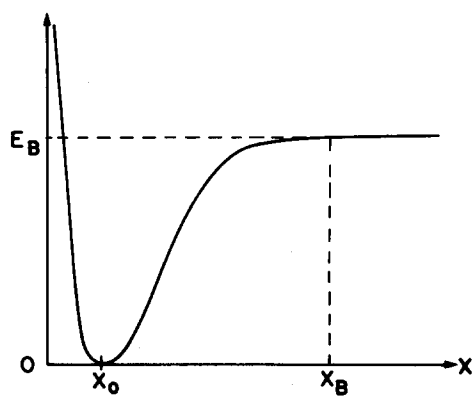

FIG. 1. A schematic representation of the potential well. x_B denotes a position such that for $x > x_B$ the coupling to the bath vanishes.

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$$r = \frac{\omega\omega_B}{2\pi\gamma} \exp\left(\frac{-E_B}{kT}\right) \quad \text{(case A)}, \tag{5a}$$

$$r = \gamma \frac{E_B}{kT} \exp\left(\frac{-E_B}{kT}\right) \quad \text{(case B)}. \tag{5b}$$

Here r is the escape rate, ω is the frequency at the bottom of the potential well, and ω_B is the "frequency" associated with the second derivative of the potential at the barrier.

In addition to the results in Eqs. (5), the rate expression associated with the transition state theory (TST)

$$r = \frac{\omega}{2\pi} \exp\left(\frac{-E_B}{kT}\right) \tag{6}$$

is often used. This result is obtained by calculating the outgoing flux at the point x_B, assuming that there is thermal equilibrium between bound and unbound particles and that $E_B \gg kT$. Kramers[1] also obtained a result which extrapolates between the high friction limit [Eq. (5a) and between the TST result Eq. (6)]

$$r = \frac{\omega}{2\pi\omega_B}\left(\sqrt{\left(\frac{\gamma}{2}\right)^2 + \omega_B^2} - \frac{\gamma}{2}\right)\exp\left(\frac{-E_B}{kT}\right). \tag{7}$$

These results yield Eq. (6) for $\gamma \to 0$ and Eq. (5a) for $\gamma \to \infty$.

The ranges of validity of these different results for the escape rate has never been fully explored. Equation (5a) is expected to be valid when the rate determining process is the change of the particle's position against the resistance imposed by friction forces. Equation (5b) is expected to be valid when the coupling to the thermal bath is so weak that energy exchange between the bath and the particle becomes rate limiting. It should be kept in mind however, that if passing through x_B is our criterion for escape, the low friction result Eq. (5b) (which express the rate in which particles attain the energy E_B) should be corrected to

$$r = f \frac{\gamma E_B}{kT} \exp\left(\frac{-E_B}{kT}\right). \tag{8}$$

Here f is the exit probability, i.e., the fraction of molecules that, once attained the energy E_B, proceed to move out of the well without going down to energies smaller than E_B and f is expected to be close to one in the low friction limit.

Also, as is well known, the TST result Eq. (6) may be corrected by taking into account only that part of the outgoing flux which originates below the energy E_B.[6] This may be expressed by

$$r = s \frac{\omega}{2\pi} \exp\left(\frac{-E_B}{kT}\right), \tag{9}$$

where s is the sticking coefficient, i.e., the fraction of equilibrium trajectories which start out of the well and in the direction of the barrier, which lead to capture (defined as the event where the particle energy E goes below E_B). We note in passing that in the low friction limit the results Eqs. (8) and (9) should be identical, resulting in a relation between the exit probability f and the sticking probability s:

$$s = 2\pi \frac{\gamma}{\omega kT} \frac{E_B}{kT} f \tag{10}$$

and for very low friction ($f \to 1$)

$$s = 2\pi \frac{\gamma E_B}{\omega kT}. \tag{11}$$

In the last few years several extensions of the Kramers theory were given. In particular we note the extension of the result of Eq. (7) to a multidimensional case by Grote and Hynes,[7] the inclusion of non-Markovian effects in the barrier region by the same authors,[8] and the corrections to the low friction limit (obtained as terms of higher powers in γ, using however, models for thermal relaxation different from Kramers') by Skinner and Wolynes.[9] New mathematical developments have been recently reviewed by Schuss.[10]

The purpose of the present paper is to extend Kramers' theory in yet another direction by including non-Markovian effects in the low friction limit.[11] Obviously, in most cases involving chemical systems the Markovian representation Eq. (1) is not valid. As usual it is based on the assumption that the time scale associated with the motion of the thermal bath is much shorter than any relevant molecular time scale. While this assumption holds, e.g., for atomic diffusion in solids, it is practically never realized in cases where the coordinate x is a molecular vibrational coordinate, because the correlation time associated with the thermal bath is usually much longer than a typical molecular vibrational period. Even if x is the desorption coordinate for a physisorbed atom on a surface, the Markovian assumption is usually inappropriate: the bath (surface motion) correlation time is often of the same order of magnitude as the period associated with the motion along x.[12]

These observations should be of no consequence for the escape rate in strong and moderate friction cases, where the particle may be considered to be essentially in thermal equilibrium within the well and where the dynamics takes place only near the barrier top. Non-Markovian effects may be important also for barrier dynamics, however, this depends on the relation between the barrier frequency (renormalized by the presence of friction) and the friction. Grote and Hynes[8] have treated this case and have shown that memory effects in barrier dynamics may lead to a smaller effective friction and thus to a larger range of validity of the TST result (which is the low friction limit of barrier dynamics models). In contrast, we focus on cases where well dynamics is important. Among such cases are (a) the low friction limit where energy accumulation becomes the rate determining step, as seen by the result of Eq. (5b), (b) reactions occurring under nonequilibrium or nonsteady state situations, such as dissociation or surface desorption following a temperature jump, and (c) reactions occurring under the effect of time varying external fields, such as the radiation field.

In all these cases well dynamics is important and becomes dominant in the low friction case. Obviously

well dynamics is governed by energy accumulation and relaxation processes. In addition to Kramers' low friction treatment [Eq. (5b)] and to related studies, the approach usually taken is based on a master equation for the population of the quantum mechanical levels of the particle in the well, where the transition rate between any two levels is obtained from quantum mechanical perturbation theory.[13] In many situations this is a cumbersome and difficult task. Intuition and experience tells us that classical mechanics should be adequate in many such cases (when the potential well supports many bound levels). Classical energy relaxation studies have indeed been carried out for non-Markovian cases using Langevin dynamic simulations.[14] Such simulations are again expensive and time consuming because of the many time scales (molecular frequency, bath dynamics, energy relaxation, and reaction rate) involved. In analogy to Kramers, we expect that also in non-Markoffian systems it should be possible to eliminate the short time scales associated with the fast molecular and bath motions and to focus on the relatively slow energy variation. In fact Zwanzig[15] has developed a procedure for reducing the classical Hamilton's equations of motion for a one dimensional particle interacting with a non-Markovian heat bath. Using the assumptions that: (a) the environment always remains in thermal equilibrium and (b) that it is enough to keep only the lowest nonvanishing power of the particle-bath interaction, Zwanzig[15] has obtained a Fokker–Planck equation for the action variable of the particle. Very recently Grote and Hynes[16] used Zwanzig's result to derive explicit forms for the action and energy diffusion equations and used it to discuss the rate of molecular dissociation and isomerization for molecules in dense environments in the energy diffusion controlled limit.

In what follows we describe an alternative procedure which uses the generalized Langevin equation (GLE) as a starting point. Our procedure leads to an equation analogous to Eq. (4) for non-Markovian systems which is similar to the result obtained by Zwanzig.[15] This equation may be solved analytically in some cases, or else may be used (itself or its Langevin analog) in a stochastic simulation which is much easier and cheaper than that based on the full system's dynamics.

Our model is described in Sec. II. The reduction procedure which leads to a Fokker–Planck equation in energy (or action) space is presented in Sec. III. In Sec. IV we analyze our result, apply it to some special cases, and test its validity against a full scale Langevin dynamics calculation.

II. THEORY

Our starting point is the GLE

$$\ddot{x} = -\frac{1}{M}\frac{\partial V(x)}{\partial x} - \int_0^t d\tau\, Z(t-\tau)\,\dot{x}(\tau) + \frac{1}{M}R(t)\ , \tag{12}$$

where R is a Gaussian noise with $\langle R\rangle = 0$ and

$$\langle R(t_1)R(t_2)\rangle = Z(t_1 - t_2)\,MkT\ . \tag{13}$$

The memory function $Z(t)$ is characterized by the correlation time which provides the time scale for its decay to zero and by its Fourier components

$$\hat{Z}_n(\omega) = \int_0^\infty dt\, Z(t)\exp(-in\omega t) \tag{14}$$

with

$$\hat{Z}_0(\omega) = \int_0^\infty dt\, Z(t) = \gamma\ . \tag{15}$$

For specificity we shall often refer to the simple case

$$Z(t) = (\gamma/\tau_c)\exp(-t/\tau_c)\ , \tag{16a}$$

$$\hat{Z}_n(\omega) = \gamma/(1 + in\omega\tau_c)\ , \tag{16b}$$

where γ is the Markovian friction while, as we shall see, the actual friction (rate of energy transfer) for a well motion with frequency ω is related to the Fourier components $|\hat{Z}_n(\omega)|$. Apart from the overall reaction (escape) rate our problem is characterized by the time scales associated with $\hat{Z}(\omega)$, τ_c, and ω. We assume

$$\gamma(\text{or } |\hat{Z}_n(\omega)|) \ll 1/\tau_c \ll \omega\ . \tag{17}$$

The right inequality implies that we cannot use the Markovian starting point, Eq. (1), while the left inequality suggests that it should be possible to get a Markoffian description of the energy transfer process.

Lax[17] has described a procedure for deriving a Markovian-Fokker–Planck equation corresponding to a Langevin equation with short but finite correlation time. His procedure can be used in principle for our present treatment. Lax,[17] however, limits himself to the standard second-order iteration procedure which is not sufficient in our case as discussed below. In what follows we use an alternative route.

III. THE REDUCTION PROCEDURE

We start from Eq. (12), and rewrite it in terms of the action (J) and angle (ϕ) coordinates. First we show (Appendix A) that Eq. (12) may be rewritten in the form

$$\dot{J} = M\frac{\partial x}{\partial \phi}\left[-\int_0^t d\tau\, Z(t-\tau)\,v(\tau) + \frac{1}{M}R(t)\right]\ , \tag{18a}$$

$$\dot{\phi} = \omega(J) - M\frac{\partial x}{\partial J}\left[-\int_0^t d\tau\, Z(t-\tau)\,v(\tau) + \frac{1}{M}R(t)\right]\ , \tag{18b}$$

where $v = \dot{x}$ is the velocity and where $\omega(J) = dH(J)/dJ$, H being the Hamiltonian for the deterministic part of the particle's motion. We note that the canonical transformation $(x, Mv) \to (J, \phi)$ is defined using this deterministic Hamiltonian. This implies that x and v, considered as functions of J and ϕ, may be expanded in the form

$$x(J,\phi) = \sum_{n=-\infty}^{\infty} x_n(J)\exp(in\phi)\ , \tag{19a}$$

$$v(J,\phi) = \sum_{n=-\infty}^{\infty} v_n(J)\exp(in\phi)\ , \tag{19b}$$

with

$$x_n = x_{-n}^*\ ;\quad v_n = v_{-n}^*\ . \tag{20}$$

The expansion coefficients x_n and v_n are related by[18]

$$v_n(J) = in\omega(J)\,x_n(J)\ . \tag{21}$$

We further note that for a one dimensional motion as

considered here it is always possible to choose the origin of ϕ so that x and v are even and odd functions of ϕ, respectively. With this choice we have

$$x_n = x_{-n} \quad [\mathrm{Im}(x_n) = 0] \tag{22}$$
$$v_n = -v_{-n} \quad [\mathrm{Re}(v_n) = 0] \ .$$

Inserting Eqs. (19) into Eq. (18) we get

$$\dot{J} = -iM \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} n x_n e^{in\phi} \int_0^t d\tau\, Z(t-\tau)\, v_m e^{im\phi} + iR(t) \sum_{n=-\infty}^{\infty} n x_n e^{in\phi} \ , \tag{23}$$

$$\dot{\phi} = \omega(J) + M \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \frac{\partial x_n}{\partial J} e^{in\phi} \int_0^t d\tau\, Z(t-\tau)\, v_m e^{im\phi} - R(t) \sum_{n=-\infty}^{\infty} \frac{\partial x_n}{\partial J} e^{in\phi} \ . \tag{24}$$

We now introduce our main approximation, based on the time scale ordering, Eq. (17). The memory kernel $Z(t)$ decays to zero in times of orders τ_c. For such short times we can write $|t-\tau| \lesssim \tau_c$,

$$\phi(\tau) \simeq \phi(t) - \omega(t-\tau) \ , \tag{25}$$

$$v_m(\tau) \simeq v_m(t) \ . \tag{26}$$

Therefore,

$$\int_0^t d\tau\, Z(t-\tau)\, v_m(\tau)\, e^{im\phi(\tau)} \simeq v_m(t)\, e^{im\phi(t)} \times \int_0^t d\tau\, Z(t-\tau)\, e^{-im\omega(t-\tau)} \tag{27}$$

and for $t \gg t_c$,

$$\int_0^t d\tau\, Z(t-\tau)\, v_m(\tau)\, e^{im\phi(\tau)} \simeq v_m(t)\, e^{im\phi(t)}\, \hat{Z}_m(\omega) \ , \tag{28}$$

where $\hat{Z}_m(\omega)$ is defined by Eq. (14).

Substituting Eq. (28) into Eqs. (23) and (24) finally leads to

$$\dot{J} = -iM \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} n x_n v_m \hat{Z}_m e^{i(n+m)\phi} + iR(t) \sum_{n=-\infty}^{\infty} n x_n e^{in\phi} \ , \tag{29}$$

$$\dot{\phi} = \omega + M \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} x_n' v_m \hat{Z}_m e^{i(n+m)\phi} - R(t) \sum_{n=-\infty}^{\infty} x_n' e^{in\phi} \ , \tag{30}$$

where $x_n' = dx_n/dJ$. Despite their appearance these equations are not Markovian because the random force $R(t)$ is characterized by the finite correlation time τ_c.

The time evolution of the probability distribution $P(J, \phi, t)$ is determined by the equation

$$\frac{\partial P}{\partial t} = \lim_{\tau \to 0+} \left\{ \frac{1}{\tau} \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \sum_{\substack{m,k=0 \\ (m+k=n)}} \left(\frac{\partial}{\partial J}\right)^m \left(\frac{\partial}{\partial \phi}\right)^k [\langle (\Delta J_t)^m (\Delta\phi_t)^k \rangle P] \right\} , \tag{31}$$

where $\Delta W_t = \Delta W_t(\tau) = W(t+\tau) - W(t)$ (W is J or ϕ). The limit in Eq. (31) should be understood as taking $\tau \ll \gamma^{-1}$. However τ is kept larger than τ_c (and ω^{-1}) in order to yield a coarse grained Markovian equation. Our task is therefore to evaluate moments of the form $\langle (\Delta J_t)^m (\Delta\phi_t)^k \rangle$. The standard procedure is to use

$$\Delta J_t(\tau) = \int_0^\tau ds\, \dot{J}(J(t+s), \phi(t+s), t+s) \ , \tag{32}$$

where $\dot{J}(J, \phi, t)$ is given by Eq. (29) as a basis for iteration in the form

$$\Delta J_t^{(l)}(\tau) = \int_0^\tau ds\, \dot{J}(J(t) + \Delta J_t^{(l-1)}(s), \phi(t) + \Delta\phi_t^{(l-1)}(s), t+s) \ , \tag{33}$$

where (l) denotes the lth iteration stage. A similar interation procedure is used to evaluate $\Delta\phi$.

In the Markovian case (where τ_c is the shortest time scale) it is usually found[17] that: (a) moments of the form $\langle (\Delta J)^m (\Delta\phi)^k \rangle$ with $m+k > 2$ are of order τ^n, $n \geq 2$ and therefore do not contribute to Eq. (31) and (b) all the relevant terms (i.e., terms of order τ) which contribute to the first and second moments ($m+k = 1$ or 2) are obtained at the second iteration stage. This leads to the standard Fokker–Planck equation.

The present, non-Markovian case is different: terms of order τ are obtained in all orders of the iteration procedure, forcing us in principle to consider an infinite number of contributions to Eq. (31). In order to simplify our notation we introduce the following function of J:

$$\sigma_n(J) = inx_n(J) \ , \tag{34}$$
$$\mu_n(J) = dx_n(J)/dJ \ , \tag{35}$$
$$B_{nm}(J) = iMnx_n(J)\, v_m(J)\, \hat{Z}_m[\omega(J)] \ , \tag{36}$$
$$C_{nm}(J) = M[dx_n(J)/dJ]\, v_m(J)\, \hat{Z}_m[\omega(J)] \ . \tag{37}$$

In terms of which Eqs. (29) and (30) take the form

$$\dot{J} = -\sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} B_{nm}(J) \exp[i(n+m)\phi] + R(t) \sum_{n=-\infty}^{\infty} \sigma_n(J) \exp(in\phi), \tag{38}$$

$$\dot{\phi} = \omega(J) + \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} C_{nm}(J) \exp[i(n+m)\phi] - R(t) \sum_{n=-\infty}^{\infty} \mu_n(J) \exp(in\phi) \ . \tag{39}$$

The equations for ΔJ_t and $\Delta\phi_t$ are

$$\Delta J_t(\tau) = -\sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \int_0^\tau ds\, B_{nm}[J(t) + \Delta J_t(s)] \exp\{i(n+m)[\phi(t) + \Delta\phi_t(s)]\} + \sum_{n=-\infty}^{\infty} \int_0^\tau ds\, R(s)\, \sigma_n[J(t) + \Delta J_t(s)] \exp\{in[\phi(t) + \Delta\phi_t(s)]\} \tag{40}$$

and

$$\Delta\phi_t(\tau) = \int_0^\tau ds\, \omega[J(t)+\Delta J_t(s)] + \sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty} \int_0^\tau ds\, C_{nm}[J(t)+\Delta J_t(s)] \exp\{i(n+m)[\phi(t)+\Delta\phi_t(s)]\}$$
$$- \sum_{n=-\infty}^{\infty} \int_0^\tau ds\, R(s)\, \mu_n[J(t)+\Delta J_t(s)] \exp\{in[\phi(t)+\Delta\phi_t(s)]\} \ . \tag{41}$$

Equation (40) and (41) are now used for a systematic iteration procedure as defined by Eq. (33), starting from $\Delta J_t^{(0)}(\tau)=0$ and $\Delta\phi_t^{(0)}(\tau)=\omega[J(t)]\tau$. Details are provided in Appendix B. Here we give only the main intermediate and final results. Inserting $\Delta J_t^{(0)}$ and $\Delta\phi_t^{(0)}$ into the right-hand side of Eqs. (40) and (41) we obtain

$$\Delta J_t^{(1)}(\tau) = \tau \sum_{n=-\infty}^{\infty} B_{n,-n} + \sum_{n=-\infty}^{\infty} \sigma_n e^{in\phi} \int_0^\tau ds\, R(s)\, e^{in\omega s} \ , \tag{42}$$

$$\Delta\phi_t^{(1)}(\tau) = \omega\tau + \tau \sum_{n=-\infty}^{\infty} C_{n,-n} - \sum_{n=-\infty}^{\infty} \mu_n e^{in\phi} \int_0^\tau ds\, R(s)\, e^{in\omega s} \ . \tag{43}$$

Inserting these results in Eqs. (40) and (41) we obtain Eqs. (B5) and (B6) for $\Delta J_t^{(2)}$ and $\Delta\phi_t^{(2)}$. Inserting these again into Eqs. (40) and (41) leads to Eqs. (B7) and (B8) for $\Delta J_t^{(3)}$ and $\Delta\phi_t^{(3)}$. This last interation step is not necessary in the Markovian case. However, in the present treatment, terms which appear in the third iteration step make non-negligible contributions to $\langle\Delta J_t\rangle$ and $\langle\Delta\phi_t\rangle$.

In calculating the moments $\langle[\Delta J_t(\tau)]^m[\Delta\phi_t(\tau)]^k\rangle$ needed in Eq. (31) we systematically neglect terms which are of order $\tau^n (n>1)$ or $[\hat{Z}(\omega)/\omega]^n$ $(n\geq 1)$. Neglecting terms which are of high order in τ is implied by Eq. (31). Neglecting terms of order $\hat{Z}(\omega)/\omega$ corresponds to the low friction limit [Eq. (17)]. We note that $\hat{Z}(\omega)/\omega \ll 1$ may be satisfied even if $\gamma[=\hat{Z}(\omega=0)] \ll \omega$ is not satisfied [see Eq. (16b)]. We find that, as in the Markovian case, only first and second moments yield terms which are not negligible by these criteria. The final results are

$$\langle\Delta J_t(\tau)\rangle = -2\tau M \sum_{n=1}^{\infty} n^2 \left(\omega - kT\frac{d}{dJ}\right)(|x_n|^2 \hat{Z}_n^c) \ , \tag{44}$$

$$\langle\Delta\phi_t(\tau)\rangle = \omega\tau + \tau M \sum_{n=1}^{\infty} n \left(\omega - kT\frac{d}{dJ}\right)\left(\frac{d|x_n|^2}{dJ}\hat{Z}_n^s\right) \ , \tag{45}$$

$$\langle[\Delta J_t(\tau)]^2\rangle = 4\tau M\, kT \sum_{n=1}^{\infty} n^2 |x_n|^2 \hat{Z}_n^c \ , \tag{46}$$

$$\langle[\Delta\phi_t(\tau)]^2\rangle = 4\tau M\, kT \sum_{n=1}^{\infty} \left|\frac{dx_n}{dJ}\right|^2 \hat{Z}_n^c \ , \tag{47}$$

$$\langle\Delta J_t(\tau)\,\Delta\phi_t(\tau)\rangle = 0 \ , \tag{48}$$

where

$$\hat{Z}_n^c = \int_0^\infty dt\, Z(t)\cos(n\omega t) \ , \tag{49a}$$

$$\hat{Z}_n^s = \int_0^\infty dt\, Z(t)\sin(n\omega t) \ . \tag{49b}$$

Inserting these results into Eq. (31) [with $n>2$ terms in Eq. (31) disregarded] and defining

$$\epsilon(J) = 2M \sum_{n=1}^{\infty} n^2 |x_n|^2 \hat{Z}_n^c \ , \tag{50}$$

$$\Gamma(J) = 2M\, kT \sum_{n=1}^{\infty} \left|\frac{dx_n}{dJ}\right|^2 \hat{Z}_n^c \ , \tag{51}$$

$$\Omega(J) = \omega(J) + M\left(\omega(J) - kT\frac{d}{dJ}\right)\sum_{n=1}^{\infty} n \left|\frac{dx_n}{dJ}\right|^2 \hat{Z}_n^s \ . \tag{52}$$

We get a Fokker–Planck equation for $P(J,\phi,t)$,

$$\frac{\partial P(J,\phi,t)}{\partial t} = \frac{\partial}{\partial J}\left\{\epsilon(J)\left[kT\frac{\partial}{\partial J} + \omega(J)\right]P\right\}$$
$$+ \Gamma(J)\frac{\partial^2 P}{\partial\phi^2} - \Omega(J)\frac{\partial P}{\partial\phi} \ . \tag{53}$$

Equation (53) is our final general result for the action-angle probability distribution. If at $t=0$, $P(J,\phi)=P(J)$, independent of ϕ, it will remain independent of ϕ at all time and will satisfy the equation

$$\frac{\partial P(J,t)}{\partial t} = \frac{\partial}{\partial J}\left\{\epsilon(J)\left[kT\frac{\partial}{\partial J} + \omega(J)\right]P\right\} \tag{54}$$

which is our final practical result.

IV. DISCUSSION

Our final result, Eqs. (54) and (50) constitutes a diffusion equation for the action variable J associated with a particle moving in a one dimensional potential well under the influence of a heat bath characterized by Eqs. (13) and (17). The energy $H(J)$ is determined from

$$H(J) = \int^J dJ'\, \omega(J') \ . \tag{55}$$

The time evolution of the probability distribution $P(J)$ is determined by the two functions $\omega(J)$ and $\epsilon(J)$. The function $\omega(J)$ is the (action dependent) frequency which is determined by the potential function. The function $\epsilon(J)$ is determined by the deterministic motion of the particle (i.e., the coefficients x_n of Eq. (19a) and by the properties of the thermal environment, through the factors $\hat{Z}_n^c$.

Consider the behavior of our result in some special limits. At equilibrium $\partial P/\partial t = 0$ and Eq. (54) yields the Boltzmann distribution

$$P_{eq}(J) \sim \exp[-H(J)/kT] \ . \tag{56}$$

In the Markovian limit $Z(t)=2\gamma\delta(t)$ and $\hat{Z}_n(\omega)=\gamma$. We get

$$\epsilon(J) = 2\gamma M \sum_{n=1}^{\infty} n^2 |x_n|^2 \ . \tag{57}$$

This may be simplified further by using the identiy

$$J = 2M\omega \sum_{n=1}^{\infty} n^2 |x_n|^2$$

(see Appendix D). This leads to

$$\epsilon(J) = \gamma J/\omega(J) \tag{58}$$

so that

$$\frac{\partial P}{\partial t} = \gamma \frac{\partial}{\partial J}\left\{\left(\frac{J}{\omega(J)}\right)\left[kT\frac{\partial}{\partial J} + \omega(J)\right]P\right\} . \tag{59}$$

This is Kramers' energy diffusion equation in the Markovian limit.[1]

Finally consider the harmonic oscillator limit. In this case Eq. (19a) takes the form

$$x(J,\phi) = \left(\frac{J}{2M\omega}\right)^{1/2}(e^{i\phi} + e^{-i\phi}) \tag{60}$$

so that

$$x_n(J) = \left(\frac{J}{2M\omega}\right)^{1/2}\delta_{|n|,1} \tag{61}$$

and

$$\epsilon(J) = 2M|x_1|^2\hat{Z}_1^c = \frac{J}{\omega}\hat{Z}_1^c . \tag{62}$$

Substituting into Eq. (54) now leads to

$$\frac{\partial P}{\partial t} = \hat{Z}_1^c(\omega)\frac{\partial}{\partial J}\left[\frac{J}{\omega}\left(kT\frac{\partial}{\partial J} + \omega\right)P\right] . \tag{63}$$

This result is the same as that obtained in the Markoffian limit[1] with γ replaced by the frequency dependent relaxation rate

$$\hat{Z}_1^c(\omega) = (MkT)^{-1}\int_0^\infty d\tau \cos(\omega\tau)\langle R(0)R(\tau)\rangle . \tag{64}$$

This result for the relaxation rate is the classical analog of the energy relaxation rate obtained for the harmonic oscillator in quantum perturbation theory.[19] It is interesting to note that all relaxation rates $\hat{Z}_n(\omega)$ have the typical form of a Fourier transform of a second-order time correlation function in analogy to results obtained in quantum perturbation treatments. Such treatments involve a second-order expansion in the system-thermal bath coupling. Similarly, Zwanzig's derivation of a classical Fokker–Planck equation for the non-Markovian case[15] involves a second-order expansion in the system bath coupling. We obtain an equivalent result by expanding in $\hat{Z}/\omega$. Since $\hat{Z}$ is second order in the system bath coupling and ω is related to the system's Hamiltonian [cf. Eq. (55)] the two expansions are essentially equivalent.

In order to proceed with a solution of Eq. (54) we need to know the functions $\omega(J)$ and $\epsilon(J)$ for the particular potential well. In particular, to evaluate $\epsilon(J)$ we usually have to truncate the series Eq. (50) and to evaluate the remaining sum numerically. For a Morse oscillator this may be carried out quite easily. The potential is

$$V(x) = D\{\exp[-2(x-x_0)/a] - 2\exp[-(x-x_0)/a]\} . \tag{65}$$

In terms of the action angle variables we have

$$H(J) = -D(1-\omega_0 J/2D)^2 , \tag{66}$$

$$\omega(J) = dH/dJ = \omega_0(1-\omega_0 J/2D) , \tag{67}$$

$$x(J,\phi) = x_0 + a\ln\{[1-\sqrt{1-\lambda^2}\cos(\phi)]/\lambda^2\} , \tag{68}$$

where

$$\lambda = 1 - \omega_0 J/2D \tag{69}$$

and where

$$\omega_0 = (2D/Ma^2)^{1/2} \tag{70}$$

is the frequency at the bottom.

The evaluation of $x_n(J)$ is described in Appendix E. The result is

$$n^2|x_n(J)|^2 = a^2\left(\frac{\omega_0 J}{4D-\omega_0 J}\right)^n , \quad n \geq 1 . \tag{71}$$

Note that Eq. (71) implies

$$\sum_{n=1}^{\infty} n^2|x_n|^2 = a^2\omega_0 J/(4D - 2\omega_0 J) ,$$

which together with Eq. (67) leads to the identity discussed in Appendix D. We should also note that the value of J at dissociation (to be denoted J_d), which satisfies $H(J_d) = 0$, is

$$J_d = 2D/\omega_0 . \tag{72}$$

Therefore, for $J \leq J_d$ we have $\omega_0 J/(4D-\omega_0 J) \leq 1$, where the identity is obtained for $J = J_d$. Thus, the series defining $\epsilon(J)$ [Eq. (50)] converges for all energies except at dissociation, provided that $\hat{Z}_n^c$ does not increase exponentially with n. In some cases $\hat{Z}_n^c$ decreases with n rapidly enough for the series to converge even for $J = J_d$.

Given the result of Eq. (71), $\epsilon(J)$ may be evaluated for any given model for the bath [i.e., a given functional for $\hat{Z}_n^c(\omega)$]. For the particular (though probably unphysical) case

$$Z(t) = \frac{2\gamma\tau_c}{\pi}(t^2+\tau_c^2)^{-1} , \tag{73a}$$

$$\hat{Z}_n^c(\omega) = \gamma\exp(-n\omega\tau_c) . \tag{73b}$$

Equations (50) and (71) lead to

$$\epsilon(J) = \gamma J\frac{2\exp[-\omega(J)\tau_c]}{\omega_0\{1-\exp[-\omega(J)\tau_c]\} + \omega(J)\{1+\exp[-\omega(J)\tau_c]\}} . \tag{74}$$

In other cases the series Eq. (50) may be evaluated numerically after truncation.

Equation (54) may be used to obtain an expression for the mean first passage time for energy relaxation or accumulation in the oscillator. A general result based on Eq. (54) is[20]

$$\tau_{MFP}(J_0,J) = \frac{1}{kT}\int_{J_0}^{J} dx\,\frac{\exp[H(x)/kT]}{\epsilon(x)}\int_0^x dy\exp\left[\frac{-H(y)}{kT}\right] , \tag{75}$$

where τ_{MFP} is the mean first passage time for reaching J, starting from an initial action J_0. This may be used to obtain the rate of relaxation processes within the model or the rate of activated processes in the low friction limit, where the energy accumulation becomes the rate determining step. For the steady state dissociation rate, we need to evaluate the average of $\tau_{MFP}(J,J_B)$ over the steady state distribution within the well[21]:

$$k_{dis} = \left[\int_0^{J_B} dJ\,P_{SS}(J)\,\tau_{MFP}(J,J_B)\right]^{-1} . \tag{76}$$

For a deep enough well the steady state distribution $P_{SS}(J)$ may be approximated by the Boltzmann distribution

$$P_{SS}(J) \simeq P_{eq}(J) = kT\,[1-\exp(-E_B/kT)]^{-1}\,\omega(J) \times \exp[-H(J)/kT]\ . \tag{77}$$

Using this and Eq. (75) in Eq. (76) we get (after integration by parts)

$$k_{dis} = kT\,[1-\exp(-E_B/kT)] \times \left(\int_0^{J_B} \frac{dJ}{\epsilon(J)} \left\{\exp\left[\frac{H(J)}{kT}\right]-1\right\}\int_0^{J} dx \exp\left[\frac{-H(x)}{kT}\right]\right)^{-1}\ . \tag{78}$$

If the well is very deep ($E_B \gg kT$), we may further simplify Eq. (78) by noticing that the main contribution to the integral over J comes from large J, so that the integral over x may be approximated by $\int_0^\infty dx \exp(-\omega_0 x/kT) = kT/\omega_0$ (ω_0 is the frequency at the bottom of the well). In the remaining integral,

$$\int_0^{J_B} \frac{dJ}{\epsilon(J)} \left\{\exp\left[\frac{H(J)}{kT}\right]-1\right\}$$

the integrand is sharply peaked near $J = J_B$ so that it can be approximated by

$$[\epsilon(J_B)\,\omega(J_B)]^{-1} \int_0^{E_B} dE \exp(E/kT) \simeq kT\,[\epsilon(J_B)\,\omega(J_B)]^{-1} \exp(E_B/kT)\ .$$

Equation (78) then leads to

$$k_{dis} = \frac{\omega_0 \epsilon(J_B)\omega(J_B)}{kT} \exp\left(\frac{-E_B}{kT}\right)\ .$$

When the barrier is identified with the threshold for dissociation ($J_B = J_d$, $E_B = E_d$), we have $\omega(J) = 0$; however, $\epsilon(J)\,\omega(J) \to \gamma J_d$ when $J \to J_d$, as implied by Eqs. (57) and (58). Thus, in this limit the rate becomes

$$k_{dis} = \gamma \frac{\omega_0 J_d}{kT} \exp\left(\frac{-E_d}{kT}\right)\ . \tag{79}$$

Note that for a Morse oscillator $\omega_0 J_d = 2E_d$ while for a truncated harmonic oscillator $\omega_0 J_d = E_d$. More important is the implication that in this limit of a very deep well, the non-Markovian nature of the thermal bath does not affect the dissociation rate (in agreement with Grote and Hynes[18]). This results from the assumption that the steady state distribution within the well is approximated well by a Boltzmann distribution up to energies for which the well frequency is low enough for the Markovian limit to be valid.

When a dissociation process is considered we usually face the problem that, since $\omega(J) \to 0$ for $J \to J_d$, the low friction limit $\hat{Z}/\omega \ll 1$ cannot be used close to the dissociation threshold. The validity of the present approach to this situation depends on the observable considered. A steady state dissociation rate is often determined by the dynamics near the potential barrier where the low friction limit may indeed be inappropriate. On the other hand, if the rate is associated with a nonequilibrium process (e.g., following a temperature jump) the dynamics may be determined mostly by the energy accumulation within the well, and the deviation from the low friction limit near the dissociation threshold may not cause appreciable errors. We demonstrate this by comparing $\tau_{MFP}(0, J_d)$ for a Morse oscillator, obtained from Eq. (75) and from simulations using stochastic classical trajectories based on Eqs. (12) and (13), where the thermal bath is characterized by Eqs. (16). The parameters used are $D = 2.5\,kT$ and $\gamma/\omega_0 = 0.04$. In Fig. 2 we plot τ_{MFP} as a function of τ_d: the full line is obtained from Eq. (75) and the points with error bars from the numerical simulations. It is seen that the agreement between the two calculations is good even though the low friction limit should not work near the threshold as discussed above. This is particularly remarkable in view of the relatively shallow well used (deeper wells present no difficulties for an evaluation based on Eq. (75), however the simulation becomes prohibitively costly). We note that the (CDC 6600) computer time needed to obtain the five points in Fig. 2 was about 1000 times longer than the time necessary to get the full line.

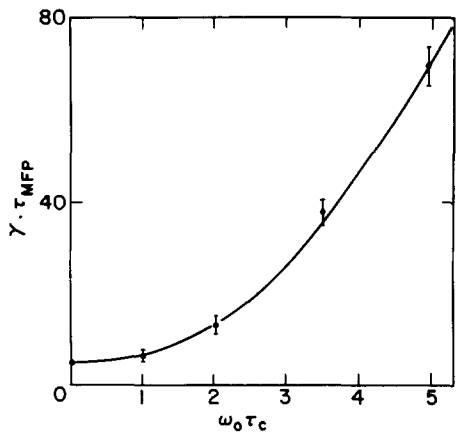

FIG. 2. Mean first past time τ_{MFP} $(0, J_B)$ for a Morse oscillator as a function of the bath correlation time τ_C for the model given by Eq. (16). ω_0 is the frequency at the bottom of the Morse potential. The threshold energy is $E(J_B) = 2.5$ kT. The solid line results from numerical integration of Eq. (75). Full circles results of numerical simulations based on Eq. (12).

The procedure developed here may be used to study non-Markoffian effects in relaxation and activated processes associated with molecular dynamics in dense phases. Another area where the present procedure is useful is the problem of desorption from solid surfaces.[12] In addition our approach may be used to discuss problems where the system interacts both with a heat bath and with an external force. This may provide a framework for studying the effect of a radiation field on activated rate processes. These problems will be discussed in future publications.

It should be stressed again that the calculations described above deal only with energy accumulation and relaxation rates, and in order to identify, e.g., the rate in Eq. (78) with a dissociation rate, we have to assume that the upwards flux (in energy space) crossing the threshold energy for dissociation is the same as the outwards flux (in position space) crossing the no return point X_B. This implies that the exit probability

f, defined in Sec. I, is unity. While this may be a good approximation in many weak coupling situations, f must be smaller than unity in many others. This problem and the dependence of f on the physical parameters will be discussed elsewhere.

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APPENDIX A

Here we start from Eq. (12) in the form

$$\dot{x} = v \ ,$$

$$\dot{v} = -\frac{1}{M}\frac{\partial V(x)}{\partial x} + Q(t) \ ,$$

$$Q(t) = -\int_0^t d\tau\, Z(t-\tau)\, v(\tau) + \frac{1}{M} R(t) \ , \tag{A1}$$

and show its equivalence to Eqs. (18). To this end we introduce the Jacobian matrix

$$\mathbf{Y} \equiv \begin{pmatrix} \frac{\partial x}{\partial J} & \frac{\partial x}{\partial \phi} \\ \frac{\partial v}{\partial J} & \frac{\partial v}{\partial \phi} \end{pmatrix} , \tag{A2}$$

which satisfies the following relations:

$$\det|\mathbf{Y}| = -\frac{1}{M} \ , \tag{A3}$$

$$\mathbf{Y}^{-1} = -M \begin{pmatrix} \frac{\partial v}{\partial \phi} & -\frac{\partial x}{\partial \phi} \\ -\frac{\partial v}{\partial J} & \frac{\partial x}{\partial J} \end{pmatrix} . \tag{A4}$$

Next we use

$$\begin{pmatrix} \dot{J} \\ \dot{\phi} \end{pmatrix} = \mathbf{Y}^{-1} \begin{pmatrix} \dot{x} \\ \dot{v} \end{pmatrix} = \mathbf{Y}^{-1} \begin{pmatrix} M^{-1}(\partial H/\partial v) \\ -M^{-1}(\partial H/\partial x) + Q(t) \end{pmatrix} , \tag{A5}$$

where

$$H = \tfrac{1}{2} M v^2 + V(x) \tag{A6}$$

is the Hamiltonian for the *deterministic* part of the motion. Equations (A4) and (A5) lead to

$$\dot{J} = -\frac{\partial H}{\partial \phi} + M \frac{\partial x}{\partial \phi} Q(t) \ ,$$

$$\dot{\phi} = \frac{\partial H}{\partial J} - M \frac{\partial x}{\partial J} Q(t) \ ,$$

which with the definition of $Q(t)$ [Eq. (A1)] and using $\partial H/\partial \phi = 0$, $\partial H/\partial J = \omega(J)$ results in Eqs. (18).

APPENDIX B

Here we provide some details of the calculation that leads from Eqs. (40)–(43) to Eqs. (44)–(48).

First iteration

Inserting Eqs. (42) and (43) into the right-hand side of Eq. (40) we obtain

$$\Delta J_t^{(1)}(\tau) = -\sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty} B_{nm} \exp[i(n+m)\phi] \int_0^\tau ds \exp[i(n+m)\omega s] + \sum_{n=-\infty}^{\infty} \sigma_n \exp(in\phi) \int_0^\tau ds\, R(s) \exp(in\omega s) \ . \tag{B1}$$

Here (and below) we have suppressed the notation concerning the t dependence of parameters like $B_{nm}\{=B_{nm}[J(t)]\}$, $\sigma_n\{=\sigma_n[J(t)]\}$, $\omega\{=\omega[J(t)]\}$, and $\phi[=\phi(t)]$. Since $\omega\tau \gg 1$ we we may replace

$$\int_0^\tau ds \exp[i(n+m)\omega s]$$

by $\delta_{n,-m}$, leading to

$$\Delta J_t^{(1)}(\tau) = -\tau \sum_{n=-\infty}^{\infty} B_{n,-n} + \sum_{n=-\infty}^{\infty} \sigma_n \exp(in\phi) \int_0^\tau ds\, R(s) \exp(in\omega s) \ . \tag{B2}$$

In a similar way we get from Eq. (41),

$$\Delta\phi_t^{(1)}(\tau) = \omega\tau + \tau \sum_{n=-\infty}^{\infty} C_{n,-n} - \sum_{n=-\infty}^{\infty} \mu_n \exp(in\phi) \int_0^\tau ds\, R(s) \exp(in\omega s) \ . \tag{B3}$$

Second iteration

Next we insert Eqs. (B2) and (B3) into the right-hand side of Eqs. (40) and (41). Proceeding with Eq. (40) we further expand functions of $\Delta J_t(s)$ and of $\Delta\phi_t(s)$ about $\Delta J_t^{(0)}(s) = 0$ and $\Delta\phi_t^{(0)}(s) = \omega s$ {e.g., $B_{nm}[J(t) + \Delta J_t(s)] = B_{nm} + B'_{nm}\,\Delta J_t(s)$, where $B_{nm} = B_{nm}[J(t)]$ and $B'_{nm} = (dB_{nm}/dJ)_{J=J(t)}$}. We first limit ourselves to terms up to first order resulting from such expansions. This leads to

$$\Delta J_t^{(2)}(\tau) = \Delta J_t^{(1)}(\tau) - \sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty} B'_{nm} \exp[i(n+m)\phi] \int_0^\tau ds\, \Delta J_t^{(1)}(s) \exp[i(n+m)\omega s] - \sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty} B_{nm} \exp[i(n+m)\phi] \int_0^\tau ds\, i(n+m)[\Delta\phi_t^{(1)}(s) - \omega s] \exp[i(n+m)\omega s] + \sum_{n=-\infty}^{\infty} \sigma'_n \exp(in\phi) \int_0^\tau ds\, R(s)\, \Delta J_t^{(1)}(s) \exp(in\omega s) + \sum_{n=-\infty}^{\infty} \sigma_n \exp(in\phi) \int_0^\tau ds\, R(s)\, in[\Delta\phi_t^{(1)}(s) - \omega s] \exp(in\omega s) \ . \tag{B4}$$

When Eqs. (B2) are inserted into Eq. (B4) we may make further simplifications by noting that integrals of the form $\int_0^\tau ds\, sF(s)$, where $F(s)$ is finite for $s \to 0$, yield terms of order τ^n, $n > 1$. Such terms may therefore be disregarded. We obtain

$$\Delta J_t^{(2)}(\tau) = \Delta J_t^{(1)}(\tau) - \sum_{n,l,m=-\infty}^{\infty}\sum\sum [B'_{nm}\sigma_l - i(n+m)B_{nm}\mu_l]\exp[i(n+m+l)\phi]\int_0^\tau ds\int_0^s ds_1 R(s_1)\exp[i(n+m)\omega s + il\omega s_1]$$
$$+ \sum_{n=-\infty}^{\infty}\sum_{l=-\infty}^{\infty}(\sigma_n\sigma_l - in\sigma_n\mu_l)\exp[i(n+l)\phi]\int_0^\tau ds\int_0^s ds_1 R(s)R(s_1)\exp(in\omega s + il\omega s_1)\ . \tag{B5}$$

Similarly we get

$$\Delta\phi_t^{(2)}(\tau) = \Delta\phi_t^{(1)}(\tau) + \omega'\sum_{n=-\infty}^{\infty}\sigma_n\exp(in\phi)\int_0^\tau ds\int_0^s ds_1 R(s_1)\exp(in\omega s_1)$$
$$+ \sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\sum_{l=-\infty}^{\infty}[C'_{nm}\sigma_l - i(n+m)C_{nm}\mu_l]\exp[i(n+m+l)\phi]\int_0^\tau ds\int_0^s ds_1\exp[i(n+m)\omega s + il\omega s_1]$$
$$- \sum_{n=-\infty}^{\infty}\sum_{l=-\infty}^{\infty}(\mu'_n\sigma_l - in\mu_n\mu_l)\exp[i(n+l)\phi]\int_0^\tau ds\int_0^s ds_1 R(s)R(s_1)\exp(in\omega s + il\omega s_1)\ . \tag{B6}$$

Third iteration

Inserting Eqs. (B5) and (B6) into the right-hand side of Eqs. (40) and (41) we proceed to obtain $\Delta J_t^{(3)}$ and $\Delta\phi_t^{(3)}$.

It is convenient to write the results in the forms

$$\Delta J_t^{(3)}(\tau) = \Delta J_t^{(2)}(\tau) - \sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}B'_{nm}\exp[i(n+m)\phi]\int_0^\tau ds\,[\Delta J_t^{(2)}(s) - \Delta J_t^{(1)}(s)]\exp[i(n+m)\omega s]$$
$$- \sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}i(n+m)B_{nm}\exp[i(n+m)\phi]\int_0^\tau ds\,[\Delta\phi_t^{(2)}(s) - \Delta\phi_t^{(1)}(s)]\exp[i(n+m)\omega s]$$
$$+ \sum_{n=-\infty}^{\infty}\sigma'_n\exp(in\phi)\int_0^\tau ds\,[\Delta J_t^{(2)}(s) - \Delta J_t^{(1)}(s)]R(s)\exp(in\omega s)$$
$$+ \sum_{n=-\infty}^{\infty}in\sigma_n\exp(in\phi)\int_0^\tau ds\,[\Delta\phi_t^{(2)}(s) - \Delta\phi_t^{(1)}(s)]R(s)\exp(in\omega s)\ , \tag{B7}$$

$$\Delta\phi_t^{(3)}(\tau) = \Delta\phi_t^{(2)}(\tau) + \omega'\int_0^\tau ds\,[\Delta J_t^{(2)}(s) - \Delta J_t^{(1)}(s)] + \sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}C'_{nm}\exp[i(n+m)\phi]\int_0^\tau ds\,[\Delta J_t^{(2)}(s) - \Delta J_t^{(1)}(s)]\exp[i(n+m)\omega s]$$
$$+ \sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}i(n+m)C_{nm}\exp[i(n+m)\phi]\int_0^\tau ds\,[\Delta\phi_t^{(2)}(s) - \Delta\phi_t^{(1)}(s)]\exp[i(n+m)\phi]$$
$$- \sum_{n=-\infty}^{\infty}\mu'_n\exp(in\phi)\int_0^\tau ds\,[\Delta J_t^{(2)}(s) - \Delta J_t^{(1)}(s)]R(s)\exp(in\omega s)$$
$$- \sum_{n=-\infty}^{\infty}in\mu_n\exp(in\phi)\int_0^\tau ds\,[\Delta\phi_t^{(2)}(s) - \Delta\phi_t^{(1)}(s)]R(s)\exp(in\omega s)\ . \tag{B8}$$

As we discuss below, terms of order τ obtained from further iterations are small [of order $\hat{Z}_n/\omega$; $\hat{Z}_n$ is defined by Eq. (14)] and may be neglected. We therefore proceed now to calculate the moments $\langle(\Delta J)^m(\Delta\phi)^k\rangle$ needed in Eq. (31).

Calculation of $\langle\Delta J_t^{(3)}(\tau)\rangle$ and $\langle\Delta\phi_t^{(3)}(\tau)\rangle$

Consider first $\langle\Delta J_t^{(2)}(\tau)\rangle$. Using $\langle R(s)\rangle = 0$ and $\langle R(s)R(s_1)\rangle = CZ(s-s_1)$, $(C = MkT)$, we get from Eqs. (B2) and (B5),

$$\langle\Delta J_t^{(2)}(\tau)\rangle = -\tau\sum_{n=-\infty}^{\infty}B_{n,-n} + \sum_{n=-\infty}^{\infty}\sum_{l=-\infty}^{\infty}(\sigma'_n\sigma_l - i\sigma_n\mu_l)$$
$$\times\exp[i(n+l)\phi]C\int_0^\tau ds\int_0^s ds_1 Z(s-s_1)$$
$$\times\exp(in\omega s + il\omega s_1)\ . \tag{B9}$$

The integral appearing in Eq. (B9) is evaluated in Appendix C. Using Eqs. (C1) and (C2) we get [disregarding terms of order $\hat{Z}(\omega)/\omega$]

$$\langle\Delta J_t^{(2)}(\tau)\rangle = \tau\sum_{n=-\infty}^{\infty}[-B_{n,-n} + C\hat{Z}_n(\omega)(\sigma_n\sigma'_{-n} + in\mu_n\sigma_{-n})]$$
$$= \tau\sum_{n=-\infty}^{\infty}\left[-Mn^2\omega|x_n|^2\hat{Z}_n(\omega) + Cn^2\frac{d|x_n|^2}{dJ}\hat{Z}_n(\omega)\right]\ . \tag{B10}$$

To get the second equality we have also used Eqs. (34)–(36) and Eq. (21).

Consider now the contribution of the second term on the right-hand side of Eq. (B7). Using Eq. (B5) it can be cast in the form

$$- \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} B'_{nm}(\sigma'_k \sigma_l - ik\sigma_k \mu_l)$$

$$\times \exp[i(k+l+m+n)\phi] C \int_0^\tau ds \int_0^s ds_1 \int_0^{s_1} ds_2 Z(s_1 - s_2)$$

$$\times \exp\{i\omega[(n+m)s + ks_1 + ls_2]\} \ . \quad \text{(B11)}$$

The integral appearing in this result is shown in Appendix C to be negligible within our approximations [for $n+m=0$ we obtain a term of order τ^2, otherwise we get terms of order $\hat{Z}(\omega)/\omega$]. Thus, this term does not contribute to $\langle \Delta J_t^{(3)}(\tau) \rangle$.

In a similar way we can show that the contributions from the third and fourth terms in Eq. (B7) are negligible. However, the last term of Eq. (B7),

$$(\text{last}) = \sum_{n=-\infty}^{\infty} in\sigma_n \exp(in\phi)$$

$$\times \int_0^\tau ds \, [\Delta\phi_t^{(2)}(s) - \Delta\phi_t^{(1)}(s)] R(s) \exp(in\omega s)$$

leads to a non-negligible contribution. This results from the term containing ω' in $\Delta\phi_t^{(2)}(\tau) - \Delta\phi_t^{(1)}(\tau)$ Eq. (B6). When inserted to (last) and the average taken we obtain

$$C\omega' \sum_{l=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} in\sigma_l \sigma_n \exp[i(n+l)\phi]$$

$$\times \int_0^\tau ds \int_0^s ds_1 \int_0^{s_1} ds_2 Z(s - s_2) \exp[i\omega(ns + ls_2)] \ . \quad \text{(B12)}$$

The integral appearing here is a special case of the integral Eq. (C5) evaluated in Appendix C. Using Eq. (C10) with $j=2$ the term of Eq. (B12) becomes

$$C\tau \sum_{n=-\infty}^{\infty} \sigma_n \sigma_{-n} \omega' \frac{d\hat{Z}_n}{d\omega} = C\tau \sum_{n=-\infty}^{\infty} \sigma_n \sigma_{-n} \frac{d\hat{Z}_n}{dJ} \quad \text{(B13)}$$

which, using Eq. (34), becomes

$$C\tau \sum_{n=-\infty}^{\infty} n^2 |x_n|^2 \frac{d\hat{Z}_n}{dJ} \ . \quad \text{(B14)}$$

Combining the contributions of Eqs. (B10) and (B14) to $\langle \Delta J_t^{(3)}(\tau) \rangle$ we finally obtain

$$\langle \Delta J_t^{(3)}(\tau) \rangle = \tau M \sum_{n=-\infty}^{\infty} n^2 \left[-\omega |x_n|^2 \hat{Z}_n + kT \frac{d}{dJ} (|x_n|^2 \hat{Z}_n) \right] . \quad \text{(B15)}$$

Introducing

$$\hat{Z}_n^c(\omega) = \int_0^\infty dt \, Z(t) \cos(n\omega t) \ , \quad \text{(B16)}$$

$$\hat{Z}_n^s(\omega) = \int_0^\infty dt \, Z(t) \sin(n\omega t) \ , \quad \text{(B17)}$$

so that $\hat{Z}_n(\omega) = \hat{Z}_n^c(\omega) - i\hat{Z}_n^s(\omega)$, Eq. (B15) may be recast in the form

$$\langle \Delta J_t^{(3)}(\tau) \rangle = 2\tau M \sum_{n=1}^{\infty} n^2 \left[-\omega |x_n|^2 \hat{Z}_n^c + kT \frac{d}{dJ} (|x_n|^2 Z_n^c) \right] . \quad \text{(B18)}$$

A similar calculation using Eq. (B8) results in

$$\langle \Delta\phi_t^{(3)}(\tau) \rangle = \omega\tau + \tau M \sum_{n=1}^{\infty} n \left(\omega - kT \frac{d}{d\tau} \right) \frac{d|x_n|^2}{dJ} \hat{Z}_n^s \ . \quad \text{(B19)}$$

It should be noted that in the reduction procedure for the analogous Markovian problem all relevant terms are obtained in the second iteration step. Here we found a contribution at the third iteration level. In fact, as noted by Lax,[17] terms of order τ which are relevant for Eq. (31) appear in the non-Markovian case in all orders of the iteration procedure. However, examination of the contributions obtained at the fourth and higher iteration steps shows that such terms are always multiplied by powers of the smallness parameter $\hat{Z}_n(\omega)/\omega$, and may therefore be neglected. The integral $I_{n,l}^{(j)}$ [Eq. (C5)] is an example for a contribution appearing at the $j+1$ iteration step. The result Eq. (C10) contains the factor $d^{j-1}\hat{Z}_l(\omega)/d\omega^{j-1}$ which is of order $[\hat{Z}_l(\omega)/\omega]^{j-1}$ so that any term arising from the jth iteration step, $j \geq 3$ contains this smallness parameter. This is true also for the contribution of Eq. (B13) arising at the third iteration step. This, and a corresponding term in $\langle \Delta\phi_t^{(3)}(\tau) \rangle$, are unique in that they also contain $d\omega/dJ$ yielding $d\hat{Z}_l/dJ$ instead of $d\hat{Z}_l/d\omega$.

Calculation of second moments

In calculating $\langle (\Delta J_t)^2 \rangle$, $\langle (\Delta\phi_t)^2 \rangle$, and $\langle \Delta J_t \, \Delta\phi_t \rangle$ we observe that contributions arising from terms which do not appear in $\Delta J_t^{(1)}$ and $\Delta\phi_t^{(1)}$ contain at least three time integrals with one Z function or four such integrals with two Z functions in the integrand. All such contributions can be shown to be either of order τ^N, $N>1$, or of order $[\hat{Z}_n(\omega)/\omega]^N$, $N \geq 1$, and may thus be neglected in our approximation. As an example, we evaluate in Appendix C the contribution to $\langle [\Delta J_t(\tau)]^2 \rangle$ arising from the third term of Eq. (B5). The desired second-order moments may therefore be obtained from Eqs. (B2) and (B3). Equation (B2) leads to

$$\langle [\Delta J_t(\tau)]^2 \rangle = \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \sigma_n \sigma_m \exp[i(n+m)\phi]$$

$$\times \int_0^\tau ds \int_0^\tau ds_1 \langle R(s) R(s_1) \rangle \exp(in\omega s + in\omega s_1) \ , \quad \text{(B20)}$$

which in a way similar to that used to yield Eq. (C2) from Eq. (C1), results in

$$\langle (\Delta J_t)^2 \rangle = 2\tau MkT \sum_{n=-\infty}^{\infty} \sigma_n \sigma_{-n} \hat{Z}_n^c \ . \quad \text{(B21)}$$

In a similar way Eqs. (B2) and (B3) lead to

$$\langle \Delta J_t \, \Delta\phi_t \rangle = 2\tau MkT \sum_{n=-\infty}^{\infty} \sigma_n \mu_{-n} \hat{Z}_n^c \ , \quad \text{(B22)}$$

$$\langle (\Delta\phi_t)^2 \rangle = 2\tau MkT \sum_{n=-\infty}^{\infty} \mu_n \mu_{-n} \hat{Z}_n^c \ . \quad \text{(B23)}$$

Using Eqs. (34) and (35) and Eq. (22) we finally get

$$\langle (\Delta J_t)^2 \rangle = 4\tau MkT \sum_{n=1}^{\infty} n^2 |x_n|^2 \hat{Z}_n^c \ , \quad \text{(B24)}$$

$$\langle \Delta J_t \, \Delta\phi_t \rangle = 0 \ , \quad \text{(B25)}$$

$$\langle (\Delta\phi_t)^2 \rangle = 4\tau MkT \sum_{n=1}^{\infty} \left| \frac{dx_n}{dJ} \right|^2 \hat{Z}_n^c \ . \quad \text{(B26)}$$

In obtaining the results of Eqs. (B18) and (B19) and Eqs. (B24) and (B25) we have limited ourselves to terms up to first order in expansions such as $B_{nm}(J + \Delta J)$

$= B_{nm}(J) + (dB_{nm}/dJ)\,\Delta J + \cdots$ [see discussion before Eq. (B4)]. It may be shown using methods similar to those used in Appendix C, that contributions from higher terms are negligible, being of order $\tau^n (n > 1)$ or $(Z/\omega)^n$ $(n \geq 1)$.

APPENDIX C

Here we evaluate approximately some integrals which are used in the reduction procedure described in Appendix B. Consider first

$$I_{nl}(\tau) = \int_0^\tau ds \int_0^s ds_1 Z(s - s_1) \exp(in\omega s + il\omega s_1) \ , \quad \text{(C1)}$$

which appear, e.g., in Eq. (B9). Introducing a new variable $x = s - s_1$ we get

$$I_{nl}(\tau) = \int_0^\tau ds \exp[i(n+l)\omega s] \int_0^s dx\, Z(x) \exp(-il\omega x)$$

$$= \int_0^\tau ds \exp[i(n+l)\omega s] \int_0^\tau dx\, Z(x) \exp(-il\omega x)$$

$$- \int_0^\tau ds \exp[i(n+l)\omega s] \int_s^\tau dx\, Z(x) \exp(-il\omega x) \ .$$

The first term is approximately $Z_l(\omega)\,\delta_{n,-l}\,\tau$ while the second one may be evaluated by parts

$$\int_0^\tau ds \left(\exp[i(n+l)\omega s]\right) \left(\int_s^\tau dx\, Z(x) \exp(-il\omega x) \right)$$

$$= \left(\int_s^\tau dx\, Z(x) \exp(-il\omega x) \right) \frac{\exp[i(n+l)\omega s]}{i(n+l)\omega} \Bigg|_{s=0}^{s=\tau}$$

$$+ \int_0^\tau ds\, Z(s) \frac{\exp(in\omega s)}{i(n+l)\omega} = \frac{\hat{Z}_{-n}(\omega) - \hat{Z}_l(\omega)}{i(n+l)\omega} \ .$$

Thus,

$$I_{nl}(\tau) \simeq \tau \hat{Z}_l(\omega)\,\delta_{n,-l} + O[\hat{Z}(\omega)/\omega] \ . \quad \text{(C2)}$$

Next consider the integral

$$I_{n;kl}(\tau) = \int_0^\tau ds \exp(in\omega s) \int_0^s ds_1 \int_0^{s_1} ds_2 Z(s_1 - s_2)$$

$$\times \exp(ik\omega s_1 + il\omega s_2) \ , \quad \text{(C3)}$$

which appears in Eq. (B11). We rewrite it in the form

$$I_{n;kl}(\tau) = I_{kl}(\tau) \int_0^\tau ds \exp(in\omega s)$$

$$- \int_0^\tau ds \exp(in\omega s) \int_s^\tau ds_1 \int_0^{s_1} ds_2 Z(s_1 - s_2)$$

$$\times \exp(ik\omega s_1 + il\omega s_2) \ .$$

The multiple integral may be evaluated by parts in a way similar to what was done above, resulting in

$$I_{n;kl}(\tau) = \frac{1}{in\omega} \{[\exp(in\omega\tau) - 1] + (1 - \delta_{n,0}) \exp(in\omega\tau)\}$$

$$\times I_{kl}(\tau) - \frac{1}{in\omega} I_{n+k,l}(\tau) \ , \quad \text{(C4)}$$

where the two-index integrals I_{kl} are given by Eq. (C2). The result contains terms of order τ^2 or of order $\hat{Z}(\omega)/\omega$.

We further consider the integral

$$I_{n,l}^{(j)} \equiv \int_0^\tau ds \int_0^s ds_1 \int_0^{s_1} ds_2 \cdots \int_0^{s_{j-1}} ds_j Z(s - s_j)$$

$$\times \exp(in\omega s + il\omega s_j) \ . \quad \text{(C5)}$$

Rewrite it in the form

$$I_{n,l}^{(j)} = \int_0^\tau ds \exp[i(n+l)\omega s]\, G_j(s) \ , \quad \text{(C6)}$$

$$G_j(s) = \int_0^s ds_1 \int_0^{s_1} ds_2 \cdots \int_0^{s_{j-1}} ds_j F(s - s_j) \ , \quad \text{(C7)}$$

$$F(s - s_j) = Z(s - s_j) \exp[-il\omega(s - s_j)] \ . \quad \text{(C8)}$$

Using repeatedly the relation

$$\int_0^x dy \int_0^y dz = \int_0^x dz \int_z^x dy$$

we obtain from Eq. (C7),

$$G_j(s) = \int_0^s ds_j \int_{s_j}^s ds_1 \int_{s_j}^{s_1} ds_2 \int_{s_j}^{s_2} ds_3 \cdots \int_{s_j}^{s_{j-2}} ds_{j-1} F(s - s_j) \ .$$

Introduce the transformation

$$x_l = s - s_l \ ; \quad dx_l = -ds_l \quad (l = 1, 2, \ldots, j-1)$$

$$y = s - s_j \ ; \quad dy = -ds_j$$

to get

$$G_j(s) = \int_0^s dy \int_0^y dx_1 \int_{x_1}^y dx_2 \int_{x_2}^y dx_3 \cdots \int_{x_{j-2}}^y dx_{j-1} F(y)$$

$$= \int_0^s dy \frac{y^{j-1}}{(j-1)!} F(y) \ .$$

Inserting this result into Eq. (C6) we get

$$I_{n,l}^{(j)} = \frac{1}{(j-1)!} \int_0^\tau ds \exp[i(n+l)\omega s]$$

$$\times \int_0^s dy\, y^{j-1} Z(y) \exp(-il\omega s) \ . \quad \text{(C9)}$$

In order to extract the term of order t and of lowest order in $\hat{Z}(\omega)/\omega$ we may repeat the development that lead from Eq. (C1) to Eq. (C2) to get

$$I_{n,l}^{(j)} \simeq \frac{1}{(j-1)!} \left(\frac{i}{l}\right)^{j-1} \frac{d^{j-1} \hat{Z}_l(\omega)}{d\omega^{j-1}} \tau \delta_{n,-l} \ . \quad \text{(C10)}$$

Next consider the contribution to $\langle [\Delta J_t(\tau)]^2 \rangle$ made by the third term of Eq. (B5). This term has the form

$$\sum_{n=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} A_{n,l} \int_0^\tau ds \int_0^s ds_1 R(s) R(s_1) \exp(in\omega s + il\omega s_1) \ ,$$

where A_n are functions of $J(t)$ and $\phi(t)$. The contribution to $\langle [\Delta J_t(\tau)]^2 \rangle$ contains the integral

$$\int_0^\tau ds \int_0^s ds_1 \int_0^\tau dr \int_0^r dr_1 \exp[i\omega(ns + ls_1 + mr + kr_1)]$$

$$\times \langle R(s) R(s_1) R(r) R(r_1) \rangle \ . \quad \text{(C11)}$$

Since R is Gaussian we have $\langle R(s)R(s_1)R(s_2)R(s_3)\rangle = \langle R(s)R(s_1)\rangle \langle R(s_2)R(s_3)\rangle +$ two permutations. We proceed with one of these contributions arising from the term $\langle R(s)R(s_2)\rangle \langle R(s_1)R(s_3)\rangle = C^2 Z(s - s_2) Z(s_1 - s_2)$, $(C = MkT)$. Furthermore we consider one representative part of the integral, namely

$$I_{nl,mk} = \int_0^{\tau} ds \int_0^{s} ds_1 \int_0^{s_1} ds_2 \int_0^{s_2} ds_3 \times \exp[i\omega(ks + ls_1 + ms_2 + ns_3)]\, Z(s - s_2)\, Z(s_1 - s_3) \ . \tag{C12}$$

This may be rewritten in the form

$$I_{nl,mk} = \int_0^{\tau} ds \int_0^{s} ds_2 \exp[i\omega(ks + ms_2)]\, Z(s - s_2)\, g(s_1, s_2) \ , \tag{C13}$$

$$g(s_1 s_2) = \int_{s_2}^{s} ds_1 \exp[i\omega(l+n)\, s_1] \int_{s_1 - s_2}^{s_1} dx \exp(-i\omega n x)\, Z(x) \ . \tag{C14}$$

In most situations the magnitude of the integral $\int_{s_1-s_2}^{s_1} dx \exp(-i\omega n x)\, Z(x)$ will be maximized for $s_1 = s_2$. Using this upper bound we get

$$g(s_1 s_2) = \delta_{l,-n}(s - s_2) \int_0^{s_2} dx \exp(-i\omega n x)\, Z(x) \ , \tag{C15}$$

where we have also replaced the integral over s_1 by $\delta_{l,-n}(s - s_2)$. Corrections to this term are of order $\hat{Z}/\omega$. Inserting into Eq. (C13) we get

$$I_{nl,mk} \simeq \delta_{l,-n} \int_0^{\tau} ds \exp[i\omega(k+m)s]\, f(s) \ , \tag{C16}$$

$$f(s) = \int_0^{s} ds_2 \exp(-i\omega m s_2)\, Z(s_2)\, s_2 \int_0^{s-s_2} dx \exp(-i\omega n x)\, Z(x) . \tag{C17}$$

An upper bound estimate on the magnitude of $f(s)$ is obtained by replacing the upper limits of the integrals (s and $s - s_2$) by τ. We then get

$$|I_{nl,mk}| \leq \left| \delta_{l,-n}\, \delta_{k,-m}\, \frac{i}{m} \left[\frac{d}{d\omega} \hat{Z}(\omega) \right] \hat{Z}(\omega)\, \tau \right| \ , \tag{C18}$$

which is negligibly small because of the appearance of $d\hat{Z}/d\omega$. In similar ways we can show that other contributions to Eq. (C11) are small so that the term containing Eq. (C11) may be neglected in the calculation of $\langle [\Delta J_t(\tau)]^2 \rangle$.

APPENDIX D

To show that $J = M\omega(J) \sum_{n=-\infty}^{\infty} n^2 |x_n(J)|^2$ we start from

$$J = \frac{M}{2\pi} \oint v(x)\, dx = \frac{M}{2\pi} \int_0^{2\pi} v(J, \phi)\, \frac{\partial x(J, \phi)}{\partial \phi}\, d\phi$$

and use Eqs. (19) to get

$$J = \frac{M}{2\pi} \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} im\, v_n(J)\, x_m(J) \int_0^{2\pi} d\phi \exp[i(n+m)\phi]$$

$$= -iM \sum_{n=-\infty}^{\infty} n v_n x_{-n}$$

which, using Eq. (21) leads to the desired result.

APPENDIX E

Starting from (for a Morse oscillator)

$$x(J, \phi) = x_0 + a \ln\left[\frac{1 - \sqrt{1-\lambda^2}\cos(\phi)}{\lambda^2} \right] \tag{E1}$$

we wish to obtain the coefficient x_n in the expansion

$$x(J, \phi) = \sum_{n=-\infty}^{\infty} x_n \exp(in\phi) \ , \tag{E2}$$

x_n is given by

$$x_n(J) = \frac{1}{2\pi} \int_0^{2\pi} d\phi \exp(-in\phi)\, x(J, \phi) = x_0 \delta_{n,0} + \frac{(-1)^n}{2\pi} \times \int_{-\pi}^{\pi} d\phi \exp(in\phi) \ln\{[1 + \sqrt{1-\lambda^2}\cos(\phi)]/\lambda^2\} \ . \tag{E3}$$

The integral in Eq. (E3) may be evaluated by using the integral

$$\frac{1}{2\pi} \int_{-\pi}^{\pi} d\phi \exp(in\phi) \ln[1 + A^2 - 2A\cos(\phi)] = -\frac{A^n}{n} \ . \tag{E4}$$

The result is

$$x_n(J) = \left[x_0 - \ln\left(\frac{2\lambda^2}{1+\lambda} \right) \right] \delta_{n,0} + \frac{a}{n} \left(\frac{1-\lambda}{1+\lambda} \right)^{n/2} \ . \tag{E5}$$

Substituting Eq. (69) for λ leads to Eq. (71).

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