Kramers problem and energy diffusion

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Abstract: The thermally activated escape of a Brownian particle over a potential barrier can be treated by the Smoluchowski equation if the high friction limit is considered. If the friction is weak, however, a different approach must be taken which is based on the concept of energy diffusion. The associated Kramers problem is to determine the rate at which the particle escapes from the potential well defining the barrier. In this work, through theory and simulations, we quantify the escape time as the mean first-passage time taken by the particle to cross the barrier by considering the energy diffusion approach.

I. INTRODUCTION

The problem of the thermally activated escape from a potential well is important in almost all scientific disciplines and has received considerable attention since the seminal work by Kramers [1]. The problem is formulated by considering a particle under the action of an external potential and immersed in a bath that induces a stochastic force on the particle because of thermal fluctuations. Due to the stochastic force, the particle undergoes Brownian motion and is able to escape from the potential well and cross the associated barrier at a rate that depends on the shape of the external potential and the temperature [2].

A statistical treatment of the problem can be obtained by means of the Fokker-Planck equations [3], giving the probability of finding the particle with a specific a position and velocity at a given time. In the limit of high friction, the Fokker-Planck equation reduces to the Smoluchowski equation describing the Brownian motion of the particle as a diffusion process in space and time. In the case of weak friction, the thermal noise produces slow changes of the particle's energy and a different strategy must be implemented which is based on the concept of *energy diffusion* [2].

In this work, we follow the energy diffusion approach to describe the escape of a Brownian particle from a potential well in the case of weak friction. We do so by computing the escape time as the mean-first passage time taken by the particle to cross the barrier introduced by the external potential [2]. In addition, we test the theoretical predictions by performing Monte Carlo (MC) simulations in the canonical ensemble by adapting the method used in [4]. For large barrier energies as compared to the thermal energy, the simulations show an exponential behavior of the mean-first passage time, in agreement with the theoretical result. We also sample the distribution of first passage times and observe that they follow an exponential distribution in time.

The work is organized as follows. In Sec. II we develop the Fokker-Plank equation for the energy evolution, in Sec. III we obtain the expression for the escape time and in Sec. IV we describe the model for the external potential and obtain an asymptotic expression for the escape time. In Sec. V we present the results of our MC simulations and, finally, in Sec. VI we draw our conclusions.

II. ENERGY DIFFUSION

The Langevin equations describe the motion of particles coupled to an environment with thermal noise at temperature T. For a single particle characterized by position x and momentum p at time t in a one-dimensional system with an external potential $U(x)$, these equations take the form

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{p}{m}, \tag{1}$$

$$\frac{\mathrm{d}p}{\mathrm{d}t} = -\frac{\mathrm{d}}{\mathrm{d}x}U(x) - \zeta\frac{p}{m} + F_p(t), \tag{2}$$

where m is the mass of the particle, ζ is the friction coefficient and $F_p(t)$ is the stochastic force satisfying the fluctuation-dissipation theorem

$$\langle F_p(t)F_p(t')\rangle = 2\zeta k_B T\delta(t-t') \tag{3}$$

describing the noise induced by the thermal bath, k_B being the Boltzmann constant. The associated Fokker-Planck equation for the distribution function $\mathcal{P}(x,p,t)$ characterizing the dynamics of the particle is given by

$$\frac{\partial\mathcal{P}}{\partial t} + \left(\frac{p}{m}\frac{\partial\mathcal{P}}{\partial x} + F_U\frac{\partial\mathcal{P}}{\partial p}\right) = \frac{\partial}{\partial p}\left(\zeta k_{\mathrm{B}}T\frac{\partial\mathcal{P}}{\partial p} + \zeta\frac{p}{m}\mathcal{P}\right), \tag{4}$$

where $F_U = -dU/dx$ is the force derived from the external potential. Here it is assumed that $U(x)$ introduces a potential well that traps the particle and an energy barrier that the particle must overcome in order to escape from the well. Due to thermal fluctuations, the particle eventually acquires enough energy to cross the barrier and escape from the well. We want study the time that the particle takes to cross the potential barrier, that is, the escape time.

In this work we focus on the case of a weak friction, in which the dynamics of the system is driven by slow changes of the energy which are produced by the noise

and friction. In order to quantify the dynamics of the system, a Fokker-Planck equation describing a energy diffusion process can be obtained by taking the distribution function $\mathcal{P}(x,p,t)$ as the starting point [2]. As shown in [5], taking $P(x,v,t)=\tilde{P}(E,t)$ and replacing it in equation (4) leads to an evolution equation for $\tilde{P}(E,t)$. The dependence on coordinates in the obtained equation can be eliminated by performing a microcanonical average, thus giving an equation for the evolution of the energy. The distribution of energies is then given by $P(E,t)=\Omega(E)\tilde{P}(E,t)$, where

$$\Omega(E)=\int \mathrm{d}x\,\mathrm{d}p\,\delta(E-H) \tag{5}$$

is the microcanonical density of states. When considering an initial value problem, the distribution of energies can be written as $P(E,t|E_0)$, so it corresponds to the probability density of finding the particle with energy E at time t, given that at $t=0$ the energy of the particle was E_0. According to the previous procedure, this probability satisfies the Fokker-Planck equation [2, 4]

$$\frac{\partial}{\partial t}P(E,t|E_0)=\mathcal{L}_E P(E,t|E_0), \tag{6}$$

which has to be solved with the initial condition $P(E,0|E_0)=\delta(E-E_0)$ and the Fokker-Planck operator is given by

$$\mathcal{L}_E=-\frac{\partial}{\partial E}v(E)+\frac{\partial}{\partial E}D(E)\frac{\partial}{\partial E}. \tag{7}$$

The operator is defined in terms of the energy diffusion coefficient given by

$$D(E)=\frac{\zeta k_B T}{m}\frac{I(E)}{\Omega(E)}, \tag{8}$$

and the drift

$$v(E)=-D(E)\beta\frac{\partial}{\partial E}F(E), \tag{9}$$

where $\beta=1/k_BT$ and

$$F(E)=E-k_BT\ln\Omega(E) \tag{10}$$

is the free energy of the particle in terms of the instantaneous energy E. In the expressions above we have introduced the number of microstates

$$I(E)=\int \mathrm{d}x\,\mathrm{d}p\,\Theta(E-H), \tag{11}$$

where $\Theta(x)$ is the step function and

$$H=\frac{p^2}{2m}+U(x) \tag{12}$$

is the Hamiltonian of the particle when it is decoupled from the environment.

In view of the above expressions, we see that the evolution of the energy is determined by the functions $I(E)$ and $\Omega(E)$. The number of microstates given by (11) can be written more explicitly as

$$\begin{aligned} I(E)&=\int_{-\infty}^{\infty}\mathrm{d}x\int_{p^2/(2m)+U(x)\leq E}\mathrm{d}p \\ &=2\sqrt{2m}\int_{U(x)\leq E}\mathrm{d}x\,\sqrt{[E-U(x)]}, \end{aligned} \tag{13}$$

where the integration range over x is given by the condition $E-U(x)\geq 0$ (meaning that the kinetic energy is non-negative). The factor 2 in the second line above appears because the integral over p is twice the integral over positive values of p. Finally, the density of states (5) can be found by noting that it is related to $I(E)$ according to

$$\Omega(E)=\frac{\mathrm{d}I(E)}{\mathrm{d}E}. \tag{14}$$

Taking the Fokker-Planck equation (6) as the starting point, in the next section we formally compute es escape time as the mean-first passage time for the particle to cross the potential barrier.

III. MEAN FIRST-PASSAGE TIME

As mentioned in the previous section, we want to obtain an expression for the average time taken by the particle to reach the barrier energy for the first time, escaping thus from the potential well. This mean first-passage time can be obtained on the basis of the survival probability, defined as the probability of all the starting points being at the energy domain D at time t,

$$S(E_0,t)=\int_D dE P(E,t|E_0), \tag{15}$$

where we recall that E_0 is the initial energy of the particle. In the case under consideration, the domain of energies is $[0,E_b]$, since the particle cannot have an energy lower than the potential minimum (which is 0) and escapes from the potential well when reaching the energy of the barrier E_b. In terms of the above probability, the distribution of first-passage times $\rho(t,E_0)$ can be found by considering

$$S(E_0,t)-S(E_0,t+dt)=\rho(t,E_0)dt, \tag{16}$$

so it is given by [2]

$$\rho(t,E_0)=-\frac{dS(E_0,t)}{dt}. \tag{17}$$

Hence, given the initial energy E_0 in the potential well, the mean first-passage time is defined as the first moment of t,

$$\tau(E_0)=\int_0^{\infty}dt\,t\rho(E_0,t). \tag{18}$$

Moreover, replacing (17) in (18) and integrating by parts leads to

$$\tau(E_0) = \int_0^\infty dt S(E_0, t), \tag{19}$$

where we have used that $S(E_0, t)$ vanishes in the limit $t \to \infty$. Then, using (15) and integrating (6) gives

$$\begin{aligned} \tau(E_0) &= \int_0^\infty dt \int_D dE P(E, t|E_0) \\ &= \int_0^\infty dt \int_D dE e^{t\mathcal{L}_{E_0}} \delta(E - E_0). \end{aligned} \tag{20}$$

If we apply the Fokker-Planck operator and use (6) again, we arrive to [2]

$$\mathcal{L}^\dagger_{E_0} \tau(E_0) = -1, \tag{21}$$

where $\mathcal{L}^\dagger_{E_0}$ is the adjoint to the Fokker-Planck operator $\mathcal{L}_E$, given by

$$\mathcal{L}^\dagger_{E_0} = e^{\beta F(E_0)} \frac{\partial}{\partial E_0} e^{-\beta F(E_0)} D(E_0) \frac{\partial}{\partial E_0}. \tag{22}$$

The next step is to isolate $\tau(E_0)$ in (21) using (22) and taking the appropriate boundary conditions on ∂D, the boundary of the domain D [3, 6]. From equation (21), we see that

$$\frac{\partial}{\partial E_0} \tau(E_0) = -\frac{e^{\beta F(E_0)}}{D(E_0)} \int_0^{E_0} dE' e^{-\beta F(E_0)}, \tag{23}$$

where we have used the reflecting boundary condition

$$\left. \frac{\partial}{\partial E_0} \tau(E_0) \right|_{E_0 = 0} = 0. \tag{24}$$

Integrating equation (23) gives the mean-first passage time as

$$\tau(E_0) = \int_{E_0}^{E_b} dE \frac{e^{\beta F(E)}}{D(E)} \int_0^E dE' e^{-\beta F(E_0)}, \tag{25}$$

where here we have imposed the absorbing boundary condition $\tau(E_b) = 0$ at the energy of the barrier, meaning that if the initial energy is $E_0 = E_b$, the particle immediately leaves the energy domain. Taking into account equations (8) and (10) for the energy diffusion coefficient and the free energy, respectively, we finally get [2]

$$\tau(E_0) = \frac{m}{\zeta k_B T} \int_{E_0}^{E_b} dE \, \frac{e^{\beta E}}{I(E)} \int_0^E dE' \, \Omega(E') e^{-\beta E'}. \tag{26}$$

We remark that the initial energy can be arbitrary within the energy domain, but below we consider that it corresponds to the energy of the particle at a potential minimum. We also highlight that in the considered situation, corresponding to the low friction limit, the mean first-passage is proportional to $1/\zeta$, in contrast to what happens in the high friction limit for which the escape time is proportional to ζ.

IV. THE MODEL

In order to define the problem and quantify the escape time, we consider the double-well potential

$$U(x) = \frac{a^2}{4b} - \frac{a}{2}(x - x_b)^2 + \frac{b}{4}(x - x_b)^4, \qquad a, b > 0, \tag{27}$$

where $x_b = (a/b)^{1/2}$ in such a way that it is symmetric around x_b, one minimum is located at $x = 0$, the local maximum is at $x = x_b$ and the position of the other minimum is $x = 2x_b$. Although we are interested in describing the escape from a single potential well, the above potential facilitates the implementation of the numerical simulations that we present in Sec. V.

The potential (27) is zero at the local minima, while the local maximum is given by

$$E_b \equiv U(x_b) = \frac{a^2}{4b}, \tag{28}$$

and characterizes the height of the barrier between the two minima. Furthermore, close to the minimum at the origin, the potential behaves as

$$U(x) = ax^2 + \mathcal{O}(x^3). \tag{29}$$

Thus, taking

$$a = \frac{m\omega_0^2}{2}, \qquad b = \frac{a^2}{4E_b} = \frac{m^2\omega_0^4}{16E_b}, \tag{30}$$

we can define the shape of the potential in terms of the frequency ω_0 and the energy E_b as input parameters for a given mass m. In particular, the position of the barrier becomes

$$x_b = \left(\frac{8E_b}{m\omega_0^2} \right)^{1/2}, \tag{31}$$

and the potential can be rewritten as

$$U(x) = \frac{m\omega_0^2}{8} x^2 \left(\sqrt{\frac{m\omega_0^2}{8E_b}} x - 2 \right)^2. \tag{32}$$

Since the potential is zero at the minima, we emphasize that the energy must be taken as $E \geq 0$.

As we show below, the behaviour of $\Omega(E)$ for small energies is required to obtain an asymptotic expression for the escape time. For this reason, we now concentrate on the situation in which the motion of the particle is confined close to the minimum at $x = 0$ with small E, and compute $I(E)$ under these conditions. Close to this minimum, the potential takes the form $U(x) \simeq m\omega_0^2 x^2/2$ and the two roots of the equation $E - U(x) = 0$ are given by $-x_E$ and x_E, where $x_E = \sqrt{2E/(m\omega_0^2)}$. Hence, from equation (13), for small E the number of microstates becomes

$$I(E) = 2\sqrt{2mE} \int_{-x_E}^{x_E} \mathrm{d}x \sqrt{1 - (x/x_E)^2}. \tag{33}$$

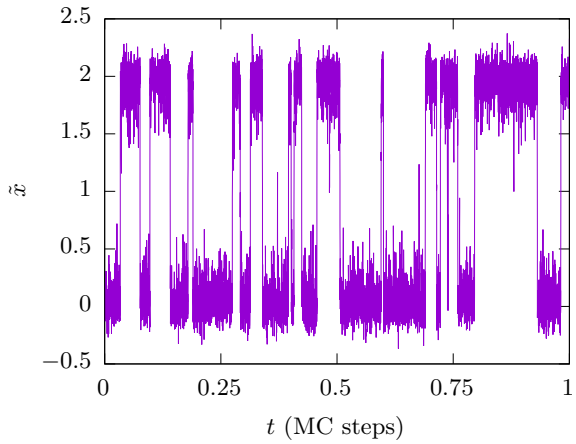

FIG. 1: MC simulations of the trajectory of the particle in the double-well potential. We observe oscillations between the two minima at $\tilde{x} = 0$ and $\tilde{x} = 2$. Here we take $\alpha = 5$.

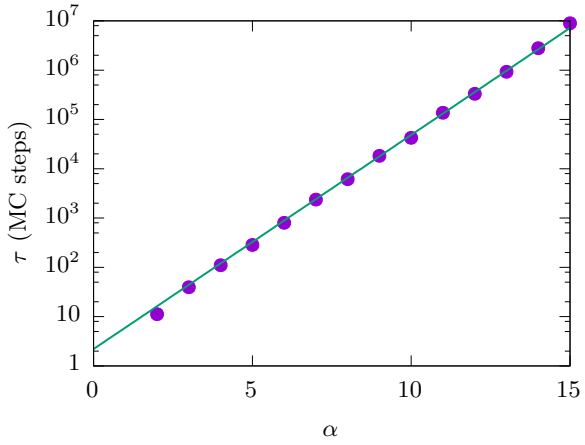

FIG. 2: MC simulations where we observe the exponential behaviour for large α. The solid line corresponds to the approximated expression $\tau = \tau_0 e^{\alpha}$ with $\tau_0 = (2.2 \pm 0.2)$ MC steps as obtained by fitting the simulations.

Performing now the change of variables $x = x_E \sin\varphi$, the above expression can be computed as

$$I(E) = \frac{4}{\omega_0} E \int_{-\pi/2}^{\pi/2} \mathrm{d}\varphi \ \cos^2\varphi = \frac{2\pi}{\omega_0} E. \tag{34}$$

Therefore, using equation (14), for E close to zero the density of states is given by

$$\Omega(E) = \frac{2\pi}{\omega_0}. \tag{35}$$

Taking into account the result in equation (35) and considering the following arguments, as discussed in [2], we obtain an expression for the mean first-passage time that is valid when there is a relatively large potential barrier as compared with $k_{\mathrm{B}}T$. Coming back to expression (26) for $\tau(E_0)$, we note that the second integral is dominated by small E' due to the exponential damping, while the first one is dominated by E near E_b. Since each integral leads to a factor β, using (35) the mean-first passage time (26) can be approximated as

$$\tau = \frac{2\pi m}{\zeta} \frac{k_{\mathrm{B}} T e^{\beta E_b}}{\omega_0 I(E_b)}. \tag{36}$$

We then observe that for relatively large βE_b, the escape time follows the exponential law $\tau \sim \tau_0 e^{\beta E_b}$, which we test below by implementing MC simulations.

V. SIMULATIONS

In order to test the validity of the exponential law found for the mean-first passage time τ, we perform MC simulations of a single particle evolving under the action of the external potential $U(x)$ given by (32) in the canonical ensemble at temperature T. In the simulations and in the following discussion, we use rescaled variables for energy and position which are defined as $\tilde{E} = E/E_b$ and $\tilde{x} = x/x_b$, respectively. Accordingly, for the external potential we use $\tilde{U} = U/E_b$. We also define

$$\alpha = \frac{E_b}{k_{\mathrm{B}} T} \tag{37}$$

which accounts for the ratio of the energy at the potential barrier to the thermal energy. It is also the variable that we can vary in the simulations. In Fig. 1, we show the evolution of the particle in the double-well potential for $\alpha = 5$.

In the MC simulations, we follow the standard Metropolis algorithm in which random displacements are performed that can be accepted or not depending on the energy of the particle in each MC step. We utilize a calibration procedure to set the maximum displacement in order to achieve an acceptance ratio of 50%. The considered initial energy for the particle is $\tilde{E}_0 = 1/(2\alpha)$ (kinetic energy at temperature T), meaning that $\tilde{U} = 0$, and we choose to put the particle in the first potential well, that is in $\tilde{x} = 0$. Performing the random displacements, the particle achieves the potential barrier, for which $\tilde{E} = 1$, after a certain number of MC steps that we consider as the unit of time t. We then count the number of MC in each realization of the simulation and the mean-first passage time τ corresponds to the average over several realizations. For each potential barrier, we average over 10^3 realizations.

We see two different ways of performance, depending on the α. On one hand, when we have have a large α the result has an exponential behaviour, since $\tau \sim \tau_0 e^{\beta E_b}$ with $\beta E_b = \alpha$, obtaining the mean first-passage time shown in Fig. 2. We fit the result for relatively large α to an exponential of the form $\tau_0 e^{\alpha}$, allowing to obtain a value for τ_0. In this way, for the results in Fig. 2 we obtain $\tau_0 = (2.2 \pm 0.2)$ MC steps. On the other hand,

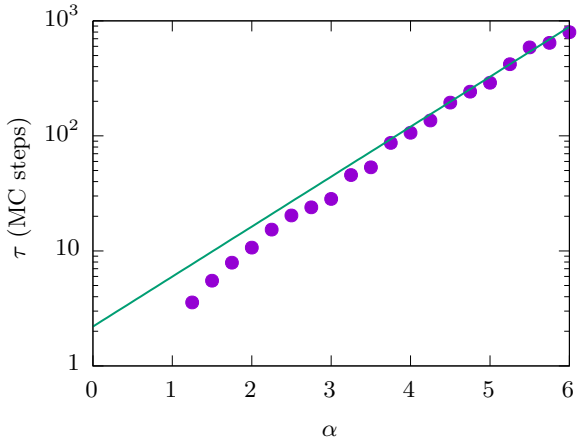

FIG. 3: MC simulations showing the deviation from the exponential behaviour for small α.

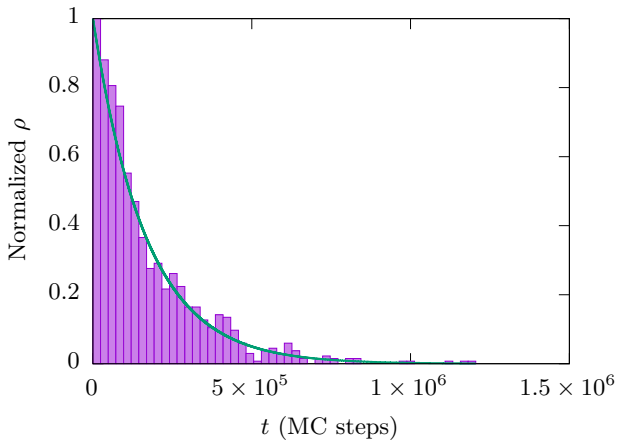

FIG. 4: Histogram of the escape times for $\alpha = 11$ using MC simulations. The normalized first-passage time distribution (solid line) is superimposed to the boxes.

when α is small (near enough to 1), meaning that the potential barrier and thermal energy are similar, the exponential behaviour does not fit well, see Fig. 3. We note that for small α, the mean first-passage times are close to 1, meaning that in most of the realizations the particle escapes from the potential well after one or very few MC steps. This behaviour does not allow for a correct calibration of the maximum displacement, so the MC method is not reliable in this case.

To get insight into the escape process, we take the times needed to reach the energy barrier in all realizations for a specific α and construct a histogram, shown in Fig. 4. This allows us to analyze the first-passage time distribution $\rho(E_0, t)$. As shown in [7], the survival probability at late times takes the form $S(E_0, t) = e^{-t/\tau(E_0)}$ and therefore, using (17), we obtain the exponential distribution $\rho(E_0, t) = e^{-t/\tau(E_0)}/\tau(E_0)$. The normalized first-passage distribution is also shown in Fig. 4, highlighting the exponential behavior observed in the simulations.

VI. CONCLUSIONS

In conclusion, we studied the problem of the escape of a particle from a potential well in the low friction limit by means of an energy diffusion approach. We performed a theoretical analysis describing the average time to reach the barrier, the mean first-passage time τ, which was complemented by MC simulations in the canonical ensemble. We obtained the behaviour of the mean first-passage time as a function of the ratio of the barrier energy to the thermal energy, denoted as α, and the simulations confirm the expected exponential behaviour when this ratio is large enough. However, in the simulations we observed that the behavior of τ is not exponential when the barrier energy is similar to the thermal energy. On the one hand, this is expected from a theoretical point of view. On the other hand, the MC simulations are problematic in this regime since the small values of the first-passage times prevent from a good calibration of the acceptance rate, which implicitly define the time scale in the simulations. To study the problem when α is close to 1, it would be interesting to implement a different simulation technique such as molecular dynamics or directly solving the Langevin equations.

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