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LETTER TO THE EDITOR

# Escape over a fluctuating barrier: the white noise limit

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**Abstract.** We examine the problem of diffusion over a fluctuating barrier in the limit where the barrier fluctuations are extremely fast compared with all other timescales in the problem. In the white noise limit, decay of probability from the metastable state is exponential with a characteristic timescale exhibiting Arrhenius behaviour. For small but finite correlation times for the fluctuating part of the potential, the effective barrier increases with the correlation time. Implications for liquids above the glass transition are discussed.

Transport and relaxation properties of a viscous liquid slightly above the glass transition appear to be activated, but in many cases are non-exponential in their time dependence and non-Arrhenius in their temperature dependence [1]. Typically, an atom may not be able to diffuse or relax unless other atoms or groups of atoms rearrange themselves to create a more favourable environment for some such process to take place. Since the barrier to diffusion depends on these other atoms, which are subject to thermal fluctuations themselves, one needs to understand the problem of barrier crossing when the barrier is itself fluctuating due to random thermal noise or other processes. This problem is also relevant to other physical situations, such as oxygen binding to haemoglobin [2, 3].

In a previous paper [4], we began a systematic study of the problem of escape over a fluctuating barrier. We studied the mean exit times in the cases when the timescale $\tau_c$ for the barrier fluctuation was very long compared with that for crossing the average static barrier, when $\tau_c$ was small compared with the static barrier crossing time but large compared with microscopic timescales in the problem, and when the barrier fluctuations were due to a white noise process. We studied the simplest possible model in which a single 'test particle' diffused over a single fluctuating barrier, which is an oversimplification in several respects: $\tau_c$ is almost certainly a (decreasing) function of temperature, and collective effects, feedback processes, and self-consistency are ignored. The model is nonetheless a reasonable approximation for some physical processes, for example when the 'gate' atoms have a large (real or effective) mass compared with the diffusing atom, or when the barrier arises from collective motions of many degrees of freedom. More importantly, the understanding gained from studying this simple model should be quite useful for studying more complicated,

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realistic models and provides a first step in that direction. The model presented here is related in spirit to various models currently under study, such as stochastic resonance [5] and coloured noise activated barrier crossing [6], but investigates a completely different phenomenon.

In this letter we present a more thorough study of a simple model of escape over a fluctuating barrier in the white noise limit. In particular, we discuss the time dependence of probability decay inside the metastable state, and present an expansion in $\tau_c$ of the mean exit time about the white noise result. The white noise limit itself displays both exponential and Arrhenius behaviour, which is perhaps not surprising in view of the clear-cut separation of timescales in that problem. For small but finite $\tau_c$, we find that the mean exit time *increases* with $\tau_c$, which is consistent with the results of other cases discussed in [4], and may have interesting implications for non-Arrhenius behaviour in glasses.

We choose to work with a simple model in which the barrier fluctuations are Gaussian, Markovian, and stationary, hence an Ornstein–Uhlenbeck process [7]. If the correlation time of the fluctuations is $\tau_c$, the barrier fluctuations are controlled by the process $\xi(t)$ governed by the equation

$$\dot{\xi} = -\frac{1}{\tau_c}\,\xi(t) + \sqrt{\frac{2}{\tau_c}}\,\eta_1(t) \tag{1}$$

where $\eta_1(t)$ is $\delta$-correlated white noise, and all times are taken to be dimensionless. For convenience, we separate the potential into a static part $V(x)$ (which we take to be of the Kramers form with a local minimum at $x=0$) and a fluctuating part $W(x)$ (see figure 1). Diffusion across the barrier in the high friction limit is governed by the Langevin equation

$$\dot{x} = -\left(V'(x) + \sqrt{\frac{T}{\tau_c}}\,\xi(t)\,W'(x)\right) + \sqrt{2T}\,\eta_2(t) \tag{2}$$

where $\xi(t)$ is governed by (1), $\eta_2(t)$ is $\delta$-correlated white noise, and primes denote derivatives with respect to $x$. The $\sqrt{1/\tau_c}$ factor ensures a sensible white noise limit, and the $\sqrt{T}$ prefactor of the fluctuating term in the potential comes from a very simple picture of a 'gate' controlled by atoms oscillating in harmonic wells due to random thermal noise. While this temperature dependence is actually more general than this simple picture suggests, there may well exist situations with more complicated temperature dependences. We will only consider a $\sqrt{T}$ amplitude for the fluctuations here, because it is both simple and natural, leaving other situations for future work.

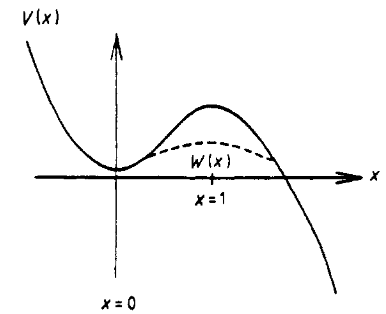


**Figure 1.** The potential $V(x)$ is static, and $W(x)$ represents the fluctuating component: $V_{\text{total}} = V + W\sqrt{T/\tau_c}\,\xi$.

Equations (1) and (2) define our model in the general case; we will now examine the situation $\tau_c \to 0$. We will first study the properties of the model in the strict white noise limit, and then ask what happens when $\tau_c$ is small but finite.

The fast variable $\xi$ can be adiabatically eliminated in the white noise limit to yield a Fokker–Planck equation for the probability density function $p(x, t)$ (we will explicitly demonstrate this procedure later):

$$\frac{\partial}{\partial t} p(x, t) = \frac{\partial}{\partial x}\left( V'(x) + T\frac{\partial}{\partial x} + TW'(x)\frac{\partial}{\partial x} W'(x)\right) p(x, t). \tag{3}$$

We first ask for the behaviour of the mean exit time from the local minimum at $x = 0$ to $x = \infty$ for an ensemble of particles. The mean time $\tau(x)$ for a particle to diffuse from $x$ to $\infty$ is found from the solution of the differential equation [8]:

$$-(V' - TW'W'')\frac{\partial \tau}{\partial x} + T(1 + (W')^2)\frac{\partial^2 \tau}{\partial x^2} = -1 \tag{4}$$

where we use natural boundary conditions at $-\infty$ and an absorbing barrier at $+\infty$. The average exit time from $x = 0$ is then [4]

$$\langle \tau \rangle = \frac{1}{T}\int_0^\infty \mathrm{d}x \exp\left(1/T \int_0^x \mathrm{d}y \frac{V'(y)}{1 + W'(y)^2}\right)(1 + W'(x)^2)^{-1/2} \int_{-\infty}^x \mathrm{d}z$$
$$\times \exp\left(-1/T \int_0^z \mathrm{d}u \frac{V'(u)}{1 + W'(u)^2}\right)(1 + W'(z)^2)^{-1/2}. \tag{5}$$

It is immediately clear that the effective barrier to escape is lowered from what it would be if the fluctuating part were absent. This is because the particle has many opportunities to escape from times when the barrier is relatively low; it need not wait for a sufficiently large thermal kick to take it over a relatively high barrier, as it would if there were no fluctuating part to the potential. While the 'effective barrier' at first sight appears to be non-Arrhenius, a steepest descent calculation of (5) at low temperature yields an Arrhenius temperature dependence of the mean exit time in an effective potential given by

$$\psi(x) = \int_0^x \mathrm{d}y \frac{V'(y)}{1 + W'(y)^2}. \tag{6}$$

Numerical evaluation of the full integral (5) confirms this picture [4].

The time dependence of escape of probability from the well can be found by integrating (3) numerically. We studied the simple case where

$$V(x) = \tfrac{1}{2}x^2 - \tfrac{1}{3}x^3 \qquad W(x) = D\,\mathrm{e}^{-\alpha(x-1)^2} \tag{7}$$

and examined the time dependence of the quantity $f(t) = \int_{-\infty}^{\infty} p(x, t)\,\mathrm{d}x$ given the initial condition $p(x, 0) = \delta(x)$. We confined ourselves to study of the regime where temperature was low ($\leq 0.05$) compared with the static barrier height, which was 0.1667, $\alpha$ varied between 5 and 10, and $D$ was kept smaller than 0.2. In this way we were able to concentrate on the regime of interest, that is, where separation of the exit time into a product of a prefactor and an exponential is sensible. We found that $f(t) \sim \mathrm{e}^{-t/\langle\tau\rangle}$ to excellent precision for $f(t) < 0.99$. Furthermore, we found excellent agreement between the $\langle\tau\rangle$ computed from this integration of (3) and the mean exit time computed directly from (5).

We now have a good understanding of our model in the white noise limit; we would like to have further information about its behaviour near but not exactly at this limit. We will use the singular perturbation technique of Doering, Hagan and Levermore [6] (DHL). We begin by writing the full Fokker–Planck equation for arbitrary $\tau_c$, derived from equations (1) and (2):

$$\frac{\partial}{\partial t} p(x, \xi, t) = [\varepsilon^{-2}\partial_\xi(\xi+\partial_\xi) + \varepsilon^{-1}(\sqrt{T}\,\xi\partial_x W'(x)) + \partial_x V'(x) + T\partial_{xx}]p(x, \xi, t) \tag{8}$$

where $\varepsilon = \sqrt{\tau_c}$. For convenience we shall define the operators $L_0 = \partial_\xi(\xi+\partial_\xi)$, $L_1 = \sqrt{T}\xi\partial_x W'(x)$, and $L_2 = \partial_x V'(x) + T\partial_{xx}$. Let the initial condition be $p(x, \xi, 0) = \delta(x)p_0(\xi)$, where $p_0(\xi) = (1/\sqrt{2\pi})\,\mathrm{e}^{-\xi^2/2}$ is the stationary distribution of $\xi$. Define the quantity $G(x, \xi) = \int_0^\infty p(x, \xi, t)\,\mathrm{d}t$; then integrating (8) from $t = 0$ to $t = \infty$ yields the equation

$$[\varepsilon^{-2}L_0 + \varepsilon^{-1}L_1 + L_2]G(x, \xi) = -\delta(x)p_0(\xi). \tag{9}$$

Equation (9) is valid when $p$ vanishes sufficiently quickly as $t \to \infty$. The mean time for a particle starting at $x = 0$ to reach infinity is given by

$$\langle\tau\rangle = \int_{-\infty}^{\infty} \mathrm{d}\xi \int_{-\infty}^{\infty} \mathrm{d}x\, G(x, \xi).$$

We will always assume a static potential, like that of (7), which approaches $-\infty$ as $x \to \infty$; our results are easily generalisable for other forms of the potential. Finally, we use natural boundary conditions at $x = -\infty$ and an absorbing barrier at $x = \infty$; the special boundary considerations of DHL do not apply here since the diffusing particle is being driven by a white noise process.

Following DHL, we insert the ansatz

$$G(x, \xi) = G_0(x, \xi) + \varepsilon G_1(x, \xi) + \varepsilon^2 G_2(x, \xi) + \ldots \tag{10}$$

into (9) and collect terms of the same power in $\varepsilon$. We therefore have

$$L_0 G_n(x, \xi) = -L_1 G_{n-1}(x, \xi) - L_2 G_{n-2}(x, \xi) - \delta_{n,2}\delta(x)p_0(\xi) \tag{11}$$

with $G_n(x, \xi) = 0$ for $n < 0$. The eigenfunctions of the operator $L_0$ are simply related to the Hermite polynomials [9] $He_n(\xi)$:

$$L_0 p_n(\xi) = -np_n(\xi) \qquad p_n(\xi) = He_n(\xi)p_0(\xi). \tag{12}$$

For $n = 0$, we have $G_0(x, \xi) = p_0(\xi)r_0(x)$, with $r_0(x)$ a function to be determined. Substituting this into (11), we find $G_1(x, \xi) = p_0(\xi)r_1(x) + \sqrt{T}p_1(\xi)\partial_x W'(x)r_0(x)$, with $r_1(x)$ also to be determined. These functions are determined by substituting our expressions for $G_0(x, \xi)$ and $G_1(x, \xi)$ into (11) with $n = 2$, noting that the operator $L_0$ has a zero eigenvalue and is in general not invertible, and therefore demanding that the coefficient of $p_0$ vanish. This restricts the space of functions of $\xi$ to that subspace on which $L_0$ is invertible, namely that subspace spanned by the $p_n(\xi)$s for $n \geq 1$. For more details, see DHL.

In this way, the following differential equations for the first few $r_n(x)$s are obtained:

$$[\partial_x V'(x) + T\partial_{xx} + T\partial_x W'(x)\partial_x W'(x)]r_0(x) = -\delta(x) \tag{13a}$$

$$[\partial_x V'(x) + T\partial_{xx} + T\partial_x W'(x)\partial_x W'(x)]r_1(x) = 0 \tag{13b}$$

$$\begin{aligned}[\partial_x V'(x) + T\partial_{xx} + T\partial_x W'(x)\partial_x W'(x)]r_2(x) \\ = -[T^2\partial_x W'(x)\partial_x W'(x)\partial_x W'(x)\partial_x W'(x) \\ + T(\partial_x W'(x))(\partial_x V'(x) + T\partial_{xx})(\partial_x W'(x))]r_0(x).\end{aligned} \tag{13c}$$

The right-hand side of $(13c)$ is simply $-[L_1'(L_1'^2+L_2)L_1']r_0$, where $L_1'$ is $L_1/\xi$; $L_1'^2+L_2$ is the white noise operator. The function $r_2(x)$ is related to $G_2$ by the equation

$$G_2(x,\xi)=p_0(\xi)r_2(x)+\sqrt{T}\,p_1(\xi)\partial_x W'(x)r_1(x)+\frac{T}{2}p_2(\xi)\partial_x W'(x)\partial_x W'(x)r_0(x). \tag{14}$$

The solution to $(13a)$ which satisfies our boundary conditions is

$$r_0(x)=\begin{cases}\dfrac{1}{T}\dfrac{e^{-\psi(x)/T}}{\sqrt{1+W'(x)^2}}\displaystyle\int_0^\infty dx'\frac{e^{\psi(x')/T}}{\sqrt{1+W'(x')^2}} & x\leqslant 0\\[2ex] \dfrac{1}{T}\dfrac{e^{-\psi(x)/T}}{\sqrt{1+W'(x)^2}}\displaystyle\int_x^\infty dx'\frac{e^{\psi(x')/T}}{\sqrt{1+W'(x')^2}} & x\geqslant 0.\end{cases} \tag{15}$$

There is *no* non-vanishing solution to $(13b)$ which satisfies the boundary conditions. The solution to $(13c)$ is

$$\begin{aligned}r_2(x)=T\int_{-\infty}^{\infty}&dx'g(x,x')\times[T\partial_{x'}W'(x')\partial_{x'}W'(x')\partial_{x'}W'(x')\partial_{x'}W'(x')\\&+(\partial_x' W'(x'))(\partial_{x'}V'(x')+T\partial_{x'x'})(\partial_x' W'(x'))]r_0(x')\end{aligned} \tag{16}$$

where $g(x,x')$ is the Green function for the white noise Fokker–Planck operator (i.e. $g(x,x')$ is just $r_0(x)$ given by (15) with the zero in the lower limit of the first integral replaced with $x'$, and where the first integral in (15) is valid for $x\leqslant x'$ and the second for $x\geqslant x'$).

Equation (16) can be simplified to

$$\begin{aligned}r_2(x)=\delta(x)&+V''(x)r_0(x)+V'(x)r_0'(x)+Tr_0''(x)\\&-T\int_{-\infty}^{\infty}dx'\,g(x,x')\times\partial_{x'}[V'(x')W''(x')-W'(x')V''(x')\\&+T\partial_{x'}W''(x')+TW''(x')\partial_{x'}]\partial_{x'}W'(x')r_0(x').\end{aligned} \tag{17}$$

Since $\int_{-\infty}^{\infty}p_i(z)\,dz=0$, $i\neq 0$, only the coefficients of $p_0$ in the $G_n$s contribute to the mean exit time. With (15) we recover (3) for the mean exit time in the white noise limit.

The lowest order correction $\tau_2$ is equal to $\tau_c\int_{-\infty}^{\infty}dx\,r_2(x)$. We have numerically integrated (17) for temperatures ranging from 0.02 to 0.05 (or from about one eighth to one third the static average barrier height), and using $V(x)$ and $W(x)$ as given in (7), with $D=1$ and $\alpha$ ranging from 3 to 10. In all cases studied, the lowest order correction $\tau_2/\tau_c$ to the white noise limit was *positive*, and obeyed an Arrhenius temperature dependence. Figure 2 shows the first-order correction term $\tau_2/\tau_c$ against temperature for the case $\alpha=10$.

Hence, we find that the mean exit time *increases* as $\tau_c$ increases. This is consistent with results found in [4] for other regimes; in all cases studied thus far, the mean exit time has been a monotonically increasing function of $\tau_c$. This result is of particular interest for the study of glassy liquids, since any reasonable model for a gating process, whether the gate atoms are in a harmonic potential or are activated from one local minimum to another, has $\tau_c$ monotonically decreasing as temperature increases. Therefore, our model implies an effective barrier to diffusion or flow which *decreases* as temperature increases, in qualitative agreement with observations on fragile liquids [10]. The simplicity of the model studied here precludes more than a qualitative comparison at this stage.

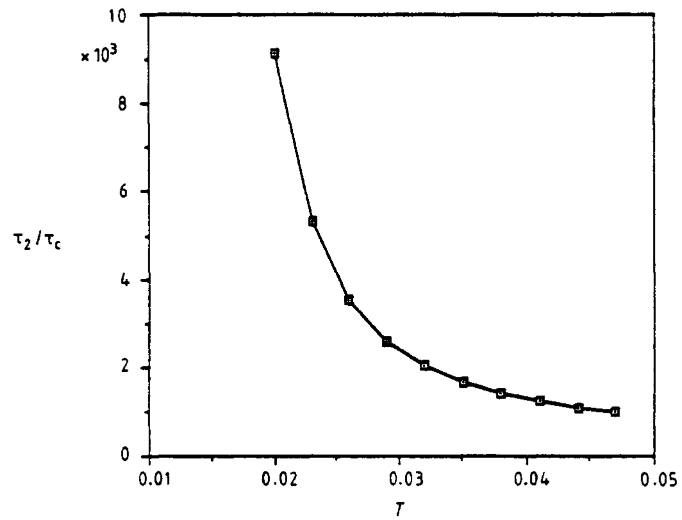


**Figure 2.** Plot of the first order correction $\tau_2/\tau_c$ against temperature for the case $D = 1$, $\alpha = 10$.

Work in progress includes a study of the time and temperature dependence of the solution of the full Fokker-Planck equation (8) for the full range of possible values of $\tau_c$. Feedback effects, in which $\tau_c$ itself is affected by crossing events, will also be examined. These results will be reported in a future publication.

One of us (DLS) wishes to acknowledge a helpful discussion with B Stein.

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