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Entropy production and rectification efficiency in colloid transport along a pulsating channel

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Abstract
We study the current rectification of particles moving in a pulsating channel under the influence of an applied force. We have shown the existence of different rectification scenarios in which entropic and energetic effects compete. The effect can be quantified by means of a rectification coefficient that is analyzed in terms of the force, the frequency and the diffusion coefficient. The energetic cost of the motion of the particles expressed in terms of the entropy production depends on the importance of the entropic contribution to the total force. Rectification is more important at low values of the applied force when entropic effects become dominant. In this regime, the entropy production is not invariant under reversal of the applied force. The phenomenon observed could be used to optimize transport in microfluidic devices or in biological channels.

Keywords: transport in confined systems, soft condensed matter, entropic transport

(Some figures may appear in colour only in the online journal)

1. Introduction

Particle current rectification is an important mechanism that controls transport at small scales. It is based on the breaking of the intrinsic randomness of Brownian fluctuations thus facilitating the motion of the particles in a preferred direction [1, 2]. The mechanism takes place when a time-space symmetry is broken giving rise to the failure of detailed balance conditions and consequently to the appearance of a net current. This is what happens when particles move under the influence of an asymmetric (ratchet) potential of energetic or entropic nature or under the action of time-periodic forces [3–5].

Current rectification has also been predicted in transport through confined structures having irregular boundaries [5–15]. In this situation, the entropy (a function of the number of states accessible to the particles) is not a constant along the transport direction and entropic forces related to the entropy gradient act on the particles. Transport in the presence of entropic barriers, or entropic transport, plays an important role at the mesoscale and has been subject of many studies [16–22].

A new entropic rectification mechanism has recently been proposed for the case in which the channel through which particle move undergoes periodic deformations. Periodic changes of the channel structure result in time-dependent entropic barriers that gives rise to peculiar transport properties. It has been found that channel pulsations may induce current reversal and resonant effects [23–25].

In this article, we study the efficiency of the entropic rectification process in a pulsating channel by quantifying the phenomenon through a rectification coefficient that is analyzed in terms of the force applied, the height of the barrier and the diffusion coefficient. The coefficient characterizes the different rectification regimes. Rectification is also studied

under the prism of the energy dissipation in the process, or equivalently of the entropy production. We will show that at high values of the applied force the entropy production is practically invariant under inversion of the force. At small values of the force, when entropic effects are dominant, the symmetry is broken.

The article is organized as follows. In section 2, we briefly review the entropic transport model for a pulsating channel. Section 3 is devoted to the analysis of the rectification coefficient. In section 4, we analyze the energetic cost of the rectification mechanism by computing the entropy production from the knowledge of the particle current and the force. Finally, in section 5 we present our main conclusions.

2. Entropic transport model for pulsating channels

We study the confined diffusion of N non-interacting Brownian particles through a 2D periodic channel whose walls may vary periodically in time. They consist of contiguous units of length $2L$ formed by two subunits of length L, as is shown in figure 1.

The shape of the boundaries of the channel is periodically modulated in time with the height given by:

$$h(x,t) = \begin{cases} a_1(t)x^2 + \frac{d}{2} & ; & 0 \leqslant x \leqslant \frac{b}{2} \\ -a_1(t)(x-b)^2 + s(t) & ; & \frac{b}{2} < x \leqslant b \\ -a_2(t)(x-b)^2 + s(t) & ; & b < x \leqslant \frac{L+b}{2} \\ a_2(t)(x-L)^2 + \frac{d}{2} & ; & \frac{L+b}{2} < x \leqslant L \end{cases} \tag{1}$$

Here b indicates the location of the point of maximum width and d is the width of the bottleneck. The time-dependent coefficients are $a_1(t) = \frac{2[s(t)-d/2]}{b^2}$, $a_2(t) = \frac{2[s(t)-d/2]}{(L-b)^2}$ and $s(t) = s_0 + s_1 \sin(\omega t + \Phi)$. The values of the parameters are set to guarantee the asymmetry of the subunits. The phase difference between adjacent subunits in one unit cell is given by:

$$\Phi = \begin{cases} 0 & ; & x \in [0,L] \\ \pi & ; & x \in (L,2L] \end{cases} \tag{2}$$

A phase lag $\Phi = \pi$ means that consecutive subunits can shrink and enlarge alternatively such that the total volume does not change much, a realistic situation that may be observed in transport of particles through channels.

We will analyze the transport properties by means of the Fick–Jacobs equation, that governs the dynamics of the probability distribution of the ensemble of non-interacting Brownian particles

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[D(x,t)\frac{\partial P(x,t)}{\partial x} - \frac{D(x,t)}{k_B T}F_{\text{eff}}(x,t)P(x,t)\right]. \tag{3}$$

Here $D(x,t)$ is an effective diffusion coefficient, that in our two-dimensional case is given by

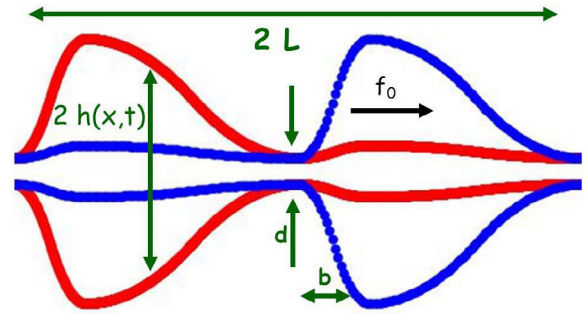$$D(x,t) = d_0(1 + h'(x,t)^2)^{(-1/3)} \tag{4}$$

Figure 1. Snapshot of a unit of the channel oscillating out of phase with period T for two different times. The solid (red) line corresponds to $t = 0$ and the dotted (blue) line corresponds to $t = T/2$.

where d_0 corresponds to the diffusion coefficient of the particles when they move in an unbounded medium and $F_{\text{eff}}(x,t)$ is an effective force acting along the x-direction which is related to the energetic and entropic barrier contributions to the free energy $A(x,t)$:

$$F_{\text{eff}}(x,t) = -\frac{\partial A(x,t)}{\partial x} = F_0 + k_B T \frac{h'(x,t)}{h(x,t)} \tag{5}$$

with $A(x,t) \doteq E - TS = -F_0 x - k_B T \ln h(x,t)$.

From equation (3), we can identify the instantaneous particle current

$$\mathscr{J}(x,t) = -\left[D(x,t)\frac{\partial P(x,t)}{\partial x} - \frac{D(x,t)}{k_B T}F_{\text{eff}}(x,t)P(x,t)\right]. \tag{6}$$

The Fick–Jacobs approximation assumes that the probability density reaches equilibrium in the transverse direction much faster than in the longitudinal one. This requirement is fulfilled if $|h'(x,t)| \ll 1$ for all times and positions, that is, when the cross section of the tube varies smoothly.

For the sake of simplicity, we use dimensionless quantities. We scale lengths with the unit length $L_o = 2L$, times with the diffusion time $\tau_{\text{dif}} = L_o^2 \gamma/(k_B T_R)$ with γ the Stokes' friction of a spherical particle of reference radius r and T_R some reference temperature, energies with $k_B T_R$, forces with $k_B T_R/L_o$ and currents with L_o/τ_{dif}. We define the dimensionless diffusion coefficient $D_0 = T/T_R$ that represents a reduced temperature. A typical diffusion constant in colloids in aqueous solution is $d_0 \approx 10^{-12}$ m^2 s^{-1}. Therefore a typical Brownian time scale or average time for a particle to diffuse a distance equal to its diameter is of the order of 1–100 s, for particles of sizes from 1 to 10 μm and velocities in the range 10^{-1}–1 (μm) s^{-1}. Besides, the validity of the Fick–Jacobs approach requires that the dimensionless frequency ω has to be smaller than one, this implies that modulations must be smaller than 20π rad s^{-1}. These values are of the same order as the ones considered in recent experiments on transport of molecules in confined media subjected to entropic barriers and to a driving force [17].

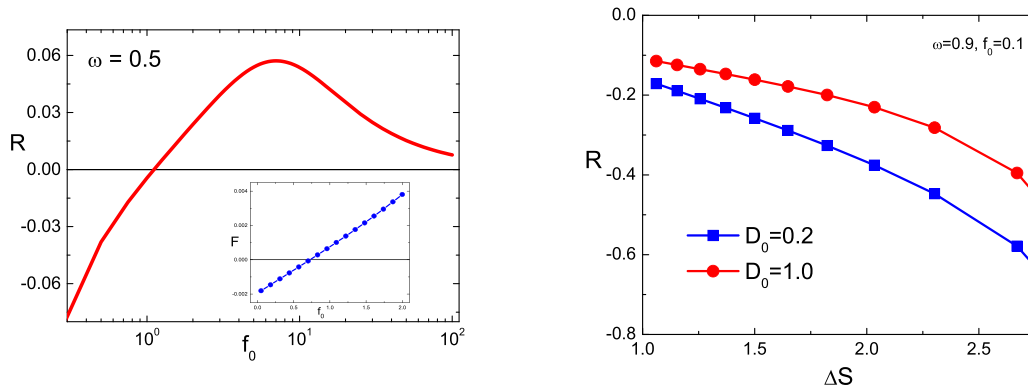We can express the effective force in terms of dimensionless variables as:

Figure 2. Rectification coefficient as a function of the applied force and the entropic barrier. Left panel: R versus f_0 for $\omega = 0.5$ and $\Delta_S = 2.15$. Inset: average mean force F versus versus f_0. Right panel: R versus ΔS for low and high diffusion ($D_0 = 0.2, 1$). $\omega = 0.9$ and $f_0 = 0.1$ Other parameters are: $s_0 = 0.45$, $s_1 = 0.2$, $b = 0.25$, $L = 1$.

$$\mathscr{F}_{\text{eff}}(x,t) = f_0 \left(1 + \frac{1}{f_0} \frac{h'(x,t)}{h(x,t)} \right) \tag{7}$$

where the second term indicates the ratio between entropic and energy forces. This equation shows that the effective force can equivalently be controlled by variations of the force, temperature and period of the cell. The effect of a small force would then be tantamount to the effect of the temperature.

In addition to the requirements for the validity of the Fick–Jacobs equation such as a smooth channel and slow oscillations, we assume high fluid viscosity and low particle density conditions. Therefore, under these assumptions we can neglect hydrodynamic particle-wall and particle-particle interaction effects in the motion of the particles.

3. Rectification efficiency

From the dimensionless Fick–Jacobs equation, we obtain numerically the probability density $P(x,t)$ with periodic boundary conditions at $x = 0, 1$. We introduce the mean particle current as

$$j(t) = \int_0^1 \tilde{\mathscr{J}}(x,t) \mathrm{d}x \tag{8}$$

with $\tilde{\mathscr{J}}(x,t)$ the dimensionless form of the probability current given in equation (6). The average current J is given by the time average of the particle current $j(t)$ in a time period $\tau = 2\pi/\omega$

$$J = \frac{1}{\tau} \int_{t_0}^{\tau+t_0} j(t) \mathrm{d}t. \tag{9}$$

The particle current rectification strength achieved in the motion of colloids along the channel can be quantified through the rectification coefficient:

$$R = \frac{J(f_0) - J(-f_0)}{J(f_0) + J(-f_0)}. \tag{10}$$

In the left panel of figure 2, we observe a rectification of the particle current as a function of f_0. We find that R changes

from negative to positive values as long $|f_0|$ increases. The inversion of R occurs for a critical value $f_0 = f_R$, that in our case is $f_R \approx 1$. This phenomenon relies on a change over between a regime dominated by the entropic barrier to one dominated by the energy one. In the inset of the left panel of figure 2, we plot the time average force F as a function of f_0 (positive), that is defined as:

$$F = \frac{1}{\tau} \int_{t_0}^{\tau+t_0} f(t) \mathrm{d}t \tag{11}$$

with $f(t)$ the ensamble average of $\mathscr{F}_{\text{eff}}(x,t)$ at a given time.

For low external forces, F is negative due to the geometry of the channel. However as f_0 increases, F becomes positive. The inversion of R can be understood from the behavior of F. We observe that the crossing of the horizontal axis occurs around the same value of f_0, for both R and F. For low but positive values of f_0, F is negative so the entropic forces dominates the transport. For high and positive f_0, F becomes positive then the energy barrier dominates. In other words, when the external force is very strong the dynamical response due to entropic forces is washed out. As the asymmetric contributions given by the geometry are negligible, the particle current takes the same values for a positive and negative f_0. This crossover relies on the relative importance between both contribution as it is expressed by the ratio in the second term of equation (7).

To show the competition of the different relevant time scales, we plot in figure 3 the dependence of R on D_0 and ω. In the energy dominated regime and low diffusion, R is more negative as long the pulsation is faster. In this situation, the time scale corresponding to the diffusion process is large and the faster time scale of the entropic ratcheting dominates the dynamics. For larger D_0, diffusive time scale dominates and R saturates to a value independent of ω.

The situation is similar for low diffusion in the entropic regime, however R achieves a higher absolute value. That is, the entropy barriers enhance the role of the asymmetric confinement on the motion of colloids, effect that is washed out in the energy regime (larger f_0). For large diffusion, R tends to be independent of ω but always negative.

In figure 3 we observe a reversal of R when it is represented as a function of D_0. As long f_0 increases, R becomes
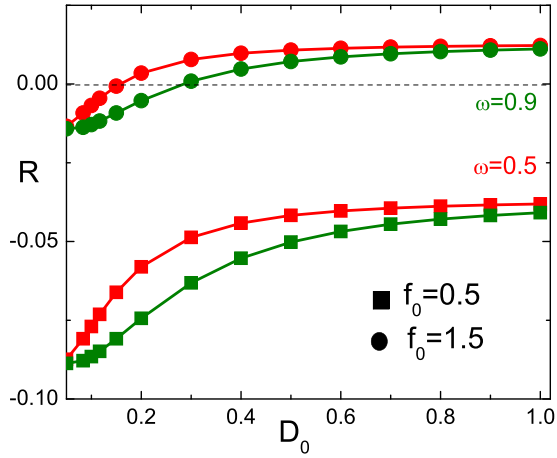
Figure 3. Rectification coefficient R versus D_0 for $\omega = 0.5$ (red) and $\omega = 0.9$ (green). $f_0 = 1.5$ (circle), $f_0 = 0.5$ (square) and $\Delta_S = 2.15$ and other parameters as in figure 2.

less negative and inversion takes place. The value of D_0 for which inversion occurs depends on ω. As long the diffusion time is smaller, the channel has to oscillates faster to produce the same inversion phenomena. This fact suggests the presence of a scaling regime in which the reversal phenomena scales with $D_0/(L^2\omega)$, for a constant f_0.

The role played by the asymmetry of the channel is related to the entropic barriers. In the right panel of figure 2, we plot R versus ΔS, defined as the highest value achieved by the entropic barrier during its oscillation: $\Delta S \equiv \ln(2(s_0 + s_1)/d)$. We observe that in the entropic regime, rectification efficiency can be improved for larger ΔS and lower values of D_0.

4. Entropy production

The different rectification scenarios found can also be analyzed in terms of the energetic cost of the particle transport which can quantified by means of the entropy production rate $\sigma(x, t)$. The dimensionless quantity (scaled in units of τ_{dif}/k_B) is the product of the flux $\tilde{\mathscr{J}}(x, t)$ and the effective driving force (or $\frac{\partial\mu}{\partial x}$ with μ the chemical potential) $\mathscr{F}_{eff}^\mu(x, t) = \frac{1}{\rho}\frac{\partial\rho}{\partial x} - \mathscr{F}_{eff}(x, t)$ that includes the enthalpic contribution:

$$\sigma(x, t) = -\tilde{\mathscr{J}}(x, t)\mathscr{F}_{eff}^\mu(x, t). \tag{12}$$

In the linear regime where the flux is proportional to the force $\mathscr{F}_{eff}^\mu(x, t)$, the entropy production is proportional to the force squared and thus depends on the applied force and the entropic force or equivalently on the shape of the channel. The scaling behavior found for the effective force would then give rise to a scaling of the entropy production. The entropy production averaged over a period of time and space

$$\sigma_P = \frac{1}{\tau}\int_{t_0}^{\tau+t_0}dt\int_0^1 dx\sigma(x, t) \tag{13}$$

characterizes the dissipation inherent to particle transport.

In figure 4, we plot the entropy production normalized to the value obtained when $\omega \to 0$. Both quantities are positive and consequently the ratio is also positive for all frequencies.

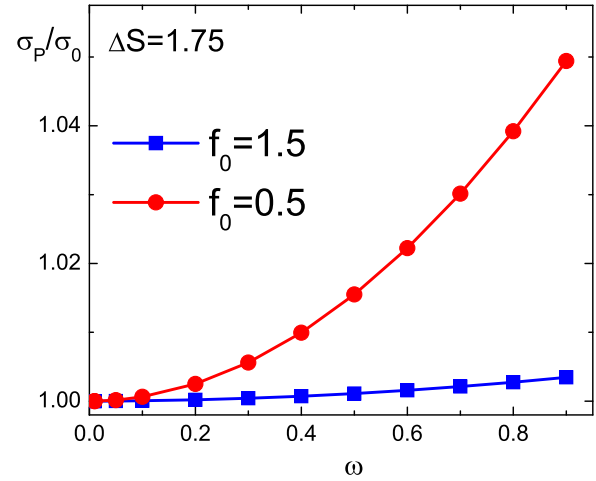**Figure 4.** Reduced entropy production: $\sigma_P(\omega)/\sigma_0(\omega \to 0)$ versus ω, for $f_0 = 1.5$ (green) and $f_0 = 0.5$ (red). $\Delta_S = 1.75$ and other parameters as in figure 2.
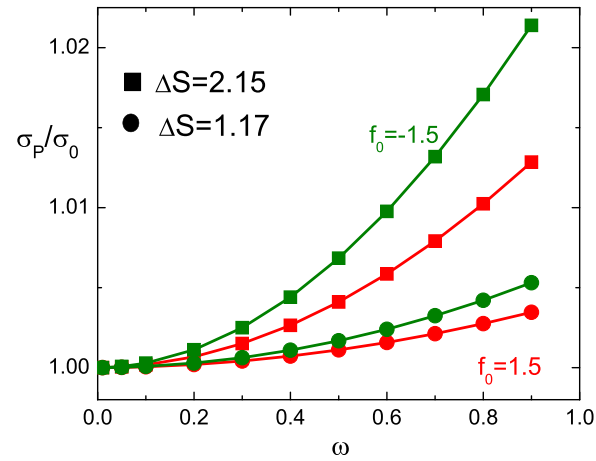

Figure 5. $\sigma_0(\omega)/\sigma_P(\omega \to 0)$ versus ω for $\Delta_S = 2.15$ (squares) and $\Delta_S = 1.17$ (circles). $f_0 = 1.5$ (red) and $f_0 = -1.5$ (green). Parameters as in figure 2.

For a given ω, larger ratios are achieved in the entropic regime because the motion of the colloids is mainly ruled by the time-modulated entropic forces. In the entropic regime, the entropy production takes a value slightly larger than the static one, thus the dissipation increases.

In figure 5, we observe that a reversal of f_0 yields different values of the ratio σ_P/σ_0 that depends on the specific shape of the channel given by ΔS.

It is interesting to analyze how a reversal of the direction of f_0 affects the entropy production when the diffusion coefficient changes. In figure 6, the ratio $\sigma_P(f_0)/\sigma_P(-f_0)$ is pictured as a function of D_0, for two different frequencies. This figure clearly shows the presence of the two quite distinct regimes dominated by entropic and energy forces.

When the effect of the external force dominates, the left/right asymmetry vanishes, consequently the entropy production is the same in both directions. This effect is enhanced when the colloids diffuse faster (larger D_0) and tends to be independent of ω. As long f_0 becomes larger, the system can be thought as colloids moving in a symmetric channel.
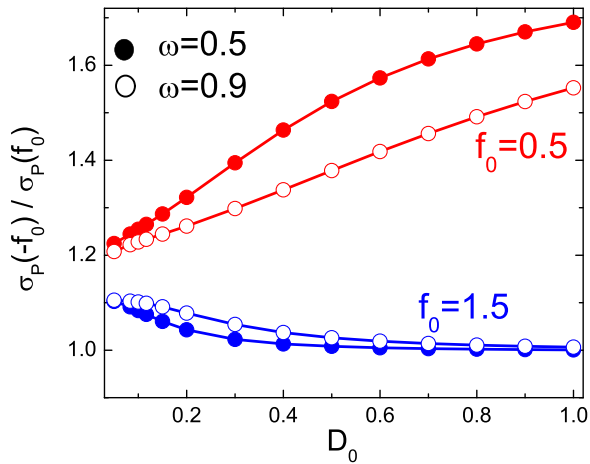
Figure 6. $\sigma_P(-f_0)/\sigma_p(f_0)$ versus D_0 for $\omega = 0.5$ (full circles) and $\omega = 0.9$ (empty circles). $f_0 = 0.5$ (red), $f_0 = 1.5$ (blue) and $\Delta_S = 2.15$ in all cases.

However, in the entropic regime the time scales related to frequencies and diffusion evenly play a relevant role. A diffusion time smaller than the characteristic time of the pulsation implies that the particle takes many time periods to travel a distance equal to one unit of the channel. Therefore, the effect of the time-dependent constraints imposed by the confinement is enhanced and the entropy production is larger, with different values for the forward and backward directions.

The behavior described suggests an interesting mechanism to induce transport of particles through microchannels. When external forces are small, the entropic ratcheting induced by pulsations becomes the leading mechanism in the transport process. It can be used to improve the rectification efficiency and to control the entropy production, reducing the dissipation.

5. Conclusions

In this article, we have analyzed the efficiency of the particle current rectification process observed in channels whose shape is modulated periodically. We have proposed a rectification coefficient that measures the difference between the particle current induced by a given force acting along both directions of the channel. We have identified two rectification regimes. At low values of the forces, when entropic effects become important, rectification may be relevant. On the contrary, at high forces the effect of the entropic barrier fades away and rectification considerably diminishes.

We have examined the rectification regimes in terms of the entropy production which has been computed as a function of the applied force, the oscillation frequency the strength of the entropic barrier and the diffusion coefficient. The analysis of this quantity shows the existence of situations of minimum dissipation that can be selected upon varying these quantities. At high values of the force, the entropy production is invariant

under inversion of the applied force. This invariance is broken at low forces when entropic effects become important.

The results obtained indicate how channels should be designed for a controllable current and dissipation and why existing structures in nature such as protein channels and pumps undergo their main functions on the basis of their particular forms.

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