The generalized Kramers’ theory for nonequilibrium open one-dimensional systems

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(August 6, 2018)

Abstract

The Kramers’ theory of activated processes is generalized for nonequilibrium open one-dimensional systems. We consider both the internal noise due to thermal bath and the external noise which are stationary, Gaussian and are characterized by arbitrary decaying correlation functions. We stress the role of a nonequilibrium stationary state distribution for this open system which is reminiscent of an equilibrium Boltzmann distribution in calculation of rate. The generalized rate expression we derive here reduces to the specific limiting cases pertaining to the closed and open systems for thermal and non-thermal steady state activation processes.

PACS number(s) : 05.40.-a, 02.50.Ey, 05.70.Ln, 82.20.-w
I. INTRODUCTION

Ever since the seminal work of Kramers on the diffusion model of chemical reactions was published about half a century ago, the theory of activated processes has become a central issue in many areas of science, notably in chemical physics, nonlinear optics and condensed matter physics. Kramers considered a model Brownian particle trapped in a one-dimensional well representing the reactant state which is separated by a barrier of finite height from a deeper well signifying the product state. 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 and many of its variants have served as standard paradigms in various problems of physical and chemical kinetics to understand the rate in multidimensional systems in the overdamped and underdamped limits, effect of anharmonicities, rate enhancement by parametric fluctuations, the role of non-Gaussian white noise, role of a relaxing bath, quantum and semiclassical corrections to classical rate and related similar aspects. The vast body of literature has been the subject of several reviews and monograph.

The common feature of overwhelming majority of the aforesaid treatments is that the system is thermodynamically closed which means that the noise of the medium is of internal origin so that the dissipation and fluctuations get related through the fluctuation-dissipation relation. However, in a number of situations the system is thermodynamically open, i.e., when the system is driven by an external noise which is independent of system’s characteristic damping. The distinctive feature of the dynamics in this case is the absence of any fluctuation-dissipation relation. While in the former case a zero current steady state situation is characterized by an equilibrium Boltzmann distribution, the corresponding situation in the latter case is defined only by a steady state condition, if attainable. It may therefore be anticipated that the independence of fluctuations and dissipation tends to make the steady state distribution function depend on the strength and correlation time of external
noise as well as on the dissipation of the system. The elucidation of the role of this steady state distribution in rate theory is worth-pursuing.

Our aim in this paper is to generalize Kramers’ theory of activated processes for external noise in this context. We thus allow the Brownian particle in a potential field to be driven by both external and internal stationary and Gaussian noise fluctuations with arbitrary decaying correlation functions. 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 over the barrier in the intermediate to strong damping regime within an unified description. The theory we develop here follows closely the original flux over population method of Farkas. The distinctive aspect, however, is the consideration of a steady state distribution instead of the equilibrium Boltzmann distribution for determination of quasi-stationary population in the source well. This affects the generalized rate expression significantly in two ways. First, the dynamics around the bottom of the source well exhibits the dependence of steady state distribution on the dissipation. Second, the rate expression remains valid even in absence of any internal thermal noise. We mention, in passing, that the former point had earlier been rightly emphasized by Mel’nikov as a specific requirement for a general theory.

Some pertinent points regarding the rate theory for nonequilibrium systems may be in order. It is well-known that though thermodynamically closed systems with homogenous boundary conditions possess in general time-independent solutions, the driven or open systems may settle down to complicated multiple steady states when one takes into account of nonlinearity of the system in full. Secondly in most nonequilibrium systems the lack of detailed balance symmetry gives rise to severe problem in determination of stationary probability density for multidimensional problem. Because of its one-dimensional and linearized description the present treatment is free from these difficulties. It is important to point out that the externally generated nonequilibrium fluctuations can bias the Brownian motion of a particle in an anisotropic medium and may used for design of molecular motors and pumps. The nonequilibrium, non-thermal systems has also been investigated by a number
of worker in different contexts, e.g., for examining the role of colour noise in stationary probabilities, the properties of nonlinear systems, the nature of cross-over, the effect of monochromatic noise, the rate of diffusion-limited coagulation processes, etc.

The outlay of the paper is as follows: In Sec.II we generalize Kramers’ theory of reaction rate for external noise. The stationary, Gaussian noise processes are of both external and internal type with arbitrary decaying correlation functions. A general form of steady state distribution function in the source well and a rate expression for barrier crossing dynamics for the nonequilibrium open system have been pointed out. In Sec.III we explicitly calculate the detailed form of the rate expressions for the specific cases. The paper is concluded in Sec.IV.

II. GENERALIZATION OF KRAMERS’ THEORY FOR EXTERNAL NOISE

We consider the motion of a particle of unit mass moving in a Kramers’ type potential $V(x)$ such that it is acted upon by random forces $f(t)$ and $e(t)$ of both internal and external origin, respectively, in terms of the following generalized Langevin equation

$$\ddot{x} + \int_0^t \gamma(t-\tau) \dot{x}(\tau) d\tau + V'(x) = f(t) + e(t) ,$$

where the friction kernel $\gamma(t)$ is connected to internal noise $f(t)$ by the wellknown fluctuation-dissipation relationship

$$\langle f(t)f(t') \rangle = k_B T \gamma(t-t') .$$

We assume that both the noises $f(t)$ and $e(t)$ are stationary and Gaussian. Their correlation times may be of arbitrary decaying type. The external noise is independent of the memory kernel and there is no corresponding fluctuation-dissipation relation. We further assume, without any loss of generality, that $f(t)$ is independent of $e(t)$ so that we have

$$\langle f(t)e(t) \rangle = 0 .$$
The external noise modifies the dynamics of activation in two ways. First, it influences the dynamics in the region around the barrier top so that the effective stationary flux across it gets modified. Second, in presence of this noise the equilibrium distribution of the source well is disturbed so that one has to consider a new stationary distribution, if any, instead of the standard Boltzmann distribution. This new stationary distribution must be a solution of the generalized Fokker-Planck equation around the bottom of the source well region and serve as an appropriate boundary condition analogous to Kramers’ problem. We consider these two aspects separately in the next two subsections.

A. Fokker-Planck dynamics at the barrier top

We consider the potential \( V(x) \) as shown in Fig.1. Linearizing the potential around the barrier top at \( x = 0 \) we write

\[
V(x \approx 0) = V(0) - \frac{1}{2} \omega_b^2 x^2 + \ldots ; \quad \omega_b^2 > 0 .
\]

Thus the Langevin equation takes the following form

\[
\ddot{x} + \int_0^t \gamma(t - \tau) \dot{x}(\tau) \, d\tau - \omega_b^2 x = F(t)
\]

where

\[
F(t) = f(t) + e(t) .
\]

The general solution of Eq.(3) is given by,

\[
x(t) = \langle x(t) \rangle + \int_0^t M_b(t - \tau) \, F(\tau) \, d\tau
\]

where

\[
\langle x(t) \rangle = v_0 M_b(t) + x_0 \chi^b(t)
\]

with \( x_0 = x(0) \) and \( v_0 = \dot{x}(0) \) being the initial position and velocity of the Brownian particle that are assumed to be nonrandom, and
\[ \chi^b_x(t) = 1 + \omega_b^2 \int_0^t M_b(\tau) \, d\tau . \]  

(9)

The kernel \( M_b(t) \) is the Laplace inversion of,

\[ \tilde{M}_b(s) = \frac{1}{s^2 + s\tilde{\gamma}(s) - \omega_b^2} \]  

(10)

with

\[ \tilde{\gamma}(s) = \int_0^\infty e^{-st} \gamma(t) \, dt . \]

The time derivative of Eq.(7) gives

\[ v(t) = \langle v(t) \rangle + \int_0^t m_b(t - \tau) \, F(\tau) \, d\tau \]  

(11)

with

\[ \langle v(t) \rangle = v_0 m_b(t) + \omega_b^2 x_0 M_b(t) \]  

(12)

and

\[ m_b(t) = \frac{dM_b(t)}{dt} . \]  

(13)

Now using the symmetry of the correlation function,

\[ \langle F(t)F(t') \rangle = C(t - t') = C(t' - t) \]

we compute the explicit expressions of the variances in terms of \( M_b(t) \) and \( m_b(t) \) as,

\[ \sigma_{xx}^2(t) \equiv \langle [x(t) - \langle x(t) \rangle]^2 \rangle \]

\[ = 2 \int_0^t M_b(t_1) \, dt_1 \int_0^{t_1} M_b(t_2) \, C(t_1 - t_2) \, dt_2 \]  

(14a)

\[ \sigma_{vv}^2(t) \equiv \langle [v(t) - \langle v(t) \rangle]^2 \rangle \]

\[ = 2 \int_0^t m_b(t_1) \, dt_1 \int_0^{t_1} m_b(t_2) \, C(t_1 - t_2) \, dt_2 \]  

(14b)

\[ \sigma_{xv}^2(t) \equiv \langle [x(t) - \langle x(t) \rangle] [v(t) - \langle v(t) \rangle] \rangle \]

\[ = \int_0^t M_b(t_1) \, dt_1 \int_0^t m_b(t_2) \, C(t_1 - t_2) \, dt_2 \]  

(14c)
and from (14a) and (14c) we see that
\[ \sigma^2_{xx}(t) = \frac{1}{2} \dot{\sigma}^2_{xx}(t). \] (14d)

While calculating the variances it should be remembered that by virtue of Eq.(6)
\[ C(t - t') = \langle f(t)f(t') \rangle + \langle e(t)e(t') \rangle. \] (15)

Since, in principle we know all the average quantities and variances of the linear system driven by Gaussian noise one can make use of the characteristic function method to write down the Fokker-Planck equation for phase space distribution function \( p(x,v,t) \) near the barrier top
\[ \partial_t p(x,v,t) + v \partial_x p(x,v,t) + \dot{\overline{\omega}}^2_b(t) x \partial_v p(x,v,t) + \phi_b(t) \partial^2_{vv} p(x,v,t) + \psi_b(t) \partial_{vvx} p(x,v,t) \] (16)
with
\[ \overline{\gamma}_b(t) = -d \frac{dt}{dt} \ln \Lambda_b(t), \] (17a)
\[ \overline{\omega}_b^2(t) = -\frac{M_b(t) \dot{m}_b(t) + m_b^2(t)}{\Lambda_b(t)}, \] (17b)
\[ \Lambda_b(t) = -\frac{m_b(t)}{\overline{\omega}_b^2} \left\{ 1 + \omega_b^2 \int_0^t M_b(\tau) d\tau \right\} + M_b^2(t), \] (17c)
\[ \phi_b(t) = \overline{\omega}_b^2(t) \sigma^2_{xx} + \overline{\gamma}_b(t) \sigma^2_{vv} + \frac{1}{2} \dot{\sigma}^2_{vv} \quad \text{and} \]
\[ \psi_b(t) = \overline{\omega}_b^2(t) \sigma^2_{xx} + \overline{\gamma}_b(t) \sigma^2_{vv} + \sigma^2_{xx} - \sigma^2_{vv} \] (17d)

Regarding the Fokker-Planck equation (16) three points are to be noted. First, although bounded the time dependent functions \( \overline{\gamma}_b(t), \phi_b(t) \) and \( \psi_b(t) \) may not always provide long time limits. These play a decisive role in the calculation of non-Markovian Kramers’ rate. Therefore, in general, one has to work out frequency \( \overline{\omega}_b(t) \) and friction \( \overline{\gamma}_b(t) \) functions for analytically tractable models. Second, when the noise is purely internal (i.e., there exist a fluctuation-dissipation relation) we have
\[ \phi_b(t) = k_B T \bar{\gamma}_b(t) \quad \text{and} \quad \psi_b(t) = \frac{k_B T}{\omega_b^2} [\omega_b^2(t) - \omega_b^2(t)] . \]  

(18)

Third, for pure external noise with Markovian relaxation, i.e., \( \gamma(t) = \gamma \delta(t) \) we have

\[ \bar{\gamma}_b(t) = \gamma, \quad \bar{\omega}_b^2(t) = \omega_b^2, \quad \phi_b(t) = \int_0^t C(t') m_b(t') \, dt' \quad \text{and} \quad \psi_b(t) = \int_0^t C(t') M_b(t') \, dt' . \]  

(19)

### B. Stationary distribution in the source well

In order to calculate the stationary distribution near the bottom of the left well we now linearize the potential \( V(x) \) around \( x = x_a \). The corresponding Fokker-Planck equation can be constructed using the above-mentioned technique to obtain

\[
\left[ \frac{\partial}{\partial t} + v \frac{\partial}{\partial x} - \bar{\omega}_0^2(t) x \frac{\partial}{\partial v} \right] p(x, v, t) = \bar{\gamma}_0(t) \frac{\partial}{\partial v} v p(x, v, t) + \phi_0(t) \frac{\partial^2}{\partial v^2} p(x, v, t) + \psi_0(t) \frac{\partial^2}{\partial v \partial x} p(x, v, t) \]

(20)

with

\[
\bar{\gamma}_0(t) = -\frac{d}{dt} \ln \Upsilon_0(t) , \quad \bar{\omega}_0^2(t) = -\frac{M_0(t) \bar{m}_0(t) + m_0^2(t)}{\Upsilon_0(t)} ,
\]

(21a)

\[
\Upsilon_0(t) = -\frac{m_0(t)}{\omega_0^2} \left\{ 1 - \omega_0^2 \int_0^t M_0(\tau) \, d\tau \right\} + M_0^2(t) ,
\]

(21b)

\[
\phi_0(t) = \bar{\omega}_0^2(t) \sigma_{xx}^2 + \bar{\gamma}_0(t) \sigma_{vv}^2 + \frac{1}{2} \sigma_{v}^2 \quad \text{and} \quad \psi_0(t) = \bar{\omega}_0^2(t) \sigma_{xx}^2 + \bar{\gamma}_0(t) \sigma_{xx}^2 + \bar{\sigma}^2_{xx} - \sigma_{vv}^2 .
\]

(21c)

(21d)

(21e)

Here the subscripts ‘0’ signifies the dynamical quantities corresponding to the bottom of the left well.

It may be easily checked that the stationary solution of Eq. (20) is given by

\[
p_{st}^0(x, v) = \frac{1}{Z} \exp \left[ -\frac{v^2}{2D_0} - \frac{\bar{V}(x)}{D_0 + \psi_0} \right]
\]

(22)

where, \( D_0 = \phi_0/\bar{\gamma}_0; \psi_0, \phi_0 \) and \( \bar{\gamma}_0 \) are the values at long time limit and \( Z \) is the normalization constant. Here \( \bar{V}(x) \) is the renormalized linearized potential with a renormalization in its frequency.
It must be emphasized that the distribution (22) is not an equilibrium distribution. This stationary distribution for the open system plays the role of an equilibrium distribution for the closed system which may be however recovered in the absence of external noise terms. We also point out in passing that because of the linearized potential $\tilde{V}(x)$ the steady state is unique and the question of multiple steady states does not arise.

C. Stationary current across the barrier

In the spirit of Kramers’ celebrated ansatz we now demand a solution of the Eq.(16) at the stationary limit of the type

$$p_{st}(x, v) = \exp \left[-\frac{v^2}{2D_b} - \frac{\tilde{V}(x)}{D_b + \psi_b}\right] \xi(x, v)$$

with $D_b = \phi_b/\bar{\gamma}_b$ and $\psi_b$ are the long time limits of the corresponding time dependent quantities specific for the barrier top region. The notable difference from the Kramers ansatz is that the exponential factor in (23) is not the Boltzmann factor but pertains to the dynamics at the barrier top.

The ansatz of the form (23) denoting the steady state distribution is motivated by the local analysis near the bottom and top of the barrier in the Kramers’ sense. For a nonequilibrium system, as in the present problem of external time-dependent potential field, the relative population of the two regions, in general, depends on the global properties of the potential. Thus although at equilibrium the probability density is given by a Boltzmann distribution, the external modulation of the potential requires energy input and drives the system away from equilibrium, disturbing the Boltzmann distribution. At this point one may anticipate the signature of dynamics in the Kramers’-like ansatz (23) compared to the standard Kramers’ ansatz for closed system (i.e., when the external field is absent). Thus while in the latter case one considers a complete factorization of the equilibrium part (Boltzmann) and the dynamical part, $\xi(x, v)$, the ansatz (23) incorporates the additional dynamical contribution through dissipation and the strength of the noise into the exponential
part. This explicit dynamical modification of Kramers’ ansatz in the form of (23) is valid so long as the extra dynamical contribution in the exponential factor in (23) does not become too severe, i.e., the amplitude of the external noise field is not too strong. To put it in a more quantitative way, this implies (assuming for simplicity $D_0 \approx D_b \sim D$, $\psi_0 \simeq \psi_b \sim \psi$) that the thermal length scale, i.e., the maximum value of $\sqrt{D + \psi/\gamma}$ on which the velocity of the particle is thermalized, should be shorter than the other characteristic length scales of the system, e.g.,

$$\sqrt{D + \psi/\gamma} < \sqrt{D/\omega_b^2} \left( \text{or } \sqrt{D/\omega_0^2} \right).$$

(24)

These considerations are necessary for making spatial diffusion regime and quasi-stationary condition meaningful in the present context.

Now inserting (23) in (16) in the steady state we get

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

(25)

At this point we set

$$u = v + ax ,$$  

(26)

and with the help of the transformation (26), Eq.(23) is reduced to the following form

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

(27)

Now, let

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

(28)

where $\lambda$ is a constant to be determined later.

From (26) and (28) we have

$$a_\pm = -\frac{B}{2A} \pm \sqrt{\frac{B^2}{4A^2} + \frac{C}{A}}.$$  

(29)

with
\[ A = 1 + \frac{\psi_b}{D_b}, \quad B = \bar{\gamma}_b \quad \text{and} \quad C = \frac{D_b}{D_b + \psi_b\bar{\omega}_b^2}. \]  

(30)

By virtue of the relation (28), Eq. (27) becomes

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

(31)

where

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

(32)

The general solution of the homogenous differential equation (31) is

\[ \xi(u) = F_2 \int_0^u \exp \left( -\frac{1}{2} \Lambda u^2 \right) \, du + F_1, \]  

(33)

where \( F_1 \) and \( F_2 \) are the constants of integration.

The integral in the Eq. (33) converges for \( |u| \to \infty \) if only \( \Lambda \) is positive. The positivity of \( \Lambda \) depends on the sign of \( a \); so by virtue of Eqs. (26) and (28) we find that the negative root of \( a \), i.e., \( a^- \), guarantees the positivity of \( \Lambda \) since

\[ -\lambda a = C. \]  

(34)

To determine the value of \( F_1 \) and \( F_2 \) we impose the first boundary condition on \( \xi \)

\[ \xi(x, v) \to 0 \quad \text{for} \quad x \to +\infty \quad \text{and all} \quad v. \]  

(35)

This condition yields

\[ F_1 = F_2 \left( \frac{\pi}{2\Lambda} \right)^{1/2}. \]  

(36)

Inserting (36) into (33) we have as usual

\[ \xi(u) = F_2 \left[ \left( \frac{\pi}{2\Lambda} \right)^{1/2} + \int_0^u \exp \left( -\frac{1}{2} \Lambda u^2 \right) \, du \right]. \]  

(37)

Since we are to calculate the current around the barrier top, we expand the renormalized potential \( \tilde{V}(x) \) around \( x \approx 0 \)
\[
\tilde{V}(x) \simeq \tilde{V}(0) - \frac{1}{2}\omega^2_b x^2 .
\]  

(38)

Thus with the help of (37) and (38), Eq. (23) becomes

\[
p_{st}(x \approx 0, v) = F_2 e^{-\frac{\tilde{V}(0)}{2\bar{b}} + \frac{v^2}{2\bar{b}} + F(x \approx 0, v) e^{-\frac{v^2}{2\bar{b}}}}
\]

(39)

with

\[
F(x, v) = \int_0^u \exp \left( -\frac{1}{2}\Lambda u^2 \right) du .
\]

(40)

Now defining the steady state current \( j \) across the barrier by

\[
j = \int_{-\infty}^{+\infty} v p_{st}(x \approx 0, v) dv
\]

(41)

we have using Eq. (33)

\[
j = F_2 D_b \frac{\sqrt{2\pi}}{(\Lambda + D_b^{-1})^{1/2}} \exp \left[ -\frac{\tilde{V}(0)}{D_b + \psi_b} \right] .
\]

(42)

D. Stationary population in the left well

Having obtained the steady state current over the barrier top we now look for the value of the undetermined constant \( F_2 \) in Eq. (42) in terms of the population in the left well. We show that this may be done by matching two appropriate reduced probability distributions at the bottom of the left well.

To do so we return to the Eq. (23) which describes the steady state distribution at the barrier top. Again with the help of (37) we have

\[
p_{st}(x, v) = F_2 \left[ \left( \frac{\pi}{2\Lambda} \right)^{1/2} + \int_0^u \exp \left( -\frac{1}{2}\Lambda u^2 \right) du \right] \exp \left[ -\frac{v^2}{2D_b} - \frac{\tilde{V}(x)}{D_b + \psi_b} \right] .
\]

(43)

We first note that, as \( x \rightarrow -\infty \), the pre-exponential factor in \( p_{st}(x, v) \) reduces to the following form

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

(44)
We now define a reduced distribution function in $x$

$$
\tilde{p}_{st}(x) = \int_{-\infty}^{+\infty} p_{st}(x,v) \, dv .
$$

(45)

Hence we have from (44) and (45)

$$
\tilde{p}_{st}(x) = 2\pi F_2 \left( \frac{D_b}{\Lambda} \right)^{1/2} \exp \left[ -\frac{\tilde{V}(x)}{D_b + \psi_b} \right] .
$$

(46)

Similarly we derive the reduced distribution function in the left well, around $x \approx x_a$ using (22) as

$$
\tilde{p}_0^{st}(x) = \frac{1}{Z} \sqrt{2\pi D_0} \exp \left[ -\frac{\tilde{V}(x_a)}{D_0 + \psi_0} \right] .
$$

(47)

where we have employed, the expansion of $\tilde{V}(x)$ as

$$
\tilde{V}(x) \simeq \tilde{V}(x_a) + \frac{1}{2} \bar{\omega}_0^2 (x - x_a)^2 , \quad x \approx x_a
$$

(48)

and $Z$ as the normalization constant.

At this juncture we impose the second boundary condition that, at $x = x_a$ the reduced distribution function (46) must go over to stationary reduced distribution function (47) at the bottom of the left well. Thus we have

$$
\tilde{p}_0^{st}(x = x_a) = \tilde{p}_{st}(x = x_a) .
$$

(49)

The above condition is used to determine the undetermined constant $F_2$ in terms of the normalization constant $Z$ of Eq.(22)

$$
F_2 = \frac{1}{Z} \left( \frac{\Lambda}{2\pi} \right)^{1/2} \left( \frac{D_0}{D_b} \right)^{1/2} \exp \left[ -\frac{\tilde{V}(x_a)}{D_0 + \psi_0} \right] \exp \left[ \tilde{V}(0) - \frac{1}{2} \bar{\omega}_0^2 x_a^2 \right] .
$$

(50)

Evaluating the normalization constant by explicitly using the relation

$$
\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \tilde{p}_0^{st}(x,v) \, dx \, dv = 1
$$

(51)

and then inserting its value in (50) we obtain

$$
F_2 = \frac{\bar{\omega}_0}{2\pi} \left( \frac{\Lambda}{2\pi} \right)^{1/2} \frac{1}{D_b^{1/2}(D_0 + \psi_0)^{1/2}} \exp \left[ \tilde{V}(0) - \frac{1}{2} \bar{\omega}_0^2 x_a^2 \right] .
$$

(52)
Making use of the relation \( \tilde{V}(x_a) = \tilde{V}(0) - \frac{1}{2} \tilde{\omega}_0^2 x_a^2 \) in (52) and then the value of \( F_2 \) in Eq.(12) we arrive at the expression for the normalized current or barrier crossing rate

\[
k = \frac{\tilde{\omega}_0}{2\pi} \frac{D_b}{(D_0 + \psi_0)^{1/2}} \left( \frac{\Lambda}{1 + \Lambda D_b} \right)^{1/2} \exp \left[ -\frac{E}{D_b + \psi_b} \right].
\] (53)

where the activation energy \( E \) is defined as

\[
E = \tilde{V}(0) - \tilde{V}(x_a),
\]
as shown in Fig.1. Since the temperature due to internal thermal noise, the strength of the external noise and damping constant are buried in the parameters \( D_0, D_b, \psi_0, \psi_b \) and \( \Lambda \) the general expression (53) looks somewhat cumbersome. We note that the subscripts ‘0’ and ‘b’ in \( D \) or \( \psi \) refer to the well or the barrier top region, respectively. We discuss it in greater detail in the next section.

**III. GENERALIZED KRAMERS’ RATE : INTERNAL VS. EXTERNAL NOISE**

Eq.(53) is the central result of this paper. This generalizes the Kramers’ expression for rate of the activated processes for the nonequilibrium open systems. Both the internal and the external noises may be of arbitrary long correlation time. It is important to note that the pre-exponential dynamical factors as well as the exponential factor are modified due to the openness of the system. The modification of the exponential factor is due to the fact that depending on the strength of the external noise \( e(t) \) the system settles down to a stationary distribution which does not coincide with the usual equilibrium Boltzmann distribution. The system therefore attains the steady state at a different ‘effective’ temperature. This aspect will be clarified in greater detail when we consider the limiting case in subsection D. In general, both the factors in the rate depend on the strength of the noise, correlation time of fluctuations of both external and internal noise processes and dissipation. The rate is spatial-diffusion-limited and is valid for intermediate to strong damping regime. This validity must be appreciated in the present context of driven system in the sense that
while on the one hand thermal length scale of the system must be short compared to other
characteristic length scales of the system corresponding to the inequality (24), dissipation
should also obey the restriction that during one round trip of the particle in phase space
(in action, angle space) under purely deterministic motion corresponding to (4), the energy
dissipated is greater than the thermal energy, i.e.,
\[ \gamma I(E) > \sqrt{D + \psi} \]  
(54)
where \( I(E) \), the action, is equivalent to unperturbed energy \( E \) in the weak friction limit.
Both the inequalities (24) and (54) are therefore relevant for quantifying the spatial-diffusion-
limited intermediate to strong damping regime. In what follows we shall be concerned with
several limiting situations to illustrate the general result (53) systematically for both thermal
and non-thermal activated processes.

A. Internal white noise

We first consider the case with no external noise and the internal thermal noise is \( \delta \)-correlated. To this end we set
\[ e(t) = 0 \quad \text{and} \quad \langle f(t)f(t') \rangle = k_B T \gamma \delta(t-t') \]  
(55)
Making use of the abbreviations in Eqs.(17) and (21) it follows after some algebra that
\[ \psi_0 = \psi_b = 0, \quad D_b = D_0 = k_B T, \quad \Lambda = \frac{\lambda}{\gamma k_B T}, \]
\[ \lambda = -(a_+ + \gamma) \quad \text{and} \quad a_\pm = -\frac{\gamma}{2} \pm \sqrt{\frac{\gamma^2}{4} + \omega_b^2}. \]
The above relations reduce the general expression (53) to classical expression for Kramers’
rate, namely,
\[ k = \frac{\omega_0}{2\pi \omega_b} \left[ \left( \frac{\gamma^2}{4} + \omega_b^2 \right)^{1/2} - \frac{\gamma}{2} \right] e^{-E/k_B T}. \]
(56)
B. Internal colour noise

Next we consider the case with no external noise but the internal noise is of Ornstein-Uhlenbeck type\cite{31,32}. Thus we have

\[ e(t) = 0 \quad \text{and} \quad \langle f(t)f(t') \rangle = \frac{D}{\tau_c} e^{-|t-t'|/\tau_c}. \quad (57) \]

Here \( D \) denotes the strength while \( \tau_c \) refers to the correlation time of the noise. Again from Eqs.(17), (18) and (21) along with (57) we derive the following relations

\[ D_0 = D_b = k_B T, \]
\[ \psi_0 = d_0 k_B T; \quad 1 + d_0 = \bar{\omega}_0^2 / \omega_0^2, \]
\[ \psi_b = d_b k_B T; \quad 1 + d_b = \bar{\omega}_b^2 / \omega_b^2, \]
\[ \lambda = -[\bar{\gamma}_b + (1 + d_b)a_-] \quad \text{and} \]
\[ a_\pm = \frac{1}{1 + d_b} \left[ -\frac{\bar{\gamma}_b}{2} \pm \sqrt{\left(\frac{\bar{\gamma}_b^2}{4} + \bar{\omega}_b^2\right)} \right]. \]

and hence the rate becomes

\[ k = \frac{\omega_0}{2\pi\omega_b} \left[ \left(\frac{\bar{\gamma}_b^2}{4} + \bar{\omega}_b^2\right)^{1/2} - \frac{\bar{\gamma}_b}{2} \right] e^{-E/k_B T}. \quad (58) \]

whereby we recover the result of Grote-Hynes\cite{33} and Hänge-Mojtaba\cite{34} obtained several years ago.

C. External colour noise

Next we consider the case where the noise is completely due to of external source and the external noise is of Ornstein-Uhlenbeck type\cite{31,32} so that we set

\[ f(t) = 0 \quad \text{and} \quad \langle e(t)e(t') \rangle = \frac{D}{\tau_c} e^{-|t-t'|/\tau_c}. \quad (59) \]

Note that since in this case the dissipation is independent of fluctuations we may assume Markovian relaxation so that \( \gamma(t) = \gamma \delta(t) \) (see also Eqs.(18) and (19)).
The above condition (59) when used in Eqs.(17), (19) and (21) we obtain after some lengthy algebra

\[
\phi_0 = \frac{D}{1 + \gamma \tau_c + \omega_0^2 \tau_c^2}, \quad \phi_b = \frac{D}{1 + \gamma \tau_c - \omega_b^2 \tau_c^2}; \\
\psi_0 = \frac{D \tau_c}{1 + \gamma \tau_c + \omega_0^2 \tau_c^2}, \quad \psi_b = \frac{D \tau_c}{1 + \gamma \tau_c - \omega_b^2 \tau_c^2}; \\
\lambda = -[\gamma + (1 + \gamma \tau_c) a_-] \quad \text{and} \\
a_\pm = \frac{1}{1 + \gamma \tau_c} \left[ -\frac{\gamma}{2} \pm \sqrt{\frac{\gamma^2}{4} + \omega_b^2} \right].
\]

and the rate becomes

\[
k = \frac{\omega_0}{2\pi \omega_b} \left( \frac{1 + \gamma \tau_c + \omega_0^2 \tau_c^2}{1 + \gamma \tau_c - \omega_b^2 \tau_c^2} \right)^{1/2} \left[ \left( \frac{\gamma^2}{4} + \omega_b^2 \right)^{1/2} - \frac{\gamma}{2} \right] \exp \left[ -\frac{\gamma(1 + \gamma \tau_c - \omega_b^2 \tau_c^2)}{D(1 + \gamma \tau_c)} E \right]. \tag{60}
\]

It is interesting to note that the expression (60) denotes the external noise-induced barrier crossing rate which crucially depends on the strength \(D\) and correlation time \(\tau_c\) of the coloured noise. The absence of temperature and the appearance of dissipation \(\gamma\) explicitly demonstrates the non-thermal origin of the noise processes as well as the absence of fluctuation-dissipation relation.

**D. Internal and external white noise**

We finally consider both the internal and external noise to be \(\delta\)-correlated, i.e.,

\[
\langle e(t)e(t') \rangle = 2\alpha \delta(t - t') \quad \text{and} \quad \langle f(t)f(t') \rangle = \gamma k_B T \delta(t - t') \tag{61}
\]

\(\alpha\) being the strength of the external white noise. Hence, by virtue of (15), (17) and (21) we have

\[
D_0 = D_b = k_B T + \frac{\alpha}{\gamma}, \quad \psi_0 = \psi_b = 0, \\
\lambda = -(a_- + \gamma) \quad \text{and} \quad a_\pm = -\frac{\gamma}{2} \pm \sqrt{\frac{\gamma^2}{4} + \omega_b^2}.
\]

Hence the rate becomes
\[ k = \frac{\omega_0}{2\pi \omega_b} \left[ \left( \frac{\gamma^2}{4} + \omega_0^2 \right)^{1/2} - \frac{\gamma}{2} \right] \exp \left[ \frac{E}{k_B T + (\alpha/\gamma)} \right]. \]  \hspace{1cm} (62)

In the limit \( \alpha \to 0 \) we recover the Kramers original result \((56)\) for pure internal white noise. We note here that \( \alpha/(\gamma k_B) \) defines a new ‘effective’ temperature due to external noise. The effective temperature which depends on the strength of the external noise had been discussed earlier by Bravo et. al. in a somewhat different context. We note that while in the latter case the bath is driven by external fluctuations, the present treatment concerns the direct driving of the reaction co-ordinate by external noise.

**IV. CONCLUSIONS**

In this paper we have generalized Kramers’ theory of activated processes for nonequilibrium open systems. The theory takes into account of both internal and external Gaussian noise fluctuations with arbitrary decaying correlation functions in an unified way. The treatment is valid for intermediate to strong damping regime for spatial diffusive processes.

The main conclusions of our study are summarized as follows;

(i) We have shown that not only the motion at the barrier top is influenced by the dynamics, it has an important role to play in establishing the stationary state near the bottom of the source well for the open systems. Thus the stationary distribution function in the well depends crucially on the correlation time of the external noise processes as well as on damping. This is distinctly a different situation (but analogous) as compared to an equilibrium Boltzmann distribution in the source well for standard Kramers’ theory for closed systems.

(ii) Provided the long time limits of the moments for the stochastic processes exist, the expression for Kramers’ rate for barrier crossing for open systems we derive here, is general.

(iii) We have checked and examined the various limits of the generalized rate expression to obtain Kramers’ rate, its non-Markovian counterpart as well as the other cases for specific external noise processes in presence and absence of the internal noise.
(iv) We have shown that a rate for barrier crossing dynamics induced by purely non-thermal Gaussian noise can be derived as an interesting limiting case of the generalized rate expression.

We conclude by noting that since the validity of the rate expression derived in the paper depends on the existence of long time limit of the moments for the stochastic processes, the theory cannot be directly extended to, say, fractal noise processes. These and the related noise processes remain outside the scope of the present treatment. Suitable extension of the Kramers’ theory in this direction is worth-pursuing.

ACKNOWLEDGMENTS

SKB is indebted to Council of Scientific and Industrial Research (C.S.I.R.), Government of India for partial financial support.
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FIGURES

FIG. 1. A schematic plot of Kramers’ type potential used in the text.
Fig. (1)