The generalized Kramers’ theory for an external noise driven bath

Jyotipratim Ray Chaudhuri, Suman Kumar Banik and Deb Shankar Ray *

Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India.

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Abstract

We consider a system-reservoir model where the reservoir is modulated by an external noise. Both the internal noise of the reservoir and the external noise are stationary, Gaussian and are characterized by arbitrary decaying correlation functions. Based on a relation between the dissipation of the system and the response function of the reservoir driven by external noise we derive the generalized Kramers’ rate for this nonequilibrium open system.

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*e-mail : pcdsr@mahendra.iacs.res.in
I. INTRODUCTION

More than half a century ago Kramers proposed a diffusion model for chemical reactions in terms of the theory of Brownian motion in phase space [1]. Since then the model and several of its variants have been ubiquitous in many areas of physics, chemistry and biology for understanding the nature of activated processes in classical [2–9], quantum and semiclassical [10–17] systems, in general. These have become the subject of several reviews [3,16–18] and monograph [19] in the recent past.

In the majority of these treatments one is essentially concerned with an equilibrium thermal bath at a finite temperature which stimulates the reaction co-ordinate to cross the activation energy barrier. The inherent noise of the medium is of internal origin. This implies that the dissipative force which the system experiences in course of its motion in the medium and the stochastic force acting on the system as a result of random impact from the constituents of the medium arise from a common mechanism. From a microscopic point of view the system-reservoir Hamiltonian description [20–23] developed over the decades suggests that the coupling of the system and the reservoir co-ordinates determines both the noise and the dissipative terms in the Langevin equation describing the motion of the system. It is therefore not difficult to anticipate that these two entities get related through a fluctuation-dissipation relation [24] (these systems are sometimes classified as thermodynamically closed system in contrast to the systems driven by external noise in nonequilibrium statistical mechanics [25]). 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 usual internal noise of the reservoir. Since the polarization fluctuations of the reservoir crucially depend on its response functions, one can further envisage a connection between the dissipation of the system and the response function of the reservoir due to the external noise from a microscopic point of view.

In the present paper we explore this connection in the context of activated rate processes when the reservoir is modulated by an external noise. Specifically our object here is to
calculate the generalized Kramers’ rate for the steady state of a nonequilibrium open system. Both the internal and the external noises are Gaussian, stationary and are characterized by arbitrary decaying correlation functions. While the internal noise of the reservoir is thermal, the external noise may be of thermal or non-thermal type. We consider the stochastic motion to be spatial diffusion limited and calculate the rate of escape in the intermediate to strong damping regime. We further mention that nonequilibrium, non-thermal systems have also been investigated phenomenologically by a number of workers in several other contexts, e.g., for examining the role of color noise in stationary probabilities [26], properties of nonlinear systems [27], nature of crossover [28], rate of diffusion limited coagulation processes [29], effect of monochromatic noise [30], etc. While these treatments concern direct driving of the system by an external noise the present consideration is based on modulation of the bath. A number of different situations depicting the modulation of the bath by an external noise may be physically relevant. As, for example, we consider a simple unimolecular conversion (say, an isomerization reaction) from $A \rightarrow B$. The reaction is carried out in a photochemically active solvent under the influence of external fluctuating light intensity. Since the fluctuations in the light intensity result in the fluctuations in the polarization of the solvent molecules, the effective reaction field around the reactant system gets modified. Provided the required stationarity of this nonequilibrium open system is maintained (which is not difficult in view of the experiments performed in the studies of external noise-induced transitions in photochemical systems [31]) the dynamics of barrier crossing becomes amenable to the present theoretical analysis that follows.

The remaining part of this paper is organized as follows: In Sec. II we discuss a system-reservoir model where the later is modulated by an external noise and establish an interesting connection between the dissipation of the system and the response function of the reservoir due to external noise. The stochastic motion in a linearized potential field is described in terms of a Fokker-Planck equation in Sec. III. Based on the traditional flux over population method [32] we derive in Sec. IV the generalized expression for the Krmaers’ rate of escape from a metastable well. The general theory is illustrated with a specific example in Sec. V.
II. THE SYSTEM-RESERVOIR MODEL : THE RESERVOIR MODULATED BY EXTERNAL NOISE

We consider a classical particle of mass $M$ is coupled to a heat bath of $N$ harmonic oscillators. The various modes of heat bath are perturbed by an external random force. The interaction between external force and bath co-ordinates is added as a new term ($H_{int}$) in the standard system-reservoir Hamiltonian of Zwanzig form [22]. The total Hamiltonian is given by

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

In Eq.(1), $x$ and $p$ are the co-ordinate and momentum of the system particle; $(q_i, p_i)$ are the variables associated with the $i$-th oscillator and $\omega_i$ and $m_i$ are the corresponding frequency and mass respectively. $a_i(x)$ measures the interaction between the particle and the bath. $V(x)$ is the potential energy of the particle. $H_{int}$ is assumed to be of the form

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

The coupling function $\kappa_i$ measures the strength of interaction and $\epsilon(t)$ is the external noise which we assume to be stationary and Gaussian with zero mean, i.e., $\langle \epsilon(t) \rangle = 0$.

We now consider the interaction between the system and the heat bath to be linear, i.e.,

$$a_i(x) = g_i x , \quad (3)$$

and then eliminate the bath degrees of freedom in the usual way [20,22,23] to obtain the following generalized Langevin equation

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

$$\dot{v} = -\frac{dV}{dx} - \int_0^t dt' \gamma(t-t') v(t') + f(t) + \pi(t) \quad (4)$$

[ while constructing Eq.(4) we have set $M$ and $m_i$ equal to unity ] where
\[
\gamma(t) = \sum_{i=1}^{N} g_i^2 \omega_i^2 \cos \omega_i t .
\] (5)

\( f(t) \) is the fluctuation generated through the coupling between the system and the heat bath and is given by

\[
f(t) = \sum_{i=1}^{N} g_i \left\{ [q_i(0) - g_i x(0)] \omega_i^2 \cos \omega_i t + v_i(0) \omega_i \sin \omega_i t \right\} .
\] (6)

\( f(t) \) thus depends on the coupling functions \( g_i \) and the normal mode initial conditions, which we assume to be canonically distributed. The statistical properties of \( f(t) \) can then be summarized in the following equations;

\[
\langle f(t) \rangle = 0 \quad \text{and} \quad (7a)
\]
\[
\langle f(t)f(t') \rangle = k_B T \gamma(t-t') .
\] (7b)

In Eq.(4), \( \pi(t) \) is a force term driven by the external noise \( \epsilon(t) \) and is given by

\[
\pi(t) = - \int_0^t \varphi(t-t') \epsilon(t') \, dt' ,
\] (8)

where

\[
\varphi(t) = \sum_{i=1}^{N} g_i \kappa_i \omega_i \sin \omega_i t .
\] (9)

The statistical properties of \( \pi(t) \) are determined by the normal mode distribution of the bath, the coupling of the system with the bath, the coupling of the bath with the external noise and the external noise itself. It may also be noted that the external noise \( \epsilon(t) \) and the internal noise \( f(t) \) are independent of each other because they have been generated from different origin. Eq.(8) is reminiscent of the familiar linear relation between the polarization and the external field where \( \pi \) and \( \epsilon \) play the role of the former and the later, respectively. \( \varphi(t) \) can then be interpreted as a response function of the reservoir due to external noise \( \epsilon(t) \).

In the continuum limit \( \gamma(t) \) and \( \varphi(t) \) reduce to the following forms

\[
\gamma(t) = \int d\omega \mathcal{D}(\omega) \, g^2(\omega) \omega^2 \cos \omega t
\] (10)
and

\[ \varphi(t) = \int d\omega \, D(\omega) \, \kappa(\omega) \, \omega \, g(\omega) \, \sin \omega t . \]  \hspace{1cm} (11)

where \( D(\omega) \) is the density of modes of the heat bath. If the coupling functions \( g(\omega) \) and \( \kappa(\omega) \) are assumed to be of the following forms \[33\] to obtain a finite result in the continuum limit,

\[ g(\omega) = \frac{g_0}{\sqrt{\tau_c} \, \omega} \quad \text{and} \quad \kappa(\omega) = \sqrt{\tau_c} \, \omega \, \kappa_0 \]

where \( g_0 \) and \( \kappa_0 \) are constants and \( \tau_c \) is the correlation time, i.e., \( \tau_c^{-1} \) is the cutoff frequency of the harmonic oscillators then the expressions for \( \gamma(t) \) and \( \varphi(t) \) reduce to

\[ \gamma(t) = \frac{g_0^2}{\tau_c} \int d\omega \, D(\omega) \, \cos \omega t \]  \hspace{1cm} (12)

and

\[ \varphi(t) = g_0 \, \kappa_0 \int d\omega \, D(\omega) \, \omega \, \sin \omega t . \]  \hspace{1cm} (13)

From the above two relations, we obtain

\[ \frac{d\gamma}{dt} = -\frac{g_0}{\kappa_0} \frac{1}{\tau_c} \varphi(t) . \]  \hspace{1cm} (14)

Eq.(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.(8) ]. Such a relation for the open system can be anticipated in view of the fact that both the dissipation and the response function 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. In what follows we shall be concerned with the consequences of this relation in terms of the Langevin description in the next section ( Eq.(15) ).

III. GENERALIZED FOKKER-PLANCK DESCRIPTION OF THE LINEARIZED MOTION

We now consider the system to be a harmonically bound particle of unit mass and of frequency \( \omega_0 \). Then because of Eq.(8) the Langevin equation (4) becomes
\[ \dot{x} = v \,, \]
\[ \dot{v} = -\omega_0^2 x - \int_0^t dt' \gamma(t-t') v(t') + f(t) - \int_0^t dt' \varphi(t-t') \epsilon(t') \]  \hspace{1cm} (15)

The Laplace transform of Eq. (15) allows us to write a formal solution for the displacement of the form

\[ x(t) = \langle x(t) \rangle + \int_0^t dt' h(t-t') f(t') - \frac{\kappa_0}{g_0} \tau_c \omega_0^2 \int_0^t dt' h(t-t') \epsilon(t') \]
\[ -\frac{\kappa_0}{g_0} \tau_c \int_0^t dt' h_2(t-t') \epsilon(t') \]  \hspace{1cm} (16)

where we have made use of the relation (14) explicitly.

Here

\[ \langle x(t) \rangle = \chi_x(t)x(0) + h(t)v(0) \]  \hspace{1cm} (17)

with \(x(0)\) and \(v(0)\) being the initial position and initial velocity of the oscillator, respectively, which are nonrandom and

\[ \chi_x(t) = \left[ 1 - \omega_0^2 \int_0^t h(\tau) \, d\tau \right] \]  \hspace{1cm} (18)

The kernel \(h(t)\) is the Laplace inversion of

\[ \tilde{h}(s) = \frac{1}{s^2 + \tilde{\gamma}(s) s + \omega_0^2} \]  \hspace{1cm} (19)

where, \(\tilde{\gamma}(s) = \int_0^\infty e^{-st} \gamma(t) \, dt\), is the Laplace transform of the friction kernel \(\gamma(t)\), and

\[ h_2(t) = \frac{d^2 h(t)}{dt^2} \]  \hspace{1cm} (20)

The time derivative of Eq. (15) yields

\[ v(t) = \langle v(t) \rangle + \int_0^t dt' h_1(t-t') f(t') - \frac{\kappa_0}{g_0} \tau_c \omega_0^2 \int_0^t dt' h_1(t-t') \epsilon(t') \]
\[ -\frac{\kappa_0}{g_0} \tau_c \int_0^t dt' h_3(t-t') \epsilon(t') \]  \hspace{1cm} (21)

where

\[ \langle v(t) \rangle = -\omega_0^2 h(t) + v(0) h_1(t) \]  \hspace{1cm} (22)
\[ h_1(t) = \frac{dh(t)}{dt} \]  

(23)

and

\[ h_3(t) = \frac{d^3h(t)}{dt^3} . \]  

(24)

Next we calculate the variances. From the formal solution of \( x(t) \) and \( v(t) \), the explicit expressions for the variances are obtained which are given below:

\[
\sigma_{xx}^2(t) = \langle [x(t) - \langle x(t) \rangle]^2 \rangle \\
= 2 \int_0^t dt_1 h(t_1) \int_0^{t_1} dt_2 h(t_2) \langle f(t_1)f(t_2) \rangle + 2 \left( \frac{\kappa_0}{\gamma_c \omega_0} \right)^2 \int_0^t dt_1 h(t_1) \int_0^{t_1} dt_2 h(t_2) \langle \epsilon(t_1)\epsilon(t_2) \rangle + 2 \left( \frac{\kappa_0}{\gamma_c} \right)^2 \int_0^t dt_1 h_2(t_1) \int_0^{t_1} dt_2 h_2(t_2) \langle \epsilon(t_1)\epsilon(t_2) \rangle + 2 \left( \frac{\kappa_0}{\gamma_c} \right)^2 \omega_0^2 \int_0^t dt_1 h(t_1) \int_0^{t_1} dt_2 h_2(t_2) \langle \epsilon(t_1)\epsilon(t_2) \rangle,  
\]

(25)

\[
\sigma_{vv}^2(t) = \langle [v(t) - \langle v(t) \rangle]^2 \rangle \\
= 2 \int_0^t dt_1 h_1(t_1) \int_0^{t_1} dt_2 h_2(t_2) \langle f(t_1)f(t_2) \rangle + 2 \left( \frac{\kappa_0}{\gamma_c \omega_0} \right)^2 \int_0^t dt_1 h_1(t_1) \int_0^{t_1} dt_2 h_1(t_2) \langle \epsilon(t_1)\epsilon(t_2) \rangle + 2 \left( \frac{\kappa_0}{\gamma_c} \right)^2 \int_0^t dt_1 h_3(t_1) \int_0^{t_1} dt_2 h_3(t_2) \langle \epsilon(t_1)\epsilon(t_2) \rangle + 2 \left( \frac{\kappa_0}{\gamma_c} \right)^2 \omega_0^2 \int_0^t dt_1 h_1(t_1) \int_0^{t_1} dt_2 h_3(t_2) \langle \epsilon(t_1)\epsilon(t_2) \rangle,  
\]

(26)

and

\[
\sigma_{xv}^2(t) = \langle [x(t) - \langle x(t) \rangle][v(t) - \langle v(t) \rangle] \rangle  \\
= \frac{1}{2} \sigma_{xx}^2(t)  
\]

(27)

where we have assumed that the noises \( f(t) \) and \( \epsilon(t) \) are symmetric with respect to the time argument and have made use the fact that \( f(t) \) and \( \epsilon(t) \) are uncorrelated.
Due to the Gaussian property of the noises $f(t)$ and $\epsilon(t)$ and the linearity of the Langevin equation (13), we see that the joint probability density $p(x, v, t)$ of the oscillator must be Gaussian. The joint characteristic function associated with the density is

$$\tilde{p}(\mu, \rho, t) = \exp \left\{ i \langle x(t) \rangle \mu + i \langle v(t) \rangle \rho - \frac{1}{2} \left[ \sigma_{xx}^2(t) \mu^2 + 2 \sigma_{xv}^2(t) \rho \mu + \sigma_{vv}^2(t) \rho^2 \right] \right\}.$$  \hspace{1cm} (28)

Using the method of characteristic function [34,35] and the above expression (28) we find the general Fokker-Planck equation associated with the probability density function $p(x, v, t)$ for the process (15);

$$\frac{\partial p}{\partial t} = -v \frac{\partial p}{\partial x} + \bar{\omega}_0^2(t) x \frac{\partial p}{\partial v} + \bar{\gamma}(t) \frac{\partial}{\partial v}(vp) + \phi(t) \frac{\partial^2 p}{\partial v^2} + \psi(t) \frac{\partial^2 p}{\partial v \partial x},$$  \hspace{1cm} (29)

where

$$\bar{\gamma}(t) = -\frac{d}{dt} \ln \Upsilon(t),$$

$$\bar{\omega}_0^2(t) = \frac{-h(t) h_1(t) + h_1^2(t)}{\Upsilon(t)} \text{ and }$$

$$\Upsilon(t) = \frac{h_1(t)}{\omega_0^2} \left[ 1 - \omega_0^2 \int_0^t d\tau \ h(\tau) \right] + h^2(t).$$

The functions $\phi(t)$ and $\psi(t)$ are defined by

$$\phi(t) = \bar{\omega}_0^2(t) \sigma_{xv}^2 + \bar{\gamma} \sigma_{vv}^2 + \frac{1}{2} \bar{\sigma}_{xx}^2,$$

$$\psi(t) = \sigma_{xv}^2 + \bar{\gamma}(t) \sigma_{xv}^2 + \bar{\omega}_0^2 \sigma_{xx}^2 - \sigma_{vv}^2.$$  \hspace{1cm} (30)

where the covariances are to be calculated for a particular given noise process.

For the internal noise processes Carmeli and Nitzan [36] and Hanggi [37] have shown that for several models the various time dependent parameters $\bar{\omega}_0^2(t)$, $\bar{\gamma}(t)$, etc. do exist asymptotically as $t \to \infty$. The above consideration shows that $h(t)$, $h_1(t)$, etc. do not depend on the nature of the noise but depend only on the relaxation $\bar{\gamma}(t)$.

We now discuss the asymptotic properties of $\phi(t)$ and $\psi(t)$, which in turn are dependent on the variances $\sigma_{xx}^2(t)$ and $\sigma_{vv}^2(t)$, as $t \to \infty$ since they play a significant role in our further analysis that follows.
From Eqs. (23) and (26), we may write

$$\sigma^2_{xx}(t) = \sigma_{xx}^{2(i)}(t) + \sigma_{xx}^{2(e)}(t)$$

and

$$\sigma^2_{vv}(t) = \sigma_{vv}^{2(i)}(t) + \sigma_{vv}^{2(e)}(t).$$

where ‘i’ denotes the part corresponding to internal noise \( f(t) \) and ‘e’ corresponds to the external noise \( \epsilon(t) \). Since the average velocity of the oscillator is zero as \( t \to \infty \) we see from Eq.(22) that \( h(t) \) and \( h_1(t) \) must be zero as \( t \to \infty \). Also from Eq.(17) we observe that the function \( \chi_x(t) \) must decay to zero for long times. Hence, from Eq.(18) we see that the stationary value of the integral of \( h(t) \) is \( 1/\omega_0^2 \), i.e.,

$$\int_0^\infty h(t) \, dt = \frac{1}{\omega_0^2}. \quad (31)$$

Now, \( \sigma_{xx}^{2(i)}(t) \) and \( \sigma_{vv}^{2(i)}(t) \) of Eqs.(24) and (29) can be written in the form

$$\sigma_{xx}^{2(i)}(t) = 2 \int_0^t dt_1 h(t_1) \int_0^{t_1} dt_2 h(t_2) \langle f(t_1) f(t_2) \rangle$$

$$= k_B T \left[ 2 \int_0^t d\tau h(\tau) - h^2(t) - \omega_0^2 \left\{ \int_0^t d\tau h(\tau) \right\}^2 \right] \quad (32)$$

and

$$\sigma_{vv}^{2(i)}(t) = 2 \int_0^t dt_1 h_1(t_1) \int_0^{t_1} dt_2 h_1(t_2) \langle f(t_1) f(t_2) \rangle$$

$$= k_B T \left[ 1 - h_1^2(t) - \omega_0^2 h^2(t) \right]. \quad (33)$$

From the above two expressions [ Eqs.(32) and (33) ] we see that

$$\sigma_{xx}^{2(i)}(\infty) = \frac{k_B T}{\omega_0^2} \quad \text{and} \quad \sigma_{vv}^{2(i)}(\infty) = k_B T. \quad (34)$$

It is important to note that these stationary values are not related to the intensity and correlation time of the internal noise.

We next consider the parts, \( \sigma_{xx}^{2(e)}(t) \) and \( \sigma_{vv}^{2(e)}(t) \), due to the presence of the external noise. The Laplace transform of Eq.(16) yields the expression
\[
\bar{x}(s) - \langle \bar{x}(s) \rangle = \tilde{h}(s) \bar{f}(s) - \frac{\kappa_0}{g_0} \tau_c \omega_0^2 \tilde{h}(s) \bar{e}(s) - \frac{\kappa_0}{g_0} \tau_c s^2 \tilde{h}(s) \bar{e}(s)
\]  
(35)

where

\[
\langle \bar{x}(s) \rangle = \left\{ \frac{1}{s} - \frac{\omega_0^2}{s^2 + s \gamma(s) + \omega_0^2} \right\} x(0) + \frac{1}{s^2 + s \gamma(s) + \omega_0^2} v(0)
\]

\[
= \left\{ \frac{1}{s} - \omega_0^2 \frac{\tilde{h}(s)}{s} \right\} x(0) + \tilde{h}(s)v(0).
\]  
(36)

From the above equation (35) we can calculate the variance \(\sigma_{xx}^2\) in the Laplace-transformed space which can be identified as the Laplace transform of Eq.(25). Thus, for the part \(\sigma_{xx}^{(e)}(t)\) we observe that, \(\sigma_{xx}^{(e)}(s)\) contains terms like \(\left( \frac{\kappa_0}{g_0} \tau_c \omega_0^2 \tilde{h}(s) \right)^2 \langle \bar{e}^2(s) \rangle\). Since, we have assumed the stationarity of the noise \(\epsilon(t)\), we conclude that if \(\tilde{C}(0)\) exists \(\langle \epsilon(t)\rangle\), then the stationary value of \(\sigma_{xx}^{(e)}(t)\) exists and becomes a constant that depends on the correlation time and the strength of the noise. Similar argument is also valid for \(\sigma_{vv}^{(e)}(t)\).

Summarizing the above discussions we note that,

(i) the internal noise-driven parts of \(\sigma_{xx}^2(t)\) and \(\sigma_{vv}^2(t)\), i.e., \(\sigma_{xx}^{(i)}\) and \(\sigma_{vv}^{(i)}\) approach the fixed values which are independent of the noise correlation and the intensity as \(t \to \infty\),

(ii) the external noise driven parts of variances also approach the constant values at the stationary \((t \to \infty)\) limit which are dependent on the strength and the correlation time of the noise.

Hence we conclude, following the Refs.[36,37] and our preceding discussions that even in presence of an external noise the coefficients of the Fokker-Planck equation (29) do exist asymptotically and we write its steady state version for the asymptotic values of the parameters as,

\[-v \frac{\partial p}{\partial x} + \omega_0^2 v \frac{\partial p}{\partial v} + \gamma \frac{\partial}{\partial v}(vp) + \phi(\infty) \frac{\partial^2 p}{\partial v^2} + \psi(\infty) \frac{\partial^2 p}{\partial v \partial x} = 0,\]

(37)

where, \(\omega_0^2, \gamma, \phi(\infty), \psi(\infty),\) etc. are to be calculated from the general definition (30) for the steady state.

The general steady state solution of the above equation (37) is

\[p_{st}(x,v) = \frac{1}{Z} \exp \left[ - \left\{ \frac{v^2}{2D_0} + \frac{\omega_0^2 x}{2(D_0 + \psi(\infty))} \right\} \right].\]

(38)
where

\[ D_0 = \frac{\phi(\infty)}{\bar{\gamma}} \]  

(39)

and \( Z \) is the normalization constant. The solution (38) can be verified by direct substitution.

The distribution (38) is not an equilibrium distribution. This stationary distribution for the nonequilibrium open system plays the role of an equilibrium distribution of the closed system which may, however, be recovered in the absence of external noise term.

Some further pertinent points regarding rate theory for nonequilibrium systems may be in order. It is well-known that the equilibrium state of a closed thermodynamic system with homogenous boundary conditions is time-independent. The open, e.g., the driven system on the other hand, may show up the complicated spatio-temporal structures or may settle down to multiple steady states [31]. The external noise may then induce transitions between them. It is, however, important to realize that these features originate only when one takes into account of the nonlinearity of the system in full and the external noise drives the system directly. Secondly, in most open nonequilibrium systems the lack of detail balance symmetry gives rise to severe problem in the determination of the stationary probability distribution for multidimensional problems [38]. At this juncture three points are to be noted. First, for the present problem we have made use of the linearization of the potential at the bottom and at top of the barrier (as is done in Kramers’ [1] and in most of the post-Kramers’ development [7, 9, 16, 36]) which precludes the existence of a multiple steady states. Second, the external noise considered here drives the bath rather than the system directly. Third, the problem is one-dimensional. Thus, an unique stationary probability density which is an essential requirement for the mean first passage time or flux over population method (as in the present case) for the calculation of rate and which is readily obtainable in the case of closed equilibrium system, can also be obtained for this open nonequilibrium system.
IV. KRAMERS’ ESCAPE RATE

We now turn to the problem of decay of a metastable state. To this end we consider as usual a ‘Brownian particle’ moving in a one-dimensional double well potential $V(x)$. In Kramers’ approach, the particle coordinate $x$ corresponds to the reaction coordinate and its values at the minima of the potential $V(x)$ denotes the reactant and product states. The maxima of $V(x)$ at $x_b$ separating these states corresponds to the activated complex. All the remaining degrees of freedom of both reactant and solvent molecules constitute a heat bath at temperature $T$. Our object is to calculate the essential modification of Kramers’ rate when the bath modes are perturbed by an external random force when the system has attained a steady state.

Linearizing the motion around barrier top at $x = x_b$ the Langevin equation (4) can be written down as

\[
\dot{y} = v ,
\]
\[
\dot{v} = \omega^2_b y - \int_0^t dt' \gamma(t - t') v(t') + f(t) + \pi(t) ,
\]

where, $y = x - x_b$ and the barrier frequency $\omega^2_b$ is defined by

\[
V(y) = V_b - \frac{1}{2} \omega^2_b y^2 ; \quad \omega^2_b > 0 .
\]

Correspondingly the motion of the particle is governed by the Fokker-Planck equation (29)

\[
\frac{\partial p}{\partial t} = -v \frac{\partial p}{\partial y} - \omega^2_b(t) y \frac{\partial p}{\partial v} + \gamma_b(t) \frac{\partial}{\partial v}(vp) + \phi_b(t) \frac{\partial^2 p}{\partial v^2} + \psi_b(t) \frac{\partial^2 p}{\partial v \partial y} ,
\]

where, the suffix ‘b’ indicates that all the coefficients are to be calculated using the general definition (30) for the barrier top region.

It is apparent from Eqs.(37) and (12) that since the dynamics is non-Markovian and the system is thermodynamically open one has to deal with the renormalized frequencies $\tilde{\omega}_0$ and $\tilde{\omega}_b$ near the bottom or top of the well, respectively. Following Kramers we make the ansatz that the nonequilibrium, steady state probability $p_b$, generating a nonvanishing diffusion current $j$, across the barrier is given by
\[ p_b(x, v) = \exp \left[ -\left\{ \frac{v^2}{2D_b} + \frac{\tilde{V}(x)}{D_b + \psi_b(\infty)} \right\} \right] \xi(x, v) \]  

(43)

where

\[ D_b = \frac{\phi_b(\infty)}{\tilde{\gamma}_b} . \]  

(44)

\( \tilde{V}(x) \) is the renormalized linear potential as

\[ \tilde{V}(x) = V(x_0) + \frac{1}{2} \tilde{\omega}_0^2 (x - x_0)^2 , \]  

near the bottom

\[ \tilde{V}(x) = V(x_b) - \frac{1}{2} \tilde{\omega}_b^2 (x - x_b)^2 , \]  

near the top

(45)

with \( \tilde{\omega}_0^2, \tilde{\omega}_b^2 > 0 \). The unknown function \( \xi(x, v) \) obeys the natural boundary condition that for \( x \to \infty \), \( \xi(x, v) \) vanishes.

The ansatz of the form (43) denoting the steady state distribution is motivated by the local analysis near the bottom and the top of the barrier in the Kramers' sense [1]. For a stationary nonequilibrium system, on the other hand, the relative population of the two regions, in general, depends on the global properties of the potential leading to an additional factor in the rate expression. Although because of the Kramers’ type ansatz [1] which is valid for the local analysis, such a consideration is outside the scope of the present treatment, we point out a distinctive feature in the ansatz (43) compared to Kramers’ ansatz. While in the latter case one considers a complete factorization of the equilibrium part (Boltzmann) and the dynamical part, the ansatz (43) incorporates the additional dynamical contribution through dissipation and strength of the noise into the exponential part. This modification of Kramers’ ansatz (by dynamics) is due to nonequilibrium nature of the system. Thus unlike Kramers’, the exponential factors in (43) and in the stationary distribution (38) which serves as a boundary condition are markedly different. While a global analysis may even modify the standard Kramers’ result our aim here is to understand the modification of the rate due to modulation of the bath driven by an external noise, within the perview of Kramers’ type ansatz. The internal consistency of the treatment, however, can be checked by recovering the Kramers’ result when the external noise is switched off.
From equation (42), using (43) we obtain the equation for \( \xi(y,v) \) in the steady state in the neighborhood of \( x_b \), the equation

\[- \left( 1 + \frac{\psi_b(\infty)}{D_b} \right) v \frac{\partial \xi}{\partial y} - \left[ \frac{D_b}{D_b + \psi_b(\infty)} \bar{\omega}_b^2 y + \bar{\gamma}_b v \right] \frac{\partial \xi}{\partial v} + \phi_b(\infty) \frac{\partial^2 \xi}{\partial v^2} + \psi_b(\infty) \frac{\partial^2 \xi}{\partial v \partial y} = 0 \].  

(46)

We then make use of the following transformation

\[ u = v + ay \quad , \quad y = x - x_b \]

where \( a \) is a constant to be determined. We obtain from Eq.(46)

\[ \{ \phi_b(\infty) + a\psi_b(\infty) \} \frac{d^2 \xi}{du^2} - \left[ \frac{D_b}{D_b + \psi_b(\infty)} \bar{\omega}_b^2 x + \left\{ \bar{\gamma}_b + a \left( 1 + \frac{\psi_b(\infty)}{D_b} \right) \right\} v \right] \frac{d\xi}{du} = 0 \].  

(47)

Putting

\[ \frac{D_b}{D_b + \psi_b(\infty)} \bar{\omega}_b^2 x + \left\{ \bar{\gamma}_b + a \left( 1 + \frac{\psi_b(\infty)}{D_b} \right) \right\} v = -\lambda u \],  

(48)

(where \( \lambda \) being another constant to be determined) we obtain the ordinary differential equation for \( \xi(u) \)

\[ \frac{d^2 \xi}{du^2} + \Lambda u \frac{d\xi}{du} = 0 \].  

(49)

where

\[ \Lambda = \frac{\lambda}{\phi_b(\infty) + a\psi_b(\infty)} \].  

(50)

and the two constants \( \lambda \) and \( a \) must satisfy the simultaneous relations

\[- \lambda a = \frac{D_b}{D_b + \psi_b(\infty)} \bar{\omega}_b^2 \],  

(51a)

\[- \lambda = \bar{\gamma}_b + a \left( 1 + \frac{\psi_b(\infty)}{D_b} \right) \].  

(51b)

This implies that, the constant \( a \) must satisfy the quadratic equation

\[ \frac{D_b + \psi_b(\infty)}{D_b} a^2 + \bar{\gamma}_b a - \frac{D_b}{D_b + \psi_b(\infty)} \bar{\omega}_b^2 = 0 \].  

(52)

which allows
\[ a_\pm = \frac{D_b}{2(D_b + \psi_b(\infty))} \left\{ -\bar{\gamma}_b \pm \sqrt{\bar{\gamma}_b^2 + 4\bar{\omega}_b^2} \right\} . \]  

(53)

The general solution of Eq.(49) is

\[ \xi(u) = F_2 \int_0^u \exp \left( -\frac{\Lambda z^2}{2} \right) \, dz + F_1 \]  

(54)

where \( F_1 \) and \( F_2 \) are constants of integration. We look for a solution which vanishes for large \( x \). For this to happen the integral in (54) should remain finite for \( |u| \to +\infty \). This implies that \( \Lambda > 0 \) so that only \( a_- \) becomes relevant. Then the requirement \( p_b(x, v) \to 0 \) for \( x \to +\infty \) yields

\[ F_1 = F_2 \sqrt{\frac{\pi}{2\Lambda}} . \]  

(55)

Thus we have

\[ \xi(u) = F_2 \left[ \sqrt{\frac{\pi}{2\Lambda}} + \int_0^u \exp \left( -\frac{\Lambda z^2}{2} \right) \, dz \right] \]  

and correspondingly

\[ p_b(x, v) = F_2 \left[ \sqrt{\frac{\pi}{2\Lambda}} + \int_0^u \exp \left( -\frac{\Lambda z^2}{2} \right) \, dz \right] \exp \left[ -\left\{ \frac{v^2}{2D_b} + \frac{\tilde{V}(x)}{D_b + \psi_b(\infty)} \right\} \right] . \]  

(56)

The current across the barrier associated with this distribution is given by

\[ j = \int_{-\infty}^{+\infty} v \, p_b(x = x_b, v) \, dv \]  

which may be evaluated using (54) and the linearized version of \( \tilde{V}(x) \), namely, \( \tilde{V}(x) = V(x_b) - \frac{1}{2} \bar{\omega}_b^2 (x - x_b)^2 \), as

\[ j = F_2 \left( \frac{2\pi}{\Lambda + D_b^{-1}} \right)^{1/2} D_b \exp \left[ -\frac{V(x_b)}{D_b + \psi_b(\infty)} \right] . \]  

(57)

To determine the remaining constant \( F_2 \) we proceed as follows. We first note that as \( x \to -\infty \) the pre-exponential factor in Eq.(50) reduces to the following form

\[ F_2[... ] = F_2 \left( \frac{2\pi}{\Lambda} \right)^{1/2} . \]  

(58)

We then obtain the reduced distribution function in \( x \) as
\[
\tilde{p}_b(x \to -\infty) = 2\pi F_2 \left( \frac{D_b}{\Lambda} \right)^{1/2} \exp \left[ -\frac{\tilde{V}(x)}{D_b + \psi_b(\infty)} \right],
\]

(59)

where we have used the definition for the reduced distribution as

\[
\tilde{p}(x) = \int_{-\infty}^{+\infty} p(x, v) \, dv .
\]

Similarly we derive the reduced distribution in the left well around \( x \approx x_0 \) using Eq. (38) where the linearized potential is \( \tilde{V}(x) = V(x) + \frac{1}{2} \tilde{\omega}_0^2 (x - x_0)^2 \),

\[
\tilde{p}_{st}(x) = \frac{1}{Z} \sqrt{2\pi D_0} e^{-\frac{V(x_0)}{D_0 + \psi(\infty)}} \exp \left[ -\frac{\tilde{\omega}_0^2 (x - x_0)^2}{2(D_0 + \psi(\infty))} \right],
\]

(60)

with the normalization constant \( \frac{1}{Z} \)

\[
\frac{1}{Z} = \frac{\tilde{\omega}_0}{2\pi \sqrt{D_0(D_0 + \psi(\infty))}} e^{\frac{V(x_0)}{2(D_0 + \psi(\infty))}} .
\]

The comparison of the distributions (59) and (60) near \( x = x_0 \), i.e.,

\[
\tilde{p}_{st}(x_0) = \tilde{p}_b(x_0)
\]

(61)

gives

\[
F_2 = \left( \frac{\Lambda}{D_b} \right)^{1/2} \frac{\tilde{\omega}_0}{2\pi \sqrt{2\pi(D_0 + \psi(\infty))}} \exp \left[ V(x_0) \frac{D_b}{D_0 + \psi(\infty)} \right] .
\]

(62)

Hence from (57), the normalized current or the barrier crossing rate \( k \) is given by

\[
k = \frac{\tilde{\omega}_0}{2\pi} \frac{D_b}{D_0 + \psi(\infty)} \left( \frac{\Lambda}{1 + \Lambda D_b} \right)^{1/2} \exp \left[ -\frac{E_0}{D_b + \psi_b(\infty)} \right]
\]

(63)

where \( E_0 \) is the activation energy, \( E_0 = V(x_b) - V(x_0) \). Since the temperature due to internal thermal noise, the strength of the external noise and the damping constant are buried in the parameters \( D_0, D_b, \psi_0, \psi_0 \) and \( \Lambda \) the generalized expression look somewhat cumbersome. We point out that the subscripts ‘0’ and ‘b’ in \( D \) and \( \psi \) refer to the well or barrier top region, respectively. Eq. (63) is the central result of this chapter. The dependence of the rate on the parameters can be exposed explicitly once we consider the limiting cases.
V. EXAMPLE : $\delta$-CORRELATED EXTERNAL NOISE AND ORNSTEIN-UHLENBECK INTERNAL NOISE

We consider a particular case where the external noise $\epsilon(t)$ is $\delta$-correlated and the internal noise is an Ornstein-Uhlenbeck (O-U) process, i.e.,

$$\langle \epsilon(t)\epsilon(t') \rangle = 2D\delta(t-t')$$

and

$$\langle f(t)f(t') \rangle = g_0^2 k_B T \frac{e^{-|t-t'|/\tau_c}}{\tau_c}.$$  \hspace{1cm} (64)

One can trace the origin of the above correlation function for internal noise by considering a Lorentzian type frequency distribution of the normal mode variables and Eq.(6). Consequently, from the fluctuation-dissipation relation we derive the dissipative kernel as

$$\gamma(t-t') = g_0^2 \frac{e^{-|t-t'|/\tau_c}}{\tau_c}. \hspace{1cm} (64)$$

It should be noted that for $\tau_c \to 0$, the above noise processes become $\delta$-correlated.

The correlation functions as given above and the dissipative kernel provide the required quantities for the calculation of $p_{st}(x,v)$ [Eq.(38)] and the generalized rate expression (63). Thus we have [see the Appendix]

$$\phi(\infty) = \bar{\gamma}(k_BT + D\kappa_0^2) \hspace{0.5cm} \text{and} \hspace{0.5cm} \psi(\infty) = 0. \hspace{1cm} (65)$$

which gives

$$D_0 = \frac{\phi(\infty)}{\bar{\gamma}} = k_BT + D\kappa_0^2. \hspace{1cm} (66)$$

Hence from equation (38) we see that the steady state distribution is given by

$$p_{st}(x,v) = \frac{1}{Z} \exp \left[ -\frac{\omega_0^2 x^2 + v^2}{2(k_BT + D\kappa_0^2)} \right],$$

since for a Markovian process $\bar{\omega}_0^2 = \omega_0^2$. From Eq.(67) we see that, the steady state probability density in our example does not depend on the correlation time of noise but does
depend on the strength and coupling of the external noise. The result is in agreement with the one obtained earlier by Bravo et. al. [33]

We now return to our generalized rate expression Eq.(63). For the present case we have computed [see the Appendix]

\[ \psi(\infty) = \psi_b(\infty) = 0, \]  
\[ D_0 = D_b = k_B T + D\kappa_0^2, \]  
\[ \bar{\omega}_0^2 = \omega_0^2, \bar{\omega}_b^2 = \omega_b^2, \]  
\[ \Lambda = \frac{\lambda}{g_0^2(k_B T + D\kappa_0)\kappa_0^2} \] 
\[ a_- = -\frac{g_0^2}{2} - \sqrt{\frac{g_0^2}{4} + \omega_b^2}. \]  

Using all these values, we obtain from Eq.(63)

\[ k = \frac{\omega_0}{2\pi\omega_b} \left[ \left\{ \frac{g_0^2}{4} + \omega_b^2 \right\}^{1/2} - \frac{g_0^2}{2} \right] \exp \left( -\frac{E_0}{k_B T + D\kappa_0^2} \right). \]  

If we put the external noise intensity \( D \) equal to zero, i.e., when external noise is absent, the above expression reduces to usual Kramers rate expression with \( g_0^2 = \gamma. \) We note here that \( D\kappa_0^2/k_B \) defines a new effective temperature characteristic of the steady state of the nonequilibrium open system. As expected this temperature is function of the strength of external noise intensity \( D \) and the coupling of the external noise to the bath modes.

VI. CONCLUSIONS

Based on a system-reservoir microscopic model where the reservoir is modulated by an external, stationary and Gaussian noise with arbitrary decaying correlation function, we have generalized the Kramers’ theory to calculate the steady state rate of escape from a metastable well. The main conclusions of this study are as follows:

(i) We have shown that since the reservoir is driven by the external noise and the dissipative properties of the system depend on the reservoir, a simple connection between the dissipation and the response function of the medium due to the external noise can be established.
(ii) This connection is important for realising the stationary state of the thermodynamically open system characterized by an *effective* temperature of the reservoir, which depends on the strength of the external noise.

(iii) Provided the long time limit of the moments for the stochastic processes pertaining to the external and internal noises characterized by arbitrary decaying correlation functions exist, the expression for generalized Kramers’ rate of barrier crossing for the open system we derive here is fairly general. The expression assumes simple forms in the specific limiting cases.

The creation of a typical nonequilibrium open situation by modulating a bath with the help of an external noise is not an uncommon phenomenon in applications and industrial processing. The external agency generating noise does work on the bath by stirring, pumping, agitating, etc., to which the system dissipates internally. In the present treatment we are concerned with a nonequilibrium steady state characterized by an *effective* temperature which signifies a constant throughput of energy in contrast to thermal equilibrium defined by an constant temperature. We believe that these considerations are likely to be important in other related issues in nonequilibrium open systems.

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APPENDIX A: CALCULATION OF VARIANCES

The Laplace transform of $\gamma$ in Eq.(64) is given by

$$\tilde{\gamma}(s) = \frac{g_0^2}{s\tau_c + 1},$$

and subsequently, we have
\[
\tilde{h}(s) = \frac{s\tau_c + 1}{\tau_c s^3 + s^2 + (\omega_0^2 \tau_c + g_0^2)s + \omega_0^2}.
\]

For \(\tau_c \neq 0\), the above expression can be simplified to

\[
\tilde{h}(s) = \frac{s + a}{s^3 + as^2 + bs + c_0}
\]

where

\[
a = \frac{1}{\tau_c}, \quad b = \omega_0^2 + \frac{g_0^2}{\tau_c} \text{ and } c_0 = \frac{\omega_0^2}{\tau_c}.
\]

We define the following characteristic quantity

\[
Q \equiv -\frac{a^2 b^2}{108} + \frac{b^3}{27} + \frac{a^3 c_0}{27} - \frac{ab c_0}{6} + \frac{c_0^2}{4}
\]

and distinguish the cases: \(Q > 0, \ Q = 0\) and \(Q < 0\), for which we have different forms of \(h(t)\). For the case \(Q > 0\) [we do not give here the explicit expressions for the cases \(Q = 0\) and \(Q < 0\)] we find that the inverse Laplace transform of \(\tilde{h}(s)\) reads

\[
h(t) = c_1 e^{-\Delta_1 t} + c_2 e^{-\Delta_2 t} \sin(\beta t + \alpha)
\]

(A1)

where the coefficients \(c_1, c_2, \Delta_1, \Delta_2, \beta\) and \(\alpha\) are given by

\[
\begin{align*}
\Delta_1 &= -A - B + \frac{a}{3}, \\
\Delta_2 &= \frac{1}{2}(A + B) + \frac{a}{3}, \\
\beta &= \frac{\sqrt{3}}{2}(A - B), \\
c_1 &= \frac{1}{2\Delta_2 - \Delta_1 - d}, \\
d &= \frac{a(2\Delta_2 - \Delta_1) - \Delta_2^2 - \beta^2}{a - \Delta_1}, \\
A &= \left(\frac{-a^3}{27} + \frac{ab}{6} - \frac{c_0}{2} + \sqrt{Q}\right)^{1/3}, \\
B &= \left(\frac{-a^3}{27} + \frac{ab}{6} - \frac{c_0}{2} - \sqrt{Q}\right)^{1/3}, \\
c_2 &= -\frac{c_1}{\beta}[(d - \Delta_2)^2 + \beta^2]^{1/2} \text{ and} \\
\alpha &= \tan^{-1}\left(\frac{\beta}{d - \Delta_2}\right)
\end{align*}
\]
Here we note that for a physically allowed solution \( \Delta_1, \Delta_2 \) must be positive. Since by Eq. (19) \( h(t) \) depends on the memory kernel \( \gamma(t) \) which is of decaying type and all the moments, in general, reach asymptotic constancy as shown in Sec. III, these quantities are positive (which depends on the correlation time \( \tau_c \), the strength of the noise and other potential parameters) which may be checked (after some algebra) by considering the limiting cases such as \( \tau_c \to 0 \) and \( \tau_c \to \text{large} \).

Substituting Eq. (57) into the expressions for variances [external noise is \( \delta \)-correlated], namely into (25) and (26) we have after some lengthy algebra

\[
\sigma_{xx}^2(t) = \sigma_{xx}^{2(i)}(t) + \sigma_{xx}^{2(e)}(t)
\]

where

\[
\sigma_{xx}^{2(i)}(t) = k_B T \left( c_2 R + \frac{c_1}{\Delta_1} \right) \left[ 2 - \omega_0^2 \left( c_2 R + \frac{c_1}{\Delta_1} \right) \right]
+ k_B T \left\{ -\frac{c_1}{\Delta_1} e^{-\Delta_1 t} \left[ 2 - 2 \omega_0^2 c_2 R - \frac{2\omega_0^2 c_1}{\Delta_1} + e^{-\Delta_1 t} \left( \Delta_1 c_1 + \frac{\omega_0^2 c_1}{\Delta_1} \right) \right] \right.
- \frac{2c_2 e^{-\Delta_2 t}}{\Delta_2^2 + \beta^2} \left[ 1 - \omega_0^2 c_2 R + \frac{\omega_0^2 c_1}{\Delta_1} (e^{-\Delta_1 t} - 1) \right] [\Delta_2 \sin(\beta t + \alpha) + \beta \cos(\beta t + \alpha)]
- 2c_1 c_2 e^{-(\Delta_1 + \Delta_2) t} \sin(\beta t + \alpha)
\]

\[
\frac{\Delta_2 \beta \omega_0^2 c_2 e^{-2\Delta_2 t}}{(\Delta_2^2 + \beta^2)^2} \sin 2(\beta t + \alpha) - \frac{\beta^2 \omega_0^2 c_2 e^{-2\Delta_2 t}}{(\Delta_2^2 + \beta^2)^2}
+ \left[ \frac{\omega_0^2 (2\beta^2 - \Delta_2^2)}{(\Delta_2^2 + \beta^2)^2} - 1 \right] c_2 e^{-2\Delta_2 t} \sin^2(\beta t + \alpha)
\]  

(A3)

with

\[
R = \frac{1}{\Delta_2^2 + \beta^2} (\Delta_2 \sin \alpha + \beta \cos \alpha) \quad (A4)
\]

and

\[
\sigma_{xx}^{2(e)}(t) = 2D \left( \frac{k_0}{\eta_0} \tau_c \right)^2 \left[ c_2^2 (\omega_0^4 + \Delta_1^4 + 2\omega_0^2 \Delta_1^2) I_A(t) \right.
+ c_2^2 \{ \omega_0^4 + (\Delta_2^2 - \beta^2)^2 - 4\beta^2 \Delta_2^2 + 2\omega_0^2 (\Delta_2^2 - \beta^2) \} I_B(t)
+ 2c_1 c_2 \{ \omega_0^4 + \Delta_1^2 (\Delta_2^2 - \beta^2) + \omega_0^2 (\Delta_1^2 + \Delta_2^2 - \beta^2) \} I_C(t)
- 2c_2^2 \beta \Delta_2 (\Delta_2^2 - \beta^2 + \omega_0^2) I_D(t) + 4c_2^2 \beta^2 \Delta_2^2 I_E(t) - 4c_1 c_2 \beta \Delta_2 (\Delta_1^2 + \omega_0^2) I_F(t) \right] . \quad (A5)
\]
Here the $I$’s are defined by

\begin{align*}
I_A(t) &= \int_0^t e^{-2\Delta_1 t} dt,
I_B(t) &= \int_0^t e^{-2\Delta_2 t} \sin^2(\beta t + \alpha) dt,
I_C(t) &= \int_0^t e^{-(\Delta_1 + \Delta_2) t} \sin(\beta t + \alpha) dt,
I_D(t) &= \int_0^t e^{-2\Delta_2 t} \sin 2(\beta t + \alpha) dt,
I_E(t) &= \int_0^t e^{-2\Delta_2 t} dt \quad \text{and}
I_F(t) &= \int_0^t e^{-(\Delta_1 + \Delta_2) t} \cos(\beta t + \alpha) dt.
\end{align*}

(A6a-A6f)

Similarly

\[ \sigma_{vv}^2(t) = \sigma_{vv}^{2(i)}(t) + \sigma_{vv}^{2(e)}(t) \]

where

\begin{align*}
\sigma_{vv}^{2(i)}(t) &= k_B T - \left[ (\Delta_1^2 + \omega_0^2)c_1 e^{-2\Delta_1 t} + \beta^2 c_2^2 e^{-2\Delta_2 t} 
- \beta \Delta_2 c_2^2 e^{-2\Delta_2 t} \sin 2(\beta t + \alpha) + (\Delta_2^2 + \omega_0^2 - \beta^2)c_2^2 e^{-2\Delta_2 t} \sin^2(\beta t + \alpha) 
+ e^{-(\Delta_1 + \Delta_2) t} \left\{ 2c_1 c_2 (\omega_0^2 + \Delta_1 \Delta_2) \sin(\beta t + \alpha) - 2\Delta_1 \beta c_1 c_2 \cos(\beta t + \alpha) \right\} \right] \quad \text{(A7)}
\end{align*}

and

\begin{align*}
\sigma_{vv}^{2(e)}(t) &= 2D \left( \frac{\kappa_0}{g_0} \tau_c \right)^2 \left[ c_1^2 \Delta_1^2 (\omega_0^2 + \Delta_1^2)^2 I_A(t) 
+ c_2^2 (\omega_0^2 + \Delta_2^2 - 3\beta^2)^2 \Delta_2 - (\omega_0^2 + 3\Delta_2^2 - \beta^2)^2 \beta^2 \right] I_B(t) 
+ 2c_1 c_2 \Delta_1 \Delta_2 (\omega_0^2 + \Delta_1^2)(\omega_0^2 - 3\beta^2 + \Delta_2^2) I_C(t) 
- c_2^2 \beta \Delta_2 (3\Delta_2^2 - \beta^2 + \omega_0^2)(\omega_0^2 - 3\beta^2 + \Delta_2^2) I_D(t) 
+ c_2^2 \beta^2 (\omega_0^2 - \beta^2 + 3\Delta_2^2) I_E(t) 
- 2c_1 c_2 \beta \Delta_1 (\Delta_1^2 + \omega_0^2)(\omega_0^2 + 3\Delta_2^2 - \beta^2) I_F(t) \right] \quad \text{(A8)}
\end{align*}

where, $I$’s are defined in Eq.(A6a-A6f). The explicit expression for $\sigma_{xv}^2(t)$ can be derived from Eq.(27). From Eqs.(57) and (60), we calculate the stationary values of the variances as follows,
\[
\sigma_{xx}^2(\infty) = \sigma_{xx}^{2(i)}(\infty) + \sigma_{xx}^{2(e)}(\infty)
\]

where

\[
\sigma_{xx}^{2(i)}(\infty) = k_B T \left( c_2 R + \frac{c_1}{\Delta_1} \right) \left[ 2 - \omega_0^2 \left( c_2 R + \frac{c_1}{\Delta_1} \right) \right]
\]  

(A9)

and

\[
\sigma_{xx}^{2(e)}(\infty) = 2D \left( \frac{\kappa_0}{g_0^2} \right)^2 \left[ \frac{c^2_1}{2} \frac{(\omega_0^2 + \Delta_1^2 + 2\omega_0^2 \Delta_2^2)}{2\Delta_1} + \frac{c^2_2}{4\Delta_2} \frac{1}{\Gamma^2 + 4\beta^2 \Delta_2^2} \right.
\]

\[
+ \frac{c^2_2}{4(\Delta_2^2 + \beta^2)} \left\{ \beta(\Gamma^2 - 4\beta^2 - 4\Delta_2^2 \beta) \sin 2\alpha - \Delta_2(\Gamma^2 + 4\beta^2 \Gamma - 4\Delta_2^2 \beta^2) \cos 2\alpha \right\}
\]

\[
+ 2c_1c_2 \frac{\Delta_2^2 + \omega_0^2}{(\Delta_1 + \Delta_2)^2 + \beta^2}
\]

\[
\times \left\{ \Gamma(\Delta_1 + \Delta_2) + 2\beta^2 \Delta_2 \right\} \sin \alpha + \beta \{ \Gamma - 2\Delta_2(\Delta_1 + \Delta_2) \} \cos \alpha \right\}
\]

(A10)

where

\[
\Gamma = \omega_0^2 + \Delta_2^2 - \beta^2.
\]  

(A11)

Again substituting the values of \(c_1, c_2, \Delta_1, \Delta_2, \alpha, \beta, \Gamma \) and \(R \) we obtain after a lengthy calculation the following result

\[
\sigma_{xx}^2(\infty) = \frac{k_B T + D\kappa_0^2}{\omega_0^2}.
\]  

(A12)

Similarly

\[
\sigma_{vv}^{2(e)}(\infty) = 2D \left( \frac{\kappa_0}{g_0^2} \right)^2 \left[ \frac{c^2_1}{2} \frac{(\Delta_1^2 + \omega_0^2)}{2} \right]
\]

\[
+ \frac{c^2_2}{4\Delta_2} \left\{ \beta^2(\omega_0^2 + 3\Delta_2^2 - \beta^2)^2 + \Delta_2^2(\omega_0^2 + \Delta_2^2 - 3\beta^2)^2 \right\}
\]

\[
- \frac{c^2_2}{4(\Delta_2^2 + \beta^2)}
\]

\[
\times \left\{ \beta(\Delta_2^2(\omega_0^2 + \Delta_2^2 - 3\beta^2)(\omega_0^2 + 5\Delta_2^2 + \beta^2) + \beta^3(\omega_0^2 + 3\Delta_2^2 - \beta^2)^2) \sin 2\alpha
\]

\[
+ \Delta_2^2(\omega_0^2 + 3\Delta_2^2 - \beta^2)(\omega_0^2 - \Delta_2^2 - 5\beta^2) + \Delta_2^3(\omega_0^2 + \Delta_2^2 - 3\beta^2)^2 \right\} \cos 2\alpha
\]

\[
+ 2c_1c_2 \frac{\Delta_1^2 + \omega_0^2}{(\Delta_1 + \Delta_2)^2 + \beta^2}
\]

\[
\times \left\{ \Delta_2(\Delta_1 + \Delta_2)(\omega_0^2 + \Delta_2^2 - 3\beta^2) - \beta(\Delta_1 + \Delta_2)(\omega_0^2 + 3\Delta_2^2 - \beta^2) \} \sin \alpha
\]

\[
+ \left\{ \beta(\Delta_2^2 + \omega_0^2 - 3\beta^2) - \beta(\Delta_1 + \Delta_2)(\omega_0^2 + 3\Delta_2^2 - \beta^2) \} \cos \alpha \right\}
\]

(A13)
Again putting the values of all the parameters we have,

\[ \sigma^2_{vv}(\infty) = k_B T + D\kappa_0^2. \]  

(A14)

Clearly,

\[ \sigma^2_{xx}(\infty) = 0. \]  

(A15)

The variances \( \sigma^2_{xx}(\infty) \), \( \sigma^2_{vv}(\infty) \) and \( \sigma^2_{xv}(\infty) \) yield \( \phi(\infty) \) and \( \psi(\infty) \) and other relevant quantities.
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