Theory of non-stationary activated rate processes: nonexponential relaxation kinetics

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Abstract

We have explored a simple microscopic model to simulate a thermally activated rate process where the associated bath which comprises a set of relaxing modes is not in an equilibrium state. The model captures some of the essential features of non-Markovian Langevin dynamics with a fluctuating barrier. Making use of the Fokker-Planck description we calculate the barrier dynamics in the steady state and non-stationary regimes. The Kramers-Grote-Hynes reactive frequency has been computed in closed form in the steady state to illustrate the strong dependence of the dynamic coupling of the system with the relaxing modes. The influence of nonequilibrium excitation of the bath modes and its relaxation on the kinetics of activation of the system mode is demonstrated. We derive the dressed time-dependent Kramers rate in the nonstationary regime in closed analytical form which exhibits strong non-exponential relaxation kinetics of the reaction co-ordinate. The feature can be identified as a typical non-Markovian dynamical effect.
I. Introduction

More than half a century ago Kramers\textsuperscript{1} considered the problem of activated rate processes by using a model Brownian particle trapped in a one dimensional well which is separated by a barrier of finite height from a deeper well. The particle was supposed to be immersed in a medium such that the medium exerts a frictional force on the particle but at the same time thermally activates it so that the particle may gain enough energy to cross the barrier. Over several decades the model has been the standard paradigm in many areas of physics and chemistry\textsuperscript{2}. The Kramers problem was to find the rate of escape from the well to the barrier. The motion of the particle is governed by the following phenomenological Langevin equation,

$$\ddot{x} = -\frac{1}{m} \frac{\partial V(x)}{\partial x} - \gamma \dot{x} + \frac{1}{m} F(t) ,$$  \hspace{1cm} (1)

where $x$ is the coordinate of the particle of mass $m$ moving in a potential $V(x)$. $\gamma$ and $F(t)$ are the damping rate and the Gaussian stationary random force provided by the thermal bath respectively. The properties of noise can be summarized by the following two relations,

$$\langle F(t) \rangle = 0 \quad , \quad \langle F(0)F(t) \rangle = 2\gamma mK\delta(t) . \hspace{1cm} (2)$$

The Langevin equation (1) is equivalent to the Fokker-Planck equation for probability distribution $p = p(x, v, t)$ [also known as Kramers equation],

$$\frac{\partial p}{\partial t} = \frac{1}{m} \frac{\partial V(x)}{\partial x} \frac{\partial p}{\partial v} - v \frac{\partial p}{\partial x} + \gamma \left[ \frac{K}{m} \frac{\partial^2 p}{\partial v^2} + \frac{\partial}{\partial v} (vp) \right] . \hspace{1cm} (3)$$

Kramers\textsuperscript{1} obtained the steady state escape rate $k$ in the limiting cases of high and low damping rates in the following form,

$$k = \begin{cases} \frac{\omega_{\text{ei}}}{2\pi\gamma} \exp\left[-\frac{E_i}{K}\right] & \gamma \longrightarrow \infty , \\ \gamma \frac{E_i}{K} \exp\left[-\frac{E_i}{K}\right] & \gamma \longrightarrow 0 \end{cases} . \hspace{1cm} (4)$$
where $\omega_o$ and $\omega_b$ are the frequencies associated with the curvature of the potential at the bottom of the well and at the barrier top, respectively. $E_b$ refers to the depth of the well. Kramers has also derived an expression for ‘intermediate’ value of $\gamma$:

$$k = \frac{\omega_b}{2\pi\omega_b} \left\{ \left[ \left( \frac{\gamma}{2} \right)^2 + \omega_b^2 \right]^{\frac{1}{2}} - \frac{\gamma}{2} \right\} \exp(-E_b/KT).$$

For non-Markovian random processes where one takes into account of the short internal time scales of the system compared to that of the thermal bath, the Langevin equation (1) gets replaced by its non-Markovian counterpart \cite{3,4}, sometimes called the generalized Langevin equation (GLE);

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

(5)

where $R(t)$ is Gaussian but non-Markovian such that

$$\langle R(t) \rangle = 0, \quad \langle R(0)R(t) \rangle = Z(t)mKT.$$ 

(6)

The memory function $Z(t)$ is expressed in terms of Fourier-Laplace components

$$Z_n(\omega) = \int_0^\infty dt Z(t)e^{-i\omega t}$$

(7)

with

$$Z_0(\omega) = \gamma$$

Based on equation (5) Adelman\cite{5} obtained the generalized Fokker-Planck equation for a Brownian oscillator with a parabolic potential as given by;

$$\frac{\partial p}{\partial t} = -\omega_b^2 x \frac{\partial p}{\partial v} - v \frac{\partial p}{\partial x} + \gamma \frac{\partial}{\partial v}(vp) + \gamma \frac{KT}{m} \frac{\partial^2 p}{\partial v^2} + \frac{KT}{m} \left( \frac{\omega_b^2}{\omega_b^2 - 1} \right) \frac{\partial^2 p}{\partial v \partial x},$$

(8)

where $\bar{\gamma} = \bar{\gamma}(t)$ and $\bar{\omega}_b^2 = \bar{\omega}_b^2(t)$ are now functions of time [although bounded, they may not always provide long time limits] which play a decisive role in the calculation of non-Markovian Kramers rate.

Various workers have made use of generalized Langevin equation to treat the different aspects of the escape problem in the non-Markovian regime. For example, Grote
and Hynes$^4$ considered the average motion of the particle in the vicinity of the barrier governed by GLE and found that on the average the particle is slowed down by friction and defining a reactive frequency $\lambda_r$ they showed that the average motion goes as $\exp(\pm\lambda_r t)$. The analysis of Hänggi and Mojtabai$^6$ on the other hand is based on the generalized Fokker-Planck equation of Adelman with a parabolic potential in the high friction limit. The generalized FP approach has also been adopted by Carmeli and Nitzan$^7$ to derive the expression for the steady-state escape rate in the high and low friction limit in the Markovian as well as non-Markovian regimes. A comprehensive overview has been given in Ref.(2).

While the early post-Kramers development as summarized above is largely phenomenological, an interesting advancement in the theory of activated rate processes was made when the generalized Langevin equation was realized in terms of a microscopic model which comprises a system coupled linearly to a discrete set of harmonic oscillators. Using the properties of the bath and a normal mode analysis it was shown$^8$ that the reactive frequency $\lambda_r$ defined by Grote and Hynes$^4$ for the average motion across the barrier is actually a renormalised effective barrier frequency.

The object of the present paper is twofold: First is to consider a simple variant of the system-heat bath model$^{9,10,11}$ to simulate the activated rate processes, where the associated bath is in a nonequilibrium state. The model incorporates some of the essential features of Langevin dynamics with a fluctuating barrier which had been heuristically and phenomenologically proposed earlier in several occasions.$^{10,13−17}$ While the majority of the treatments of the phenomenological fluctuating barrier rest on the reduction of the equations to overdamped limit$^5,10,14$, thus restricting the validity of the solutions in the large time limit, we take full account of the inertial terms in our calculation of barrier dynamics and probability distribution function both in the long time and in the short time nonstationary regimes. The Fokker-Planck description allows us to calculate Kramers-Grote-Hynes reactive frequency pertaining to these situations for
non-Markovian dynamics in closed form. Second, since the theories of activated processes traditionally deal with stationary bath, the nonstationary activated processes has remained largely overlooked so far. We specifically address this issue and examine the influence of initial excitation and subsequent relaxation of a bath modes on the activation of the reaction co-ordinate. We show that relaxation of the nonequilibrium bath modes may result in strong non-exponential kinetics and a nonstationary Kramers rate. The physical situation that has been addressed is the following:

We consider that at $t = 0_-$, the time just before the system and the bath is subjected to an external excitation, the system is appropriately thermalized. At $t = 0$, the excitation is switched on and the bath is thrown into a nonstationary state which behaves as a nonequilibrium reservoir. We follow the stochastic dynamics of the system mode after $t > 0$. The important separation of the time scales of the fluctuations of the nonequilibrium bath and the thermal bath (to which it relaxes) is that the former effectively remains stationary on the fast correlation of the thermal noise.

The outline of the paper is as follows; Following Ref. [10] we discuss in Sec.II a microscopic model to simulate an activated rate process where the system in question is not initially thermalized. Appropriate elimination of reservoir degrees of freedom leads to a nonlinear non-Markovian Langevin equation which governs the dynamics of a particle with a fluctuating barrier, stochasticity being contributed by both (additive) thermal noise and a slower (multiplicative) noisy relaxing nonequilibrium modes. The Fokker-Planck description is provided in Sec.III. The standard Markovian description and the generalized FP equation of Adelman’s form can be recovered in the appropriate limits. In Sec.IV we derive the expression for Kramers rate of barrier crossing in the non-Markovian but steady state regime and show that the Kramers-Grote-Hynes “reactive frequency” can be explicitly realized in this model in closed form. Sec.V is devoted to nonstationary aspect. We solve the time-dependent FP equation for nonstationary probability density and calculate the corresponding current. An expression
for Kramers rate in the nonstationary regime in closed analytical form is derived. The paper is concluded in Sec.VI.

II. The model and the Langevin equation

We consider a model consisting of a system mode coupled to a set of relaxing modes considered as a semi-infinite dimensional system ($\{q_k\}$-subsystem) which effectively constitutes a nonequilibrium bath. This, in turn, is in contact with a thermally equilibrated reservoir. Both the reservoirs are composed of two sets of harmonic oscillators characterized by the frequency sets $\{\omega_k\}$ and $\{\Omega_j\}$ for the nonequilibrium and the equilibrium bath, respectively. The system-reservoir combination evolves under the total Hamiltonian

$$
H = \frac{p^2}{2m} + V(x) + \frac{1}{2} \sum_j (P_j^2 + \Omega_j^2 Q_j^2) + \frac{1}{2} \sum_k (p_k^2 + \omega_k^2 q_k^2) - x \sum_j K_j Q_j - g(x) \sum_k q_k - \sum_{j,k} \alpha_{jk} q_k Q_j ,
$$

(9)

the first two terms on the right hand side describe the system mode. The Hamiltonian for the thermal and nonequilibrium baths are described by the sets $\{Q_j, P_j\}$ and $\{q_j, p_j\}$ for coordinates and momenta, respectively. The coupling terms containing $K_j$ refers to the usual system-thermal bath linear coupling. The last two terms indicate the coupling of the nonequilibrium bath to the system and the thermal bath modes, respectively. Since in the present problem, $H$ is considered to be classical and temperature, $T$ high for the thermally activated problem we note that quantum effects do not play any significant role. Hamiltonian (9) is a simpler variant of that treated in Ref.[10]. For simplicity we take $m = 1$ in (9) and for rest of the treatment. As shown in Ref. [10] the model (9) captures the essential features of fluctuating barrier dynamics. We recall the relevant aspect in the following discussions.
Eliminating the equilibrium reservoir variables \( \{ Q_j, P_j \} \) in an appropriate way \(^9,^{10}\) one may show that the nonequilibrium bath modes obey the following equations of motion,

\[
\ddot{q}_k + \gamma \dot{q}_k + \omega^2_k q_k = g(x) + \eta_k(t) .
\]  

(10)

This takes into account of the average dissipation (\( \gamma \)) of the nonequilibrium reservoir modes \( q_k \) due to its coupling to thermal reservoir which induces fluctuations \( \eta_k(t) \) characterized by \( \langle \eta_k(t) \rangle = 0 \) and the usual fluctuation-dissipation theorem \( \langle \eta_k(t) \eta_k(0) \rangle = 2\gamma K T \delta(t) \). We mention here that moving from Eq.(9) to (10) generate cross terms of the form \( \sum_j \gamma_{kj} q_j \), which are neglected for \( j \neq k \).

Proceeding similarly to eliminate the thermal reservoir variables from the equations of motion of the system mode one obtains

\[
\ddot{x} + \gamma_{eq} \dot{x} + V'(x) = \xi_{eq}(t) + g'(x) \sum_k q_k ,
\]  

(11)

where \( \gamma_{eq} \) refers to the dissipation coefficient of the system mode due to its direct coupling to the thermal bath providing fluctuations \( \xi_{eq}(t) \). Here we have

\[
\langle \xi_{eq}(t) \rangle = 0 \text{ and } \langle \xi_{eq}(t) \xi_{eq}(0) \rangle = 2\gamma_{eq} K T \delta(t) .
\]

Now making use of the formal solutions of Eq.(10)\(^{10}\) which takes into account of the relaxation of the nonequilibrium modes and integrating over the nonequilibrium modes with a Debye type frequency distribution of the form,

\[
\rho(\omega) = \begin{cases} 
3\omega^2/2\omega_c^3 & \text{for } |\omega| \leq \omega_c \\
0 & \text{for } |\omega| > \omega_c 
\end{cases}
\]

where \( \omega_c \) is the high frequency Debye cut-off, one finally arrives at the following Langevin equation of motion for the system mode,

\[
\ddot{x} + \Gamma(x) \dot{x} + \tilde{V}'(x) = \xi_{eq}(t) + g'(x) \xi_{eq}(t) .
\]  

(12)
Here $\Gamma(x)$ is a system coordinate dependent dissipation constant composed of $\gamma_{eq}$ and $\gamma_{neq}$ as follows,

$$\Gamma(x) = \gamma_{eq} + \gamma_{neq}[g'(x)]^2.$$  \hspace{1cm} (13)

$\xi_{neq}$ refers to the fluctuations of the nonequilibrium bath modes which effectively cause a damping of the system mode by an amount $\gamma_{neq}[g'(x)]^2$.

Eq.(12) also includes the modification of the potential $V(x)$ in which the particle moves as

$$\tilde{V}(x) = V(x) - \frac{\omega_c}{\pi} \gamma_{neq} \, g^2(x).$$  \hspace{1cm} (14)

Eq.(12) thus describes the effective dynamics of a particle in a modified barrier, where the metastability of the well originates from the dynamic coupling $g(x)$ of the system mode with the nonequilibrium bath modes. It is necessary to stress here that $g(x)$, in general, is nonlinear. This nonlinearity has two immediate consequences. First, by virtue of the term $\tilde{V}'(x)$ in Eq.(12) it gives rise to a fluctuating barrier. Second, the term $g'(x)\xi_{neq}(t)$ imparts a multiplicative noise term in Eq.(12) in addition to the usual additive noise term $\xi_{eq}(t)$. We point out here that the problem of diffusion over a fluctuating barrier\textsuperscript{13–17} of similar nature has been addressed earlier by a number of workers from the phenomenological point of view. For example, Stein et.al.\textsuperscript{14} have calculated the decay of probability from the metastable state in the white noise limit and also for short finite correlation times for the fluctuating part of the potential. Riemann and Elston\textsuperscript{15} have calculated an asymptotic rate formula when the particle is subjected to both dichotomous and thermal noise.

The treatment followed in the aforesaid cases concerns overdamped situation and, in general, the validity is restricted to long time limit. In the present problem, however, we look at the stochastic process right from the moment the nonequilibrium excitation (followed by the relaxation) sets in. We are therefore forced to take into consideration of the inertial term in Eq.(12) on its usual footing.
We now turn to the another aspect of the problem. In order to define the problem described by Eq.(12) completely, it is further necessary to state the properties of fluctuations of the nonequilibrium bath $\xi_{\text{neq}}(t)$. We have first for Gaussian noise

$$\langle \xi_{\text{neq}}(t) \rangle = 0.$$ 

Also the essential properties of $\xi_{\text{neq}}(t)$ explicitly depend on the nonequilibrium state of the intermediate oscillator modes $\{q_k\}$ through $U(\omega, t)$, the energy density distribution function at time $t$ in terms of the following fluctuation-dissipation relation\textsuperscript{10} for the nonequilibrium bath,

$$\begin{align*}
U(\omega, t) &= \frac{1}{4\gamma_{\text{neq}}} \int_{-\infty}^{+\infty} d\tau \langle \xi_{\text{neq}}(t)\xi_{\text{neq}}(t+\tau) \rangle e^{i\omega\tau} \\
&= \frac{1}{2}KT + e^{-\gamma t/2} \left[ U(\omega, 0) - \frac{1}{2}KT \right].
\end{align*}$$

(15)

$[U(\omega, 0) - \frac{1}{2}KT]$ is a measure of departure of energy density from thermal average at $t = 0$. The exponential term implies that this deviation due to the initial excitation decays asymptotically to zero as $t \to \infty$, so that one recovers the usual fluctuation-dissipation relation for the thermal bath. With the above specification of correlation function of $\xi_{\text{neq}}$ Eq.(15) thus attributes the nonstationary character of the $\{q_k\}$-subsystem.

In passing, we stress that the above derivation\textsuperscript{10} is based on the assumption that $\xi_{\text{neq}}$ is effectively stationary on the fast correlation of the thermal modes. This is a necessary requirement for the systematic separation of time scales involved in the dynamics. We point out that the effective dynamics sets no choice on any special form of coupling $g(x)$ between the system mode and the relaxing mode and as such this may be of arbitrary nonsingular type for our problem we have considered here.
III. The generalized Fokker-Planck description

Eq.(12) is the required Langevin equation for the particle moving in a modified potential $\tilde{V}(x)$ [Eq.(14)] and damped by a coordinate-dependent friction $\Gamma(x)$ [Eq.(13)] due to its linear coupling to a thermal bath and nonlinear coupling to the $\{q_k\}$-subsystem characterized by fluctuations $\xi_{\text{neq}}(t)$. Before proceeding further a few pertinent points are to be noted to stress some distinct and important aspects of the model.

First, depending on the system-$\{q_k\}$-subsystem coupling $g(x)$ both the modified potential $\tilde{V}(x)$ as well as $\Gamma(x)$ are, in general, nonlinear. So the stochastic differential equation (12) is nonlinear. Again, the stochasticity in Eq.(12) is composed of two parts: $\xi_{\text{eq}}(t)$ is an additive noise due to thermal bath while $\xi_{\text{neq}}g'(x)$ is a multiplicative contribution due to nonlinear coupling to $\{q_k\}$-subsystem. It is thus important to note that the presence of multiplicative noise and a fluctuating barrier are associated with nonlinearity in $g(x)$.

Second, the Langevin equation (12) is non-Markovian. The origin of this non-Markovian nature lies in the decaying term in Eq.(15) where the decay explicitly expresses the initial nonequilibrium nature of the $\{q_k\}$-subsystem following the sudden excitation at $t = 0$. This non-Markovian feature is thus not to be confused with that arises due to the usual frequency dependence of the dissipation constant.

Third, although the modification of $V(x)$ is due to the specific choice of the Debye model for the mode density which has so far been commonly used, the theory remains effectively unchanged as one goes over to more complicated spectrum.

We now rewrite Eq.(12) in the form,

$$
\dot{u}_1 = F_1(u_1, u_2, t; \xi_{\text{neq}}, \xi_{\text{eq}})\dot{u}_2 = F_2(u_1, u_2, t; \xi_{\text{neq}}, \xi_{\text{eq}}) \tag{16}
$$
where we use the following abbreviations,

\[
\begin{align*}
  u_1 &= x \\
  u_2 &= v
\end{align*}
\]  
(17)

and

\[
\begin{align*}
  F_1 &= v \\
  F_2 &= -\Gamma(x)v - \tilde{V}'(x) + \xi_{eq}(t) + g'(x)\xi_{neq}(t)
\end{align*}
\]  
(18)

The vector \( u \) with components \( u_1 \) and \( u_2 \) thus represents a point in a 2-dimensional ‘phase space’ and the Eq.(16) determines the velocity at each point in this phase space. The conservation of points now asserts the following linear equation of motion for density \( \rho(u, t) \) in ‘phase space’,

\[
\frac{\partial}{\partial t} \rho(u, t) = -\sum_{n=1}^{2} \frac{\partial}{\partial u_n} F_n(u, t; \xi_{neq}, \xi_{eq}) \rho(u, t)
\]

or more compactly

\[
\frac{\partial \rho}{\partial t} = -\nabla \cdot F \rho .
\]  
(19)

Our next task is to find out a differential equation whose average solution is given by \( \langle \rho \rangle \) where the stochastic averaging has to be performed over two noise processes \( \xi_{neq} \) and \( \xi_{eq} \). To this end we note that \( \nabla \cdot F \) can be partitioned into two parts; a constant part \( \nabla \cdot F_0 \) and a fluctuating part \( \nabla \cdot F_1(t) \), containing these noises. Thus we write

\[
\nabla \cdot F(u, t; \xi_{neq}, \xi_{eq}) = \nabla \cdot F_0(u) + \epsilon \nabla \cdot F_1(u, t; \xi_{neq}, \xi_{eq})
\]  
(20)

where \( \epsilon \) is a parameter (we put it as an external parameter to keep track of the order of the perturbation expansion in \( \epsilon \tau_c \), where \( \tau_c \) is the correlation time of fluctuation of \( \xi_{neq}(t) \); we put \( \epsilon = 1 \) at the end of calculation) and also note that \( \langle F_1(t) \rangle = 0 \). Eq.(19) therefore takes the following form,

\[
\dot{\rho}(u, t) = (A_0 + \epsilon A_1) \rho(u, t)
\]  
(21)
where $A_0 = -\nabla \cdot F_0$, $A_1 = -\nabla \cdot F_1$. The symbol $\nabla$ is used for the operator that differentiate everything that comes after it with respect to $u$.

Making use of one of the main results for the theory of linear equation of the form (21) with multiplicative noise, we derive an average equation for $\rho$ \(\langle \rho \rangle = p(u, t)\), the probability density of $u(t)$ ; for details refer to Van Kampen\textsuperscript{12},

\[
\dot{p} = \left\{ A_0 + \epsilon^2 \int_0^\infty \langle A_1(t) \exp(\tau A_0) A_1(t-\tau) \rangle \exp(-\tau A_0) \right\} p . \tag{22}
\]

The above result is based on second order cumulant expansion and is valid in the case that fluctuations are small but rapid and the correlation time $\tau_c$ is short but finite, i.e.,

\[\langle A_1(t) A_1(t') \rangle = 0 \text{ for } |t - t'| > \tau_c .\]

The Eq.(22) is exact in the limit correlation time $\tau_c$ tends to zero. Using the expressions for $A_0$ and $A_1$ we obtain

\[
\frac{\partial p(u, t)}{\partial t} = \left\{ -\nabla \cdot F_0 + \epsilon^2 \int_0^\infty d\tau \langle \nabla \cdot F_1(t) \exp(-\tau \nabla \cdot F_0) \nabla \cdot F_1(t-\tau) \rangle \exp(\tau \nabla \cdot F_0) \right\} p(u, t) . \tag{23}
\]

The operator $\exp(-\tau \nabla \cdot F_0)$ in the above equation provides the solution of the equation

\[
\frac{\partial f(u, t)}{\partial t} = -\nabla \cdot F_0 f(u, t) , \tag{24}
\]

($f$ signifies the unperturbed part of $\rho$) which can be found explicitly in terms of characteristics curves. The equation

\[
\dot{u} = F_0(u) \tag{25}
\]

for fixed $t$ determines a mapping from $u(\tau = 0)$ to $u(\tau)$, i.e., $u \rightarrow u^\tau$ with inverse $(u^\tau)^{-\tau} = u$. The solution of Eq.(24) is

\[
f(u, t) = f(u^{-t}, 0) \left| \frac{d(u^{-t})}{d(u)} \right| = \exp(-t \nabla \cdot F_0) f(u, 0) , \tag{26}
\]
\[ \frac{|d(u^{-t})|}{d(u)} \] being a Jacobian determinant. The effect of \( \exp(-t \nabla \cdot F_0) \) on \( f(u) \) is as follows:

\[ \exp(-t \nabla \cdot F_0) f(u, 0) = f(u^{-t}, 0) \left| \frac{d(u^{-t})}{d(u)} \right|. \tag{27} \]

The above simplification when put in Eq.(23) yields

\[ \frac{\partial}{\partial t} p(u, t) = \nabla \cdot \left\{ -F_0 + \epsilon^2 \int_0^{\infty} \left| \frac{d(u^{-\tau})}{d(u)} \right| \langle F_1(u, t) \nabla_{-\tau} \cdot F_1(u^{-\tau}, t - \tau) \rangle \left| \frac{d(u)}{d(u^{-\tau})} \right| d\tau \right\} p(u, t). \tag{28} \]

\( \nabla_{-\tau} \) denotes differentiation with respect to \( u_{-\tau} \). We now identify,

\[
\begin{align*}
  u_1 &= x \\
  u_2 &= v \\
  F_{01} &= v, \quad F_{11} = 0 \\
  F_{02} &= -\Gamma(x)v - \bar{V}'(x), \quad F_{12} = \xi_{eq}(t) + g'(x)\xi_{neq}(t)
\end{align*}
\]

In this notation Eq.(28) now reduces to

\[ \frac{\partial p}{\partial t} = -\frac{\partial}{\partial x} (vp) + \frac{\partial}{\partial v} \left\{ \Gamma v + \bar{V}'(x) \right\} p \\
  + \frac{\partial}{\partial v} \int_0^{\infty} d\tau \langle [\xi_{eq}(t) + g'(x)\xi_{neq}(t)] \left[ \frac{\partial}{\partial v} (\xi_{eq}(t - \tau) + g'(x^{-\tau})\xi_{neq}(t - \tau)) \right] \rangle p, \tag{30} \]

where we have used the fact that the Jacobian obey the equation

\[ \frac{d}{dt} \log \left| \frac{d(x^t, v^t)}{d(x, v)} \right| = \frac{\partial}{\partial x} v + \frac{\partial}{\partial v} \{ -\Gamma v + \bar{V}'(x) \} = -\Gamma \tag{31} \]

so that Jacobian equals to \( e^{-\Gamma t} \).

As a next approximation we consider the ‘unpurterbed’ part of Eq.(16) and take the variation of \( v \) during \( \tau_c \) into account to first order in \( \tau_c \). Thus we have

\[ x^{-\tau} = x - \tau v; \quad v^{-\tau} = v + \Gamma \tau v + \tau \bar{V}'(x). \quad \tag{32} \]
Neglecting terms $\mathcal{O}(\tau^2)$ Eq.(32) yields,

$$\frac{\partial}{\partial v} = (1 - \Gamma) \frac{\partial}{\partial v} + \tau \frac{\partial}{\partial x}. \quad (33)$$

Taking into consideration of Eq.(33), Eq.(30) can be simplified after some algebra to the following form,

$$\frac{\partial}{\partial t} p(x, v, t) = -\frac{\partial}{\partial x} (vp) + \frac{\partial}{\partial v} \left\{ \Gamma(x)v + \nabla^\prime(x) - 2g'(x)g''(x)I_{nn} \right\} p$$

$$+ \left\{ I_{ee} + [g'(x)]^2 I_{nn} \right\} \frac{\partial^2 p}{\partial v \partial x}$$

$$+ \left\{ J_{ee} - \Gamma(x)I_{ee} + [g'(x)]^2 J_{nn} - \Gamma(x)[g'(x)]^2 I_{nn} - vg'(x)g''(x)I_{nn} \right\} \frac{\partial^2 p}{\partial v^2}, \quad (34)$$

where,

$$\begin{align*}
I_{ee} &= \int_0^\infty d\tau \langle \xi_{eq}(t)\xi_{eq}(t-\tau) \rangle \\
I_{nn} &= \int_0^\infty d\tau \langle \xi_{neq}(t)\xi_{neq}(t-\tau) \rangle \\
J_{ee} &= \int_0^\infty d\tau \langle \xi_{eq}(t)\xi_{eq}(t-\tau) \rangle \\
J_{nn} &= \int_0^\infty d\tau \langle \xi_{neq}(t)\xi_{neq}(t-\tau) \rangle
\end{align*} \quad (35)$$

The subscripts $ee$ and $nn$ in the above expressions for the integrals over the correlation functions refer to equilibrium and nonequilibrium baths, respectively. In deriving the last Eq.(34) we have assumed that the two reservoirs are uncorrelated. Eq.(34) is the required generalized Fokker-Planck equation for our problem.

In order to allow ourselves a fair comparison with Fokker-Planck equation of other forms, we first turn to the diffusion terms in Eq.(34). The coefficients are coordinate $(x)$ dependent. It is customary to get rid of this dependence by approximating the coefficients at the barrier top (say, $x = 0$) [one may also use mean field or steady state solutions of Eq.(34) obtained by neglecting the fluctuation terms and putting appropriate stationary condition in the diffusion coefficients].
The drift term in Eq.(34) refers to the presence of a dressed potential of the form,

\[ R(x) = \tilde{V}(x) - [g'(x)]^2 I_{nn} \]

or

\[ R(x) = V(x) - \frac{\omega_c}{\pi} \gamma_{\text{neq}} g^2(x) - [g'(x)]^2 I_{nn} . \]  

(36)

The modification of the potential is essentially due to the nonlinear coupling of the system to the nonequilibrium modes. \( I_{nn} \) is a non-Markovian small contribution and therefore the third term in (36) may be neglected without any loss of generality. For the rest of the treatment we use \( R(x) \approx \tilde{V}(x) \). At the vicinity of the barrier top \( x = 0 \), \( \tilde{V}'(x) \) may be approximated, as usual, by a parabolic potential, i.e.,

\[ \tilde{V}(x) \approx \tilde{E}_b - \frac{1}{2} \tilde{\omega}_b^2 x^2 \]  

(37)

with

\[ V(x) \approx E_b - \frac{1}{2} \omega_b^2 x^2 . \]  

(38)

For convenience, one may set \( g(0) = 0 \) in the Taylor series expansion for \( g(x) \) (carried out at the barrier top \( x = 0 \)), without any loss of generality. And one obtains

\[ \tilde{E}_b = E_b \]  

(39)

and

\[ \tilde{\omega}_b^2 = \omega_b^2 + \frac{2 \omega_c \gamma_{\text{neq}}}{\pi} [g'(0)]^2 . \]  

(40)

In the linearized description, the Fokker-Planck Eq.(34) is now reduced to the following form,

\[ \frac{\partial p}{\partial t} = -v \frac{\partial p}{\partial x} + \Gamma p + \left[ \Gamma v - \bar{\omega}_b^2 x \right] \frac{\partial p}{\partial v} + A \frac{\partial^2 p}{\partial v^2} + B \frac{\partial^2 p}{\partial v \partial x} , \]  

(41)

where we have used the following abbreviations;

\[ A = J_{ee} - \Gamma(0)I_{ee} + [g'(0)]^2 J_{nn} - \Gamma(0)[g'(0)]^2 I_{nn} \]  

(42)
and
\[ B = I_{ee} + [g'(0)]^2 I_{nn} . \]  

(43)

From the last two relations we have
\[ A = [J_{ee} + g'(0)^2 J_{nn}] - \Gamma(0)B \]  

(44)

Defining \( A \) and \( B \) as
\[ A = \gamma KT \quad \text{and} \quad B = \beta KT \]  

(45)

one obtains
\[ \frac{\partial p}{\partial t} = -v \frac{\partial p}{\partial x} - \bar{\omega}^2 x \frac{\partial p}{\partial v} + \Gamma \frac{\partial}{\partial v}(vp) + \gamma KT \frac{\partial^2 p}{\partial v^2} 
+ KT \left[ \frac{J_{ee} + g'(0)^2 J_{nn}}{\Gamma(0)KT} - \frac{\gamma}{\Gamma(0)} \right] \frac{\partial^2 p}{\partial x \partial v} . \]  

(46)

Identifying
\[ \bar{\Omega}^2 = \Omega^2 \left[ \frac{J_{ee} + g'(0)^2 J_{nn}}{\Gamma(0)KT} \right] , \]  

(47)

Eq.(46) may be rewritten as,
\[ \frac{\partial}{\partial t} p(x,v,t) = -v \frac{\partial p}{\partial x} - \bar{\omega}^2 x \frac{\partial p}{\partial v} + \Gamma \frac{\partial}{\partial v}(vp) + \gamma KT \frac{\partial^2 p}{\partial v^2} 
+ KT \left[ \frac{\bar{\Omega}^2(t)}{\Omega^2} - \frac{\gamma}{\Gamma(0)} \right] \frac{\partial^2 p}{\partial x \partial v} . \]  

(48)

Here \( \bar{\gamma}(t) \) and \( \bar{\Omega}(t) \) are functions of time (due to the relaxation of the nonequilibrium modes) as defined by Eqs.(45) and (47). Or in other words nonstationary nature of the bath makes \( \bar{\Omega}(t) \) time-dependent through \( J_{nn} \) term which is essentially a non-Markovian modification.

Now the fluctuation-dissipation relations for equilibrium and nonequilibrium baths stated in Sec.II may be invoked. For equilibrium baths as noted earlier we have the
usual result;

\[ J_{ee} = \int_{0}^{\infty} d\tau \langle \xi_{eq}(t)\xi_{eq}(t-\tau) \rangle = \gamma_{eq}KT \] (49)

For the nonequilibrium version, Eq.(15) may be rearranged further to note that

\[ J_{nn} = \int_{0}^{\infty} d\tau \langle \xi_{neq}(t)\xi_{neq}(t-\tau) \rangle = \gamma_{neq}KT(1 + re^{-\frac{r}{2}t}) \] (50)

where \( r \) is a measure of the deviation from equilibrium at the initial instant and is given by \( r = \left\{ \frac{U(\omega, \omega, 0)}{2KT} - 1 \right\} \). Here \( U(\omega, t) \) defines the energy density distribution at time \( t \).

Using (49) and (50) we obtain from Eq.(47)

\[ \frac{\Omega^2(t)}{\Omega^2} = 1 + \frac{r\gamma_{neq}e^{-\frac{r}{2}t}}{\gamma_{eq} + \gamma_{neq}|g'(0)|^2} \] . (51)

In the long time limit the relation reduces to

\[ \mathcal{L}t \rightarrow \infty \bar{\Omega}(t) = \Omega \] . (52)

It is interesting to note that with the replacement \( \frac{\Omega^2(t)}{\Omega^2} \sim \frac{\omega^2}{\omega_0^2} \) (terms are of order \( 1 + \mathcal{O}(\gamma) \)) and \( \Gamma(0) \sim \tilde{\gamma} \) one recovers the Fokker-Planck equation in the Adelman’s form\(^5\) (Eq.(8)).

**IV. Non-Markovian steady state Kramers rate**

We now proceed to analyze our generalized Fokker-Planck equation (48) and calculate the steady state current and the Kramers escape rate over the barrier. The procedure we follow in this section is similar to that of Kramers supplemented by Hänggi and Mojtabai’s earlier analysis\(^6\).

As usual we make the ansatz

\[ p(x, v, t) = F(x, v, t) \exp \left[ -\frac{v^2}{2} + \tilde{V}(x) \right] \] (53)
with \( \tilde{V}(x) \) as approximated by a parabolic potential of the form [ see Eqs. (37-40) ]

\[
\tilde{V}(x) \simeq \tilde{E}_b - \frac{1}{2} \tilde{\omega}_b^2 x^2
\]

with \( \tilde{E}_b = E_b \)

and

\[
\tilde{\omega}_b^2 = \omega_b^2 + \frac{2 \omega_c \gamma_{\text{eq}}}{\pi} [g'(0)]^2
\]

as stated earlier.

We seek an equation for \( F \) of the form

\[
F(x, v, t) = F(u, t) , \quad u = v + ax .
\]

(54)

Inserting (53) and (54) in Eq. (48) we obtain

\[
\frac{\partial F}{\partial t} = \left\{ (\Gamma - \gamma) - \frac{1}{K T} (\Gamma - \tilde{\gamma}) v^2 - \frac{\tilde{\omega}_b^2}{K T} \Delta x v \right\} F
\]

\[
+ \left\{ (\Gamma - 2\gamma) - a (1 + \Delta) \right\} v - \tilde{\omega}_b^2 (1 - \Delta) x \right] \frac{\partial F}{\partial u}
\]

\[
+ KT (\gamma + \Delta a) \frac{\partial^2 F}{\partial u^2} ,
\]

(55)

where

\[
\Delta = \frac{\tilde{\Omega}^2(t)}{\Omega^2} - \frac{\tilde{\gamma}}{\Gamma(0)} .
\]

(56)

Using (51), \( \Delta \) may be rewritten as

\[
\Delta \simeq \frac{r \gamma_{\text{eq}} e^{-2 \tilde{t}}}{\gamma_{\text{eq}} + \gamma_{\text{eq}} [g'(0)]^2}
\]

(57)

for \( \Gamma \sim \tilde{\gamma} \).

Assuming \( \frac{\Delta}{K T} \) and \( (\Gamma - \gamma) \) to be very small we obtain

\[
\frac{\partial F}{\partial t} = K T \frac{\partial^2 F}{\partial u^2} - \left[ \frac{\Gamma + a (1 + \Delta)}{\Gamma + \Delta a} v + \frac{\tilde{\omega}_b^2 (1 - \Delta)}{\Gamma + \Delta a} x \right] \frac{\partial F}{\partial u} ,
\]

(58)
which may be written in the form

\[
\frac{\partial F}{\partial t} = KT \frac{\partial^2 F}{\partial u^2} + \bar{\alpha} u \frac{\partial F}{\partial u} ,
\]  

(59)

with

\[
\bar{\alpha} = -\frac{\Gamma + a(1 + \Delta)}{\Gamma + \Delta a} ,
\]  

(60)

and \(a\) is a solution of the quadratic equation

\[
a^2(1 + \Delta) + \Gamma a - \bar{\omega}_b^2(1 - \Delta) = 0 .
\]  

(61)

Since \(Lt_{t \to \infty} \Delta = 0\), the long time or steady state solution of Eq.(58) is satisfied by

\[
KT \frac{\partial^2 F}{\partial u^2} + \bar{\alpha} u \frac{\partial F}{\partial u} = 0
\]  

(62)

with

\[
Lt_{t \to \infty} \bar{\alpha}(t) = -\frac{\Gamma + a}{\Gamma} = \alpha\text{(say)} .
\]  

(63)

Since the Eqs.(62) and (63) are identical in form to the expressions obtained in the usual Kramers theory one can have the usual expressions for the probability density \(p(x, v)\) and the current \(j_s\) as

\[
p(x, v, \infty) = N \left[ \left( \frac{\pi KT}{2\alpha} \right)^{\frac{3}{2}} + \int_0^{|v|/x} dz \exp \left( -\frac{\alpha z^2}{2KT} \right) \right] \exp \left[ -\frac{v^2}{2} + \tilde{V}(x) \right]
\]  

(64)

with

\[
F_s = N \left[ \left( \frac{\pi KT}{2\alpha} \right)^{\frac{3}{2}} + \int_0^{v-|a|x} dz \exp \left( -\frac{\alpha z^2}{2KT} \right) \right]
\]  

(65)

(here the subscript \(s\) in \(F_s\) refers to steady state \(F\)) and

\[
j_s = \int_{-\infty}^{+\infty} dv \, v p(x, v) = N(KT)^{\frac{3}{2}} \left( \frac{2\pi}{\alpha + 1} \right)^{\frac{3}{2}} \exp \left( -\frac{E_b}{KT} \right)
\]  

where we have used the linearized version of \(\tilde{V}(x)\) near the top of the barrier at \(x = 0\),

\[
\tilde{V}(x) = \tilde{E}_b - \frac{1}{2} \bar{\omega}_b^2 x^2 ,
\]
with $\bar{E}_b = E_b$ and $\bar{\omega}_b$ is as given in Eq.(40) and $N$ is the normalization constant.

Employing the asymptotic distribution (just before the system is subjected to the shock at $t = 0$) of $P_w(x, v)$ for $x \to -\infty$ and at $t = 0$ from $p(x, v, t)$, where $P_w(x, v) = p(x \to -\infty, v; t = 0)$ [see Sec. V for calculation of $p(x, v, t)$], one obtains the total number of particles in the well,

$$n_a = N \int_{-\infty}^{+\infty} dv \int_{-\infty}^{+\infty} dx P_w(x, v) = N \frac{2\pi KT}{\omega_0} \left( \frac{2\pi KT}{\alpha} \right)^{\frac{1}{2}}. \quad (66)$$

Here $\omega_0$ is the frequency at the bottom of the left well. We have set the potential energy at the bottom of the left well equal to zero, for convenience.

The final result for the rate of escape in the steady state is given by

$$k = \frac{j_s}{n_a} = \frac{\omega_0 \lambda}{2\pi \bar{\omega}_b} e^{-E_b/\kappa T}, \quad (67)$$

where

$$\lambda = \left[ \left\{ \left( \frac{\Gamma}{2} \right)^2 + \bar{\omega}_b^2 \right\}^{\frac{1}{2}} - \frac{\Gamma}{2} \right]. \quad (68)$$

It is evident that $\lambda$ is reminiscent of the ‘reactive frequency’ $\lambda_r$ of Grote and Hynes$^4$. Microscopically the non-Markovian character of the dynamics in $\lambda$ enters through the explicit structure of $\Gamma$ and $\bar{\omega}_b$ which are given by

$$\Gamma = \gamma_{eq} + \gamma_{neq} [g'(0)]^2 \quad (69)$$

and

$$\bar{\omega}_b^2 = \omega_b^2 + \frac{2\omega_c \gamma_{neq} [g'(0)]^2}{\pi}. \quad (70)$$

The appearance of the reactive frequency $\lambda$ is suggestive of the fact that the particle on the average is not moving on the bare barrier with frequency $\omega_b$ but on a dressed barrier frequency $\bar{\omega}_b$ corrected by $\lambda$. Pollak$^8$ has shown that the reactive frequency $\lambda$ is exactly an imaginary frequency of a barrier that has been modified by the bath modeled as a discrete set of harmonic oscillators linearly coupled to the system. The
effect of $\lambda$ is to slow down the particle by friction near the barrier. In the present model where the generalized Langevin equation (12) describes the motion of the particle over a fluctuating barrier the essential modification of $\lambda$ and $\omega_b$ rests on the nonlinear coupling of the nonequilibrium relaxing modes with the system. Thus in addition to the properties of the bath, dynamic nature of the system-bath coupling is also significant in governing the barrier dynamics. We note in passing that the usual Markovian limit can be recovered if one puts $\gamma_{neq} = 0$ in Eq.(67) and associated quantities.

Before closing this section one pertinent point need to be mentioned. A closer look into the derivation makes it clear that Eq.(67) results from an ansatz of the form (53) where we use $\tilde{V}(x)$ in the Boltzmann factor. This choice is basically guided by the fact that the potential $V(x)$ gets dressed at $t = 0$ by initial excitation of nonequilibrium modes. This choice also makes the stationary current independent of position. However, if one uses the bare potential $V(x)$ and assume a weak dependence of $x$ on $j_s$, one obtains Eq.(67) with $\tilde{\omega}_b$ in the denominator getting replaced by $\omega_b$ itself. The main lesson is that the modification of Kramers rate (67) is essentially due to $\lambda$, the reactive frequency of Grote-Hynes, which has been recognized as an important result in view of some experimental evidence$^{18}$ of relatively weak dependence of rate on damping in the large friction limit.

V. Time-dependent solution of the generalized Fokker-Planck equation; nonstationary Kramers rate; nonexponential relaxation kinetics

We now turn to Eq.(55). Rearranging the time-dependent $\Delta$-containing terms it may be rewritten as

$$\frac{1}{\Gamma} \frac{\partial F}{\partial t} = - \left[ \frac{(\Gamma + a)v + \tilde{\omega}_b^2 x}{\Gamma} \right] \frac{\partial F}{\partial u} + KT \frac{\partial^2 F}{\partial u^2} + \Delta \left[ \frac{aKT}{\Gamma} \frac{\partial^2 F}{\partial u^2} - \frac{(av - \tilde{\omega}_b^2 x)}{\Gamma} \frac{\partial F}{\partial u} \right],$$

(71)

where $\Delta$ is defined in Eq.(57).
Let us write
\[
\frac{(\Gamma + a)v + \bar{\omega}_b^2 x}{\Gamma} = -\alpha u
\]  \hspace{1cm} (72)
and
\[
\frac{(av - \bar{\omega}_b^2 x)}{\Gamma} = -\lambda u
\]  \hspace{1cm} (73)

Here \(\alpha\) is as defined in (63) and \(\lambda\) is to be determined.

In terms of the relations (72) and (73), Eq.(71) reduces to a more compact form.
\[
\frac{1}{\Gamma} \frac{\partial F}{\partial t} = \alpha u \frac{\partial F}{\partial u} + KT \frac{\partial^2 F}{\partial u^2} + \Delta \left[ aKT \frac{\partial^2 F}{\Gamma \partial u^2} + \lambda u \frac{\partial F}{\partial u} \right].
\]  \hspace{1cm} (74)

Eq.(72) may be used to calculate the value of \(a\) as obtained from the solution of the algebraic equation
\[
a^2 + \Gamma a - \bar{\omega}_b^2 = 0.
\]  \hspace{1cm} (75)

Only the negative root of the above equation (say \(a_-\)) is the physically realizable solution corresponding to the steady state solution. This value of \(a\) determines uniquely the value of \(\lambda\) as defined in Eq.(73) to obtain
\[
\lambda = -\alpha.
\]  \hspace{1cm} (76)

We now seek a solution \(F(u,t)\) of Eq.(74) in the form
\[
F(u,t) = F_s(u)e^{-\phi(t)}.
\]  \hspace{1cm} (77)

where \(F_s(u)\) is the steady state solution obtained in the earlier section, i.e., it satisfies
\[
\alpha u \frac{\partial F_s}{\partial u} + KT \frac{\partial^2 F_s}{\partial u^2} = 0.
\]  \hspace{1cm} (78)

We require further
\[
\mathcal{L}t_{t \to \infty} \phi(t) = 0.
\]  \hspace{1cm} (79)
Substituting (77) in Eq.(74) it may be shown that the ‘space’ and the time part is separable. We obtain,

$$-\frac{1}{\Gamma} \frac{\partial \phi}{\partial t} e^{\frac{2}{\gamma} t} = \frac{C}{F_s} \left[ \lambda u \frac{\partial F_s}{\partial u} + \frac{a KT}{\Gamma} \frac{\partial^2 F_s}{\partial u^2} \right] = \text{constant} = D \text{(say)} \quad ,$$

(80)

where we have made use of the Eq.(78) and also

$$\Delta = Ce^{-\frac{2}{\gamma} t} \quad \text{with} \quad C = \frac{r \gamma_{\text{neq}}}{\gamma_{\text{eq}} + \gamma_{\text{neq}}[g'(0)]^2} .$$

On integration over time we obtain from Eq.(80), the solution

$$\phi(t) = 2D \Gamma \gamma e^{-\frac{2}{\gamma} t}$$

(81)

where $D$ is determined by the initial condition.

The time-dependent solution of Eq.(71) therefore reads as

$$F(u, t) = F_s(u) \exp \left[ -\frac{2D \Gamma}{\gamma} e^{-\frac{2}{\gamma} t} \right] .$$

(82)

Thus the corresponding probability distribution is given by,

$$p(x, v, t) = N \left[ \left( \frac{\pi KT}{2\alpha} \right)^{\frac{1}{2}} + \int_0^{|v-|a|x|} dz \exp \left( -\frac{\alpha z^2}{2KT} \right) \right]$$

$$\exp \left[ -\frac{v^2}{2} + \tilde{V}(x) \right] e^{-\frac{2D \Gamma}{\gamma} \exp\left(\frac{-2}{\gamma} t\right)} .$$

(83)

To determine $D$ we now demand that just at the moment the system (and the nonthermal bath) is subjected to external excitation at $t = 0$ and $x \to -\infty$ the distribution (75) must coincide with the usual Boltzmann distribution where the energy term in the Boltzmann factor in addition to usual kinetic and potential terms contains the initial fluctuation of energy density $\Delta U$ [$\Delta U = U(\omega, 0) - \frac{1}{2} KT$] due to excitation of the system at $t = 0$ [see Eq.(15)].
\[
p(x, v, t) \xrightarrow{t \to 0} N \left( \frac{2\pi KT}{\alpha} \right)^{\frac{1}{2}} e^{-2D\frac{v^2}{2}} e^{-\frac{1}{\kappa T} \left( \frac{v^2}{2} + \tilde{V}(x) \right)} \\
= N \left( \frac{2\pi KT}{\alpha} \right)^{\frac{1}{2}} e^{-\frac{1}{\kappa T} \left( \frac{v^2}{2} + \tilde{V}(x) + \Delta U \right)} , \text{ for } (x \to -\infty) . \tag{84}
\]

The last equality demands that
\[
D = \frac{\gamma \Delta U}{2\Gamma KT} \tag{85}
\]

[for the current to be coordinate independent the parabolic approximation of \( \tilde{V}(x) \) is to be used]. \( D \) is thus determined in terms of the relaxing mode parameters and fluctuations of the energy density distribution at \( t = 0 \).

The time-dependent probability density therefore allows us to construct nonstationary current,
\[
j(t) = \int_{-\infty}^{+\infty} dv \, v \, p(x, v, t) = j_s e^{-\frac{2Dt}{\gamma} \exp(-\frac{\gamma^2}{2} t)} , \tag{86}
\]
where \( j_s \) is the stationary or steady state current as derived in the last section.

By Eq. (74) we have,
\[
p_w(x, v) = p(x \to -\infty, v, t = 0_-) , \tag{87}
\]
which was used to calculate the number of particles \( n_a \) initially in the well just before the system was subjected to shock at \( t = 0 \). Thus non-stationary Kramers rate of transition is given by
\[
k(t) = \frac{\omega_0}{2\pi\omega_b} \left[ \left\{ \left( \frac{\Gamma}{2} \right)^2 + \omega_b^2 \right\}^{\frac{1}{2}} - \frac{\Gamma}{2} \right] e^{-\frac{E_b}{\kappa T}} e^{-\frac{2\Delta U}{\gamma} \exp(-\frac{\gamma^2}{2} t)} , \tag{88}
\]
or in terms of the steady state Kramers rate \( k \)
\[
k(t) = k \exp \left[ -\frac{\Delta U}{KT} e^{-\frac{\gamma^2}{2} t} \right] , \tag{89}
\]

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where $\Delta U$ is a measure of the initial departure from the average energy density distribution due to the preparation of the nonstationary state of the intermediate bath modes as a result of excitation at $t = 0$, and $k$ is given by

$$
k = \frac{\omega_0}{2\pi\omega_b} \left\{ \left( \frac{\Gamma}{2} \right)^2 + \frac{\omega_b^2}{\Gamma} \right\}^{1/2} e^{-E_b/KT}.
$$

The above result (88) illustrates a strong nonexponential relaxation of the system mode undergoing a nonstationary activated rate process. The origin of this is an initial preparation of nonequilibrium mode density distribution (with a deviation $\Delta U$) which eventually relaxes to an equilibrium distribution. Eq. (88) implies that the initial transient rate is different from the asymptotic steady state Kramers rate. What is immediately apparent is that the sign of $\Delta U = U(\omega, 0) - \frac{1}{2}KT$ determines whether the initial rate will be faster or slower than the steady state rate. When $\Delta U$ is negative, i.e., the contribution of thermal energy dominates, the initial rate of thermal activation of the reaction co-ordinate gets enhanced as a consequence. On the other hand, when the sudden excitation of the nonequilibrium modes provides a positive deviation $\Delta U$, the initial rate of activation becomes slower. This is because there likely to exist some time lag for the nonthermal energy gained by the few nonequilibrium modes by sudden excitation to be distributed over a range before it become available to the reaction co-ordinate as thermal energy for activation.

It is also interesting to consider the zero and high temperature limits. When $T \to 0$ both the steady state Kramers rate $k$ as well as the time-dependent factor $\exp[-\frac{\Delta U}{K} e^{-\gamma t/2}]$ goes to zero. If $T = 0$, then $k(t)$ is zero at all time. However, it seems intuitively that there should be a transient period during which the rate is finite. It may be noted that since the relaxation of the nonequilibrium bath modes (following the sudden excitation) is very slow compared to the rate of activation process, the particle undergoing barrier crossing cannot ‘sense’ this transient (ideally if the relaxation to equilibrium is adiabatic, i.e., the thermalization of the initial departure $\Delta U$ is very
slow, there should be no transient). We believe that the distinct separation of the two time-scales implied in the dynamics makes the transient unobservable. An interplay of overlapping time-scales pertaining to the relaxation of the bath and the activation of the system may give rise to transients in $k(t)$ at $T = 0$. Evidently this is outside the scope of the present treatment.

When $T$ is very high such that $\frac{1}{2}kT$ far exceeds $\mathcal{U}(\omega, 0)$ the initial rate gets strongly enhanced (since $\Delta \mathcal{U}$ is negative) and the time-dependent exponential factor becomes roughly independent of temperature. In the limit $t \to \infty$ or $\Delta \mathcal{U} \to 0$ we recover steady state Kramers rate, as expected.

The activation rate is thus consequently modified which effectively incorporates a secondary relaxation kinetics. The quasi-thermal excitations decay on the time scale $\frac{1}{\gamma}$, which is well separated from other internal time scales of the thermal bath. The dynamic nature of the coupling between the system and the nonequilibrium modes is responsible for fluctuating barrier. A closer look into the origin of the non-exponential kinetics makes it clear that the spiritual root of $D$-term is essentially the $\Delta$-containing term in Eq.(71) or $\frac{\partial^2 p}{\partial x \partial v}$ term in Eq.(46) which is a non-Markovian contribution. We thus identify the non-exponential relaxation of the system mode as a typical non-Markovian dynamical feature. In the case of very small $\gamma$ one naturally recovers the exponential relaxation and Arrhenious rate of activation of the usual kinetic scheme.

A relevant pertinent point regarding some of the related works need be considered here. Generalized Langevin equation (GLE) has been widely employed in various contexts, e.g., in the description of reactions in liquids. A search for realistic models began with the realization that friction exerted by the solvent on the solute is space dependent. A formally consistent approach to the problem of space and time dependent friction had been introduced early by Lindenberg and co-workers\textsuperscript{20,21}. Carmeli and Nitzan\textsuperscript{22} have also derived a stochastic dynamical equation which is a generalization of GLE to the case of space and time dependent friction. Pollak and Berezhkorskii\textsuperscript{25}
have demonstrated that the space and time-dependent friction model is identical to a multidimensional anisotropic but Markovian friction problem in which the reaction co-ordinate is coupled to an additional co-ordinate which is governed by a Langevin type equation. A theory for treating spatially dependent friction in the classical activated rate processes has been considered and following the method of Pollak an effective Grote-Hynes reactive frequency for this case has been obtained as a transcendental equation. More recently a general theory for thermally activated rate constants influenced by spatially dependent and time correlated friction has been proposed.

While in the above problems one is concerned with the space and time dependent friction, which is essentially a characteristic of the solvent mode structure, in the present problem we deal with effect of a secondary relaxation of intermediate oscillator modes (following an initial excitation) on the primary kinetics of the system mode. The mode density function due to initial excitation differs from its equilibrium value - a feature which is marked in the nonequilibrium fluctuation-dissipation relation. Thus the exponential relaxation in Eq.(81) is not be confused with the exponential time-dependent friction employed in earlier instances. The origin of these two exponential terms are fundamentally different. The non-exponential kinetics is essentially an offshoot of a dynamic modification of the fluctuation-dissipation theorem appropriately carried over to a nonstationary regime. This nonequilibrium nature of activated process is reflected in the nonstationary kinetics that we derive here.

The non-exponential relaxation kinetics had been explored earlier in different occasions in relation to disordered systems, viscous liquids, oxygen binding to hæmoglobin, where phenomenological fluctuating barrier models have been employed (barriers arising from the collective motions of many degrees of freedom). The present model although oversimplified in many respects captures the essential nature of influence of an initial non-thermal mode density distribution on the relaxation kinetics of the system.
VI. Conclusions

In conclusion, we consider a simple microscopic system-nonequilibrium bath model to simulate nonstationary thermally activated processes. The nonequilibrium bath is effectively realized in terms of a semi-infinite dimensional broad-band reservoir which is subsequently kept in contact with a thermal reservoir which allows the nonthermal bath to relax with a characteristic time. A systematic separation of timescales is then used to construct the appropriate Langevin equation for the particle, which is nonlinear and non-Markovian in character. Based on a strategy of Van Kampen’s expansion in $\epsilon \tau_c$ of the relevant physical quantity where $\epsilon$ is the strength and $\tau_c$ is the correlation time of fluctuations of the relaxing modes, we show that this Langevin equation can be recast into the form of a generalized Fokker-Planck equation, when the correlation time is short but finite. Adelman’s form of the Fokker-Planck equation [ Eq.(8) ] as well as the standard Markovian description can be recovered in the appropriate limits. We now summarize the main conclusions of this study:

(i) The model proposed here captures the essential features of Langevin dynamics with a fluctuating barrier. The present approach is equipped to deal with situations both in the non-stationary short time as well as stationary long time regimes. The origin of the short time non-exponential kinetics can be traced back in a non-stationary fluctuation-dissipation theorem.

(ii) We derive the expression for the steady state Kramers escape rate in the non-Markovian case and show that the Grote-Hynes ‘reactive frequency’ can be realized explicitly in terms of the microscopic parameters of the nonequilibrium relaxing modes and their arbitrary dynamic coupling to the system mode.

(iii) The central result of this paper is the derivation of a nonstationary Kramers rate in closed analytic form. This essentially illustrates the influence of an initial excitation and subsequent relaxation of the nonequilibrium bath modes on the system degree of
freedom undergoing an activated process. The system mode is shown to follow strong non-exponential kinetics.

The model considered in the present paper may be realized in a guest-host system embedded in a lattice where the immediate local neighborhood of the guest comprises intermediate oscillator modes whereas the lattice plays the role of a thermal bath. Appropriately identified reaction co-ordinate coupled to other degrees of freedom in a molecule embedded in a matrix may be another worthwhile candidate for such a scheme.

Although simple, the model thus allows us explicit solutions and in view of the prototypical role played by the present model in several earlier investigations, we hope that the conclusions drawn here will find applications in some related experiments of physics and chemistry of complex systems.

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