Kramers' escape problem with anomalous kinetics: non-exponential decay of the survival probability

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Abstract

Systems where multiple trapping or other manifestations of disorder lead to a non-local temporal evolution which results in the macroscopic observation of anomalous kinetics, are shown to exhibit a non-exponential, Mittag–Leffler decay in Kramers-type escape problems. The detailed behaviour of the survival probability is studied, and it is demonstrated that the associated escape rate is time dependent, exhibiting a turnover from a self-similar to a logarithmic pattern. Comparisons to experiment, and to local models are drawn. © 2000 Elsevier Science B.V. All rights reserved.

Traditionally, reaction rate problems [1,2] are formulated through the Smoluchowski [3] and Onsager [4] models in terms of diffusion in the presence of absorbing bodies, or in terms of the Kramers model dating back to the seminal paper of 1940 [5]. Kramers considered a point particle in phase space diffusing in the potential $V(x)$. Being initially caught in a potential hole, the particle can only escape over a potential barrier. Kramers promoted this model for the study of the dependence of the escape rate on temperature and viscosity. Alternative approaches for calculating rate reactions include the consideration of Markovian first passage time problems by Pontryagin, Andronow and Witt [6], as well as first passage time problems for the master equation considered by Landau and Teller [7], Montroll and Shuler [8],

Weiss [9], and, more recently, by Bar–Haim and Klafter [10].

Here, we focus on the Kramers approach, and in what follows we study a possible extension to system whose dynamics is non-Markovian and includes memory. Extensions of the Kramers model are considered necessary [8,11–13] although there are refined versions of the original formulation [14,15]. Such non-Markovian dynamics has been taken into consideration through generalised Langevin equations in the well-known Grote–Hynes [11] and Hänggi et al. [12] models.

On the level of the Kramers equation, these generalised models lead to a formulation which is local in time, and contains time-dependent coefficients. The associated Kramers survival probability still decays exponentially, with a frequency-dependent rate [11,12,16]. In contrast, dynamical descriptions which are related to the generalised master equation are non-local in time, and they exhibit memory on the macroscopic level of the probability density function

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(pdf) [17]. In systems where the memory decays slowly in a long-tailed, self-similar power law fashion, it has been demonstrated that fractional kinetic equations are a tailor-made approach for the description of the pdf. Within fractional dynamics, the standard kinetic equations of the Smoluchowski, Rayleigh, and Klein–Kramers type have been generalised, and thus there exists a complete theory of anomalous transport in the presence and absence of external force fields, and in phase space, in full analogy to the Brownian case [18–21]. The major advantage of the fractional formulation, due to its operator character, lies in the fact that fractional equations can, in essence, be treated with the same mathematical tools known from standard partial differential equations [22].

Fractional dynamics emerges for systems whose temporal evolution is governed by broadly distributed waiting times between individual transitions. Thus, the fractional Klein–Kramers equation and its overdamped counterpart, the fractional Fokker–Planck equation, can be derived for multiple trapping systems with broadly distributed waiting time statistics where Brownian motion patterns, described by a Langevin equation with Gaussian white noise, are regularly interrupted by an immobilisation of the test particle. In such systems, there exists no characteristic scale for the trapping times [19–21]. This kind of trapping mechanisms has been explored in amorphous semiconductors [23], in the motion of excess electrons in liquids [24], it occurs in the motion of a bead in a polymeric solution [25], and in the tracer dispersion in porous systems [26]. Multiple trapping systems with a scale-free waiting time distribution are close to thermal equilibrium, and their mean squared displacement shows subdiffusion, $\langle x^2(t)\rangle \propto t^\alpha$ with $0 < \alpha < 1$, in the force free limit [19–21].

Here we develop a model which combines the classical Kramers idea of the escape over a potential barrier with fractional dynamics. The result of this apparently simple generalisation leads to the Mittag–Leffler relaxation of the survival probability which shows a transition from a stretched exponential behaviour to an inverse power-law pattern. This Mittag–Leffler pattern replaces the exponential kinetics traditionally found in the Markovian case. Thereby, the Arrhenius activation of the associated fractional Kramers rate is preserved.

In the standard overdamped version of the Kramers problem, the escape of a particle subject to a Gaussian white noise over a potential barrier is considered in the limit of low diffusivity, i.e., where the barrier height ΔV is large in comparison to the diffusion constant K [27], compare Fig. 1. Then, the probability current over the potential barrier top near $x_{\max}$ is small, and the time change of the pdf is equally small. In this quasi-stationary situation, the probability current is approximately position independent. The temporal decay of the probability to find the particle within the potential well is then given by an exponential function [5,27]

$$p(t) = \mathrm{e}^{-r_K t}, \qquad (1)$$

where the Kramers rate is defined through [5,27]

$$r_K = \frac{1}{2\pi m\eta}\sqrt{V''(x_{\min})|V''(x_{\max})|}$$
$$\times \exp(-\beta\Delta V), \qquad (2)$$

with $\Delta V = V(x_{\max}) - V(x_{\min})$. In Eq. (2), the exponential function contains the Boltzmann factor $\beta \equiv (k_B T)^{-1}$ so that the inverse Kramers rate follows an Arrhenius activation $r_K^{-1} \propto \mathrm{e}^{E^*/T}$ with $E^* \equiv \Delta V/k_B$.

In a similar fashion, the Kramers rate in the low viscosity limit is given through [5]

$$r_K = \eta\beta\Delta V \exp(-\beta\Delta V). \qquad (3)$$

According to Kramers' treatment, the proportionality of the Kramers rate to η in the low viscosity limit
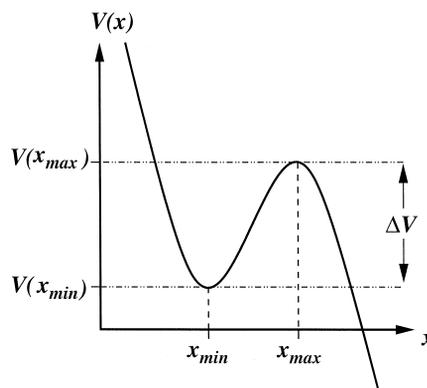
Fig. 1. Potential well in the Kramers rate model. Initially the particle is assumed to be caught in the potential hole. The x axis corresponds to a reaction coordinate.

turns over to the inverse proportionality in the high viscosity. The interpolating behaviour for arbitrary η was studied by Mel'nikov [2].

Let us now derive the fractional counterpart to the exponential decay pattern (1). To this end, we note that the solution W_α of the fractional Klein–Kramers and Fokker–Planck equations can be expressed in terms of its Brownian analogue, W_1 [19,21]. For the fractional Fokker–Planck equation, this connection is given through the scaling relation [19]

$$W_\alpha(x,u) = \frac{\eta_\alpha}{\eta} u^{\alpha-1} W_1\left(x, \frac{\eta_\alpha}{\eta} u^\alpha\right) \qquad (4)$$

in Laplace space, $W_\alpha(x,u) = \int_0^\infty dt\, e^{-ut} W_\alpha(x,t)$. In Eq. (4), η and η_α are the Brownian and fractional friction constants, the latter being a rescaled version of the former: $\eta_\alpha \equiv \eta/\vartheta$, where η is the classical friction occurring in the Langevin equation. The scale factor ϑ emerges from the competition between the characteristic time scale of the Langevin dominated motion events and the internal waiting time scale involved in the trapping dynamics [21]. Moreover, the generalised friction constant η_α satisfies the generalised Einstein–Stokes relation $K_\alpha = k_B T/(m\eta_\alpha)$, together with the generalised diffusion constant K_α [19].

The transformation (4) affects all kinetic processes associated with the fractional Fokker–Planck equation, such as the relaxation of single modes, or the Kramers escape. Application of relation (4) to the Laplace transform $p(u) = (r_K + u)^{-1}$ of the survival probability, Eq. (1), produces

$$p_\alpha(u) = \frac{1}{u + r_K^{(\alpha)} u^{1-\alpha}}, \qquad (5)$$

with the generalised, fractional Kramers rate

$$r_K^{(\alpha)} = \frac{\eta}{\eta_\alpha} r_K. \qquad (6)$$

The fraction $\eta/\eta_\alpha = \vartheta$ is thus the rescaling of the classical Kramers rate according to the parameters classifying the multiple trapping system with broadly distributed waiting times. Consequently, the Arrhenius activation nature of the Kramers rate is preserved in systems controlled by fractional dynamics.

Similarly in the underdamped case, one finds the fractional Kramers rate

$$r_K^{(\alpha)} = \eta^* \beta \Delta V \exp(-\beta \Delta V), \qquad (7)$$

where $\eta^* \equiv \vartheta\eta$ replaces the classical friction η. Thus, according to Eqs. (6) and (7), our fractional Kramers model leads to the turnover in the friction dependence from $r_K^{(\alpha)} \propto \eta^*$ to $r_K^{(\alpha)} \propto 1/\eta_\alpha$.

This seemingly complicated turnover can be reconciled with the standard picture. Indeed, on combining the elementary constant ϑ with the other constants in expressions (6) and (7), the traditional turnover $r_K^{(\alpha)} \propto \eta$ to $r_K^{(\alpha)} \propto 1/\eta$ is recovered for the fractional Kramers rate. This observation is due to the linearity of the fractional operator.

The difference between the fractional and the classical escape models lies in the temporal relaxation of the survival probability for which one finds via Laplace inversion of Eq. (5)

$$p_\alpha(t) = E_\alpha\left(-r_K^{(\alpha)} t^\alpha\right) \qquad (8)$$

for both the underdamped and the overdamped cases, in terms of the Mittag–Leffler function E_α which is defined through [28]

$$E_\alpha\left(-r_K^{(\alpha)} t^\alpha\right) = \sum_{n=0}^\infty \frac{\left(-r_K^{(\alpha)} t^\alpha\right)^n}{\Gamma(1 + \alpha n)}. \qquad (9)$$

The Mittag–Leffler function interpolates between the initial stretched exponential behaviour

$$E_\alpha\left(-r_K^{(\alpha)} t^\alpha\right) \sim \exp\left(-\frac{r_K^{(\alpha)} t^\alpha}{\Gamma(1 + \alpha)}\right) \qquad (10a)$$

and the final inverse-power law pattern

$$E_\alpha\left(-r_K^{(\alpha)} t^\alpha\right) \sim \left(r_K^{(\alpha)} \Gamma(1 - \alpha) t^\alpha\right)^{-1}. \qquad (10b)$$

In the Brownian limit $\alpha \to 1$, the Mittag–Leffler function reduces to the exponential function, and for $\alpha = 1/2$, it can be expressed in terms of the complementary error function, $E_{1/2}(-z^{1/2}) = e^z \mathrm{erfc}(z^{1/2})$.

Note that the Mittag–Leffler function is an entire function which decays completely monotonically for $0 < \alpha < 1$. It is the exact relaxation function for the underlying multiscale process, and leads to the Cole–Cole behaviour for the complex susceptibility, which is often used to describe experimental results. It can be decomposed into single Debye processes, the relaxation time distribution of which is given by a one-sided Lévy distribution [29]. Due to the fundamental relation (4), the Mittag–Leffler function is universal for fractional dynamics in the sense that for

a given anomalous exponent α, all formerly exponential patterns like mode relaxation, moment equilibration, or the survival are replaced by the Mittag–Leffler function.

Often one defines non-exponential relaxations in terms of a time dependent rate coefficient $k(t)$ through $p(t) = \exp(-k(t)t)$. For the fractional Kramers model one therefore obtains the rate coefficient $k(t) = \left| \ln E_\alpha(-r_K^{(\alpha)} t^\alpha) \right| / t$ which leads to two limiting cases, the short time self-similar behaviour

$$k(t) \sim \frac{r_K^{(\alpha)}}{t^{1-\alpha} \Gamma(1+\alpha)}, \quad t^\alpha \ll r_K^{(\alpha)}, \tag{11a}$$

and the long time logarithmic pattern

$$k(t) \sim \frac{\alpha}{t} \ln\left(t \left[r_K^{(\alpha)} \Gamma(1-\alpha) \right]^{1/\alpha} \right),$$

$$t^\alpha \gg r_K^{(\alpha)}. \tag{11b}$$

It is interesting to note that the latter, up to some constants, is given by $k(t) \sim \ln t / t$ which is in this sense universal, i.e., the functional form is independent of the waiting time index α.

Let us compare our result to the generalised Langevin models of Refs. [11,12]. The Klein–Kramers equation corresponding to this stochastic equation was derived by Wang and Tokuyama [16], and it contains time-dependent coefficients in an overall local equation. We find from their result the long-time exponential-type behaviour $p(t) \sim \exp(-f(t))$ for the case $0 < \beta < 1$, which clearly differs from our inverse power-law result, Eq. (11b). Note that, at the same time, both models correspond to subdiffusion $\langle x^2(t) \rangle \propto t^\beta$. In the generalised Langevin equation this behaviour emerges from the time-dependent friction and is basically equivalent to fractional Brownian motion [16]; in our fractional equation approach it stems solely from the memory character brought about through the broadly distributed multiple trapping mechanism. Thus, the power-law memory entering on the Langevin level leads to an exponential-type Kramers decay, whereas the same memory entering on the Klein–Kramers-level gives rise to the power-law long-time behaviour of the relaxation function.

Reactions in proteins can, as an approximation, be formulated within the Kramers reaction theory of barrier crossing [30]. The related survival dynamics,

as well as the protein dynamics itself, is however non-exponential [30–32]. Here, we propose that our fractional Kramers model can be applied to the ligand rebinding to proteins. In Fig. 2, we have reproduced the Mittag–Leffler fit to the experimental data from Iben et al. obtained from ligand CO rebinding to myoglobin after photodissociation, as investigated by Glöckle and Nonnenmacher [33]. These authors assume that the fractional parameter α features a linear temperature dependence, $\alpha(T) = 0.41 T / 120 \text{K}$ which might take the change of the protein-solvent system into account. From the data analysis they find a remarkable agreement with the Mittag–Leffler behaviour, and the Arrhenius activation $\tau = \tau_m e^{E_\tau / T}$ for the characteristic time which is related to the fractional Kramers rate through $r_K^{(\alpha)} \equiv \tau^{-\alpha}$. Thus, selecting out the temperature dependence of α, one exactly finds the Arrhenius dependence as predicted by the fractional Fokker–Planck model. The insert in Fig. 2 shows this Arrhenius activation of τ as found in Ref. [33]. Note that our model does not account for the non-Arrhenius activation found for the glassy protein behaviour by Austin et al. [31].

Due to the finiteness of experimental data windows, certain data sets allow for stretched exponential fits instead of an asymptotical power-law description like the Mittag–Leffler pattern. However, there exist cases when the stretched exponential fit leads to questionable parameters [34]. Moreover, an inappropriate fit function might lead to deviations
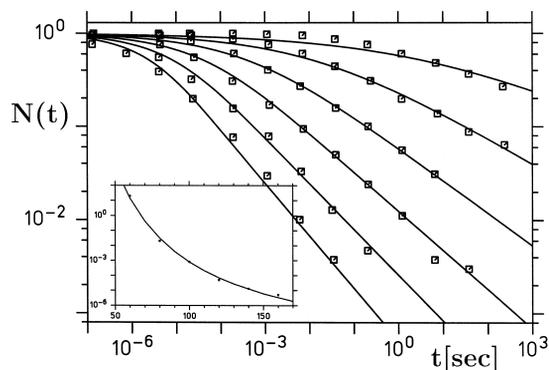
Fig. 2. Mittag–Leffler model for the rebinding of CO to Mb, after a photo dissociation. Data from Austin et al. [31]. The temperature dependence of τ_0 follows the Arrhenius law shown in the insert, with the parameters $\tau_m = 3.4 \times 10^{-10}$ s and $E_\tau = 1470$ K.

from the predicted friction dependence [30,35], or from the Arrhenius activation. In order to investigate the effects of a 'forced' exponential fit to data following the Mittag–Leffler pattern, we have produced surrogate data according to the fractional theory. The 'forced' exponential fit data then indeed reveal seeming deviations from the Arrhenius law. Such deviations might become pronounced for certain combinations of the number of data points, and the covered range. This is also the case if truncated data are fitted with an inappropriate function.

It might be questioned whether the low diffusivity condition applied to the Brownian case is equally sufficient for carrying along only the first order contribution to the survival in the fractional dynamics case. Let us assume that for the Brownian case, such higher order contributions are given through the sum $p(t) = \sum_i a_i e^{-\lambda_i t}$ so that the ratio of successive terms is found to be $f_i = (a_{i+1}/a_i) \times \exp\left(-(\lambda_{i+1} - \lambda_i)t\right)$ where $a_i > a_{i+1}$ and $\lambda_i < \lambda_{i+1}$. Conversely, the fractional analogue is given through the sum of Mittag–Leffler contributions $p_\alpha(t) = \sum_i a_i E_\alpha(-\vartheta \lambda_i t^\alpha)$. Thus, the ratio of successive contributions turns over from $f_i^{(\alpha)} = (a_{i+1}/a_i)\exp\left(-\vartheta(\lambda_{i+1} - \lambda_i)t^\alpha/\Gamma(1+\alpha)\right)$ for short times to the time independent ratio $f_i^{(\alpha)} = (a_{i+1}\lambda_i)/(a_i\lambda_{i+1})$, instead of the exponential decay in the Brownian case. Thus, for certain potential types higher order contributions might lead to a modification in the prefactor of the resulting power law decay, and a somewhat earlier inset of this self-similar regime. The general features of our results, the turnover from the stretched exponential to the inverse power law decay, remain unchanged, however. In this sense, the condition for the Brownian system carries over to the fractional dynamics system.

Concluding, we have demonstrated that the classical Kramers theory for reaction rates leads to the ubiquitous Mittag–Leffler relaxation pattern for systems where the underlying dynamics is fractional. Due to its close relation to self-similar dynamics and generalised limit theorems, the fractional approach is expected to be the appropriate physical model in a variety of complex systems in physics, chemistry and biological physics exhibiting an escape dynamics in which no characteristic time scale of the escape dynamics exists.

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