Anomalous escape governed by thermal 1/f noise

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We present an analytic study for subdiffusive escape of overdamped particles out of a cusp-shaped parabolic potential well which are driven by thermal, fractional Gaussian noise with a $1/\omega^{1-\alpha}$ power spectrum. This long-standing challenge becomes mathematically tractable by use of a generalized Langevin dynamics via its corresponding non-Markovian, time-convolutionless master equation: We find that the escape is governed asymptotically by a power law whose exponent depends exponentially on the ratio of barrier height and temperature. This result is in distinct contrast to a description with a corresponding subdiffusive fractional Fokker-Planck approach; thus providing experimentalists an amenable testbed to differentiate between the two escape scenarios.

The theme of anomalous sub-diffusion and rate kinetics continuous to flourish over the last years. This topic is driven by the availability of a Witt of intriguing experimental data, ranging from anomalous diffusion in amorphous materials, quantum dots, protein dynamics, actin networks, and biological cells [1] [2] [3] [4] [5] [6] [7] [8] [9] [10] [11]. Suitable theoretical descriptions derive from continuous to flourish over the last years. This topic is amenable testbed to differentiate between the two escape scenarios.

Thus, in contrast to the finite mean first passage time (MFPT) result in [24] our main result exhibits an infinite MFPT, being consistent with a strict subdiffusive escape dynamics. A rate description emerges only when invoking a physically plausible low frequency regularization of the noise spectrum.

GLE-approach. We start out from the GLE for a particle of mass $m$ moving in the potential $V(x)$ [13]: i.e.,

$$m\ddot{x} + \int_0^t \eta(t-t')\dot{x}(t')dt' + V'(x) = \xi(t).$$

The autocorrelation function $\langle \xi(t)\xi(t') \rangle$ of thermal Gaussian noise $\xi(t)$ and the frictional kernel $\eta(t)$ are related by the usual fluctuation-dissipation relation [13]:

$$\langle \xi(t)\xi(t') \rangle = k_BT\eta(t-t').$$

In the following we consider the overdamped limit with $m \to 0$; i.e. the velocity is thermally relaxed at each instant of time. Moreover, we assume that the particles are initially localized in a metastable parabolic well at $x_0$, cf. the inset in Fig. (1). The starting probability density then is $P(x,t=0) = \delta(x-x_0)$. The corresponding non-Markovian master equation for $P(x,t)$ for this GLE is generally not known: For arbitrary physical memory-friction $\eta(t)$ this task is known for two cases only: namely (i) a linear potential $V(x) = -F_0 x$, including the case of free diffusion, i.e. $F_0 = 0$ and (ii) a parabolic potential $V(x) = k_xx^2/2$. The procedure to obtain the master equation is well known: It is solely rooted in the Gaussian nature of $x(t)$ [18] [21] [22] [23] [24]. The result is a time-convolutionless master equation for $P(x,t)$ obeying a Fokker-Planck form with a time-dependent diffusion coefficient $D(t)$ [22] [24], reading

$$\frac{\partial P(x,t)}{\partial t} = D(t)\frac{\partial}{\partial x} \left( e^{-\beta V(x)} \frac{\partial}{\partial x} e^{\beta V(x)} P(x,t) \right).$$

Here, $\beta = 1/(k_BT)$. Notably, $D(t)$ does not depend on $x_0$, but is dependent on $V(x)$ and memory friction $\eta(t)$.
For a quadratic potential, it can be expressed via the relaxation function \( \theta(t) \) of position fluctuations as \cite{22, 24}:

\[
D(t) = -l_T^2 \frac{d}{dt} \ln \theta(t),
\]

where \( l_T = \sqrt{k_B T/\kappa} \) is the length scale of thermal fluctuations. The Laplace-transform of \( \theta(t) \) is related to the memory friction \( \eta(t) \) by \( \tilde{\theta}(s) = \tilde{\eta}(s)/[\kappa + s \tilde{\eta}(s)] \).

We next use a power-law friction kernel \( \eta(t) \), reading

\[
\eta(t) = \frac{\eta_0}{\Gamma(1-\alpha)} \frac{1}{|t|^\alpha}, \quad 0 < \alpha < 1.
\]

This friction \( \eta(t) \) yields an anomalous, free \( (V(x) = 0) \) subdiffusion with \( \langle \delta x^2(t) \rangle = 2K_\alpha t^\alpha/\Gamma(1+\alpha) \), where the anomalous diffusion coefficient \( K_\alpha = k_B T/\eta_0 \) obeys a generalized Einstein relation. For a parabolic potential this yields the relaxation function

\[
\theta(t) = E_\alpha[-(t/\tau_D)^\alpha],
\]

where \( \tau_D = (\eta_0/\kappa)^{1/\alpha} \) and \( E_\alpha(z) \) is the Mittag-Leffler function, i.e., \( E_\alpha(z) = \sum_{n=0}^{\infty} z^n/\Gamma(\alpha n + 1) \) \cite{26}. It corresponds to the Cole-Cole model of glassy dielectric media \cite{27}, whereas the limit \( \alpha \to 1 \) corresponds to an exponential relaxation with \( E_1(z) = \exp(z) \).

The thermal fGn \( \xi(t) \) is the time derivative of fractional Brownian motion (fBm) \cite{17} with a power spectrum, \( S_\xi(\omega) = 2k_B T \eta_0 \sin(\pi \alpha)/\omega^{2-\alpha} \). For this thermal fGn the GLE in \cite{11} with \( m = 0 \) can formally identically be recast as the "fractional" Langevin equation, i.e., \( \eta_0 D_\alpha^\nu x(t) + V'(x) = \xi(t) \), wherein \( D_\alpha^\nu x(t) = (1/\Gamma(1-\alpha)) \int_0^t dt' (t-t')^{-\alpha} \dot{x}(t') \) is the operator of the fractional Caputo derivative \cite{24}.

**FPG-approach.** Alternatively, if instead of the fGn dwelling in a potential in \cite{11,2}, \cite{3} we use a modeling in terms of an overdamped, fractional Fokker-Planck equation description \cite{13,14}, the probability density obeys

\[
D_\alpha^\nu P(x,t) = K_\alpha \frac{\partial}{\partial x} \left( e^{-\beta V(x)} \frac{\partial}{\partial x} e^{\beta V(x)} P(x,t) \right).
\]

This result derives from an underlying continuous time random walk description of subdiffusion \cite{11}. It has well as an associated Langevin equation in a random operational time \( t(\tau) \) \cite{28} which, however, is profoundly different from the GLE.

**Subdiffusive dynamics dwelling in a parabolic potential.** The time-convolutionless master equation \cite{3} of the GLE in \cite{11,2,5} can be solved exactly for a parabolic potential \cite{29}. We first transform \( P(x,t) \) as \( P(x,t) = \exp(-\beta V(x)/2)W(x,t) \) and separate the variables, \( W(x,t) = Y(x)\Phi(t) \), where the coordinate-dependent part yields a spectral representation, reading

\[
Y_n''(x) + \frac{\beta}{2} \kappa \left( 1 - \frac{\beta}{2} \kappa x^2 + 2\lambda_n/(\beta \kappa) \right) Y_n(x) = 0,
\]

where \( \lambda_n \) and \( Y_n(x) \) are the corresponding spectral eigenvalues and eigenfunctions. The functions \( \Phi_n(t) \) obey:

\[
\dot{\Phi}_n(t) = -\lambda_n D(t) \Phi_n(t).
\]

By use of \cite{41} the exact solutions of \cite{40} read

\[
\Phi_n(t) = [\theta(t)]^{\alpha_n},
\]

where \( \alpha_n := l_T^2 \lambda_n \). These findings yield for the explicit solution for the probability density \( P(x,t) \) the result,

\[
P(x,t) = \exp(-\beta \kappa x^2/4) \sum_n c_n Y_n(x) [\theta(t)]^{\alpha_n},
\]

where the expansion coefficients \( c_n \) are determined from the initial probability density \( P(x,t=0) \). The spectrum reads \( s_n = n, n = 0, 1, 2, \ldots \). Moreover, the functions \( Y_n(x) \) are given in terms of Hermite functions \cite{13}.

The dynamics of the probability evolution is thus ruled by the relaxation function \( \theta(t) \) in Eq. \cite{40}. Remarkably, the relaxation of the mean value \( \langle x(t) \rangle \) follows precisely to the same law as in the case of a FFP description \cite{13}.

**Escape out of parabolic cusp potential.** Let us impose next an infinitely sharp potential cutoff at \( x_c = L \gg l_T \), see the inset in Fig. \cite{11}. This sharp cut-off is identical to an absorbing boundary condition, satisfying \( P(x,t) = 0 \) for \( x \geq L \). The Gaussian approximation for the GLE therefore remains valid inside the parabolic cusp potential \cite{30}.

The solution of eq. \cite{43} for the corresponding boundary value problem now reads anew (for \( -\infty < x \leq L \)):

\[
Y_n(x) = U \left( -s_n - \frac{1}{2}, -x/l_T \right),
\]

where \( U(\nu,x) \) denotes the parabolic cylinder function. The spectrum for this case reads \( \lambda_n = s_n/l_T^2 \), being determined by the solutions of transcendental equation

\[
U \left( -s_n - \frac{1}{2}, -L/l_T \right) = 0.
\]

For \( L \to \infty \), \( s_n \) approaches again \( n \). For large \( L \gg l_T \) the decay of the survival probability inside the well \( P_{SP}(t) = \int_{-\infty}^L P_{cusp}(x,t) dx \) is ruled by the lowest eigenvalue; i.e.,

\[
P_{SP}(t) \approx [\theta(t)]^{\alpha_0}.
\]
This constitutes our first central result. The value \( s_0 \) is
given by the numerical solution of Eq. [13]. Remarkably, it is well
approximated by the inverse of the properly scaled mean first passage
time of the corresponding, memoryless Markovian problem yielding, cf. in Ref. [15]:

\[
s_0^{-1} = l_T^{-2} \int_0^L dy \int_{-\infty}^y dx \exp(\beta[V(y) - V(x)]).
\]  

(15)

This yields \( s_0 = F \left( \frac{V_0}{k_B T} \right) \), where \( V_0 = k_L^2/2 \) is the
barrier height and \( 1/F(z) = \sqrt{\pi} \int_0^{\sqrt{z}} e^{-x^2} \text{erf}(y) dy \).
For example, for \( L = 2l_T \) the exact value of \( s_0 \) is
\( s_0^{(\text{exact})} = 0.09727 \) while \( s_0^{(\text{approx})} = 0.09589 \).
The difference is already less than 1.5% and rapidly diminishes with increasing \( L \).
As a main trend, \( s_0 \) decreases approximatively exponentially \( \alpha \exp(-V_0/k_B T) \),
thus displaying a typical Arrhenius dependence.

Within the approximation of \[13\] the MFPT of the
non-Markovian escape dynamics is given by:

\[
\langle \tau \rangle = \int_0^\infty P_{\text{MFPT}}(t) dt = \int_0^\infty [\theta(t)]^s_0 dt,
\]

(16)

being indeed very distinct from the Markovian case. For the
fGn-GLE model, denoted in the following by \( P_{\text{GLE}} \),
we find from \[14\] \( P_{\text{GLE}}(t) \approx (E_\alpha [-t/(t_D)^\alpha])^s_0 \), and thus
the MFPT diverges, i.e. \( \langle \tau \rangle = \infty \).

Likewise, the high-barrier solution of the FFP equation in \[7\] is given by \( P_{\text{FFP}}(t) \approx E_\alpha [-s_0(t/t_D)^\alpha] \), yielding
again no finite value for the MFPT. The asymptotic long-
time behaviors differ distinctly in these two models:

\[
P_{\text{GLE}}(t) \sim \Gamma(1-\alpha)^{-s_0} \left( \frac{T_D}{t} \right)^{s_0\alpha},
\]

(17)

\[
P_{\text{FFP}}(t) \sim \frac{1}{s_0\Gamma(1-\alpha)} \left( \frac{T_D}{t} \right)^\alpha,
\]

(18)

where \( T_D = (\eta_0/\kappa)^1/\alpha \). In particular, for the fGn-GLE
model, the power law exponent \( s_0\alpha \) depends exponentially
on the barrier height and the (inverse) temperature.
In contrast, for the FFP-theory this power law exponent
just equals the subdiffusive power law exponent \( \alpha \).

Fig. \[1\] depicts a comparison between two escape
dynamics for \( \alpha = 1/2 \) \[2\], where \( \theta(t) = \exp(t/T_D)\text{erfc}(\sqrt{t/T_D}) \), and for \( \beta V_0 = 2 \). The FFP-
escape dynamics overall proceeds faster. The initial
kinetic stages are identical. A detection of a power-
law escape that is exponentially sensitive to temperature
would corroborate the GLE based approach; while
a temperature-independent power law decay would favor
the FFP-approach.

**Role of memory cut-off.** Both considered theoretical
models contain a physical drawback: Random forces
obeying a true \( 1/\omega^{1-\alpha} \) feature in the power spectrum
are not physical; i.e. a low-frequency regularization
must always emerge on physical grounds, (implying that
\( S(\omega = 0) \) is finite) \[22\]. To account for this physical
requirement we introduce an exponential cutoff \( \exp(-\omega_c t) \)
with a small frequency \( \omega_c \) for the memory kernel \[23\],
yielding \( S(\omega = 0) = 2k_B T \eta_0/\omega_c^{1-\alpha} \). The corresponding
relaxation function \( \theta(t) \) now exhibits an exponential
decay \( \exp(-\omega_c t) \), for \( t \geq 1/\omega_c \). The memory kernel \( \eta(t) \)
becomes integrable so that the MFPT \( \langle \tau \rangle \) exists.
As a consequence, a non-Markovian rate description now
becomes valid \[17\]. In practice, however, a feasible rate
description fails whenever the main part of the escape
dynamics occurs within a distinct non-exponential, power
law regime which extends over many temporal decades.
This feature is elucidated with Fig. \[2\]. A valid rate
description, although with an extremely small rate is re-
stored by either lowering the temperature, or likewise,
by increasing the barrier height. The top curve (high-
est barrier case) in Fig. \[2\] depicts this trend. Our results
corroborate also with the numerical simulations of

![FIG. 1: Comparison between the escape dynamics described by the fractional Fokker-Planck equation and the overdamped, non-Markovian GLE-dynamics in (1)-(5) in a parabolic cusp potential, depicted with the inset.](image1)

![FIG. 2: Survival probability for a modified fGn-GLE model using a regularization. An exponential relaxation tail emerges for \( t > \omega_c^{-1} \). The chosen parameters are: \( T_D \sim 1 \) ps, \( \omega_c \sim 1 \) hour\(^{-1} \) and \( \alpha = 1/2 \).](image2)
bistable dynamics \cite{31}, where a numerical cut-off is intrinsically present. Using a memory cut-off within the CTRW description for the FFP in Eq. \(7\) does result as well in an asymptotically finite rate. The intermediate power law will exhibit, however, also no distinct temperature dependence, being again in a clear contrast with the subdiffusive GLE description.

In conclusion, we put forward an analytical treatment of the survival probability for the non-Markovian escape from a cusp-shaped well when anomalous subdiffusion is acting. Then, the MFPT diverges which in turn invalidates a rate description. The sensible physical requirement of a low-frequency regularization enables one to restore a rate theory description that is valid for sufficiently high barriers, or very low temperatures. The single-molecular enzyme kinetics \cite{6,7} might present a suitable candidate to validate experimentally the intriguing crossover between an exponential and a power law kinetic regime which crucially depends on temperature.

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\bibitem{29} Even if the exact Green function \(P(x,t|x_0,0) = \exp[-(x-x_0\theta(t))^2/(2\theta^2(1-\theta^2(t)))/\sqrt{2\pi\theta^2(1-\theta^2(t))}\) is known \cite{23}, the resulting eigenfunctions expansion is required nevertheless for the escape problem.
\bibitem{30} Here, a non-natural boundary condition must be used. Our case of a cusp-shaped parabolic well with its a sudden drop to \(-\infty\) mimics an absorbing line, \(x \geq L \gg l_r\). Any initial distribution relaxes on the time scale \(\theta(t)\) to a quasi-equilibrium Gaussian density with a width around \(l_r\), and gradually decays due to escape.
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