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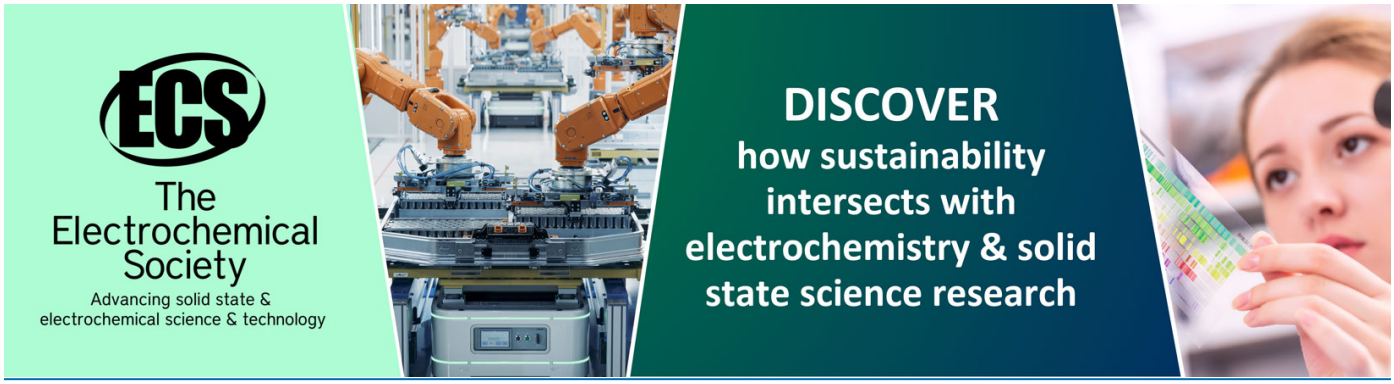

Applicability of Kramers rate formulas in the energy diffusion regime

I I Gontchar[1,2], M V Chushnyakova[2,3], A I Blesman[2]

[1] Physics and Chemistry Department, Omsk State Transport University, Omsk 644046, Russia
[2] Physics Department, Omsk State Technical University, Omsk 644050, Russia
[3] Physics Department, Akdeniz University, Antalya 07058, Turkey

Abstract. The work of nanomachines, which is a contemporary subject of the numerous investigations, is permanently affected by thermal fluctuations. Some aspects of this phenomenon might be reduced to the so-called Kramers problem concerning the decay rate of a metastable state. In the present work we compare the result of computer modelling, performed by solving the Langevin equations, with the analytical formulas for the decay rate for the case of energy diffusion regime (relatively small values of the friction strength). Qualitatively the agreement between these two approaches is rather good. However, the quantitative analysis reveals a difference of 10-20% which depends upon the thermal energy of the system.

1. Introduction

Nowadays the work of nanomachines is under extensive experimental study [1-3]. For these objects, the thermal fluctuations driving Brownian motion play an important role. Some challenges in this field are related to the so-called Kramers problem [4-6] concerning the quasistationary thermal decay rate (QDR) of a metastable state. The QDR depends significantly upon the friction strength η: at larger values of η (the spatial diffusion regime) the rate decreases with η whereas at smaller values of friction (the energy diffusion regime) opposite is predicted. The approximate formulas for the QDR obtained in [4] and modified in [7, 8] were checked thoroughly by comparing with the numerical modeling for the spatial diffusion regime [9-11]. Yet for the energy diffusion regime no quantitative tests of the approximate formulas are known. This is the goal of the present study to perform these tests.

2. Model

For this aim we model the decay process using the Langevin equations. Since in [4, 7] only the one-dimensional (1D) analytical formula was derived, we perform our modeling for 1D too. The Brownian motion is described by a dimensionless coordinate q and the conjugate momentum p. In the discrete form the equations used for modeling read:

$$p^{(n+1)} = p^{(n)}(1 - \eta m^{-1}\tau) + K\tau + gb^{(n)}\sqrt{\tau}, \quad (1)$$

$$q^{(n+1)} = q^{(n)} + \left(p^{(n)} + p^{(n+1)}\right)\tau/(2m). \quad (2)$$

The superscripts represent two moments of time separated by the time step of numerical modeling τ. The random numbers b entering the random forces have a Gaussian distribution with zero average and variance equal to 2. In equation (1) m and η are the coordinate independent inertia and friction parameters, respectively; $K = -dU/dq$ is the driving force; $g = (\theta\eta)^{1/2}$ is the amplitude of the random force; θ stands for the average thermal energy. The potential $U(q)$ is represented by two parabolas of the same stiffness C smoothly jointed at q_m.

The modeling results in a sequence of N_{tot} trajectories terminated not later than at the time moment t_D. Some of the trajectories reach the absorptive border $q_a = 2$ before t_D. The algorithm for calculating the QDR resulting from the dynamical modeling, R_D, is described in Ref. [9].

Let us now discuss the approximate formula for the QDR when there is almost no dissipation in one bounce. This formula was obtained in [4]. It reads

$$R_{KL} = \gamma \frac{\omega}{2\pi} \exp\left(-\frac{U_b}{\theta}\right). \quad (3)$$

Here ω is the frequency of oscillations near the parabolic bottom of the potential well; U_b is the barrier height.

$$\gamma = \frac{I_b \eta}{\theta m}; \quad (4)$$

I_b denotes the classical non-dissipative action at the collective energy equal to U_b:

$$I_b = 2\int_{q_l}^{q_b} \sqrt{2m[U_b - U(q)]}dq. \quad (5)$$

It is evaluated from the left turning point (q_l) up to the location of the top of the barrier (q_b). In our case $I_b = 2\pi \cdot 1.07 \cdot U_b/\omega$. Equation (3) is supposed to be valid provided $\gamma < 1$.

In [7] a modification of equation (3) was proposed allowing a smooth transition from the energy diffusion regime to the spatial diffusion regime. Denoting this modified rate as R_{KLB} we write it as

$$R_{KLB} = \frac{\delta - 1}{\delta + 1} R_{KL}. \quad (6)$$

Here

$$\delta = \left(1 + \frac{4\alpha}{\gamma}\right)^{1/2}; \quad (7)$$

α is a dimensionless adjustable parameter of the order of unity.

3. Results

In figure 1 we compare the approximate rate R_{KLB} with the numerical one R_D in the wide range of the friction strength in a qualitative manner. For convenience of a wider audience, the rates and damping coefficient are given in units of ω ($\varphi = \eta(m\omega)^{-1}$). These calculations are performed for three values of the controlling parameter $\varepsilon = U_b\theta^{-1}$. The values of R_{KLB} are calculated using $\alpha = 1.3$. In figure 1 one sees good qualitative agreement of the approximate rates with the numerical ones for all values of ε and φ. Note, that the numerical rate R_D is a subject of statistical errors which are between 1% and 2% in our calculations.

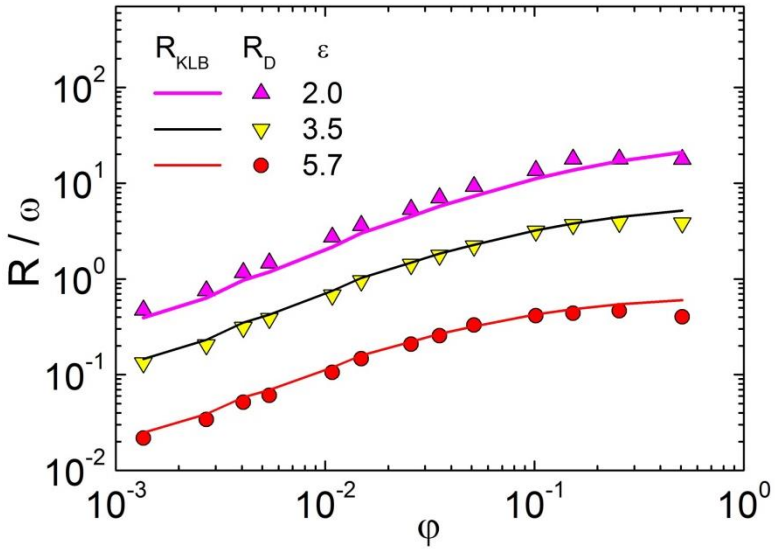

Figure 1. The decay rates R_{KLB} and R_D versus the dimensionless friction strength φ for three values of controlling parameter ε indicated in the figure.

In order to consider the problem in a more quantitative manner, in figure 2 we present the fractional difference

$$\xi = \frac{R_{KLB}}{R_D} - 1. \tag{8}$$

for the same values of the controlling parameter ε as in figure 1. Analyzing the values of ξ is more convenient because the rates themselves cover several orders of magnitude whereas the deviation of the approximate rate from the dynamical one is at most several tens percent.

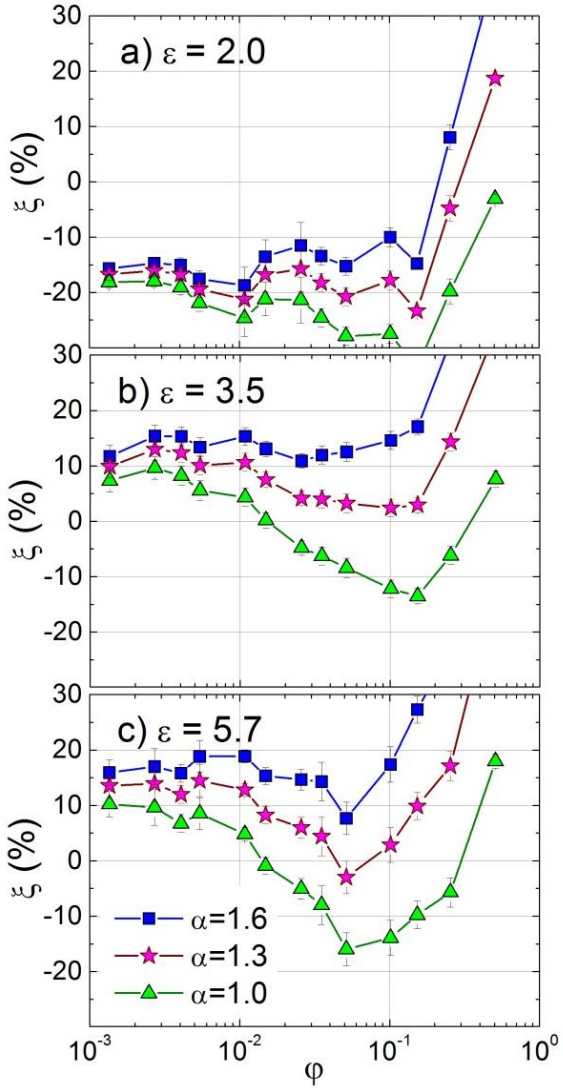

Figure 2. The fractional differences between R_{KLB} and R_D as functions of the dimensionless friction strength φ for three values of controlling parameter ε and adjustable parameter α (both are indicated in the figure).

First of all, we note in in figure 2 that no value of fitting parameter α provides an ideal agreement of R_{KLB} with R_D, i.e. the value of ξ never stays around zero within the error bars. In each panel the values of ξ corresponding to different values of α converge as φ decreases. This is expected from equations (6), (7). Another interesting feature observed in each panel is that the fractional difference ξ saturate at extremely weak friction. The saturated values are different depending upon ε. Generally speaking, the Kramers approach is expected to become poorer as ε decreases (see details in [4, 10, 12]): the larger ε the larger excess of R_D over the Kramers rate, i.e. the smaller ξ. Results presented in

figure 2c seem corresponding to this consideration. However, the value of $\xi = 10\%$ at $\varepsilon > 3$ in figures 2a and 2b is unexpected. It can be related to the circumstance that the Kramers formula (3) is obtained using the "Fokker-Planck" equation for the action variable and is approximate by itself whereas we model the decay process using the Langevin equations which are equivalent to the Fokker-Plank equation for the phase-space density.

4. Conclusions

In the present work we have compared an approximate analytical formula for the thermal decay rate in the energy diffusion regime, i. e. at small values of friction, with the exact quasistationary numerical rate R_D. The latter was obtained modeling the decay process by solving the Langevin equations. Our calculations demonstrate good qualitative agreement between the approximate rate R_{KLB} and R_D.

The quantitative comparison between these two rates shows that there is no way to reach an ideal agreement of R_{KLB} with R_D within the statistical errors of the latter which do not exceed 2%. Moreover, at extremely weak friction an approximate approach of [4] overestimates the numerical (exact) rate by 10% when all conditions of applicability of this approach are fulfilled (including the controlling parameter $\varepsilon \gg 1$). As ε becomes comparable to unity, the numerical rate exceeds the approximate one. This observation agrees with the general expectation.

Acknowledgments

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