Thermally activated escape rate in presence of long-time memory

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Kramers's original modeling of the thermally activated escape rate over a barrier is generalized for Brownian-motion theory with long-time memory.

The problem of the decay of a metastable state presents a central role in many areas of science, most notably in chemical kinetics, electron transport in semiconductors, and nonlinear optics. Limiting the discussion to one-dimensional systems, the problem can essentially be modeled by a "Brownian particle" moving in a double-well potential ϕ (see Fig. 1). This model has been popular since Kramers's original Fokker-Planck approach.[1] Since Kramers, a number of investigators have improved and clarified several points: We mention the extension to the decay of a metastable state in driven nonequilibrium systems with nonuniform diffusion,[2] the results for multidimensional systems in the overdamped and underdamped limit,[3–5] the effects of anharmonicities in the potential form,[1,5–8] the role of non-Gaussian white thermal noise (i.e., a Markov master equation description for the Brownian motion process),[7,9] the effect of a rate enhancement via parametric fluctuations,[10] and the influence of quantum tunneling.[11,12] Common to all those treatments is the assumption of a clear-cut separation of time scales between particle and inherent molecular (bath) motion.

In the model that we consider in this paper we drop this assumption. In other words, the thermal noise fluctuations are allowed to exhibit an arbitrary (nonexponential) slowly decaying memory-correlation function. This situation arises for example in biophysical transport problems,[13] catalysis,[14] and impurity diffusion.[15] Attempts to solve the problem of thermally activated escape over a barrier in this difficult situation have been rare. For the problem of diffusion of an impurity bound in a harmonic lattice, interesting results have been obtained by Rezayi and Suhl.[15] Based on their stable states picture, Grote and Hynes,[16–19] have recently discussed the effect of exponentially decaying memory correlations (for the quantum analog see Ref. 12). Their result for the rate, λ, is based on an appealing formula which expresses the rate in terms of an equilibrium reactive flux-flux correlation function.[16] However, it should be noted that their result is based on the assumption that the memory rate kernels decay rapidly compared to the reaction time scale.[16,20] Yet in another attempt one of us has recently evaluated the rate of escape in the overdamped limit by fully taking into account the anharmonicity of the potential but restricting the discussion to a fast, exponentially decaying memory function only.[21]

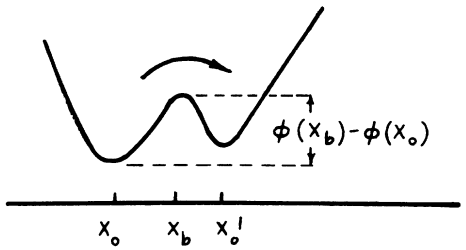

FIG. 1. Potential field used in text.

Clearly, the region around the barrier plays a crucial role in the evaluation of the rate. If we linearize the motion within this barrier region, we can model the Brownian motion in coordinate, x, and velocity, u, phase space by the following generalized Langevin equation (we use a unit mass for the particle and the notation $y=x-x_b$)

$$\begin{aligned}\dot{y}&=u\ ,\\ \dot{u}&=\omega^2 y-\int_0^t \gamma(t-\tau)u(\tau)\,d\tau+\xi(t)\ ,\end{aligned}\tag{1}$$

where the barrier frequency ω^2 is defined by

$$\phi(y)=\phi_b-\frac{\omega^2}{2}y^2+\cdots\ ,\quad \omega^2>0\ .\tag{2}$$

The thermal noise $\xi(t)$ is a stationary Gaussian random force which satisfies the fluctuation-dissipation theorem of the second kind

$$\langle\xi(\tau)\xi(0)\rangle=kT\gamma(|\tau|)\ ,\tag{3}$$

and $\gamma(\tau)$ is the (unspecified) memory function. Because of the linear structure in (1), the Gaussian noise implies that the Brownian motion process, $(y(t),u(t))$, with initial values $(\tilde{y},\tilde{u})$ at time $t_0=0$, is governed by a Gauss process. The rate of change of the probability $p_t(y,u|\tilde{y},\tilde{u})$ can be obtained in *time-convolutionless* form

$$\dot{p}_t=\Gamma(t)p_t\tag{4a}$$

with the master operator

$$\Gamma(t)=\frac{d}{dr}(p_r p_t^{-1})\bigg|_{r=t^+} . \tag{4b}$$

Using the fluctuation-dissipation theorem in (3), a cumbersome but similar calculation of the type performed in Refs. 22 and 23 yields the *non-Markov master equation*

$$\dot{p}_t=\left(-u\frac{\partial}{\partial y}-\bar{\omega}^2(t)y\frac{\partial}{\partial u}\right)p_t+\bar{\gamma}(t)\frac{\partial}{\partial u}(up_t)$$

$$+kT\bar{\gamma}(t)\frac{\partial^2}{\partial u^2}p_t+\frac{kT}{\omega^2}[\bar{\omega}^2(t)-\omega^2]\frac{\partial^2}{\partial u\,\partial y}p_t . \tag{5}$$

The functions $\bar{\gamma}(t)$ and $\bar{\omega}^2(t)$ are derived from the time-dependent correlation matrix of fluctuations as

$$\bar{\gamma}(t)=-\dot{a}(t)/a(t) , \tag{6a}$$

$$\bar{\omega}^2(t)=-b(t)/a(t) , \tag{6b}$$

where

$$a(t)=\rho_y(t)\dot{\rho}_u(t)-\dot{\rho}_y(t)\rho_u(t) , \tag{6c}$$

$$b(t)=\dot{\rho}_y(t)\ddot{\rho}_u(t)-\ddot{\rho}_y(t)\dot{\rho}_u(t) , \tag{6d}$$

with

$$\rho_y(t)=1+\omega^2\int_0^t\rho_u(\tau)\,d\tau . \tag{6e}$$

The correlation $\rho_u(t)$ is given in terms of the inverse Laplace transform (L^{-1}) by

$$\rho_u(t)=L^{-1}\left(\frac{1}{z^2-\omega^2+z\hat{\gamma}(z)}\right) , \quad \rho_u(0)=0 , \tag{6f}$$

and $\hat{\gamma}(z)$ denotes the Laplace transform of $\gamma(\tau)$. The non-Markovian master equation (5), valid only within the barrier region, cannot describe nonlinear phenomena such as the relaxation of a sharply localized unstable state around $x=x_b(y=0)$. However, Eq. (5) does allow for the evaluation of the *steady nonequilibrium* probability $p_0(y,u)$, obtained by injecting particles at the locally stable well around x_0 and removing them the moment they reach the locally stable product well around x_0'. In the limit of small thermal noise the state x_0 is a long-lived quasiequilibrium state. The nonequilibrium probability p_0, generating a nonvanishing diffusion current j_0, has thus the form

$$p_0(x,u)=\frac{1}{Z}F(x,u)\exp\left(-\frac{u^2/2+\phi(x)}{kT}\right) \tag{7}$$

with $F(x,u)$ obeying, $F(x,u)=1$ around x_0 and $F(x_0',u)=0$ at the absorbing boundary around x_0'. From (5) we obtain for $F(y,u)$ in the neighborhood of $x=x_b$ the equation (F_z' denotes the differentiation after z)

$$uF_y'+\bar{\omega}^2yF_u'=kT\bar{\gamma}F_{uu}''-\bar{\gamma}uF_u'$$

$$+\frac{kT}{\omega^2}(\bar{\omega}^2-\omega^2)\left(\frac{\omega^2y}{kT}F_u'-\frac{u}{kT}F_y'+F_{yu}''\right) \tag{8a}$$

with

$$\bar{\omega}^2=\lim_{t\to\infty}\bar{\omega}^2(t), \quad \bar{\gamma}=\lim_{t\to\infty}\bar{\gamma}(t) . \tag{8b}$$

For the solution of the crucial function F we try Kramers's ansatz (valid for not extremely small effective damping $\bar{\gamma}$)

$$F(y,u)=F(\zeta)=F(u-cy) \tag{9}$$

with c a yet undetermined constant. Therefore, we obtain with $d=(\bar{\omega}^2-\omega^2)/\omega^2$ for (8)

$$-[c(1+d)-\bar{\gamma}]uF_\zeta'+\omega^2yF_\zeta'=kT(\bar{\gamma}-dc)F_{\zeta\zeta}'' \tag{10}$$

which determines the constant c via the quadratic relation

$$c=\omega^2/[c(1+d)-\bar{\gamma}] . \tag{11}$$

With (10) and (11) and the boundary conditions $F(\zeta)\to 1$ as $\zeta\to\infty$, $F(\zeta)\to 0$ as $\zeta\to-\infty$, the solution $F(\zeta)$ is found by integration to be

$$F(\zeta)=\left(\frac{c(1+d)-\bar{\gamma}}{2\pi kT(\bar{\gamma}-dc)}\right)^{1/2}$$

$$\times\int_{-\infty}^{\zeta}\exp\left[-\left(\frac{c(1+d)-\bar{\gamma}}{2kT(\bar{\gamma}-dc)}\right)z^2\right]dz . \tag{12}$$

By expanding the potential ϕ around x_0 (see Fig. 1)

$$\phi(x)=\phi_0+\frac{\omega_0^2}{2}(x-x_0)^2+\cdots , \quad \omega_0^2>0 \tag{13}$$

we find for the occupation, n_0, of particles at x_0

$$n_0\simeq\frac{\exp(-\phi_0/kT)}{Z}\int_{-\infty}^{+\infty}\exp\left(-\frac{u^2+\omega_0^2z^2}{2kT}\right)dz\,du$$

$$=\frac{2\pi kT}{Z\omega_0}\exp\left(-\frac{\phi_0}{kT}\right) . \tag{14}$$

The rate for thermally activated escape is given by

$$\lambda=j_0/n_0 , \tag{15}$$

where the diffusion current j_0 is calculated to be

$$j_0=\int_{-\infty}^{+\infty}p_0(y=0,u)u\,du$$

$$=\frac{kT}{Z}\left(\frac{c(1+d)-\bar{\gamma}}{c}\right)^{1/2}\exp\left(-\frac{\phi_b}{kT}\right) . \tag{16}$$

With c denoting the plus sign solution of the quadrat-

ic relation (11) (this amounts to a decreasing rate with increasing effective damping $\bar{\gamma}$), we have for the rate the remarkably simple central result

$$\lambda = \frac{\omega_0}{2\pi\omega}\left[\left(\frac{\bar{\gamma}^2}{4}+\bar{\omega}^2\right)^{1/2}-\frac{\bar{\gamma}}{2}\right]\exp\left[-\frac{\phi_b-\phi_0}{kT}\right] . \quad (17)$$

In conclusion, the rate λ has the structure of Kramers's result,[1] but with the bare damping γ and bare barrier frequency ω^2 substituted in the curly brackets by the effective parameters $\bar{\gamma}$ and $\bar{\omega}^2$. In contrast to the Markov result,[1-9] the prefactor in (17) is determined by a set of four parameters: the bare frequencies ω_0 and ω *and* the effective parameters $\bar{\gamma}$ and $\bar{\omega}^2$. These effective parameters, obtained as the limits ($t\to\infty$) of the bounded expressions (6a) and (6b), incorporate the effect of the (long-time) memory function $\gamma(\tau)$ induced by the contraction of a $\sim 10^{24}$ many-body problem modeling the coupling to the heat bath. This reduction of the original huge many-body problem to a two-dimensional non-Markovian Brownian motion process (5), which in turn yields the main result (17), presents some considerable progress. With $\gamma(\tau)$ a *nonexponentially* decaying function, the reduction in (5) amounts to an equivalent Fokker-Planck dynamics in an infinite-dimensional state space.

We note that an explicit analytical evaluation of the parameters $\bar{\gamma}$ and $\bar{\omega}^2$ is particularly simple for $\hat{\rho}_u(z)$ being a *meromorphic* function: For example, with Gaussian white noise, $\langle\xi(\tau)\xi(0)\rangle = 2kT\gamma\delta(\tau)$, we recover Kramers result with $\bar{\gamma}=\gamma$, $\bar{\omega}^2=\omega^2$. If $\gamma(\tau)\equiv 0$, we find from $\bar{\gamma}=0$, $\bar{\omega}^2=\omega^2$ the well-known absolute rate theory (ART) result of Vineyard[24]

$$\lambda = \lambda^{\mathrm{ART}} = \frac{\omega_0}{2\pi}\exp\left[-\frac{\phi_b-\phi_0}{kT}\right] . \quad (18)$$

The case with an exponentially decaying memory,

$$\gamma(|\tau|) = f(\nu)\exp(-\nu|\tau|) \quad (19)$$

yields after some elementary algebra

$$\lambda = \frac{\omega_0\alpha}{2\pi\omega}\exp\left[-\frac{\phi_b-\phi_0}{kT}\right] = \frac{\alpha}{\omega}\lambda^{\mathrm{ART}} , \quad (20)$$

$$0<\alpha<\omega ,$$

where $z=\alpha$ is the single pole in the right half plane of the corresponding function $\hat{\rho}_u(z)$. The rate in (20) coincides in this particular case with the final result for the rate given in Ref. 17; despite the two completely different derivations.

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