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Escape rate for the power-law distribution in low-to-intermediate damping

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HIGHLIGHTS

- The escape rate for the power-law distribution in low-to-intermediate damping is studied.
- An expression of the escape rate for the power-law distribution is derived.
- The extra current and improvement of the absorbing boundary condition are discussed.

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ABSTRACT

Escape rate in the low-to-intermediate damping connecting the low damping with the intermediate damping is established for the power-law distribution on the basis of flux over population theory. We extend the escape rate in the low damping to the low-to-intermediate damping, and get an expression for the power-law distribution. Then we apply the escape rate for the power-law distribution to the experimental study of the excited-state isomerization, and show a good agreement with the experimental value. The extra current and the improvement of the absorbing boundary condition are discussed.

1. Introduction

In 1940, Kramers proposed a thermal escape of a Brownian particle out of a metastable well [1], and according to the very low and intermediate to high dissipative coupling to the bath, he yielded three explicit formulas of the escape rates in the low damping, intermediate-to-high damping (IHD) and very high damping respectively, all of which has been received great attentions and interests in physics, chemistry, and biology etc. [2,3]. In the IHD region, he got an expression of escape rate in the infinite barrier (i.e. the barrier height $E_C \gg k_B T$) and successfully extended it to high damping region; in the low damping region, he derived a rate in energy diffusion regime; as for the intermediate region, he had not given an expression, which was known as Kramers turnover problem. Later, plenty of researches had been continued. Carmeli et al. derived an expression for the escape rate in the Kramers model valid for the entire friction coefficient by assuming that the stationary solutions of the low damping and moderate-to-high damping overlap in some region of phase space and are equal to each other (see Eq. (17) in Ref. [4]); Büttiker et al. extended the low damping result to the larger range of damping by reconsidering absorbing boundary condition at the barrier and introducing an extra flux $J_{E>E_C}$ (see Eq. (3.11) in Ref. [5]); Pollak et al. got a general expression in non-Markov processes (see Eq. (3.33) in Ref. [6]); Hänggi et al. introduced a simple interpolation formula (see Eq. (6.1) in Ref. [7]) for the arbitrary friction coefficient. However, it has been noticed that the above bridging expressions yield results that agree roughly to within $\leq$ 20% with the numerically precise answers inside the

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turnover region; in higher dimensions and for the case of memory friction, these interpolation formulas may eventually fail seriously [7]. At the same time, more attentions need to be paid that the systems studied in above theories are all in thermal equilibrium and the distributions all follows a Maxwell–Boltzmann (MB) distribution, $\rho_{eq}(E) = \rho_0 e^{-E/k_B T}$, where E is the energy, ρ_0 is the normalization constant, k_B is the Boltzmann constant, and T is the temperature. It should be considered that a complex system far away from equilibrium has not to relax to a thermal equilibrium state with MB distribution, but often asymptotically approaches to a nonequilibrium stationary-state with power-law distributions. In these situations, the Kramers escape rate should be restudied.

In fact, plenty of the theoretical and experimental studies have shown that non-MB distributions or power-law distributions are quite common in some nonequilibrium complex systems, such as in glasses [8,9], disordered media [10–12], folding of proteins [13], single-molecule conformational dynamics [14,15], trapped ion reactions [16], chemical kinetics, and biological and ecological population dynamics [17,18], reaction–diffusion processes [19], chemical reactions [20], combustion processes [21], gene expression [22], cell reproductions [23], complex cellular networks [24], small organic molecules [25], and astrophysical and space plasmas [26]. The typical forms of such power-law distributions include the noted κ-distributions in the solar wind and space plasmas [26,27], the q-distributions in complex systems within nonextensive statistics [28], and the α-distributions noted in physics, chemistry and elsewhere like $P(E) \sim E^{-\alpha}$ with an index $\alpha > 0$ [16,19,20,25,29]. These power-law distributions may lead to processes different from those in the realm governed by Boltzmann–Gibbs statistics with MB distributions. 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 [28], by generalizing Gibbsian theory [30] to a system away from thermal equilibrium, and so forth. Recently, a stochastic dynamical theory of power-law distributions has been developed by means of studying the Brownian motion in a complex system [31,32], which lead the new fluctuation–dissipation relations (FDR) for power-law distributions, a generalized Klein–Kramers equation and a generalized Smoluchowski equation. Based on the statistical theory, one can generalize the transition state theory (TST) to the nonequilibrium systems with power-law distributions [33]; one can study the power-law reaction rate coefficient for an elementary bimolecular reaction [34], the mean first passage time for power-law distributions [35], and the escape rate for power-law distributions in the overdamped systems [36].

In this work, the Kramers escape rate for power-law distributions in the low-to-intermediate damping (LID) will be studied. The paper is organized as follows. In Section 2, a generalized escape rate in the LID region is obtained for the power-law distribution and compared with the results of the low damping Kramers' escape rate, and then we apply our theory to the excited-state isomerization of 2-alkenylanthracene in alkane. Further discussion of extra current is given in Section 3, and finally the conclusion is made in Section 4.

2. Escape rate for the power-law distribution in the LID

We have mentioned in the introduction that Büttiker et al. got a Kramer's escape rate in a wider frictional range on the assumption that the system follows the thermal equilibrium distribution. However, for the low damping systems, it is always nonequilibrium. Because the coupling to the bath is very weak and the time to reach thermal equilibrium is very long in low damping systems, the escape of particles may be established before thermal equilibrium, and thus nonequilibrium effects dominate the process [37]. Thereby, the nonequilibrium distribution, such as κ-distribution, may be used here.

Low damping or small viscosity means that the Brownian forces cause only a tiny perturbation in the undamped energy, so it is helpful to replace the momentum by the energy. In the energy region, the Klein–Kramers equation can be written [3] as

$$\frac{\partial \rho}{\partial t} = \frac{\omega(I)}{2\pi}\frac{\partial}{\partial E}(\gamma I \rho) + \frac{\omega(I)}{2\pi}\frac{\partial}{\partial E}\left(D\frac{\omega(I)}{2\pi}\frac{\partial \rho}{\partial E}\right), \tag{1}$$

where ω is the angular frequency of oscillation frequency and it satisfies $\omega(I) = 2\pi\, \mathrm{d}E/\mathrm{d}I$, D is the diffusion coefficient, γ is the friction coefficient, I is the action defined as $I(E) = \oint_{E=\mathrm{Const}} p\mathrm{d}x$. In energy space, the continuity equation [3] is

$$\frac{\partial \rho}{\partial t} = -\frac{\omega(I)}{2\pi}\frac{\partial J}{\partial E}. \tag{2}$$

Take Eq. (2) into Eq. (1) and the current J becomes

$$\begin{aligned} J &= -\frac{D\omega(I)}{2\pi}\exp\left(-\int \frac{2\pi I\gamma}{D\omega(I)}\mathrm{d}E\right)\frac{\partial}{\partial E}\left(\rho \exp\int \frac{2\pi I\gamma}{D\omega(I)}\mathrm{d}E\right) \\ &= -\frac{D\omega(I)}{2\pi}\rho_s\frac{\partial\left(\rho\rho_s^{-1}\right)}{\partial E}, \end{aligned} \tag{3}$$

where ρ_s is the stationary-state distribution $\rho_s = Z^{-1}\exp\left(-\int \frac{2\pi\gamma I}{\omega D}\mathrm{d}E\right)$, and Z is the normalization constant. In the previous work, we derived Kramers' escape rate in the low damping for the power-law distribution, and showed that the stationary-state distribution is the power-law κ-distribution [31],

$$\rho_s(E) = Z^{-1}(1-\kappa\beta E)_+^{1/\kappa}, \tag{4}$$