On the reluctance of a neutral nanoparticle to enter a charged pore

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We consider the translocation of a neutral (uncharged) nanoparticle through a pore in a thin membrane with constant surface charge density. If the concomitant Debye screening layer is sufficiently thin, the resulting forces experienced by the particle on its way through the pore are negligible. But when the Debye length becomes comparable to the pore diameter, the particle encounters a quite significant potential barrier while approaching and entering the pore, and symmetrically upon exiting the pore. The main reason is an increasing pressure which acts on the particle when it intrudes into the counter ion cloud of the Debye screening layer. In case the polarizability of the particle is different (usually smaller) than that of the ambient fluid, a second, much smaller contribution to the potential barrier is due to self-energy effects. Our numerical treatment of the problem is complemented by analytical approximations for sufficiently long cylindrical particles and pores, which agree very well with the numerics.

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I. INTRODUCTION

How can a charged object exert electric forces on an uncharged object? Generally speaking, this may be the case whenever the nominally neutral object and/or its overall neutral environment is actually composed of positive and negative constituents, which may freely move (e.g. ions in a liquid) or lead to dielectric polarization effects (e.g. electrons and protons in a solid) in the presence of an electric field, see Fig. 1.

According to textbook Electrostatics [1], any given charge in a polarizable environment gives rise to a so-called “self-energy” or “energy of charge”, which is negative and proportional to the polarizability of the environment. As a consequence, a repulsive force between the given charge and any other extended object arises in the most common case that they are both surrounded by a fluid and the polarizability of the object is lower than that of the fluid, see Fig. 1(a).

One of the best known examples is an ion (charged object) in an aqueous solution (dielectric constant of water $\epsilon_w \approx 80$) being repelled by a biological or artificial membrane (neutral object) with a typical dielectric constant $\epsilon_m$ of $2 - 5 \times 10^{-5}$ [2–6]. Here, we address the conceptually analogous case of the potential barrier which an uncharged particle encounters upon entering a charged membrane pore. The corresponding forces on the particle are closely related to the well-known phenomenon of dielectrophoresis and will henceforth be denoted as dielectric forces.

Additional important effects arise in the usual case that the ambient fluid contains positively and negatively charged ions [3–6]. As a consequence, any charged object now attracts counterions (and repels coions) from the ambient fluid (electric double layer). The characteristic extension of such a counterion “layer” or “cloud” is quantified by the so-called Debye length, typically of the order of 1 nm. At distances beyond a few Debye lengths, the charged object is thus essentially screened, i.e. it “looks” as if it were uncharged.

On the one hand, the above mentioned dielectric forces are therefore expected to be notably reduced already within the counterion layer and become negligible outside it. On the other hand, additional repulsive forces are expected when an uncharged object enters the electric double layer, see Fig. 1(b). The reason is that the prevailing like-charged ions repel each other, resulting in an excess pressure within the counterion cloud which also acts against any intruding object. While this effect bears some resemblance to osmotic pressure [7], the term counterion pressure seems more appropriate to us and will be adopted from now on.

A detailed exploration of those effects is the main sub-
of the order of $\sigma$ experimental conditions the surface charge density concentrations, and other factors, and which is screened value depends on the membrane material, pH-value, salt constant surface charge density [8–16]. The membrane is modeled as an insulator with concentrations away from the membrane). Typical experimental concentrations and preset bulk concentrations $Q \approx H$, see Fig. 1 and Refs. [8–15]. The fluid [5, 6, 29].

A fluid chamber is divided into two compartments by a thin biological or solid-state membrane (typical thickness $H \approx 20$ nm) [51], see Fig. 11 and Refs. [8–16]. The fluid chamber contains an electrolyte solution with $N_\nu$ different ionic species and preset bulk concentrations $c_{\nu,0}$ (far away from the membrane). Typical experimental concentrations $c_{\nu,0}$ range from about 10 mM to about 1000 mM [8–16]. The membrane is modeled as an insulator with constant surface charge density $\sigma$, whose quantitative value depends on the membrane material, pH-value, salt concentrations, and other factors, and which is screened by counterions in the electrolyte solution. Under typical experimental conditions the surface charge density $\sigma$ is of the order of $\sigma = -50$ mC/m$^2$ [17–22].

An uncharged, prolate particle of radius $R < Q$ and length $L \geq 2R$ is contained in the electrolyte solution. In our model, the particle is a cylinder with half spheres merged to the ends, and hence the particle becomes a sphere if $L = 2R$. Typical values in our examples below will be $R = 3$ nm and $L = 6$ – 60 nm.

The quantity of foremost interest is the net force acting on the particle due to the counterion pressure and the dielectric forces mentioned in Sec. II.

From the viewpoint of the numerical (and analytical) tractability of the problem, two further assumptions are practically unavoidable [6, 23–25], see also Sec. III.C. First, we restrict our discussion to the axisymmetric case where a particle translocates through the pore along the $z$-axis (see Fig. 2). This will also be justified by our later finding that the neutral particle is repelled by the uniformly charged membrane and pore surfaces and hence the energetically most favorable translocation path (e.g. driven by thermal noise) will be along the pore axis [19, 23–25]. Second, we restrict ourselves to steady state (time-independent) situations, and we assume, similarly as in Refs. [4, 23, 27–28], that the particle itself does not to exhibit any proper motion within the relaxation time of its environment. In other words, the particle position is a model parameter rather than a dynamical variable. The justification is, as usual, the clear cut time- and length-scale separation between the nanoparticle and the molecular degrees of freedom of the ambient fluid [5, 6, 29].

III. GENERAL FRAMEWORK

A. Basic equations

In this section we summarize the Poisson, Nernst-Planck, and Stokes equations. A more detailed discussion is provided e.g. in Refs. [16, 30–32].

The electric potential $\psi$ obeys the Poisson equation

$$- \varepsilon_0 \nabla \cdot [\varepsilon(x) \nabla \psi(x)] = \rho(x) + \rho_m(x), \quad (1)$$

where $\varepsilon_0$ is the vacuum permittivity and $\varepsilon$ the dielectric constant (relative permittivity). While the static charge density $\rho_m$ is associated with the fixed membrane surface charges, $\rho$ denotes the local charge density due to the mobile ions,

$$\rho(x) := \begin{cases} e_0 N_\Lambda \sum_{\nu=1}^{N_\nu} Z_\nu c_\nu(x) & \text{in the electrolyte solution} \\ 0 & \text{else} \end{cases} \quad (2)$$

Here, $\varepsilon_0 = 1.602 \ldots \times 10^{-19}$ C is the elementary charge and $N_\Lambda = 6.022 \ldots \times 10^{23}$/mol is Avogadro’s constant. Furthermore, $Z_\nu$ and $c_\nu$ denote the valence and the molar concentration of the $\nu$th ionic species.

The particle flux density $J_\nu$ of the $\nu$th ionic species consists of three different contributions, arising from (i) convection due to the velocity field of the fluid $u$, (ii) concentration gradients, and (iii) the electric field $E = -\nabla \psi$, and is given by the Nernst-Planck equation

$$J_\nu(x) = c_\nu(x) u(x) - D_\nu \nabla c_\nu(x) - \mu_\nu c_\nu(x) \nabla \psi(x). \quad (3)$$

The diffusion coefficient $D_\nu$ is related to the mobility $\mu_\nu$ via $\mu_\nu = Z_\nu e_0 D_\nu/k_\text{B}T$, where $k_\text{B}$ denotes Boltzmann’s
constant and $T$ the temperature. Assuming a steady state, particle number conservation implies
\[ \nabla \cdot \mathbf{J}_c(x) = 0 \text{.} \] (4)

The velocity field $\mathbf{u}$ and the pressure $p$ of the electrolyte solution are governed by the Navier-Stokes equation. Since in our present case the Reynolds number is very low, the non-linear terms in this equation can be safely neglected. Focusing on steady states and neglecting the very small effect of gravity, it is thus sufficient to solve the simpler Stokes equation
\[ \eta \Delta \mathbf{u}(x) - \nabla p(x) - \rho(x) \nabla \psi(x) = 0 \text{,} \] (5)
with $\eta$ the viscosity of the fluid. Analogously to Eq. (4), assuming an incompressible fluid and focusing on steady state solutions, mass conservation implies
\[ \nabla \cdot \mathbf{u}(x) = 0 \text{.} \] (6)

### B. Parameters and boundary conditions

The relative permittivity is assumed to be of the form
\[ \varepsilon(x) = \begin{cases} \varepsilon_w & \text{in the electrolyte solution} \\ \varepsilon_m & \text{in the membrane} \\ \varepsilon_p & \text{in the particle} \end{cases} \] (7)

While $\varepsilon_w$ is usually close to the value $\approx 80$ for water at room temperature, $\varepsilon_m$ and $\varepsilon_p$ are material dependent. A typical value for biological matter is $\varepsilon = 2$ and for solid-state membranes (e.g. SiO$_2$, SiN, Si$_3$N$_4$) $\varepsilon = 5$ [2-7, 33-36]. Typical particle permittivities $\varepsilon_p$ are in the same range and actually turn out to play a very minor role. Thus, we will usually adopt the following choices: $\varepsilon_w = 80$ and $\varepsilon_m = \varepsilon_p = 5$.

With respect to the static (fixed) surface charges we can, as detailed in [1, 6], formally set $\rho_0 = 0$ in Eq. (1) and instead work with the boundary conditions
\[ -\nabla \psi(x) \text{ continuous} \text{,} \] (8)
\[ (\varepsilon_w \nabla \psi_w(x) - \varepsilon_m \nabla \psi_m(x)) \cdot \mathbf{n}(x) = -\sigma/\varepsilon_0 \text{,} \] (9)
\[ (\varepsilon_w \nabla \psi_w(x) - \varepsilon_p \nabla \psi_p(x)) \cdot \mathbf{n}(x) = 0 \text{,} \] (10)
where $\psi_w$, $\psi_m$, and $\psi_p$ denote the electric potential at the respective side of the interface (see also Eq. (7)) and where $\mathbf{n}$ is the normal vector pointing from the membrane and the particle, respectively, into the electrolyte solution. The remaining boundary conditions for the Poisson equation (1) are chosen as $\psi(x) = 0$ at the top and bottom walls of the cylindrical fluid chamber in Fig. 2 and $\nabla \psi(x) \cdot \mathbf{n}(x) = 0$ at the cylindrical side wall.

Turning to the Nernst-Planck equation (5), the concentrations $c_p$ of the different ionic species are required to assume their bulk values $c_{p,0}$ at the top and bottom walls of the fluid chamber. On the membrane and particle walls as well as on the cylindrical side wall of the fluid chamber, we impose insulation (or reflecting) boundary conditions $\mathbf{J}_p(x) \cdot \mathbf{n}(x) = 0$. In the following, we restrict our discussion to so-called symmetric $Z : Z$ electrolytes, i.e. $N_p = 2$, $Z_1 = -Z_2 =: Z$, and $c_{1,0} = c_{2,0} =: c_0$. Moreover, in our numerical examples below we will focus on the simplest case $Z = 1$. We further adopt a typical temperature $T = 300$ K and typical diffusion coefficients $D_1 = D_2 =: D = 2 \times 10^{-9}$ m$^2$/s [16]. Accordingly, the Debye length, quantifying the extension of the electric double layer (see also Secs. [1] and [16]) takes the form
\[ \lambda_D = \sqrt{\frac{\varepsilon_0 \varepsilon_m k_B T}{2 e^2 N_A c_0}} \approx 0.305 \text{ nm} \text{.} \] (11)

With respect to the Stokes equation (5), our first assumption is that the usual no-slip boundary conditions $\mathbf{u} = 0$ are satisfied on the membrane and particle walls as well as on the cylindrical side wall of the fluid chamber (see Fig. 2). Concerning the top and bottom walls of the fluid chamber, we require that the pressure $p$ approaches some preset “bulk value” $p_0$,
\[ p(x) = p_0 \text{ .} \] (12)

Since only the gradient of $p$ matters (see Eq. (5)), we can and will set
\[ p_0 = 0 \text{ .} \] (13)
without loss of generality. Moreover, we require that the normal component of the hydrodynamic stress (see e.g. [32] for a more detailed discussion) vanishes at the top and bottom walls of the fluid chamber,
\[ \mathbf{F} = -p(x) \nabla \psi(x) = 0 \text{,} \] (14)
where $\mathbf{F}$ denotes the matrix with elements $\partial u_i/\partial x_j$ and $[\nabla \mathbf{u}]^T$ the transposed matrix. The boundary conditions [12-14] are well-known to be numerically stable provided the boundaries are sufficiently far away from the nanopore [37, 38]. Quantitatively, we found that for not too large particle lengths ($L \lesssim H$), and not too low concentrations ($c_0 \gtrsim 1$ mM), finite-size effects become negligible for fluid chambers (see Fig. 2) beyond a radius of about 40 nm and a height of about 100nm. For larger particle lengths or lower concentrations, the size of the fluid chamber was increased, so that finite size effects were again negligible.

For all examples, the viscosity of water at room temperature takes its standard value $\eta = 10^{-3}$ Pa·s and the values of the remaining parameters will be specified later.

### C. Forces on the particle

The force $\mathbf{F}$ acting on the particle in Fig. 2 can be decomposed into two contributions [32], one arising from the interaction with the electric field $\mathbf{E} = -\nabla \psi$, and
the other from the hydrodynamic interaction with the surrounding electrolyte solution,

$$\mathbf{F} = \mathbf{F}_e + \mathbf{F}_h \ .$$ (15)

The electrostatic force $\mathbf{F}_e$ can be calculated quite generally [1, 7] by integrating the Maxwell stress tensor over the particle surface $\mathcal{O}(P)$,

$$\mathbf{F}_e = \epsilon_w \epsilon_0 \oint_{\mathcal{O}(P)} \left( \mathbf{E}(x) \left| \mathbf{E}(x) \right|^T - \frac{1}{2} \left| \mathbf{E}(x) \right|^2 \right) \mathbf{n}(x) dS \ .$$ (16)

Similarly, the hydrodynamic force $\mathbf{F}_h$ follows by integrating the hydrodynamic stress tensor (also called pressure tensor) over the particle surface,

$$\mathbf{F}_h = \oint_{\mathcal{O}(P)} \left( -p(x) + \eta \left( \nabla \mathbf{u}(x) + \left[ \nabla \mathbf{u}(x) \right]^T \right) \right) \mathbf{n}(x) dS \ .$$ (17)

If $\epsilon_p = \epsilon_w$, the net electric force $\mathbf{F}_e$ on the particle must vanish. Physically, this follows by observing that for an overall constant $\epsilon$, the electric field is proportional to the field for $\epsilon = 1$, i.e. for a non-polarizable particle in vacuum. Since there are no dielectric forces in the latter case, the same applies to the former case. ($\mathbf{F}_e$ in (16) must be zero in both cases). Formally, the same follows from Poisson’s equation (1), whose right hand side vanishes within the particle region, the boundary conditions \[8, 10\], which imply a smooth behavior of $\mathbf{E}$ across the particle boundary for $\epsilon_p = \epsilon_w$, and by employing the Gauss theorem in (19). For a neutral particle with arbitrary $\epsilon_p$ it thus seems justified to henceforth identify $\mathbf{F}_e$ with the dielectric forces due to polarization or self-energy effects from \[17\] and Sec. \[1\].

D. Simplifications at thermal equilibrium

Since we are considering an isolated system (no external forces are acting) and we focus on steady state solutions, this steady state must be tantamount to thermal equilibrium. Hence all macroscopic fluxes in the system must vanish, i.e.

$$\mathbf{u}(x) = 0 \text{ and } \mathbf{J}_p(x) = 0 \ .$$ (18)

As a consequence, all boundary conditions involving $\mathbf{J}_p$ and $\mathbf{u}$ are automatically fulfilled. Furthermore, the Nernst-Planck equation (3) is formally solved by the Boltzmann-distribution

$$c_r(x) = c_{r,0} \exp \left( -\frac{Z_r e_0 \psi(x)}{k_B T} \right) \ ,$$ (19)

while Eq. (4) is trivially satisfied. Likewise, the Stokes equation (5) with boundary conditions (12) and (13) can be formally integrated, yielding for the pressure the result

$$p(x) = 2k_B T N_A c_0 \left[ \cosh \left( \frac{Z e_0 \psi(x)}{k_B T} \right) - 1 \right] \ .$$ (20)

The only remaining equation is thus Poisson’s equation (1). Concerning the two charge density terms which appear on the right hand side of this equation (1) we observe that: (i) Exploiting (19), the ion charge density \[2\] in a Z:Z electrolyte solution (see above Eq. (11)) can be rewritten as

$$\rho(x) = -2Z e_0 N_A c_0 \sinh \left( \frac{Ze_0 \psi(x)}{k_B T} \right) \ .$$ (21)

(ii) The fixed membrane surface charges $\rho_m$ are effectively accounted for by the boundary conditions \[8-11\]. By combining (11) and (21), we are thus left with the so-called Possion-Boltzmann equation for the electric potential

$$\epsilon_0 \nabla \cdot \left[ \epsilon(x) \nabla \psi(x) \right] = 2Z e_0 N_A c_0 \sinh \left( \frac{Ze_0 \psi(x)}{k_B T} \right) \ .$$ (22)

Once this equation with (7)-(10) is solved, the concentration, pressure, and charge density fields immediately follow from (19)-(21).

Turning to the forces, we first remark that $\mathbf{F}_h$ from (17) simplifies to the familiar pressure integral

$$\mathbf{F}_h = -\oint_{\mathcal{O}(P)} p(x) \mathbf{n}(x) dS \ .$$ (23)

In other words, $\mathbf{F}_h$ quantifies the counterion pressure effects from Fig. (1b) and Sec. (1).

Furthermore, for symmetry reasons the force $\mathbf{F}$ resulting from (15), (16), (23) will be parallel to the pore axis. Henceforth, this force component is denoted by $F(z)$ for any given position $z$ of the particle center in Fig. (2). Finally, the corresponding potential energy $U(z)$, from which $F(z)$ derives, follows as

$$U(z) = -\int_{z_0}^z dz' \ F(z') \ ,$$ (24)

where $z_0$ denotes the particle position when it touches the bottom wall in Fig. (2). Symmetry reasons further imply that

$$F(-z) = -F(z) \ .$$ (25)

With (24) we thus can conclude that

$$U(-z) = U(z) \ .$$ (26)

E. Numerical method

In spite of the above mentioned simplifications at thermal equilibrium, the remaining Poisson-Boltzmann equation (22), complemented by (7)-(10), and the final surface integrations in (10), (23) can only be tackled analytically in a few special cases and within certain approximations,
see e.g. Sec. IV. In all other cases, only numerical solutions are possible. It, however, turns out that the numerical treatment of the fully three-dimensional problem is still very demanding, even on modern computers, if a satisfactory numerical accuracy is required. Consequently, similar previous studies are restricted to one-dimensional [32], two-dimensional [24], or axisymmetric problems [24, 28, 42] problems. In the latter case, which is also at the focus of our present work, an effectively two-dimensional problem is readily recovered when going over to cylindrical coordinates (see e.g. [32] for the explicit expressions). Our numerical results presented below were obtained using the commercial COMSOL 4.3a Multiphysics package of coupled partial differential equation solvers, exploiting finite element methods [38].

IV. ANALYTICAL APPROXIMATIONS

For a very long particle \( (L \gg H \text{ in Fig. 2}) \), which is "fully threaded through the pore" so that both ends stick far out at either side of the pore, we are dealing with an almost translation invariant situation and the net force on the particle will be practically zero. While equation (31) still cannot be solved analytically in full generality, we will focus on approximations for two limiting cases in the following two subsections.

Once the latter problem is solved, we can exploit that \( \rho(x) = 0 \) outside the electrolyte solution and that \( \rho_m(r) = \sigma \delta(r - Q) \) to calculate the free energy per unit length according to Eq. (28) as

\[
\frac{1}{r} \frac{d}{dr} \left( r \frac{d}{dr} \psi_{1,2}(r) \right) = -2Z\varepsilon_0 N_L c_0 \frac{\varepsilon_0 \epsilon_w}{\varepsilon_0 \epsilon_w} \sinh \left( \frac{Z\varepsilon_0 \psi_{1,2}(r)}{k_B T} \right)
\]

(31)

complemented by the conditions \( \psi_{1,2}(r) = 0 \) for \( r > Q \) (overall charge neutrality of pore surface and counterions, cf. Eq. (1) and convention \( \psi_{1,2}(r \rightarrow \infty) = 0 \), \( \psi_{1,2}(r = Q) = \sigma / \epsilon_0 \epsilon_w \) (cf. Eq. (10)), \( \psi'_1(r = 0) = 0 \) (regularity at the pore center), \( \psi'_2(r = R) = 0 \) (cf. Eq. (10)), and \( \psi'_2(r) = 0 \) for \( r < R \) (cf. Eq. (10)).

A. High concentration or low surface charge

We first focus on the so-called Debye-Hückel limit \( Z\varepsilon_0 |\psi_{1}(r)|/k_B T \ll 1 \) throughout the nanopore, which is tantamount to low surface charge densities \( \sigma \) and/or
high bulk concentrations \(c_0\). The corresponding approximation for the maximum force \(F_m\) from (39) is henceforth denoted as \(F_m^m\). Referring to the Appendix I for the detailed calculation, the final result is

\[
F_m^m = \frac{\pi \sigma^2 Q}{\epsilon_0 \epsilon_w k} \left( \frac{I_0(\kappa r)}{I_1(\kappa Q)} - \frac{I_0(\kappa r) K_1(\kappa R) + K_0(\kappa r) I_1(\kappa R)}{K_1(\kappa R) I_1(\kappa Q) - I_1(\kappa R) K_1(\kappa Q)} \right)
\]

where \(\kappa := \frac{\lambda_D^{-1}}{r}\) is the inverse Debye length from (11) and \(I_k(\kappa_k)\) is the modified Bessel function of the first (second) kind and order \(k\).

Likewise, for the electric field and the pressure in the empty pore (index 1) the following approximations are provided in Appendix I:

\[
\psi_1(r) = \frac{\sigma}{\epsilon_0 \epsilon_w k} I_1(\kappa r) \label{eq:psi1}
\]

\[
p_1(r) = \frac{N_A e_0}{k_B T} \left( \frac{Z e_0 \sigma}{\epsilon_0 \epsilon_w k} I_1(\kappa Q) \right)^2 \label{eq:p1}
\]

### B. Low concentration or high surface charge

Next we turn to the case \(Z e_0 |\psi_1(r)| / k_B T \gg 1\), i.e. high surface charge densities \(\sigma\) and/or low concentrations \(c_0\). Hence, we follow Philip and Wooding [14] and exploit the approximation

\[
\sinh \left( \frac{Z e_0 \psi_1(r)}{k_B T} \right) \approx \frac{\sin(\psi_1(r))}{2} \exp \left( \frac{Z e_0 |\psi_1(r)|}{k_B T} \right) \label{eq:sinh}
\]

Making use of \(\sin(\psi_1(r)) = \sin(\sigma)\) and hence \(|\psi_1(r)| = \sin(\sigma)|\psi_1(r)|\), the first solution \(\psi_1\) of Eq. (31) with the boundary conditions discussed below is

\[
\psi_1(r) = -\text{sign}(\sigma) U_0 \left( \ln \left[ \frac{\epsilon_0 e_0 N_A a_1}{a_2} \right] + 2 \ln \left( 1 - \frac{|\sigma| Q}{a_1} \right) \right)
\]

where we have defined

\[
U_0 := \frac{k_B T}{Z e_0} ,
\]

\[
a_1 := Q \left( 4 \epsilon_0 \epsilon_w k_B T + Z e_0 |\sigma| Q \right),
\]

\[
a_2 := 8 \epsilon_0 \epsilon_w k_B T |\sigma| .
\]

The somewhat more lengthy expressions for \(\psi_2(r)\) are provided in Appendix II.

Given \(\psi_1(r)\), the pressure and the charge density follow from (20,21). With \(\sinh(\cdot)\) and an analogous approximation for \(\cosh(\cdot)\), they take the form

\[
\rho_i(r) = -\text{sign}(\sigma) Z e_0 N_A c_0 \exp \left( \frac{\text{sign}(\sigma) \psi_1(r)}{U_0} \right) \label{eq:rho_i}
\]

\[
p_i(r) = k_B T N_A c_0 \exp \left( \frac{\text{sign}(\sigma) \psi_1(r)}{U_0} \right) \label{eq:p_i}
\]

Finally, by exploiting the above results to evaluate the integral (32) we arrive at our final approximation for the maximum force \(F_m^m\) from (39), henceforth denoted as \(F_m^m\). An interesting property of this approximation \(F_m^m\) is demonstrated in Appendix III, namely that it is independent of the bulk concentration \(c_0\).

### V. NUMERICAL RESULTS

#### A. The empty pore

As a first example we consider the case of an empty pore (Fig. 2 without particle). Assuming a typical membrane surface charge density of \(\sigma = -50 \text{ mC/m}^2\) and a relatively low bulk concentration of \(c_0 = 1 \text{ mM}\) (cf. Sec. II), we have numerically solved the Poisson-Boltzmann equation (22) as detailed in Sec. III.

Fig. 3 illustrates the results for the electric potential \(\psi(x)\) and for the corresponding pressure \(p(x)\) from (20). Most remarkably, the pressure within the pore increases quite notably beyond the bulk value \(p_0 = 0 \text{ Pa}\) from Eq. (13). In fact, the counter ion pressure near the membrane surface typically may become as large as 20 bar according to Fig. 3 (d), (f), (h).

For a cross-section through the \(z = 0 \text{ plane}\) (i.e. through the pore center), Figs. (c) and (d) provide a more detailed picture of the numerically obtained fields for \(c_0 = 1 \text{ mM}\) together with the analytical approximations (37) and (42) for low concentrations.

We found a comparably good agreement even for a tenfold increased bulk concentration, i.e. for \(c_0 = 10 \text{ mM}\) (not shown). Significant deviations arise upon another tenfold increased concentration, i.e. for \(c_0 = 100 \text{ mM}\), see red lines in Fig. (e) and (f). Finally, for \(c_0 = 1000 \text{ mM}\), the analytical approximation for low concentrations is far off the numerics from Fig. (g) and (h).

Likewise, the approximations (34) and (35) for high bulk concentrations reproduce the numerical solution almost perfectly for \(c_0 = 1000 \text{ mM}\) (blue lines in Fig. (g) and (h)), develop notable deviations for \(c_0 = 10 \text{ mM}\) (Fig. (e)(f)), and completely fail for \(c_0 = 10 \text{ mM}\) and \(c_0 = 1 \text{ mM}\).

#### B. Force on the particle

What happens when an uncharged particle approaches and enters the previously considered empty pore? On the one hand, the electric potential in Fig. (a) induces a polarization of the particle, which, due to the higher polarizability of the ambient liquid, results in a net repulsion, see Fig. (a). On the other hand, the counter ion pressure in Fig. (b) generates yet another repulsive force contribution, see Fig. (b). Strictly speaking, there will also be back-reactions of the approaching particle on the “unperturbed” electric and pressure fields of the empty pore.
different contributions over the entire particle volume or of the analytical approximations \(34\) and \(35\) for low concentrations. The dielectric constants in \(7\) we re the dielectric force \(F(z)\) for particles with fixed position \(z\) along the pore axis. The different curves represent results for particles with fixed radius \(R = 3\) nm and various lengths, namely \(L = 6\) nm (black), \(L = 10\) nm (red), \(L = 18\) nm (blue), and \(L = 26\) nm (green). (Overall, the forces increase (in modulus) with particle length.) The pore radius was \(Q = 5\) nm, the membrane thickness \(H = 20\) nm, the surface charge density \(\sigma = -50\) mC/m\(^2\), and dielectric constants \(\epsilon_w = 80\), \(\epsilon_m = \epsilon_p = 5\) (cf. Eqs. \(20\)). (a) Corresponding pressure from \(20\). All pressures beyond \(2 \cdot 10^5\) Pa are displayed in deep red (see also \(d\)). (c) and (d): Radial dependence of the same fields for \(z = 0\) (i.e. in the middle of the pore), obtained numerically (symbols) and by means of the analytical approximations \(51\) and \(52\) for low concentrations (red lines). The units in \(d\) are now \(10^6\) Pa. (e) and (f): Same, but for \(c_0 = 100\) mM. In addition, the analytical approximations \(51\) and \(52\) for high concentrations are shown as blue (lower) lines. (g) and (h): Same, but for \(c_0 = 1000\) mM.

Fig. 4 exemplifies the numerically obtained forces for four different particle lengths \(L\) and two different bulk concentrations \(c_0\). Qualitatively, these results are very similar for both bulk concentrations, but the absolute values of the forces are approximately a decade larger for \(c_0 = 10\) mM than for \(c_0 = 100\) mM. Further main observations are:

(i) Although the particle is neutral, the dielectric force \(F_e(z)\) does not vanish [Figs. 4(c),(d)].

(ii) The \(z\)-dependence of this dielectric force is quite complicated, in particular if \(L \approx H\), see Fig. 2 and the green and blue lines in Figs. 4(c),(d).

(iii) The hydrodynamic force \(F_h(z)\) generated by the counterion pressure (see below \(28\)) is much larger than the dielectric force \(F_e(z)\).

(iv) The various above predicted “force plateaux” are
FIG. 5: (Color online) The maximum (or plateau) force $F^m$ (in units of pN) for the same system as in Fig. 4 (a),(c),(e), but now for a particle length of $L = 60$ nm and a variable bulk concentration $c_0$ (in units of mM) in (a) and a variable (negative) surface charge density $\sigma = -|\sigma|$ (in units of mC/m²) in (b). Symbols: Numerical solutions. Red lines (horizontal in (a), partially dashed in (b)): Approximation $F^m_g$ for low concentration or high surface charge from Sec. IV B. Blue lines: Approximation $F^m_f$ from (33) for high concentration or low surface charge. Dashed: Empirical interpolation (43) between these approximations. In (b) the red solid line corresponds to case “+” in Eq. (40) and its dashed continuation to case “−”.

Indeed observed. In particular, the total force $F(z)$ develops for sufficiently large particle lengths $L$ two symmetric, asymptotically $L$-independent “plateaux” $\pm F^m$ [Figs. 4 (e),(f)], for which we derived the analytical approximations $F^m_f$ in (33) and $F^m_g$ in Sec. IV B.

Fig. 4 (a) shows the maximum force $F^m$ as a function of the bulk concentration $c_0$ for a fixed surface charge density $\sigma = -50$ mC/m². More precisely, the numerical results were obtained by solving the Poisson-Boltzmann equation (22) for an $L = 60$ nm long particle at $z = 30$ nm, i.e. with its lower end at the center of the nanopore. The numerical solution compares very well with the two complementary asymptotic approximations $F^m_f$ from (33) and $F^m_g$ from Sec. IV B. In particular, the maximum force $F^m$ becomes (almost) constant for low $c_0$, as predicted at the end of Sec. IV B.

Analogously, in Fig. 5 (b) the surface charge density was varied while keeping the concentration $c_0$ fixed at 10 mM. In particular, $F^m$ indeed scales with $\sigma^2$ for sufficiently low surface charge densities $\sigma$, as predicted by the analytical approximation (33) (blue line).

Summarizing Fig. 5 we can say that the maximum force is well approximated by $F^m_f$ for low charge densities $\sigma$ and/or high concentrations $c_0$, and by $F^m_g$ for high charge densities and/or low concentrations. Figs. 4 (a),(b) also suggest that for arbitrary $\sigma$ and $c_0$, at least one of the two approximations $F^m_f$ or $F^m_g$ always works reasonably well. We furthermore observe that $F^m_f \ll F^m_g$ in case that $F^m_f$ is a good approximation and that $F^m_g \ll F^m_f$ in the regime of validity of the approximation $F^m_f$. This suggests the following empirical interpolation formula for the maximum force

$$F^m_{\text{emp}} = \left( \frac{1}{F^m_f} + \frac{1}{F^m_g} \right)^{-1}.$$  \hspace{1cm} (43)

The dashed lines in Figs. 4 show that this approximate “crossover” formula indeed works remarkably well for arbitrary concentrations and charge densities.

C. Potential barriers against entering the pore

Figure 6 exemplifies the potential $U(z)$ and, in particular, the potential barriers $\Delta U$ governing the pore entrance and translocation by a nanoparticle. While barriers up to a few $k_B T$ may still be surmounted by thermal activation within reasonable time-scales, larger barriers practically rule out a translocation through the pore in view of the typical Boltzmann-Arrhenius factors $\exp(-\Delta U/k_B T)$ by which thermally activated rate processes are ruled [45]. In conclusion, the translocation of neutral particles through nanopores can be greatly suppressed if the nanopore walls carry surface charges.

According to Figs. 4 and 5 and their discussion in the main text, the force $F(z)$ develops two plateaux of height $\pm F^m$, whose widths can be very roughly approximated as $\min\{L,H\}$. In combination with (24), (43) we thus arrive at the following approximation for the potential barrier,

$$\Delta U_{\text{emp}} = F^m_{\text{emp}} \min\{L,H\}.$$  \hspace{1cm} (44)

As Fig. 6 demonstrates, this simple approximation reproduced the numerically obtained barriers quite well. The deviations are mainly rooted in the fact that we cannot approximate very well the “edges” of the force plateaux in Figs. 4 (e),(f).

D. Generalizations

So far, we have restricted ourselves to particles with radii $R = 3$ nm. We have seen that, beside other factors, the potential barrier for crossing the pore strongly depends on the ion concentrations. Above $c_0 \approx 100$ mM
the barrier nearly vanishes. For these salt concentrations, the distance of the particle from the wall, \( Q - R \), is larger than a few times the Debye length \( \lambda_D \) from (11) so that the surface charge is almost entirely screened by the counterions. On the other hand, if \( Q - R \) is comparable to or smaller than the Debye length, the counterion pressure within the nanopore will significantly influence the translocation dynamics. For particle radii other than \( R = 3 \) nm, all effects will thus be qualitatively the same as for particles with \( R = 3 \) nm, if the pore radius and/or the concentration are adapted accordingly.

Next we briefly discuss how the results from Sec. VI depend on the surface charge density \( \sigma \). As tacitly anticipated in Fig. 5(b), all forces are obviously independent of the sign of those charges, i.e. they must be even functions of \( \sigma \). Moreover, they must vanish in the absence of any surface charges. Hence, the leading order behavior for small \( \sigma \) will be proportional to \( \sigma^2 \). This asymptotics as well the behavior beyond the small \( \sigma \) regime is illustrated by Fig. 6(b). Moreover, we found numerically e.g. for \( \sigma = -20 \) mC/m\(^2\) almost the same shapes of the force curves as for \( \sigma = -50 \) mC/m\(^2\) in Fig. 4 just their overall amplitudes were rescaled by the same factor of \( \approx 0.5 \) as the corresponding maximum force \( F_m \) in Fig. 3(b). A similar behavior is expected for a large range of other \( \sigma \)-values.

While the surface charge density of sulfate coated surfaces is, e.g., quite independent of the solution conditions \([17, 21]\), the surface charge density of silica (SiO\(_2\)) membranes has been reported to increase with increasing concentration \( c_\sigma \) and has typical values between -10 mC/m\(^2\) and -100 mC/m\(^2\) for \( c_\sigma \) between 1 mM and 1000 mM \([17, 20, 22, 16]\). In such a case, a more realistic modeling should take into account a reduction of the surface charge density within the pore, compared to the membrane charge density far from the pore \([17]\). We have conducted preliminary numerical investigations along these lines, indicating that the results change only quite insignificantly.

FIG. 6: (Color online) (a) Inset: The potential energy \( U(z) \) in units of the thermal energy \( k_B T \) versus \( z \) (in units of nm), obtained numerically from Eqs. (15,16,23,24), for a particle length \( L = 14 \) nm and all other parameters as in Fig. 3(a), (c), (e). The potential barrier \( \Delta U \) is indicated by the double arrow. Main figure: Potential barrier \( \Delta U \) (in units of \( k_B T \)) versus particle length \( L \) (in units of nm) for 5 different bulk concentrations \( c_\sigma \), namely (top-down) 1 mM (black), 10 mM (red), 40 mM (gray), 100 mM (green), and 1000 mM (blue). (b) The corresponding analytical estimates from (13), (14).

VI. CONCLUSIONS

We have explored the forces, experienced by an electrically neutral but in general polarizable nanorod in an electrolyte solution, which are generated by a constant surface charge density on a membrane with a cylindrical nanopore. Unless the Debye screening length \([14]\), quantifying the characteristic extension of the electric double layer, is much smaller than the minimal distance between particle and pore walls, those forces are quite notable and give rise to significant potential barriers against the particle’s entrance into the pore. The dominating contribution is due to the mutual repulsion of the counterions which screen the surface charges, resulting in an repulsive pressure force on those parts of the particle which are entering the counterion cloud. A second contribution is due to the combined net effect of all the induced dipoles in the particle and the ambient fluid. Under typical experimental conditions those dielectric forces are, however, much weaker than the counterion pressure forces. This is in striking contrast to the extensively studied opposite case of a charged particle, entering a neutral pore \([2, 9]\).

What happens if both the pore and the particle are charged? While a systematic exploration of this issue goes beyond the scope of our present paper, we briefly may point out the main features of our numerical findings in the special case that the pore and the particle both carried the same surface charge \( \sigma = -50 \) mC/m\(^2\) (all other parameters as in Fig. 4(a), (c),(e)): The forces \( F_h(z) \) exhibited almost the same shapes as those in Fig. 4(a), while their amplitudes increased by about a factor of five. The forces \( F_c(z) \) did not resemble those from Fig. 4(b) at all, rather they now were almost (but not exactly) proportional to \( F_h(z) \) with proportionality constants close to unity. As a consequence, also the total forces \( F(z) \) were similar to those from Fig. 4(e), except that the amplitudes were larger by about a factor of
ten. In particular, these findings cannot be understood by simply superimposing the cases of an uncharged particle and of an uncharged pore. We also note that while \( F_h \) can still be associated with the counterion pressure effects (cf. Fig. 1(b) and Eq. (23)), \( F_r \) now comprises not only the dielectric forces but also the only partially screened electrostatic repulsion between the equally charged particle and pore walls (cf. Fig. 1(a) and Sec. III C).

Regarding potential applications, a particularly interesting direction may be ultrafiltration [41], especially the design of sieves for uncharged (and possibly even nonpolarizable) nanoparticles, whose particle sorting characteristics can be adjusted by means of the ion concentration, see Fig. 6.

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Appendix I

In this Appendix we provide the derivation of the approximations (33)-(35).

Exploiting \( \sinh(x) \approx x \) for \(|x| \lesssim 1\) yields the Poisson-Boltzmann equation (31) in the Debye-Hückel limit

\[
\frac{1}{r} \frac{d}{dr} \left( r \frac{d}{dr} \psi_i(r) \right) = \kappa^2 \psi_i(r) ,
\]

where \( \kappa := \lambda_D^{-1} \) is the inverse Debye length, see (11).

By exploiting the above approximation \( \sinh(x) \approx x \) for \(|x| \lesssim 1\) once again in (23) and the analogous approximation \( \cosh(x) \approx 1 + x^2/2 \) for \(|x| \lesssim 1\) in (24), we obtain

\[
\rho_i(r) = -2Ze_0Na_0 \frac{Z_0e_0\psi_i(r)}{k_B T} ,
\]

\[
p_i(r) = k_B T Na_0 \left( \frac{Z_0e_0\psi_i(r)}{k_B T} \right)^2 .
\]

As a consequence, the integrand in Eq. (32) vanishes and the free energy per unit length simplifies to (47)

\[
g_i = \pi \sigma Q \psi_i(Q) .
\]

The solutions of Eq. (45) with the boundary conditions discussed below Eq. (31) are well known (see e.g. 48, 49) and are given by (34) and

\[
\psi_2(r) = \frac{\sigma}{\epsilon_0 e_0 \kappa} I_0(\kappa r) K_1(\kappa r) + K_0(\kappa r) I_1(\kappa r) - I_1(\kappa r) K_0(\kappa r) ,
\]

where \( I_k \) (\( K_k \)) is the modified Bessel function of the first (second) kind and order \( k \).

Introducing (34) and (49) into (48) and (30) yields (33). Introducing (34) into (47) yields (35).

Appendix II

In this Appendix we provide the analytical solution \( \psi_2(r) \) of the Poisson-Boltzmann equation (31) within the approximation (36), originally derived in [44, 50], and assuming different functional forms, depending on the model parameters:

\[
\psi_2(r) = \begin{cases} 
\psi_+(r) & \text{if } \ln \frac{Q}{\kappa r} < 1 \text{ and } |\sigma| > \frac{2U_0 e_0 e_w}{Q(1-\ln \frac{Q}{\kappa r})} , \\
\psi_-(r) & \text{else}
\end{cases}
\]

The function \( \psi_+ \) is given by

\[
\psi_+(r) := \text{sign}(\sigma) U_0 \ln \left( \frac{-a_3}{\kappa^2 r^2 \cos^2 \left( a_4 + \frac{1}{2} \sqrt{-a_3 \ln \frac{Q}{\kappa r}} \right) } \right) ,
\]

where \( \kappa \) is the inverse Debye length (11) and where \( U_0 \) is given by (53).

The potential \( \psi_+ \) has to satisfy the boundary conditions discussed below Eq. (31) which fix the parameters \( a_3 \) and \( a_4 \). A straightforward calculation shows that \( a_3 \) is thus given by

\[
a_3 := 4 / \tan^2(a_4) ,
\]

and that \( a_4 \) is implicitly given as the solution of

\[
\cot(a_4) \tan \left( a_4 + \cot(a_4) \ln \frac{Q}{R} \right) = 1 + \frac{Q|\sigma|}{2U_0 e_0 e_w} ,
\]

in the interval \((a_{\text{min}}, \pi/2)\) where \( a_{\text{min}} > 0 \) is implicitly defined via

\[
(\pi/2 - a_{\text{min}}) \tan(a_{\text{min}}) = \ln Q/R .
\]

Analogously, \( \psi_- \) is given by

\[
\psi_-(r) := \text{sign}(\sigma) U_0 \ln \left( \frac{4a_5a_6(\kappa r) \sqrt{a_6}}{(\kappa r)^2 [1 - a_5(\kappa r) \sqrt{a_6}]} \right) ,
\]

with

\[
a_5 := \frac{2 - \sqrt{a_6}}{(2 + \sqrt{a_6}) (\kappa R) \sqrt{a_6}} ,
\]

and \( a_6 \in (0, 4) \) being implicitly defined via

\[
\frac{(a_6 - 4) \left[ 1 - \left( \frac{Q}{\kappa r} \right)^{\sqrt{a_6}} \right]}{(2 + \sqrt{a_6}) - (2 - \sqrt{a_6}) \left( \frac{Q}{\kappa r} \right)^{\sqrt{a_6}}} = \frac{|\sigma| Q}{U_0 e_0 e_w} .
\]

Appendix III

In this Appendix we show that the approximation \( F^{m}_y \) from Sec. IV.B is independent of the bulk concentration \( c_0 \).
Introducing \( \text{sign}(\sigma) \) into (41) it follows that both \( p_1(r) \) and \( p_1(r) \) are independent of \( c_0 \). The free energy per unit length \( g_1 \) thus follows with (42) as

\[
g_1 = -\text{sign}(\sigma)\pi U_0 \ln(c_0) \left[ Q\sigma - \int_0^Q dr r \rho(r) \right] + \ldots ,
\]

(58)

where the dots refer to terms which are independent of \( c_0 \). Multiplying the integral in Eq. (55) by \( 2\pi \) yields the charge per unit length due to the mobile ions. Employing the Gauss theorem \([1]\) and the boundary conditions discussed below Eq. (51) shows that the integral equals \(-Q\sigma\) and hence

\[
g_1 = -2\text{sign}(\sigma)\pi U_0 \ln(c_0) Q\sigma + \ldots .
\]

(59)

Analogously, it can be shown that also \( g_2 \) from (52) is of the form

\[
g_2 = -2\text{sign}(\sigma)\pi U_0 \ln(c_0) Q\sigma + \ldots ,
\]

(60)

where the dots in (59) and (60) indicate in general two different terms, both of which are however independent of \( c_0 \). We thus can conclude that the maximum force \( F_{\max}^g \) from (40) is independent of \( c_0 \) as well.
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