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Kramers escape rate in overdamped systems with the power-law distribution

Zhou Yanjun, Du Jiulin *

Department of Physics, School of Science, Tianjin University, Tianjin 300072, China

HIGHLIGHTS

- The escape rate in an overdamped system with power-law distribution is studied.
- The finite barrier effect for the Kramers escape rate is discussed.
- We apply the generalized escape rate to the unfolding of titin.

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ABSTRACT

Kramers escape rate in the overdamped systems is restudied for the power-law distribution. By using the mean first passage time, we derive the escape rate with the power-law distribution and obtain the Kramers' infinite barrier escape rate in this case. We show that the escape rate with the power-law distribution extends the Kramers' overdamped result to the relatively low barrier. Furthermore, we apply the escape rate with the power-law distribution to the unfolding of titin and show a better agreement with the experimental rate than the traditional escape rate.

1. Introduction

Kramers' problem proposed for the thermal escape of a Brownian particle out of a metastable well has received great attention and interests in physics, chemistry and biology [1,2] etc., which has become the most important one of modern reaction rate theories. At first, Kramers realized a very unsatisfactory feature of transition state theory (TST) which appears to predict escape in the absence of coupling to a heat bath in contradiction to the fluctuation–dissipation theorem, and then chose the prefactor μ to remedy this defect [3]. According to the very low and intermediate-to-high dissipative coupling to the bath, he yielded three explicit formulas of μ for the escape rate in very low damping, intermediate and overdamped cases, respectively. In this paper, we focus on the overdamped systems.

When Brownian particles move in an overdamped media, the probability distribution of particles can be described by Smoluchowski equation. Kramers postulated that the barrier Brownian particles escape is high compared with thermal energy and the dissipative coupling to the bath is strong so that the systems can be in a thermal equilibrium state, a Maxwell–Boltzmann (MB) distribution always holds in the whole time, and any disturbance to the MB distribution can almost be negligible at all times [3]. Under this assumption, the escape rate is obtained. However, the assumption is farfetched in open complex systems. Nonequilibrium is the main feature of an open complex system. In fact, lots of experimental studies on complex systems have shown non-MB distributions or power-law distributions, such as glasses [4,5], disordered

* Corresponding author.
E-mail addresses: yanjunzhou@aliyun.com (Y. Zhou), jldu@tju.edu.cn (J. Du).

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media [6–8], folding of proteins [9], single-molecule conformational dynamics [10,11], trapped ion reactions [12], chemical kinetics, and biological and ecological population dynamics [13,14], reaction–diffusion processes [15], chemical reactions [16], combustion processes [17], gene expression [18], cell reproductions [19], complex cellular networks [20], small organic molecules [21], and astrophysical and space plasmas [22], etc. The typical forms of such power-law distributions have included the κ-distributions or the generalized Lorentzian distributions in the solar wind and space plasmas [22–26], the q-distributions in complex systems within nonextensive statistical mechanics [27], and those α-distributions noted in physics, chemistry and elsewhere like $P(E) \sim E^{-\alpha}$ with an index $\alpha > 0$ [12,15,16,21,23,28]. These power-law distributions may lead to processes different from those in the realm governed by Boltzmann–Gibbs statistics with MB distribution. Simultaneously, a class of statistical mechanical theories studying the power-law distributions in complex systems has been constructed, for instance, by generalizing Boltzmann entropy to Tsallis entropy [27], by generalizing Gibbsian theory [29] to a system away from thermal equilibrium, and so forth. Most recently, a generalized transition state theory (TST) for the systems with power-law distributions was studied and the generalized reaction rate formulas were presented for one-dimensional and n-dimensional Hamiltonian systems away from equilibrium [30]. The power-law TST reaction rate coefficient for an elementary bimolecular reaction was studied when the reaction takes place in the system with power-law distributions and the mean first passage time for power-law distributions was also studied [31]. These developments now naturally give rise to a possibility that Kramers escape rate can be reconsidered under the condition of power-law distributions in a complex system.

One of the most important thermal escape theories is the first passage time theory [32,33]. In an overdamped case, suppose that the motions of the particles are bounded in the finite space V with an absorbing boundary Σ, and they are governed by the Langevin equation [34],

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -(m\gamma)^{-1}\frac{\mathrm{d}U}{\mathrm{d}x} + (m\gamma)^{-1}\eta(x,t), \tag{1}$$

where m is the mass of the particle, U is a potential field, γ is the friction coefficient. Generally, the noise may be considered inhomogeneous in space and so it may be a function of the variables x, i.e. $\eta = \eta(x,t)$ is a multiplicative (space-dependent) noise. It is usually assumed that the noise is Gaussian, with zero average and delta-correlated in time t, such that it satisfies,

$$\langle \eta(x,t)\rangle = 0, \qquad \left\langle \eta(x,t)\,\eta\left(x,t'\right)\right\rangle = 2D(x)\delta\left(t-t'\right). \tag{2}$$

The correlation strength of multiplicative noise (i.e. diffusion coefficient) $D(x)$ is also a function of the variables x.

If $P(x,t)$ is the probability distribution of particles that has not left by time t, it satisfies the Smoluchowski equation,

$$\frac{\partial P(x,t)}{\partial t} = (m\gamma)^{-1}\frac{\partial}{\partial x}\left(\frac{\mathrm{d}U}{\mathrm{d}x}P(x,t)\right) + (m\gamma)^{-1}\frac{\partial}{\partial x}\left(D(x)\frac{\partial P(x,t)}{\partial x}\right), \tag{3}$$

where the initial condition and absorbing boundary condition are $P(x,0) = \delta(x-x_0)$, $P(x,t)|_{\Sigma} = 0$ respectively. It is known that when the system reaches thermal equilibrium, $D(x)$ is a constant, $D = \beta^{-1}$ and the stationary solution of Eq. (3) is an MB distribution. In the stochastic dynamical theory of power-law distributions, when the system is away from thermal equilibrium, one can consider $D(x)$ as a function of the potential energy $U(x)$, and to satisfy the generalized fluctuation–dissipation relation (FDR) for power-law distribution [34],

$$D(x) = \beta^{-1}\left[1-\kappa\beta U(x)\right], \tag{4}$$

where $\beta = 1/k_BT$, k_B is the Boltzmann constant, T is the temperature, κ is the power-law parameter and $\kappa \neq 0$ measures a distance away from thermal equilibrium. Substituting Eq. (4) into Eq. (3), one can show that the stationary-state solution is the power-law κ-distribution [34],

$$P_s(x) = Z_\kappa^{-1}\left[1-\kappa\beta U(x)\right]_+^{1/\kappa}, \tag{5}$$

where Z_κ is the normalization constant $Z_\kappa = \int \mathrm{d}x\,[1-\kappa\beta U(x)]_+^{\frac{1}{\kappa}}$. It is clear that the generalized FDR is a condition under which the power-law κ-distribution can be created from the stochastic dynamics of the Langevin equations. At the same time, we can easily find that Eq. (3) combined with Eq. (4) leads to the following time-dependent solution of the power-law distribution,

$$P(x,t) = Z_\kappa^{-1}(t)\left[1-\kappa\beta(t)\,(x-x_M(t))^2\right]_+^{\frac{1}{\kappa}}, \tag{6}$$

where $Z_\kappa(t) = \int \mathrm{d}x\left[1-\kappa\beta(t)\,(x-x_M(t))^2\right]_+^{\frac{1}{\kappa}}$ is the normalization constant at time t, $\beta(t) = 1/k_BT(t)$, $T(t)$ is the temperature at time t, $x_M(t)$ is the sym-center of the potential energy at time t. The time-dependent solution is precisely the same as the result with q-distributions (see Eq. (9) in Ref. [35]).

We introduce the Fokker–Planck operator, f, and its adjoint operator, $f^\dagger$ [32],

$$f = (m\gamma)^{-1}\frac{\partial}{\partial x}\left(\frac{\mathrm{d}U}{\mathrm{d}x}\right) + (m\gamma)^{-1}\frac{\partial}{\partial x}D(x)\frac{\partial}{\partial x}, \tag{7a}$$

$$f^\dagger = -(m\gamma)^{-1}\frac{\mathrm{d}U}{\mathrm{d}x}\frac{\partial}{\partial x} + (m\gamma)^{-1}\frac{\partial}{\partial x}D(x)\frac{\partial}{\partial x}, \tag{7b}$$