Exact solution of Smoluchowski equation for reorientational motion in Maier-Saupe potential

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Abstract

The analytic treatment of the non-inertial rotational diffusion equation, i.e., of the Smoluchowski’s one (SE), in a symmetric double-well Maier-Saupe uniaxial potential of mean torque is considered. This equation is of utmost importance in the theory of molecular rotational motion (occurring for dynamics of nematic liquid crystals, dielectric relaxation, etc.). A similar equation takes place in the theory of ferromagnetism where it is called the Brown’s one. We obtain the exact solution of SE via the confluent Heun’s function. The solution is uniformly valid for any barrier height. We apply the obtained solution to the calculation of the mean first passage time and the longitudinal correlation time and obtain their precise dependence on the barrier height. In the intermediate to high barrier (low temperature) region (i.e., when the ratio of the barrier height to the product of the Boltzmann constant and temperature is greater than $\approx 2 \div 3$) the results of our approach are in full agreement with the literature results. In the low barrier (high temperature) region our results noticeably correct the predictions of the existing theories and give appreciably greater values for the transition rates from the potential well. We conclude that our results reveal the range of validity and the accuracy of both the Kramers’ estimate for the transition rate in the high friction limit and that of the approximate approach developed by Coffey, Kalmykov, Déjardin and their coauthors. The drawbacks of our approach are its applicability only to the symmetric potential and its inability to yield an analytical expression for the smallest non-vanishing eigenvalue.

Key words: rotational motion, diffusion, confluent Heun’s function.
1 Introduction

Rotational reorientations are a particular type of motion whose utmost importance for applications can hardly be underestimated. They are ubiquitous in physics-chemical studies of liquid crystals, polymers, proteins, lipids and many other kinds of the stuff. Rotational reorientations are investigated experimentally with the help of NMR, dielectric relaxation spectroscopy, fluorescence depolarization, etc (see, e.g., [1] and refs. therein). The main theoretical tool for their investigation is the Smoluchowski’s equation (SE), i.e., non-inertial rotational diffusion equation for a rigid body in an external potential of mean torque. It is an approximation to the more general master equation (ME). The latter is one of the basic tools in non-equilibrium statistical mechanics and physical kinetics [2], [3], [4]. ME is that for the time evolution of the probability density and consequently it expresses the fundamental principle of kinetic balance. Continuous ME is an integro-differential equation and generally it is rather difficult for analytical treatment. ME is the starting point for all models of molecular reorientation [5]. In each particular case physical intuition and/or first principles calculations have to be used in order to formulate an explicit expression for the transition probability which determines the entire process. However, in only very few examples the transition probability allows an analytic solution of ME. This difficulty is the reason why (instead of looking for an analytic solution) one usually tries to find approximations to the original ME. The well-known Kramers-Moyal expansion, e.g., transforms ME into a partial differential equation of infinite order. The transition from ME (by Taylor series expansion of the jump probabilities and the probability density for infinitely small jump steps) results in the Fokker-Planck equation which is a partial differential one [2], [3], [6]. For the case when the inertial effects are negligible (overdamped limit) the latter is reduced to SE. There is a vast literature on their study and applications [2], [3], [4], [7], [8], [9], [10], [11], [12], [13], [14], [15], [16], [17], [18], [19], [20], [21], [22], [23], [24], [25], [26], [27], [28], [29], [30]. The applications of them to the dielectric spectroscopy [22], [23], [24], [28], fluorescence depolarization [15] and NMR relaxation of liquid crystals (see [31], [32], [33] and refs. therein) have been thoroughly explored. Also, the extension of the theory from ordinary diffusion to the fractional one is intensively studied (see [27], and refs. therein).

As mentioned above, SE is only an approximation to ME valid for the case of infinitely small jump steps in a space variable. According to [5] all models for molecular motion are divided into a jump process and a diffusion process. The jumps can take place between discrete set of accessible places or in the continuous region of accessible places. In the latter case the diffusion limit is that of infinitely small jump steps. There is a fundamental result that ”a diffusion process always be approximated by a jump process, not the reverse” [3]. Thus the diffusion model ([8], [10], [11], [15], [19], [20]) can be inferred
from the jump model. In this regard SE is subordinate to ME. One has to resort to SE because in the general case its treatment is easier than that of ME. SE arises in the theory of ferromagnetism (where it is called Brown’s equation) and that of molecular rotational motion in a uniaxial potential (occurring for dynamics of liquid crystals, dielectric relaxation, etc.). In its turn, a particular case of SE in a uniaxial double-well potential of the mean torque can be analyzed with the help of the effective potential comprising the Maier-Saupe one as an ingredient. The latter is widely used in the theory of rotational reorientations of nematic liquid crystals and in the theory of dielectric relaxation of rod-like molecules.

However, these numerous researches make use of the approximate treatment of SE. The latter is based on the expansion of the probability distribution function as a series of spherical harmonics. This method is well suited for the potentials of mean torque that can be expanded in terms of spherical harmonics. It results in an infinite hierarchy of differential-recurrence relations for the the moments (the expectation values of the spherical harmonics). This approach was developed by Coffey, Kalmykov, Déjardin and their coauthors in the above mentioned papers. For the sake of brevity we further call it as CKD. Its authors resort to the approximate treatment because it is widely believed that SE has no exact analytic solution or at least obtaining it is a notoriously difficult problem. As a matter of fact, the results of CKD are compared either with those of numerical solutions of SE and Fokker-Planck one or with other approximate solutions. In particular, Brown in his classical papers considered only uniaxial potential of ordinary Maier-Saupe type (without logarithmic contribution that makes it genuinely double-well one) and obtained approximate solutions of the resulting Sturm-Liouville problem in the cases of high-energy, low-energy and intermediate-energy barriers separately. Thus, it seems interesting to obtain exact solution of the problem where it is possible and to compare the above approximate results with it. In the present paper we show that for the case of symmetric potential the problem under consideration appears to be amenable to stringent analytic treatment. We obtain the exact solution for the case of SE for reorientational motion in a symmetric double-well Maier-Saupe uniaxial potential of mean torque via the confluent Heun’s function (CHF). Our solution is uniformly valid for any barrier height. The CHF is a known and by now well described special function which is a solution of the confluent Heun’s equation. We apply the obtained solution to the calculation of the mean first passage time (MFPT) and the longitudinal correlation time and obtain their precise dependence on the barrier height.

The paper is organized as follows. In Sec. 2 the problem under study is formulated. In Sec. 3 the solution of SE is presented. In Sec. 4 the probability distribution function is obtained. In Sec. 5 the general result is exemplified by
the calculation of the escape rate from a well in the double-well Maier-Saupe uniaxial potential of mean torque. Also the longitudinal correlation time is calculated. In Sec. 6 the results are discussed and the conclusions are summarized. In Appendix the numerical calculations with CHF are considered.

2 Smoluchowski equation

In the spherical frame $\mathbf{\Xi} \equiv \{\psi, \varphi\}$ (where $0 \leq \psi \leq \pi$ is the polar angle and $0 \leq \varphi \leq 2\pi$ is the azimuthal one) we introduce the conditional probability $P(\mathbf{\Xi}, t; \mathbf{\Xi}_0, 0)$ of finding the probe at orientation $\mathbf{\Xi}$ at time $t$, if the orientation was $\mathbf{\Xi}_0$ at time zero and the equilibrium distribution function $P_{eq}(\mathbf{\Xi})$. The latter represents the equilibrium probability of finding the probe at orientation $\mathbf{\Xi}$ and is connected to the anisotropic potential of mean torque $U(\mathbf{\Xi})$ through the Boltzmann distribution. In many practical situations the distribution function $P(\mathbf{\Xi}, t; \mathbf{\Xi}_0, 0)$ and $P_{eq}(\mathbf{\Xi})$ characterizing a system of interest usually depend only on the polar angle $\psi$ (that between the axis of the probe and the $z$ axis of the chosen frame). The most notable example is nematic liquid crystals in a uniaxial phase for which a rotation about the director, assumed to be the $z$ laboratory axis, should leave the system invariant. Such situations arise for axially symmetric potentials when there are no dynamical coupling between the longitudinal and the transverse modes of motion. In this case the longitudinal modes are governed by the single state variable (polar angle $\psi$ that is called colatitude [34]) while the azimuthal angle gives rise only to a steady precession round the axis $z$. As is stressed in [34] in the theory of ferromagnetism the exact Fokker-Planck equation in the single variable (i.e., SE) follows directly from the axial symmetry of the potential. In the theory of non-inertial rotational diffusion for a rigid body the requirement of strong damping is necessary besides the above one [34].

For the sake of brevity we further denote such distribution functions as

$$P(\mathbf{\Xi}, t; \mathbf{\Xi}_0, 0) = P(\psi, t; \psi_0, 0) \equiv f(\psi, t)$$

and $P_{eq}(\mathbf{\Xi}) = P_{eq}(\psi) \equiv f_{eq}(\psi) = f(\psi, t \to \infty)$. The latter is defined by the potential of mean torque $V(\psi)$ originating from the long range order of the system

$$f_{eq}(\psi) = const \, \exp \left[ -V(\psi) / (k_B T) \right]$$

The distribution function $f(\psi, t)$ must be a solution of ME or approximately of the corresponding SE. The latter is the equation for the time evolution of
the distribution function \( f(\psi, t) \). This function must be normalized so that its integral over the whole space gives

\[
\frac{1}{4\pi} \int_0^{2\pi} d\varphi \int_0^{\pi} d\psi \sin \psi \ f(\psi, t) = \frac{1}{2} \int_0^{\pi} d\psi \sin \psi \ f(\psi, t) = 1 \quad (1)
\]

The normalized initial condition takes the form

\[
f(\psi, 0) = \frac{2}{\sin \psi_0} \delta(\psi - \psi_0) \quad (2)
\]

For a uniaxial potential of mean torque \( V(\psi) \) SE under consideration is \([23],[29],[27]\)

\[
2\tau \frac{\partial f(\psi, t)}{\partial t} = \frac{\beta}{\sin \psi} \frac{\partial}{\partial \psi} \left[ \sin \psi f(\psi, t) \frac{\partial V(\psi)}{\partial \psi} \right] + \\
\frac{1}{\sin \psi} \frac{\partial}{\partial \psi} \left[ \sin \psi \frac{\partial f(\psi, t)}{\partial \psi} \right] \quad (3)
\]

where \( \tau \) is the characteristic relaxation time for isotropic non-inertial rotational diffusion (e.g., \( \tau_D \) the Dedye one for the theory of dielectric relaxation or \( \tau_N \) the Néel one for the theory of ferromagnetism) and \( \beta = 1/(k_B T) \). We introduce a new variable

\[
x = \cos \psi \quad (4)
\]

Then the equation takes the form

\[
\frac{\partial f(x, t)}{\partial t} = \frac{1}{2\tau} \frac{\partial}{\partial x} \left[ (1 - x^2) \left( \frac{\partial f(x, t)}{\partial x} + \beta f(x, t)V'(x) \right) \right] \quad (5)
\]

where the dash means the derivative over variable \( x \).

In the stationary limit \( t \to \infty \) the probability distribution function \( f(x, t) \) must tend to its equilibrium value \( f_{eq}(x) \). Thus we have

\[
\frac{\partial f(x, t)}{\partial t} = 0
\]

and

\[
f(x, t \to \infty) \to f_{eq}(x) = \text{const} \exp \left( -\frac{V(x)}{k_B T} \right) \quad (6)
\]
Fig. 1. The symmetric double-well Maier-Saupe uniaxial potential of mean torque
\[ V(\psi) = b \sin^2 \psi - k_B T \ln(\sin^2 \psi). \] It is called the double-well potential in the present paper to oppose it to the ordinary Maier-Saupe one \( U_{MS}(\psi) = b \sin^2 \psi. \) The barrier height is \( \sigma = \frac{b}{(k_B T)} - 1 - \ln \left[ \frac{b}{(k_B T)} \right]. \)

Further we consider the effective double-well potential suggested by Pastor and Szabo [40] and used also in [23], [29], [27]

\[ V(x) = U(x) - \frac{1}{\beta} \ln(1 - x^2) \quad (7) \]

where the ingredient \( U(x) \) is responsible for the barrier. The Maier-Saupe contribution is most widely used in the literature

\[ U(x) = U_{MS}(x) = b(1 - x^2) \quad (8) \]

where the parameter \( b \) defines the barrier height. We introduce the dimensionless parameter

\[ \alpha = \frac{\beta b}{2} \quad (9) \]

The obtained double-well Maier-Saupe uniaxial potential of mean torque is depicted in Fig.1. We call this potential the double-well Maier-Saupe to oppose it to the ordinary Maier-Saupe one without logarithmic contribution \( -\frac{1}{\beta} \ln(1 - x^2). \)
3 Solution of Smoluchowski’s equation

Equation (5) can be solved by separation of variables

\[ f(x,t) = \eta(x)\chi(t) \]  

(10)

Denoting the separation constant as \(-\rho\) \((\rho > 0)\) we obtain

\[ \chi(t) = \exp(-\rho t) \]  

(11)

and the equation for the function \(\eta(x)\)

\[ (1 - x^2) [\eta''_x(x) - 4\alpha x\eta'_x(x)] + 2 (\rho\tau + 1 - 2\alpha + 6\alpha x^2) \eta(x) = 0 \]  

(12)

We introduce a new variable

\[ y = x^2 \]  

(13)

The equation takes the form

\[ y(y-1)\eta''_{yy}(y) + \left[ -2\alpha y^2 + \left(2\alpha + \frac{1}{2}\right) y - \frac{1}{2}\right] \eta'_y(y) - \]

\[ \left[3\alpha y + \frac{1}{2} (\rho\tau + 1 - 2\alpha)\right] \eta(y) = 0 \]  

(14)

It belongs to a class of the so-called confluent Heun’s equation [37]. Equation (14) has fundamental solutions that can be expressed via the CHF. The latter is a known special function [37], [38]. At present it is realized explicitly in the only symbolic computational software package Maple as \texttt{HeunC} and its derivative \texttt{HeunCPrime} (see [38] for expert opinion on the merits and drawbacks of this computational tool in Maple). The fundamental solutions of (14) are

\[ \eta^{(1)}(y) = \text{HeunC} \left(-2\alpha, -1/2, -1, -\frac{5\alpha}{2}, \frac{\alpha - \rho\tau}{2}; y \right) \]  

(15)

\[ \eta^{(2)}(y) = y^{1/2}\text{HeunC} \left(-2\alpha, 1/2, -1, -\frac{5\alpha}{2}, \frac{\alpha - \rho\tau}{2}; y \right) \]  

(16)

The spectrum of the eigenvalues for the parameter \(\rho\) is defined by the boundary conditions. For the latter we impose the usual requirement that the distribution function \(f(x,t)\) must be finite at the boundary. In fact, due to the
divergence of our double-well Maier-Saupe uniaxial potential of mean torque at the boundary \( V(x) \to \infty \) at \( x \to \pm1 \) we require that \( f(x, t) \) must be zero there

\[
\lim_{x \to \pm1} f(x, t) = 0 \tag{17}
\]

The latter yields

\[
\lim_{x \to \pm1} \eta^{(i)}(x) = 0 \tag{18}
\]

for both \( i = 1, 2 \) or equivalently

\[
\lim_{y \to 1} \eta^{(i)}(y) = 0 \tag{19}
\]

We denote

\[
\Delta_n = \rho^{(1)}_n \tau \tag{20}
\]

\[
\Omega_m = \rho^{(2)}_m \tau \tag{21}
\]

The equation for the spectrum of eigenvalues of \( \Delta_n \) \((n = 1, 2, 3, \ldots)\) for \( \eta^{(1)}_n(y) \) is

\[
HeunC\left(-2\alpha, -1/2, -1, -\frac{5\alpha}{2}, \frac{\alpha - \Delta_n}{2}; y \to 1\right) = 0 \tag{22}
\]

That for the spectrum of eigenvalues of \( \Omega_m \) \((m = 1, 2, 3, \ldots)\) for \( \eta^{(2)}_m(y) \) is

\[
HeunC\left(-2\alpha, 1/2, -1, -\frac{5\alpha}{2}, \frac{\alpha - \Omega_m}{2}; y \to 1\right) = 0 \tag{23}
\]

These equations can be solved only numerically but Maple easily copes with this problem. One always obtains \( \Delta_1 = 0 \) while the lowest \( \Omega_1 \) is always nonzero and the corresponding term mainly determines the behavior of the distribution function \( f(\psi, t) \) and MFPT calculated with its help. The dependence of \( \Omega_n \) and \( \Delta_m = 0 \) on the parameter \( \alpha \) is depicted in Fig.2 and Fig.3 respectively. It should be stressed that at large barrier heights the value of \( \Omega_1 \) becomes very small as Fig.3 testifies.
Fig. 2. The dependence of the spectrum of the eigenvalues of $\Delta_n$ (obtained as the solution of (22)) on the barrier height. This spectrum characterizes the first set of eigenfunctions of the Smoluchowski’s operator $L_S$ if the Smoluchowski’s equation under study to be written in the formal way $\dot{f} = L_S f$. 

Fig. 3. The dependence of the spectrum of the eigenvalues of $\Omega_m$ (obtained as the solution of (23)) on the barrier height. This spectrum characterizes the second set of eigenfunctions of the Smoluchowski’s operator $L_S$ if the Smoluchowski’s equation under study to be written in the formal way $\dot{f} = L_S f$. 

\[ \dot{m} = f \]
4 Probability distribution function

We return to the variable $\psi$ with the help of (4) and (13). Then the general solution of SE (3) can be written as

$$f(\psi, t) = C_1 \eta_1^{(1)}(\psi) + \sum_{n=2}^{\infty} C_n \exp(-\Delta_n t/\tau) \eta_n^{(1)}(\psi) +$$

$$\sum_{m=1}^{\infty} D_m \exp(-\Omega_m t/\tau) \eta_m^{(2)}(\psi)$$

(24)

The crucial issue for the calculation of the coefficients $C_n$ and $D_m$ is the following one: being the solution of the boundary problems both $\eta_n^{(1)}(\psi)$ and $\eta_m^{(2)}(\psi)$ are full sets of the orthogonal functions

$$\int_0^\pi d\psi \sin \psi \eta_i^{(i)}(\psi)\eta_i^{(i)}(\psi) = \delta_{im}$$

(25)

for $i = 1, 2$ and any function can be expanded into a series over $\eta_n^{(1)}(\psi)$ or $\eta_m^{(2)}(\psi)$. At time $t = 0$ (24) yields (with taking into account (2))

$$\frac{2}{\sin \psi_0} \delta(\psi - \psi_0) = \sum_{n=1}^{\infty} C_n \eta_n^{(1)}(\psi) + \sum_{m=1}^{\infty} D_m \eta_m^{(2)}(\psi)$$

(26)

We can obtain the coefficients $C_n$ by expanding each $\eta_m^{(2)}(\psi)$ over the full set of $\eta_n^{(1)}(\psi)$ and those $D_m$ vice versa. We denote

$$R_n = \left[ \int_0^\pi d\psi \sin \psi \left[ \eta_n^{(1)}(\psi) \right]^2 \right]^{-1} \int_0^\pi d\psi \sin \psi \eta_n^{(1)}(\psi) \eta_m^{(2)}(\psi)$$

(27)

$$Q_n = \left[ \int_0^\pi d\psi \sin \psi \left[ \eta_m^{(2)}(\psi) \right]^2 \right]^{-1} \int_0^\pi d\psi \sin \psi \eta_m^{(2)}(\psi) \eta_n^{(1)}(\psi)$$

(28)

$$A_n = \left[ \int_0^\pi d\psi \sin \psi \left[ \eta_n^{(1)}(\psi) \right]^2 \right]^{-1} 2\eta_n^{(1)}(\psi_0)$$

(29)

$$B_m = \left[ \int_0^\pi d\psi \sin \psi \left[ \eta_m^{(2)}(\psi) \right]^2 \right]^{-1} 2\eta_m^{(2)}(\psi_0)$$

(30)
Then the coefficients $C_n$ and $D_m$ are found from the systems of algebraic equations

$$\sum_{l=1}^{\infty} C_l \left[ \delta_{ln} - \sum_{m=1}^{\infty} Q^l_m R^m_n \right] = A_n - \sum_{m=1}^{\infty} R^m_n B_m$$

(31)

and

$$\sum_{k=1}^{\infty} D_k \left[ \delta_{mk} - \sum_{n=1}^{\infty} Q^n_m R^n_k \right] = B_m - \sum_{n=1}^{\infty} Q^n_m A_n$$

(32)

respectively.

Thus, we have the explicit algorithm for obtaining the coefficients $C_n$ and $D_m$ along with the corresponding spectra $\Delta_n$ and $\Omega_m$ that makes the solution of our problem to be completed. Substitution of all these values into (24) yields the required probability distribution function. Of course, in practice the solution of the systems of algebraic equations (31) and (32) requires a truncation of the series, i.e., replacement of the infinity by some finite number $M$ that is stipulated by the computational facilities at one’s disposal. In our numerical calculations we take $M = 2$, i.e., calculate only $C_1$, $C_2$, $D_1$ and $D_2$.

5 Mean first passage time and longitudinal correlation time

To exhibit how the result obtained may be useful we calculate with its help the dependence of MFPT on the barrier height $\alpha$. Our effective Maier-Saupe uniaxial potential of mean torque (that used in, e.g., [40], [23], [29], [27]) is (see (7), (8) and (9))

$$\frac{1}{k_B T} V(\psi) = 2\alpha \sin^2 \psi - \ln \left( \sin^2 \psi \right)$$

(33)

It is depicted in Fig. 1. It has two local minima the left of which is at

$$\psi_L = \arcsin \left( \frac{1}{\sqrt{2\alpha}} \right)$$

(34)

and the maximum at

$$\psi_M = \frac{\pi}{2}$$

(35)
First we calculate the non-averaged MFTP. We set the initial condition to be the system in the left local minimum \( \psi_0 = \psi_L \). It is worthy to recall that our solution of SE \( f(\psi, t) \) is actually the conditional probability \( f(\psi, t) \equiv P(\psi, t; \psi_0, 0) \) of finding the system at orientation \( \psi \) at time \( t \), if the orientation was \( \psi_0 \) at time zero. Then, following Risken [6] we introduce the probability \( \Omega(\psi_0, t) \) of realizations which have started at \( \psi_0 = \psi_L \) and which have not yet reached one of the boundaries \( \psi = 0 \) or \( \psi = \psi_M \) up to the time \( t \)

\[
\Omega(\psi_0, t) = \int_0^{\psi_M} d\psi \sin \psi f(\psi, t)
\]

(36)

The distribution function \( w(\psi_0, T) \) for the first passage time \( T \) (we use the notations from [6] and note that this value is not to be confused with temperature which will further enter only implicitly via \( \alpha \) from (9) and via \( 1 / (k_B T) = 2\alpha/b \) is

\[
w(\psi_0, T) = -\frac{\partial \Omega(\psi_0, T)}{\partial T}
\]

(37)

The moments of the first passage time distribution are

\[
T_n(\psi_0) = \int_0^\infty dT \, T^n w(\psi_0, T)
\]

(38)

The value of interest for us here is the MFPT \( T_1 \)

\[
T_1(\psi_0) = \int_0^\infty dT \, Tw(\psi_0, T)
\]

(39)

that characterizes the ability for the system to reach the barrier top \( \psi_M \) starting from the left minimum \( \psi_0 = \psi_L \). Thus, we have to calculate the quantity

\[
T_1(\psi_0) = -\int_0^{\psi_M} d\psi \sin \psi \int_0^\infty dT \, T \frac{\partial f(\psi, T)}{\partial T}
\]

(40)

After straightforward calculations we obtain

\[
\frac{1}{\tau} T_1(\psi_0) = \frac{D_1}{\Omega_1} \int_0^{\psi_M} d\psi \sin \psi \eta_1^{(2)}(\psi) +
\]
\[
\sum_{n=1}^{\infty} \int_0^{\psi_M} d\psi \sin \psi \left[ \frac{C_n}{\Delta_n} \eta_n^{(1)}(\psi) + \frac{D_n}{\Omega_n} \eta_n^{(2)}(\psi) \right]
\] 

(41)

Finally, we calculate the averaged MFPT \( <T_1> \) for the case when the initial condition is thermodynamically averaged over the left well

\[
<T_1> = \left[ \int_0^\pi d\psi_0 \sin \psi_0 \exp \left( -\frac{V(\psi_0)}{k_B T} \right) \right]^{-1} \times 
\int_0^{\psi_M} d\psi_0 \sin \psi_0 \exp \left( -\frac{V(\psi_0)}{k_B T} \right) T_1(\psi_0)
\]

(42)

It is worthy to recall here that the coefficients \( C_n \) and \( D_n \) are the functions of the initial condition \( \psi_0 \), i.e., explicitly \( C_n \equiv C_n(\psi_0) \) and \( D_n \equiv D_n(\psi_0) \). The results of numerical calculation of \( <T_1> \) are presented in Fig.4. There the results for the averaged MFPT \( <T_1> \) obtained from our numerical calculations are compared with the analytical estimate from the Kramers’ theory for the transition rate

\[
\frac{1}{\tau} <T_1> \approx \frac{1}{\Gamma_K}
\]

(43)

If we return again to the variable \( x = \cos \psi \) and denote

\[
h(x) \equiv \frac{1}{k_B T} V(x) = 2\alpha (1 - x^2) - \ln(1 - x^2)
\]

(44)

then the Kramers’ formula takes the form [18],

\[
\Gamma_K = \frac{\sqrt{h''_{xx}(x_L) h''_{xx}(x_M)}}{2\pi} \exp \{- [h(x_M) - h(x_L)]\}
\]

(45)

Also in Fig.4 the result of CKD is presented. The latter in our case of the symmetric potential is [27], [34]

\[
\frac{1}{\tau} <T_1> \equiv \frac{1}{\tau} T_{MFPT} = 
\]

\[
4 \left[ \left( \int_{-1}^{0} dz \frac{e^{-\sigma z^2}}{1 - z^2} \int_{-1}^{\frac{z}{z'}} dz' e^{\sigma z'^2} \right)^{-1} + \left( \int_{0}^{1} dz \frac{e^{-\sigma z^2}}{1 - z^2} \int_{\frac{1}{z}}^{1} dz' e^{\sigma z'^2} \right)^{-1} \right]^{-1}
\]

(46)
Fig. 4. The dependence of the mean first passage time for the transition from the well of the symmetric double-well Maier-Saupe uniaxial potential of mean torque $V(\psi) = b \sin^2 \psi - k_B T \ln (\sin^2 \psi)$ on the parameter $b$ which characterizes the barrier height. The dots are the result of our exact approach developed in the present paper. The thin line is the result of the Kramers’ estimate for the transition rate in the high friction limit \((45)\). The thick line is the result of the approximate approach developed by Coffey, Kalmykov, Déjardin and their coauthors \((46)\) extrapolated from the ordinary Maier-Saupe potential $U_{MS}(\psi) = b \sin^2 \psi$ for which the barrier height is $\sigma = b/(k_B T)$ to our double-well one with the barrier height $\sigma = b/(k_B T) - 1 - \ln [b/(k_B T)]$.

where for our double-well Maier-Saupe potential

$$\sigma \equiv \frac{V(x_M) - V(x_L)}{k_B T} = 2\alpha - 1 - \ln(2\alpha) \quad (47)$$

Following CKD we introduce the longitudinal correlation function

$$\frac{< \cos \psi(0) \cos \psi(t) >}{< \cos^2 \psi(0) >} = \left\{ \int_0^\pi d\psi \sin \psi \int_0^\pi d\psi_0 \sin \psi_0 \cos \psi_0 \cos \psi f(\psi, t) \right\} \times$$

$$\left\{ \int_0^\pi d\psi \sin \psi \int_0^\pi d\psi_0 \sin \psi_0 (\cos \psi_0)^2 f(\psi, t) \right\}^{-1} \quad (48)$$

where the averaging $< ... >$ is carried out with the help of the obtained distribution function $f(\psi, t)$ given by \((24)\). Also, we define the longitudinal
Fig. 5. The dependence of the longitudinal correlation time for rotational motion in the symmetric double-well Maier-Saupe uniaxial potential of mean torque \( V(\psi) = b \sin^2 \psi - k_B T \ln(\sin^2 \psi) \) on the parameter \( b \) which characterizes the barrier height. The dots are the result of our exact approach developed in the present paper. The thin line is the result of the Brown’s estimate \((51)\). The thick line is the result of the approximate approach developed by Coffey, Kalmykov, Déjardin and their coauthors \((50)\) extrapolated from the ordinary Maier-Saupe potential \( U_{MS}(\psi) = b \sin^2 \psi \) for which the barrier height is \( \sigma = b/(k_B T) \) to our double-well one with the barrier height \( \sigma = b/(k_B T) - 1 - \ln [b/(k_B T)] \).

correlation time

\[
\tau_|| = \int_0^\infty dt \frac{<\cos \psi(0) \cos \psi(t)>}{<\cos^2 \psi(0)>}
\] (49)

In Fig.5 the results of calculations of the value \( \tau_|| \) are presented. They are compared with the result of CKD that in the case of the symmetric potential takes the form \((27), (34)\)

\[
\frac{1}{\tau_||}^{CKD} = \frac{3e^{\sigma}}{\sigma^2 M(3/2, 5/2, \sigma)} \int_0^1 dz \frac{ch[\sigma(1 - z^2)] - 1}{1 - z^2}
\] (50)

where \( M(a, b, z) \) is the Kummer’s function. Also, for the sake of completeness we present in Fig.5 the so-called Brown’s estimate

\[
\frac{1}{\tau_||}^{Brown} = \frac{\sqrt{\pi}e^{\sigma}}{2\sigma^{3/2}}
\] (51)
6 Results and discussion

To clarify the terminology it should be stressed that we deal with barrier heights in the energetic units (i.e., conceive it to be the ratio of its value in the natural units to the product of the Boltzmann constant and temperature). Thus, e.g., the low barrier regime may well be realized for high barriers in the natural units at sufficiently high temperatures. Namely in this sense we further use the notions of the intermediate to high barrier (low temperature) region and the low barrier (high temperature) one.

It should be stressed that the result of CKD in its more general form for an asymmetric potential (the formula (46) for our particular case of the symmetric one) is obtained for the ordinary Maier-Saupe potential \( U_{MS}(\psi) = b \sin^2 \psi \) rather than our double-well one \( V(\psi) = b \sin^2 \psi - k_B T \ln(\sin^2 \psi) \). Strictly speaking in the original CKD the parameter \( \sigma \) is \( \sigma = b/(k_B T) \) rather than (47). It is our extrapolation of the CKD result to the double-well Maier-Saupe potential by taking \( \sigma \) to be (47) that leads to some discrepancy between our calculated values for MFPT at large \( b/(k_B T) \) and those predicted by (46) as seen in Fig.4. Nevertheless, the discrepancy is insignificantly small as Fig.4 testifies. We conclude that our results agrees well with those of CKD at barrier heights greater than \( b/(k_B T) \approx 3 \div 4 \) (\( \sigma \approx 2 \div 3 \)). The Kramers’ estimate for the transition rate in the high friction limit (45) yields excellent approximation for the double-well Maier-Saupe potential at \( b/(k_B T) \) greater than \( \approx 3 \). We conclude that in the intermediate to high barrier region our results are in full agreement with the known literature ones.

In the low barrier region our results yield noticeably smaller values for MFPT than those predicted by both the Kramers’ estimate (45) and that of CKD (46). We conclude that in this region the existing theories appreciably over-estimate MFPT or in other words predict too small values for the transition rates from the potential well. Thus, our approach reveals the range of validity and the accuracy of the literature ones.

Our approach yields directly the probability distribution function rather than the statistical moments (i.e., values averaged over it). We recall that CKD enables one to obtain the reformulation of the problem as the differential-recurrence relations for the longitudinal and transverse correlation functions. A systematic way for their analysis has been suggested that yields ”exact analytic solutions for the longitudinal and transverse complex susceptibilities and correlation times for many problems of practical interest” [27]. However, in some applications (e.g., to the theory of nuclear magnetic relaxation) it is desirable to work namely with the distribution function taken alone. The virtue of our approach is in providing such option. As an example of the case where the direct averaging with distribution function is used we calculate the
longitudinal correlation time (see Fig.5). As in the previous case our results are very similar to those of CKD in the intermediate to high barrier region and correct them slightly in the the low barrier one.

Our approach yields the exact solution of SE \((3)\). Let us formally write this equation as \(\dot{f} = L_S f\) where \(L_S\) is the Smoluchowski’s operator. Then the difference of our exact solution from the approximate CKD can be explained as follows. The authors of CKD expand \(f\) over Legendre polynomials while we expand it over the eigenfunctions of \(L_S\). The latter are expressed over CHF which at present can be considered as a well tabulated special function. Efficient numerical algorithms for it are available in the literature let alone an explicit realization in Maple that makes its usage a routine problem. In fact, to deal with CHF is no harder than with Legendre polynomials. Moreover, the approximate solution leads to recurrence system for the coefficients in the expansion when those with lower indexes are related to higher ones. To cope with such system is a difficult problem in itself though it is successfully solved in the above mentioned papers. In our exact solution the coefficients in the expansion are obtained from the infinite system of algebraic equations. Strictly speaking the coefficients with different indexes in the expansion are also interrelated with each other. However, the truncation of this system by finite number of equations can be carried out up to any required index obeying the requirement of a preliminary imposed accuracy. As soon as it is done, then the resulting finite system can be trivially solved by standard methods. However, besides the advantages of our solution over the approximate one there are drawbacks. Within the framework of the approximate solution the authors of the above mentioned papers manage to obtain an analytical expression for the smallest non-vanishing eigenvalue. In our approach that is obtained as a solution of \((23)\). The latter is to be solved numerically. In the present paper we do not try to obtain an analytical expression for \(\Omega_1\) from \((23)\). Also, our approach is developed only for symmetric uniaxial potential of mean torque. The crucial substitution \((13)\) can work only for potentials with even powers of \(\cos \psi\) or \(\sin \psi\) and can not be generalized to odd powers leading to the asymmetry of the potential.

In conclusion, we revisit a rather old problem of rotational motion in a double-well potential of mean torque. The corresponding physical process is within the framework of the escape rate theory that is more than seventy years old (if to count from the cornerstone Kramers’ paper). Nevertheless, the adequate tools for its exact analytic treatment (the theory of CHF and its convenient numerical realizations) were developed only relatively recently. Their application provides a new way to rederive old and well known results and to correct them slightly. Thus, in the limited case of the symmetric double-well Maier-Saupe uniaxial potential of mean torque our exact approach reveals the range of validity and accuracy of the previous approximate ones.
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7 Appendix

Maple is very efficient for numerical search of the roots of (22) and (23). Unfortunately, the calculations of the integrals containing $HeunC$ by Maple proves to be too time consuming that makes the analysis of $\langle T_1 \rangle$ with the help of this program to be practically inconvenient. Besides, one can not control the processing at its usage [38]. For this reason, we prefer to employ the explicit numerical realization of the CHF. We find that the required accuracy can well be retained at reducing the number of terms in the definition of the CHF by a series. As a consequence the processing time is diminished substantially. For this purpose, we make use of the explicit representation of the CHF by a series [37]. It includes the three-term recurrence relation [37], [39] that in our case takes the form for the first solution of (14)

$$\eta^{(1)}(y) = HeunC\left(-2\alpha, -1/2, -1, -\frac{5\alpha}{2}, \frac{\alpha - \rho \tau}{2}; y \right) =$$

$$\sum_{k=0}^{\infty} v_k^{(1)} \left(-2\alpha, -1/2, -1, -\frac{5\alpha}{2}, \frac{\alpha - \rho \tau}{2}\right) y^k$$

(52)

where

$$A_k v_k^{(1)} = B_k v_{k-1}^{(1)} + C_k v_{k-2}^{(1)}$$

(53)

with the initial conditions $v_{-1}^{(1)} = 0, v_0^{(1)} = 1$. Here

$$A_k^{(1)} = 1 - \frac{1}{2k}$$

(54)

$$B_k^{(1)} = 1 + \frac{4\alpha - 5}{2k} + \frac{4 - 4\alpha - 2\rho \tau}{4k^2}$$

(55)

$$C_k^{(1)} = -\frac{2\alpha}{k^2} \left(k - \frac{1}{2}\right)$$

(56)

For the second solution of (14) we have

$$y^{-1/2} \eta^{(2)}(y) = HeunC\left(-2\alpha, 1/2, -1, -\frac{5\alpha}{2}, \frac{\alpha - \rho \tau}{2}; y \right) =$$
\[ \sum_{k=0}^{\infty} v_k^{(2)} \left( -2\alpha, 1/2, -1, -\frac{5\alpha}{2}, \frac{\alpha - \rho \tau}{2} \right) y^k \]  

(57)

where

\[ A_k^{(2)} v_k^{(2)} = B_k^{(2)} v_{k-1}^{(2)} + C_k^{(2)} v_{k-2}^{(2)} \]  

(58)

with the initial conditions \( v_{-1}^{(2)} = 0, v_0^{(2)} = 1 \). Here

\[ A_k^{(2)} = 1 + \frac{1}{2k} \]  

(59)

\[ B_k^{(2)} = 1 + \frac{4\alpha - 3}{2k} - \frac{\rho \tau}{2k^2} \]  

(60)

\[ C_k^{(2)} = -\frac{2\alpha}{k} \]  

(61)

To provide fast convergence of the series in (52) and (57) we truncate them, i.e., replace the infinity by some large but finite \( N \) which we choose from the requirement that the obtained values of \( \frac{< T_1 >}{\tau} \) cease to change within the limits of the required accuracy. Under these approximations we obtain an efficient numerical algorithm for calculating the integrals with the our CHF.
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