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Non-Markovian thermal relaxation at elevated temperatures

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The exit problem out of a metastable well is studied, at all temperatures, for an overdamped Brownian particle. The exact time dependent exit probability is derived for a free particle and this solution is found to contain all qualitative features characterizing the numerically analyzed escape out of a metastable well: At sufficiently large times there always exists a Markovian limit to the exit problem and the approach to this limit is governed by the initial position of the diffusing particle. Particles originating near the bottom of the well are found to approach, with decreasing temperature, the Markovian relaxation law uniformly, whereas particles originating closer to the edges of the metastable region approach this limit in a complicated, nonuniform fashion.

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Calculations of thermal relaxation rate (see, e.g., the review by Hänggi *et al.* [1]) are based on the assumption that the metastable relaxing system finds itself in a quasistationary state characterized by a time independent outward probability flux [2]. The occupation probability of the system is then given by a Markovian (exponential) decay law. This formulation of the exit problem is known to be justified [1] in the limit of low temperatures (small noise intensity); however, the question of what constitutes, for a given system, a sufficiently low temperature remains unanswered nor has the non-Markovian exit problem been systematically studied.

We solve here, at all temperatures T, the exit problem for an overdamped Brownian particle in potential $V(x)$. For simplicity we assume the potential to be symmetric, $V(x) = -V(x)$, with a single minimum at $x = 0$ where $V(0) = 0$ and we place absorbing boundaries at the edges of the interval $\langle -x_0, x_0\rangle$. The exit problem is characterized by two quantities: First, by the mean first passage (MFP) time $\tau_q(y)$ where $q = V(x_0)/k_BT$ is the reduced barrier height and y the initial position of the particle, $|y| \leq x_0$, and secondly by the probability $n_q(t,y)$ that the particle has not exited the interval $\langle -x_0, x_0\rangle$ by the time $t > 0$; obviously, $\tau_q(y) = \int_0^\infty dt\, n_q(t,y)$. In the low temperature limit, $q \to \infty$, the MFP time $\tau_q(y) \sim e^q$ is independent [1] of y and [3]

$$n_q(t,y) = \exp[-t/\tau_q(y)]. \tag{1}$$

We find that at elevated temperatures the approach to this Markovian limit is governed by the initial position of the diffusing Brownian particle and we distinguish a uniform approach regime for particles originally located near the bottom of the well and a nonuniform approach regime for particles which start off closer to the edge of the metastable region. In the first case, in particular, the high temperature non-Markovian decay is found to be slower than the exponential decay (1) at times $t < \tau_q(y)$ but comparatively faster at $t > \tau_q(y)$. This finding is of interest in that similar behavior has recently been observed (but at *low* temperatures) experimentally, in isolated ferromagnetic particles [4].

The Langevin equation (p. 197 of Ref. [5]) for an overdamped Brownian particle is

$$dx = -\eta^{-1}V'(x)dt + \sqrt{2\eta^{-1}T}dw(t) \tag{2}$$

where η is a dissipation constant, $w(t)$ is a Wiener process, and $V' = dV/dx$ [6]. Throughout the paper we shall use the dimensionless variables $x \to x/x_s$ (x_s is an arbitrary length scale) and $t \to t/t_s$ ($t_s = \eta x_s^2/T$) and the dimensionless potential $V(x) \to V(x)/k_BT$. In terms of these variables the Fokker-Planck (Smoluchowski) equation for the random process (2) becomes

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x}\left[V'(x)P + \frac{\partial P}{\partial x}\right] \tag{3}$$

where $P = P(x,t|y,0)$ is the instanteneous probability distribution of a Brownian particle initially located at the point y. We impose on Eq. (3) the absorbing (p. 136 of Ref. [5]) boundary conditions $P(\pm x_0, t|y,0) = 0$ and for simplicity restrict ourselves to the symmetric initial conditions

$$P(x,0|y,0) = [\delta(x+y) + \delta(x-y)]/2. \tag{4}$$

The probability of finding the Brownian particle in the metatstable region at $t \geq 0$ is

$$n_q(t,y) = \int_{-x_0}^{x_0} dx\, P(x,t|y,0) \overset{\text{def}}{=} 1 - \int_0^t dt'\, g_q(t',y) \tag{5}$$

where the second integral defines the exit times distribution $g_q(t,y)$. Integrating Eq. (3) over the metastable domain and making use of the symmetry of the problem we obtain further the useful representation [7]

$$\dot{n}_q(t,y) = 2P_x(x_0,t|y,0) = -g_q(t,y), \tag{6}$$

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$\dot{n}_q = dn_q/dt$, and $P_x = \partial P/\partial x$. The MFP time proper is in our case given by the simple formula (p. 139 of Ref. [5]

$$\tau_q(y) = \int_y^{x_0} dx\, e^{V(x)} \int_0^x dz\, e^{-V(z)}; \qquad (7)$$

in particular, $\tau_0(y) = (x_0^2 - y^2)/2$ for a free particle with $V'(x) \equiv 0$.

The Fokker-Planck equation (3) with the given initial and boundary conditions is solved here for the harmonic potential $V(x) = (a/2)x^2$ and for the sinusoidal potential $V(x) = 2v \sin^2 x$; in either case we set $x_0 = \pi/2$. For the harmonic potential we employ Siegert's integral equation formalism [7] in which the occupation probability $n_q(t, y)$ satisfies the equation

$$\begin{aligned} 2n_q(t,y) = {} & G(t,y) + G(t,-y) \\ & + \int_0^t dt'\, \dot{n}_q(t',y)[G(t-t',x_0) \\ & + G(t-t',-x_0)] \end{aligned} \qquad (8)$$

where $G(t,z) = \mathrm{Erf}[f(t)(1 + ze^{-at})]$, $f(t) = (a/2)^{1/2}[1 - e^{-2at}]^{-1/2}$, and $\mathrm{Erf}(x)$ is the error function. These expressions are based on the infinite-medium fundamental solution [8] of Eq. (3) for the harmonic potential,

$$\mathcal{G}(x,t|y,t') = \frac{1}{\sqrt{\pi f^2(t-t')}} \exp\left\{ -\frac{[x - ye^{-a(t-t')}]^2}{f^2(t-t')} \right\}, \qquad (9)$$

but analogous fundamental solutions for nonharmonic potentials are not known to us and for this reason we solve Eq. (3) also by expanding the Laplace transform of the distribution $P(x,t|y,0)$, $\hat{P}(x,p|y,0)$, in the Fourier series

$$\hat{P}(x,p|y,0) = \sum_{k=0}^{\infty} a_{2k+1}(p,y) \cos(2k+1)x \qquad (10)$$

which satisfies the absorbing boundary conditions. The Laplace transform of Eq. (6) yields

$$p\hat{n}_q(p,y) - 1 = 2\sum_{k=0}^{\infty}(-1)^k a_{2k+1}(2k+1) = -\hat{g}_q(p,y) \qquad (11)$$

and for the sinusoidal potential we find that the coefficients $A_{2k+1} = a_{2k+1}(2k+1)$ satisfy an infinite tridiagonal system of linear equations which is easily solved numerically with arbitrary precision [9]:

$$d_1 = (p + 1 - v)A_1 + vA_3/3, \qquad (12)$$

$$\begin{aligned} d_{2k+1} = {} & -v\sigma_{2k-1}A_{2k-1} + \sigma_{2k+1}(p)A_{2k+1} \\ & + v\sigma_{2k+3}A_{2k+3}, \end{aligned} \qquad (13)$$

$k > 0$. The coefficients of the linear system are $\sigma_{2k-1} = (2k+1)/(2k-1)$, $\sigma_{2k+3} = (2k+1)/(2k+3)$, and $\sigma_{2k+1}(p) = p/(2k+1) + 2k + 1$ and the absolute terms

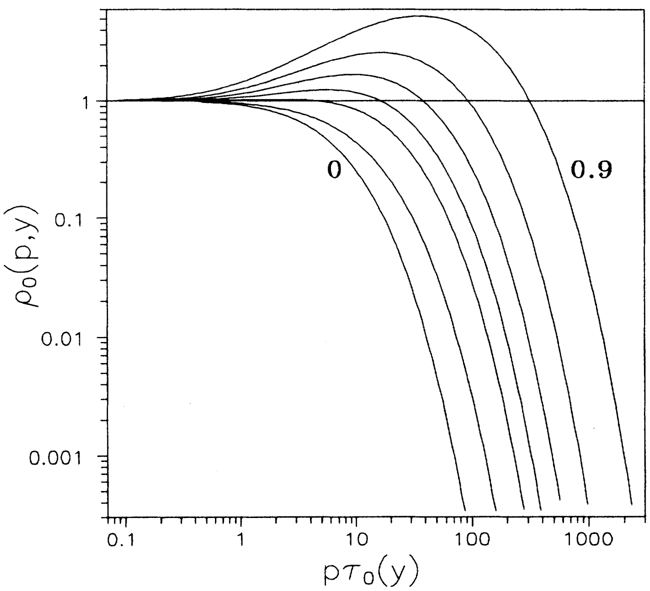

FIG. 1. The function $\rho_0(p,y) = [1 + \tau_0(y)]\hat{g}_0(p,y)$ vs $p\tau_0(y) = p(x_0^2 - y^2)/2$ for selected values of the initial position y. There is $2x_0/\pi = 1$ and, consecutively, $2y/\pi = 0$ (labeled), 0.3, 0.5, 0.6, 0.7, 0.8, and 0.9 (labeled).

are the Fourier components of the initial distribution (4), $d_{2k+1} = (2/\pi)\cos(2k+1)y$.

The Volterra integral equation (8) is particularly instructive in that it is exactly solvable in the limit of a free particle, i.e., as $a \to 0$, where we obtain [10]

$$\hat{g}_0(p,y) = \frac{\cosh y\sqrt{p}}{\cosh x_0\sqrt{p}}. \qquad (14)$$

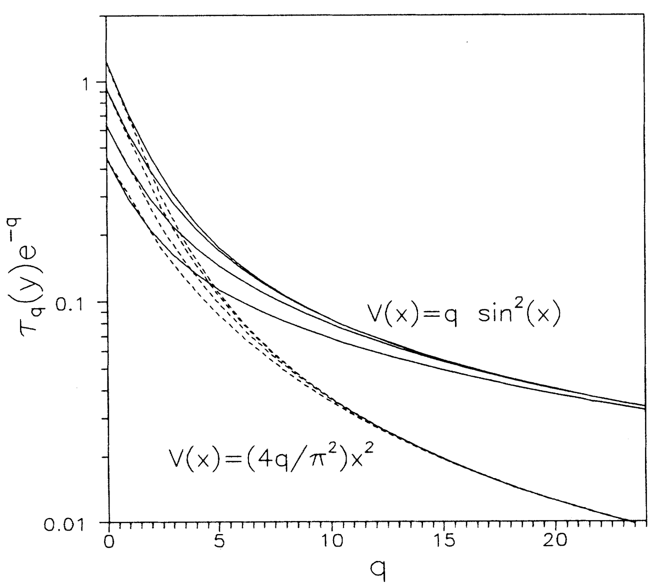

FIG. 2. The scaled MFP time $\tau_q(y)e^{-q}$, i.e., the inverse prefactor, for the two potential wells discussed in text. $2x_0/\pi = 1$ and the initial position $2y/\pi = 0$ (topmost curves), 0.5, 0.7, and 0.8 (lowermost curves). We write here $2v = q$ and $a/2 = 4q/\pi^2$ for clarity.

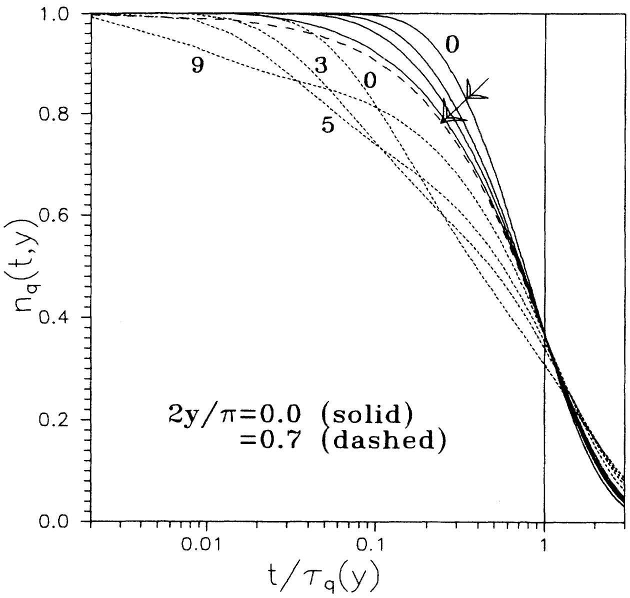

FIG. 3. Occupation probability $n_q(t, y)$ of a harmonic well vs the reduced time $t/\tau_q(y)$ for two values of the initial position $y < x_0 = \pi/2$ and $2q = 0$, 3, 5, and 9. For $y = 0$ only the free particle, $q = 0$, curve is labeled; with increasing q these curves uniformly approach the exponential decay law (1) which is shown in long dash and marked by an arrow. The remaining curves are labeled by the value of $2q$.

In particular, $\hat{g}_0(p, y) \approx [1 + \tau_0(y)p]^{-1}$ for $x_0 p^{1/2} \ll 1$, so that the long time exit behavior of a free particle is Markovian by virtue of the definition (5). The distribution of exit times for a particle in a potential field is expected to have a long time Markovian limit as well and Eq. (14) therefore represents a useful example of its possible behavior. The function $\hat{g}_0(p, y)$ monotonically decreases along the real positive p axis and is exponentially small as $p \to \infty$ but we find that a better *qualitative* insight into the non-Markovian relaxation process is gained by considering the ratio

$$\rho_q(p, y) = [1 + \tau_q(y)]\, \hat{g}_q(p, y) \tag{15}$$

which becomes identically equal to unity in the strict Markovian limit (1). For all $y/x_0 \in \langle 0, 1)$ the function $\rho_0(p, y)$ has a local extremum at $p = 0$ but for $y/x_0 \geq 5^{-1/2} \approx 0.4472$ it also has a local maximum along the real positive axis (see Fig. 1) and we shall presently show that the occurrence of this maximum heralds a significant change in the nature of the non-Markovian relaxation process and in the mode of approach towards the

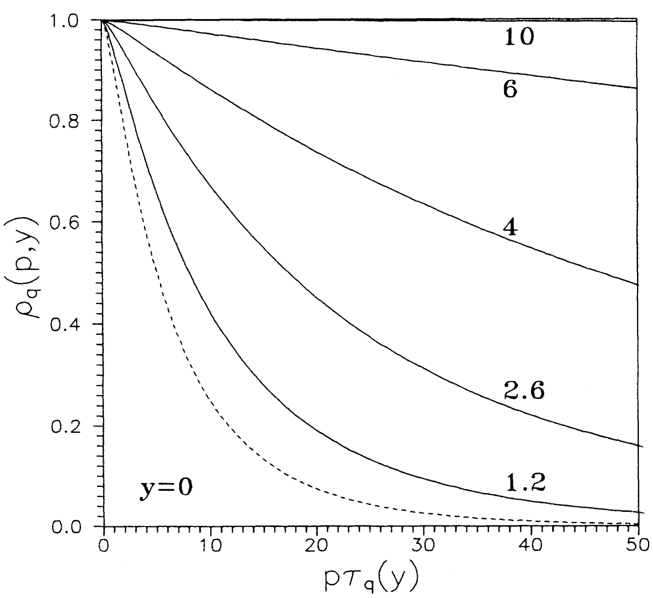

FIG. 4. The function $\rho_q(p, y)$ of Eq. (15) for a sinusoidal potential. The initial position $y = 0$, $x_0 = \pi/2$ and the values of q are given by the curve labels. Dashed line is the free particle solution of Fig. 1.

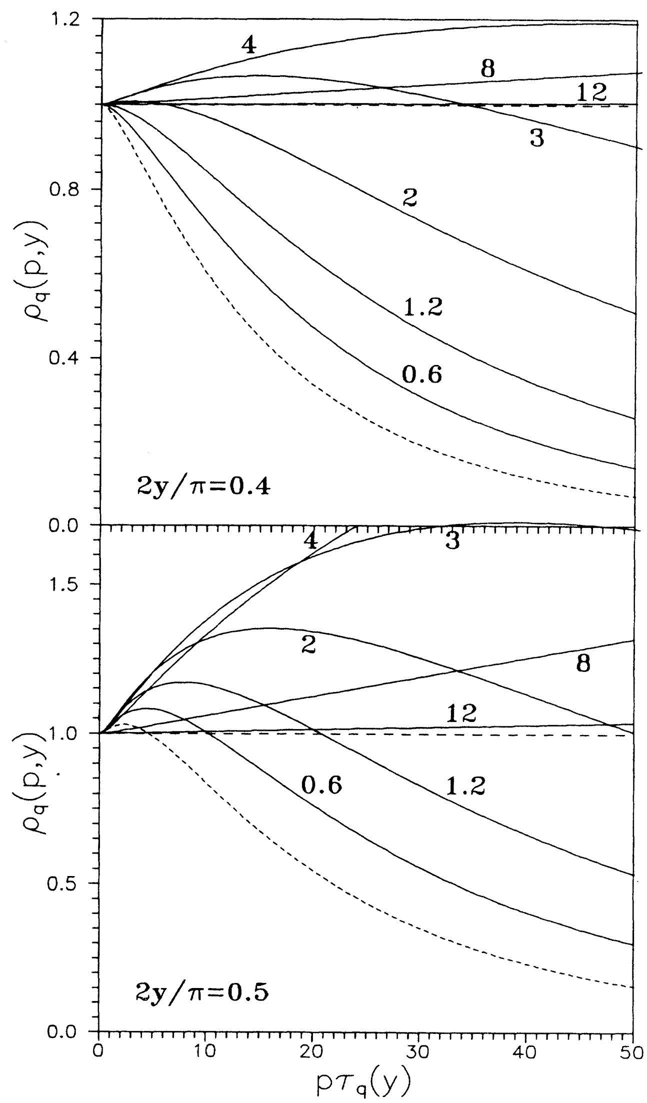

FIG. 5. The function $\rho_q(p, y)$ of Eq. (15) for a sinusoidal potential. The initial positions are $2y/\pi = 0.4$ (top) and 0.5 (bottom), $x_0 = \pi/2$, and the values of q are given by the curve labels. Dashed lines are the free particle solutions of Fig. 1.

Markovian limit. Further qualitative insight is obtained by comparing the MFP times (7) for the two potentials. According to Fig. 2 $\tau_q(y)$ for the harmonic potential is, at a given q, always smaller than for the sinusoidal potential but, at the same time, it becomes independent of the initial position y at lower values of q. The rate with which the curves $\tau_q(y)$ converge is apparently related to the well shape and Fig. 2 suggests that escape out of a harmonic well reaches its Markovian limit at higher temperatures (smaller q) than escape out of the smooth sinusoidal well.

The foregoing discussion allows us now to interpret the results of numerical calculations. Equation (8) for the probability out of the harmonic well yields the real time solutions $n_q(t,y)$ which we plot in Fig. 3 while Eq. (11) yields only the Laplace transform of the exit times distribution out of the sinusoidal well and in Figs. 4 and 5 we plot the ratio $\rho_q(p,y)$ of Eq. (15). The two families of plots are, however, closely related and will be discussed together.

According to Fig. 3 the non-Markovian relaxation from inital position $y = 0$ is slower than the exponential law (1) at times $t < \tau_q(0)$ but faster than (1) for $t > \tau_q(0)$. It is not clear to us whether the fact that $n_q[\tau_q(0),0] = e^{-1}$ for all q is an artifact of the harmonic potential, though apparently this effect is not related to the symmetry imposed on the problem since the common intercept does not exist for any $y > 0$. Plots of the ratio $\rho_q(p,0)$ are presented (for the sinusoidal potential) in Fig. 4. With increasing q these curves uniformly approach the Markovian limit $\rho_q(p,0) \equiv 1$ and this behavior is also quite obvious from the real time plots of Fig. 3. At the same time, however, there is $\lim_{p\to\infty} \rho_q(p,y) = 0$ so that the very short time exit behavior is always nonexponential. Essentially the same behavior is found also for sufficiently small $y > 0$, $2y/\pi \lesssim 0.3$; in this case, however, the common intercept is only approximate, located at $t > \tau_q(y)$. It should also be noted that at barrier heights q for which the escape out of the harmonic well is almost Markovian the plots of Fig. 4 are decidedly non-Markovian, quite in accordance with our analysis of the MFP times of Fig. 2.

A qualitatively distinct, nonuniform approach to the Markovian limit is found for large values of the initial position y where the function $\rho_0(p,y)$ has a local maximum along the real positive axis. The nature of this nonuniform mode of approach is readily apparent from Fig. 5 (bottom) where we present plots of the function $\rho_q(p,y)$ for $2y/\pi = 0.5$. The limiting behavior is not so clearly discernible from the complicated real time behavior of the probabilities $n_q(t,y)$ which are shown for $2y/\pi = 0.5$ in Fig. 3. These curves, however, offer a marked difference to the time dependence of the uniform mode discussed in the previous section: At extremely short times the decay is, as before, slower than the exponential law (1), however, it becomes significantly faster in its intermediate states and slows down again at large times, $t > \tau_q(y)$. In other words, apart from its initial stage the relaxation process now exhibits behavior exactly opposite to the time dependence of the uniform mode discussed in the preceding paragraph.

From the extremal properties of the free particle function $\rho_0(p,y)$ we deduced that the nonuniform mode sets in at $y/x_0 = 5^{-1/2}$ but Fig. 5 (top) shows that for $V'(x) \not\equiv 0$ the critical value is, in fact, less, $y/x_0 < 1/5^{-1/2}$. The small q curves here resemble those of the uniform mode whereas for intermediate and large q values they develop characteristics of the nonuniform mode. The real time functions $n_q(t,y)$ interpolate between the uniform and nonuniform modes of behavior as well.

In summary, we find that the free particle solution (14) contains all qualitative features characterizing thermally activated escape out of a metastable well. In particular, the Markovian limit of exponential decay always exists at sufficiently large times and so do the uniform and nonuniform approach modes. If the diffusing particle is confined in a metastable well then the Markovian limit is attained at shorter times, the transition point between the uniform and nonuniform modes is shifted towards lower values but no qualitatively new feature is introduced.

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