Escape rate from a metastable state weakly interacting with a heat bath driven by external noise

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Based on a system-reservoir model, where the reservoir is driven by an external stationary, Gaussian noise with arbitrary decaying correlation function, we study the escape rate from a metastable state in the energy diffusion regime. For the open system we derive the Fokker-Planck equation in the energy space and subsequently calculate the generalized non-Markovian escape rate from a metastable well in the energy diffusion domain. By considering the dynamics in a model cubic potential we show that the results obtained from numerical simulation are in good agreement with the theoretical prediction. It has been also shown numerically that the well-known turnover feature can be restored from our model.

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I. INTRODUCTION

Ever since Kramers proposed his seminal work [1] for chemical reaction in terms of the theory of Brownian motion in phase space, the model and its several variants remain ubiquitous in many areas of natural sciences. Through the years it has been a subject of several theoretical [2–8] and experimental [9–11] investigations for understanding the nature of activated rate processes. In the majority of these treatments, one is essentially concerned with a thermally equilibrated bath, which simulates the reaction coordinate to cross the activation energy barrier. The inherent noise of the medium is of internal origin, which implies that the dissipative force which the system experiences in the course of its motion in the medium and the stochastic force acting on the system as a result of the random impact from the constituents of the medium arise from a common mechanism. From a microscopic point of view, the system-reservoir Hamiltonian description [12,13] suggests that the coupling of the system and the reservoir coordinates determines both the noise and the dissipative terms in the Langevin equation describing the motion of the system and therefore these two entities get related through a fluctuation-dissipation relation [14], which is the characteristics of a thermodynamically closed system in contrast to the systems driven by external noise [15,16]. However, when the reservoir is modulated by an external noise, it is likely that it induces fluctuations in the polarization of the reservoir. These fluctuations in turn may drive the system in addition to the usual internal noise of the reservoir. Since the fluctuations of the reservoir crucially depend on the response function, one can envisage a connection between the dissipation of the system and the response function of the reservoir due to external noise, from a microscopic standpoint [17]. At this point it is important to mention that a direct driving of the system coordinate breaks the fluctuation-dissipation relation and can generate biased directed motion that can be seen in ratchets and molecular motors [18]. On the other hand, bath modulation by an external noise agency preserves the fluctuation dissipation relation, as a result of which the well-known Kramers' turnover feature can be restored.

In many cases involving chemical systems the Markovian representation of the Langevin equation is not valid. In the Markovian description the time scale associated with the motion of the thermal bath is much shorter than any relevant molecular time scale. This assumption is practically never realized in cases where the system coordinate is a molecular vibrational coordinate, because the correlation time associated with the thermal bath is usually much longer than a typical molecular vibrational period. This observation is of no consequence for the escape rate in the strong and moderate friction cases, where the particle is 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 crossing dynamics; however, this depends on the relation between the barrier frequency (renormalized by the presence of the friction) and the friction coefficient. But in the low-friction limit, where the well dynamics is important, energy accumulation becomes the rate-determining step. Furthermore, for reactions occurring under the nonequilibrium situation, the well dynamics becomes crucial and becomes dominant in the low-friction regime. Obviously the well dynamics is governed by energy accumulation and relaxation processes. In addition to Kramers' treatment at low-friction, there are several treatments that deal with such a situation, among which Zwanzig [19], using the assumption that the reservoir is always in thermal equilibrium, developed a procedure for reducing the classical Hamilton's equations of motion for a one-dimensional particle interacting with a non-Markovian heat bath. The escape of a particle from a potential well has been treated using a generalized Langevin equation in the low-friction limit by Carmeli and Nitzan (CN) [20]. Thereafter a detailed classical analysis reveals that the rate is significantly modified by memory effects when compared to the corresponding Kramers' theory.

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While nonequilibrium and nonthermal systems have also been investigated phenomenologically by a number of workers in several contexts [16,21–25], these treatments are concerned mainly with direct driving of the system by an external noise or a time-dependent field—e.g., for examining the role of color noise in the stationary probabilities [21], properties of nonlinear systems [22], nature of crossover [23], effect of monochromatic noise [24], and chemical reaction dynamics in anisotropic solvents [25]. In the present paper we consider a system-reservoir model where the reservoir is modulated by an external noise. Our object here is to explore the role of reservoir response on the system dynamics and to calculate the generalized escape rate from a metastable state for a nonequilibrium open system in the energy diffusion regime.

A number of different situations depicting the modulation of the bath may be of physically relevant. Though the dynamics of a Brownian particle in a uniform solvent is well known, it is less clear when the response of the solvent will be time dependent, as in the case of the dynamical properties of suspension in a liquid crystal when projected onto an anisotropic stochastic equation of motion or in the diffusion and reaction in supercritical liquids and growth in living polymerization [25,26]. Also space-dependent friction may be realized from the presence of a stochastic potential in the Langevin equation [27]. As another example, we consider a simple unimolecular conversion from $A \to B$—say, an isomerization reaction. The reaction can be carried out in a photochemically active solvent under the influence the external fluctuating light intensity. Since the fluctuation in the light intensity results in fluctuations in the polarization of the solvent molecules, the effective reaction field around the reactant system gets modified [28]. In passing we mention that the escape rate in the energy diffusion regime is just not a theoretical issue today but has been a subject of experimental investigation over the last two decades [11].

The outlay of the paper is as follows. In Sec. II we discuss a system-reservoir model where the latter is modulated by an external noise and establish an important connection between the dissipation of the system and the response function of the reservoir due to the external noise. The stochastic motion in energy space and Fokker-Planck equation has been constructed in Sec. III. We solve the problem of energy-diffusion controlled-rate processes in Sec. IV. An explicit example with a cubic potential is worked out to illustrate the theory in Sec. V. The paper is concluded in Sec. VI.

II. THE MODEL: HEAT BATH MODULATED BY EXTERNAL NOISE

We consider a classical particle of mass M bilinearly coupled to a heat bath consisting of N harmonic oscillators driven by an external noise. The total Hamiltonian of such a composite system can be written as [12,13]

$$H = \frac{p^2}{2M} + V(x) + \frac{1}{2}\sum_{i=1}^{N}\left\{\frac{p_i^2}{m_i} + m_i\omega_i^2(q_i - g_i x)^2\right\} + H_{int}. \tag{2.1}$$

In the above equation, x and p are the coordinate and momentum of the system particle, respectively, and $V(x)$ is the potential energy of the system. (q_i,p_i) are the variables for the ith oscillator having frequency ω_i and mass m_i. g_i is the coupling constant for the system-bath interaction. H_{int} is the interaction term between the heat bath and the external noise, $\epsilon(t)$, with the following form:

$$H_{int} = \frac{1}{2}\sum_{i=1}^{N} \kappa_i q_i \epsilon(t). \tag{2.2}$$

The type of interaction we have considered between the heat bath and the external noise, H_{int} is commonly known as the *dipole interaction* [29]. In Eq. (2.2), κ_i denotes the strength of the interaction. We consider $\epsilon(t)$ to be a stationary, Gaussian noise process with zero mean and arbitrary correlation function

$$\langle \epsilon(t)\rangle_e = 0, \quad \langle \epsilon(t)\epsilon(t')\rangle_e = 2D\Psi(t-t'), \tag{2.3}$$

where D is the external noise strength, $\Psi(t-t')$ is the external noise kernel, and $\langle \ldots \rangle_e$ implies averaging over the external noise processes.

Eliminating the bath degrees of freedom in the usual way (and putting M and m_i equal to 1) we obtain the following generalized Langevin equation:

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

$$\dot{v} = -\frac{dV}{dx} - \int_0^t dt'\,\gamma(t-t')v(t') + f(t) + \pi(t), \tag{2.4}$$

where

$$\gamma(t) = \sum_{i=1}^{N} g_i^2\omega_i^2 \cos\omega_i t \tag{2.5}$$

and $f(t)$ is the thermal fluctuation generated due to the system-reservoir interaction and is given by

$$f(t) = \sum_{i=1}^{N} g_i\{[q_i(0) - g_i x(0)]\omega_i^2 \cos\omega_i t + v_i(0)\omega_i \sin\omega_i t\}. \tag{2.6}$$

In Eq. (2.4), $\pi(t)$ is the fluctuating force term generated due to the external stochastic driving $\epsilon(t)$ and is given by

$$\pi(t) = -\int_0^t \varphi(t-t')\epsilon(t')dt', \tag{2.7}$$

where

$$\varphi(t) = \sum_{i=1}^{N} g_i\kappa_i\omega_i \sin\omega_i t. \tag{2.8}$$

The form of Eq. (2.4) therefore suggests that the system is driven by two forcing functions $f(t)$ and $\pi(t)$. The initial conditions of the bath oscillators for a fixed choice of the initial condition of the system degrees of freedom determines $f(t)$. To define the statistical properties of $f(t)$, we assume that the *initial distribution* is one in which the bath is equilibrated at $t=0$ in the presence of the system but in the absence of an external noise agency such that $\langle f(t)\rangle=0$ and $\langle f(t)f(t')\rangle=k_BT\gamma(t-t')$.

Now, at $t=0_+$, the external noise agency is switched on and the bath is modulated by $\epsilon(t)$. The system is governed by Eq. (2.4), where apart from the internal noise $f(t)$, another fluctuating force $\pi(t)$ appears, which depends on the external noise $\epsilon(t)$. Therefore, one can define an effective noise $\xi(t)[=f(t)+\pi(t)]$ whose correlation is given by

$$\langle\langle\xi(t)\xi(t')\rangle\rangle = k_BT\gamma(t-t') + 2D\int_0^t dt''\int_0^{t'} dt'''\varphi(t-t'')\times\varphi(t'-t''')\Psi(t''-t''') = C(t-t')(\text{say}), \tag{2.9}$$

along with $\langle\langle\xi(t)\rangle\rangle=0$, where $\langle\langle\ldots\rangle\rangle$ means we have taken two averages independently. While writing Eq. (2.9) we made the assumption $\langle\langle\xi(t)\xi(t')\rangle\rangle=C(t-t')$ which cannot be proved unless the structure of $\varphi(t)$ is explicitly given. However, as we shall see in Sec. V and in the following discussion that it is a valid assumption [see Eqs. (2.15)–(2.17) and (5.5)] for a particular choice of the coupling coefficients $g(\omega)$ and $\kappa(\omega)$ [see Eqs. (2.10) and (2.11)] and for a stationary external noise processes [see Eq. (5.1)]. It should be emphasized that the above relation (2.9) is not a fluctuation-dissipation relation due to the appearance of the external noise intensity. Rather it serves as a *thermodynamic consistency condition*.

Let us now digress a little bit about $\pi(t)$. The statistical properties of $\pi(t)$ are determined by the normal-mode density of the bath frequencies, the coupling of the system with the bath, the coupling of the bath with the external noise, and the external noise itself. Equation (2.7) is reminiscent of the familiar linear relation between the polarization and external field, where π and ϵ play the role of the former and latter, respectively. $\varphi(t)$ can then be interpreted as a response function of the reservoir due to external noise $\epsilon(t)$. The very structure of $\pi(t)$ suggests that this forcing function, although originating from an external force, is different from a direct driving force acting on the system. The distinction lies at the very nature of the bath characteristics (rather than system characteristics) as reflected in the relations (2.7) and (2.8).

In order to obtain a finite result in the continuum limit, the coupling functions $g_i=g(\omega)$ and $\kappa_i=\kappa(\omega)$ are chosen [30] as $g(\omega)=g_0/\sqrt{\tau_c}\omega$ and $\kappa(\omega)=\kappa_0\omega\sqrt{\tau_c}$. Consequently $\gamma(t)$ and $\varphi(t)$ reduce to the following forms:

$$\gamma(t) = \frac{g_0^2}{\tau_c}\int d\omega\mathcal{D}(\omega)\cos\omega t \tag{2.10}$$

and

$$\varphi(t) = g_0\kappa_0\int d\omega\mathcal{D}(\omega)\omega\sin\omega t, \tag{2.11}$$

where g_0 and κ_0 are constants and $1/\tau_c$ is the cutoff frequency of the oscillator (τ_c may be characterized as the correlation time of the bath [15] and for $\tau_c\to 0$ we obtain a δ-correlated noise process). $\mathcal{D}(\omega)$ is the density of modes of the heat bath which is assumed to be a Lorentzian:

$$\mathcal{D}(\omega) = \frac{2}{\pi\tau_c(\omega^2+\tau_c^{-2})}. \tag{2.12}$$

This assumption resembles broadly the behavior of the hydrodynamical modes in a macroscopic system [31]. This form of density of modes, along with the expressions of $g(\omega)$ and $\kappa(\omega)$, allows us to write for the expression of $\varphi(t)$ as

$$\varphi(t) = (g_0\kappa_0/\tau_c)\exp(-t/\tau_c). \tag{2.13}$$

From Eqs. (2.10) and (2.11) one obtains [17]

$$\frac{d\gamma}{dt} = -\frac{g_0}{\kappa_0}\frac{1}{\tau_c}\varphi(t). \tag{2.14}$$

Equation (2.14) is an important content of the present model. This expresses how the dissipative kernel $\gamma(t)$ depends on the response function $\varphi(t)$ of the medium due to external noise $\epsilon(t)$ [see Eq. (2.7)]. Such a relation for the open system can be anticipated in view of the fact that both the dissipation and response functions crucially depend on the properties of the reservoir, especially on its density of modes and its coupling to the system and the external noise source.

To continue, if we assume that $\epsilon(t)$ is a δ-correlated noise—i.e., $\langle\epsilon(t)\epsilon(t')\rangle=2D\delta(t-t')$—then the correlation function of $\pi(t)$ is represented as

$$\langle\pi(t)\pi(t')\rangle = D(g_0\kappa_0)^2\tau_c^{-1}\exp(-|t-t'|/\tau_c), \tag{2.15}$$

where we have neglected the transient terms $(t,t'>\tau_c)$. This equation shows how the heat bath dresses the external noise. Though the external noise is a δ-correlated noise, the system encounters it as an Ornstein-Uhlenbeck nose with the same correlation time as the internal noise but with an intensity depending on the couplings and external noise strength. On the other hand, if the external noise is an Ornstein-Uhlenbeck process with $\langle\epsilon(t)\epsilon(t')\rangle=(D/\tau')\exp(-|t-t'|/\tau')$ where D and τ' are the strength and correlation time of the noise, respectively, the correlation function of $\pi(t)$ is found to be

$$\langle\pi(t)\pi(t')\rangle = \frac{(Dg_0\kappa_0)^2}{(\tau'/\tau_c)^2-1}\frac{\tau'}{\tau_c}\left\{\frac{1}{\tau_c}\exp\left(-\frac{|t-t'|}{\tau'}\right) - \frac{1}{\tau'}\exp\left(-\frac{|t-t'|}{\tau_c}\right)\right\}, \tag{2.16}$$

where we have neglected the transient terms. The dressed external noise $\pi(t)$ now has a more complicated correlation function with two correlation times τ_c and τ'. If the external noise-correlation time is much larger than the internal noise correlation time—i.e., $\tau'\gg\tau_c$—which is more realistic, then the dressed noise is dominated by the external noise—i.e.,

$$\langle\pi(t)\pi(t')\rangle = \{(Dg_0\kappa_0)^2/\tau'\}\exp[-|t-t'|/\tau']. \tag{2.17}$$

On the other hand, when the external noise correlation time is smaller than the internal one, we recover Eq. (2.15).

III. KRAMERS' EQUATION IN ENERGY SPACE

To start with we first define the Fourier transform of $C(t)$ and $\gamma(t)$ as

$$\hat{C}_n(\omega) = \int_0^\infty dt C(t)\exp(-in\omega t), \quad (3.1)$$

$$\hat{\gamma}_n(\omega) = \int_0^\infty dt \gamma(t)\exp(-in\omega t). \quad (3.2)$$

In the absence of external stochastic driving force $\epsilon(t)$, the fluctuation-dissipation relation $\langle f(t)f(t')\rangle = k_B T\gamma(t-t')$ can be expressed in the Fourier domain as [now $C(t-t') = \langle f(t)f(t')\rangle$]

$$\hat{C}_n^c(\omega) = k_B T \hat{\gamma}_n^c,$$

where $\hat{C}_n^c(\omega)$ and $\hat{\gamma}_n^c$ are the cosine components of $\hat{C}_n$ and $\hat{\gamma}_n$, respectively. Unless the explicit form of $\epsilon(t)$ is specified, it is difficult to express the thermodynamic consistency relation (2.9) in the Fourier domain. Without losing generality we thus will use the general form (3.1) and (3.2) to derive the Fokker-Planck equation until we use explicit form of $\epsilon(t)$. Conventionally the low-friction regime assumes the relation $\gamma \ll \omega \ll 1/\tau_c$, where γ is the friction arising due to interaction with the heat bath, evaluated in the Markovian limit. τ_c is the correlation time of the noise due to the heat bath, and ω is the linearized system frequency. Such a relation was also considered by Kramers in the low-friction regime as well as for the white-noise case. But in this paper we are concerned not only the low-friction regime but also with the non-Markovian effect due to the heat bath. In this context we consider the following time scales in the dynamics relevant for energy diffusion in the non-Markovian limit [20]:

$$\gamma \ll 1/\tau_c \ll \omega. \quad (3.3)$$

The separation of time scales in Eq. (3.3) now allows us to write Eq. (2.4) as the action (J) and the angle (ϕ) coordinates:

$$\dot{J} = \frac{\partial x}{\partial \phi}\left[-\int_0^t d\tau\gamma(t-\tau)v(\tau) + \xi(t)\right], \quad (3.4)$$

$$\dot{\phi} = \omega(J) - \frac{\partial x}{\partial J}\left[-\int_0^t d\tau\gamma(t-\tau)v(\tau) + \xi(t)\right], \quad (3.5)$$

where v represents the velocity of the particle and for the deterministic part of the system's Hamiltonian, $H = v^2/2 + V(x)$, we can write

$$\omega(J) = \frac{dH(J)}{dJ}. \quad (3.6)$$

Since the canonical transformation $(x,v)\to(J,\phi)$ has been done with the deterministic part of the Hamiltonian, it is implied that x and v can be expanded in terms of J and ϕ,

$$x(J,\phi) = \sum_{n=-\infty}^{\infty} x_n(J)\exp(in\phi), \quad (3.7a)$$

$$v(J,\phi) = \sum_{n=-\infty}^{\infty} v_n(J)\exp(in\phi), \quad (3.7b)$$

along with $x_n = x_{-n}^*$ and $v_n = v_{-n}^*$. Differentiating Eq. (3.7a) with respect to time and noting that in the action-angle variable space $\dot{\phi} = \omega(J)$ we can write

$$v_n(J) = in\omega(J)x_n(J). \quad (3.8)$$

Since we are dealing with the dynamics in one dimension only, we can choose J and ϕ in such a way that we can make the simplification $x = (1/2)\sum_{n=-\infty}^{\infty}[x_n\exp(in\phi) + x_n^*\exp(-in\phi)]$ for $x = x^*$. With the choice of phase $x = x_{-n}$ [since $\mathrm{Im}(x_n) = 0$], x may be further expressed as $x = \sum_{n=-\infty}^{\infty} x_n \cos n\phi$. Similarly using Eq. (3.8) we get $v = \sum_{n=-\infty}^{\infty} v_n \sin n\phi$ for $v_n = -v_{-n}$ [since $\mathrm{Re}(v_n) = 0$]. Now inserting Eqs. (3.7a) and (3.7b) into Eqs. (3.4) and (3.5) we obtain

$$\dot{J} = -i\sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty} n x_n \exp(in\phi)\int_0^t d\tau\gamma(t-\tau)v_m\exp(im\phi) + i\xi(t)\sum_{n=-\infty}^{\infty} n x_n\exp(in\phi), \quad (3.9)$$

$$\dot{\phi} = \omega(J) + \sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\frac{\partial x_n}{\partial J}\exp(in\phi)\int_0^t d\tau\gamma(t-\tau)v_m\exp(im\phi) - \xi(t)\sum_{n=-\infty}^{\infty}\frac{\partial x_n}{\partial J}\exp(in\phi). \quad (3.10)$$

In Eqs. (3.9) and (3.10), the argument of the damping memory kernel γ is $(t-\tau)$. Now γ decays to zero within the correlation time τ_c. So, to deal with the integrals of Eqs. (3.9) and (3.10), it is reasonable to divide the range of integration into two parts: (a) $|t-\tau| \leq \tau_c$ and (b) $t \gg \tau_c$. Thus following CN [20] we can write

$$\phi(t) = \phi[\tau + (t-\tau)] \simeq \phi(\tau) + \left.\frac{\partial\phi}{\partial t}\right|_{t=\tau}(t-\tau),$$

neglecting higher terms of τ_c. It follows that

$$\phi(\tau) \simeq \phi(t) - (t-\tau)\omega, \quad v_m(\tau) \simeq v_m(t). \quad (3.11)$$

Equation (3.11) is reasonable approximation so far as the use of Eqs. (3.9) and (3.10) is concerned. Within the integral, we therefore manipulate the behavior of ϕ and v_m for a time up to which $\gamma(t-\tau)$ exists and also for the observational time at which γ has decayed to zero. So, more specifically, we can write, for $|t-\tau| \leq \tau_c$,

$$\int_0^t d\tau\gamma(t-\tau)v_m(\tau)\exp[im\phi(\tau)] \simeq v_m(t)\exp[im\phi(t)]\int_0^t d\tau\gamma(t-\tau)\exp[-im(t-\tau)\omega], \quad (3.12)$$

and for $t \gg \tau_c$, using Eq. (3.2), we have

$$\int_0^t d\tau\gamma(t-\tau)v_m(\tau)\exp[im\phi(\tau)] \simeq v_m(t)\exp[im\phi(t)]\hat{\gamma}_m(\omega). \tag{3.13}$$

Putting Eq. (3.13) which takes into account the observational time scale, into Eqs. (3.9) and (3.10) we get

$$\dot{J} = -i\sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty} n x_n v_m \hat{\gamma}_m(\omega)\exp[i(n+m)\phi] + i\xi(t)\sum_{n=-\infty}^{\infty} n x_n \exp(in\phi), \tag{3.14}$$

$$\dot{\phi} = \omega(J) + \sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\frac{\partial x_n}{\partial J} v_m \hat{\gamma}_m(\omega)\exp[i(n+m)\phi] - \xi(t)\sum_{n=-\infty}^{\infty}\frac{\partial x_n}{\partial J}\exp(in\phi). \tag{3.15}$$

Now we are in a position to formulate the Fokker-Planck equation. For this we follow the method proposed by CN [20] which is based on Kramers-Moyal expansion of the transition probability that connects the probability distribution function $P(J,\phi,t)$ at time t with that of $P(J,\phi,t+\tau)$ at a later time $t+\tau$ for small τ, given that we know the moments of the distribution. The time evolution of the probability distribution $P(J,\phi,t)$ is determined by the equation

$$\frac{\partial P}{\partial t} = \lim_{\tau\to 0+}\left[\frac{1}{\tau}\sum_{n=1}^{\infty}\frac{(-1)^n}{n!}\sum_{m,k=0;(m+k=n)}\left(\frac{\partial}{\partial J}\right)^m \times\left(\frac{\partial}{\partial\phi}\right)^k\{\langle\langle(\Delta J_t)^m(\Delta\phi_t)^k\rangle\rangle P\}\right], \tag{3.16}$$

where $\Delta J_t = \Delta J_t(\tau) = J(t+\tau) - J(t)$ and $\Delta\phi_t = \Delta\phi_t(\tau) = \phi(t+\tau) - \phi(\tau)$. At this juncture it is worth recalling that τ is the coarse-grained time scale over which the probability distribution function evolves, whereas τ_c is the correlation time, which due to low damping is much smaller than τ. The low value of γ prompts us to take $1/\gamma$ as the largest time scale for the entire problem. However, the reciprocal of the frequency of oscillation—i.e., $1/\omega$—is the smallest time scale. Our task is now to calculate moments of the form $\langle\langle(\Delta J_t)^m(\Delta\phi_t)^k\rangle\rangle$ where $\langle\langle\cdots\rangle\rangle$ means that we have taken the two averages independently.

To evaluate the moments we make use of the following standard procedure [20,32]:

$$\Delta J_t(\tau) = \int_0^\tau ds\dot{J}[J(t+s),\phi(t+s),t+s], \tag{3.17}$$

$$\Delta\phi_t(\tau) = \int_0^\tau ds\dot{\phi}[J(t+s),\phi(t+s),t+s], \tag{3.18}$$

where $\dot{J}$ and $\dot{\phi}$ are given by Eqs. (3.14) and (3.15), respectively.

The non-Markovian nature—i.e., τ_c is finite but $\tau_c < \tau$—of the present problem allows us to consider all orders of τ in Eq. (3.16). But since $\partial P/\partial t$ is evaluated in the limit $\tau\to 0_+$, terms linear in τ are taken while all the higher powers are neglected. We then recast Eqs. (3.14) and (3.15) in the following form:

$$\dot{J} = -\sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty} B_{nm}(J)\exp[i(n+m)\phi] + \xi(t)\sum_{n=-\infty}^{\infty}\sigma_n(J)\exp(in\phi), \tag{3.19}$$

$$\dot{\phi} = \omega(J) + \sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty} C_{nm}(J)\exp[i(n+m)\phi] - \xi(t)\sum_{n=-\infty}^{\infty}\mu_n(J)\exp(in\phi), \tag{3.20}$$

where

$$\sigma_n(J) = inx_n(J), \tag{3.21}$$

$$\mu_n(J) = \frac{dx_n(J)}{dJ}, \tag{3.22}$$

$$B_{nm}(J) = inx_n(J)v_m(J)\hat{\gamma}_m[\omega(J)], \tag{3.23}$$

$$C_{nm}(J) = \left[\frac{dx_n(J)}{dJ}\right]v_m(J)\hat{\gamma}_m[\omega(J)]. \tag{3.24}$$

Finally the moments can be calculated using the standard iterative process prescribed by CN [20] and they are of the following form:

$$\langle\langle\Delta J_t(\tau)\rangle\rangle = -2\tau\sum_{n=1}^{\infty} n^2\left[\omega|x_n|^2\hat{\gamma}_n^c(\omega) - \frac{d}{dJ}\{|x_n|^2\hat{C}_n^c(\omega)\}\right], \tag{3.25}$$

$$\langle\langle\Delta\phi_t(\tau)\rangle\rangle = \omega\tau + \tau\sum_{n=1}^{\infty} n\left[\omega\hat{\gamma}_n^s(\omega)\frac{d|x_n|^2}{dJ} - \frac{d}{dJ}\left(\hat{C}_n^s(\omega)\frac{d|x_n|^2}{dJ}\right)\right], \tag{3.26}$$

$$\langle\langle[\Delta J_t(\tau)]^2\rangle\rangle = 4\tau\sum_{n=1}^{\infty} n^2|x_n|^2\hat{C}_n^c(\omega), \tag{3.27}$$

$$\langle\langle[\Delta\phi_t(\tau)]^2\rangle\rangle = 4\tau\sum_{n=1}^{\infty} n^2\left|\frac{dx_n}{dJ}\right|^2\hat{C}_n^c(\omega), \tag{3.28}$$

$$\langle\langle\Delta J_t(\tau)\Delta\phi_t(\tau)\rangle\rangle = 0, \tag{3.29}$$

where

$$\hat{\gamma}_n^c = \int_0^\infty dt\gamma(t)\cos(n\omega t), \tag{3.30a}$$

$$\hat{\gamma}_n^s = \int_0^\infty dt\gamma(t)\sin(n\omega t), \tag{3.30b}$$

$$\hat{C}_n^c = \int_0^\infty dt C(t)\cos(n\omega t), \tag{3.30c}$$

$$\hat{C}_n^s = \int_0^\infty dt C(t)\sin(n\omega t). \tag{3.30d}$$

Also,

$$\hat{\gamma}_n(\omega) = \hat{\gamma}_n^c(\omega) - i\hat{\gamma}_n^s(\omega), \tag{3.30e}$$

$$\hat{C}_n(\omega) = \hat{C}_n^c(\omega) - i\hat{C}_n^s(\omega). \tag{3.30f}$$

In the absence of the external noise $\epsilon(t)$, $\hat{C}_n(\omega)$ reduces to $\hat{C}_n(\omega)=k_BT\hat{\gamma}_n(\omega)$ for which Eqs. (3.25)–(3.29) become [20]

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

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

$$\langle [\Delta J_t(\tau)]^2\rangle = 4\tau k_BT\sum_{n=1}^{\infty} n^2|x_n|^2\hat{\gamma}_n^c,$$

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

$$\langle \Delta J_t(\tau)\Delta\phi_t(\tau)\rangle = 0.$$

Note that in the above unnumbered equations there is only one averaging $\langle\cdots\rangle$ instead of two averaging $\langle\langle\cdots\rangle\rangle$ used in this article. This is due to the fact that in the present model we make an extra averaging over the external noise processes in addition to the usual thermal averaging procedure.

Inserting Eqs. (3.25)–(3.29) into Eq. (3.16) and neglecting terms with $n>2$ we obtain the Fokker-Planck equation for $P(J,\phi,t)$ as

$$\frac{\partial P(J,\phi,t)}{\partial t} = \frac{\partial}{\partial J}\left[\varepsilon(J)\left\{\frac{\hat{C}_n^c(\omega)}{\hat{\gamma}_n^c(\omega)}\frac{\partial}{\partial J} + \omega(J)\right\}P\right] + \Gamma(J)\frac{\partial^P}{\partial\phi^2} - \Omega(J)\frac{\partial P}{\partial\phi}, \tag{3.31}$$

where

$$\varepsilon(J) = 2\sum_{n=1}^{\infty} n^2|x_n|^2\hat{\gamma}_n^c(\omega), \tag{3.32}$$

$$\Gamma(J) = 2\sum_{n=1}^{\infty} n^2\left|\frac{dx_n}{dJ}\right|^2\hat{C}_n^c(\omega), \tag{3.33}$$

$$\Omega(J) = \omega + \sum_{n=1}^{\infty} n\left[\omega\hat{\gamma}_n^s\frac{d|x_n|^2}{dJ} - \frac{d}{dJ}\left(\hat{C}_n^s\frac{d|x_n|^2}{dJ}\right)\right]. \tag{3.34}$$

For a distribution function that is initially $(t=0)$ independent of ϕ the diffusion equation in action space becomes

$$\frac{\partial P(J,t)}{\partial t} = \frac{\partial}{\partial J}\left[\varepsilon(J)\left\{\Lambda\frac{\partial}{\partial J} + \omega(J)\right\}P\right], \tag{3.35}$$

where

$$\Lambda = \Lambda(\omega_0) \simeq \frac{\hat{C}_n^c(\omega_0)}{\hat{\gamma}_n^c(\omega_0)}. \tag{3.36}$$

Here ω_0 is the linearized frequency and Λ plays the typical role of k_BT which for $\epsilon(t)=0$ becomes equal to k_BT. Now by virtue of Eq. (3.6), $\omega(J)=\partial H/\partial J=dE/dJ$. Expressing

$$\omega(J) = \nu(E), \tag{3.37}$$

we have

$$\frac{\partial}{\partial J} = \nu(E)\frac{\partial}{\partial E}. \tag{3.38}$$

With this transformation, for an external noise driven bath, the Kramers equation for energy diffusion [Eq. (3.35)] becomes

$$\frac{\partial P(E,t)}{\partial t} = \frac{\partial}{\partial E}\left[D(E)\left(\frac{\partial}{\partial E} + \frac{1}{\Lambda}\right)\nu(E)P(E,t)\right], \tag{3.39}$$

with the following diffusion coefficient:

$$D(E) = \nu(E)2\Lambda(\omega_0)\sum_{n=1}^{\infty} n^2|x_n|^2\int_0^\infty dt\gamma(t)\cos[n\nu(E)t]. \tag{3.40}$$

Equation (3.39) *is the first key result of the present article*. The equation is valid for arbitrary temperature and noise correlation. The prime quantities that determine the equation for energy diffusion (3.39) are the diffusion coefficient D; the open system analog of k_BT, Λ; and the frequency of the dynamical system, $\nu(E)$. Although the expression for the diffusion coefficient (3.40) looks bit complicated and formal due to the appearance of the Fourier coefficients x_n in the summation, it is possible to read the various terms in $D(E)$ in the following way. $D(E)$ is essentially an approximate product of three term $\Lambda(\omega_0)$, $\int_0^\infty dt\gamma(t)\cos[n\nu(E)t]$, and $\nu(E)\sum_{n=1}^\infty n^2|x_n|^2$, where the n dependences of the latter two contributions have been separated out for interpretation. The first term is an analog of k_BT for the open system, the integral is the Fourier transform of the memory kernel, while the sum can be shown to be equal to J (see Appendix D of CN [20]), the action variable. For a system only coupled to a heat bath—i.e., for no external driving—$D(E)$ reduces to the expression derived by CN [20].

IV. ENERGY-DIFFUSION-CONTROLLED RATE OF ESCAPE

The classical treatment of memory effects in the energy-diffusion-controlled escape is now well documented in the literature [20,33,34]. To address the corresponding problem for the open system we first rewrite the Kramers' equation (3.39) in the form of a continuity equation

$$\frac{\partial P(E,t)}{\partial t} + \frac{\partial j_E}{\partial E} = 0, \tag{4.1}$$

where j_E is the stationary flux along the energy coordinate and is given by

$$j_E = -D(E)\left[\frac{\partial}{\partial E} + \frac{1}{\Lambda}\right]\nu(E)P_{st}(E), \tag{4.2}$$

with P_{st} being the stationary probability distribution. For zero current condition, we have the stationary distribution, p_{st} at the source well

$$p_{st}(E) = \frac{N^{-1}}{\nu(E)}\exp(-E/\Lambda), \tag{4.3}$$

where N is the normalization constant. Here it is important to mention that for $\epsilon(t)=0$, one has $p_{st}=P_{eq}$. We now define the rate of escape, k, as flux over population [35],

$$k = j_E/n_a, \tag{4.4}$$

where n_a is the total population at the source well,

$$n_a = \int_0^{E_b} P(E)dE. \tag{4.5}$$

Here E_b is the value of the activation barrier. Following Büttiker, Harris, and Landauer (BHL) [36] we use a Kramers-like ansatz

$$P(E) = \eta(E)p_{st}(E) \tag{4.6}$$

to arrive at

$$j_E = -D(E)\nu(E)p_{st}(E)\frac{\partial\eta(E)}{\partial E}. \tag{4.7}$$

Integrating the above expression from $E=E_1 \simeq \Lambda$ to $E=E_b$, one derives an expression for energy independent current j_E (with $E \leqslant E_b$) as

$$j_E = \frac{\eta(\Lambda) - \eta(E_b)}{\int_\Lambda^{E_b} dE/D(E)\nu(E)p_{st}(E)} = [1-\eta(E_b)]D(E_b)\frac{N^{-1}}{\Lambda}\exp(-E_b/\Lambda), \tag{4.8}$$

where we have used the boundary condition $\eta(\Lambda) \simeq 1$.

Following the original reasoning by BHL we now allow an outflow j_{out} from each energy range E to $E+dE$, with each E satisfying the condition $E \geqslant E_b$. Then we can write

$$dj_{out} = \alpha\nu(E)\eta(E)p_{st}(E)dE, \tag{4.9}$$

which is compensated by a divergence in the vertical flow:

$$\frac{dj_E}{dE} = \alpha\nu(E)\eta(E)p_{st}(E). \tag{4.10}$$

Here α is a parameter that has been set approximately equal to 1 by BHL, though in general the parameter α is not always equal to 1 [5,37]. Inserting the expression for nonequilibrium current [Eq. (4.7)] in the above expression we obtain an ordinary differential equation for $\eta(E)$:

$$D(E)\frac{d^2\eta}{dE^2} + \left[\frac{dD}{dE} - \frac{D(E)}{\Lambda}\right]\frac{d\eta}{dE} - \alpha\eta(E) = 0. \tag{4.11}$$

Within a small energy range above E_b one can assume essentially a constant diffusion coefficient—i.e., $dD(E)/dE|_{E\simeq E_b}=0$ for $E \geqslant E_b$. Now substituting a trial solution of the form $\eta(E)=\mathcal{C}\exp(sE/\Lambda)$ for $s<0$, in Eq. (4.11) we have

$$s_- = \frac{1}{2}\left[\left(1+\frac{4\alpha\Lambda^2}{D(E_b)}\right)^{1/2} - 1\right]. \tag{4.12}$$

Setting $\eta(E)=\eta(E_b)\exp[s(E-E_b)/\Lambda]$ and putting this into Eq. (4.7) and comparing this with the right-hand side of Eq. (4.8) we have

$$\eta(E_b) = 1/(1-s) \quad \text{for } s<0. \tag{4.13}$$

Thus the escape rate k can be written as

$$k = j_E\left[\int_0^{E_b}\eta(E)p_{st}(E)dE\right]^{-1}. \tag{4.14}$$

Making use of Eq. (4.13) in Eq. (4.8) and the resulting expression for j_E in Eq. (4.14) we obtain

$$k = \frac{-s}{1-s}\left[\frac{\int_0^{E_b}\eta(E)p_{st}(E)dE}{(N^{-1}/\Lambda)D(E_b)\exp(-E_b/\Lambda)}\right]^{-1}. \tag{4.15}$$

For the dynamics at the bottom we have $\eta \to 1$. For ω_0 being the frequency at the bottom of the source well we now calculate the total population of the source well,

$$n_a = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} p_{st}(E)dxdp = N^{-1}(2\pi\Lambda/\omega_0). \tag{4.16}$$

So for the external-noise-driven heat bath the non-Markovian rate of escape from a metastable well in the low-friction regime is given by

$$k = \left[\frac{\{1+[4\alpha\Lambda^2/D(E_b)]\}^{1/2}-1}{\{1+[4\alpha\Lambda^2/D(E_b)]\}^{1/2}+1}\right]\frac{D(E_b)}{\Lambda^2}\omega_0\exp(-E_b/\Lambda). \tag{4.17}$$

Equation (4.17) *is the second key result of present paper.*

V. SPECIFIC EXAMPLE: HEAT BATH DRIVEN BY EXTERNAL COLOR NOISE

As a specific example, we consider that the heat bath is modulated externally by a colored noise $\epsilon(t)$ with noise correlation

$$\langle \epsilon(t)\epsilon(t')\rangle = \frac{D_e}{\tau_e}\exp\left[-\frac{|t-t'|}{\tau_e}\right], \tag{5.1}$$

where D_e and τ_e are the strength and the correlation time of the external noise, respectively. In addition to that we also consider the internal noise $f(t)$ to be white. The effective Gaussian Ornstein-Uhlenbeck noise $\xi(t)=f(t)+\pi(t)$ will have an intensity D_R and a correlation time τ_R given by [15]

$$D_R = \int_0^\infty \langle \xi(t)\xi(0)\rangle dt, \tag{5.2}$$

$$\tau_R = \frac{1}{D_R}\int_0^\infty t\langle \xi(t)\xi(0)\rangle dt. \tag{5.3}$$

Following the above definitions and using Eq. (2.17) we have

$$D_R = g_0^2(k_BT + D_e\kappa_0^2), \quad \tau_R = \frac{D_e g_0^2\kappa_0^2}{D_R}\tau_e. \tag{5.4}$$

It is important to mention here that since we are treating the internal noise processes to be a δ-correlated one ($\tau_c \to 0$), τ_c does not appear explicitly in the expression of D_R and τ_R. With this the effective noise $\xi(t)$ becomes a colored noise and its correlation is given by

$$\langle\langle \xi(t)\xi(t')\rangle\rangle = \frac{D_R}{\tau_R}\exp\left[-\frac{|t-t'|}{\tau_R}\right]. \tag{5.5}$$

To study the dynamics we consider a model cubic potential of the form $V(x)=Ax^2-Bx^3$ where A and B are two constant parameters with $A>0$ and $B>0$. The diffusion coefficient $D(E_b)$ in the internal white noise limit reduces to

$$D(E_b) = g_0^2\Lambda(\omega_0)J, \tag{5.6}$$

where the action J is represented as [20]

$$J = 2\nu(E_b)\sum_{n=1}^{\infty} n^2|x_n|^2 \tag{5.7}$$

and can be calculated using the following standard form:

$$J = \frac{1}{\pi}\int_{x_1}^{x_2} v\,dx, \tag{5.8}$$

where x_1 and x_2 are the two turning points of oscillation for which v is equal to zero and they both correspond to total system energy E. In principle, they are the first two roots (in ascending order of magnitude) of the cubic equation

$$-Ax^2 + Bx^3 + E = 0. \tag{5.9}$$

For an external-color-noise-driven heat bath $\Lambda(\omega_0)$ [see Eq. (3.36)] reduces to

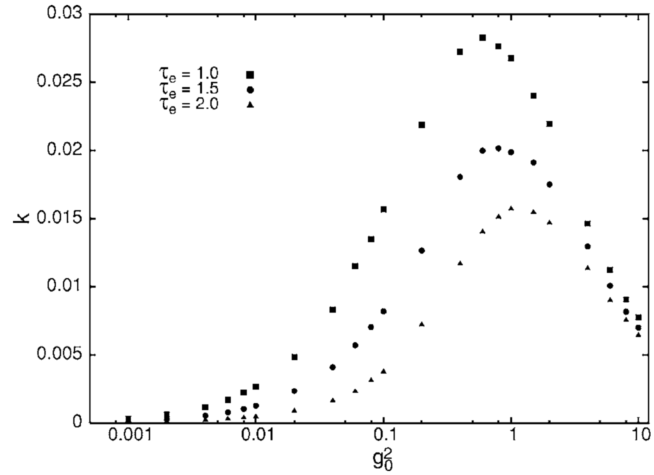

FIG. 1. Turnover phenomenon for an external-color-noise-driven bath. Parameters used are $k_BT=0.1$, $D_e=1.0$, $\kappa_0^2=5.0$, $\alpha=1.0$, $A=0.5$, and $E_b=5.0$ (scale arbitrary).

$$\Lambda(\omega_0) = \frac{k_BT + D_e\kappa_0^2}{1+\omega_0^2\tau_e^2}. \tag{5.10}$$

We then numerically solve the Langevin equation (2.4) using the second-order stochastic Heun algorithm [38,39]. To ensure the stability of our simulation we have used a small time step $\Delta t=0.001$ with $\Delta t/\tau_R \ll 1$. The numerical rate has been defined as the inverse of the mean first-passage time [40,41]. The mean first-passage time has been calculated by averaging over 5000 trajectories. The value of the other parameters used are given in the caption of Figs. 1 and 2

In his dynamical theory of chemical reactions Kramers identified two distinct regimes of stationary nonequilibrium states in terms of dissipation constant (γ). The essential result of Kramers' theory is that the rate varies linearly in the weak dissipation regime (characterized as the diffusion of energy) and inversely in the intermediate to strong damping

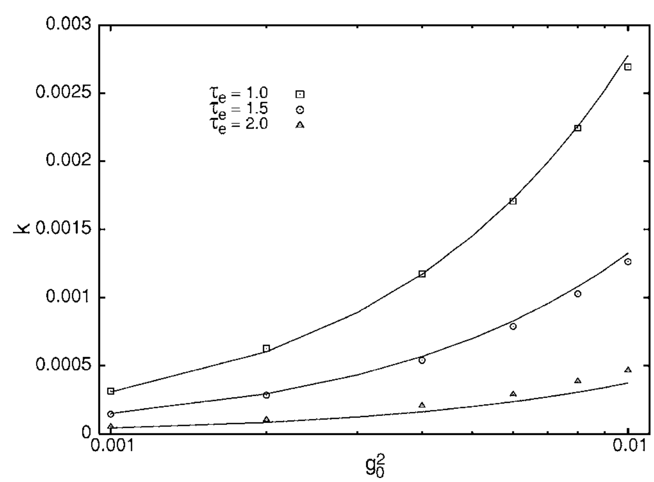

FIG. 2. Barrier crossing rate in the low-friction regime ($0.001 \leq g_0^2 \leq 0.01$), a comparison between the theoretical prediction, Eq. (4.17) (solid lines) and Langevin simulation. Parameters used are $k_BT=0.1$, $D_e=1.0$, $\kappa_0^2=5.0$, $\alpha=1.0$, $A=0.5$, and $E_b=5.0$ (scale arbitrary).

regime (spatial-diffusion-limited regime). That is, in between the two regimes the rate constant as a function of dissipation constant exhibits a bell-shaped curve known as Kramers' turnover [4,5]. In the traditional system reservoir model the dissipation and fluctuation, both originating from a common source, the reservoir, are connected through the fluctuation-dissipation relation. A typical signature of this relation can be seen through the turnover phenomenon in Kramers' dynamics. Whereas for a thermodynamic open system where the heat bath is modulated by an external noise, both the dissipation and response functions depend on the properties of the reservoir, mainly on its density of modes and its coupling to the system and the external noise source. By virtue of this connection between the dissipation and external noise sources, Eq. (2.9) plays the typical role of the thermodynamic consistency relation, an analog of the fluctuation-dissipation relation for a thermodynamic closed system, for which one can expect a turnoverlike feature in Kramers' dynamics (for the open system). So for the external-color-noise-driven bath we first wanted to check whether Kramers' turnover feature can be restored from our model. In Fig. 1 we have plotted the rate constant k obtained from Langevin simulation for a wide range of damping constant g_0^2 for different values of external noise correlation time τ_e. The figure shows usual Kramers' turnover of the rate constant with variation of the damping constant. The shift of the maxima occurs as the external noise correlation time varies, a typical effect of the bath modulation.

Next we compared the theoretical result (4.17) with the numerical simulation data. In Fig. 2 we have plotted the rate constant k against the damping constant g_0^2 in the weak-damping domain ($0.001 \leqslant g_0^2 \leqslant 0.01$) for different values of the external noise correlation time τ_e. What we observe is that the agreement between the theoretical prediction and numerical simulation is quite satisfactory.

VI. CONCLUSION

Based on a simple system-reservoir Hamiltonian approach, we have studied the behavior of a subsystem coupled to a heat bath where the heat bath is modulated by an external stationary, Gaussian noise process with arbitrary decaying correlation function, thereby making the system thermodynamically open. For such an open system we have analytically derived the generalized steady-state Kramers' escape rate from a metastable well in the low-friction regime. The main conclusions of the present work are the following.

(i) Since the reservoir is driven by the external noise and the dissipative properties of the system depend on the reservoir, we have established a simple relation between the dissipation and response functions of the medium due to external noise. This relation is important for identifying the effective temperature of the heat bath characterizing the stationary state of the thermodynamically open system.

(ii) We then followed the dynamics of the open system in the energy space and derived the corresponding Fokker-Planck equation with diffusion coefficient containing the effective temperaturelike quantity which is an open-system analog of k_BT. Following the standard approach we then derived the generalized non-Markovian Kramers' escape rate from a metastable well in the energy diffusion regime.

(iii) From the point of view of the realistic situation we considered the special case where the internal noise is white and the external noise is colored and have calculated the escape rate for a model cubic potential. We have shown that the theoretical prediction agrees reasonably well with numerical simulation. In addition to that we have also shown that our model recovers the turnover feature of the Kramers' dynamics when the external noise modulates the reservoir.

(iv) Finally, as shown in the present work one can easily tune the external-noise parameters from outside which can be used to study the effect of several kinds of noise properties—e.g., long-tail Gaussian noise [7]—in the Kramers' dynamics. Another suitable candidate for studying the escape rate dynamics can be irreversibly driven environments [42,43]. In our future communication we would like to pursue such a theoretical analysis.

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