Entropic Transport: Kinetics, Scaling, and Control Mechanisms

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We show that transport in the presence of *entropic* barriers exhibits peculiar characteristics which makes it distinctly different from that occurring through energy barriers. The constrained dynamics yields a scaling regime for the particle current and the diffusion coefficient in terms of the ratio between the work done to the particles and available thermal energy. This interesting property, genuine to the entropic nature of the barriers, can be utilized to effectively control transport through quasi-one-dimensional structures in which irregularities or tortuosity of the boundaries cause entropic effects. The accuracy of the kinetic description has been corroborated by simulations. Applications to different dynamic situations involving entropic barriers are outlined.

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Transport through quasi-one-dimensional structures as pores, ion channels, and zeolites is ubiquitous in biological and physicochemical systems and constitute a basic mechanism in processes as catalysis, osmosis, and particle separation [1–6]. A common characteristic of these systems is the confinement arising from the presence of boundaries which very often exhibit an irregular geometry. Variations of the shape of the structure along the propagation direction implies changes in the number of accessible states of the particles. Consequently, entropy is spatially varying, and the system evolves through entropic barriers, which controls the transport, promoting or hampering the transfer of mass and energy to certain regions. Motion in the system can be induced 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 objectives of major importance in the dynamical characterization of those systems.

Our purpose in this Letter is to demonstrate that entropic transport exhibits striking features, sometimes counterintuitive, which are different from those observed in the more familiar case with energy barriers [7]. We propose a general scenario describing the dynamics through entropic barriers and show the existence of a scaling regime for the current of particles and the effective diffusion coefficient. The presence of this regime might have important implications in the control of transport.

Entropic transport.—The origin of the entropic barriers can be inherent to the intimate nature of the system or may emerge as a consequence of a coarsening of the description employed. A typical example presents the motion of a Brownian particle in an enclosure of varying cross section. This basic situation constitutes the starting point in the study of transport processes in the type of confined systems that are very often encountered at subcellular level, nanoporous materials, and in microfluidic applications. As shown in Ref. [8], the complicated boundary conditions of the diffusion equation in irregular channels can be greatly simplified by introducing an entropic potential that accounts for the reduced space accessible for the diffusion of the Brownian particle. The resulting kinetic equation describing the evolution of the probability distribution is known as the Fick-Jacobs equation [8,9] and constitutes an approximation to the full dynamics. The validity of that equation has only been analyzed for diffusion in the absence of a driving force in whose case many of the transport processes previously mentioned could not take place. This is so, since thermal diffusion alone may not be able to induce transitions of the particles through the entropic barrier.

In typical transport processes through pores or channels, motion of the suspended particles is induced by application of an external driving force F that is directed along their axis. The over-damped dynamics of a biased Brownian particle within the tube (see Fig. 1) then reads:

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

where η is the friction coefficient of the particle, k_B the Boltzmann constant, T the temperature, $F = |\vec{F}|$ a constant force in x direction, and $\vec{\xi}(t)$ is Gaussian white noise with zero mean and correlation function: $\langle \xi_i(t)\xi_j(t')\rangle = 2\delta_{ij}\delta(t - t')$ for $i, j = x, y, z$. The reflecting boundary conditions ensure the confinement of the dynamics within the tube.

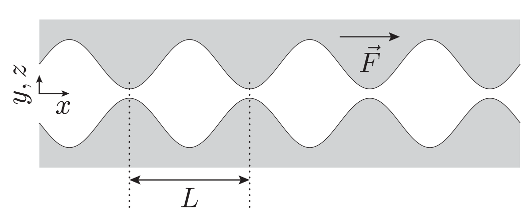

FIG. 1. Schematic diagram of the tube confining the motion of the biased Brownian particles. The half-width ω is a periodic function of x with periodicity L.

Reduction of the dimensionality.—As mentioned previously, the dynamics of the particles along the axis of the 3D tube or a 2D channel (see Fig. 1) can be recast into the *Fick-Jacobs equation*; i.e.,

$$\frac{\partial P}{\partial t} = D_0 \frac{\partial}{\partial x}\left[s(x) \frac{\partial}{\partial x} \frac{P}{s(x)} \right] \tag{2}$$

obtained from the 3D (or 2D) Smoluchowski equation after elimination of y and z coordinates by assuming equilibrium in the orthogonal directions. Here $P(x, t)$ is the probability distribution function, D_0 the diffusion coefficient, and $s(x)$ is the cross-sectional area for a (3D) tube or the width for a (2D) channel. This description is in principle valid for $|\omega'(x)| \ll 1$, where $\omega(x)$ is the radius of the tube (or the half-width of the channel in 2D) and the prime refers to the first derivative. It has been shown that the introduction of a x-dependent diffusion coefficient considerably improves the accuracy of the kinetic equation extending its validity to more winding structures [8,10]. The expression

$$D(x) = \frac{D_0}{[1 + \omega'(x)^2]^{\alpha}}, \tag{3}$$

where $D_0 = k_B T/\eta$ and $\alpha = 1/3, 1/2$ for two and three dimensions, respectively, was shown to appropriately account for the curvature effects [10].

In the presence of a constant force F along the direction of the tube the Fick-Jacobs equation can be recast into the following expression [10]

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x}\left[D(x) \frac{\partial P}{\partial x} + \frac{D(x)}{k_B T} \frac{\partial A(x)}{\partial x} P \right] \tag{4}$$

which defines a free energy $A(x) := E - TS = -Fx - T k_B \ln h(x)$, where $E = -Fx$ is the energy, $S = k_B \ln h(x)$ the entropy, $h(x)$ the dimensionless width $2\omega(x)/L$ in 2D, and the dimensionless transverse cross section $\pi[\omega(x)/L]^2$ of the tube in 3D. For a symmetric channel with periodicity L, the free energy assumes the form of a periodic tilted potential.

Universal scaling for the particle current and effective diffusion.—The key quantities in transport through quasi-one-dimensional structures are the average particle current, or equivalently the nonlinear mobility, and the effective diffusion coefficient. While in the case of an energy barrier, the driving force F and the temperature T are two independent variables, for entropic transport, both current and effective diffusion are controlled by a universal scaling parameter:

$$f := \frac{FL}{k_B T}. \tag{5}$$

For the average particle current and the nonlinear mobility $\mu(f)$ we find an expression similar to the Stratonovich formula [11]

$$\mu(f) := \frac{\langle \dot{x} \rangle}{F} = \frac{1}{\eta} \frac{1 - \exp(-f)}{\int_0^1 dz I(z, f)} f^{-1}, \tag{6a}$$

where

$$I(z, f) := \{1 + [\hat{\omega}'(z)]^2\}^{\alpha} \hat{h}^{-1}(z) \exp(-fz) \times \int_{z-1}^{z} d\tilde{z}\, \hat{h}(\tilde{z}) \exp(f\tilde{z}), \tag{6b}$$

depends only on the dimensionless variable $z = x/L$, the scaling parameter f, and the shape of the tube given in terms of the dimensionless half-width $\hat{\omega}(z) := w(x)/L$ and its first derivative. Here $\hat{h}(z) := h(x)$.

The effective diffusion coefficient could be expressed in terms of moments of the first passage time for a Brownian particle arriving at $x_0 + L$ while starting out from x_0 [11]. A detailed analysis shows that the effective diffusion coefficient also scales with $FL/k_B T$ as:

$$\frac{D_{\text{eff}}}{D_0} = \frac{\int_0^1 dz \int_{z-1}^{z} d\tilde{z} \mathcal{N}(z, \tilde{z}, f)}{[\int_0^1 dz I(z, f)]^3}, \tag{7a}$$

with

$$\mathcal{N}(z, \tilde{z}, f) := \left(\frac{1 + [\hat{\omega}'(z)]^2}{1 + [\hat{\omega}'(\tilde{z})]^2} \right)^{\alpha} \frac{\hat{h}(\tilde{z})}{\hat{h}(z)} [I(\tilde{z}, f)]^2 \exp(-fz + f\tilde{z}). \tag{7b}$$

Numerical simulations.—A model of a 2D periodic channel is sketched in Fig. 1; the shape is described by $\omega(x) = a \sin(2\pi x/L) + b$. Here, a is the parameter that controls the slope of the walls, the width of the channel is $2\omega(x)$, and the width at the bottleneck is $2(b - a)$.

The scaling behaviors, predicted above, have been corroborated by Brownian dynamic simulations performed by integration of the dimensionless Langevin equation, which is equivalent to Eq. (1), within the stochastic Euler algorithm. Therefore, lengths are scaled by the periodicity L of the tube, time by $\tau := L^2 \eta/(k_B T_{\text{room}})$—the corresponding characteristic diffusion time at room temperature T_{room}—and the force by $F_0 := \eta L/\tau$. The mean velocity in x direction, $\langle \dot{x} \rangle = \lim_{t\to\infty} x(t)/t$, and the corresponding effective diffusion coefficient, $D_{\text{eff}} = 1/2 \lim_{t\to\infty} (\langle x^2(t) \rangle - \langle x(t) \rangle^2)/t$, are obtained as an average over $3 \cdot 10^4$ trajectories.

Results for the particle current and the effective diffusion coefficient as a function of the applied force for the case $a = 1/(2\pi)$, $b = 1.02/(2\pi)$, and $L = 1$ are presented in Fig. 2 and Fig. 3 for different values of the noise strength (i.e., the temperature). The particle current increases monotonically with the force, but *decreases* upon increasing the level of noise. The effective diffusion coefficient exhibits a nonmonotonic behavior with the appearance of a peak which becomes more pronounced at low noise levels (see Fig. 3). When both quantities are represented as a function of the scaling parameter f (see Figs. 4 and 5) all curves collapse to the scaled solution which evidences the

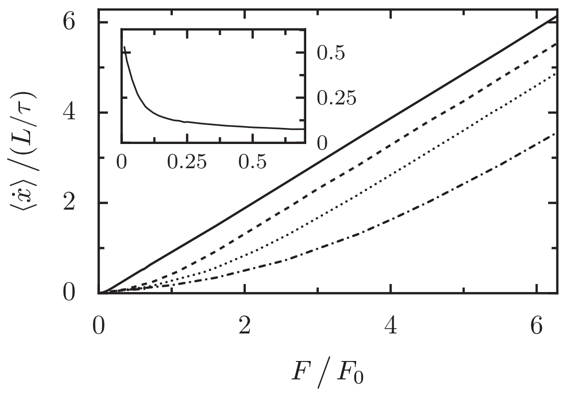

FIG. 2. Numerically determined force dependence of particle current for a symmetric two-dimensional channel with the shape defined by the half-width $\omega(x) = [\sin(2\pi x/L) + 1.02]/(2\pi)$, $L = 1$, and for the values of T/T_{room}: 0.01 (solid line), 0.1 (dashed line), 0.2 (dotted line), and 0.4 (dash-dotted line). The inset depicts the dependence of the particle current $\langle \dot{x} \rangle / (L/\tau)$ on the dimensionless temperature T/T_{room} for the force value: $F/F_0 = 0.628$. Contrary to the case of energetic barriers, the particle current declines with increasing temperature.

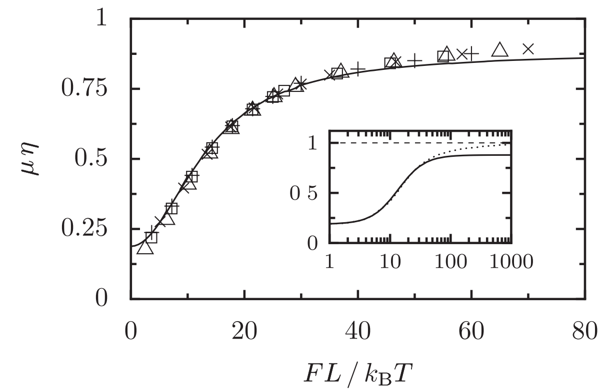

FIG. 4. Graph for the scaled nonlinear mobility. In the Langevin simulation the different symbols correspond to different values of T/T_{room}: 0.01 (crosses), 0.1 (pluses), 0.2 (squares), 0.4 (triangles). The relative error of the simulation results is 0.01. The Fick-Jacobs results, Eq. (6), correspond to the solid lines. The inset depicts the long range behavior (the dotted line depicts the numerical results). The numerical values for the scaled nonlinear mobility approach, in the limit $f \to \infty$, to the value 1 (dashed horizontal line).

excellent agreement of simulations results with the scaling behavior predicted for those quantities. Therefore, whereas in the case of transport through energetic barriers the force (or tilt) and the temperature are two independent parameters, the entropic transport is controlled by a single parameter f. Another important result shown in Fig. 3 is the presence of a peak in the diffusion and the fact that the effective diffusion can be much larger than bulk diffusion. Thus the phenomenon of enhancement of the diffusion, linked to the dynamics of particles in periodic tilted energetic potentials, also takes place when barriers hindering the transport have an entropic nature.

In Figs. 4 and 5 we have also represented the nonlinear mobility and effective diffusion coefficient predicted by Eqs. (6) and (7) obtained from the Fick-Jacobs equation. At low values of the scaling variable f the results match perfectly with the simulations whereas deviations occur at higher values of f. The scaled nonlinear mobility and the effective diffusion coefficient approximates for $f \to \infty$ values different from the value 1. The accuracy of the Fick-Jacobs description worsens at large f because the assumption of equilibration in the transverse direction, which supports the elimination of the y, z coordinates, fails at high values of the applied force. The agreement substantially improves when the shape of the tube does not change too fast, i.e., when $|\omega'(x)|$ is smaller, which can be achieved for instance by increasing the period L of the

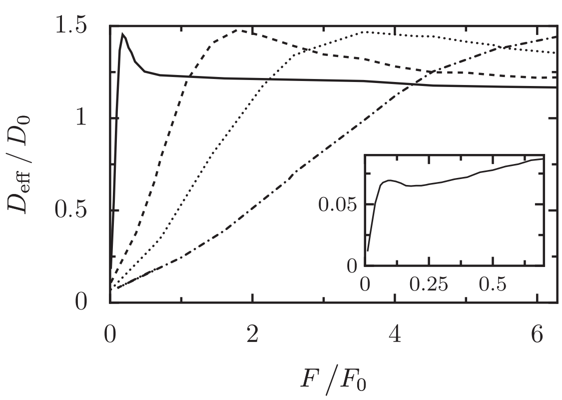

FIG. 3. The effective diffusion coefficient vs the external bias. The parameters for the various lines correspond to those detailed in Fig. 2. The inset depicts the effective diffusion coefficient $D_{\text{eff}}/(L^2/\tau)$ vs dimensionless temperature T/T_{room}.

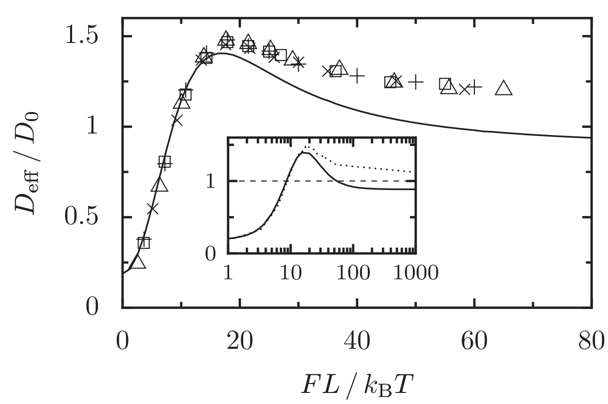

FIG. 5. Same as in Fig. 4, but for the effective diffusion coefficient. The relative error of the simulation results is 0.1. The Fick-Jacobs results, Eq. (7), correspond to the solid lines. The inset depicts the long range behavior (the dotted line depicts the numerical results). The numerical values for the scaled nonlinear mobility approach, in the limit $f \to \infty$, to the value 1 (dashed horizontal line).

shape oscillations of the channel. In situations where the roughness of the channel is not very extreme, the Fick-Jacobs description provides a very good approximation to the transport for values of the external work of some tens of $k_B T$'s. In fact, that is the range of energies relevant to most transport processes in biological systems.

The peculiar behavior of the particle current and effective diffusion coefficient as a function of temperature is depicted in the insets of Figs. 2 and 3. Contrary to the case of an energetic barrier, the particle current *decreases* upon increasing the temperature. In the presence of energetic barriers, the temperature facilitates the activation (the overcoming of the barriers) and thus tends to increase the particle current. However, when transport is controlled by entropic factors, the temperature dictates the strength of the entropic potential, and thus an increase of temperature leads to a reduction of the particle current. The effective diffusion coefficient as a function of the temperature also manifests a striking behavior with the presence of a peak, and the existence of a range of temperatures where the effective diffusion coefficient decreases upon increasing the temperature. It is important to remark that, since the transport characteristics scale as $FL/k_B T$, the peculiar regimes can be obtained not only by changing the temperature but also by modifying the strength of the force.

Applications.—An example in which the entropic nature of the transport becomes more evident is the case of micro and nanoporous materials, such as zeolites. These materials have a regular structure with channels of different width and well-defined geometry. This peculiar structure confers them an outstanding ability to act as molecular sieves, that is currently exploited in chemically clean separation of mixtures, ion exchange, and petrochemical cracking. Driven by their economic and scientific importance, these materials have been studied extensively experimentally and more recently by computer simulations. For instance, the diffusion has been found to decrease with temperature in some range of temperatures [12]; and the existence of an optimal value of the diffusion as a function of the temperature has also been observed [13]. In fact, the dependence of the effective diffusion coefficient on temperature reported in Ref. [13] behaves just as the one predicted here with Fig. 3. Finally, values of diffusion coefficients higher than the bulk, consistent with the phenomenon of diffusion enhancement predicted by our model, have also been reported [14]. Our simple model thus accounts for all these behaviors and shows that they are not specific of a particular zeolite structure but they arise from the entropic nature of the transport.

Conclusions.—In summary, we have shown that transport phenomena in systems in the presence of entropic barriers exhibit some features radically different from conventional transport through energetic barriers. The effect of confinement can be recast in terms of an entropic potential, and the dynamics of the system can be accurately described by means of the Fick-Jacobs equation. We have shown the existence of a scaling regime in the dynamics. The particle current and the effective diffusion coefficient are controlled by a single parameter f that measures the relative importance of the external work done to the particle and the thermal energy. The scaling in f thus opens up the possibility of tuning and controlling the efficiency of transport in confined systems by a proper combination of temperature and applied field. In situations in which the temperature can only be varied in a very limited range, as frequently occurs in biological systems, the existence of scaling implies that the same transport regime can be accomplished by the application of an external force. The analysis presented could be applied to a wide variety of situations, such as biological transport through ion channels and membrane pores, or the portage in molecular sieves or polymer gels, where entropic effects play a very important role.

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