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Nonequilibrium fluctuation induced escape from a metastable state

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Abstract. Based on a simple microscopic model where the bath is in a non-equilibrium state we study the escape from a metastable state in the over-damped limit. Making use of Fokker-Planck-Smoluchowski description we derive the time dependent escape rate in the non-stationary regime in closed analytical form which brings on to fore a strong non-exponential kinetic of the system mode.

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The problem of activated rate processes deals with the escape of a Brownian particle from a metastable state under the influence of thermal fluctuations generated by the immediate surrounding to which the Brownian particle is in close contact. Based on nonequilibrium statistical mechanics Kramers [1] proposed a framework for the phenomenon which over several decades became a standard paradigm for theoretical and experimental investigation in many areas of natural science [2–6]. To the best of our knowledge majority of the post Kramers developments of the theory have been made in the stationary domain with few approaches in the non-stationary regime within the framework of reactive flux formalism [2]. However, few attempts have been made to deal the problem using nonequilibrium, non-stationary formalism [7–9].

In their work Millonas and Ray [7] proposed a theoretical framework for studying the dynamics of escape rate from a metastable state in the over-damped limit. Because of the nonequilibrium fluctuations of the bath mode an in built fluctuating barrier appears in the effective potential of the nonlinear Langevin equation of the system variable. Using path integral formalism the authors then derived a time dependent escape rate. Motivated by this work [7] we prescribe here an alternative method to derive the time dependent escape rate using the Fokker-Planck-Smoluchowski description. The object of the present work is twofold: first, to consider a simple variant of system-bath model [7] to study the activated rate processes, where the associated heat bath is in nonequilibrium state. The model incorporates some of the essential features of Langevin dynamics with a fluctuating barrier which has been phenomenologically proposed earlier [7,10]. Second, since the theories of activated rate processes traditionally deal with stationary bath, the non-stationary activated rate processes have remained largely overlooked so far. We specifically address this issue and examine the influence of initial excitation and subsequent relaxation of bath modes on the activation of the reaction coordinates within the framework of Fokker-Planck-Smoluchowski equation. In spite of the fact that our development bears a close kinship with the work of Millonas and Ray [7], it is crucial to highlight that while Millonas and Ray have used an explicit path integral approach towards the solution of the problem, we, on the contrary, implement a naive differential equation based approach which leads us to a *closed analytical expression for the time-dependent escape rate*. We also mention that in this work we have explicitly calculated the *non-exponential kinetics* of the system mode, where the associated bath is not in thermal equilibrium. The closed form of the final expression of our approach brings with it the twin advantages of being capable of (1) handling the non-stationary phenomena, and (2) tracing the trajectory of how a system coupled with a non-equilibrium bath reaches the stationary state in a computationally economic manner.

To make the present work self consistent we describe the essential features of the model proposed by Millonas and Ray [7]. The physical situation that has been addressed is the following. At $t = 0_-$, the time just before the system and the bath are subjected to an external

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excitations, the system is approximately thermalized. At $t = 0$, the excitation is switched on and the bath is thrown into a non-stationary state which behaves as a nonequilibrium bath. We follow the stochastic dynamics of the system mode after $t > 0$. The important separation of the time scale of the fluctuations of the nonequilibrium bath and the thermal bath is that the former effectively remains stationary on the fast correlation time scale of the thermal noise.

The model consists 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 bath. Both the baths are composed of two sets of harmonic oscillators characterized by the frequency sets $\{\omega_k\}$ and $\{\Omega_j\}$ for the nonequilibrium and equilibrium baths, respectively. The system-bath combination evolves under the total Hamiltonian [7]

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

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 coordinate and momenta, respectively. The coupling terms containing κ_j refer to the usual system-bath linear coupling. The last two terms indicate the coupling of the nonequilibrium bath to the system and the thermal bath modes, respectively. In the present problem H is considered to be classical and the temperature T is high for the thermally activated problem, so that the quantum effects do not play any significant role. For simplicity we take mass, $m = 1$ in equation (1) and for the rest of the treatment. The form of the nonequilibrium bath, a set of phonons, is chosen for both simplicity and because of its generic relationship to many condensed matter systems.

Elimination of equilibrium reservoir variables $\{Q_j, P_j\}$ in an appropriate way we have the equation of motion for the nonequilibrium bath modes as [8,11,12]

$$\ddot{q}_k + \gamma \dot{q}_k + \omega_k^2 q_k = g(x) + \eta_k(t). \quad (2)$$

This takes into account the average dissipation (γ) of the nonequilibrium bath modes q_k due to their coupling to the thermal bath which induces fluctuations $\eta_k(t)$ characterized by $\langle \eta_k(t) \rangle = 0$ and $\langle \eta_j(t)\eta_k(t') \rangle = 2\gamma k_B T \delta(t - t')\delta_{jk}$. In moving from equations (1) to (2) the cross terms of the form $\sum_j \gamma_{kj} q_j$ has been neglected for $j \neq k$. Proceeding similarly to eliminate the thermal bath variables from the equation of motion of the system mode, we get

$$\ddot{x} + \gamma_{eq}\dot{x} + V'(x) = \xi_{eq}(t) + g'(x)\sum_k q_k, \quad (3)$$

where γ_{eq} refers to the dissipation coefficient of the system mode due to its coupling to the thermal bath providing fluctuations $\xi_{eq}(t)$ with the properties,

$$\langle \xi_{eq}(t) \rangle = 0, \langle \xi_{eq}(t)\xi_{eq}(t') \rangle = 2\gamma_{eq} k_B T \delta(t - t'). \quad (4)$$

Now making use of the formal solution of equation (2) 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

$$\mathcal{D}(\omega) = 3\omega^2/2\omega_c^3 \;\; for \;\; |\omega| \leq \omega_c$$
$$= 0 \;\; for \;\; |\omega| > \omega_c$$

where ω_c is the high frequency Debye-cut-off, we finally arrive at the following Langevin equation of motion for the system mode,

$$\ddot{x} + \Gamma(x)\dot{x} + \tilde{V}'(x) = \xi_{eq}(t) + g'(x)\xi_{neq}(t). \quad (5)$$

Here $\Gamma(x)$ is a system coordinate dependent dissipation constant and is given by

$$\Gamma(x) = \gamma_{eq} + \gamma_{neq}[g'(x)]^2 \quad (6)$$

and $\xi_{neq}(t)$ refers to the fluctuations of the nonequilibrium bath modes which effectively cause a damping of the system mode by an amount $\gamma_{neq}[g'(x)]^2$. Equation (5) also includes the modification of the bare potential $V(x)$

$$\tilde{V}(x) = V(x) - \frac{\omega_c}{\pi}\gamma_{neq} g^2(x). \quad (7)$$

Equation (5) 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.

In order to define the dynamics described by equation (5) completely it is necessary to state the properties of the fluctuations of the nonequilibrium bath $\xi_{neq}(t)$, which is assumed to be Gaussian with zero mean $\langle \xi_{neq}(t) \rangle = 0$. Also the essential properties of $\xi_{neq}(t)$ 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 fluctuation-dissipation relation for the nonequilibrium bath [7]

$$u(\omega, t) = \frac{1}{4\gamma_{neq}} \int_{-\infty}^{+\infty} d\tau \langle \xi_{neq}(t)\xi_{neq}(t + \tau) \rangle e^{i\omega\tau}$$
$$= \frac{1}{2}k_B T + e^{-\gamma t/2}\left[u(\omega, 0) - \frac{1}{2}k_B T\right], \quad (8)$$

where $[u(\omega, 0) - k_B T/2]$ is a measure of departure of energy density from thermal average at $t = 0$. The exponential term implies that 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 ξ_{neq}, Equation (8) thus attributes the non-stationary character of $\{q_k\}$-subsystem.

On time scales larger than the inverse friction coefficient $1/\gamma_{eq}$, we can in most particular cases consider

the over-damped limit of the Langevin equation. This in turn corresponds to the adiabatic elimination of the fast variables, inertia term, from the equation of motion by putting $\ddot{x} = 0$ for homogeneous systems. In contrast, for the case of inhomogeneous system the above method of elimination does not work properly and Sancho et al. [13] have given a proper prescription for the elimination of fast variables. Using the method of Sancho et al. the formal master equation for the probability density of the process $P(x,t) = \langle \rho(x,t) \rangle$ is given by

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x}\left\{\frac{\tilde{V}'(x)}{\Gamma(x)}P\right\} + \gamma_{eq}k_BT\frac{\partial}{\partial x}\left\{\frac{1}{\Gamma(x)}\frac{\partial}{\partial x}\frac{1}{\Gamma(x)}P\right\} + \gamma_{neq}k_BT\left(1+re^{-\gamma t/2}\right)\frac{\partial}{\partial x}\left\{\frac{g'(x)}{\Gamma(x)}\frac{\partial}{\partial x}\frac{g'(x)}{\Gamma(x)}P\right\} + \gamma_{neq}k_BT\left(1+re^{-\gamma t/2}\right)\frac{\partial}{\partial x}\left\{\frac{g'(x)g''(x)}{\Gamma^2(x)}P\right\} \quad (9)$$

where $r = \{[u(\omega \to 0,0)/2k_BT] - 1\}$ is a measure of the deviation from equilibrium at the initial instant. Equation (9) is the Fokker-Planck-Smoluchowski equation where the associated bath is in nonequilibrium state, and is the *first key result of this paper*. Under stationary condition (at $t \to \infty$) $\partial P/\partial t = 0$ and the stationary distribution obeys the equation

$$k_BT\frac{dP_{st}(x)}{dx} + \tilde{V}'(x)P_{st}(x) = 0 \quad (10)$$

which has the solution

$$P_{st}(x) = N\exp\left[-\frac{1}{k_BT}\int^x \tilde{V}'(x')dx'\right] \quad (11)$$

where N is the normalization constant. In ordinary Stratonovich description the Langevin equation corresponding to the Fokker-Planck-Smoluchowski equation (9) is given by

$$\dot{x} = -\frac{\tilde{V}'(x)}{\Gamma(x)} - \frac{D(t)g''(x)g'(x)}{\Gamma^2(x)} + \frac{1}{\Gamma(x)}\xi_{eq}(t) + \frac{g'(x)}{\Gamma(x)}\xi_{neq}(t) \quad (12)$$

where

$$D(t) = \gamma_{neq}k_BT(1+\gamma e^{-\gamma t/2}) \quad (13)$$

is the time-dependent diffusion constant due to the relaxation of nonequilibrium bath. Using equations (9) or (12) the escape rate from a metastable state can be calculated via steepest descent method [14]

$$k = \frac{\tilde{\omega}_0\tilde{\omega}_b}{2\pi\Gamma(x_b)}\exp\left(-\frac{\tilde{E}_b}{k_BT}\right) \quad (14)$$

where k is the Kramers activation rate, with $\tilde{E}_b = \tilde{V}'(x_b) - \tilde{V}'(x_0)$ is the modified activation energy and $\tilde{\omega}_b = [\tilde{V}''(x_b)]^{1/2}$, $\tilde{\omega}_0 = [\tilde{V}''(x_0)]^{1/2}$ are the modified frequencies at the barrier top and the bottom of the potential well, respectively. x_b denotes the position of the barrier top and x_0 is the position of the bottom of the potential well. In equation (14) Γ has been evaluated at the top of the barrier. In the absence of the nonequilibrium bath (14) reduces to standard Kramers' expression [1],

$$k = \frac{\omega_0\omega_b}{2\pi\gamma}\exp\left(-\frac{E_b}{k_BT}\right). \quad (15)$$

To obtain the time dependent rate $k(t)$, let us consider that the time dependent solution of equation (9) is given by

$$P(x,t) = P_{st}(x)e^{-\phi(t)} \quad (16)$$

where ϕ is a function of t only and $\lim_{t\to\infty}\phi(t) = 0$. $P_{st}(x)$ is the steady state solution of equation (9). Substitution of (16) in (9) separates the space and time parts and we have the equation for $\phi(t)$ as

$$-\frac{d\phi}{dt}e^{\gamma t/2} = \text{const.} = \alpha(say) \quad (17)$$

which after integration over time gives

$$\phi(t) = \frac{2\alpha}{\gamma}e^{-\gamma t/2} \quad (18)$$

where α can be determined by initial condition. The time dependent solution of equation (9) therefore reads

$$P(x,t) = P_{st}(x)\exp\left[-\frac{2\alpha}{\gamma}e^{-\gamma t/2}\right]. \quad (19)$$

To determine α we now assume that [8] just at the moment the system (and the non-thermal bath) is subjected to external excitation at $t = 0$, the distribution must coincide with the usual Boltzmann distribution where the energy term in the Boltzmann factor in addition to the usual kinetic and potential energy terms, contains the initial fluctuations of energy density $\Delta u[=u(\omega,0) - k_BT/2]$ due to excitation of the system at $t = 0$. This gives $\alpha = (\gamma/2)(\Delta u/k_BT)$. α is thus determined in terms of relaxing mode parameters and fluctuations of the energy density distribution at $t = 0$. The time dependent rate is then derived as [14]

$$k(t) = k\exp\left[-\frac{\Delta u}{k_BT}e^{-\frac{\gamma}{2}t}\right] \quad (20)$$

where Δu is the measure of the initial departure from the average energy density distribution due to the preparation of the non-stationary state of the intermediate bath modes as a result of excitation at $t = 0$ and k is given by equation (14). The above result, equation (20), *which is the second key result of this paper*, illustrates a strong non-exponential kinetic of the system mode undergoing a non-stationary activated rate processes in the over-damped regime. The origin of this is an initial preparation of nonequilibrium mode density distribution which eventually relaxes to an equilibrium distribution. Equation (20) implies that the initial transient rate is different from the asymptotic steady state Kramers' rate. The sign of Δu determines whether the initial rate will be faster or

slower than the steady state rate. This is because there exists a time lag for the non-thermal energy gained by the few nonequilibrium modes by sudden excitation to be distributed over a range before it becomes available to the reaction coordinate as thermal energy for activation.

In conclusion, based on a system-reservoir model, where the reservoir is in a non-equilibrium state, we have provided an analytic model to derive the closed time-dependent escape rate from a metastable state induced by non-equilibrium fluctuations. We have explicitly calculated the *non-exponential kinetics* of the system mode, where the associated bath is not in thermal equilibrium. Our methodology takes care of the non-stationary phenomena, and simultaneously traces the barrier dynamics of a system when it is coupled with a non-equilibrium bath. Not only that our approach may serve as a potential avenue towards the explanation of non-stationary transport processes and rachet problems envisaged in various chemically and biologically interesting systems. The work in this direction is in progress in our group.

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