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Two-dimensional Diffusion with a Transverse Gravitational Force: Analytical, Numerical and Simulations Results

Two-dimensional Diffusion with a Transverse Gravitational Force: Analytical, Numerical and Simulations Results

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Abstract. Using the Kalinay and Percus projection method a new effective diffusion coefficient is found. This diffusivity generalizes the well-known results previously reported in the literature. Specifically, it is a coefficient that can be applied to two-dimensional asymmetrical channels under an external gravitational-like potential. Furthermore, Brownian Dynamics simulations are performed, and their agreement with the theoretical results is shown. Also, the Mean First-Passage Time is studied for two-dimensional straight conical channels, where the analytical results are analyzed to understand its applicability range using numerical methods, which are compared with Brownian Dynamics simulations. A remarkable result is also presented: the Mean First-Passage Time assumes a minimum at finite values of the external potential amplitude.

1. Introduction

The diffusion coefficient is a quantity that can be used to describe transport in a system. For a free system, it is customary to use a diffusion constant (D_0). Once confinement or external field influence is imposed, it is necessary to extend the model by using the effective diffusive coefficient [1] (D_{eff} or $D(x)$) that, in this case, depends on the x-coordinate. Second Fick's law provides us [2] with a basic description of free systems but Fick-Jacobs [3] and even better, Fick-Jacobs-Zwanzig [4] equations improve the models. Later Reguera and Rubi proposed [5] a new heuristically-found coefficient enhancing Zwanzig's result. Kalinay and Percus used their method [6], named projection method [7] to make an even better description of diffusive systems. The last procedure was used by Kalinay himself [8] to describe a symmetrical channel under transverse gravitational force.

Using the so-called projection method, we are looking to derive an effective diffusion coefficient for narrow channels that generalizes previously reported results. This is, a position-dependant diffusion coefficient for two-dimensional asymmetric channels under a transverse gravitational external field [9]. To be consistent, it must contain the well-known previous results for symmetric channels with external gravitational force, as well as asymmetrical cases where the transverse field goes to zero, and also, the cases where the asymmetry of the system and external potential fields are absent.

Instead of the experimental way to compare the theoretical models, a computational approach can be used to verify their range of applicability [10]. For our kind of models, i.e., point-like

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and non-interacting particles, it is appropriate to use Brownian dynamics simulations [1] with the addition of an external force which is the gravitational one.

2. Previous Works

For quasi-one-dimensional channels, one can map noninteracting point-like particle motion onto an effective one-dimensional (1D) description in terms of the diffusion along the midline of the channel $y_0(x)$, as a function of the longitudinal coordinate x. The so-called Fick-Jacobs (FJ) approach consists of eliminating transverse stochastic degrees of freedom by assuming fast equilibration in such a direction. The associated approximate description relies on the modified Fick-Jacobs-like equation derived by Zwanzig (Zw) for the probability density in the channel $c(x,t)$ [4]

$$\frac{\partial c(x,t)}{\partial t} = \frac{\partial}{\partial x}\left\{ D(x) w(x) \frac{\partial}{\partial x}\left[\frac{c(x,t)}{w(x)}\right]\right\}, \tag{1}$$

where $D(x)$ is a position-dependent diffusion coefficient and $w(x)$ the channel width. The effective 1D probability density, $c(x,t)$, is related to the 2D probability density $\rho(x,y,t)$ by

$$c(x,t) = \int_{w(x)} \rho(x,y,t)dy. \tag{2}$$

In fact, equation (1) is formally equivalent to the Smoluchowski equation [4]

$$\frac{\partial \rho(x,y,t)}{\partial t} = \left(D_x \frac{\partial}{\partial x} e^{-\beta U(x,y)} \frac{\partial}{\partial x} e^{\beta U(x,y)} + D_y \frac{\partial}{\partial y} e^{-\beta U(x,y)} \frac{\partial}{\partial y} e^{\beta U(x,y)} \right) \rho(x,y,t). \tag{3}$$

The expression for the position-dependent effective diffusion coefficient for a narrow 2D channel of varying width that has a straight midline derived by Zw is as follows [4]:

$$D(x) \approx D_{Zw}(x) = \frac{D_0}{1 + \frac{1}{12} w'^2(x)}, \tag{4}$$

where $w'(x) = dw(x)/dx$. Later, Reguera and Rubi (RR) generalized Zwanzig's expression, and based on heuristic arguments, they suggested [5],

$$D(x) \approx D_{RR}(x) = \frac{D_0}{\left[1 + \frac{1}{4} w'^2(x)\right]^{\eta}}, \tag{5}$$

where $\eta = 1/3$ and $1/2$, for 2D channels and three-dimensional tubes, respectively. For cases in which the diffusion of a Brownian particle takes place in a narrow 2D channel with a non-straight midline and varying width, i.e., an asymmetric channel, Bradley (Br) generalized Zwanzig's equation as follows [11]:

$$D(x) \approx D_{Br}(x) = \frac{D_0}{1 + y_0'^2(x) + \frac{1}{12} w'^2(x)}, \tag{6}$$

where $y_0(x)$ is the center line of the channel. By setting $y'(x) = 0$ in equation (6), we arrive to equation (4). When diffusion takes place into a tilted 1D line, by setting $w'(x) = 0$, equation (6) reads as,

$$D(x) \approx D_{1D}(x) = \frac{D_0}{1 + y_0'^2(x)}. \tag{7}$$

3. Projection Method

A brief outline of the projection method [1] will be stated in this section. The first step is to take the 2D Smoluchowski Eq. (3), choosing for this particular case a gravitational-like potential $U(y) = Gy$, where $g \equiv \beta G$. Now the one-dimensional density is calculated by taking the integral of the particle density $\rho(x, y, t)$

$$c(x,t) = \int_{h_1(x)}^{h_2(x)} \rho(x,y,t)\, dy. \tag{8}$$

This should be done inside the system's boundaries. The next step is to obtain an equilibrium solution for density by assuming $D_y \to \infty$, this is a transverse-directional equilibrium. This solution can be easily written as

$$\rho_0(x,y,t) = \frac{1}{A(x)}\, e^{-gy} c(x,t), \tag{9}$$

where $A(x)$ is a normalization function that contains boundaries and potential information encoded inside. Now we can see ρ as the result of a perturbative series in $\epsilon \equiv D_x/D_y$

$$\rho(x,y,t) = e^{-gy} \sum_{n=0}^{\infty} \epsilon^n \hat{\omega}_n(x,y,\partial_x) \frac{c(x,t)}{A(x)}. \tag{10}$$

After applying the usual techniques for series solutions, the key assumption of a stationary regime for long times ($\partial_t c(x,t) = 0$) is made, then we can find $D(x)$.

3.1. Developments made with the projection method

Using the projection method, Kalinay and Percus (KP) obtained the following for a 2D channel [7]:

$$D(x) \approx D_{KP}(x) = \frac{\arctan\left(w'(x)/2\right)}{w'(x)/2} D_0. \tag{11}$$

Later, assuming that the channel width is a slowly varying function of x, $|dw(x)/dx| = |w'(x)| \ll 1$, Dagdug and Pineda (DP) obtained the following equation for an asymmetric channel [12]:

$$D(x) \approx D_{DP}(x) = D_0 \left[\frac{\arctan\left(y_0'(x) + \frac{w'(x)}{2}\right)}{w'(x)} - \frac{\arctan\left(y_0'(x) - \frac{w'(x)}{2}\right)}{w'(x)} \right]. \tag{12}$$

This last equation generalizes KP's result for symmetric to asymmetric channels and reduces to the latter when the channel has a straight midline parallel to the x-axis, and $y'(x) = 0$, Eq. (11). Moreover, the equation obtained by Bradley, Eq. (6), is a truncated expansion of equation (12) when the Taylor series is kept up to the first order in $w'(x)$ and $y_0'(x)$. By the same means, Kalinay [8] obtained the following coefficient considering an entropic and gravitational-like potential coexistence inside a symmetric channel:

$$\begin{aligned}\frac{D_{Kg}(x)}{D_0} \approx & 1 - \frac{h'^2}{\sinh^2 gh}\left(1 + \cosh^2 gh - 2gh \coth gh\right) \\ & + \frac{h'^4}{\sinh^6 gh}\Bigg(\sinh^4 gh \cosh^2 gh - \frac{gh}{2}\sinh 2gh \\ & \times \left(17\sinh^2 gh + 36\right) + gh^2\left(7\sinh^4 gh + 40\sinh^2 gh + 36\right)\Bigg).\end{aligned} \tag{13}$$

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Inspired by RR's work, Kalinay proposed to write Eq. (13) with the same structure as Eq. (5), but with the exponent η dependent on $gh(x)$, namely,

$$\eta(gh) = \frac{1}{\sinh^2 gh}\left(1 + \cosh^2 gh - 2gh \coth gh\right), \tag{14}$$

where $\eta(gh(x))$ goes from 1/3 to 1, from negligible G to the strong field case, respectively.

4. Brownian Dynamics Simulations

Simulations were performed using Fortran, and C codes, parallelizing the execution of the programs. All realizations were made with $\Delta t = 10^{-8}$ and 5.0×10^4 particles. The probe channels have a period of $L = 1$ and external potential $G = 0, 5, 10, 20, 50,$ *(for $n \to w$ also 10^5)*. The simulation realizations were conducted with channel boundaries' defined by $h_2(x) = \lambda x + 0.1 = -h_1(x)$.

5. Results

5.1. Effective Diffusion Coefficient

Following the method proposed by KP, we found that the known results for two-dimensional narrow channels could be generalized by

$$\begin{aligned}\frac{D(x)}{D_0} = 1 &- \frac{w'^2}{4\sinh^2\left[\frac{1}{2}gw\right]}\left\{1 + \cosh^2\left[\frac{1}{2}gw\right] - gw\coth\left[\frac{1}{2}gw\right]\right\} \\ &- y_0'\left\{y_0' - w'\coth\left[\frac{1}{2}gw\right] + \frac{1}{2}gww'\operatorname{csch}^2\left[\frac{1}{2}gw\right]\right\},\end{aligned} \tag{15}$$

and approximately written using the RR interpolation formula (5) with

$$\begin{aligned}\eta = &\frac{1}{\sinh^2\left[\frac{1}{2}gw\right]}\left\{1 + \cosh^2\left[\frac{1}{2}gw\right] - gw\coth\left[\frac{1}{2}gw\right]\right\} \\ &+ 4\frac{y_0'}{w'^2}\left\{y_0' - w'\coth\left[\frac{1}{2}gw\right] + \frac{1}{2}gww'\operatorname{csch}^2\left[\frac{1}{2}gw\right]\right\}.\end{aligned} \tag{16}$$

Above equations contains the channel width $w(x) = h_2(x) - h_1(x)$, the midline $y_0(x) = \left[h1(x) + h_2(x)\right]/2$ and their respective derivatives.

5.2. Mean First-passage Time

The Mean First-passage time (MFPT) is the probability of a diffusing particle being absorbed by a boundary for the first time. Considering a one-dimensional system, it satisfies the following equation[13]:

$$\frac{1}{A(x_0)}\frac{\mathrm{d}}{\mathrm{d}x_0}\left[D(x_0)\,A(x_0)\,\frac{\mathrm{d}\tau(x_0)}{\mathrm{d}x_0}\right] = -1, \tag{17}$$

where $\tau(x_0)$ is the MFPT, x_0 is the initial position of the Brownian particle, and the normalization function A contains information about the entropy and energy barriers. Furthermore, for a two-dimensional system of length L and variable width $w(x)$ under the influence of a transverse gravitational-like external field G, where the boundaries define a straight conical shape, we need to consider two separate cases, which are

$$\tau(x_0) \rightarrow \begin{cases} \tau_{n \rightarrow w} = \tau(x_0 = 0 \rightarrow L) \\ \tau_{w \rightarrow n} = \tau(x_0 = L \rightarrow 0) \end{cases}, \tag{18}$$

which represents the transitions of the particle from the narrow to the wide end of the channel ($n \rightarrow w$), and the transition from the wide to the narrow end of the channel ($w \rightarrow n$), respectively. Both cases are depicted in the panels of Figure 3.

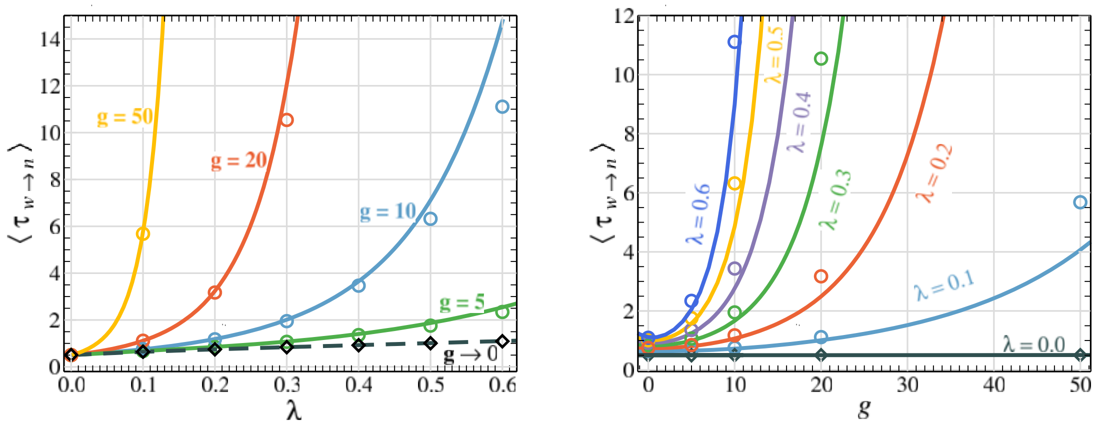

Figure 1. MFPT for wide-to-narrow channels where the predicted theoretical (numerical) values are shown as continuous lines, while the values obtained from Brownian dynamics simulations are depicted as symbols. The channel of length $L = 1$ is formed by reflecting boundaries $h_1(x) = -\lambda x - 0.1$ and $h_2(x) = \lambda x + 0.1$. The limiting case $g \rightarrow 0$ is also shown by a black dashed line. The left figure shows the MFPT as a function of the slope of the boundaries λ, while the right figure shows the MFPT as a function of the strength of the external field g.

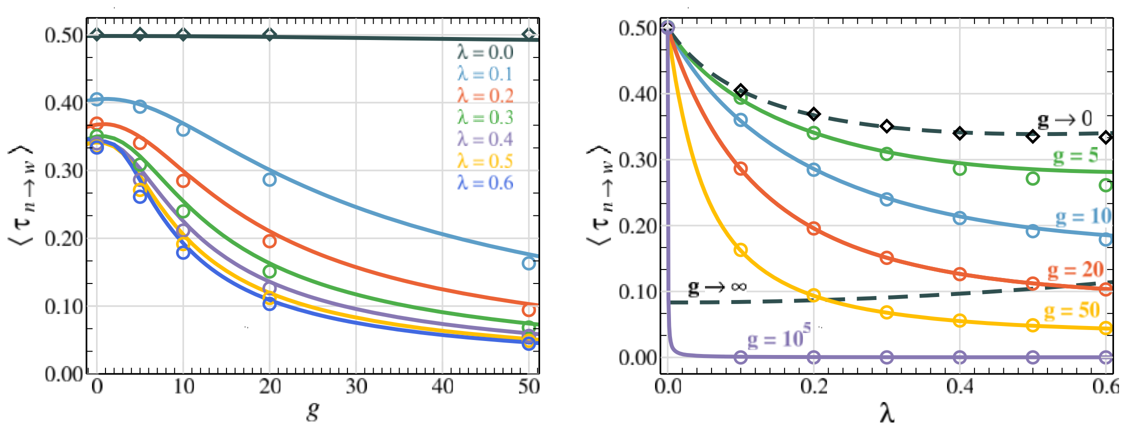

Figure 2. MFPT for narrow-to-wide channels where the predicted theoretical (numerical) values are shown as continuous lines, while the values obtained from Brownian dynamics simulations are depicted as symbols. The channel of length $L = 1$ is formed by reflecting boundaries $h_1(x) = -\lambda x - 0.1$ and $h_2(x) = \lambda x + 0.1$. The limiting cases $g \rightarrow 0$ and $g \rightarrow \infty$ are also shown by black dashed lines. The left figure shows the MFPT as a function of the slope of the boundaries λ, while the right figure shows the MFPT as a function of the strength of the external field g.

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The boundary conditions to solve the Eq. (17) are

$$\tau_{n\to w}(x_0)\Big|_{x_0=L} = \frac{\mathrm{d}\tau_{n\to w}(x_0)}{\mathrm{d}x_0}\Big|_{x_0=0} = 0, \tag{19}$$

and

$$\tau_{w\to n}(x_0)\Big|_{x_0=0} = \frac{\mathrm{d}\tau_{w\to n}(x_0)}{\mathrm{d}x_0}\Big|_{x_0=L} = 0. \tag{20}$$

The solutions for the equation (17) are found in terms of quadratures:

$$\tau_{n\to w}(x_0) = \int_{x_0}^{L} \frac{\mathrm{d}x}{D(x)A(x)} \int_0^x A(y)\,\mathrm{d}y, \tag{21}$$

$$\tau_{w\to n}(x_0) = \int_0^{x_0} \frac{\mathrm{d}x}{D(x)A(x)} \int_x^L A(y)\,\mathrm{d}y. \tag{22}$$

6. Conclusions

We obtained a theoretical expression for the MFPT, which has to be solved numerically because of the complexity of the diffusivity. Also, Brownian dynamics simulations were performed to check the agreement with the theoretical results in the narrow-to-wide and the wide-to-narrow cases. Despite some deviations observed for the wide-to-narrow case at intermediate channel boundary slopes and larger g values, the general predictions of the approximate Fick-Jacobs equation (1D description) are validated.

In the narrow-to-wide setting a remarkable effect is observed as the MFPT is not bounded by the limiting case $g \to \infty$. This result can be interpreted as an optimum interplay between the entropic potential exerted by the channel boundaries and the gravitational-like force acting

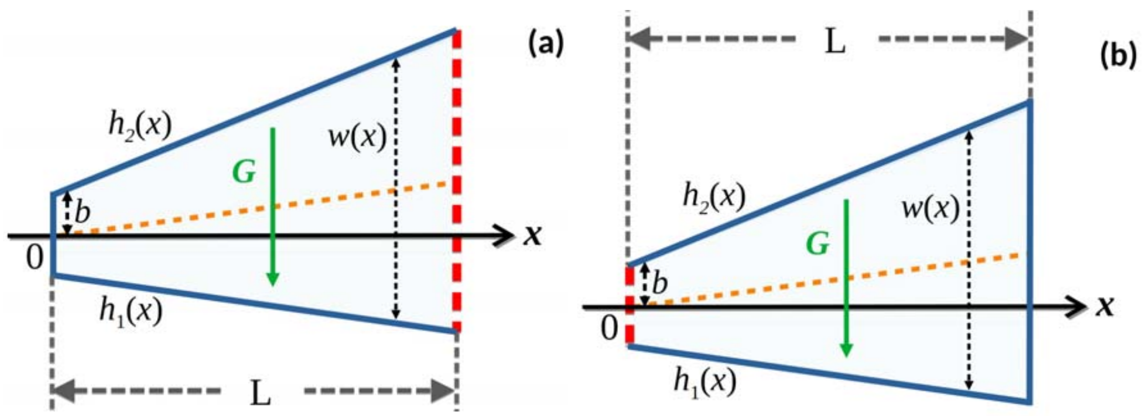

Figure 3. Depiction of a two-dimensional asymmetric conical channel with straight walls under a gravitational-like (constant) force G represented as a downwards arrow. The upper boundary is defined by $h_2(x) = \lambda_2 x + b$, while the lower boundary is given by $h_1(x) = \lambda_1 x - b$. The straight midline of the channel is $y_0(x) = [h_1(x)+h_2(x)]/2$, and its variable width is $w(x) = h_2(x) - h_1(x)$. The panel (a) is an expanding channel, this is, a narrow-to-wide ($n \to w$) particle transition and a reflected boundary is located at $x = 0$, and the particle is removed from the channel by an absorbing boundary at $x = L$. Panel (b) shows a narrowing channel, where the particle's transition is from a wide-to-narrow ends ($w \to n$), in such case, the hard reflecting boundary is placed at $x = L$ and the absorbing wall is present in the position $x = 0$.

over the system. This interplay is not present in the case where the external force is very high as the particle is pinned down to the channel wall vanishing the effect of the entropic force.

Control over exit time can be made by changing the boundaries and the external potentials applied to the diffusive system. This may allow the development of applications such as particle separation, gatting, catalysis, and fluid mixing, among others.

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