Computer simulating of nanoprocesses:
Thermal jumps over a low barrier in the overdamped regime

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Abstract. We model numerically the process of a thermally activated decay of a metastable state over a low barrier in the overdamped regime. This process is typical for the recent nanoscale experiments reported in the literature. Within the framework of a novel unified computer code, two ways of modeling are applied: (i) the partial differential equation (Smoluchowski equation) and (ii) the stochastic ordinary differential equation (Langevin equation for the generalized coordinate). The advantages and disadvantages of both approaches are discussed and analyzed. Special attention is paid to the transient stage of the process yet the quasistationary stage is considered as well.

1. Introduction

Single-molecule manipulating experiments reported in [1–3] are all in the nanoscale and consequently are subjects of significant thermal fluctuations. These fluctuations result in jumps over a barrier and must be accounted for when extracting information from the experimental data [4,5]. The approximate analytical formulas derived in [6,7] are not expected to be applicable in the case of a low barrier which is typical for the single-molecule pulling experiments [1,2]. Moreover, hunting a simple analytical formula for the lifetime of a particle in the well [8,9] sometimes leads to results that are shown [10] to be misleading.

Thus, for the case of the low barrier, numerical modeling of the decay process is of particular importance. There are two ways of effective modeling in the overdamped regime: (i) the partial differential equation (Smoluchowski equation, SE) and (ii) the stochastic ordinary differential equation (Langevin equation for the generalized coordinate, LEq). We have acquired some experience in both approaches in our previous studies [11–13], yet the problem of the low barrier has not been addressed in those articles. In the present study, we focus on the comparison between the SE and LEq and on the analysis of the advantages and disadvantages of both approaches. Earlier, the numerical solutions of these equations have been realized within the framework of two different computer codes [11,12]. Recently, we have unified these two codes. Thus, we can compare the relevant results under the same values of the input parameters.
2. Smoluchowski equation (SE)

In [14], it was demonstrated that the decay rate is defined mostly by two dimensionless parameters: a governing parameter $G$ and a damping parameter $\varphi$. These parameters read

$$ G = \frac{U_b}{\theta}, $$

$$ \varphi = \frac{\eta \tau_c}{2\pi m}. $$

Here $U_b$ is the height of the potential barrier limiting the potential well (sometimes the terms “pocket” or “trap” are used); $\theta$ is the average thermal barrier height of the vibrational motion; $\tau_c$ is the period of oscillations near the bottom of the trap; $m$ and $\eta$ are the inertia and friction parameters. In the present study, we are interested in the overdamped (spatial diffusion) regime which corresponds to $\varphi \gg 1 \ [15,16]$. To be more concise, all calculations here are performed for $\varphi = 15$. This does not restrict our results because both the SE and LEq are self-modelling, i.e.

$$ \eta_2 R_{at}(t/\eta_2, \eta_2) = \eta_1 R_{at}(t/\eta_1, \eta_1). $$

Here $R_{at}(t/\eta_1, \eta_1)$ denotes the time-dependent decay rate obtained at the given value of the friction parameter $\eta_1$.

The Smoluchowski equation for the probability density $\rho(q,t)$ reads [15]

$$ \frac{\partial \rho(q,t)}{\partial t} = - \frac{\partial}{\partial q} \left( \frac{\rho U(q)}{\eta} + \frac{\varphi \partial \rho}{\eta} \right). $$

(4)

Here $q$ denotes the dimensionless generalized coordinate of a fictitious Brownian particle; $U(q)$ stands for the potential energy; $j$ denotes the probability flux. In this work, we consider a barrier of the parabolic shape.

For solving Eq. (4), the following numerical scheme is applied

$$ \eta \frac{\rho_i^1 - \rho_i^0}{h_t} = \rho_i^0 \left( \frac{d^2 U}{dq^2} \right)_i + \frac{(dU)}{(dq)}_i \frac{\rho_i^{1+1} - \rho_i^{1-1}}{2h_q} + \frac{\varphi}{\eta} \frac{\rho_i^{1+1} - 2\rho_i^{0} + \rho_i^{1-1}}{h_q^2}. $$

(5)

Here $h_t$ and $h_q$ are the mesh steps for time and coordinate, respectively; $\rho_i^0 = \rho(t,q_i)$, $\rho_i^1 = \rho(t + h_t,q_i)$, $\rho_i^{1+1} = \rho(t + h_t,q_i + h_q)$, etc. Thus, the partial differential equation (4) is reduced to a system of linear equations with unknown values $\rho_i^1, \rho_i^{1-1}, \rho_i^{1+1}$. The matrix of the coefficients has a tridiagonal form and the system is solved by the Thomas algorithm [17].

In order to succeed with this algorithm, one must have a small probability density at the leftmost and rightmost points of the coordinate domain. Therefore, we use the potential energy of the following form

$$ U(q) = \begin{cases} 
\frac{C_c(q-q_c)^2}{2} & \text{at } q < q_m; \\
U_b - \frac{C_b(q-q_b)^2}{2} & \text{at } q_m < q < q_{mm}; \\
U_w + \frac{C_w(q-q_w)^2}{2} & \text{at } q_{mm} < q. 
\end{cases} $$

(6)

Here the subscript “$c$” indicates the bottom of the left well (trap), “$b$” refers to the barrier top, $C_c(b,w)$ denotes the stiffness. The input parameters for the potential energy are $U_b$, $q_c$, $q_b$, $q_{mm}$, $q_w$, and $r_{cb} = C_c / C_b$. The values $q_m, C_c, C_b, C_w, U_w$ are found from the continuity conditions for the potential energy and its first and second derivatives at the matching points $q_m$ and $q_{mm}$. In this work, $q_c = 1.0$, $q_b = 1.6$, $r_{cb} = 1.0$; the potential landscape is shown in Fig 1 in different scales. The two curves correspond to two different sets $q_{mm}$ and $q_w$: the curve with the shallower right well corresponds to $q_{mm} = 3.0$ and $q_w = 4.0$ (thick solid line) whereas the deeper one is obtained with $q_{mm} = 4.0$ and $q_w = 5.5$ (line
with circles). The potential energy represented by two smoothly joined parabolas and used in [12] is also shown in Fig. 1 by the dashed line. One sees in Fig. 1b that all three potential profiles coincide in the vicinity of the metastable state and barrier.

To run the scheme (5), we have to define the left and right border points. These points ($q_L$ and $q_R$) are the solutions of the equation $U(q) = k_e U_b$, i.e. the intersections of the thick horizontal line and the curve $U(q)$ in Fig. 1a. In the present calculations, $k_e = 70$ is used.

![Figure 1](image-url)  
**Figure 1.** Coordinate dependence of the potential energies used in the present work (blue solid line – shallow, line with circles – deep) and in [12] (red dashed line) in different scales.
The initial condition for the probability density reads

$$\rho(q, t = 0) = \begin{cases} 
(2\pi\sigma_0^2)^{-1/2}\exp\left[-\frac{(q - q_c)^2}{2\sigma_0^2}\right] & \text{at } q < q_b \\
0 & \text{at } q > q_b 
\end{cases}$$

with $\sigma_0^2=0.0030$. This value of $\sigma_0^2$ is significantly smaller than the variance of the quasi-equilibrium distribution (0.090).

The decay rate via the point $q_a$ is evaluated using the flux-over-population method:

$$R_{Sat}(t) = \frac{j(t, q_a)}{\int_{q_L}^{q_a} \rho(q, t) dq}.$$  \hspace{1cm} (8)

The rates resulting from the SE are presented in Fig. 2. We try calculating these rates for both deep and shallow potential profiles of Fig. 1 at several points $q_d = 1.4, 1.6, 2.0, 3.2, 4.0,$ and 5.0. Calculations at $q_a = 1.4, 1.6, 2.0$ terminate successfully for both potentials resulting in the rates which are potential-independent (i.e. they are the same for the shallow and deep right pockets). However, for the shallow pocket, calculations crashed for $q_a \geq 3.2$, namely, it is impossible to determine the decay rate. With the deep potential, the SE modeling results in reasonable rates not only at $q_a = 1.4, 1.6, 2.0$, but for $q_a = 3.2, 4.0$ too, and crashes at $q_a \geq 5.0$. This demonstrates that even the second well with the depth $50U_b$ might be not enough to provide the numerical solution of the SE. This is an unpleasant feature of the approach based on this equation.

Let us stress one more feature of the rates in Fig. 2. Their quasistationary values are the same at all values of $q_a$, although the transient behavior depends upon the value of $q_a$ significantly. We will see below that it is not so in the case of the LEq modeling.

![Figure 2](image-url)

**Figure 2.** Time evolution of the decay rate calculated using Eq. (8) with different positions of $q_a$. $G = 1.00$, $\varphi = 15$. $R_{Sat}$ and $t$ are shown in arbitrary units, for other details see text.
3. Reduced Langevin equation (LEq)

Let us now study the same problem using the LEq which reads in the numerical form

\[ q^{(n+1)} = q^{(n)} + \frac{1}{\eta} \left( \frac{dU}{dq} \right)^{(n)} \tau + b^{(n)} \sqrt{\frac{\theta}{\tau}}. \]  

(9)

Here the superscripts refer to the consequent time moments \( t^{(n)} = n\tau; b^{(n)} \) are the Gaussian random numbers with zero average and variance equal to 2. These numbers are obtained by means of the Marsaglia method [18] and a uniform random number generator built by us using the results of [19]. The generator is based on the “long integer” values of C-language and its period is estimated as \( 2^{64} = 1.84 \times 10^{19} \) which is sufficient for our needs. Note, that using a standard generator based on “integer” values, we sometimes face the periodic behavior of the pseudo-random numbers.

Solving Eq. (9) at each time step \( \tau \), we model \( N_{at} \) trajectories. Each trajectory starts at \( q_c \) and runs no longer than \( t_B \). Some trajectories reach the absorbing border \( q_a \) at \( t_a \), i.e. the metastable state decays. The time-dependent rate decay is evaluated as

\[ R_{Lat}(t) = \frac{1}{N_{tot} - N_{at}} \frac{\Delta N_{at}}{\Delta t}. \]  

(10)

Here \( N_{at} \) denotes the number of trajectories arriving at \( q_a \) by the time moment \( t \); \( \Delta N_{at} \) is the number of trajectories coming at \( q_a \) during the time lapse \( \Delta t \). Typical dependencies \( R_{Lat}(t) \) for different potential shapes at large value of the damping parameter are presented, e.g., in [12]. However, in that work, a harmonic potential formed by two smoothly joint parabolas was used (dashed line in Fig. 1), whereas in the present work this potential is supplemented either by a deep or shallow tail.

Therefore, in Fig. 3 we show the rates \( R_{Lat}(t) \) for two potentials of Fig. 1. The same values of \( q_a \) are used here as in Fig. 2. However, one now realizes that the meaning of \( q_a \) in these two types of calculations is different. In the present modeling, \( q_a \) indicates the absorptive border. Therefore, one sees in Fig. 3a that, as \( q_a \) moves closer to the barrier, the quasistationary rate becomes larger. This is the effect of the backscattering considered in detail in [20]. Note, that in the calculations presented in Fig. 3a, the tail of the potential does not matter since the absorptive border is very close to \( q_b \).

Comparing Figs. 3b and 3c one sees, that as the absorptive border moves further from \( q_b \), the difference in the deep and shallow potentials becomes more significant. For the deep potential (Fig. 3b), the time-dependent rates calculated at \( q_a = 3.2 \) and 4.0 look very much the same: the rate \( R_{Lat}(q_a = 4.0) \) is just shifted to somewhat larger times corresponding to the longer descent from the barrier.

In Fig. 3c, the rate \( R_{Lat}(q_a = 4.0) \) is not even shown because it takes extremely long time for this rate to reach the quasistationary value. The rate \( R_{Lat}(q_a = 3.2) \) is significantly shifted to longer times. The reason for that is the different behavior of the deep and shallow potentials displayed in Fig. 1c. The shallow potential is more gradual near \( q_a = 3.2 \) making the rate to rise slower.

One more feature of the rates is seen when one compares Figs. 3b and 3c. Namely, after different transient behavior, the rates calculated at \( q_a = 2.0, 3.2, \) and 4.0 reach approximately the same value \( R_B = 3 \).

Note, that it takes significantly longer computer modeling (by a factor of 100) to obtain the rates \( R_{Lat} \) in comparison with \( R_{Sat} \). This is a disadvantage of the Langevin approach. But the advantage of this approach is that it never crashes. Moreover, for the case of a cusped (edge-shaped) potential considered in [6,13,21] the SE modeling does not work at all due to a strong discontinuity of the force, whereas the LEq modeling works without any problems. This seems to be an important advantage of the Langevin approach since the cusped potential is applicable for the electron transfer chemical reactions [22].
Figure 3. The time evolution of the dynamical decay rate (oscillating curve with symbols) with its quasistationary value (thin horizontal line) for shallow and deep potential profiles at different values of \( q_a \). \( G = 1.00 \), \( \varphi = 15 \).

4. Direct comparison of the LEq and SE rates
In Fig. 4, we present the results of the direct comparison between the time-dependent rates resulting from the LEq and SE modeling for low barrier (\( G \leq 1 \)) at the same conditions. These rates are evaluated
at $q_a = 3.2$ for the deep potential, therefore the effect of the variations of $q_a$ mentioned in the previous section is insignificant. We observe in each panel of Fig. 4 that the rates $R_{Lat}(t)$ and $R_{Sat}(t)$ are in very good agreement. The only difference is that the rate $R_{Sat}(t)$ always attains its quasistationary value slightly earlier than the rate $R_{Lat}(t)$ does. This is definitely due to the final width of $\rho(q, t = 0)$ (see Eq. (7)).

![Figure 4](image-url)

**Figure 4.** The time-dependent rates $R_{Lat}(t)$ (curves with triangles), their quasistationary values (horizontal lines), and $R_{Sat}(t)$ (curves without symbols) calculated for four values of the governing parameter. $\varphi = 15$. $q_a = 3.2$, the deep potential.

5. Conclusions

In the present work, the numerical modeling of the thermally activated decay of a metastable state over a low barrier in the overdamped regime is performed. This is a typical situation in the nanoprocesses like single molecular pulling experiments [4,5].

Two ways of modeling are applied: (i) the partial differential equation (Smoluchowski equation, SE) and (ii) the stochastic ordinary differential equation (Langevin equation for the generalized coordinate $q$, LEq). The time evolution of the rates and their quasistationary values appeared to be very close within the applied two approaches provided they are calculated well beyond the barrier.

The SE allows to perform calculations significantly faster. For the successful numerical solution of this equation, it is necessary to supplement the potential energy profile with an additional deep well to the right of the metastable state. However, with some potential tails the SE calculations crash. The LEq calculations are by a factor of 100 longer. Yet these calculations do not have such a problem.

The point at which the rate is determined in these two approaches has different meanings: in the case of the SE, it is just the registration point, whereas in the case of the LEq, it is the absorption point (point of no return).
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