

DEBYE LENGTH MATCHES CHANNEL BOTTLENECK: CORRUGATION-GOVERNED REGIME IN TRACER DIFFUSION THROUGH A VARYING-SECTION CHANNEL

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ABSTRACT

We study the motion of charged and neutral tracers, in an electrolyte embedded in a varying section channel. Making use of systematic approximations, we map the convection diffusion equation governing the motion of tracers density in an effective 1D equation describing the dynamic along the channel where its varying-section is encoded as an effective entropic potential. This simplified approach allows us to characterize tracer diffusion in semi-confined environment by measuring its mean first passage time (MFPT). We disentangle the MFPT dependence upon channel geometry, electrolyte properties and tracers charge even at equilibrium. Such behavior can be exploited in different biological as well as synthetic situation whenever relevant phenomena can be triggered by the presence of few particles.

INTRODUCTION

The motion of charged tracers in an electrolyte has become a matter of interest due to its implication in both biological situations as well in the development of micro- nano- fluidic devices. In many cases tracers move in an electrolyte that is embedded in a channel or in a porous media. Due to the interaction with the electrolyte, the walls of the channel or the porous media accumulate net charge. Hence a net, screened, electrostatic field develops inside the channel. This feature is at the basis of phenomena such as electro-osmosis and it has been exploited for micro- nano-pumping. The currents in these devices generally relies on the control of some external force as hydrostatic or electrostatic fields. Tuning the external forcing leads to the control of particle currents as it happens, e.g. in sodium-potassium pumping in neurons.

An alternative route to current control relies on the geometrical confinement provided by the channel itself. It has been shown [1],[2] that the rectification provided by local variation in channel section can strongly affect particle transport. Moreover, the geometrically-induced current control is affected by the inhomogeneous distribution of particles along the radial direction [1]. This is the case of neutral tracers under an external field as gravity, or of charged tracers embedded in an electrolyte confined in charged-wall channel. Recently different groups [3], [4] have characterized the flow in varying-section channels when the electrostatic field generated by the charge channel walls is characterized by a screening (Debye) length, k^{-1} , that is vanishing small compared to the channel half-amplitude, $h(x)$.

However, the regime where k^{-1} is comparable to the channel bottleneck leads to a competition between electrostatic driving and geometric confinement and can lead to new dynamic scenarios where channel modulation plays a relevant role in charged tracer transport. Such regime has already shown interesting features as current inversion and negative mobility for forced electrolytes [5].

In this piece of work we show that, even at equilibrium, a sig-

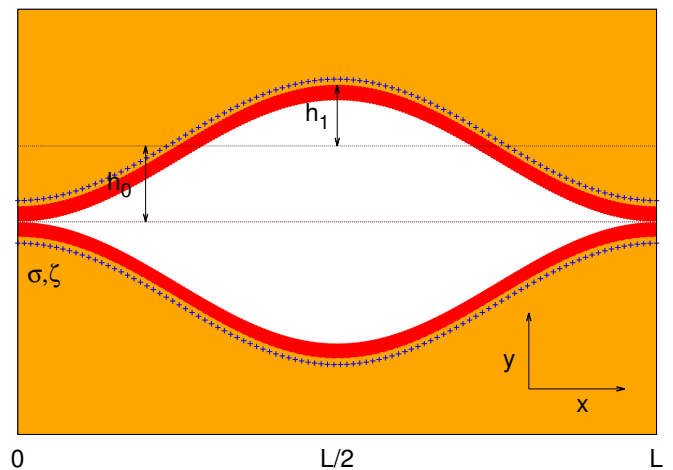


Figure 1. Electrostatic field inside a varying-section channel whose bottleneck amplitude $h_0 - h_1$ is comparable with the Debye double layer thickness k^{-1} .

nature of the interplay between the local rectification provided by the varying-section channel and the inhomogeneous distribution of charged tracers, provided by the transverse electrostatic field, can be read out from the tracers mean first passage time (MFPT) along the channel. Our results show a remarkable dependence of the MFPT on particle charge as well as on channel corrugation. For positively charged channel walls, positive (negative) tracers are depleted (attracted) towards the channel walls and their MFPT is enlarged (reduced) respectively. We expect such features to be relevant for several biological situations where channel walls are made by bilipidic membrane while the cytoplasm or physiologic solution particles are transported is rich in salt. In the latter situation the MFPT is a key quantity since cell fate might be determined by the recognition of, low concentrated, receptors. On the other hand in synthetic

situations such as nuclear waste containers or pattern forming system, a charge-dependence of the MFPT can lead to enlargement of the half-life of the former as well to, transitory, pattern formation/deformation for the latter.

To capture the main features of such an interplay between the geometrically induced local rectification provided by the varying-section channel and the electrostatic field we study a $z-z$ electrolyte embedded in a conducting channel (similar results have been obtained for an insulating channel). To keep an analytical insight we assume a highly diluted ion concentration and a small ζ potential on the channel walls, i.e. $\beta e \zeta \ll 1$ where $\beta^{-1} = k_B T$ is the inverse temperature (being k_B the Boltzmann constant) and e the elementary charge. This choice keeps the electrostatic field inside the channel in the linear regime hence allowing for a Debye-Huckel approximation to the electrostatics inside the channel. In order to gain insight in the properties of the MFPT of charged tracers and the which are the most relevant parameters determining their dynamic, we will assume that the channel amplitude, $h(x)$, varies slowly, i.e. $\partial_x h(x) \ll 1$. Such assumption allows for a projection of the $2D-3D$ convection diffusion equation to an effective $1D$ equation, where the varying-section of the channel will enter as an entropic effective potential. This approximation, called Fick-Jacobs, has been used and validated in many different scenarios [6], [1], [7].

The structure of the text is the following: in section II we will derive the Fick-Jacobs equation for charged tracers moving in a varying-section channel, in section III we will present our results while in section IV we will summarize our conclusions.

THEORETICAL FRAMEWORK: EQUILIBRIUM

The motion of suspension of charged particles is characterized by a convection-diffusion equation, that in the overdamped regime, reads:

$$\partial_t P(x, y, t) = D \beta \nabla \cdot (P(x, y, t) \nabla U(x, y)) + D \nabla^2 P(x, y, t) \quad (1)$$

where D is the diffusion coefficient and $U(x, y)$ is the total conservative potential acting on the particles. When particles are embedded in a confined region as is the case for tracers moving across a channel, the boundary condition of eq. 1 along the channel longitudinal axis will vary according to its channel amplitude. If the channel section varies only along the x -direction and it is constant in z , the free space accessible to the center of mass of a point-like particle is $2h(x)L_z$, being $h(x)$ the half-width of the channel along the y -direction and L_z the width along the z -direction. For such a situation, we encode the presence of the channel and the electrostatic potential in the overall potential $U(x, y, z)$ defined as:

$$\begin{aligned} U(x, y, z) &= U(x + L, y, z) \\ U(x, y, z) &= \psi(x, y), |y| \leq h(x) \ \& \ |z| \leq L_z/2 \\ U(x, y, z) &= \infty, |y| > h(x) \ \text{or} \ |z| > L_z/2 \end{aligned} \quad (2)$$

that is periodic along the longitudinal direction, x , and confines the particles inside the channel.

In order to find the electrostatic potential, $\psi(x, y)$, inside the channel, we should solve the, $2D$, Poisson equation:

$$\partial_x^2 \psi(x, y) + \partial_y^2 \psi(x, y) = -\frac{\rho_q(x, y)}{\epsilon} \quad (3)$$

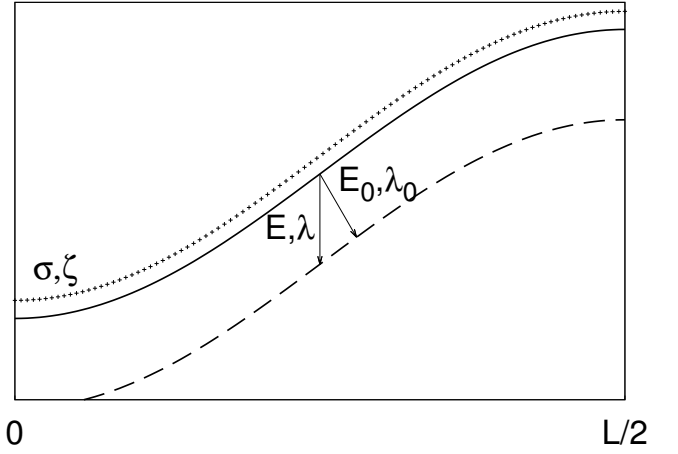


Figure 2. Debye double layer inside a varying-section channel. The Debye length $k_0^{-1} = \lambda_0$ is shown as well as the approximated Debye length $k^{-1} = \lambda$.

with the boundary condition given by eq. 3, being $\rho_q = \rho_0 \exp(-\beta z e \psi(x, y))$ the, equilibrium, charge density inside the channel in the absence of tracers. Assuming smoothly-varying channel walls, $\partial_x h \ll 1$, we can take advantage of the lubrication approximation, $\partial_x^2 \psi(x, y) \ll \partial_y^2 \psi(x, y)$. In this way we can reduce eq. 3 to a $1D$ equation for the potential $\psi(x, y)$. Such an approximation introduces an error in the electrostatic field that can be estimated. In fact we know that, prior to our lubrication approximation, the electrostatic field is perpendicular to the channel wall. Hence, for varying-section channel, we should count for the projection of the electrostatic field along the radial direction as shown in fig. 2 when solving the Poisson equation. For a smoothly-varying channel amplitude, the projected electrostatic field reads:

$$E = E_0 \cos(\alpha) \quad (4)$$

with $\alpha = \arctan[\partial_x h(x)]$. Due to the smoothness of the variation of channel amplitude, we have $\partial_x h(x) \ll 1$ hence leading to a second order correction in $\partial_x h(x)$ for the electrostatic field

$$E = E_0 \left[1 - \frac{1}{2} (\partial_x h(x))^2 \right]. \quad (5)$$

In the following we will neglect such correction assuming, $E = E_0$ along the channel. For low salt concentration in the electrolyte and small ζ potential on channel walls, we can further simplify eq. 3 by linearizing the charge density $\rho_q(x, y) \simeq \rho_0 (1 - \beta z e \psi(x, y))$, hence getting:

$$\psi(x, y) = \zeta \frac{\cosh(ky)}{\cosh(kh(x))} \quad (6)$$

for a channel made by conducting walls or

$$\psi(x, y) = \frac{\sigma}{2\epsilon} \frac{\cosh(ky)}{\sinh(kh(x))} \quad (7)$$

for an insulating-walls channel characterized by a constant surface-density of electric charge σ , being ϵ the dielectric con-

stant of the electrolyte. Such assumption, known as Debye-Huckel approximation, allows to identify the screening length, k_0^{-1} , of the electrostatic potential as $k_0^2 = \beta z e \rho_0 / \epsilon$. The approximation made for the electrostatic field reflects in the Debye length. Fig. 2 shows the common origin of the corrections for both the Debye length and the electrostatic field, provided by the change in the channel section. Consistently with the choice for the electrostatic field, we can assume constant Debye length, $k^{-1} = k_0^{-1}$, along the channel by safely ignoring the second order correction given by eq. 5.

Under the assumption of smoothly varying-section channels, $\partial_x h \ll 1$, we can approximate the radial profile of the probability distribution function (pdf), $P(x, y, t)$, of a tracer of charge q by its profile at equilibrium, i.e we can factorize the pdf by assuming:

$$P(x, y, z, t) = p(x, t) \frac{e^{-\beta q \Psi(x, y)}}{e^{-\beta A(x)}} \quad (8)$$

$$e^{-\beta A(x)} = \int_{-L_z/2}^{L_z/2} \int_{-h(x)}^{h(x)} e^{-\beta q \Psi(x, y)} dy dz.$$

By integration over dy, dz we obtain:

$$\dot{p}(x, t) = \partial_x D [\beta p(x, t) \partial_x A(x) + \partial_x p(x, t)] \quad (9)$$

where we have assumed vanishing small tracers concentration so not to perturb the equilibrium electrostatic potential $\Psi(x, y)$. Eq. 9 encodes both the confining as well as the electrostatic potential given by eq. 3 in the free energy $A(x)$. Since all the quantities of interest are independent of z , without loss of generality we can assume $\int_{-L_z/2}^{L_z/2} dz = 1$. Defining the average, x -dependent, electrostatic energy as:

$$\langle V(x) \rangle = e^{\beta A(x)} \int_{-h(x)}^{h(x)} q \Psi(x, y) e^{-\beta q \Psi(x, y)} dy \quad (10)$$

from eq. 8 we can define the entropy along the channel as $TS(x) = \langle V(x) \rangle - A(x)$ hence getting:

$$S(x) = \ln \left[\int_{-h(x)}^{h(x)} e^{-\beta q \Psi(x, y)} dy \right] + \beta \langle V(x) \rangle. \quad (11)$$

In the linear regime $\beta q \Psi(x, y) \ll 1$; we can linearize eq. 11 getting:

$$S(x) \simeq \ln(2h(x))$$

where the entropy has a clear geometric interpretation, being the logarithm of the space, $2h(x)$, accessible to the center of mass of the tracer. Accordingly, we introduce the entropy barrier, ΔS , defined as:

$$\Delta S = \ln \left(\frac{h_{max}}{h_{min}} \right) \quad (12)$$

that represent the difference, in the entropic potential, evaluated at the maximum, h_{max} , and minimum, h_{min} of channel aperture.

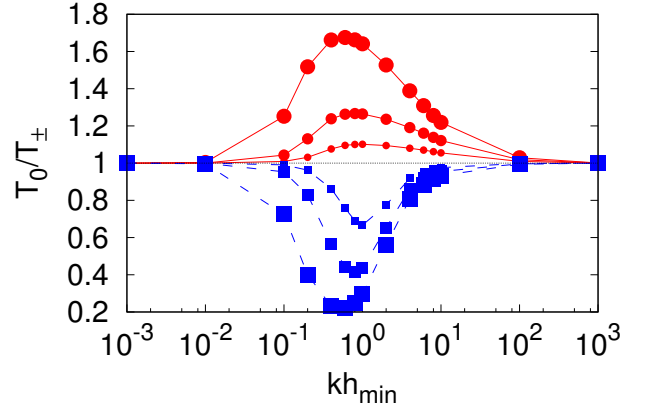


Figure 3. Filled points: inverse of the MFPT, $1/T_{\pm}$, normalized by the MFPT of neutral tracers T_0 , as a function of the inverse Debye length, k^{-1} , normalized by the minimum channel amplitude h_{min} for positive, $\beta q \zeta = 3$, (blue squares) or negative, $\beta q \zeta = -3$, (red dots) tracers in a conducting channel characterized by $\Delta S = 2.2$.

RESULTS

In the present work we analyze the motion of charged tracers in a channel characterized by conducting walls (similar results have been obtained for the case of insulating channel walls) whose half section along the y -direction is characterized by

$$h(x) = h_0 + h_1 \sin \frac{2\pi}{L}(x + \phi) \quad (13)$$

where h_0 is the, average channel section, and h_1 is the, possible, modulation, while we assume the channel to be flat along the z -direction. ϕ controls the channel shape with respect to its boundaries fixed at $x = 0$ and $x = L$. According to eq. 13 we have $h_{max} = h_0 + h_1$ and $h_{min} = h_0 - h_1$.

In order to characterize the geometrically induced contribution to the diffusion of charged tracers at equilibrium, we choose to analyze the first passage time distribution. In particular we focus on the mean of such distribution, i.e. the mean first passage time (MFPT) tracers take to pass through the channel. Such quantity has a twofold interest. On one hand, the MFPT captures, even at equilibrium where electrostatic current vanishes, the role played by the geometrically-induced potential. On the other hand, it is an interesting quantity for situations like ion trapping or chemical segregation as happens in nuclear waste containers. In the following we assume that one of the ends of the channel, namely the one at $x = 0$, is in contact with a reservoir of tracers and we are interested in the MFPT of positive negative or neutral tracers, $t_{\pm,0}(x)$, tracers take to diffuse from x to the other end of channel situated at $x = L$. Such situation leads to a reflecting boundary condition on the end of the channel in contact with the reservoir, i.e at $x = 0$, and to an absorbing condition on the other end, at $x = L$. Taking advantage of the 1D projection, eq. 9, we can calculate the x -dependent MFPT, $t(x)$, which reads [8]:

$$\beta D \partial_x A(x) \partial_x t_{\pm,0}(x) + D \partial_x^2 t_{\pm,0}(x) = -1 \quad (14)$$

By numerically solving eq. 14 the MFPT of tracers crossing the channel is given by $T_{\pm,0} = t_{\pm,0}(0)$. Fig. 3 shows the MFPTs

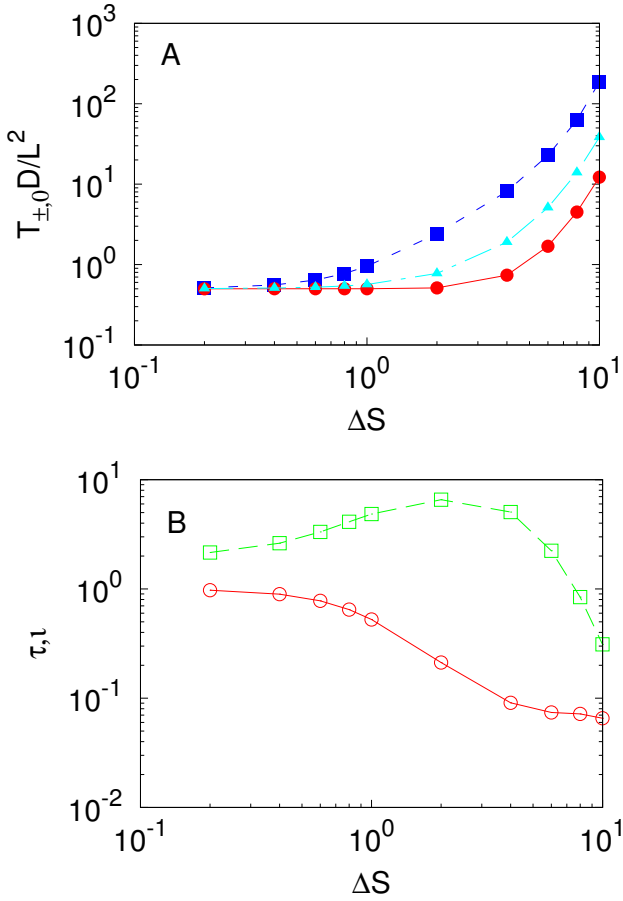


Figure 4. A: MFPT, T , normalized by L^2/D , as a function of the entropic barrier ΔS for positive (blue squares), $\beta q \zeta = 3$, or negative (red dots), $\beta q \zeta = -3$, tracers in a channel with $kh_{min} = 1$. B: ratio of the MFPTs (red circles), $\tau = T_-/T_+$, and “current” (green squares), $i = \frac{2L^3}{\sigma D} \frac{|\rho_+ T_- - \rho_- T_+|}{T_- T_+}$, with T_{\pm} the MFPT of positive (negative) tracers and σ the charge density on the channel walls as a function of the entropic barrier ΔS for the same parameters as panel A.

for positive (blue squares) as well negative tracers (red dots) across a varying-section channel normalized by the MFPT of neutral tracers, T_0 , whose MFPT does not depend on k^{-1} . When the Debye length k^{-1} is comparable with the channel minimum amplitude, h_{min} , negative tracers, attracted towards the positive charged walls, benefit from the modulation induced by the corrugation of the channel and their MFPT is smaller than the one corresponding to neutral tracers. Positive tracers, depleted from the channel walls, experience an enhanced electrostatic barrier at the channel bottleneck that increases their MFPT. Interestingly such a modulation in the MFPT for charged tracers vanishes for $kh_{min} \ll 1$ as well as for $kh_{min} \gg 1$, underlying the relevance of the regime, $kh_{min} \sim 1$, under study.

The dependence of the MFPTs on the entropy barrier is shown in fig. 4.A. While for vanishing values of ΔS all tracers show the same MFPT, a monotonous increase in the MFPT for all tracers is registered upon increasing ΔS . The increase in the MFPT even for neutral tracers is of solely entropic origin. Hence fig. 4.A confirms the enhanced sensitivity of positive tracers with respect to negative ones upon variation of the geometry of the channel. The relative behavior of positive with respect to negative tracers can be useful for application as chemical segregation or particle separation. The ratio of the MFPTs for positive and negative tracers, $\tau = \frac{T_-}{T_+}$ is shown in fig. 4.B.

For vanishing values of ΔS , positive and negative tracers experience the same MFPT while for increasing ΔS negative tracers can be as faster as an order of magnitude leading to a ratio of the order of $\tau \sim 10^{-1}$. The asymmetry in the MFPT for positive and negative tracers suggest the onset of net currents as a response to fluctuations in tracers density. In the spirit of linear response theory, we can define the adimensional current $i = \frac{2L^3}{\sigma D} \frac{|\rho_+ T_- - \rho_- T_+|}{T_- T_+}$. Fig. 4.B shows that the asymmetry in tracer motion leads to an effective current, suggesting that entropic rectification can give rise to non-negligible electrostatic currents with a non-monotonous dependence on channel corrugation. This indicates that one can exploit geometrical modulation to tune electrostatic currents. This requires a more detailed analysis.

CONCLUSIONS

The motion of charge tracers suspended in an electrolyte embedded in a channel with charged walls is strongly affected by the geometry of the channel. The geometrical confinement introduces an effective potential due to the local bias induced by the varying section of the channel. Such feature is captured by neutral tracers whose MFPT is modulated by the channel shape through the amplitude of the entropy barrier, ΔS . The dependence of the MFPT of charged tracers upon different parameters, such as the Debye length k^{-1} and the entropy barrier ΔS , allows for a particle-diffusion control mechanism relying on the geometrical properties of the channel as well as on the electrolyte properties encoded in the Debye length k^{-1} . The MFPT of charged tracers is very sensitive to tracers charge q . According to it, tracers are depleted or attracted to the channel walls hence experiencing different energetic barriers. Such a dependence leads to an additional control parameter that can be exploited to promote/reduce the crossing of the channel by charged tracers as registered in extensive numerical simulations [9].

The phenomenology we have just described has a twofold interest. It shows that interesting behavior, such as particle current inversion or negative mobility, observed when the system is drive out of equilibrium [5] can be captured even studying the properties of the system at equilibrium. By analyzing the MFPT we have been able to show that when the Debye length matches the channel bottleneck, i.e. $kh_{min} \sim 1$ novel effects can rise to due the overlap between the geometrically induced local bias in the diffusion and the geometrically modulated electrostatic field inside the channel. Such an interplay leads to a non-trivial behavior of the MFPT upon different parameters. On the other hand in situations such as cellular signaling, gene regulation or chemical segregation where many phenomena are triggered by the capture of few molecules rather than on the steady state concentration, one is interested in the time a few tracers reach the target rather than on the steady values. For such situations our study shows that in the case in which particles have to diffuse across an inhomogeneous (porous) media, such inhomogeneity can lead to significant advances or delays of the typical triggering time.

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