Quantization of the Smoluchowski equation and the problem of quantum tunneling at zero temperature

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Abstract

In this article we address the problem of quantum tunneling of a non-Markovian Brownian particle away from thermal equilibrium. We calculate the Kramers escape rate at low temperature (including the zero temperature case) in the Smoluchowski limit (strong friction regime). Our main findings are: (i) our quantum escape rate is valid far from the thermal equilibrium and is non-Markovian, but it becomes Markovian as the correlation time vanishes; (ii) at thermodynamic equilibrium we obtain a non-Markovian quantum rate that predicts a superfluidity phenomenon in the Markovian limit at low and zero temperatures.
I Introduction: Quantum tunneling

Let us consider a quantum particle moving in a double-well potential. The transition of this particle over the barrier potential from a metastable state toward another state is known as quantum tunneling. This phenomenon takes place in many areas of physics (e.g., in condensed matter physics), chemistry, astronomy, and biology [1, 2, 3]. From the experimental standpoint quantum tunneling has been investigated on the basis of rate experiment performed in the following areas [2]: Tunneling in biophysical transport, quantum diffusion in solids, chemical conversion processes, tunneling in ferromagnetic materials, electron tunneling in amorphous alloys, nucleation of vortices in HeII, escape of electrons from the surface of liquid helium, low-temperature Josephson-junction systems, tunneling of protons on hydrated protein powders, and many others.

In isolated systems quantum tunneling process has been studied making use of the Schrödinger equation [4], whereas in open systems, i.e., systems immersed in a reservoir undergoing Brownian motion, we cannot follow such approach since there is no wavefunction describing a Brownian particle, for instance. The nontrivial issue is therefore to find out a manner of elaborating a theory of quantum transport so as to clarify the role played by dissipation and fluctuation on quantum tunneling. To be complete this theory has to take into account not only equilibrium and Markovian properties but also non-Markovian and non-equilibrium features [5].

The usual Hamiltonian approach for describing open systems is as follows. Imagine an environment consisting of a set of harmonic oscillators coupled to the Brownian particle. Once found the Hamiltonian function of whole system (particle plus environment), canonical quantization procedure could be employed. The Feynman path integral formalism is used to derive equations of motion for the reduced density matrix describing the quantum motion of the Brownian particle alone. On the basis of this method Caldeira and Leggett [6] have quantized the Kramers equation [7] and analyzed quantum tunneling [8]. More recently, following the Caldeira–Leggett approach Ankerhold at al. [9] have derived a quantum Smoluchowski equation and explored its physical meaning applying it to chemical reactions, mesoscopic physics, and charge transfer in molecules. Meanwhile, other works [10] have revealed some drawbacks underlying such quantum Smoluchowski equation,
since it violates the Second Law of Thermodynamics, for instance. From our point of view the restlessness over this internal inconsistency leads us to search for alternative ways of quantizing the Smoluchowski equation, thereby eschewing any \textit{ad hoc} procedures as achieved in Ref.\cite{10}.

Another Hamiltonian approach \cite{11} has been developed and used in \cite{12} to derive a quantum Smoluchowski equation and investigate the issue of quantum tunneling at zero temperature, in contrast with Ankerhold et al.’s survey. Such alternative way does not depend on the path integral formalism, but is based on the canonical quantization.

In recent years, we have put forward a non-Hamiltonian method for quantizing open systems \cite{13,14,15}. There we start directly with the stochastic dynamics (Langevin and Fokker–Planck equations) and quantize it by making use of a Fourier transform carrying the Planck constant. Accordingly, our approach is independent of path integral techniques and is not based on canonical quantization.

In order to contribute to a general theory of quantum tunneling within a non-Hamiltonian framework we have already started in \cite{15} we organize our article as follows:

I. Introduction: Quantum tunneling
II. Our generalized Langevin equation
III. Our non-Markovian Smoluchowski equation
IV. Quantization of our Smoluchowski equation
V. Quantum tunneling
VI. Summary and discussions
Appendix: Derivation of our Fokker–Planck equation [Eq.(13)]

\section{Our generalized Langevin equation}

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

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

(1)

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

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

(2)

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 [2, 3],

\[ \frac{dP}{dt} = -\frac{dV}{dX} - \gamma P + b_1 \Psi \quad ; \quad \frac{dX}{dt} = \frac{P}{m} , \]  

(3)

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

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

(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

\[
\frac{dp}{dt} = -\frac{dV(x)}{dx} - \gamma \frac{p}{m} \quad ; \quad \frac{dx}{dt} = \frac{p}{m}. \tag{5}
\]

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 \( \Psi \)

\[
\langle \Psi(t')\Psi(t'') \rangle = (D/t_c^2)^{1/3}e^{-(t''-t')/t_c} \quad ; \quad \langle \Psi \rangle = 0, \tag{6}
\]

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):

\[
\frac{dP}{dt} = -\frac{dV}{dX} - \int_0^t \beta(t-\tau) \frac{P(\tau)}{m} d\tau + b_1 \Psi \quad ; \quad \frac{dX}{dt} = \frac{P}{m}. \tag{7}
\]

Both the frictional kernel \( \beta(t-\tau) \) and the fluctuating function \( \Psi(t) \) are coupled by means of the dissipation-fluctuation theorem [16]

\[
\langle \Psi(t')\Psi(t'') \rangle = \kappa_B T \beta(t-\tau).
\]

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 [16].

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

\[
P = P + \Delta P, \tag{8}
\]

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

\[
b_2 = b_2(t) = \int_0^t \langle \Psi(t') \rangle dt'. \tag{9}
\]
Accordingly, the Langevin equations (3) turn out to be written as

\[ \frac{d\bar{P}}{dt} = -\frac{dV}{dX} - \frac{\gamma}{m} \bar{P} + b_1 \Psi; \quad \frac{dX}{dt} = \frac{\bar{P}}{m} + b_2 \Psi, \tag{10} \]

in phase space \((X, \bar{P})\), with

\[ \langle \Psi(t') \Psi(t'') \rangle = \left( \frac{D}{t_c^2} \right)^{1/3} e^{-(t''-t')/t_c}; \quad \langle \Psi \rangle = \left( \frac{C}{t_c^2} \right)^{1/3} e^{-t/t_c}, \tag{11} \]

and

\[ b_1 = \left( \frac{D}{t_c^2} \right)^{1/3} (1 - e^{-t/t_c}); \quad b_2 = \left( \frac{C}{t_c} \right)^{1/3} (1 - e^{-t/t_c}). \tag{12} \]

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) and (12), are our generalized Langevin equations.

III Our non-Markovian Smoluchowski equation

Equations (10), (11) and (12) generate the following Fokker–Planck equation in phase space \((x, \bar{p})\) (for details, see Appendix)

\[ \frac{\partial F}{\partial t} = -\frac{\partial (A_x F)}{\partial x} - \frac{\partial (A_x \bar{p} F)}{\partial \bar{p}} + \frac{A_{xx}}{2} \frac{\partial^2 F}{\partial x^2} + A_{xp} \frac{\partial^2 F}{\partial x \partial \bar{p}} + \frac{A_{\bar{p}\bar{p}}}{2} \frac{\partial^2 F}{\partial \bar{p}^2}, \tag{13} \]

where

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

The quantities

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

and

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

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

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

\[ \sqrt{A_{xx}A_{\bar{p}\bar{p}}} = A_{x\bar{p}}. \tag{14} \]

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

\[ F(x, \bar{p}) = \frac{1}{\sqrt{2\pi mk_B T}} e^{-\{p^2/2mk_BT\} e^{-\{kx^2/2k_BT\}}} \tag{15} \]

into our Fokker–Planck equation (13) it is too easy to verify that (15) cannot become its solution. This means that our stochastic process, described by (10–13), holds always away from the thermal equilibrium. That leads us to think that the physical meaning of the relation (14), 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 (14) is broken up and our generalized momentum \( \bar{P} \) in Eq.(8) equals to \( P \). Consequently, Eq.(13) reduces to the non-Markovian Kramers equation in phase space \((x,p)\)

\[ \frac{\partial F}{\partial t} = - \frac{p}{m} \frac{\partial F}{\partial x} + \frac{\partial}{\partial p} \left[ \left( \frac{dV}{dx} + \frac{\gamma}{m} p \right) F \right] + \frac{D}{2} \frac{1 - e^{-t/t_c}}{e^{-t/t_c}} \frac{\partial^2}{\partial p^2} F. \tag{16} \]

In the Markovian steady regime characterized by \( t \gg t_c \), or formally \( t_c \to 0 \), the MB distribution (15) with \( \bar{p} = p \) turns out to be a solution to (16), thereby determining the diffusion coefficient as being equal to \( A_{pp} = D = 2\gamma\kappa_B T \). It is worth noting that according to both the phase space equations (13) and (16) the following fluctuating relation is valid

\[ \langle \Delta X \Delta P \rangle > 0, \]

where \( \Delta X = \sqrt{\langle X^2 \rangle - \langle X \rangle^2} \), and \( \Delta P = \sqrt{\langle P^2 \rangle - \langle P \rangle^2} \).

On the other hand, inserting \( F(x, \bar{p}, t) = f(x, t) \delta(\bar{p}) \) into (13) and taking into account the high friction condition

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

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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
\[
\frac{\partial f(x, t)}{\partial t} = -\frac{1}{\gamma} \frac{\partial}{\partial x} \left[ \mathcal{K}(x, t)f(x, t) \right] + \frac{A_{xx}}{2} \frac{\partial^2 f(x, t)}{\partial x^2},
\]
(17)
where
\[
\mathcal{K}(x, t) = -\frac{dV}{dx} + \gamma \left( \frac{C^2}{tc} \right)^{1/3} \left( e^{-t/t_c} - e^{-2t/t_c} \right).
\]
Replacing (15) into (17) we obtain $A_{xx} = 2\kappa B T/\gamma$ in both stationary and Markovian regimes.

Considering $V = 0$ (free particle) and $C = 0$ from our equation (12) we derive the non-Markovian Rayleigh equation in $p$-space
\[
\frac{\partial g(p, t)}{\partial t} = \frac{\gamma}{m} \frac{\partial}{\partial p} \left[ pg(p, t) \right] + D(1 - e^{-t/t_c})^2 \frac{\partial^2}{\partial p^2} g(p, t),
\]
(18)
with
\[
g(p, t) = \int \mathcal{F}(x, p, t) dx.
\]
At thermal equilibrium we find $D_{pp} = \gamma k_B T$ as being the diffusion coefficient in momentum space after inserting (15) into (18). For both (16) and (18) the fluctuating relation
\[
\Delta X \Delta P = 0
\]
is satisfied.

From the mathematical viewpoint we note that we can derive the Kramers equation (16), the Smoluchowski equation (17), and the Rayleigh equation (18) as special cases of our equation of motion (13). That physically means that all the physics encapsulated into these equations of motion (16), (17), and (18) are in principle contained in our Eq.(13).

In the next sections we wish to survey the quantization of our Smoluchowki equation (17), thereby tackling the problem of quantum tunneling at zero temperature in the strong friction regime.
IV Quantization of our Smoluchowski equation

We start with the non-Markovian Smoluchowski equation (17) at points $x_1$ and $x_2$; we multiply the first equation by $f(x_2, t)$ and the second one by $f(x_1, t)$. We add the resulting equations and obtain the following evolution equation for the function $\xi = \xi(x_1, x_2, t) = f(x_1, t)f(x_2, t)$:

$$\frac{\partial \xi}{\partial t} = -\frac{1}{\gamma} \left( \frac{\partial}{\partial x_1} \mathcal{K}(x_1, t) + \frac{\partial}{\partial x_2} \mathcal{K}(x_2, t) \right) \xi + 2A_{xx} \frac{\partial^2 \xi}{\partial p^2}. \quad (19)$$

We now perform the change of variables

$$x = \frac{x_1 + x_2}{2}, \quad \eta = x_1 - x_2.$$

We define our quantization process by introducing the following Fourier transform $[13, 14, 15]$

$$F(x, p, t) = \frac{1}{2\pi\hbar} \int \xi(x, \eta, t) e^{ip\eta/\hbar} d\eta, \quad (20)$$

$h$ being the Planck constant $\hbar$ divided by $2\pi$ and $p = m dx/dt$ the physical momentum. Inserting (20) into (19) we arrive at our non-Gaussian, non-Markovian equation of motion in quantum phase space $(x, p; \hbar)$

$$\frac{\partial F}{\partial t} = -\frac{1}{\gamma} (\mathcal{O}F + \mathcal{A}F + \mathcal{B}F) + \frac{\mathcal{D}(t)}{2} \frac{\partial^2 F}{\partial x^2} - 2\mathcal{D}(t) \frac{p^2}{\hbar^2} F, \quad (21)$$

with

$$\mathcal{O}F = 2 \sum_{s=1,3,5,...} \frac{1}{(s-1)!(2s-1)} \frac{\partial^s \mathcal{K}(x, t)}{\partial x^s} \frac{\partial^{s-1} F}{\partial p^{s-1}}, \quad (22)$$

$$\mathcal{A}F = \sum_{r=0,2,4,...} \frac{1}{r!2^r} \frac{\partial^r \mathcal{K}(x, t)}{\partial x^r} \mathcal{D}(t) \frac{\partial^{r+1} F}{\partial p^{r+1}}, \quad (23)$$

$$\mathcal{B}F = 2 \sum_{s=1,3,5,...} \frac{1}{s!2^s s+1} \frac{\partial^s \mathcal{K}(x, t)}{\partial x^s} \left\{ s \frac{\partial^{s-1} F}{\partial p^{s-1}} + p \frac{\partial^s F}{\partial p^s} \right\}, \quad (24)$$

and

$$\mathcal{D}(t) = (DC^2)^{1/3}(1 - e^{-t/t_c})^2. \quad (25)$$
Our quantum Smoluchowski equation (21) is valid far from the thermal equilibrium and for nonlinear external forces. We emphasize that according to our quantization procedure, based on the Fourier transformation (20), our Eq. (21) has to obey the Heisenberg fluctuating relation

$$\Delta X \Delta P \geq \frac{\hbar}{2},$$

thus restoring the stochastic character of momentum variable in the quantum domain. In the classical limit, $\hbar \to 0$, we recover the classical expression $\Delta X \Delta P \geq 0$. Most specifically, assuming

$$F(x, p, t) = f(x, t)\delta(p)$$

our quantum equation (21) leads to the classical Smoluchowski equation (17), since

$$\int OFdp = 2\frac{\partial K}{\partial x}f(x, t),$$
$$\int AFdp = K\frac{\partial f(x, t)}{\partial x},$$
$$\int BFdp = -\frac{\partial K}{\partial x}f(x, t).$$

### IV.1 Harmonic oscillator

Let us consider $V = \frac{kx^2}{2}$, $k$ being a constant. Equation (21) turns out to be written as

$$\frac{\partial F}{\partial t} = \frac{k}{\gamma}F + \frac{k}{\gamma}[x + h(t)]\frac{\partial F}{\partial x} + \frac{D(t)}{2}\frac{\partial^2 F}{\partial x^2} - \frac{k}{\gamma}p\frac{\partial F}{\partial p} - 2D(t)\frac{p^2}{\hbar^2}F,$$  

where

$$h(t) = \frac{\gamma}{k}\left(\frac{C^2}{t_c}\right)^{1/3}(e^{-2t/t_c} - e^{-t/t_c}).$$

With the initial condition

$$F(x, p, t = 0) = \frac{\sqrt{ab}}{\pi\hbar}e^{-ap^2/\hbar - bx^2/\hbar},$$  

(27)
\( a \) and \( b \) being Gaussian parameters, the solution for (26) reads

\[
F(x,p,t) = \frac{1}{2\pi} \left( \frac{A(t)}{B(t)} \right)^{1/2} e^{-A(t)p^2 - [x-c(t)]^2/4B(t)},
\]

where

\[
A(t) = \left\{ \frac{a}{\hbar} - 2\frac{g(t)}{\hbar^2} \right\} e^{-2kt/\gamma} + \frac{2g(t)}{\hbar^2},
\]

\[
B(t) = \left\{ \frac{\hbar}{4b} - \frac{g(t)}{2} \right\} e^{-2kt/\gamma} + \frac{g(t)}{2},
\]

\[
c(t) = (1 - e^{-kt/\gamma})\mu(t),
\]

\[
g(t) = \gamma(C^2D)^{1/3} \left\{ \frac{1}{2k} - 2tc e^{-t/te} - e^{-t/te} + \frac{te^{-2t/te}}{2(kt_e - \gamma)} \right\},
\]

and

\[
\mu(t) = \left( \frac{C}{t_c} \right)^{2/3} \left\{ \frac{e^{-2t/te}}{2} - e^{-t/te} \right\}.
\]

Solution (28) leads to

\[
\Delta X = \sqrt{2B(t)},
\]

\[
\Delta P = \frac{1}{\sqrt{2A(t)}},
\]

that is,

\[
\Delta X \Delta P = \sqrt{\frac{B(t)}{A(t)}} \geq \frac{\hbar}{2}.
\]

V Quantum tunneling

Now, let \( t = \Delta\tau \) be a fixed time interval for observing the Brownian particle such that we have a steady solution for (26), that is, \( \partial F/\partial t|_{t=\Delta\tau} = 0 \). During \( \Delta\tau \) the system is therefore stationary. In this context, we aim at to calculate the quantum Kramers escape rate of a Brownian particle over a potential barrier in the strong friction regime.

We consider a Brownian particle moving in a double-well potential \( V(x) \). The barrier top is located at point \( x_b \), while the two bottom wells is at \( x_a \).
and $x_c$, such that $V(x_a) = V(x_c) = 0$, $x_a < x_b$. The starting point is our solution (28) we modify according to

$$F(x, p, \Delta \tau) = \alpha \phi(x, p) e^{-A(\Delta \tau)p^2 - [x - c(\Delta \tau)]^2 / 4B(\Delta \tau)}, \quad \alpha = \text{constant.} \quad (37)$$

Inserting (37) into the steady version of (26) we derive the ordinary differential equation for the function $\phi(x, p)$

$$\frac{D\gamma}{2k} \frac{d^2 \phi}{d\xi^2} = \frac{\xi}{d\xi} \phi, \quad \xi = p - x, \quad (38)$$

since

$$B(\Delta \tau) = \frac{D\gamma}{4k}, \quad (39)$$

$$A(\Delta \tau) = \frac{D\gamma}{kh^2}, \quad (40)$$

$$h(\Delta \tau) = -c(\Delta \tau). \quad (41)$$

From (39) and (40) we determine the parameters of Gaussian function (27) as being

$$a = \frac{D\gamma}{h} \left\{ \frac{1}{k} + 2u \left( 1 - e^{k\Delta \tau / \gamma} \right) \right\}, \quad (42)$$

and

$$b = \frac{h}{D\gamma} \left\{ \frac{1}{k} + 2u \left( 1 - e^{k\Delta \tau / \gamma} \right) \right\}, \quad (43)$$

with

$$u = u(\Delta \tau) = \left\{ -2t_c e^{-\Delta \tau / t_c} + \frac{t_c e^{-2\Delta \tau / t_c}}{2(kt_c - \gamma)} \right\}. \quad (44)$$

It follows then that $ab = 1$, whereas from the identity (41) we have the following relation among the time scales $\Delta \tau$ (the observation time), $t_c$ (the correlation time), and $t_r = \gamma / k$ (the relaxation time):

$$t_c^{1/3} = \frac{(e^{-\Delta \tau/t_c} - 1)(e^{-\Delta \tau/t_c} - 2)}{2t_r (e^{-\Delta \tau/t_c} - 1)} \quad (45)$$

A solution to the differential equation (38) is given by

$$\phi(\xi) = \sqrt{-\frac{k}{\pi D\gamma}} \int_{-\infty}^{\xi} e^{(k/D\gamma)\xi^2} d\xi, \quad k < 0, \quad (46)$$
wherein we have used the boundary condition \( \phi(\xi \to +\infty) = 1 \). This result confirms the fact that the region around the barrier at \( x_b \), in which the curvature of the potential is negative, is quite relevant in the calculation of the diffusion current, as we will see below. Substituting (46), (39), and (40) into (37) and expanding the ensuing \( F(x, p) \) around \( x_b \) we obtain

\[
F = \alpha e^{-2V(x_b)/D\gamma} \sqrt{\frac{m\omega_b^2}{\pi D\gamma}} e^{-(D\gamma/m\omega_b^2h^2)p^2+(m\omega_b^2/D\gamma)(x-x_b-c)^2} \int_{-\infty}^{\xi} e^{-(m\omega_b^2/D\gamma)\xi^2} d\xi,
\]

(47)

with \( k_b = -m\omega_b^2 \). At point \( x = x_b \) we find the following diffusion current

\[
j_b = \int F(x = x_b, p) \frac{p}{m} dp = \frac{\alpha \omega_b^2 h^2 e^{(m\omega_b^2/c^2/D\gamma)}}{2D\gamma \sqrt{1 - (D\gamma/m\omega_b^2h)^2}} e^{-2V(x_b)/D\gamma},
\]

(48)

where

\[
c = c(\Delta\tau) = (1 - e^{m\omega_b^2\Delta\tau/D\gamma}) \left( \frac{C}{t_c} \right)^{2/3} \left\{ \frac{e^{-2\Delta\tau/t_c}}{2} - e^{-\Delta\tau/t_c} \right\}.
\]

(49)

Our result (48) is valid provided

\[
m\omega_b^2 h > D\gamma.
\]

(50)

At the vicinity of \( x_a \) we cannot use the stationary solution (47), since it is only valid for negative curvature \( k < 0 \), hence we use the (nonnormalized) function

\[
F(x, p) = \alpha e^{-(D\gamma/kh^2)p^2-(k/D\gamma)(x-c)^2}
\]

to finding the number of Brownian particles injected around \( x_a \):

\[
\nu_a = \int \int F(x, p) dx dp = \alpha \pi h.
\]

Using \( \nu_a \) and the current (48) the non-Markovian quantum Kramers escape rate at non-equilibrium regime reads

\[
\Gamma = \frac{j_a}{\nu_a} = \frac{\omega_b^2 h e^{m\omega_b^2/c^2/D\gamma}}{2\pi D\gamma \sqrt{1 - (D\gamma/m\omega_b^2h)^2}} e^{-2V(x_b)/D\gamma}.
\]

(51)
In the Markovian limit $\Delta \tau \gg t_c$, or formally $t_c \to 0$, from (51) we obtain

$$\Gamma = \frac{\omega_b^2 \hbar}{2\pi D \gamma \sqrt{1 - \left(\frac{D \gamma \omega_b^2 \hbar}{m} \right)^2}} e^{-2V(x_b)/D \gamma}.$$  \hspace{1cm} (52)

Non-Markovian properties are therefore responsible for the enhancement of the quantum tunneling rate far from the thermal equilibrium.

We want now to evaluate the diffusion coefficient $D$ present in (51) or (52) using the well-established principles of equilibrium thermodynamics. To this end, let us assume that during $\Delta \tau$ our open system has attained a thermal equilibrium situation in which is valid the principle of energy equipartition

$$\langle E \rangle = \frac{\langle P^2 \rangle}{2m} + \frac{k}{2} \langle X^2 \rangle = \kappa_B T$$ \hspace{1cm} (53)

that associates the stochastic dynamics of the Brownian particle (e.g., its average total energy) to equilibrium thermodynamics underlying the thermal environment (Boltzmann’s constant $\kappa_B$ and temperature $T$).

Replacing (39) and (40) into (34) and (35), respectively, we find

$$\langle X^2 \rangle = \frac{D \gamma}{2k},$$  \hspace{1cm} (54)

$$\langle P^2 \rangle = \frac{k \hbar^2}{2\gamma D}$$ \hspace{1cm} (55)

that lead to the following equation according to (53)

$$D^2 - \frac{4\kappa_B T}{\gamma} D + \frac{k \hbar^2}{m \gamma^2} = 0,$$ \hspace{1cm} (56)

whose solution is the quantum diffusion coefficient [18]

$$D = \frac{2\kappa_B T}{\gamma} + \frac{1}{\gamma} \sqrt{(2\kappa_B T)^2 - (\hbar \Omega)^2}; \quad \Omega^2 = k/m, \quad k > 0,$$ \hspace{1cm} (57)

valid for any finite temperature $T \geq \hbar \Omega/2\kappa_B$, or

$$D = \frac{2\kappa_B T}{\gamma} + \frac{1}{\gamma} \sqrt{(2\kappa_B T)^2 + (\hbar \omega)^2}; \quad \omega^2 = -k/m, \quad k < 0,$$ \hspace{1cm} (58)
valid for any finite temperature $T \geq 0$. At high temperature, $\kappa_B T \gg \hbar \Omega, \hbar \omega$, both (57) and (58) lead to the classical diffusion coefficient $D = 4\kappa_B T/\gamma$. On the other hand, at low temperature so that the quantum energy of the Brownian particle is equal to the thermal energy of the reservoir, i.e., $\kappa_B T = \hbar \Omega/2 = \hbar \omega/2$, (57) and (58) lead to $D = \hbar \Omega/\gamma$ and $D = \hbar \omega(1 + \sqrt{2})/\gamma$, respectively. At lower temperature, $\kappa_B T \ll \hbar \omega$, from (58) we obtain $D =\hbar \omega/\gamma$ which in turn leads to $D = \hbar \omega/\gamma$ at zero temperature.

Due to the condition (50) the non-Markovian quantum Kramers escape rate is thereby constrained to the low-temperature realm ($T < \hbar \omega/\kappa_B$)

$$\Gamma = \frac{\omega^2_B \hbar e^{m \omega_B^2 c^2/(\omega_B h + 2\kappa_B T)}}{2\pi (\omega_B h + 2\kappa_B T) \sqrt{1 - [(\omega_B h + 2\kappa_B T)/m \omega_B^2 h]^2}} e^{-2V(x_b)/(\omega_B h + 2\kappa_B T)} \tag{59}$$

that in the Markovian limit leads to

$$\Gamma = \frac{\omega^2_B \hbar}{2\pi (\omega_B h + 2\kappa_B T) \sqrt{1 - [(\omega_B h + 2\kappa_B T)/m \omega_B^2 h]^2}} e^{-2V(x_b)/(\omega_B h + 2\kappa_B T)}. \tag{60}$$

At zero temperature from (59) we obtain the non-Markovian rate

$$\Gamma = \frac{\omega_B e^{m \omega_B c^2/\hbar}}{2\pi \sqrt{1 - (1/m \omega_B)^2}} e^{-2V(x_b)/\omega_B \hbar}, \tag{61}$$

whereas in the Markovian case we derive

$$\Gamma = \frac{\omega_B}{2\pi \sqrt{1 - (1/m \omega_B)^2}} e^{-2V(x_b)/\omega_B \hbar}. \tag{62}$$

that is the same result obtained in our previous work [15].

We wish to point out that our Markovian results (60) and (62) are independent of the friction constant $\gamma$ at thermal equilibrium. This means that over the barrier at low temperatures (including zero temperature) Brownian particles may decay into a metastable well around $x_c$ at high temperatures. This may take place without violating the Second Law of Thermodynamics since in the quantum domain at low temperatures the particles could flux overcoming any dissipative mechanism (superfluidity phenomenon!).

So far we have considered the thermal environment as having a general nature. Supposing then that the thermal reservoir consists of a set of many
harmonic oscillators we can generalize the equipartition theorem of energy (53) taking into account the quantum nature of the heat bath:

\[
\langle E \rangle = \frac{\langle P^2 \rangle}{2m} + \frac{k}{2}\langle X^2 \rangle = (\hbar \nu / 2) \coth(\hbar \nu / 2\kappa_B T).
\] (63)

[\nu = (k/m)^{1/2} for \( k > 0 \), and \( \nu = (-k/m)^{1/2} \) for \( k < 0 \)]. It follows then the equation \( D^2 - 4\langle E \rangle D/\gamma + k\hbar^2/m\gamma^2 = 0 \) that yields the solution

\[
D = \frac{h\Omega}{\gamma \coth \frac{h\Omega}{2\kappa_B T}} + \frac{\Omega h}{\gamma} \sqrt{\coth^2 \frac{h\Omega}{2\kappa_B T} - 1}; \quad \Omega^2 = k/m, \quad k > 0,
\] (64)

or

\[
D = \frac{h\omega}{\gamma \coth \frac{h\omega}{2\kappa_B T}} + \frac{\omega h}{\gamma} \sqrt{\coth^2 \frac{h\omega}{2\kappa_B T} + 1}; \quad \omega^2 = -k/m, \quad k < 0.
\] (65)

At high temperature, \( \kappa_B T \gg h\Omega, h\omega \), both (64) and (65) lead to \( D = 4\kappa_B T/\gamma \). At low temperature, \( \kappa_B T \ll h\Omega, h\omega \), (including zero temperature \( T = 0 \)), (64) and (65) lead to \( D = h\Omega/\gamma \) and \( D = h\omega(1 + \sqrt{2})/\gamma \), respectively. Hence we obtain the non-Markovian quantum Kramers escape rate (52) as being given by the expression

\[
\Gamma = \frac{\omega_b e^{\omega_b^2 e^2 / h\omega_b(1 + \sqrt{2})}}{2\pi(1 + \sqrt{2}) \sqrt{1 - [(1 + \sqrt{2})/m\omega_b]^2}} e^{-2V(x_b) / h\omega_b(1 + \sqrt{2})}.
\] (66)

In the Markovian limit we obtain

\[
\Gamma = \frac{\omega_b}{2\pi(1 + \sqrt{2}) \sqrt{1 - [(1 + \sqrt{2})/m\omega_b]^2}} e^{-2V(x_b) / h\omega_b(1 + \sqrt{2})}
\] (67)

that exhibits the influence of the zero-point energy of the thermal reservoir upon the quantum tunneling rate of our Brownian particle at zero temperature. Eq.(67) is also independent of frictional constant \( \gamma \), thus leading to the superfluidity phenomenon.

**VI Summary and discussions**

In this paper we have addressed the issue of quantum tunneling at low (including zero temperature) for non-Markovian open systems away from the
thermal equilibrium. From our quantum Smoluchowski equation (21) we have derived the non-equilibrium, non-Markovian quantum escape rate (51) that does depend on both the friction and diffusion coefficients.

We have thus provided an alternative method of quantizing the Smoluchowski equation taking into account non-Markovian and non-equilibrium effects. This result, coming from our non-Hamiltonian account, is novel and is not present in others approaches \cite{9, 12, 19, 20}.

At low temperature and in the Markovian regime our quantum Kramers escape rates (60) and (67) are independent of damping constant $\gamma$. That is, dissipation has no effect on the quantum tunneling, thus giving rise to superfluidity. This result has been misunderstood by Ankerhold et al.\cite{19} that state: “This finding (...) contracts existing theoretical results verified by experimental data”. This statement is incorrect since Ao et al.\cite{21} have arrived at our same conclusion by studying Landau–Zener tunneling in a dissipative environment: “no effect of dissipation is present at zero temperature”.

We hope our present work could foster development of experimental researches on quantum tunneling in overdamped open systems in order that we can compare our theoretical predictions with experimental data.

In a forthcoming paper \cite{22} we pursue our non-Hamiltonian approach in surveying quantum tunneling effects from the quantization of our non-equilibrium, non-Markovian Fokker–Planck equation (13) and of the Rayleigh equation (18), as well as quantum tunneling in the small friction regime (energy diffusion).

To conclude, we want to point out that non-linear effects due to the external potential can be also analyzed through our quantum Smoluchowski equation (21)

$$\frac{\partial F}{\partial t} = \frac{1}{\gamma} \left( x^2 \frac{\partial F}{\partial x} + \frac{1}{4} \frac{\partial^3 F}{\partial x \partial p^2} + 2xF - 2xp \frac{\partial F}{\partial p} \right) + \frac{D(t) \partial^2 F}{2 \partial x^2} - 2D(t) \frac{p^2}{\hbar^2} F$$

for the cubic potential $V = x^3/3$, for instance.
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Appendix: Derivation of our Fokker–Planck equation \[ \text{[Eq.(13)]} \]

In this appendix we want to show in somewhat details how we could explicitly construct the Fokker–Planck equation (13) from the system of stochastic differential equations [13]

\[
\frac{d\bar{P}}{dt} = -\frac{dV}{dX} \frac{\gamma}{m} \bar{P} + b_1 \Psi ; \quad \frac{dX}{dt} = \frac{\bar{P}}{m} + b_2 \Psi.
\]

Equations (69) yield the results

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

and

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

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

\[
A_p = \lim_{\Delta t \to 0} \frac{\langle \Delta \bar{P} \rangle}{\Delta t} = -\frac{dV}{dX} \frac{\gamma}{m} \bar{P} + \frac{1}{m} \int_t^{t+\Delta t} b_1(t') \langle \Psi(t') \rangle dt', \]

\[
A_{pp} = \lim_{\Delta t \to 0} \frac{\langle (\Delta \bar{P})^2 \rangle}{\Delta t} = -2 \left( \frac{dV}{dX} + \frac{\gamma}{m} \bar{P} \right) \lim_{\Delta t \to 0} \int_t^{t+\Delta t} b_1(t') \langle \Psi(t') \rangle dt' + \lim_{\Delta t \to 0} \frac{1}{\Delta t} \int_t^{t+\Delta t} \int_t^{t+\Delta t} b_1(t') b_1(t'') \langle \Psi(t') \Psi(t'') \rangle dt' dt'',
\]

\[
A_x = \lim_{\Delta t \to 0} \frac{\langle \Delta X \rangle}{\Delta t} = \frac{\bar{P}}{m} + \frac{1}{m} \lim_{\Delta t \to 0} \int_t^{t+\Delta t} \int_t^s b_1(t') \langle \Psi(t') \rangle dt' ds + \lim_{\Delta t \to 0} \int_t^{t+\Delta t} b_2(t') \langle \Psi(t') \rangle dt'.
\]
\[ A_{xx} = \lim_{\Delta t \to 0} \frac{\langle (\Delta X)^2 \rangle}{\Delta t} = I_1 + I_2 + I_3 + I_4 \] (75)

with

\[ I_1 = \frac{2\bar{P}}{m^2} \int_t^{t+\Delta t} \int_t^s b_1(t') \langle \psi(t') \rangle dt' ds, \] (76)

\[ I_2 = \frac{2\bar{P}}{m} \int_t^{t+\Delta t} b_2(t') \langle \psi(t') \rangle dt', \] (77)

\[ I_3 = \frac{1}{m^2} \lim_{\Delta t \to 0} \int_t^{t+\Delta t} \int_t^{t+\Delta t} \int_t^s b_1(t') b_1(t'') \langle \psi(t') \psi(t'') \rangle dt' dt'' ds, \] (78)

\[ I_4 = \frac{2}{m} \lim_{\Delta t \to 0} \int_t^{t+\Delta t} \int_t^{t+\Delta t} \int_t^s b_1(t') b_2(t'') \langle \psi(t') \psi(t'') \rangle dt' dt'' ds, \] (79)

\[ I_5 = \int_t^{t+\Delta t} \int_t^{t+\Delta t} b_1(t') b_2(t'') \langle \psi(t') \psi(t'') \rangle dt' dt'', \] (80)

and

\[ A_{xp} = \lim_{\Delta t \to 0} \frac{\langle \Delta X \Delta \bar{P} \rangle}{\Delta t} = \xi_1 + \xi_2 + \xi_3 + \xi_4 + \xi_5, \] (81)

where

\[ \xi_1 = \frac{\bar{P}}{m} \int_t^{t+\Delta t} b_1(t') \langle \psi(t') \rangle dt', \] (82)

\[ \xi_2 = -\frac{1}{m} \left( \frac{dV}{dX} + \frac{\gamma}{m} \bar{P} \right) \int_t^{t+\Delta t} \int_t^s b_1(t') \langle \psi(t') \rangle dt' ds, \] (83)

\[ \xi_3 = \frac{1}{m} \lim_{\Delta t \to 0} \frac{1}{\Delta t} \int_t^{t+\Delta t} \int_t^{t+\Delta t} \int_t^s b_1(t') b_1(t'') \langle \psi(t') \psi(t'') \rangle dt' dt'' ds, \] (84)

\[ \xi_4 = -\frac{\bar{P}}{m} \int_t^{t+\Delta t} b_2(t') \langle \psi(t') \rangle dt', \] (85)

\[ \xi_5 = \lim_{\Delta t \to 0} \frac{1}{\Delta t} \int_t^{t+\Delta t} \int_t^{t+\Delta t} b_2(t') b_2(t'') \langle \psi(t') \psi(t'') \rangle dt' dt''. \] (86)

After using our definitions
\[ \langle \Psi(t') \Psi(t'') \rangle = \left( D / t_c^2 \right)^{1/3} e^{-(t''-t')/t_c}; \quad \langle \Psi \rangle = \left( C / t_c^2 \right)^{1/3} e^{-t'/t_c}, \tag{87} \]

and
\[
\begin{align*}
 b_1 &= \int_0^t \langle \Psi(t') \Psi(t'') \rangle dt'' = (Dt_c)^{1/3}(1 - e^{-t/t_c}), \\
 b_2 &= \int_0^t \langle \Psi(t') \rangle dt' = (Ct_c)^{1/3}(1 - e^{-t/t_c}). \tag{88} \end{align*}
\]

into (72–75) and (81) we obtain our Fokker–Planck equation (13) with the coefficients
\[
\begin{align*}
 A_x &= (\bar{\rho} / m) + \left( \frac{C^2}{t_c} \right)^{1/3} \left( e^{-t/t_c} - e^{-2t/t_c} \right), \\
 A_{\bar{p}} &= -kx - \left( \frac{\gamma}{m} \right) \bar{p} + \left( \frac{CD}{t_c} \right)^{1/3} \left( e^{-t/t_c} - e^{-2t/t_c} \right), \\
 A_{xx} &= (C^2 D)^{1/3}(1 - e^{-t/t_c})^2, \\
 A_{\bar{p}\bar{p}} &= D(1 - e^{-t/t_c})^2. \tag{90, 91, 92, 93, 94} \end{align*}
\]
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