Two ways for finding the thermal decay rate at weak friction

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Abstract. We model the thermal decay of a metastable state at weak friction (the underdamped regime), the phenomenon which might be met in many branches of natural and technical sciences. The profile of the metastable state is considered as a pure parabola. We quantitatively compare the decay rate obtained from the phase space dynamics with the rate coming from the approximate energy diffusion approach which should be correct in the case of relatively weak friction. Both the phase space and energy diffusion dynamics employ the Langevin-type equations, however for the different stochastic variables. The results of the comparison reveal that the level of agreement between these two approaches depends not only upon the damping parameter (as qualitatively expected) but also upon the thermal energy.

1. Introduction

There is much in common in such different processes as the fission process of excited atomic nuclei [1–3], chemical reactions [4–6], and the single molecular pulling experiments [7–9]. All these (and many other) processes can be viewed as a thermal induced decay of a metastable state. Accounting for thermal fluctuations is vital for the functioning and performance of the micro- and nanomotors [10–12] as well as for the superconducting nanowires [13–15].

Arrhenius was the first who found the quantitative law of this phenomenon [16] considering purely statistical arguments. Much later Kramers, in his seminal work [17], incorporated the dynamical ingredients into the description of the thermal induced decay. Depending on the friction strength, Kramers separated two limiting regimes of random motion and thermal decay: the energy diffusion regime and the overdamped regime. Nowadays it is known that the former is applicable, for instance, for the phase slippage phenomena in superconducting nanowires [13–15] whereas the latter is realized in the biological problems [8,18].

In the present work, we compare quantitatively two ways for describing the decay process at weak friction: the Energy Diffusion (ED) approach and the Phase Space Diffusion (PSD) approach. Although it is clear that the latter is more accurate (we will call it exact), it is not known what is the amount of the deviation of the former from this exact approach. This is the purpose of the present work to quantify the deviation.

The decay process is characterized by the decay rate whose time-dependence is a subject of the initial conditions. The definition of the time-dependent decay rate in the discrete form reads

$$R_a(t) = \frac{1}{N_{tot} - N_at} \frac{\Delta N_{at}}{\Delta t}. \quad (1)$$
Here \( N_{at} \) is the number of Brownian particles reaching the absorptive border by the time moment \( t \), \( \Delta N_{at} \) is the number of particles attaining this border during the time interval \( \Delta t \). This definition does not depend upon the way of describing the decay process and is used below both for the ED and PSD. Note, that after some transient stage the rate reaches its quasistationary value which does not depend upon the initial conditions (see, e.g. Fig. 3 in [19]).

2. Model
In the ED approach the motion of a Brownian particle is described either by the energy (\( E \)) diffusion equation

\[
\frac{\partial g}{\partial t} = \beta \frac{\partial}{\partial E} \left( E g + \theta E \frac{\partial g}{\partial E} \right)
\]

(2)

for the probability density \( g(E,t) \) or by the following stochastic differential equation (ED Langevin equation, EDLE):

\[
E_{n+1} = E_n - \beta (E_n - \theta) \tau + \sqrt{\beta \theta E_n \tau} b_n.
\]

(3)

Here \( E_n (E_{n+1}) \) is the energy of the Brownian particle at the time moment \( t_n \) (\( t_{n+1} \)), \( \beta \) is the damping coefficient, \( \theta \) is the mean thermal energy, \( \tau \) is the time step of the modeling, \( b_n \) is the random number possessing a normal distribution with zero average and variance 2. We use the latter approach according to our previous experience [2,20,21].

Equations (2) and (3) imply that the potential pocket is parametrized by a parabola (the “edge” potential, Fig. 1; see also Fig. 2 in [17]). This is the only potential for which the action is proportional to the energy:

\[
I = E \tau_c.
\]

(4)

Here \( \tau_c \) is the period of oscillation near the bottom of the well.

![Figure 1](image_url)  
**Figure 1.** The edge potential used in the present work is shown as a function of the generalized coordinate. The particles initially are located in the left well (at \( q_c \)) and are eliminated from the consideration (“absorbed”) as soon as they cross the barrier in the case of ED approach or when they reach \( q_a \) in the case of PSD approach. Note that potential is normalized and thus dimensionless.
Since Eq. (3) was not used in the literature before, we performed its validation in the following way. The normalized stationary (equilibrium) distribution of the Brownian particles in the well according to Eq. (2) (or Eq. (3)) with zero flux reads
\[ g_{eq} = \theta^{-1} \exp(-EG/U_b). \] (5)
It results in the relation \( \langle E/U_b \rangle = 1/G \). Our calculations for the different values of parameter \( G \) demonstrate good agreement with this average value within the statistical errors which do not exceed 2%.

The initial value of the energy is \( E_0 = 0.01\theta \); we have checked that the results of the modeling do not depend upon \( E_0 \) as long as \( E_0 < 0.1\theta \). The modeling is terminated when either the time lapse \( t_{\beta} \) is expired or the energy of the particle exceeds the barrier height \( U_b \). The structure of Eq. (3) shows that, provided \( \theta \) is kept constant, for any two different values of the damping coefficient, the equality
\[ \frac{R_{a1}(t\beta_1)}{\beta_1} = \frac{R_{a2}(t\beta_2)}{\beta_2} \] (6)
holds (self-similarity property). This makes the EDLE very attractive from the computer time point of view.

However, the EDLE is only approximate: it is expected to produce the physically correct result at very small values of \( \beta \). The PSD approach is applicable at any friction strength. Thus, we simulate the decay process of the same metastable state by means of the phase space Langevin equations which in numerical form (Euler-Maruyama method, [22]) read
\[ p_{n+1} = p_n - [\beta p_n + C(q_n - q_c)]\tau + \sqrt{m\beta\theta\tau} b_n, \] (7)
\[ q_{n+1} = q_n + \frac{p_{n+1} + p_n}{2m} \tau. \] (8)
This sort of equations is widely used in the modern literature [3,23–25]. Here \( p_n \) \( (p_{n+1}) \) and \( q_n \) \( (q_{n+1}) \) are the particle momentum and coordinate at the time moment \( t_n \) \( (t_{n+1}) \), \( m \) stands for the inertia parameter and \( C \) denotes the potential stiffness. All the trajectories start from the bottom of the well at \( q_c = 1.0 \) with zero momentum. The modeling is finished when either the time lapse \( t_{\beta} \) is expired or the particle coordinate reaches the barrier value \( q_b = 1.6 \). Note, that due to weak damping the backscattering of the particles (the return to the potential well) absents [26]. Computer modeling of Eqs. (7) and (8) is much more time consuming. Moreover, the resulting decay rate depends upon the damping coefficient in non-monotonic manner. This is the price paid for the generality of these equations.

3. Results
In Fig. 2 we compare the results of ED and PSD approaches qualitatively. For this goal the rates \( R_{aE}/\beta_E \) as functions of \( t\beta_E \) and \( R_{aPS}/\beta_{PS} \) as functions of \( t\beta_{PS} \) are shown for two values of the governing parameter
\[ G = U_b \theta^{-1} \] (9)
and two values of the damping parameter
\[ \varphi = \beta \omega^{-1}. \] (10)
Here \( \omega = (C/m)^{1/2} \). There are the values of the damping parameter that quantify the notion of “weak friction”. Usually in the literature one finds that the energy diffusion regime is established at \( \varphi < 1 \). The time-dependent rates \( R_{aE} \) and \( R_{aPS} \) are obtained from the numerical modeling using Eq. (1). The corresponding quasistationary rates \( R_{DE} \) and \( R_{DPS} \) (horizontal lines) are calculated according to the routine described in [27]. The statistical errors of \( R_{DE} \) and \( R_{DPS} \) are within 2%.
The quantity $\beta_E (\beta_{PS})$ is the value of the damping coefficient with which the numerical simulation according to the ED (PSD) approach is executed. One observes the best agreement between two approaches in figure 2a, i.e. at the smallest value of the damping parameter (this is to be expected) and for the smallest value of the governing parameter (this seems to be a novel and unexpected result).

![Diagram](image)

**Figure 2.** Typical time dependent rates (wriggling lines) and their quasistationary values (horizontal lines) for two values of $G$ and two values of $\varphi$ which are indicated in the figure. Oscillating lines without (with) symbols correspond to the ED (PSD) approaches.

At the largest values $G$ and $\varphi$ (figure 1d) the approximate ED approach overestimates the exact (PSD) quasistationary rate by a factor of 2.

In order to quantify this observation, we present in figure 3 the ratio

$$r_{EPS} = \frac{R_{DE}\beta_{PS}}{R_{DPS}\beta_E}$$

as a function of $\varphi$ for three values of the governing parameter.

Indeed, the ratio increases (i.e. the ED approach works worse) as the damping parameter increases. Only at $\varphi = 10^{-3}$ the ratio approaches the unity whereas as $\varphi$ increases the curves corresponding to different values of $G$ diverge. This means that the sensitivity of the ratio to the damping parameter increases with $G$.

In Ref. [28], a nonlinear dependence of $R_{DE}$ upon $\beta$ was proposed in order to improve the original Kramers linear dependence and to match the two analytical rates in the turnover region $\varphi \approx 1$. Our modeling does not indicate any deviation of $R_{DE}$ from the linear dependence upon $\beta$ (or $\varphi$).
Figure 3. Dependence of the ratio $r_{EPS}$ (see Eq. (11)) upon the damping parameter for three values of $G$ indicated in the figure.

4. Conclusions
We have performed numerical calculations of the thermal decay rate of a metastable state in the domain of the friction strength corresponding to the energy diffusion regime. This have been done by means of two approaches. The first one is the approximation neglecting dissipation in one bounce of the Brownian particle in the potential well (the energy diffusion approach). The second one is much more exact: the random motion is modeled in the phase space (the phase space diffusion approach). Comparing these two approaches enable us to estimate the accuracy (and systematic errors) of the former approach. In particular, it has turned out that the accuracy of the energy diffusion approach depends not only upon the dissipation (which qualitatively is to be expected) but upon the governing parameter as well, i.e. upon the height of the potential barrier comparing to the thermal energy. Using our results may help to other researches saving computer resources and avoiding inaccuracies related with application of the faster energy diffusion approach.

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