Diffusion over an entropic barrier: Non-Arrhenius behavior

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We have examined the temperature dependence of noise-induced escape rate of Brownian particles between two distinct regions in a two-dimensional enclosure through a narrow bottleneck. Varying cross section of the confinement results in an effective entropic barrier in reduced dimension. The strong non-Arrhenius dependence of the escape rate is observed, which can be explained in terms of a crossover between entropy-dominated regime and energy-dominated regime in presence of an interplay of gravitational bias and thermal motion.

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The model of diffusion of particles over a potential barrier under thermal activation lies at the heart of rate processes in physical, chemical, and biological sciences over many decades [1–5]. The potential barrier of the underlying model is energetic in nature. However, for the particles at the mesoscopic level when constrained to move in a confined space in two or three dimensions with uneven boundaries, the boundary effects come into play in a significant way. One encounters an effective entropic barrier in the free energy expression in Fick-Jacobs equation [6], which is equivalent to a Smoluchowski equation in reduced dimension. Irregular geometrical constraints, may thus, play a key role in rate theory and transport processes [7–10]. In early 1990s, Zwanzig [11,12] was the first to address the problem of diffusion of particles through a narrow tube of varying cross-section to show how the stochastic dynamics is governed by position-dependent diffusivity in reduced dimension. Subsequently the concept of entropic barrier and the associated problems [11–20] have been investigated in several issues related to transport in periodic channels [18], in thermal activation in bistable potential exhibiting entropic variants of stochastic resonance [16] and resonant activation [17]. Since Fick-Jacobs equation involves forces of both energetic and entropic origin, it is worthwhile to explore the relative role of the two factors in temperature dependence of kinetics when an interplay of gravitational bias (due to the mass of the mesoscopic particles) and thermal motion is important for stochastic dynamics. In what follows we study this interplay in the temperature variation of the escape rate of Brownian particles through a narrow bottleneck between two lobes of a bilobal confinement in two dimensions. The particles are subjected to an overdamped dynamics and a constant gravitational bias through the transverse direction. We observe a non-Arrhenius behavior particularly when the value of the constant bias is very low. This nonlinearity diminishes when the value of the bias is increased. The observed non-Arrhenius behavior is essentially an entropic effect experienced by the resident particles due to the uneven boundaries of the enclosure. This is related to the shape and size of the confinement and can be understood in terms of a crossover of the rate between energy-dominated region and entropy-dominated region when the constant bias is varied. Although the non-Arrhenius behavior of the transition rate is expected according to the theory developed within Fick-Jacobs approximation [16], for the parameter regime of small values of gravitational force or higher temperature, the transition region of the parameters where both entropic and energetic characteristic of the barrier is important needs a further careful examination. This is particularly necessary for understanding the limits of validity of the approximation in the region.

We describe the overdamped dynamics of a Brownian particle in a confined geometry of two-dimensional space subjected to a constant force G acting along the transverse direction by means of the following Langevin equation:

$$\gamma(d\vec{r}/dt) = -G\vec{e_y} + \sqrt{\gamma k_B T}\vec{\xi}(t). \tag{1}$$

Here $\vec{r}$ denotes the position vector of the particle, γ is the friction coefficient, $\vec{e_x}$, $\vec{e_y}$ are the unit vectors along x and y directions, respectively. The fluctuating term $\vec{\xi}(t) = [\xi_x(t), \xi_y(t)]$ is characterized by zero-mean, Gaussian random thermal noise and obeys the fluctuation-dissipation relation,

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

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

The confinement can be accounted for by imposing reflecting boundaries on the system. The walls as shown in Fig. 1(a) can be described by the following equation:

$$B_l(x) = L_y(x/L_x)^4 - 2L_y(x/L_x)^2 - c/2 = -B_u(x). \tag{3}$$

The geometrical parameters are L_x, L_y, and c. Here x and y are position coordinates and B_l, B_u correspond to the lower and the upper boundary functions of the system, respectively. L_x corresponds to the distance between the bottle-neck position and the position of maximal width, L_y refers to the narrowing of the boundary function, and c to the remaining width at the bottleneck. Consequently, $2\omega(x) = B_u(x) - B_l(x)$ gives the local width of the structure. For convenience, we make use of the dimensionless description of the Langevin dynamics and scale all lengths by characteristic length L_x, i.e., $\tilde{x} = x/L_x$, $\tilde{y} = y/L_x$. This implies $\tilde{c} = c/L_x$ and $\tilde{B}_l = B_l/L_x = -\tilde{B}_u$, and $\tau = (\gamma L_x^2/k_B T_R)$, the corresponding characteristic

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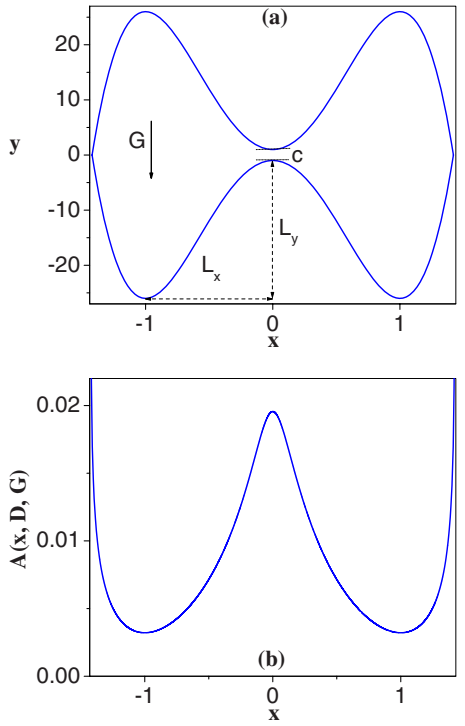

FIG. 1. (Color online) (a) A schematic plot of the two-dimensional space of the particle with the boundaries expressed by Eqs. (1) and (3) with model structure parameters. (b) A plot of spatial variation of the effective potential $A(x,D,G)$ in 1D for the same system with G/D ratio=1.

diffusion time at an arbitrary, but irrelevant reference temperature T_R, so that $\tilde{t}=t/\tau$, and the scaled value of the transverse constant bias is given by $\tilde{G}=G/F_R$ where $F_R=(\gamma L_x/\tau)$. The noise terms have been made dimensionless by proper scaling factors. In the following we shall omit the tilde symbols for clarity. In dimensionless form the Langevin equation becomes,

$$\frac{d\vec{r}}{dt} = -G\vec{e_y} + \sqrt{D}\vec{\xi}(t), \tag{4}$$

where $\sqrt{D}\vec{\xi}(t)$ is the scaled noise term and the boundary functions now read as

$$B_l(x) = -B_u(x) = -\omega(x) = ax^4 - bx^2 - c/2, \tag{5}$$

where the aspect ratio $a=L_y/L_x$ and $b=2a$. Our emphasis in this study is to explore 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 description of the system can now be given as Langevin equation in two perpendicular directions by the following dimensionless equations:

$$\frac{dx}{dt} = \sqrt{D}\xi_x(t),$$

$$\frac{dy}{dt} = -G + \sqrt{D}\xi_y(t), \tag{6}$$

where $\xi_x(t)$ and $\xi_y(t)$ are the x and y components of the additive noise term. The Fokker-Planck description [21] corresponding to Langevin dynamics [Eq. (6)] is given by

$$\frac{\partial P(x,y,t)}{\partial t} = D\frac{\partial}{\partial x}e^{-\Psi(x,y)}\frac{\partial}{\partial x}[e^{\Psi(x,y)}P(x,y,t)] + D\frac{\partial}{\partial y}e^{-\Psi(x,y)}\frac{\partial}{\partial y}[e^{\Psi(x,y)}P(x,y,t)], \tag{7}$$

where the potential function is written as $\Psi(x,y)=Gy/D$.

The above Fokker-Planck description of motion of the Brownian particle in two dimensions in an enclosure of the spatially varying cross-section can be simplified by introducing an effective potential in one dimension. This reduction of dimension can be achieved by employing a marginal probability distribution $P(x,t)$ along x direction and a conditional local equilibrium probability of y at a given x, $\rho(y;x)$. The key point is to assume a local equilibrium along y direction so that we may write

$$P(x,y,t) \cong P(x,t)\rho(y;x),$$

$$P(x,t) = \int dy P(x,y,t). \tag{8}$$

This results in Fick-Jacobs equation,

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[D\frac{\partial}{\partial x}P(x,t) + A'(x,D,G)P(x,t)\right], \tag{9}$$

where the effective potential [16] experienced by the Brownian particle is given by

$$A(x,D,G) = -D\ ln\left[\frac{2D}{G}\sinh\left(\frac{Gw(x)}{D}\right)\right], \tag{10}$$

A' refers to the spatial derivative along x. The entropic potential $A(x,D,G)$ for the confinement is described by Eq. (10) and shown in Fig. 1(b).

With a barrier height $\Delta A \gg D$, thermal activation causes the transitions between the states with a Kramers' rate [1]

$$r_k(D) = \frac{\sqrt{|A''(x_{max})|A''(x_{min})}}{2\pi}\exp\left[-\frac{\Delta A}{D}\right] \tag{11}$$

$A''(x_{min})$ and $A''(x_{max})$ are the squares of the linearized frequencies at the minimum and maximum of the effective potential, respectively. For the potential given by Eq. (10) the corresponding rate of transition from the left lobe to the right lobe is found to be [16]

$$r_k(D) = \frac{Ga}{\pi}\frac{\sqrt{2\sinh\left(\frac{Gc}{D}\right)\sinh\left(\frac{G(c+b)}{D}\right)}}{\sinh^2\left(\frac{G(c+b)}{2D}\right)}. \tag{12}$$

Another (although not exactly same) way of calculating the rate of transition is to compute the mean first passage time,

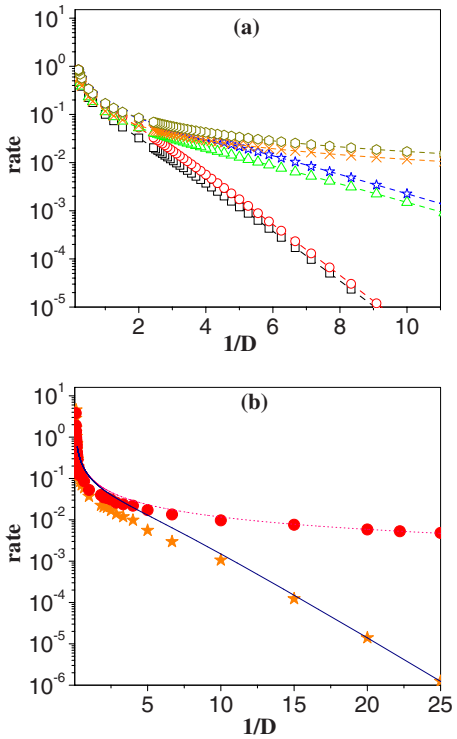

FIG. 2. (Color online) (a) The analytical plot obtained from Eq. (15) of escape rate versus $1/D$ for $G=0.05$ (red circular points), $G=0.02$ (blue stared point), 0.000 01 (dark yellow hexagonal point) respectively and the same plot obtained from Eq. (12) for $G=0.05$ (black squared points), $G=0.02$ (green triangular points), 0.000 01 (orange crossed points) respectively. (b) A comparison between numerical and analytical results [obtained from Eq. (15)] of escape rate versus $1/D$ for $G=0.02$ (blue line and orange stared point), 0.000 01 (red line and red circular point), respectively. In both cases lines represent the analytical results where points stand for numerical data.

$[t(x)]$ (MFPT). This is done [1,2,16] by rearranging Eq. (9) and we finally obtain

$$t(x) = \frac{1}{D}\int_{x}^{x_s} dy \int_{x_r}^{y} dz \exp\left[-\frac{A(y,D,G) - A(z,D,G)}{D}\right], \tag{13}$$

where x_r and x_s denote the reflecting boundary with

$$\frac{\partial t(x_r)}{\partial x} = 0 \tag{14}$$

and the absorbing boundary with $t(x_s)=0$, respectively. The time scale of the barrier crossing process is given by 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 $x=x_s=1$

$$r_t = \frac{1}{t(-x_0)}. \tag{15}$$

For our present problem we have chosen the parameter set $a=25.0$, $b=2a$, and $c=2.0$. Thus

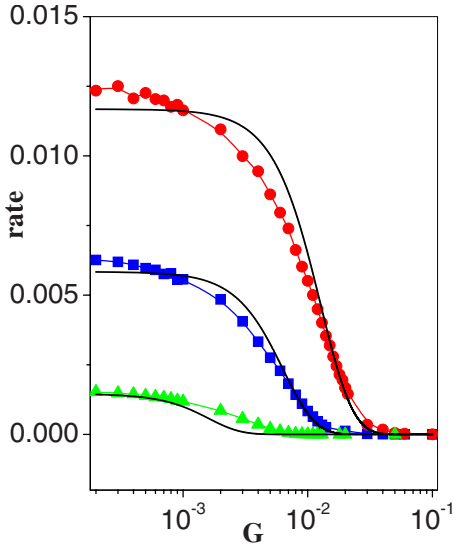

FIG. 3. (Color online) Numerical plot of rate versus G for $D=0.1$ (red line and circular point), 0.05 (blue line and squared point), 0.025 (green line and triangular point) respectively. The black lines represent the analytic results obtained from Eq. (15) for the similar parameter sets.

$$t(-x_0) = \frac{1}{D}\int_{-1}^{1} dx \exp\left[\frac{A(x)}{D}\right]\int_{x_r}^{x} dy \exp\left[-\frac{A(y)}{D}\right] \tag{16}$$

Using Eqs. (16) and (10) we obtain

$$t(-x_0) = \frac{1}{D}\int_{-1}^{1} dx \operatorname{cosech}\left(\frac{G\omega(x)}{D}\right)\int_{x_r}^{x} dy \sinh\left(\frac{G\omega(y)}{D}\right). \tag{17}$$

We now proceed to simulate numerically the mean first passage time (τ) by solving Eq. (6) and taking care of the confinement of the particles in terms of Eq. (5). 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 $x=-1$, $y=-25.0$, we make use of the reflecting and absorbing boundaries of the system set at $x=-1.45$ and $x=+1$, respectively, irrespective of y coordinate. The averaging is carried out over 10^5 realization of trajectories and the time step $\triangle t$ used for numerical integration is 10^{-4}. $1/\tau$, the inverse of the numerical mean first passage time thus obtained is defined as the escape rate [22] of the particle from one lobe to the other. Calculations of MFPT from numerical simulations for similar systems but without any transverse field were performed previously [23,25,26].

We now calculate the escape rate (analytical) in two different ways using Eqs. (12) and (15). Figure 2(a) shows the variation of the escape rate on a log scale as a function of the inverse of scaled temperature $(1/D)$ for several values of gravitational force (G). The variation, in general, is nonlinear and depicts two distinct regions. At low temperature (or high $1/D$) the particles mainly diffuse downwards for large values of G. This implies that the barrier is energetic and therefore one observes Arrhenius behavior due to thermal activation in

this regime. On the other hand at high temperature (low $1/D$) the particles can explore the entire volume of the enclosure for relatively small values of G. The particles feel the entropic barrier and the activation is characteristically non-Arrhenius in nature. In Fig. 2(b) we have compared the analytical results with the numerical simulation data for different values of G. The comparison is also made in Fig. 3 where we have plotted the variation of rate vs G for several values of dimensionless temperature (D). It is apparent that the escape rate exhibits a crossover from entropy-dominated regime to energy-dominated regime with the 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. A closer look at Figs. 2(b) and 3, however, suggests that the analytic results are in good agreement with numerics only in the low temperature region and for higher values of G.

Summarizing the above results we now make two observations. First, high $G\omega(x)/D(\gg 1)$ ratio characterizes the Arrhenius behavior of thermal activation. On the other hand, low $G\omega(x)/D(\ll 1)$ ratio is characteristic of the non-Arrhenius behavior of the transition rate. The latter is mainly governed by the shape of the channel. Second, the analytic prediction agrees well with numerical simulation data in two dimensions only in the Arrhenius regime. It is also clear that the data obtained by simulations do not coincide with analytic predictions for low G and at high temperature, i.e., in the non-Arrhenius regime. This deviation may be caused by the simplicity of the Fick-Jacobs-like approximation [24]. In order to obtain better agreement with the results obtained by solving the original problem in higher dimensions one-dimensional treatment should be improved or extended. Ideally such an extension may be made by replacing the simple integration over transverse coordinate [as done in Eq. (8)] by a more rigorous mapping of Eq. (7) onto longitudinal coordinate x. An approach in this spirit has been advocated recently [27,28] for diffusion.

In conclusion, we have shown an interesting nonlinear behavior in Arrhenius plot of the temperature dependence of noise-induced escape rate of particles through a bottleneck in a two-dimensional enclosure. Its origin lies on geometry of the confinement. By varying the strength of the constant bias along the transverse direction (G), it is possible to tune the extent of dominance of entropic factor. We hope that the observed temperature dependence of noise-induced escape may be relevant in several areas of biological context like cells, ion channels as well as in microporus media, where the thermally activated particles for which the bias force due to gravity is not negligible, are forced to undergo constrained motion.

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