From Entropic to Energetic: The Transformation Behavior of Potential Barriers

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The diffusion of biased Brownian particles over an entropic barrier in a confined medium is investigated. By altering the direction of the external bias, the nature of the potential barriers changes from purely entropic to energetic. The strong non-Arrhenius dependence of the escape rate is observed due to a crossover between the entropy-dominated regime and energy-dominated regime under the cooperative effect of external bias and thermal motion.

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I. INTRODUCTION

Diffusion of particles over a potential barrier under thermal activation has been a classic paradigm for investigating rate processes in physical, chemical, and biological sciences over many decades [1–3]. Effective control of the mass and charge transport requires a deep understanding of the diffusion mechanism involving small objects whose size ranges from the nano- to the microscale. Thereby, diffusive transport can either be described in terms of a macroscopic description which is given by Fick’s second law or as a stochastic process accounting for the erratic motion of suspended microscopic particles. This erratic motion was first systematically studied by the botanist Robert Brown, its related theories played a central role in the development of both the foundations of thermodynamics and the dynamical interpretation of statistical physics, so diffusion of microscopic (Brownian) particles is often referred to as Brownian motion [4, 5]. In general, energetic barriers are more frequent in problems of solid-state physics (metals and semiconductors, photonic crystals, and coupled Josephson junctions) [6–8] and entropic barriers are often encountered in soft-condensed matter and biological systems [9, 10]. Especially when the system is scaled down to a mesoscopic level and constrained to move in a confined space in two or three dimensions with uneven boundaries, the boundary effects come into play in a nontrivial way. In the frame of the Fick-Jacobs equation [11], an effective entropic barrier in the free energy expression is equivalent to a Smoluchowski equation in the reduced dimension. Irregular geometry plays a key role in transport processes [12–14].

Zwanzig originally addressed the diffusion problem of particles through a narrow tube of varying cross-section to show how the stochastic dynamics is governed by position-
dependent diffusivity in reduced dimensions [15]. Subsequently, the concept of an entropic barrier and the associated problems [16–20] were investigated in several issues related to transport in periodic channels [19], thermal activation in a bistable potential exhibiting entropic variants of stochastic resonance [20, 21], and resonant activation [22]. Burada and co-workers considered a Brownian particle moving in a confined medium and provided an analytical tool to analyze transport characteristics in periodic confined structures [23]. Ghosh et al. put forward the concept of ‘geometricstochastic resonance’, considering such a manifestation of stochastic resonance requires neither energetic nor entropic barriers, but a purely geometric effect [24]. In their most recent investigation, they studied the inertial effects on Brownian transport through narrow pores, and gave some detailed discussion on potential applications to colloidal systems [25, 26]. Huang et al. considered the dynamics of the particle influences by a driving force with both Gaussian and compound Poisson noises [27]. The pioneering researches mainly focused on the basis that there is a deterministic direction of the bias. Actually, in the real world, the direction of the bias is usually random, so that we introduce the bias angle to describe the stochastic direction of bias. Besides, since the Fick-Jacobs equation involves forces of both energetic and entropic origin, it is significant to investigate the relationship between these two factors. The paper is organized as follows: in Section II, we give the model for the Brownian motion of a particle in a two-dimensional confined space and discuss the nature of the potential barriers. In Section III, we investigate the diffusive motion of particles to explore the non-Arrhenius behavior of the escape rate of thermal noise and particle radius. Finally, a conclusion summarizes this paper in Section IV.

II. THE NATURE OF THE POTENTIAL BARRIERS

The overdamped Brownian particle in a confined geometry subjected to the constant force $\vec{F}$ can be described by the Langevin equation written as [28]

$$\gamma \frac{d\vec{s}}{dt} = \vec{F} + \sqrt{\gamma k_B T} \vec{\xi}(t)$$

(1)

with

$$\vec{F} = f \vec{e}_x - g \vec{e}_y,$$

(2)

where $f = |\vec{F}| \cos \theta$ and $g = |\vec{F}| \sin \theta$ denote the force components along and perpendicular to the 2D channel direction, respectively. $\vec{s}$ describes the position of the particle in two dimensions, $\gamma$ is the friction coefficient, $\vec{e}_x$, $\vec{e}_y$ are the unit vectors along the $x$ and $y$ directions, respectively. The fluctuating term $\vec{\xi}(t) = [\xi_x(t), \xi_y(t)]$ is characterized by zero-mean and has the following statistical properties:

$$\langle \xi_i(t) \rangle = 0,$$

(3)

$$\langle \xi_i(t) \rangle \langle \xi_j(t) \rangle = 2\delta_{ij}(t - t'), \text{ for } i, j = x, y.$$

(4)
FIG. 1: The schematic plot of the two-dimensional space of the particle with the boundary expressed by Equation (4).

The confinement can be accounted for by imposing reflecting boundaries on the system. The walls shown in Figure 1 could be described by the following equation:

$$B_l(x) = -B_u(x) = L_y(x/L_x)^4 - 2L_y(x/L_x)^2 - c/2,$$

where $B_l(x)$ and $B_u(x)$ correspond to the lower and upper boundary functions, $L_x$ denotes the distance between the middle point of the bottleneck and the position of the maximal width, $L_y$ refers to the narrowing of the boundary functions, and $c$ to the remaining width of the bottleneck. Consequently,

$$w(x) = (B_u(x) - B_l(x))/2$$

gives the local width of the structure.

To proceed further we employ the dimensionless description of the dynamics with the help of following scaled quantities: $\bar{x} = x/L_x$ and $\bar{y} = y/L_x$. This ensures the scaled boundary functions and the local width as $\bar{B}_l(\bar{x}) = B_l(x)/L_x = -\bar{B}_u(\bar{x})$ and $\bar{w}(\bar{x}) = w(x)/L_x$. The time $t$ is scaled as $\bar{t} = t/\tau$, where $\tau = \gamma L_x^2/kT_R$ with $T_R$ as a reference temperature. $\tau$ is essentially the time taken by the particle to diffuse a distance $L_x$ at temperature $T_R$. 
With a Langevin description, the system can now be reduced in two directions by the following dimensionless equations:

\[
\frac{dx}{dt} = f + \sqrt{D} \xi_x(t), \quad \frac{dy}{dt} = -g + \sqrt{D} \xi_y(t),
\]  

(7)

and the boundary function (5) reads:

\[
w(x) = -ax^4 + bx^2 + c/2,
\]  

(8)

with the rescaled temperature \( D = T/T_R \). At the same time, we defined the aspect ratio \( a = L_y/L_x \) and \( b = 2a \), i.e., \( a \) and \( b \) are appropriately scaled constants. Our emphasis in this work is to study the temperature dependence of the escape rate of the enclosed Brownian particles from the position with maximum local half-width of the left lobe to that of the right lobe through the narrow bottleneck.

The Fokker-Planck description corresponding to the Langevin dynamics [Eq. (7)] is given by [30]:

\[
\frac{\partial P(x, t)}{\partial t} = D \frac{\partial}{\partial x} \left[ \exp \left( \frac{-u(x, y)}{D} \right) \frac{\partial}{\partial x} \exp \left( \frac{-u(x, y)}{D} \right) P(x, y, t) \right] + D \frac{\partial}{\partial y} \left[ \exp \left( \frac{-u(x, y)}{D} \right) \frac{\partial}{\partial x} \exp \left( \frac{-u(x, y)}{D} \right) P(x, y, t) \right],
\]  

(9)

where the potential function is written as \( u(x, y) = gy/D \). We use reflecting boundary conditions at the confining walls.

The above description of motion of the Brownian particle in two dimensions in an enclosure of spatially varying cross section can be simplified by introducing an effective potential in one dimension. This dimensional reduction can be achieved by employing a marginal probability distribution \( P(x, t) \) along the \( x \) direction and a conditional local equilibrium probability of \( y \) at a given \( x, \sigma(y; x) \), and assuming a local equilibrium along the \( y \) direction as follows:

\[
P(x, y, t) = P(x, t) \sigma(y; x).
\]  

(10)

This results in the FJ equation

\[
\frac{\partial P(x, t)}{\partial t} = \frac{\partial}{\partial x} \left[ D \frac{\partial}{\partial x} P(x, t) + A'(x, D, g) P(x, t) \right],
\]  

(11)

\( A' \) refers to the spatial derivative along \( x \), the effective potential experienced by the Brownian particle is given by

\[
A(x, \theta) = -fx - D \ln \left[ \frac{2D}{g} \sinh \left( \frac{gw(x)}{D} \right) \right].
\]  

(12)

Note that the free energy \( A(x, \theta) \) can be tuned by altering the aspect ratio \( gw(x)/D \). Consequently, it is significant to analyze the two limiting situations for the free energy \( A(x, \theta) \) that can be obtained depending on the angle of the bias.
Assuming the bias direction is parallel to the channel direction, i.e., when $\theta = 0$, the dimensionless free-energy function (12) modifies into the form

$$A(x) = -|\vec{F}|x - D \ln[2w(x)], \quad (13)$$

resembling a potential function with purely entropic barriers [14, 17–21].

The other limiting case is that the bias is perpendicular to the channel direction, the corresponding angle is $\theta = \frac{\pi}{2}$, Eq. (12) turns into

$$A(x) = -D \ln \left[ 2D \frac{|\vec{F}| \sinh\left( \frac{|\vec{F}|w(x)}{D} \right)}{\vec{F}} \right]. \quad (14)$$

This effective potential depends on the absolute value of the bias, the noise strength, and the geometry of the structure in a nontrivial way [20]. It is interesting that even in the limit of small noise ($D \to 0$), the effective potential exhibits energetic barriers persisting.

We can see that by changing the angle of the applied bias one can effectively steer the nature of the potential barriers, this means that the nature of the potential can be changed from entropic to energetic. Between the two limiting cases, at a finite angle of the applied bias, the free-function will have both an entropic and an energetic contribution. For small noise strengths it is purely energetic, but for strong noise strengths it is purely entropic [21].

III. THE NON-ARRHENIUS PHENOMENON BASED ON THE TRANSITION BEHAVIOR

Consider the limiting case of $\theta = \frac{\pi}{2}$, i.e., Brownian particles in a confined geometry subjected to a transverse force $g$ described by the following Langevin equation:

$$\gamma \left( \frac{d\vec{s}}{dt} \right) = -g\vec{e}_y + \sqrt{\gamma k_B T} \vec{\xi}(t). \quad (15)$$

According to Equation (14), the effective potential experienced by the Brownian particle is given by

$$A(x, D, g) = -D \ln \left[ 2D \frac{g \sinh\left( \frac{g w(x)}{D} \right)}{g} \right]. \quad (16)$$

The entropic potential $A(x, D, g)$ for the confinement is governed by Eq. (16) and shown in Fig. 2. To calculate the rate of transition, we compute the mean first passage time (MFPT) by rearranging the Ficks-Jacob equation (10) and finally obtain

$$t(x) = \frac{1}{D} \int_x^{x_s} dy \int_{y}^{y_r} dz \exp \left[ -\frac{A(y, D, g) - A(z, D, g)}{D} \right], \quad (17)$$

where $x_r$ and $x_s$ denote the reflecting boundary with $\frac{\partial t(x_r)}{\partial x} = 0$ and the absorbing boundary with $t(x_s) = 0$, respectively. The time scale of the barrier crossing process is given by
FIG. 2: A plot of spatial variation of the effective potential $A(x,D,g)$ in one dimension with $g/D = 1$.

the MFPT, which is inversely proportional to the rate of escape from the initial well at $x = -x_0 = -1$ (left-well minimum) to the bottom of the final well at $x = x_s = 1$

$$r_t = \frac{1}{t(-x_0)}.$$ (18)

For the present problem, the parameter set is chosen as $a = 25$, $b = 2a = 50$, and $c = 2$. Consequently, we obtain the first passage time from the left well (the initial well) to the right well (the final well) as

$$t(-x_0) = \frac{1}{D} \int_{-1}^{1} dx \exp\left[\frac{A(x)}{D}\right] \int_{x}^{x_s} dy \exp\left[-\frac{A(y)}{D}\right].$$ (19)

Employing Eqs. (16) and (18), we get

$$t(-x_0) = \frac{1}{D} \int_{-1}^{1} dx \exp\left[-\ln\left(\frac{2D}{g}\right)\sinh\left(\frac{gw(x)}{D}\right)\right] \int_{x}^{x_s} dy \exp\ln\left[\frac{2D}{g}\right] \sinh\left(\frac{gw(y)}{D}\right)$$

$$= \frac{1}{D} \int_{-1}^{1} dx \frac{g}{2D \sinh\left(\frac{gw(x)}{D}\right)} \int_{x}^{x_s} dy \frac{2D}{g} \sinh\left(\frac{gw(y)}{D}\right).$$ (20)
To calculate the first passage time taken by a Brownian particle to escape from one lobe to the other starting from an initial position at \( x = -1 \), \( y = -25 \), we make use of the reflecting and absorbing boundaries of the system set at \( x = -1.45 \) and \( x = +1 \), respectively, irrespective of the \( y \) coordinate.

The inverse of the numerical mean first passage time thus obtained is defined as the escape rate of the particle from one lobe to the other [31]. According to Eq. (20), we have plotted the variation of rate \( R \) vs \( g \) for several values of dimensionless temperature \( D \) in Fig. 3. It shows that the escape rate exhibits a crossover from the entropy-dominated regime to the energy-dominated regime with an increase of \( g \). The extent of dominance of either zone and the range of crossover regime are significantly influenced by temperature. A lower temperature makes the crossover zone smaller. At higher temperature the entropic dominance persists for a larger value of \( g \). The presentation of Figure 3 is the same as that in the previously performed work [29], which summarized the entropic factor \( gw(x)/D \) ratio as the characteristic of distinguishing between the Arrhenius region and the non-Arrhenius region of the transition rate. The latter is mainly governed by the shape of the channel.

IV. DISCUSSION AND CONCLUSIONS

The potential barrier of the underlying model and many of its variants are energetic in nature. However, when the system is scaled down to a mesoscopic level and constrained to move in a confined space in two or three dimensions with uneven boundaries, the boundary effects come into play in a novel way. In this paper, we adopt the Fick-Jacobs approximation to explore the relative role of energetic origin and entropic origin in the temperature dependence of the kinetics when an interplay of applied bias and thermal motion has been considered. We can effectively steer the nature of the potential barriers from entropic to energetic by changing the angle of the applied bias. In the special case of \( \theta = \frac{\pi}{2} \), the factor \( gw(x)/D \) is critical to the transition behavior of particles. If \( gw(x)/D \gg 1 \), the Arrhenius behavior of thermal activation is obviously observed. On the other hand, \( gw(x)/D \ll 1 \) is characteristic of the non-Arrhenius behavior of the transition rate. It is possible for us to tune the applied bias and the shape of the barrier to control the transport of Brownian particles in narrow confined structures. This temperature dependence of noise-induced escape may be relevant in several areas of biology like cells, ion channels, and in microporous media. It is worthy to deeply study this topic for its wide range of applications [32–34], including particle separation, catalysis, fluid mixing, and so on. In a real experiment, the bias \( \vec{F} \) could be realized through an electric field.

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FIG. 3: The transition rate $R$ as a function of the bias $g$, the scaled temperature $D$ takes 0.03, 0.1, 0.3 respectively.

References