Entropic particle transport in periodic channels

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1. Introduction

The phenomenon of entropic transport is ubiquitous in biological cells, ion channels, nano-porous materials, zeolites and microfluidic devices etched with grooves and chambers. Instead of diffusing freely in the host liquid phase the Brownian particles frequently undergo a constrained motion (Liu et al., 1999; Siwy et al., 2005; Berezhkovskii and Bezrukov, 2005; Hille, 2001; Barrer, 1978; Chou and Lohse, 1999; Kettner et al., 2000; Matthias and Müller, 2003; Ai and Liu, 2006; Volkmuth and Austin, 1992; Nixon and Slater, 2002; Chang and Yethiraj, 2006). The geometric restrictions to the system's dynamics results in entropic barriers and regulate the transport of particles yielding important effects exhibiting peculiar properties. The results have prominent implications in processes such as catalysis, osmosis and particle separation (Liu et al., 1999; Siwy et al., 2005; Berezhkovskii and Bezrukov, 2005; Hille, 2001; Barrer, 1978; Chou and Lohse, 1999; Kettner et al., 2000; Matthias and Müller, 2003; Ai and Liu, 2006; Volkmuth and Austin, 1992; Nixon and Slater, 2002; Chang and Yethiraj, 2006) and, as well, for the noise-induced transport in periodic potential landscapes that lack reflection symmetry (Brownian ratchet systems) (Hänggi et al., 2005; Astumian and Hänggi, 2002; Reimann and Hänggi, 2002) or Brownian motor transport occurring in arrays of periodically arranged asymmetric obstacles, termed "entropic" ratchet devices (Derenyi and Astumian, 1998). Motion in these systems can be induced by imposing different concentrations at the ends of the channel, or by the presence of external driving forces supplying the particles with the energy necessary to proceed. The study of the kinetics of the entropic transport, the properties of transport coefficients in far from equilibrium situations and the possibility for transport control mechanisms are pertinent objectives in the dynamical characterization of those systems.

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Because the role of inertia for the motion of the particles through these structures can typically be neglected the Brownian dynamics can safely be analyzed by solving the Smoluchowski equation in the domain defined by the available free space upon imposing the appropriate boundary conditions. Whereas this method has been very successful when the boundaries of the system possess a rectangular shape, the challenge to solve the boundary value problem in the case of nontrivial, corrugated domains represents a difficult task. A way to circumvent this difficulty consists in coarsening the description by reducing the dimensionality of the system, keeping only the main direction of transport, but taking into account the physically available space by means of an entropic potential. The resulting kinetic equation for the probability distribution, the so called Fick–Jacobs (FJ) equation, is similar in form to the Smoluchowski equation, but now contains an entropic term. The entropic nature of this term leads to a genuine dynamics which is distinctly different from that observed when the potential is of energetic origin (Reguera et al., 2006). It has been shown that the FJ equation can provide a very accurate description of entropic transport in channels of varying cross-section (Reguera et al., 2006; Burada et al., 2007; Kosinska et al., 2008). However, the derivation of the FJ equation entails a tacit approximation: the particle distribution in the transverse direction is assumed to equilibrate much faster than in the main (unconstrained) direction of transport. This equilibration justifies the coarsening of the description leading in turn to a simplification of the dynamics, but raises the question about its validity when an *external force is applied*. To establish the validity criterion of a FJ description for such biased diffusion in confined media is, due to the ubiquity of this situation, a subject of primary importance.

Our objective with this work is to investigate in greater detail the FJ-approximation for biased diffusion and to set up a corresponding criterion describing its regime of validity. We will analyze the biased movement of Brownian particles in 2D periodic channels of varying cross-section and formulate different criteria for the validity of such a FJ-description. On the basis of our numerical and analytical results we recapitulate the striking and sometimes counterintuitive features (Reguera et al., 2006), which arises from entropic transport and which are different from those observed in the more familiar case with energetic, metastable landscapes (Hänggi et al., 1990).

2. Diffusion in Confined Systems

Transport through pores or channels (like the one depicted in Fig. 1) may be caused by different particle concentrations maintained at the ends of the channel, or by the application of external forces acting on the particles. Here we will exclusively consider the case of force driven transport. The external driving force is denoted by $\vec{F} = F\vec{e}_x$. It points into the direction of the channel axis. In general, the dynamics of a suspended Brownian particle is overdamped (Purcell, 1977) and well described by the Langevin equation:

$$\eta \frac{d\vec{x}}{d\tilde{t}} = \vec{F} + \sqrt{\eta k_B T}\,\vec{\xi}(\tilde{t}). \tag{1}$$

where $\tilde{t}$ is the time, $\vec{x}$ the position vector of the particle, η its friction coefficient, k_B the Boltzmann constant and T is the temperature. The thermal fluctuating forces which the surrounding fluid exerts on the particle are modeled by zero-mean Gaussian white noise $\vec{\xi}(\tilde{t})$, obeying the fluctuation–dissipation relation $\langle \xi_i(\tilde{t})\xi_j(\tilde{t}')\rangle = 2\delta_{ij}\delta(\tilde{t}-\tilde{t}')$ for $i, j = x, y, z$.

In addition to Eq. (1), the full problem is set up by imposing reflecting boundary conditions at the channel walls. The form of the channel will be specified below.

To further simplify the treatment of this model we introduce dimensionless variables. We measure all lengths in units of the period L, i.e.

$$\vec{x} = L\vec{r}, \tag{2}$$

where $\vec{r}$ is the dimensionless position vector of the particle. As unit of time τ we choose twice the time it takes for the particle to diffusively cover the distance L which is given by $\tau = L^2\eta/(k_B T)$, hence

$$\tilde{t} = \tau t. \tag{3}$$

In these dimensionless variables the Langevin equation reads

$$\frac{d\vec{r}}{dt} = \vec{f} + \vec{\xi}(t). \tag{4}$$

where $\langle\vec{\xi}(t)\rangle = 0$ and $\langle\vec{\xi}(t)\vec{\xi}(t')\rangle = 2\delta_{i,j}\delta(t-t')$ for $i, j = x, y, z$ and where the dimensionless force

$$\vec{f} = f\vec{e}_x \quad \text{and } f = \frac{LF}{k_B T} \tag{5}$$

contains the dimensionless parameter f that characterizes the force as the ratio of the work which it performs on the particle along a distance of the length of the period and the thermal energy. The corresponding Fokker–Planck equation for the time evolution of the probability distribution $P(\vec{r}, t)$ takes the form (Risken, 1989; Hänggi and Thomas, 1982):

$$\frac{\partial P(\vec{r}, t)}{\partial t} = -\vec{\nabla}\vec{J}(\vec{r}, t), \tag{6a}$$

where $\vec{J}(\vec{r}, t)$ is the probability current:

$$\vec{J}(\vec{r}, t) = (\vec{f} - \vec{\nabla})P(\vec{r}, t), \tag{6b}$$

Note that for channels with similar geometry, which are related by a scale transformation $\vec{x} \to \lambda\vec{x}$, $\lambda > 0$, the transport properties are determined by the single dimensionless parameter f which subsumes the period lengths, the force and the temperature of the surrounding fluid.

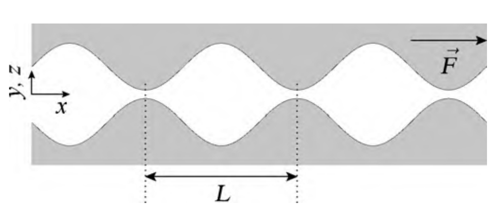

Fig. 1. Schematic diagram of a channel confining the motion of forced Brownian particles. The half-width ω is a periodic function of x with periodicity L.

The reflection of particles at the channel walls leads to a vanishing probability current at the boundaries. Therefore, the boundary conditions at the channel walls are

$$\vec{J}(\vec{r},t)\vec{n} = 0 \quad \vec{r} \in \text{channel wall}. \tag{7}$$

where $\vec{n}$ denotes the normal vector field at the channel walls.

The boundary of a 2D periodic channel which is mirror symmetric about its axis is given by the periodic functions $y = \pm\omega(x)$, i.e. $\omega(x+1) = \omega(x)$ for all x, where x and y are the Cartesian components of $\vec{r}$. In this case, the boundary condition becomes

$$\frac{\mathrm{d}\omega(x)}{\mathrm{d}x}\left[fP(x,y,t) - \frac{\partial P(x,y,t)}{\partial x}\right] + \frac{\partial P(x,y,t)}{\partial y} = 0, \tag{8}$$

at $y = \pm\omega(x)$. Except for a straight channel with $\omega = const$, there are no periodic channel shapes for which an exact analytical solution of the Fokker–Planck Eq. (6) with boundary conditions (8) is known. Approximate solutions though can be obtained on the basis of an one-dimensional diffusion problem in an effective potential. Narrow channel openings, which act as geometric hindrances in the full model, show up as entropic barriers in this one-dimensional approximation (Reguera et al., 2006; Burada et al., 2007; Jacobs, 1967; Zwanzig, 1992; Reguera and Rubí, 2001; Kalinay and Percus, 2006). This approach is valid under conditions that will be discussed below in some detail.

3. The Fick–Jacobs Approximation

In the absence of an external force, i.e. for $\vec{f} = 0$, it was shown (Jacobs, 1967; Zwanzig, 1992; Reguera and Rubí, 2001; Kalinay and Percus, 2006) that the dynamics of particles in confined structures (such as that of Fig. 1) can be described approximatively by the FJ equation, with a spatially dependent diffusion coefficient:

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x}\left(D(x)\omega(x)\frac{\partial}{\partial x}\frac{P}{\omega(x)}\right). \tag{9}$$

This 1D equation is obtained from the full 2D Smoluchowski equation upon the elimination of the transversal y coordinate assuming fast equilibration in the transversal channel direction. Here $P(x,t) = \int_{-\omega(x)}^{\omega(x)} \mathrm{d}y\, P(x,y,t)$ denotes the marginal probability density along the axis of the channel. We note that for three-dimensional channels an analogue approximate Fokker–Planck equation holds in which the function $\omega(x)$ is to be replaced by $\pi\omega^2(x)$ (area of cross-section). In the original work by Jacobs (1967) the 1D diffusion coefficient $D(x)$ is constant and equals the bare diffusion constant which is unity in the present dimensionless variables. Later, Zwanzig (1992) and Reguera and Rubí (2001) proposed different spatially dependent forms of the 1D diffusion coefficient.

3.1. Spatially Dependent 1D Diffusion Coefficients

The 1D diffusion coefficient suggested by Zwanzig results from a systematic expansion in terms of the gradient of the boundary function $\omega(x)$. In leading order he obtained $D(x) = 1 - \gamma\omega'(x)^2 + \ldots$, where $\gamma = 1/3$ for the considered 2D structure (for a 3D structure, $\gamma = 1/2$) and the prime denotes the derivative with respect to x. Interpreting this result as the first two terms of a geometric series Zwanzig proposed his resummed expression for the 1D diffusion coefficient reading

$$D_{\mathrm{Z}}(x) = \frac{1}{1+\gamma\omega'(x)^2}. \tag{10}$$

Reguera and Rubí (2001) put forward a different form of the 1D diffusion coefficient:

$$D_{\mathrm{RR}}(x) = \frac{1}{(1+\omega'(x)^2)^{\gamma}}, \tag{11}$$

which also can be considered as a resummation of Zwanzig's perturbational result. Yet another form of the 1D diffusion coefficient was proposed by Kalinay and Percus (2006). For the biased diffusion discussed here the results obtained with the Kalinay–Percus diffusion coefficient differ only little from those obtained by the Reguera-Rubí diffusion coefficient. Therefore we do not further consider the Kalinay–Percus diffusion coefficient.

3.2. Constant Bias along the Channel Direction

In the presence of a constant force F along the direction of the channel the FJ Eq. (9) can be recast into the form (Reguera et al., 2006; Burada et al., 2007; Reguera and Rubí, 2001):

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x}D(x)\left(\frac{\partial P}{\partial x} + \frac{\mathrm{d}A(x)}{\mathrm{d}x}P\right) \tag{12}$$

with the dimensionless free energy $A(x) := E - S = -f\,x - \ln\omega(x)$. In physical dimensions the energy is $\tilde{E} \equiv k_{\mathrm{B}}TE = -F\tilde{x}$ ($\tilde{x} = xL$) and the dimensional entropic contribution is $\tilde{S} \equiv k_{\mathrm{B}}TS = k_{\mathrm{B}}T\,\ln\omega$. For a periodic channel this free energy assumes the form of a tilted periodic potential. In the absence of a force the free energy is purely entropic and Eq. (12) reduces to the FJ Eq. (9). On the other hand, for a straight channel the entropic contribution vanishes and the particle is solely driven by the external force.

3.3. Nonlinear Mobility and Effective Diffusion

Key quantities of particle transport through periodic channels are the average *particle current*, or equivalently the nonlinear *mobility*, and the *effective diffusion coefficient*. For a particle moving in a one-dimensional tilted periodic potential the heights ΔV of the barriers separating the potential wells provide an additional energy scale apart from the work of the force FL and the thermal energy $k_{\mathrm{B}}T$. Hence, at least two dimensionless parameters, say $\Delta E/(k_{\mathrm{B}}T)$ and $FL/(k_{\mathrm{B}}T)$ govern the transport properties of these systems. In contrast, as already noted in the context of the full 2D model the transport through channels is governed by the single dimensionless parameter $f = FL/(k_{\mathrm{B}}T)$. This, of course, remains to hold true in the one-dimensional approximation which models the transversal spatial variation in terms of an entropic potential.

For any non-negative force the average particle current in periodic structures can be obtained from (Reimann et al., 2001):

$$\langle \dot{x} \rangle = \langle t(x_0 \to x_0 + 1) \rangle^{-1} \tag{13}$$

where $t(a \to b)$ denotes the first time of a particle which starts at $x = a$ to arrive at $x = b$. The angular brackets refer to an average over the fluctuating force. Note that the resulting mean first passage time $\langle t(x_0 \to x_0 + 1)\rangle$ diverges for a vanishing force and consequently leads to a vanishing current. A positive force prevents the particle to make far excursions to the left, hence leading to a finite mean first passage time as well as a finite current. Within the one-dimensional approximation, cf. Eq. (12), the moments of the first passage time $t(a \to b)$ can be determined recursively by means of

$$\langle t^n(a \to b) \rangle = n \int_a^b \mathrm{d}x \frac{1}{D(x)} \exp(A(x)) \int_{-\infty}^x \mathrm{d}y \times \exp(-A(y)) \langle t^{n-1}(y \to b) \rangle. \tag{14}$$

For $n = 0$ the starting value of the iteration is given by $\langle t^0(a \to b)\rangle = 1$.

The nonlinear mobility $\mu(f)$. is defined by

$$\mu(f) = \frac{\langle \dot{x} \rangle}{f}. \tag{15}$$

Using Eqs. (13) and (14) one can obtain the following Stratonovich formula for the nonlinear mobility (Reguera et al., 2006)

$$\mu(f) = \frac{1 - \exp(-f)}{f \int_0^1 \mathrm{d}z\, I(z, f)}, \tag{16a}$$

where

$$I(z, f) := \frac{h^{-1}(z)}{D(z)} \exp(-fz) \int_{z-1}^{z} \mathrm{d}\tilde{z}\, h(\tilde{z}) \exp(f\tilde{z}), \tag{16b}$$

depends on the dimensionless position z, the force f and the shape of the tube given in terms of the half-width $\omega(x)$ and its first derivative.

The effective diffusion coefficient is defined as the asymptotic behavior of the variance of the position

$$D_{\mathrm{eff}} = \lim_{t \to \infty} \frac{\langle x^2(t) \rangle - \langle x(t) \rangle^2}{2t}. \tag{17}$$

It is related to the first two moments of the first passage time by the expression (Reimann et al., 2001; Lindner et al., 2001):

$$D_{\mathrm{eff}} = \frac{\langle t^2(x_0 \to x_0 + 1) \rangle - \langle t(x_0 \to x_0 + 1) \rangle^2}{2 \langle t(x_0 \to x_0 + 1) \rangle^3}. \tag{18}$$

After some algebra it can be transformed to read

$$D_{\mathrm{eff}} = \frac{\int_0^1 \mathrm{d}z \int_{z-1}^{z} \mathrm{d}\tilde{z}\, \mathcal{N}(z, \tilde{z}, f)}{\left[\int_0^1 \mathrm{d}z I(z, f)\right]^3}, \tag{19a}$$

where

$$\mathcal{N}(z, \tilde{z}, f) := \frac{D(\tilde{z})}{h(z)} \frac{h(\tilde{z})}{D(z)} [I(\tilde{z}, f)]^2 \exp(-fz + f\tilde{z}). \tag{19b}$$

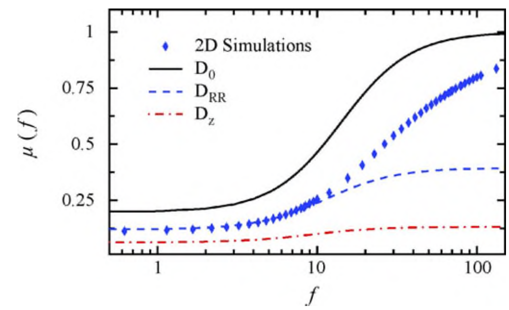

Fig. 2. (Color online) The dependence of the nonlinear mobility of a Brownian particle within a 2D channel with half-width $\omega(x) = \sin(2\pi x) + 1.02$ is depicted *vs.* the dimensionless force $f = FL/k_B T$. The symbols correspond to the numerically simulated exact values, cf. Eq. (21), and the lines to the analytically calculated, approximative values, cf. Eq. (16), with the diffusion coefficients: $D_0 = 1$ (solid line); $D_{\mathrm{RR}}(x)$ (dashed line), cf. Eq. (11), and $D_{\mathrm{Z}}(x)$ (dashed-dotted line), cf. Eq. (10).

3.4. Exact Numerics for the 2D Channel

The predicted dependence of the average particle current and the effective diffusion coefficient, predicted above, was compared with Brownian dynamic simulations performed by a numerical integration of the Langevin equation Eq. (4), within the stochastic Euler-algorithm. The shape of the exemplarily taken 2D channel is described by

$$\omega(x) := a \sin(2\pi x) + b, \tag{20}$$

where $b > a$. The sum and difference of the two parameters $a + b$ and $b - a$ give half of the maximal and the minimal width of the channel, respectively. Moreover, a controls the slope of the channel walls which determines the one-dimensional diffusion coefficient $D(x)$.

For the considered channel configuration, cf. Eq. (20), the boundary condition becomes $\omega(x) = a(\sin(2\pi x) + \kappa)$, where $\kappa = b/a = 1.02$ throughout this paper. For a we chose values between 1 and $1/2\pi$. This choice of parameters corresponds to rather short channels for $a = 1$ and a more elongated one for $a = 1/2\pi$. In all cases the width of the widest opening of the channel is larger by a factor of 100 than the width at narrowest opening. One may therefore expect strong entropic effects for these channels. The particle current and effective diffusion coefficient were derived from an ensemble-average of about 3×10^4 trajectories:

$$\langle \dot{x} \rangle = \lim_{t \to \infty} \frac{\langle x(t) \rangle}{t}, \tag{21}$$

and Eq. (17), respectively.

Fig. 2 demonstrates that the resummed one-dimensional diffusion coefficient $D_{\mathrm{RR}}(x)$ leads to a considerably better agreement with the numerical results than the constant diffusion and the diffusion coefficient $D_{\mathrm{Z}}(x)$ proposed by Zwanzig. Therefore we used $D_{\mathrm{RR}}(x)$ for all following calculations.

4. Validity of the Fick–Jacobs Description in the Presence of a Constant Bias

The reduction of dimensionality leading to the FJ equation relies on the assumption of equilibration in the transverse direction which results in an almost uniform distribution of the transversal positions y at fixed values of the longitudinal coordinate x. One can formulate two different sets of criteria determining first, whether the FJ equation describes the relaxation towards the stationary state, say in presence of periodic boundary conditions, or second, whether the stationary state, but not necessarily the relaxation towards this state, can be described by the FJ equation.

Although we here are mainly interested in the second, weaker, type of criteria which are sufficient to guarantee the validity of the transport properties predicted by the FJ equation, we shortly formulate stronger criteria which must be satisfied if the FJ equation is employed to determine the relaxation towards equilibrium. Then, of course, the time scale of equilibration in transversal direction τ_T must be short compared to the relevant time scales in longitudinal direction, τ_L (Burada et al., 2007). The time scale τ_T can be estimated by the time to diffusively cover the widest transversal distance of the channel. It therefore is given by

$$\tau_T = 2(a+b)^2. \tag{22}$$

The time scales characterizing the longitudinal motion are the diffusion time τ_{dL} over the length of a period, which is one in our dimensionless variables, and the time τ_{fL} it takes to drag a particle over this distance by applying the force f. These times are given by

$$\tau_{dL} = 1/2 \quad \text{and}\, \tau_{fL} = 1/f \tag{23}$$

Hence, a necessary condition, that the FJ equation reliably describes transient processes can be formulated as

$$2(a+b)^2 \ll \min(1/2, 1/f) \tag{24}$$

This condition is fulfilled only for rather elongated channels being at least five times as long as wide.

As already mentioned in the presence of periodic boundary conditions in the longitudinal direction, the particle distribution described by the Fokker–Planck Eq. (6) approaches a stationary distribution. Even in the case if the first criterion (24) is violated the stationary solution of the FJ Eq. (12) may still yield the correct marginal probability density provided transversal cuts of the two-dimensional stationary probability density are practically constant. Such a uniform distribution in transversal direction strictly holds in the absence of externally imposed concentration differences if the force f vanishes or if the channel is straight. For channels with varying width the narrow positions confine the positions of particles. From there they are dragged by the force and at the same time they perform a diffusive motion until the channel narrows again. The required uniform distribution in the transversal direction can only be achieved if the diffusional motion is fast enough in comparison to the deterministic drift under the influence of f. In other words, the diffusional spreading within the time the force drags the particle from the narrowest to the widest place in the channel must be at least of the order of the widest channel width. This leads to the second, weaker,

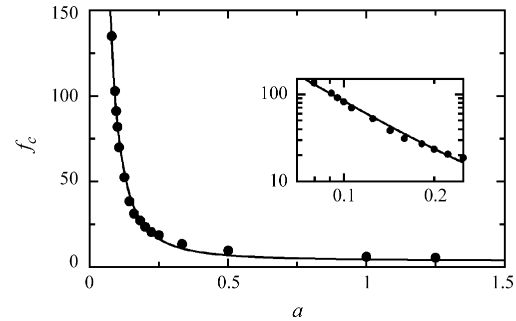

Fig. 3. The dependence of the critical value of the dimensionless force f_c on the parameter a for 2D channels defined by the dimensionless boundary function $\omega(x) = a(\sin(2\pi x) + 1.02)$ is depicted. For $f < f_c$ the accuracy of the Fick–Jacobs approximation is $\sim 1\%$ (in comparison with the exact 2D simulational results). The solid line demonstrates the a^{-2}-dependence of the critical values predicted by Eq. (25). The inset depicts the same data on a logarithmic scale.

criterion

$$(a+b)^2 \le \frac{1}{2f} \Leftrightarrow f \le \frac{1}{a^2}\frac{1}{2(1+\kappa)^2} \propto \frac{1}{a^2}. \tag{25}$$

Eq. (25) provides an estimate of the minimum forcing above which the FJ description is expected to fail in providing an accurate description of the transport properties in the long time limit. The quantitative value of the critical force depends on the level of the prescribed accuracy. The criterion demonstrates how the validity of the equilibrium approximation depends on the relevant parameters of the problem and is concordant with that found for a different scaling in Burada et al. (2007).

In order to test the accuracy of the FJ description, we evaluated the behavior of the nonlinear mobility as a function of the scaled force f, for different values of a according to Eq. (16) and compared it with numerical simulations of the corresponding full two-dimensional problem. The value of the dimensionless force f up to which the FJ approximation with spatially dependent diffusion coefficient $D_{RR}(x)$ provides an accurate description depends on a just as predicted by Eq. (25), cf. Fig. 3. For large values of a the FJ equation starts to deviate from the numerically exact behavior already for rather small forces f, whereas for small values of a larger forces may be applied without violating the FJ equation.

In Fig. 4 the dependence of the nonlinear mobility on the force f is displayed for two different values of the parameter a characterizing the geometry of the channel. For the channel with $a = 1$ which, at its widest opening, is approximately four time as wide as it is long, the predictions of the equilibration assumptions fails at smaller f-values than in the case of $a = 1/2\pi$.

5. Transport Characteristics: Anomalous Temperature Dependence and Enhancement of Diffusion

Transport in one-dimensional periodic *energetic* potentials behaves very differently from one-dimensional periodic systems with *entropic* barriers. The fundamental difference lies

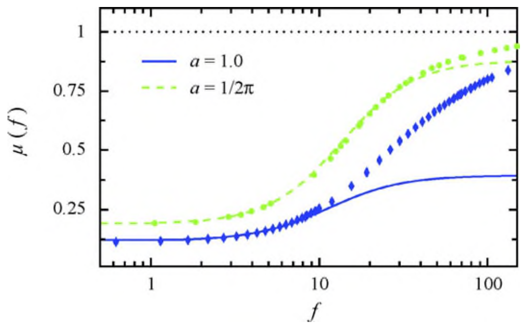

Fig. 4. (Color online) The numerically simulated (symbols) and analytically calculated (cf. Eq. (16) – lines) dependence of the scaled nonlinear mobility $\mu(f)$ vs. the dimensionless force $f = FL/k_B T$ is depicted for two 2D channel geometries. For both channels the scaled half-width is given by $\omega(x) = a(\sin(2\pi x) + 1.02)$; $a = 1$: diamonds and solid line (blue), $a = 1/(2\pi)$: circles and dashed line (green). The dotted line indicates the deterministic limit $\mu(f) = \langle \dot{x} \rangle / f = 1$.

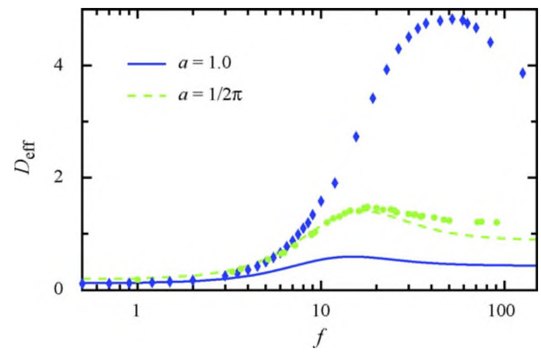

Fig. 5. (Color online) The numerically simulated (symbols) and analytically calculated (cf. Eq. (19) – lines) dependence of the effective diffusion coefficient D_{eff} is depicted *vs.* the dimensionless force $f = FL/k_B T$ for two channels in 2D. For both channels the scaled half-width is given by $\omega(x) = a(\sin(2\pi x) + 1.02)$; $a = 1$: diamonds and solid line(blue), $a = 1/(2\pi)$: circles and dashed line (green).

in the temperature dependence of these models. Decreasing temperature in an energetic periodic potential decreases the transition rates from one period to the neighboring by decreasing the Arrhenius factor $\exp\{-\Delta V/(k_B T)\}$ where ΔV denotes the activation energy necessary to proceed by a period (Hänggi et al., 1990). Hence decreasing temperature leads to a decreasing mobility. For a one-dimensional periodic system with an entropic potential, a decrease of temperature leads to an increase of the dimensionless force parameter f and consequently to an increase of the mobility, cf. Fig. 4.

On the other hand, the dependence of the dynamics on the geometry parameter a clearly reflects the entropic effects on the mobility. A channel with a larger a value has wider openings and therefore provides more space where the particle can sojourn. This longer residence time within a period of the channel diminishes the throughput and consequently the mobility. This is corroborated by the results of our calculations depicted in Fig. 4. For all values of f, an increase in value of a leads to a decrease in the mobility. This holds not only where the FJ equation applies but also for large values of f where it fails.

Another interesting effect can be observed for the effective diffusion if looked as a function of the force f. Already the expression for the effective diffusion (19) which follows rigorously from the FJ equation displays a maximum as a function of f which may even exceed the value 1 of the bare diffusion, cf. Fig. 5. For $f \to \infty$ the periodic stationary distribution approaches a delta function along the x axis and the effective diffusion approaches the bare value 1. If one decreases the force to finite but still large values then the stationary distribution acquires a finite width in the transversal direction with a “crowded” region in front of the narrowest place of the channel (Burada et al., 2007). The transport becomes more noisy and consequently the effective diffusion exceeds the bare value 1. On the other hand if one starts at $f = 0$ the entropic barriers diminish the diffusion such that the effective diffusion is less than bare diffusion. Consequently, somewhere in between there must be a value of f with maximal effective diffusion. For $a = 1$ and $b = 1.02$ the value of the force at the maximal effective diffusion is outside the regime of validity of the FJ equation. The numerical simulations give a much more pronounced peak of the effective diffusion. For the less entropic channel with $a = 1/2\pi$ the maximum is at the border of the regime of validity of the FJ equation, but the enhancement of the effective diffusion constant is less pronounced than for the larger value $a = 1$. These observations lead us to the conclusion that entropic effects increase the randomness of transport through a channel and in this way decrease the mobility and increase the effective diffusion. A similar enhancement of effective diffusion was found in titled periodic *energetic* potentials (Reimann et al., 2001; Lindner et al., 2001; Constantini and Marchesoni, 1999).

6. Conclusions

In summary, we demonstrated that transport phenomena in periodic channels with varying width exhibit some features that are radically different from conventional transport occurring in energetic periodic potential landscapes. The most striking difference between these two physical situations lies in the fact that for a fixed channel geometry the dynamics is completely characterized by a single parameter $f = FL/(k_B T)$ which combines the external force F causing a drift, the period length L of the channel, and the thermal energy $k_B T$, which is a measure of the strength of the acting fluctuating forces. Transport in periodic energetic potentials depends, at least, on one further parameter which is the height of the highest barrier separating neighboring periods. This leads to an opposite temperature dependence of the mobility. While the mobility of a particle in an energetic potential increases with increasing temperature the mobility of a particle in a channel of periodically varying width decreases. The incorporation of the spatial variation of the channel width as an entropic potential in the FJ equation allows a qualitative understanding of the dependence of the transport properties on the channel geometry.

The effective diffusion exhibits a non-monotonic dependence versus the dimensionless force f. It starts out at small f with a value that is less than the bare diffusion constant, reaches a maximum with increasing f and finally approaches the value of the bare diffusion from above.

It is known from the literature that, under certain conditions, the two-dimensional Fokker–Planck equation governing the time dependence of the probability density of a particle in the channel can be approximated by a one-dimensional Fokker–Planck equation: It is termed the Fick–Jacobs equation and contains an entropic potential and a position dependent diffusion coefficient. Various forms of the diffusion coefficient can be found in the literature. A comparison of different forms for a particular channel geometry leads to the conclusion that the expression recently suggested by Reguera and Rubí yields the most favorable agreement. In principle the FJ equation describes both the transient behavior of a particle and also the stationary behavior of the particle dynamics which is approached in the limit of large times, provided appropriate boundary conditions confining the motion in the direction of the channel axis are applied. In order to study stationary transport, periodic boundary conditions must be invoked. We formulated criteria for the validity of the FJ equation for both the transient and the stationary regimes and found that the restrictions imposed by the criterion in the stationary regime are much less serious than those for the transient dynamics. The estimates, which are based on simple dynamical arguments, were corroborated by our numerical simulations.

We restricted our analysis to two-dimensional channels. A generalization of the presented methods to three-dimensional pores with varying cross-section is in principle straightforward. We also confined ourselves to channels with a mirror symmetry about a vertical axis which in the present case can be chosen at $x = 1/4$. For periodic channel shapes without this symmetry ratchet like transport can be expected even if the unbiased force f of vanishing temporal average changes periodically in time.

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