Memory effect on thermally activated escape rates

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Non-Markovian thermal Brownian motion of a particle over a barrier is studied using thermal noise with a small but finite bath-memory correlation time. Starting from the corresponding non-Markovian Smoluchowski master equation, valid in the over-damped limit, the rate of escape λ is evaluated, and it is shown that a renormalization of the bare damping occurs. The modeling of the rate λ for a special class of bistable, driven non-Markovian nonequilibrium systems is sketched.

There is a multitude of processes in physics and chemistry that involve activated escape of a "particle" over a barrier. This important problem has been tackled by many others with different methods. Treating the effect of the coupling with the "heat bath" by a friction coefficient γ, the results in Kramer's original 1940 paper[1] represent a milestone. Kramers showed that equilbrium theories generally overestimate the reaction rate (for a more modern discussion of the problem see Refs. 2 and 3). Efforts to generalize Kramer's formulas to multidimensional systems have been discussed by Brinkman,[4] Landauer and Swanson,[5] and Langer.[6] Some other recent generalizations include the discussion of moderate damping,[7,8] catalysis at metal surfaces,[9] and the effect of a rate enhancement via parametric fluctuations.[10] Common to all those various treatments is the *assumption of a clear-cut separation of time scales of particle and heat bath motion.* In practice, this assumption amounts to the use of a thermal white noise, i.e., noise which is delta correlated in time. In many situations this assumption can be justified. However, for problems like the desorption from solids, impurity diffusion in solids,[11] or biophysical transport,[12] the coupling of the particle motion to physically relevant but often not clearly preceivable slow physical modes plays an important role. In the latter case, the friction becomes nonlocal in time (memory) implying via the fluctuation-dissipation theorem of the second kind a nonwhite thermal noise. For the problem of impurity diffusion in a solid, in which the heat bath moves slowly compared to the particle, Rezayi and Suhl[11] have recently presented an interesting attempt at solving the problem of the escape rate in such a situation.

Our goal in this report is somewhat more modest. We consider a heavy Brownian particle in an external field $\phi(x)$, as, for example, sketched in Fig. 1, which still moves slowly compared with the degrees of freedom of the bath. However, the particle does *not* move so slowly that the persistence effects of the random noise can totally be neglected. In other words, after having extracted the nonlinear slow motion of the particle the residual motion on the particle, exerted by the bath, decays on a fast but finite time-scale α. This approach presents an improvement over the usual Brownian motion theory with thermal white noise[1–10] and consequently provides some insight into the validity of the white noise approximation. A main mathematical complication associated with such an improved Brownian motion theory is the *loss of the Markovian character* present in the white-noise limit and thus also loss of the ordinary well-known Fokker-Planck description.[1–9]

For a phenomenological modeling of a non-Markovian Brownian motion theory with a fast but finite bath-memory correlation time $\alpha \equiv 1/2\nu$ we start from the microscopic theory of Brownian motion in external fields as investigated by Kim and Oppenheim.[13] With a unit particle mass $M=1$, the nonlinear generalized Langevin equation

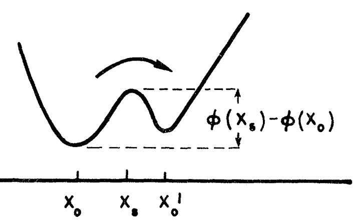

FIG. 1. Potential field used in text.

in coordinate, x, and velocity, u, phase space can be cast into the form[13,14] (we restrict the discussion to a one-dimension reaction path)

$$\dot{x}=u\ ,$$
$$\dot{u}=-\phi'(x)-\int_0^t\gamma(\tau)u(t-\tau)d\tau+\xi(t)\ . \tag{1}$$

Here, $\gamma(\tau)$ denotes a nonlocal friction coefficient, $\xi(t)$ is a nonwhite stationary thermal random noise, and the prime denotes differentiation with respect to the coordinate x. The nonlinear generalized Langevin equation in (1) can only be regarded as a model in the absence of any rigorous derivation. Generally, the nonlocal damping will depend functionally on the phase-space variables.[14] The noise $\xi(t)$ satisfies the fluctuation-dissipation theorem of the second kind[14]:

$$\langle\xi(\tau)\xi(0)\rangle=kT\gamma(\tau)\ . \tag{2}$$

Here, k is Boltzmann's constant, T the temperature, and the expectation $\langle\cdots\rangle$ is over the random realizations. With

$$\dot{u}=-\phi'(x)-\left[\int_0^t\gamma(\tau)d\tau\right]u+\left[\int_0^t\gamma(\tau)\tau\,dt\right]\dot{u}+\cdots+\xi(t)\ , \tag{3}$$

and neglecting on the rhs of (3) terms of order $O(\hat{\gamma}(\alpha)\alpha)$ (small bath-memory relaxation time α) as well as transient effects we obtain

$$\dot{u}=-\phi'(x)-\hat{\gamma}u+\xi(t)\ , \tag{4}$$

where $\hat{\gamma}$ presents a renormalized damping

$$\hat{\gamma}=\hat{\gamma}\left[\alpha=\frac{1}{2\nu}\right]=\int_0^\infty\gamma(\tau)d\tau=\frac{1}{2kT}\int_{-\infty}^{\infty}\langle\xi(\tau)\xi(0)\rangle d\tau\ . \tag{5}$$

Our interest is in the large friction limit, i.e., $\hat{\gamma}>>2\omega_0$ (Refs. 3 and 12), with ω_0 a typical undamped angular frequency of a locally stable potential well. Assuming that the force $-\phi'(x)$ does not change appreciably over distances of the order $(kT/\hat{\gamma}^2)^{1/2}$ (see Ref. 15) we can eliminate adiabatically the velocity variable u yielding the nonlinear non-Markovian Langevin equation

$$\dot{x}=-\frac{\phi'(x)}{\hat{\gamma}}+\frac{\xi(t)}{\hat{\gamma}}\ . \tag{6}$$

Owing to the finite correlation time of the thermal noise $\xi(t)$, the Langevin equation (6) does *not* correspond to the Fokker-Planck-Smoluchowski equation describing the rate of change of the probability

$$p_t(x)=\langle\delta(x(t)-x)\rangle\ . \tag{7}$$

For a general noise $\xi(t)$ satisfying (2), it is generally impossible to derive a closed equation for the rate of change of the probability $p_t(x)$.[16] In what follows, we model the thermal fluctuations by a stationary telegraphic random noise. In other words we set $\xi(t)\equiv\eta(t)$, with

$$\eta(t)=a(-1)^{n(t)}\ , \tag{8}$$

where $n(t)$ is a Poisson process with counting parameter ν, a denotes a step random variable of vanishing mean, and probability ρ_a

$$\rho_a=\tfrac{1}{2}[\delta(a-(2\nu kT\hat{\gamma})^{1/2})+\delta(a+(2\nu kT\hat{\gamma})^{1/2})]\ . \tag{9}$$

For the fluctuation-dissipation theorem (2), we obtain with (8) the explicit result

$$\langle\xi(\tau)\xi(0)\rangle=\langle\eta(\tau)\eta(0)\rangle=2kT\hat{\gamma}(\alpha)\nu\exp(-2\nu|\tau|)\ . \tag{10}$$

In the limit $\nu\to\infty$, the noise $\eta(t)$ approaches *Gaussian white noise* and (10) reduces to the familiar Einstein relation

$$\langle\eta(\tau)\eta(0)\rangle=2kT\gamma\delta(\tau)\ ,$$

with γ denoting a *bare* friction

$$\gamma=\lim_{\nu\to\infty}\int_0^\infty\gamma(\tau)d\tau=\lim_{\nu\to\infty}\hat{\gamma}(\alpha=1/2\nu)\ . \tag{11}$$

Also note that with a small relaxation time $\alpha=1/2\nu<1/\hat{\gamma}$, the telegraphic random noise $\eta(t)$ is close to a physically more realistic *nonwhite* Gaussian noise. With the notation $f(x)=-\phi'(x)/\hat{\gamma}$, we obtain for the rate of change of the probability $p_t(x)$ from (6) and (7)

$$\dot{p}_t(x)=-\frac{\partial}{\partial x}[f(x)p_t(x)]-\frac{1}{\hat{\gamma}}\frac{\partial}{\partial x}\langle\eta(t)\delta(x(t)-x)\rangle\ . \tag{12}$$

Now, with $R_t(\eta(s))=\delta(x(t)-x)$ being a functional of the noise $\eta(s)$, $t\geq s\geq 0$, the expectation in (12) can be evaluated by use of a formula by Klyatskin[17] which in our case reads

$$\langle \eta(t) R_t(\eta(s)) \rangle = 2kT\hat{\gamma}\nu \int_0^t d\tau \left\langle \frac{\delta}{\delta\eta(\tau)} R_t(\eta(s)\Theta(\tau - s^-)) \right\rangle \exp -2\nu(t-\tau) \ . \tag{13a}$$

Θ is the Heaviside step function. By virtue of the functional derivative

$$\frac{\delta}{\delta\eta(\tau)}[\delta(x(\tau)-x)] = -\frac{1}{\hat{\gamma}}\frac{\partial}{\partial x}\delta(x(\tau)-x) \ , \tag{13b}$$

we obtain after elementary calculations the *non-Markovian Smoluchowski master equation*

$$\dot{p}_t(x) = -\frac{\partial}{\partial x}[f(x)p_t(x)] + \frac{2\nu kT}{\hat{\gamma}}\frac{\partial}{\partial x}\int_0^t \exp\left[-\left[2\nu + \frac{\partial}{\partial x}f(x)\right](t-\tau)\right]\frac{\partial}{\partial x}p_\tau(x)d\tau$$

$$\equiv -\frac{\partial}{\partial x}j(x,t) \ . \tag{14}$$

In the equilibrium state $j=0$, the stationary probability $\bar{p}(x)$ obeys

$$j = 0 = f(x)\bar{p}(x) - \frac{2\nu kT}{\hat{\gamma}}\left[2\nu + \frac{\partial}{\partial x}f(x)\right]^{-1}\frac{\partial}{\partial x}\bar{p}(x) \ , \tag{15}$$

yielding

$$\bar{p}(x) = \frac{Z^{-1}}{kT - \dfrac{[\phi'(x)]^2}{2\nu\hat{\gamma}}}\exp\int^x \frac{-\phi'(y)dy}{kT - [\phi'(y)]^2/2\nu\hat{\gamma}}\,\Theta\left[\frac{2\nu kT}{\hat{\gamma}} - \left[\frac{\phi'(x)}{\hat{\gamma}}\right]^2\right] . \tag{16a}$$

With $\alpha = 1/2\nu < 1/\hat{\gamma}$ small, $\bar{p}(x)$ is well represented by

$$\bar{p}(x) = Z^{-1}\exp[-\phi(x)/kT] \ . \tag{16b}$$

The calculation of the rate of escape λ is accomplished following the ideas of Kramers.[1] We inject particles at x_0 and remove them the moment they reach the second locally stable region around x_0'. The resulting stationary *nonequilibrium* current j_0 builds up a total integrated density proportional to the escape time $\tau_0 = 1/\lambda$. If $p_0(x)$ denotes the nonequilibrium probability we have

$$j_0\lambda^{-1} \sim \int_{x_0}^{x_0'} p_0(x)dx \ . \tag{17}$$

Solving (15) with $j=0$ substituted by $j_0 \neq 0$ for the nonequilibrium probability density $p_0(x)$ we have in virtue of the boundary condition $p_0(x_0')=0$ (x_0': absorbing boundary)

$$p_0(x) = g(x)\bar{p}(x) \tag{18}$$

where

$$g(x) = -j_0\int_{x_0'}^x \frac{[2\nu + f'(y)]dy}{\bar{p}(y)[2\nu kT/\hat{\gamma} - f^2(y)]} \ . \tag{19}$$

With (17)–(19) we obtain for the rate λ our main result

$$\lambda = \left[\int_{x_0}^{x_0'} dx\, \exp\frac{-\phi(x)}{kT}\int_x^{x_0'}\left[\frac{1 - \phi''(y)/2\nu\hat{\gamma}}{\dfrac{kT}{\hat{\gamma}} - \left[\dfrac{\phi'(y)}{\hat{\gamma}}\right]^2 \Big/ 2\nu}\right]\exp\frac{\phi(y)}{kT}dy\right]^{-1} . \tag{20}$$

This main result holds independent of the specific shape of the external bimodel field $\phi(x)$, (e.g., also for a domed barrier region). The result requires only that τ_0 is much larger than the characteristic time for reaching local equilibrium in each potential valley; i.e., $\tau_0 >> 1/\omega_0$, so that the metastable equilibrium probabilities near x_0 and x_0' are long lived yielding a well-defined rate λ. In the limit $\nu \to \infty$ (i.e., $\alpha \to 0$) the result in (20) reduces to the Smoluchowski equation result

$$\lambda=\frac{kT}{\gamma}\left[\int_{x_0}^{x_0'}\exp-\frac{\phi(x)}{kT}dx\int_{x}^{x_0'}\exp\frac{\phi(y)}{kT}dy\right]^{-1} . \quad (21)$$

Setting

$$\phi'(y)\simeq\phi'(x_s)=0,\ \ \phi''(x_s)=\omega^2(x_s)<0 ,$$

we can for approximately harmonic potential extrema near $\{x_0,x_s,x_0'\}$ considerably simplify the rate in (20) to give the approximate result

$$\lambda\simeq\frac{\omega(x_0)\,|\,\omega(x_s)\,|}{2\pi\bar{\gamma}(\alpha)}\times\exp\{-[\phi(x_s)-\phi(x_0)]/kT\} , \quad (22)$$

with

$$\bar{\gamma}(\alpha)=\hat{\gamma}[1-\phi''(x_s)/2\nu\hat{\gamma}]\simeq\hat{\gamma}(\alpha) . \quad (23)$$

The rate in (23) just coincides in structure with the formula of Kramers.[1-9] The bare friction γ, (11), is substituted by the renormalized friction $\bar{\gamma}(\alpha)\approx\hat{\gamma}(\alpha)$, which incorporates the effects of a small but finite correlation time α of the nonwhite thermal noise. Throughout the paper, we did not specify any particular form for the renormalized friction $\hat{\gamma}(\alpha)$. A specific dependence of $\hat{\gamma}(\alpha)$ on α is a result of one (or possibly several different) special physical mechanisms for the damping.

Further, a calculation of the rate of escape for bistable, driven nonequilibrium systems (e.g., optical bistability,[18,19] nonlinear Esaki diode[20]) of the type $\dot{x}=\beta(x)+\eta(t)$, with $\eta(t)$ characterizing telegraphic *external* nonwhite noise, i.e., its strength and memory-correlation time $\alpha=1/2\nu$ can be arbitrarily structured by the experimenter, is rather straightforward by carrying through the ideas and solutions, (14), (16), and (19), presented in this paper: The escape rate λ is influenced by the amplitude $\sigma=\langle a^2\rangle_{\rho_a}$, the memory-correlation time $\alpha=1/2\nu$ and related, by the corresponding form of the stationary probability $\bar{p}(x)$. With (x_1,x_2) denoting the stable states of the deterministic drift $\beta(x)$, we obtain

$$\lambda=\left[\int_{x_1}^{x_2}dx\,\bar{p}(x)\int_{x}^{x_2}\frac{[1+\beta'(y)/2\nu]}{\bar{p}(y)[\sigma-\beta^2(y)]/2\nu}dy\right]^{-1} , \quad (24a)$$

where

$$\bar{p}(x)=\frac{Z^{-1}}{\sigma-\beta^2(x)}\exp 2\nu\int^{x}\frac{\beta(y)dy}{\sigma-\beta^2(y)}\Theta(\sigma-\beta^2(x)) , \quad (24b)$$

with σ large enough such that $\bar{p}(x)$ has a support on $[x_1,x_2]$.

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