Generalization of the classical Kramers rate for non-Markovian open systems out of equilibrium

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Abstract

We analyze the behavior of a Brownian particle moving in a double-well potential. The escape probability of this particle over the potential barrier from a metastable state toward another state is known as the Kramers problem. In this work we generalize Kramers’ rate theory to the case of an environment always out of thermodynamic equilibrium reckoning with non-Markovian effects.
I Introduction: Metastability and fluctuations

We consider a Brownian particle immersed in an environment (e.g., a fluid) under the influence of an external potential. Due to the environmental fluctuations the escape rate of this particle over the barrier separating two metastable states—in a double-well potential, for instance—is known as the Kramers problem [1, 2], even though the rate theory has been already tackled by van’t Hoff and Arrhenius as late as 1880 [2]. For many years this phenomenon has had various applications in physical, chemical, astronomical, and biological systems [1, 2, 3, 4]. Originally, Kramers [1] investigated the Brownian movement in a reservoir at thermodynamic equilibrium taking into account only Markovian effects. He also worked out a method for calculating the escape probability from a Fokker–Planck equation (nowadays known as the Kramers equation) associated with a given set of Langevin equations. Even then, several generalizations of this Kramers’ pioneering work have arisen in the literature with experimental verifications [2, 3, 5, 6], e.g., in Josephson junction measuring the decay of the supercurrent.

In the theory of escape rate non-Markov and/or nonequilibrium features are commonly introduced through memory effects contained in the friction kernel present in generalized Langevin equations and using either the Fokker–Planck equation found by Adelman and Mazo [7] or a non-Markovian Smoluchowski equation [8], or yet using the Fokker–Planck equation in energy picture [9]. The equilibrium Kramers rate using only the non-Markovian generalized Langevin equation is investigated in [10]. In nonequilibrium situations the Kramers theory has been also studied in Markovian open systems with oscillating barriers [11], as well as in periodically driven stochastic systems [12].

It should be remarked that a feature common to all above approaches is that the mean value of the stochastic term present in the Langevin equations is zero. Following a diverse way, in the present paper we propose a generalization of the Langevin equations and construct the respective Fokker-Planck equation. In this context we evaluate the Kramers escape rate away from the equilibrium taking into account non-Markovian effects related to different time scales inherent in the Brownian dynamics. As recently pointed out by Pollak and Talkner [13] these topics are still poorly understood despite their ongoing relevance for rate theory.
Our paper is organized as follows:
I. Introduction: Metastability and fluctuations
II. Generalizing the Langevin approach
III. Our Fokker–Planck equation
IV. Kramers rate: nonequilibrium and non-Markov
V. Summary and perspectives
Appendix A: Derivation of our Fokker–Planck equation [Eq.(12)]
Appendix B: An example

II Generalizing the Langevin approach

As a physical model of a stochastic process we consider a particle with mass $m$ immersed into an environment. This particle undergoing a Brownian motion is characterized by the stochastic position $X = X(t)$ and the stochastic momentum $P = P(t)$, while the environment is specified by a random variable $\Psi = \Psi(t)$. Such physical quantities could be intertwined through the relations

$$X = Q + \Delta Q; \quad P = m \frac{dX}{dt},$$

where $\Delta Q = \alpha b_1(t)\Psi(t)$, $t$ being a parameter, called time, and $\alpha$ a dimensional constant such that $\Delta Q$ has dimension of length. $d/dt$ denotes a differential operator acting upon $X$, and $b_1(t)$ a time-dependent parameter measuring the strength of the environment effects upon the particle. We define it as being

$$b_1 = b_1(t) = \int_0^t \langle \Psi(t')\Psi(t'') \rangle dt'',$$

where the mean

$$\langle \Psi(t')\Psi(t'') \rangle = \int \int \psi(t')\psi(t'') D_{XP\Psi}(x,p,\psi,t) dx dp d\psi =$$

$$\int \psi(t')\psi(t'') D_{\Psi}(\psi,t) d\psi$$

is calculated in terms of the joint probability density function $D_{XP\Psi}(x,p,\psi,t)$ or the probability density $D_{\Psi}(\psi,t)$.

One assumes the motion of the Brownian particle moving in an external potential $V(X)$ to be described by the stochastic differential equations in
phase space \((X, P)\), known as Langevin’s equations \([14]\),

\[
\begin{align*}
\frac{dP}{dt} &= -\frac{dV}{dX} - \frac{\gamma}{m} P + b_1 \Psi ; \\
\frac{dX}{dt} &= \frac{P}{m},
\end{align*}
\]  

(3)

where \(-\gamma P/m\) denotes a (memoryless) frictional force activating the particle motion. There \(\Psi\) has the statistical properties

\[
\langle \Psi(t')\Psi(t'') \rangle = 2D^{1/3}\delta(t'' - t') ; \quad \langle \Psi \rangle = 0,
\]  

(4)

making the stochastic process Markovian. \(\delta(t'' - t')\) is the Dirac delta function and \(D\) is a constant – to be determined by the physics of the problem – such that \(b_1 \Psi = D^{1/3}\) in Eq.(3) has in fact dimension of newton.

It is important to note that as the environmental parameter \(b_1(t)\) does vanish, the stochastic quantities \(P\) and \(X\) reduce to the respective deterministic values \(p = mdq/dt\) and \(x = q\), provided \(D_{XP}(x, p) = \delta(x - q)\delta(p - p')\). Physically, that means that the initially open system becomes isolated from its environment and turns out to be described by Newton’s equations

\[
\begin{align*}
\frac{dp}{dt} &= -\frac{dV(x)}{dx} - \frac{\gamma}{m} p ; \\
\frac{dx}{dt} &= \frac{p}{m}.
\end{align*}
\]  

(5)

For this reason one says that the Langevin equations (3) are a generalization of Newton’s equations (5).

In the literature \([2]\) the non-Markovian character is introduced by means of the following statistical properties of \(\Psi\)

\[
\langle \Psi(t')\Psi(t'') \rangle = (D/t_c^2)^{1/3}e^{-(t'' - t')/t_c} ; \quad \langle \Psi \rangle = 0,
\]  

(6)

where \(t'' > t'\) and \(t_c\) is the correlation time between the Brownian particle and its environment. One takes into account a memory friction kernel in the Langevin equations (3):

\[
\begin{align*}
\frac{dP}{dt} &= -\frac{dV}{dX} - \int_0^t \beta(t - \tau) \frac{P(\tau)}{m} d\tau + b_1 \Psi ; \\
\frac{dX}{dt} &= \frac{P}{m}.
\end{align*}
\]  

(7)

Both the frictional kernel \(\beta(t - \tau)\) and the fluctuating function \(\Psi(t)\) are coupled by means of the dissipation-fluctuation theorem \([15]\)

\[
\langle \Psi(t')\Psi(t'') \rangle = \kappa_B T \beta(t - \tau).
\]
Physically, such a theorem assures that the Brownian particle will always attain the thermal equilibrium of the heat bath characterized by Boltzmann’s constant $\kappa_B$ and the temperature $T$. As $\beta(t - \tau) = 2\gamma \delta(t - \tau)$ and the correlation time $t_c$ tends to zero, i.e., $t_c \to 0$, the expression (6) reduces to (4) while (7) reproduces (3). Thereby, the stochastic dynamics (7), along with the statistical properties (6), are called the generalized Langevin equations [15].

In the present paper our purpose is to make another extension of the Langevin approach. To begin with, we hold the definition of $X$ in (1) and generalize the stochastic momentum $P = dX/dt$ according to

$$\bar P = P + \Delta P,$$

where $\Delta P = -mb_2(t)\Psi(t)$, with $b_2(t)$ defined as

$$b_2 = b_2(t) = \int_0^t \langle \Psi(t') \rangle dt'.$$

Accordingly, the Langevin equations (3) turn out to be written as

$$\frac{d\bar P}{dt} = -\frac{dV}{dx} - \frac{\gamma}{m} \bar P + b_1 \Psi ; \quad \frac{dX}{dt} = \frac{\bar P}{m} + b_2 \Psi,$$

in phase space $(X, \bar P)$, with

$$\langle \Psi(t') \Psi(t'') \rangle = (D/t_c^2)^{1/3} e^{-(t'' - t')/t_c} ; \quad \langle \Psi \rangle = (C/t_c^2)^{1/3} e^{-t'/t_c}. \quad (11)$$

As the constant $C$ vanishes, we recover from (10) the usual Langevin equations (3) as a special case. In short, equations in (10), together with (11), are our generalized Langevin equations.

### III Our Fokker–Planck equation

Considering a Brownian particle in a harmonic potential $V = kx^2/2$, Equations (10) and (11) generate the following Fokker–Planck equation in phase space $(x, \bar p)$ (for details, see Appendix A)

$$\frac{\partial F}{\partial t} = -\frac{\partial (A_x F)}{\partial x} - \frac{\partial (A_{\bar p} F)}{\partial \bar p} + \frac{A_{xx}}{2} \frac{\partial^2 F}{\partial x^2} + A_{xp} \frac{\partial^2 F}{\partial x \partial \bar p} + \frac{A_{\bar p\bar p}}{2} \frac{\partial^2 F}{\partial \bar p^2}, \quad (12)$$

5
where 

\[ F = F(x, \bar{p}, t) = \int D_{X \Psi}(x, \bar{p}, \psi, t) d\psi. \]

The quantities

\[ A_x = (\bar{p}/m) + (C^2/t_c)^{1/3}(e^{-t/t_c} - e^{-2t/t_c}), \]

and

\[ A_{\bar{p}} = -kx - (\gamma/m)\bar{p} + (CD/t_c)^{1/3}(e^{-t/t_c} - e^{-2t/t_c}) \]

are the drift coefficients, whereas the time-dependent diffusion coefficients are given by

\[ A_{xx} = (C^2D)^{1/3}(1 - e^{-t/t_c})^2, \]

\[ A_{x\bar{p}} = (D^2C)^{1/3}(1 - e^{-t/t_c})^2, \]

and

\[ A_{\bar{p}\bar{p}} = D(1 - e^{-t/t_c})^2. \]

Combining \( A_{xx}, A_{x\bar{p}}, \) and \( A_{\bar{p}\bar{p}} \) we notice that they satisfy the relation

\[ \sqrt{A_{xx}A_{\bar{p}\bar{p}}} = A_{x\bar{p}}. \] (13)

Moreover, on replacing the Maxwell–Boltzmann (MB) distribution

\[ F(x, \bar{p}) = \frac{1}{\sqrt{2\pi m k_B T}} e^{-\left(\frac{\bar{p}^2}{2m k_B T}\right)} e^{-\left(kx^2/2\kappa_B T\right)} \] (14)

into our Fokker–Planck equation (12) it is too easy to verify that (14) cannot become its solution. This means that our stochastic process, described by (10–12), holds always away from the thermal equilibrium. That leads us to think that the physical meaning of the relation (13), which is a consequence of our assumption \( \langle \Psi \rangle \neq 0 \) in (11), is connected with nonequilibrium characteristics underlying the environment. In fact, as \( C = 0 \) the constraint (13) is broken up and our generalized momentum \( \bar{P} \) in Eq.(8) becomes equal to \( P \). Consequently, Eq.(12) reduces to the non-Markovian Kramers equation in phase space \((x, p)\)

\[ \frac{\partial F}{\partial t} = -\frac{p}{m} \frac{\partial F}{\partial x} - \frac{\partial}{\partial p} \left[ \left(-kx - \frac{\gamma}{m} p\right) F \right] + \frac{D(1 - e^{-t/t_c})^2}{2} \frac{\partial^2}{\partial p^2} F. \] (15)

In the Markovian steady regime characterized by \( t \gg t_c \), or formally \( t_c \to 0 \), the MB distribution (14) with \( \bar{p} = p \) turns out to be a solution to (15), thereby determining the diffusion coefficient as being equal to \( A_{\bar{p}\bar{p}} = D = 2\gamma k_B T \).
On the other hand, inserting \( \mathcal{F}(x, \bar{p}, t) = f(x, t)\delta(\bar{p}) \) into (12) and taking into account the high friction condition

\[
\gamma \frac{\bar{p}}{m} = -kx,
\]

obtained from Newton’s equations (5) on neglecting inertial effects (\( |d\bar{p}/dt| \ll |\gamma \bar{p}/m| \)), we arrive at the non-Markovian Smoluchowski equation in position space

\[
\frac{\partial f(x, t)}{\partial t} = -\frac{1}{\gamma} \frac{\partial}{\partial x} [K(x, t)f(x, t)] + \frac{A_{xx}}{2} \frac{\partial^2 f(x, t)}{\partial x^2},
\]  

(16)

where

\[
K(x, t) = -kx + \gamma (C^2/t_c)^{1/3} (e^{-t/t_c} - e^{-2t/t_c}).
\]

Replacing (14) into (16) we obtain \( A_{xx} = 2\kappa_B T/\gamma \) in both stationary and Markovian regimes.

Considering \( V = 0 \) and \( C = 0 \) from our equation (12) we derive the non-Markovian Rayleigh equation in \( p \)-space

\[
\frac{\partial g(p, t)}{\partial t} = \frac{\gamma}{m} \frac{\partial}{\partial p} [pg(p, t)] + \frac{D(1 - e^{-t/t_c})^2}{2} \frac{\partial^2}{\partial p^2} g(p, t),
\]  

(17)

with

\[
g(p, t) = \int D_X P(x, p, t) dx.
\]

From the mathematical viewpoint we note that we can derive the Kramers equation (15), the Smoluchowski equation (16), and the Rayleigh equation (17) as special cases of our equation of motion (12). Physically, that means that all the physics encapsulated into these equations of motion (15), (16), and (17) are in principle contained in our Eq.(12).

**IV Kramers rate: Nonequilibrium and non-Markov**

In order to provide a physical significance to our equation of motion (12) we are going to evaluate the Kramers rate. This problem consists on calculating the escape probability of a Brownian particle over a potential barrier.
in a presence of an environment away from equilibrium and having non-Markovian features.

We follow the Kramers’ approach [1, 16, 17, 18] for calculating escape rate. We start with the non-Markovian Kramers equation (15) and derive a stationary equation as we assume that during a given fixed time interval \( t = \Delta \tau \) for observing the Brownian particle, the function \( \mathcal{F} \) can be factorised as

\[
\mathcal{F}(x, p, t) = e^{\gamma t/m} F(x, p)|_{t=\Delta \tau}.
\]  

Inserting (18) into (15) leads to the stationary Kramers equation

\[
-\frac{p}{m} \frac{\partial F}{\partial x} - \frac{\partial}{\partial p} \left[ \left( -kx - \frac{\gamma}{m} p \right) F \right] + \frac{D(1 - e^{-\Delta \tau/\tau_c})}{2} \frac{\partial^2}{\partial p^2} F = 0.
\]  

(19)

After the change of variable according to

\[
\xi = p - ax
\]  

Eq.(19) turns into

\[
\frac{d^2 F}{d\xi^2} = -A \xi \frac{dF}{d\xi},
\]  

(21)

where

\[
A = \frac{2(a - \gamma)}{mD(1 - e^{-\Delta \tau/\tau_c})}.
\]  

(22)

Solution to (21) is given by [after using condition \( F(\xi = \infty) = 1 \)]

\[
F(\xi) = \left( \frac{A}{2\pi} \right)^{1/2} \int_{-\infty}^{\xi} e^{-A\xi^2/2} d\xi,
\]  

(23)

provided \( A > 0 \), i.e.,

\[
a = \frac{1}{2} \left( \gamma + \sqrt{\gamma^2 - 4mk} \right), \quad k > 0.
\]  

(24)

Following Kramers \([1]\) and using (23) we build up the following function

\[
\mathcal{W}(x, p) = e^{-\beta[(p^2/2m) + V(x)]} F(\xi = p - ax),
\]  

(25)
where the parameter $\beta$ has dimension of $1/\text{joule}$, so that the exponential in (25) is dimensionless. [Notice that on account of the temperature concept cannot generally be defined in nonequilibrium situations we could not employ the thermodynamic identity $\beta = 1/\kappa_B T$.] From (26) and (27) we notice that $\beta$ should be restricted to the values $0 < \beta < \infty$.

In a double-well potential $V(x)$ the barrier top is located at point $x_b$, whereas the metastable wells are at $x_a$ and $x_c$, with $x_c > x_a$ such that $V(x_a) = V(x_c) = 0$. To find out the probability current (flux) over the potential barrier located at $x = x_b$, i.e.,

$$j_b = \int_{-\infty}^{+\infty} W(x = x_b, p) \frac{p}{m} dp,$$

we expand $V(x)$ and $\xi$ about $x_b$:

$$V(x) \approx V(x_b) - (m\omega_b^2/2)(x - x_b)^2,$$

and

$$\xi = p - a(x - x_b).$$

$\omega_b$ is the oscillation frequency over the barrier. Consequently, using (25) we find the probability current

$$j_b = \frac{1}{\beta} \left( \frac{Am}{Am + \beta} \right)^{1/2} e^{-\beta V(x_b)}$$

with $a$ in (24) and (22) given by

$$a = \frac{1}{2} \left( \gamma + \sqrt{\gamma^2 + 4m^2\omega_b^2} \right).$$

The number of particles $\nu_a$ in the metastable state around $x_a$ can be calculated with (25) in the limit $\xi \to \infty$ as being

$$\nu_a = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-\beta[(p^2/2m) + (k_a x^2/2)]} dp dx = \frac{2\pi}{\omega_a \beta}, \quad k_a = m\omega_a^2.$$
Using (26) and (27) we derive the nonequilibrium and non-Markov escape rate
\[ \Gamma_{\text{neq}} = \frac{j_b}{\nu_a} = \frac{\omega_a}{2\pi} \left( \frac{Am}{Am + \beta} \right)^{1/2} e^{-\beta V(x_b)}. \] (28)

Physical regimes related to the time scales \( \Delta \tau \) (observation time) and \( t_c \) (correlation time):

i) For \( \Delta \tau = t_c \), the non-Markovian, non-equilibrium escape rate is given by (28) with
\[ A \approx 3 \frac{(a - \gamma)}{mD}; \]

ii) while for \( \Delta \tau \ll t_c \) \((t_c \to \infty)\), the system holds highly non-Markovian at non-equilibrium situation having the rate (28) with
\[ A \approx \frac{2t_c(a - \gamma)}{mD\Delta \tau}; \]

iii) for \( \Delta \tau \gg t_c \) \((t_c \to 0)\) the Markovian regime is attained along with the equilibrium state. In this context, \( \beta = 1/\kappa_B T \) and the diffusion constant can be calculated as being \( D = 2\gamma \kappa_B T \). Thereby, from (28) we obtain the well-known Markovian Kramers rate at thermodynamic equilibrium
\[ \Gamma_{\text{eq}} = \frac{\omega_a}{2\pi m\omega_b} \left[ \sqrt{\frac{\gamma^2}{4} + m^2\omega_b^2} - \frac{\gamma}{2} \right] e^{-V(x_b)/\kappa_B T}. \] (29)

Now we want to extend Kramers’ approach to our Fokker–Planck equation (12). To this end, we assume again the function
\[ \mathcal{F}(x, \bar{p}, t) = e^{\gamma t/m} F(x, \bar{p}) \]
to be a solution to Eq.(12) during a fixed time interval \( \Delta \tau \) (a time of observation). As above we perform the variable change \( \xi = \bar{p} - ax \) and derive the following ordinary differential equation from (12)
\[ \frac{d^2 F}{d\xi^2} = - (A\xi - B) \frac{dF}{d\xi}; \] (30)
where
\[ A = \frac{2(a - \gamma)}{m \left( a\sqrt{A_{xx}} + \sqrt{A_{\bar{p}\bar{p}}^2} \right)^2} ; \quad B = \frac{2b(\Delta\tau)[1 + a(C/D)^{1/3}]}{(a\sqrt{A_{xx}} + \sqrt{A_{\bar{p}\bar{p}}})^2}, \]  
with
\[ b(\Delta\tau) = (CD/t_c)^{1/3}(e^{-\Delta\tau/t_c} - e^{-2\Delta\tau/t_c}), \]
\[ A_{xx} = (C^2D)^{1/3}(1 - e^{-\Delta\tau/t_c})^2, \]
\[ A_{\bar{p}\bar{p}} = (D^2C)^{1/3}(1 - e^{-\Delta\tau/t_c})^2, \]
\[ A_{x\bar{p}} = D(1 - e^{-\Delta\tau/t_c}), \]

and
\[ a = \frac{1}{2} \left( \gamma \pm \sqrt{\gamma^2 - 4mk} \right). \]

Solution to (30) is given by [after using condition \( F(\xi = \infty) = 1 \)]
\[ F(\xi) = \left( \frac{A}{2\pi} \right)^{1/2} e^{-B^2/2A} \int_{-\infty}^{\xi} e^{-(A/2)\xi^2 + B\xi} d\xi, \]  
provided \( A > 0 \), i.e.,
\[ a = \frac{1}{2} \left( \gamma + \sqrt{\gamma^2 - 4mk} \right), \quad k > 0. \]  

We build up the function
\[ W(x, \bar{p}) = e^{-\beta[\bar{p}^2/(2m) + V(x) + \xi]} F(\xi = \bar{p} - ax). \]  

As supposed above, let the Brownian particle be to move in a double-well potential \( V(x) \), in which the barrier top is located at point \( x_b \), whereas the metastable wells are at \( x_a \) and \( x_c \), with \( x_c > x_a \) such that \( V(x_a) = V(x_c) = 0 \). In order to find the flux over the potential barrier located at \( x = x_b \),
\[ j_b = \int_{-\infty}^{+\infty} W(x = x_b, \bar{p}) (\bar{p}/m) d\bar{p}, \]
we expand \( V(x) \) and \( \xi \) about \( x_b \):
\[ V(x) \approx V(x_b) - (m\omega_b^2/2)(x - x_b)^2, \]
and

\[ \xi = \bar{p} - a(x - x_b). \]

After inserting (34), with (32) and (33), into \( j_b \) we find

\[ j_b = \frac{1}{\beta} \left( \frac{Am}{Am + \beta} \right)^{1/2} e^{-\beta B^2/2A(Am+\beta)} e^{-\beta V(x_b)} \]  

(35)

while the number of particles \( \nu_a \) in the metastable state around \( x_a \) is given by

\[ \nu_a = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-\beta[(\bar{p}^2/2m) + (k_a x^2/2)]} d\bar{p}dx = \frac{2\pi}{\beta \omega_a}, \quad k_a = m \omega_a^2. \]  

(36)

With \( j_b \) and \( \nu_a \) we obtain then the nonequilibrium and non-Markovian escape rate in the stationary regime

\[ \Gamma_{\text{neq}} = \frac{j_b}{\nu_a} = \frac{\omega_a}{2\pi} \left( \frac{Am}{Am + \beta} \right)^{1/2} e^{-\beta B^2/2A(Am+\beta)} e^{-\beta V(x_b)}, \]  

(37)

where \( A \) and \( B \) are given by (31) with

\[ a = \frac{1}{2} \left( \gamma + \sqrt{\gamma^2 + 4m^2\omega_b^2} \right). \]

On account of the exponential term the performance of the escape rate (37) is thoroughly controlled by the nonequilibrium parameter \( \beta \). [As \( C = 0 \), our rate (37) reduces to Eq.(28)].

In the Markovian limit, \( t_c \to 0 \), Eq.(37) leads to

\[ \Gamma_{\text{neq}} = \frac{\omega_a}{2\pi} \left( \frac{2(a - \gamma)}{2(a - \gamma) + \beta \left( a\sqrt{C^2D}1/3 + \sqrt{D} \right)} \right)^{1/2} e^{-\beta V(x_b)}, \]  

(38)

whereas for \( C = 0, D = 2\gamma \kappa_B T, \) and \( \beta = (1/\kappa_B T) \) our result (37), via (38), reproduces the Markovian escape rate (29) found by Kramers for a Brownian particle immersed in a thermal reservoir at thermodynamic equilibrium.
Comparing our result (38) with (29) we arrive at the relation

$$\frac{\Gamma_{\text{neq}}}{\Gamma_{\text{eq}}} = \frac{2m\omega b}{\sqrt{2(a - \gamma)}} \frac{1}{\sqrt{2(a - \gamma) + \beta \left( a\sqrt{(C^2D)^{1/3}} + \sqrt{D} \right)^2}} e^{V(x_b)(1 - \beta \kappa B T) / \kappa B T}.$$  

(39)

As $\beta < 1/\kappa B T$ our nonequilibrium rate $\Gamma_{\text{neq}}$ is enhanced in comparison with the equilibrium Kramers rate $\Gamma_{\text{eq}}$. On the contrary, for $\beta > 1/\kappa B T$ we find $\Gamma_{\text{neq}} < \Gamma_{\text{eq}}$.

Although our escape rate $\Gamma_{\text{neq}}$ (38) cannot be defined for $\beta = 0$ we may conjecture about the mathematical behavior of $\Gamma_{\text{neq}} / \Gamma_{\text{eq}}$ as $\beta \to 0$ corresponding to the extreme physical situation $\beta \ll 1/\kappa B T$. From (39) we obtain then the result

$$\frac{\Gamma_{\text{neq}}}{\Gamma_{\text{eq}}} = \frac{2m\omega b}{\sqrt{\gamma^2 + 4m^2 \omega_b^2}} e^{V(x_b) / \kappa B T}.$$  

(40)

which leads to

$$\frac{\Gamma_{\text{neq}}}{\Gamma_{\text{eq}}} = \frac{\gamma}{2m\omega b} e^{V(x_b) / \kappa B T}.$$  

(41)

for $\gamma \gg 2m\omega_b$ (or formally $\gamma \to \infty$), and to

$$\frac{\Gamma_{\text{neq}}}{\Gamma_{\text{eq}}} = e^{V(x_b) / \kappa B T}.$$  

(42)

for $\gamma \to 0$ (or physically $\gamma \ll 2m\omega_b$). By considering the case $\gamma = 2m\omega_b$, from Eq.(40) we derive

$$\frac{\Gamma_{\text{neq}}}{\Gamma_{\text{eq}}} = (1 + \sqrt{2}) e^{V(x_b) / \kappa B T}.$$  

(43)

By comparing (37) with (38) we can evaluate the influence of the non-Markovian effects on escape rates out equilibrium. The exponential term

$$e^{-\beta B^2 / 2A(\lambda + \beta)}$$

therefore does account for diminishing the probability of escape in the non-Markovian regime.
Before closing this section we want to emphasize that our general escape rate (37) has been obtained in the aftermath of the hypothesis $\langle \Psi \rangle \neq 0$ assumed in Eqs. (10–12), noticing that $t$ is the evolution time of the Brownian particle immersed in a fluid, $\Delta \tau$ denotes an observation time necessary to detect generally nonequilibrium physical properties at the stationary state, and $t_c$ the correlation time responsible for non-Markovian features.

V Summary and perspectives

In this paper we have investigated the metastability phenomenon in the presence of fluctuations. In Section II we have obtained the generalized Langevin equations (10) on the basis of an extension of the stochastic momentum (8) taking into account the nonvanishing average value of the random function $\Psi$.

In Section III we have built up a Fokker–Planck equation [Eq.(12)] from which we have found out the non-Markovian escape rate away from the equilibrium (37). As compared to the equilibrium rate our result (39) predicts that the probability of escape may decrease or increase in the nonequilibrium regime. The parameter $\beta$ controls the performance of such escape rate.

Throughout our article we have deemed the stochastic system to hold at a nonequilibrium state even in steady situations. Which of many possible physical mechanisms is responsible for approaching it to the equilibrium state? The Markovian character, i.e., as the correlation time $t_c$ is too tiny in comparison with the observation time $\Delta \tau$, seems to be a strong criterion to attain the equilibrium state, provided in our result (38) the constant $C$ does vanish. It is worth remembering that $C$ has been introduced in Eq.(11) for $\langle \Psi \rangle \neq 0$.

Quantum and nonlinear effects of the potential barrier will be studied in a forthcoming work [19]. We hope thus our present approach could contribute to the formulation of a general theory of escape rate and stimulate experimental researches in the area of non-Markovian escape rate in systems away from thermal equilibrium.
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Appendix A: Derivation of our Fokker–Planck equation [Eq.(12)]

In this appendix we want to show in somewhat details how we could explicitly construct the Fokker–Planck equation (12) from the system of stochastic differential equations [20]

$$\frac{d\bar{P}}{dt} = -\frac{dV}{dX} - \gamma \bar{P} + b_1 \Psi; \quad \frac{dX}{dt} = \frac{\bar{P}}{m} + b_2 \Psi.$$  \hfill (44)

Equations (44) yield the results

$$\Delta \bar{P} = -\left(\frac{dV}{dX} + \frac{\gamma \bar{P}}{m}\right) \Delta t + \int_t^{t+\Delta t} b_1(t')\langle \Psi(t') \rangle dt' \hfill (45)$$

and

$$\Delta X = \frac{\bar{P}}{m} \Delta t - \left(\frac{dV}{dX} + \frac{\gamma \bar{P}}{m}\right) \left(\frac{\Delta t}{m}\right)^2 + \frac{1}{m} \int_t^{t+\Delta t} \int_s^{t+\Delta t} b_1(t')\langle \Psi(t') \rangle dt'ds + \int_t^{t+\Delta t} b_2(t')\langle \Psi(t') \rangle dt'. \hfill (46)$$

Using $\Delta \bar{P} = \bar{P}(t+\Delta t) - \bar{P}(t)$ and $\Delta X = X(t+\Delta t) - X(t)$ we calculate the following quantities

$$A_\bar{P} = \lim_{\Delta t \to 0} \langle \Delta \bar{P} \rangle \frac{\Delta t}{\Delta t} = -\frac{dV}{dX} - \frac{\gamma \bar{P}}{m} + \lim_{\Delta t \to 0} \frac{1}{\Delta t} \int_t^{t+\Delta t} b_1(t')\langle \Phi(t') \rangle dt', \hfill (47)$$

$$A_{\bar{P}\bar{P}} = \lim_{\Delta t \to 0} \langle (\Delta \bar{P})^2 \rangle \frac{\Delta t}{\Delta t} = -2 \left(\frac{dV}{dX} + \frac{\gamma \bar{P}}{m}\right) \lim_{\Delta t \to 0} \int_t^{t+\Delta t} b_1(t')\langle \Phi(t') \rangle dt' + \lim_{\Delta t \to 0} \int_t^{t+\Delta t} b_1(t')b_1(t'')\langle \Phi(t')\Phi(t'') \rangle dt' dt'', \hfill (48)$$

$$A_x = \lim_{\Delta t \to 0} \langle \Delta X \rangle \frac{\Delta t}{\Delta t} = \frac{\bar{P}}{m} + \lim_{\Delta t \to 0} \int_t^{t+\Delta t} \int_s^{t+\Delta t} b_1(t')\langle \Psi(t') \rangle dt'ds + \lim_{\Delta t \to 0} \int_t^{t+\Delta t} b_2(t')\langle \Psi(t') \rangle dt', \hfill (49)$$
\[ A_{xx} = \lim_{\Delta t \to 0} \frac{\langle (\Delta X)^2 \rangle}{\Delta t} = I_1 + I_2 + I_3 + I_4 \]  

with

\[ I_1 = \frac{2\bar{P}}{m^2} \int_t^{t+\Delta t} \int_t^{s} b_1(t') \langle \Psi(t') \rangle dt' ds, \]

\[ I_2 = \frac{2\bar{P}}{m} \int_t^{t+\Delta t} b_2(t') \langle \Psi(t') \rangle dt', \]

\[ I_3 = \frac{1}{m^2} \lim_{\Delta t \to 0} \int_t^{t+\Delta t} \int_t^{s} \int_t^{r} b_1(t') b_1(t'') \langle \Psi(t') \Psi(t'') \rangle dt' dt'' dr ds, \]

\[ I_4 = \frac{2}{m} \lim_{\Delta t \to 0} \int_t^{t+\Delta t} \int_t^{s} \int_t^{r} b_1(t') b_2(t'') \langle \Psi(t') \Psi(t'') \rangle dt' dt'' ds, \]

\[ I_5 = \int_t^{t+\Delta t} \int_t^{s} b_1(t') b_2(t'') \langle \Psi(t') \Psi(t'') \rangle dt' dt'', \]

and

\[ A_{xp} = \lim_{\Delta t \to 0} \frac{\langle \Delta X \Delta \bar{P} \rangle}{\Delta t} = \xi_1 + \xi_2 + \xi_3 + \xi_4 + \xi_5, \]

where

\[ \xi_1 = \frac{\bar{P}}{m} \int_t^{t+\Delta t} b_1(t') \langle \Psi(t') \rangle dt', \]

\[ \xi_2 = -\frac{1}{m} \left( \frac{dV}{dX} + \frac{\gamma m}{\bar{P}} \right) \int_t^{t+\Delta t} \int_t^{s} b_1(t') \langle \Psi(t') \rangle dt' ds, \]

\[ \xi_3 = \frac{1}{m} \lim_{\Delta t \to 0} \frac{1}{\Delta t} \int_t^{t+\Delta t} \int_t^{s} \int_t^{r} b_1(t') b_1(t'') \langle \Psi(t') \Psi(t'') \rangle dt' dt'' ds, \]

\[ \xi_4 = -\frac{\bar{P}}{m} \int_t^{t+\Delta t} b_2(t') \langle \Psi(t') \rangle dt', \]

\[ \xi_5 = \lim_{\Delta t \to 0} \frac{1}{\Delta t} \int_t^{t+\Delta t} \int_t^{s} \int_t^{r} b_2(t') b_2(t'') \langle \Psi(t') \Psi(t'') \rangle dt' dt''. \]

After using our definitions

\[ \langle \Psi(t') \Psi(t'') \rangle = (D/t_c^2)^{1/3} e^{-(t''-t')/t_c}; \quad \langle \Psi \rangle = (C/t_c^2)^{1/3} e^{-t/t_c}, \]
and

\[ b_1 = \int_0^t \langle \Psi(t')\Psi(t'') \rangle dt'' = (Dt_c)^{1/3}(1 - e^{-t/t_c}), \quad (63) \]

\[ b_2 = \int_0^t \langle \Psi(t') \rangle dt' = (Ct_c)^{1/3}(1 - e^{-t/t_c}). \quad (64) \]

into (47–50) and (56) we obtain our Fokker–Planck equation (12) with the coefficients

\[ A_x = (\bar{p}/m) + \left( \frac{C^2}{t_c} \right)^{1/3} (e^{-t/t_c} - e^{-2t/t_c}), \quad (65) \]

\[ A_{\bar{p}} = -kx - \left( \frac{\gamma}{m} \right) \bar{p} + \left( \frac{CD}{t_c} \right)^{1/3} (e^{-t/t_c} - e^{-2t/t_c}), \quad (66) \]

\[ A_{xx} = (C^2 D)^{1/3}(1 - e^{-t/t_c})^2, \quad (67) \]

\[ A_{x\bar{p}} = (D^2 C)^{1/3}(1 - e^{-t/t_c})^2, \quad (68) \]

\[ A_{\bar{p}\bar{p}} = D(1 - e^{-t/t_c})^2. \quad (69) \]
Appendix B: An example

In Sect. IV we have derived our main result, Eq. (37), depending on the phenomenological quantities $C$ and $D$ through the relations $A$ and $B$ [see Eq. (31)]. It would be pretty catchy whether we could a priori calculate them by means of the environmental physics, that is, employing a theory of nonequilibrium thermodynamics. Unfortunately, at the moment there is no such theory. Yet, we can envisage the following physical situation: We imagine an environment having $I_1$, $I_2$, and $I_3$ as subsystems, such that within $I_1$ the Brownian particle is described by our Fokker–Planck equation (12), while within $I_2$ it is described by the Kramers equation (15), and within $I_3$ its dynamics turns out to be governed by the Smoluchowski equation (16). As outlined in Sect. III, supposing the equilibrium Maxwell–Boltzmann distribution (14) to be a boundary condition in the regions $I_2$ and $I_3$, we determine from (15) the phase-space diffusion coefficient $A_{\bar{p}\bar{p}} = 2\gamma B_T$, and from (16) the $x$-space diffusion coefficient $A_{xx} = 2\kappa B_T/\gamma$. Owing to the constraint (13) we find $A_{x\bar{p}} = 2\kappa B_T$. [In contrast with $A_{xx}$ and $A_{\bar{p}\bar{p}}$, it is interesting to note that the phase-space diffusion coefficient $A_{x\bar{p}}$ is independent of the friction constant $\gamma$. That absence of a dissipation-fluctuation relation indicates a nonequilibrium physical situation]. Therefore, as a whole our medium $I = I_1 + I_2 + I_3$ could be considered as a thermal reservoir away from the equilibrium but with locally defined temperature concept. That Brownian particle is then characterized by our non-Markovian Langevin equations

$$\frac{d\bar{p}}{dt} = \frac{-dV}{dX} - \frac{\gamma}{m} \bar{p} + \left[\frac{2t_c\gamma B_T(1 - e^{-t/t_c})}{m}\right]^{1/3} \Psi, \quad (70)$$

$$\frac{dX}{dt} = \frac{\bar{p}}{m} + \left[\frac{2t_c\kappa B_T}{\gamma^2(1 - e^{-t/t_c})}\right]^{1/3} \Psi, \quad (71)$$

and by the corresponding Fokker–Planck equation (12) in the form

$$\frac{\partial F}{\partial t} = -\frac{\partial (A_x F)}{\partial x} - \frac{\partial (A_{\bar{p}} F)}{\partial \bar{p}} + \frac{\kappa B_T}{\gamma} \frac{\partial^2 F}{\partial x^2} + 2\kappa B_T \frac{\partial^2 F}{\partial x \partial \bar{p}} + \gamma \kappa B_T \frac{\partial^2 F}{\partial \bar{p}^2}, \quad (72)$$

with

$$A_x = \frac{\bar{p}}{m} + \left[\frac{(2\kappa B_T)^2}{t_c^4(1 - e^{-t/t_c})}\right]^{1/3} e^{-t/t_c}, \quad (73)$$

$$A_{\bar{p}} = -kx - \frac{\gamma \bar{p}}{m} + \left[\frac{(2\kappa B_T)^2}{t_c \gamma(1 - e^{-t/t_c})}\right]^{1/3} e^{-t/t_c}. \quad (74)$$
In the nonequilibrium region the Kramers rate is given by (37) with \( \beta = 1/\kappa_B T \) and
\[
\mathcal{A} = \frac{2(a - \gamma)}{m \sqrt{2\kappa_B T/\gamma + \sqrt{2\gamma \kappa_B T}}}.
\] (75)
\[
\mathcal{B} = \frac{Am}{(a - \gamma)} \frac{(2\kappa_B T)^{2/3}}{(\gamma t_c)^{1/3}} e^{-\Delta \tau/t_c} \left[ 1 + \frac{a(1 - e^{-\Delta \tau/t_c})}{\gamma} \right] \left( 1 - e^{-\Delta \tau/t_c} \right)^{2/3}. \] (76)

In the case \( \gamma \gg 2m\omega_b \) and \( a \approx \gamma + (m^2 \omega_b^2/\gamma) \), the rate reads
\[
\Gamma = \frac{m\omega_a \omega_b}{4\pi \gamma} e^{-(1/4m\omega_b^2)(2\kappa_B T)/(\gamma t_c)^2} u(\Delta \tau) e^{-V(x_b)/\kappa_B T} \] (77)

with
\[
u(\Delta \tau) = (2 - e^{-\Delta \tau/t_c})^2 (1 - e^{-\Delta \tau/t_c})^{4/3} e^{-2\Delta \tau/t_c}. \] (78)

We note that (77) may be written as
\[
\Gamma_{\text{neq}} = \frac{1}{2} e^{-(1/4m\omega_b^2)(2\kappa_B T)/(\gamma t_c)^2} u(\Delta \tau) \Gamma_{\text{eq}} \] (79)
relating the nonequilibrium rate \( \Gamma_{\text{neq}} \) to the equilibrium one
\[
\Gamma_{\text{eq}} = \frac{m\omega_a \omega_b}{2\pi \gamma} e^{-V(x_b)/\kappa_B T} \] (80)
which is obtained from (29) for \( \gamma \gg 2m\omega_b \). In the Markovian limit, \( \Delta \tau \gg t_c \), the nonequilibrium rate (79) reduces to \( \Gamma_{\text{neq}} = \Gamma_{\text{eq}}/2 \).

On the other hand, for the low friction case, \( \gamma \ll m\omega_b \), we obtain
\[
\Gamma'_{\text{neq}} = \sqrt{\frac{\gamma}{m\omega_b}} e^{-(1/4m^2 \omega_b^2)(2\kappa_B T/\gamma t_c)^2} \nu(\Delta \tau) \Gamma'_{\text{eq}} \] (81)
with
\[
\nu(\Delta \tau) = \left[ 1 + \left( \frac{1}{2} + \frac{m\omega_b}{\gamma} \right) (1 - e^{-\Delta \tau/t_c}) \right] \left( 1 - e^{-\Delta \tau/t_c} \right)^{4/3} e^{-2\Delta \tau/t_c}. \] (82)

In Eq.(81), \( \Gamma'_\text{eq} = (\omega_a/\pi) e^{-V(x_b)/\kappa_B T} \) is obtained from (29) as \( \gamma \to 0 \). In the Markovian limit, \( \Delta \tau \gg t_c \), it follows that \( \Gamma'_{\text{neq}} = (\gamma/m\omega_b)^{1/2} \Gamma'_{\text{eq}} \).
On the basis of our stochastic model for a non-Markovian Brownian particle out equilibrium, from Eqs. (79) and (81) we draw the conclusion that the performance of the nonequilibrium escape rate is too small compared to the equilibrium situation.
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