Average lifetimes of a metastable state at low barrier in the overdamped regime

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Abstract. Thermal decay of a metastable state is a process revealing itself in particular in the contemporary single-molecule pulling experiments. Unfortunately, some approaches used for the interpretations of these experiments in the literature are incorrect and misleading. We prove this statement in the present work. For this aim, the most important characteristic of the decay process which is the average lifetime of a Brownian particle in a metastable state is considered. For this state two typical potentials are used: the Lennard-Jones and cubic potentials. We concentrate on the case of strong friction (overdamped regime) and low barrier since these conditions are typical for the mentioned experiments. We calculate the average lifetimes using five approaches, including dynamical modeling, and compare them with each other.

1. Introduction

The problem of thermal decay of a metastable state in presence of friction is encountered in many fields of the natural sciences: physics of nuclear fission [1–3], chemical physics [4–6], physics of Josephson junctions [7–9], biology [10,11], etc. For the first time, this problem was considered dynamically (i.e. accounting for the dissipative effects) by Kramers in his famous paper [12]. That is why this problem is called the Kramers problem [13–15]. Further works mostly were devoted to the generalization of the Kramers’ results for the multi-dimensional case [16–18], to their elaboration [19–21], to their extension for the non-Markovian processes [5,20] and to the case of the microcanonical ensemble [22–24].

Relatively recently new experimental works appear on stretching of the single polymer molecule [10,25,26]. To extract the information on the binding energy from these experiments, the authors of these works apply the Kramers formalism too. However, there is a distinct feature in these experiments which leads us out of the framework of the usual approach. Namely, in these experiments, the height of the barrier $U_b$, which a fictitious Brownian particle must overcome, becomes rather small in comparison with the average thermal energy $k_B T$ ($k_B$ denotes the Boltzmann constant, $T$ stands for the temperature). So, the governing parameter

$$G = \frac{U_b}{k_B T},$$

is smaller than unity, $G < 1$). The second dimensionless value characterizing the Kramers problem is a damping parameter.
\[ \varphi = \frac{\eta}{\sqrt{mC}}. \]  

Here \( \eta \) and \( m \) denote the friction and inertia parameters, respectively; \( C \) stands for the stiffness of the potential well. For the single-molecule pulling experiments, the typical value of \( \varphi \) is rather large \( (\varphi \approx 10) \). At this value, the Brownian motion proceeds in the overdamped regime. Physically, it means that (i) momentum relaxation happens much faster than the coordinate relaxation and (ii) the kinetic energy of the Brownian particle dissipates totally during one bounce in the well.

In his work [12], Kramers derived an approximate formula for the quasistationary rate in the overdamped regime

\[ R_{K0} = \frac{\omega^2}{2\pi\beta} \exp(-G). \]  

Here \( \omega = \sqrt{C/m}, \beta = \eta/m. \) The accuracy of this formula becomes worse as the governing parameter decreases. However, this is equation (3) which is taken for the analysis of the data on the single-molecule pulling experiments in [25]. In [27], this approach has been criticized and a formula has been proposed which is claimed to provide a better description of the decay process for the case of a low barrier. Moreover, in [27] Eq. (3) is interpreted as “the Kramers theory” and is declared to “break down dramatically” at \( G \leq 1 \). Our present work is motivated by the paper [27] and we are going to demonstrate that the Kramers theory, if applied correctly, works reasonably well for the low barrier systems, too, contrary to what is claimed in [27].

### 2. The model

We performed our calculations for two potential profiles used in [27]. They are shown in Fig. 1.

![Diagram](image1.png)

**Figure 1.** Two potentials used in [27] and in the present work: the thin line with a barrier corresponds to the cubic potential; the thick line denotes the Lennard-Jones potential. The arrows indicate the bottom of the well and (only for the cubic potential) the barrier position. Note that the potentials are divided by the barrier height of the cubic potential.

The potential with a barrier is a cubic one; it reads:

\[ U(q) = \sum_{i=0}^{3} a_i q^i. \]
The coefficients \( a_i \) are defined by the conditions

\[
0 = \sum_{i=1}^{3} i a_i q_i^{i-1} \quad \text{at} \quad q = q_c \quad \text{and} \quad q = q_b,
\]

(5)

\[
U_b = \sum_{i=0}^{3} a_i q_i^i, \quad 0 = \sum_{i=0}^{3} a_i q_i^i.
\]

(6)

The input parameters for the potential are as follows: \( U_b = 6, \ q_c = 1.0, \ q_b = 1.6. \)

The second potential is the Lennard-Jones one whose parameters are adjusted to make the depth of well equal to \(-U_b\) and to have the stiffness at \( q_c \) close to the one of the cubic potential. All calculations below have been performed at \( \varphi = 15 \), the value of \( G \) has been varied.

In the present work, we model the decay process solving numerically the stochastic ordinary differential equation in the configuration space (the Langevin equation for the coordinate \( q \), LEq). In doing so, we use our expertise from the previous studies [28,29]. The LEq has a form

\[
dq = -\frac{1}{\eta} \frac{dU}{dq} \, dt + \sqrt{\frac{2k_B T}{\eta}} \, dW.
\]

(7)

Here the increment of the Wiener process, \( dW \), has the normal distribution with zero average and the variance \( dt \). To solve Eq. (7), the Euler scheme is applied (see, e.g. [29]).

Each trajectory starts at the bottom of the potential pocket and is modeled until either (i) a predefined time lapse \( t_d \) is expired or (ii) an absorbing border (sink) \( q_s \) is reached. In the latter case, we deal with the useful trajectory. The numerical (‘n’) time-dependent decay rate calculated at the sink (‘s’) reads

\[
R_{sn}(t_j) = \frac{1}{N_{tot} - N_{s}(t_j)} \frac{\Delta N_s}{\Delta t}.
\]

(8)

Here \( N_s(t_j) \) is the number of trajectories reaching \( q_s \) by the time moment \( t_j \); \( \Delta N_s \) represents the number of trajectories arriving at the sink during the time lapse \( \Delta t \) between \( t_j \) and \( t_{j+1} = t_j + \Delta t \).

3. The numerical rates

Typical time-dependent rates normalized to their quasistationary values \( R_{sd} \) are presented in Fig. 2 (oscillating curves with symbols). The rates calculated with the cubic and LJ potentials are presented in the left and right columns, respectively. One sees, that even for the low barrier systems, the quasistationary values of the rates are established. These values are evaluated by a universal automatized method described in [30,31].

The statistical errors of \( R_{sd} \) do not exceed 3%. Generally speaking, the time dependences of the rates are similar at low \( (G = 0.3) \) and high \( (G = 2.0) \) barrier and for both potentials employed.

The dependence of the quasistationary rate upon the value of \( q_s \) is a special question. For the case of the barrier consisting of two smoothly matched parabolas, this question was studied in detail in [32]. The cubic potential is rather similar to that one, therefore one expects a similar dependence of \( R_{sd} \) upon \( q_s \). This dependence obtained in the present study is shown in Fig 3. Our expectation for the cubic potential is confirmed: as \( q_s \) increases \( R_{sd} \) first decreases and then stabilizes becoming independent upon \( q_s \). For the case of the Lennard-Jones potential, the decrease of \( R_{sd} \) with \( q_s \) is also observed; however, there is no saturation at all. This happens due to the fact that this potential does not possess a pronounced descent beyond the barrier.
Figure 2. Typical time-dependent rates $R_{sn}(t)$ divided by their quasistationary values $R_{sd}$ (the curves with symbols). The horizontal lines correspond to the unity and guide the eye.
Figure 3. The dependence of the quasistationary rates $R_{SD}$ upon the position of the sink $q_s$. Squares – LJ potential, circles – cubic potential. The statistical errors (2%) are within the symbols.

4. Average (characteristic) lifetimes

In fact, in [27] some average (characteristic) lifetimes of the Brownian particle at the metastable state, not the quasistationary rates, were discussed. The average lifetime is indeed very close to the inverse quasistationary rate, however, only in the case of a high barrier. Meanwhile, the work [27] is claimed to be focused on the opposite case, $G < 1$.

In the present work, we calculate the mean (characteristic) lifetime using five approaches. The first one is based on the results of the dynamical modeling and reads:

$$\tau_{SD} = R_{SD}^{-1}. \quad (9)$$

The second approach is to find the mean time of the first passage at the absorbing point (sink) [33–35]

$$\tau_{MFPT} = \frac{\eta}{k_B T} \int_{q_c}^{x_c} dy \exp\left(\frac{U(y)}{k_B T}\right) \int_{-\infty}^{y} dz \exp\left(-\frac{U(z)}{k_B T}\right). \quad (10)$$

In [27] this equation, although with an undefined adjusting multiplier instead of $\eta/(k_B T)$, was used and called, by some reason, an “Ornstein-Uhlenbeck method”. As far as we know, no such method is known in the literature. There are either the Ornstein-Uhlenbeck process [34,36,37] or the Ornstein-Uhlenbeck noise [4,5]. In fact, Eq. (10) is derived from the Smoluchowski equation for the probability density $f(q,t)$ [4,34]:

$$\frac{\partial f}{\partial t} = \frac{1}{\eta} \frac{\partial}{\partial q} \left( df + k_B T \frac{\partial f}{\partial q} \right). \quad (11)$$

Therefore, there cannot be any undefined adjusting multiplier in Eq. (10).

The third approach consists in finding the value $\tau_{KI}$ which is inverse to the integral Kramers rate [29,38]

$$\tau_{KI} = \frac{\eta}{k_B T} \int_{q_c}^{q_s} dy \exp\left(\frac{U(y)}{k_B T}\right) \int_{-\infty}^{q_b} dz \exp\left(-\frac{U(z)}{k_B T}\right). \quad (12)$$

We would like to comment on this equation somewhat more. Inverse to this equation, what we called the integral Kramers rate, was derived for the overdamped case by Kramers in [12]. However, Kramers did not write this equation explicitly, because in the absence of computers it was useless. Nevertheless,
in some later publications the formula for the integral Kramers rate has been written down (see, e.g., Eq. (5.109) in the Risken’s book [34], Eq. (3) in [29], and Eq. (2) in [38]).

Comparing Eqs. (10) and (12) one sees that they are very similar. The difference is that in Eq. (10) for τMFPT the integrals are coupled and one needs evaluating the double integral whereas in Eq. (12) the integrals are decoupled and one needs calculating just two one-dimensional integrals. Note, that the authors of [27] in their work stress an advantage of the approximate formulas, not including any integrals, in comparison with the (exact!) equation for τMFPT. We believe that these advantages left in the 20th century. Presently, using modern software and computers it is as fast to compute a one-dimensional integral as to evaluate a formula not including integrals.

Yet, we include in our analysis a “simplified Kramers time”

$$\tau_{K0} = \frac{2\pi\beta}{\omega^2} \exp(G)$$

(13)
too (compare to Eq. (3)). Note, that the times τK0 and τKI cannot be evaluated for the LJ potential due to the absence of the barrier top at finite values of the coordinate.

Finally, we compute the most exact (‘m’) numerical lifetime (or decay time) [39] resulting from the dynamical calculations

$$\tau_{SNM} = N_{tot}^{-1} \sum_{i=1}^{N_{SD}} t_{si} + (N_{tot} - N_{SD})(t_D + R_{SD}^{-1}).$$

(14)

Here the summation is performed over all the $N_{SD}$ trajectories which arrive at the sink during the time lapse of the dynamical modeling, $t_D$. The remaining $N_{tot} - N_{SD}$ trajectories decay in the quasistationary regime with the mean lifetime $t_D + R_{SD}^{-1}$. We have performed some test calculations varying $t_D$ and have found the variation of $\tau_{SNM}$ within the framework of the numerical errors.

In many cases (though, not always) the five characteristic times are close to each other. That is why we compare those by means of the following fractional differences:

$$\xi_{SD} = \tau_{SNM} \tau_{SD}^{-1} - 1,$$

(15)

$$\xi_{MFPT} = \tau_{SNM} \tau_{MFPT}^{-1} - 1,$$

(16)

$$\xi_{KI} = \tau_{SNM} \tau_{KI}^{-1} - 1,$$

(17)

$$\xi_{K0} = \tau_{SNM} \tau_{K0}^{-1} - 1.$$  

(18)

In Fig. 4, some of the characteristic times (Figs. 4a and 4c) as well as the fractional differences (Figs. 4b and 4d) are shown. The upper row of panels corresponds to the cubic potential whereas the lower row is for the Lennard-Jones potential. For the cubic potential, we present the most different times $\tau_{SNM}$ and $\tau_{K0}$ (Fig. 4a). Even these values appear to be hardly distinguished at all values of the governing parameter including $G < 1$. Thus, the statement of [27] about the “dramatic breakdown of the Kramers theory” is not correct. For the cubic potential, even for extremely small $G = 0.1 \tau_{K0}$ exceeds $\tau_{SNM}$ only by a factor of 2. This is to be expected because Eq. (13) is approximately valid for the quasistationary regime whereas at small $G$ most of the decays happen in the transient stage. Remember, that for the Lennard-Jones potential, $\tau_{K0}$ and $\tau_{KI}$ are not defined. Therefore, in Fig. 4c only $\tau_{SNM}$ is displayed and in Fig. 4d $\xi_{K0}$ and $\xi_{KI}$ are not shown.
Figure 4. As functions of \( G \) the following quantities are shown: The numerical mean lifetime \( \tau_{\text{snm}} \) [Eq. (14); panels (a) and (c)] and the fractional differences [Eqs. (15)-(18); panels (b) and (d)]. The value \( \xi_{K0} \) absents in panel (d) because \( \tau_{K0}^{-1} \) is not defined for the LJ potential. For the cubic potential, the absolute value of \( \xi_{K0} \) becomes rather large at \( G < 1 \) (the corresponding time \( \tau_{K0} \) appears in panel (a)).

5. Conclusions

This study might be timely for the recent nanoscale experiments with relatively low barriers [10,25,26]. In the analysis of these experiments, the model of the thermal decay of a metastable state is usually invoked. In our work, the decay process has been modeled solving the stochastic (Langevin) equation numerically. We have analyzed five approaches for finding the characteristic (mean) lifetime of a Brownian particle in a potential well in the overdamped regime (the damping parameter \( \varphi = 15 \)). We mostly have concentrated on the low barrier case (the governing parameter \( G < 1 \)). Our present work has been triggered by the article [27] where many of the statements we have found to be incorrect and misleading. This has been proved in the present work.

The approximate times resulting from the mean first passage time approach (Eq. (10)) and from the (inverse) integral Kramers formula (Eq. (12)) for the cubic potential appeared to be in good agreement with the exact mean lifetime \( \tau_{\text{snm}} \) resulting from the numerical modeling and Eq. (14): the largest difference has been 15\% at \( G = 0.1 \) (see Fig. 4b). Of course, the latter method requires the longest computer time.

To finalize, let us note that a similar study was published by us recently [40]. However, in that work, the cases of strong friction and low barrier were not emphasized. The integral Kramers formula and the mean first passage time approaches were not considered, too. In addition, that study was performed for a different potential (two smoothly matched parabolas).
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