Coupled electrokinetic transport through a nanoporous membrane: a theoretical approach

O. Liot
Université de Toulouse, INPT, UPS, IMFT (Institut de Mécanique des Fluides de Toulouse), Allée Camille Soula, F-31400 Toulouse, France
Institut Lumière Matière, Université Lyon 1, CNRS, UMR 5306,
10 rue Ada Byron, 69622 Villeurbanne Cedex, France

C. Sempere, C. Ybert, and A.-L. Biance
Institut Lumière Matière, Université Lyon 1, CNRS, UMR 5306,
10 rue Ada Byron, 69622 Villeurbanne Cedex, France
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Liquid transport through nanopore is central into many applications, from water purification to biosensing or energy harvesting. Ultimately thin nanopores are of major interest in these applications to increase driving potential and reduce as much as possible dissipation sources. We investigate here theoretically the efficiency of the electrical power generation through an ultrathin nanoporous membrane by means of streaming current (electrical current induced by ionic flow in the vicinity of the liquid/solid interface) or electroosmosis (flow rate induced by an electrical potential). Upscaling from one unique pore to a nanoporous membrane is not straightforward when we consider low aspect ratio nanopore because of 3D entrance effects, which lead to interactions between the pores. Whereas these interactions have already been considered for direct transport (hydrodynamic permeability of the membrane, ionic conductance), specific effects appear when coupled transports are considered. We derive here the expression of the electroosmotic mobility for a nanoporous membrane including surface conduction, and we show that (i) it depends mainly of the distance between the pores and (ii) it is sublinear with the number of pores. Varying the pore spatial organization (square, hexagonal, disordered structure) reveals that these transport properties are only dependent on one parameter, the porosity of the membrane. Finally, when considering energy conversion yield, it is shown that increasing the number of pores is deleterious, and a non-monotonic behavior with salt concentration is reported.

I. INTRODUCTION

Transport properties (ionic/chemical/mass/thermal transport) in a liquid at the nanoscale (nanofluidics) is principally affected by surface interactions [1-5]. Such transport phenomena are coupled and have many applications, in biosensing and DNA sequencing [6], in natural objects [7,8], in material science [9,10], and, more importantly, to harvest energy (thermal or chemical energy in electricity for example [11-14]) or for remediation [15], water treatment [16] or desalination [17,18]. As another example, pierced graphene monolayer has been the ultimate target for water filtration [19], which involves simultaneously fluid transport through a membrane and electrostatic exclusion by the pores.

The investigation of these coupled transports (so-called electrokinetic phenomena – EK) dates back to the XIXth century [20] and concern the coupled flux (flow rate, ionic current...) associated with the application of different potentials in a system (thermal, chemical potential, pressure or voltage gradients). These coupled fluxes result from interactions with surfaces and are enhanced at the nanoscale, where the surface to volume ratio diverges. In an insulating solid nanochannel containing an ionic solution, some ionic charges are present at the liquid-solid interface and a diffuse layer of counter ions (electrical double layer, EDL) forms in the vicinity of the surface. The typical width of this layer is the Debye length and scales as [1]:

$$\kappa^{-1} \propto \frac{1}{\sqrt{I}},$$

where $I = \sum c_i z_i^2$ is the ionic strength of the solution, with $c_i$ the concentration of ionic specie $i$ and $z_i$ its valence. These ions can be put into motion thanks to a pressure driving (for example) and will generate an ionic current, the so-called streaming current.

In this context, the use of nanopores (ultrathin channels with low aspect ratio) seems promising to increase potential gradient (inversely proportional to the channel length), reduce dissipation and then enhance EK transport and energy conversion yield. In this nanopore geometry, however, so-called entrance effects, due to convergence of flow streams at the entrance of the pore, have to be taken into account. Entrance hydrodynamic permeability has been derived for more than one century [21], whereas entrance effects concerning ionic electroosmotic [22] and diffusio-osmotic transport [24] is still a subject of active research.

However, most of studies so far focus on one nanopore or one nanochannel. Nevertheless, to design macroscopic membranes with large pore density for energy harvesting, some insights are compulsory to understand the influence of the interactions between pores during EK transport. Sub-additive electric conductance was experimentally observed and modelled for ionic transport through an assembly of nanopores [25]. It leads to a pore conductance scaling as the square root of the number of pores for a 2D array. In addition, the more the pore are isolated, the higher will be the resulting current

*olivier.liot@imft.fr*
Despite a seemingly analogous system, when considering the hydrodynamic permeability, theoretical analysis [27] and experiments [13] show that pore interactions result in a slight increase of the permeability of the membrane.

However, to our knowledge, no study has focused yet on pore interaction influence on coupled transport properties and especially on energy harvesting efficiency, although it is central to understand the salient features necessary to improve and optimise applied systems such as osmotic energy power plants [11][13]. This work aims to study both analytically and numerically the coupled electrokinetic transports (in particular streaming current and electroosmosis) through a multi-pore membrane. In particular, the effects of the spatial arrangements of the pores (ordered and disordered membranes) and of the number of pores on energy harvesting efficiency and yield is investigated.

The article is organized as follows. First, a theoretical development to determine the electrokinetic transport coefficients for one pore taking into account entrance effects and then for an assembly of pore is proposed. Secondly, a numerical solution for hydrodynamic permeability and ionic conductance, as well as for electroosmotic mobility in various types of membranes is proposed and discussed. Finally, energy harvesting yield is calculated and analyzed.

II. THEORETICAL DEVELOPMENT

Compared to previous works on electric [25] and fluidic [13][27] transport through multi-pore membrane, the main difficulty for studying streaming current or electroosmosis lies in the coupling between ions and fluid transports. Such coupling could have complex consequences on entrance effects, which are at the origin of pore interactions. Moreover, surface-conduction dominated electric transport through nanopores [22] could affect coupled transport too. We will first derive the transport properties of one nanopore, taking into account entrance effects. We will then consider an assembly of nanopores and derive scaling laws to predict how the transport is affected by interactions with neighbouring pores. Finally, we will derive the full expression of EK transport coefficients for a membrane with N pores organized with a known geometry, taking into account entrance effects and surface conduction.

A. Electrokinetic transport coefficients for one pore

For one isolated pore, the electrokinetic coupling for one pore is given by the linear response theory, formalized here by the Onsager matrix [28]:

$$
\begin{pmatrix}
Q \\
I
\end{pmatrix} =
\begin{pmatrix}
K_h & \mu_{eo} \\
\mu_{eo} & K_e
\end{pmatrix}
\begin{pmatrix}
\Delta P \\
\Delta V
\end{pmatrix},
$$

(2)

We denote $Q$ the fluid flow rate through the pore, $I$ the electrical current, $\Delta P$ the external pressure gradient and $\Delta V$ the potential difference applied to the pore. The coefficients of the Onsager matrix are: $K_h$ the hydrodynamic permeability of the pore, $K_e$ the electric conductance, and $\mu_{eo}$ the electroosmotic mobility. Note that due to Onsager reciprocity, the same coefficient $\mu_{eo}$ appears for both electroosmosis and streaming current.

We decompose the problem in two parts: the inner part inside the nanopore and the access part, as depicted in Fig. 1. The fluxes (flow rate, ionic current) are conserved in the different zones because access regions and pore are serial connected. These flux can then be linked to local quantities applying in these zones. For the inner pore region, it reads:

$$
\begin{pmatrix}
Q \\
I
\end{pmatrix} =
\begin{pmatrix}
K_h^i & \mu_{eo}^i \\
\mu_{eo}^i & K_e^i
\end{pmatrix}
\begin{pmatrix}
\Delta P^i \\
\Delta V^i
\end{pmatrix},
$$

(3)

where index $i$ is for the inside-pore region. The transport coefficients inside the pore ($K_h^i$, $\mu_{eo}^i$ and $K_e^i$) are well-known.

Concerning the access region, indexed by $a$, we neglect cross-over phenomena which could occur in the diffusive layer of the membrane [29], which means that there is no electroosmotic flow outside the pore. Thus, fluxes are similarly connected to local properties:

$$
\begin{pmatrix}
Q \\
I
\end{pmatrix} =
\begin{pmatrix}
K_h^a & 0 \\
0 & K_e^a
\end{pmatrix}
\begin{pmatrix}
\Delta P^a \\
\Delta V^a
\end{pmatrix}.
$$

(4)

Considering that the nanopore is symmetric, two access contributions shall be considered, the pore’s inlet and outlet. Then, the potentials can be decomposed as $\Delta P = \Delta P^i + 2\Delta P^a$ and $\Delta V = \Delta V^i + 2\Delta V^a$. To determine electrical conductivity and electroosmotic mobility of the system, we first assume a configuration where no pressure gradient is applied ($\Delta P = 0$). Balancing fluxes in access and inner regions,

$$
Q = \mu_{eo}^i \Delta V = K_h^i \Delta P^i + \mu_{eo}^i \Delta V^i = K_h^a \Delta P^a,
$$

$$
I = K_e \Delta V = \mu_{eo}^i \Delta P^i + K_e^i \Delta V^i = K_e^a \Delta V^a,
$$

we get the following relations between the potentials:
\[ \Delta P^i = -2 \frac{\mu_{eo}}{K_h^i} \Delta V \]  

\[ \Delta V^i = \left(1 - 2\frac{K_e}{K_h^i} \right) \Delta V. \]  

Inserting these in eqs. 5 and 6, we get a linear system on \( K_e \) and \( \mu_{eo} \) which can be solved as:

\[ K_e = \frac{1 + 2k_e(1 - \alpha^i)}{1 + 2(k_e + k_h) + 4k_e k_h(1 - \alpha^i)} K_e^i, \]  

\[ \mu_{eo} = \frac{1}{1 + 2(k_e + k_h) + 4k_e k_h(1 - \alpha^i)} \mu_{eo}^i. \]  

with \( k_h = K_h^i / K_h^o, k_e = K_e^i / K_e^o \) and \( \alpha^i = (\mu_{eo}^i)^2 / (K_e^i K_h^i) \). To get the hydrodynamic permeability, we follow the same reasoning in a configuration where \( \Delta V = 0 \), which results in

\[ K_h = \frac{1 + 2k_e(1 - \alpha^i)}{1 + 2(k_e + k_h) + 4k_e k_h(1 - \alpha^i)} K_h^i, \]  

and we obtain the same expression as previously for \( \mu_{eo} \), satisfying Onsager reciprocity theorem [28].

**B. Electroosmotic mobility for a multi-pore membrane: effect of the number of pores.**

We now consider a 2D array of \( N \) pores of radius \( a \) on a membrane of thickness \( h \) with \( h = 2a \). We focus on scaling of total coupled transport coefficient with the number of pores crossing the membrane. On the one hand, coefficients corresponding to inner do not include entrance effects and so pore interactions. Inner hydraulic and electric resistances are independent, and nanopores are disposed in parallel from the hydrodynamic and electrical point of view. Then, when \( N \to \infty \), \( K_e^i N \approx NK_e^1 \), \( K_h^i N \approx NK_h^1 \) and \( \mu_{eo}^i N \approx N \mu_{eo}^1 \). The subscript \( N \) refers to the total value for \( N \) pores.

For the access quantity, previous work [25] showed that \( K_e^o N \propto \sqrt{N} \). Concerning the hydrodynamic transport, the physical origin of an entrance effect is the focusing of streamlines at the interface between large reservoir and thin pore. Since a viscous flow dissipates energy when streamlines change in direction, we have an access resistance \( R_h^o = 1/K_h^o \). Previous works [21] [30] [31] showed that \( R_h^o = 3\pi \eta a^2 / 8h \) where \( \eta \) is the dynamic viscosity of the fluid. This access resistance is also valid for the pore outlet resistance. Other studies [32] [33] put forward that the total resistance of the pore crossing a membrane is very close to the sum of Poiseuille and access resistances. In the case of membranes where \( h \sim a \), the access resistance cannot be neglected. Indeed \( R_h^i = 1/K_h^i = 8\eta h / (\pi a^4) \) so \( R_h^i / R_h^o \sim h / a \sim 1 \).

To take into account hydrodynamic interactions between pores, we use previous work from Tio and Sadhal [34]. At first order, only pairwise interactions are considered. They showed that the access resistance of a pore labelled \( m \) among other pores labeled \( n \) is:

\[ R_{h,m} = \frac{3\eta}{2a^3} \left(1 - \sum_{n\neq m} \left[\frac{2}{3\pi} \left(\frac{a}{L_{n,m}}\right)^3 + \frac{6}{5\pi} \left(\frac{a}{L_{n,m}}\right)^5\right] + \frac{18}{7\pi} \left(\frac{a}{L_{n,m}}\right)^7 + \ldots \right). \]  

\( L_{n,m} \) represents the center-to-center distance between pore \( m \) and pore \( n \). We denote as \( L \) the typical distance between two pore centers. We can shrink the previous equation, introducing \( \lambda_m \):

\[ R_h = R_h^2 \left(1 - 2\pi \sum_{i=2}^{\infty} \sum_{p=1}^{\infty} \frac{3^{p-1}}{2p + 1} \left(\frac{1}{L_{i,n,m}}\right)^{2p+1}\right). \]  

\[ = R_h^2 (1 - \lambda^m). \]

\(|r_{n,m}| \) is the dimensionless positions of the pores in units of \( L \). For large \( N \), because we have parallel resistances, we get:

\[ K_{h,N}^o \approx K_h^o N, \quad K_{h,N}^i \approx K_h^i \sum_{m} \frac{1}{1 - \lambda^m}. \]  

When \( L/a > 3 \), i.e. space between two pores’ edge is only one pore radius, we can consider only the first term of \( \lambda^m \). For \( N \to \infty \), \( \sum_{n\neq m} \left(\frac{1}{|r_{n,m}|}\right)^3 \) tends towards a constant (close to 11 for a hexagonal array). Thus, since \( \lambda^m \) tends to a constant \( \Lambda \) for large \( N \), we have the following scaling:

\[ K_{h,N}^o \approx K_h^o \frac{1}{1 - \Lambda} \propto N. \]

Despite a seemingly analogous problem, we observe a large difference with electrical conductance. Due to the constant correction \( 1/(1 - \Lambda) > 1 \), we have here a flow rate increase thanks to hydrodynamic interactions between pores, as observed previously [27]. Moreover, whereas pore interactions tend to a sub-linear behaviour of \( K_e^o N \), we obtain a linear scaling for the access hydrodynamic permeability.

Let us now apply a pressure drop through a membrane made of \( N \to \infty \) nanopores, but no electric potential difference (\( \Delta V = 0 \)). Thus we get for the streaming current \( I_{stream} = \mu_{eo,N} \Delta P \). Using eq. 10 and previous scalings, we can write for large \( N \):

\[ \mu_{eo,N} \propto \sqrt{N}. \]  

Similarly to the electric transport [25], the electroosmotic transport adopts a sub-linear scaling with the number of pores.
C. Transport coefficients for a membrane pierced with \( N \) identical pores with any spatial organization.

To upscale experimentally the coupled transport value through a large multi-pore membrane, some studies at the scale of a few pores have allowed to capture main interaction mechanisms between the pores. Such an approach has been used to investigate filtration by dedicated membrane for example [35,37] or for the study of electric transport (direct transport) [25]. Numerically, we are able to by-pass this step and estimate directly the behaviour of a very large membrane. Previous works [25,27] show that at least two main parameters drive the membrane response to an external driving: inter-pore distance and lattice or randomly-ordered pores) and we show its effect on transport coefficients. We then want to specify the coefficients \( K_e, K_h \) and \( \mu_{eo} \) derived in the previous subsection, eqs. 9, 10 and 11.

We recall first the expressions of the inner Onsager coefficients for a cylindrical nanopore [22, 23, 31]:

\[
K^i_h = \frac{\pi a^4}{8\eta h}, \tag{18}
\]

\[
K^i_e = \kappa_h \frac{\pi a^2}{h} + \kappa_s \frac{2\pi a}{h}, \tag{19}
\]

\[
\mu^i_{eo} = -\frac{\varepsilon_0^2 \pi a^2}{\eta h}. \tag{20}
\]

with \( \eta \) the fluid dynamic viscosity, \( \varepsilon \) is the fluid dielectric constant, \( \kappa_h \) the bulk conductivity of the solution and \( \zeta \) the membrane zeta potential. These expressions of \( K^i_e \) and \( \mu^i_{eo} \) are taken in the limit of no EDL overlap, \( a > \kappa^{-1} \). The electric conductance takes into account surface effects inside the pore, with \( \kappa_s = \kappa_h \Sigma \) the surface conductivity [22]. \( \Sigma \) is the surface charge density, \( e \) the elementary electric charge and \( c_0 \) the electrolyte concentration. We denote as \( l_{Du} = \kappa_e / \kappa_h \) the Dukhin length which represents the competition between bulk and surface conduction [2].

The access direct transport coefficients have also been derived [22, 31]:

\[
K^a_h = \frac{a^3}{3\eta}, \tag{21}
\]

\[
K^a_e = 2\kappa_h (2a + l_{Du}). \tag{22}
\]

Note that the access electric conductance also takes into account a surface contribution proposed by Lee et al. [22].

From these results we can explicit the following coefficients:

\[
k_h = \frac{3\pi a}{16h}, \tag{23}
\]

\[
k_e = \frac{\pi a}{2h} \left( \frac{a + 2l_{Du}}{2a + l_{Du}} \right), \tag{24}
\]

\[
\alpha' = \frac{8\varepsilon_0^2 \zeta^2}{\eta a \kappa_h (a + 2l_{Du})}. \tag{25}
\]

To keep only dominant terms in expressions of \( K_e, K_h \) and \( \mu_{eo} \), we estimate the order of magnitude of \( \alpha' \) for common situations. We consider water with dissolved \( K^+ \) and \( Cl^- \) ions, flowing through a membrane of silicon nitride (Si\(_3\)N\(_4\)) at ambient temperature and \( pH \approx 6 \), values consistent with previous experimental works [22, 25]. Table I lists the values used to estimate \( \alpha' \). We recall that \( \kappa_h = (\lambda_{K^+} + \lambda_{Cl^-})c_0 \) where \( \lambda_{K^+} \) and \( \lambda_{Cl^-} \) are the molar ionic conductivity for \( K^+ \) and \( Cl^- \) respectively. We consider concentrations between 0.001 mol.L\(^{-1}\) (M) and 1 mol.L\(^{-1}\). In addition, we set [23] \( |\Sigma| = 20 \text{mC.m}^{-2} \).

| Name          | Symbol | Value  | Unit   |
|---------------|--------|--------|--------|
| Dielectric constant | \( \varepsilon \) | \( 6.95 \times 10^{-10} \) | F.m\(^{-1} \) |
| Zeta potential | \( \zeta \) | -30 | -     |
| Dynamic viscosity | \( \eta \) | \( 1.0 \times 10^{-3} \) | Pa.s |
| Pore radius    | \( a \) | 25 | nm     |
| Salt concentration | \( c_0 \) | 0.001 – 1 | mol.L\(^{-1} \) |
| Bulk conductivity | \( \kappa_h \) | \( 1.49 \times 10^{-2} – 14.9 \) | S.m\(^{-1} \) |
| Dukhin length  | \( l_{Du} \) | 0.104 – 104 | nm |

TABLE I. Values used to compute \( \alpha' \).

Within these conditions, \( \alpha' \) varies between \( 1.2 \times 10^{-4} \) and \( 2.1 \times 10^{-2} \), thus \( \alpha' \ll 1 \). We then approximate the electric conductance, hydraulic permeability and electroosmotic mobility by:

\[
K_h \simeq \frac{1}{1 + 2k_h} K^h, \tag{26}
\]

\[
K_e \simeq \frac{1}{1 + 2k_e} K^e, \tag{27}
\]

\[
\mu_{eo} \simeq \frac{1}{(1 + 2k_e)(1 + 2k_h)} \mu^e_{eo}. \tag{28}
\]

We observe that direct transport coefficients, \( K_h \) and \( K_e \), do not include coupling term: electric conductance depends only on electric terms and hydraulic conductance is a function of hydraulic quantities only. Coupling effects affect only the electroosmotic mobility. We simplify these expressions by defining the following coefficients:

\[
\beta_h = \frac{1}{1 + 2k_h}, \tag{29}
\]

\[
\beta_e = \frac{1}{1 + 2k_e}, \tag{30}
\]

\[
\beta_{eo} = \frac{1}{(1 + 2k_e)(1 + 2k_h)}. \tag{31}
\]
We notice that $\beta_{eo} = \beta_1 \beta_b$. As expected, these coefficients are lower than 1, because access resistance has indeed to be added to the inner one.

Actually, these coefficients $\beta$ are relative to the one-pore case. They include implicitly, via $k_e$ and $k_h$, the access hydraulic permeability and electric conductance. For a multipore scale, each $\beta$ is different for each pore and depends on the spatial environment made by the other pores. Following the same notations as in the previous subsection, we name $\beta^m_h$, $\beta^m_e$ and $\beta^m_{eo}$ the coefficients $\beta$ for the pore $m$ for the three kinds of transport (hydraulic, electric, coupled). So for each pore $m$ we get $K^m_h = \beta^m_h K^i_h$ (note that inner coefficients are independent of the considered pore, if we consider identical pores). We have the analogous relation for the electric and coupled transports. Using the same convention, we obtain:

$$\beta^m_h = \frac{1}{1 + 2k^m_h},$$
$$\beta^m_e = \frac{1}{1 + 2k^m_e},$$
$$\beta^m_{eo} = \frac{1}{(1 + 2k^m_e)(1 + 2k^m_h)},$$

with $k^m = K^i_h / K^m_h$ and $k_e = K^i_e / K^m_e$.

$K^m$ can be determined by inverting eq.\textsuperscript{12}. The estimation of $K^m$ necessitates the estimation of $\beta^m_{eo}$. Lee et al.\textsuperscript{22} showed that due to surface conduction, the effective radius of the access zone for electrical conductance is $R_{eff} = a + 0.5L_{Du}$. We then extend the work from Gadaleta et al.\textsuperscript{23} by considering pair interactions between access zones, and adding the surface conductance term. We write (introducing $\gamma^m$ for the right-hand term with the sum):

$$K^m_e = 2k_e(2a + L_{Du}) \left(1 + \sum_{n,m=0} a + 0.5L_{Du} \right)^{-1},$$
$$K^m_e = 2k_e(2a + L_{Du})(1 + \gamma^m)^{-1},$$

and we obtain the following equations for $k^m$ and $k_h$:

$$k^m_h = \frac{3\pi a}{16h} (1 - \lambda^m) = k_h (1 - \lambda^m),$$
$$k^m_e = \frac{\pi a}{2h} \left( \frac{a + 2L_{Du}}{2a + L_{Du}} \right) (1 + \gamma^m) = k_e (1 + \gamma^m).$$

One can notice that for an isolated pore, $\gamma^m = \lambda^m = 0$ and we recover expressions of eqs.\textsuperscript{23} and \textsuperscript{24}.

The total hydraulic permeability, electric conductance and electroosmotic mobility can be computed for membrane pierced with $N$ pores, provided we know all the distances between each pores in the membrane. The coefficients read

$$K_{h,N} = K_h^i \sum_m \beta^m_h,$$
$$K_{e,N} = K_e^i \sum_m \beta^m_e,$$
$$\mu_{eo,N} = \mu_{eo}^i \sum_m \beta^m_{eo}.$$
close enough to each others, as observed previously. We do not observe any influence of the number of pores since the hydrodynamic pore interaction is a short-range effect scaling as \((L/a)^{-3}\) at best. Finally, the expressions of \(\beta_h\) and \(\beta_m\) do not imply electric component so the hydrodynamic transport does not depend on the electrolyte concentration.

Fig. 2 shows a comparison of \(K_{h,N}/NK_h\) between three different membrane configurations: hexagonal lattice, square lattice and random lattice. The last one corresponds to 2D Random Sequential Adsorption \([41]\) whose maximal porosity \(\varepsilon\) is about 0.46. Porosity is defined as the ratio between the surfaces of the pore to the total surface of the membrane. Fig. 3 shows curves plotted as a function of \(1/\varepsilon\) instead of \(L/a\) to normalize the different configurations but keeping the same trend: when \(1/\varepsilon\) rises, \(L/a\) too. On the contrary to previous results \([27]\), we do not observe any noticeable differences when changing the pore spatial organisation. Jensen et al. \([27]\) made computations using only the third order in \(a/L_{n,m}\) (see eq. 12) whereas we took as far as the 9th order. But the difference observed is due to changes in porosity. For a given \(L/a\), membrane porosity depends on the pore spatial arrangement. Since the porosity is higher for a hexagonal lattice than for a square lattice, it is unavoidable to have lower hydraulic resistance. The porosity is actually the only relevant parameter and normalisation using \(\varepsilon\) collapses the curves of hydraulic permeability. Inset in fig. 3 shows a zoom at small \(1/\varepsilon\). It reveals very slight differences at high porosity, but the highest accessible porosity is different for each configuration: \(K_{h,N}/NK_h\) ratio can reach higher values for hexagonal lattice which can access a higher porosity.

### B. Electrical transport

We consider here again a square-lattice membrane. Fig. 4 shows \(K_{e,N}/NK_e\) as a function of \(L/a\) ratio for different values of \(N\). To compute this ratio for an aqueous solution of potassium chloride, we fixed \(|\Sigma| = 20 \text{ mC.m}^{-2}\) (consistent for Si₃N₄ membranes \([22]\)), \(a = 25 \text{ nm}\) and \(h = 50 \text{ nm}\). The ratio is plotted in a range \(l_{Du}/a \in [2.6 \times 10^{-3}, 26]\) corresponding to salt concentration \(c_0 \in [1, 10^{-4}] \text{ M}\). The salt concentration range is represented by the hatched area on each plot. Note that \(c_0 = 10^{-4} \text{ M}\) corresponds to \(\kappa^{-1} = 30 \text{ nm}\), which is a limit for non-overlapping EDL inside the pore.

FIG. 2. Ratio between total hydraulic permeability \(K_{h,N}\) and the one for \(N\) isolated pore \(K_{h,N}^{isolated}\) versus \(L/a\) for a square-lattice membrane. Three \(N\) are plotted. For the computation, we used \(h = 50 \text{ nm}\) and \(a = 25 \text{ nm}\).

FIG. 3. Ratio between total hydraulic permeability \(K_{h,N}\) and the one for \(N\) isolated pore \(K_{h,N}^{isolated}\) versus \(1/\varepsilon\). Square lattice, hexagonal lattice and random lattice are compared. Two \(N\) are plotted. Inset is a zoom of the main plot. For the computation, we used \(h = 50 \text{ nm}, a = 25 \text{ nm}\).

FIG. 4. Ratio between total electric conductance \(K_{e,N}\) and the one for \(N\) isolated pore \(K_{e,N}^{isolated}\) versus \(L/a\) for a square-lattice membrane. Three \(N\) are plotted. Each hatched area represents the range \(l_{Du}/a \in [2.6 \times 10^{-3}, 26]\) corresponding to salt concentration \(c_0 \in [1, 10^{-4}] \text{ M}\). For the computation, we used \(|\Sigma| = 20 \text{ mC.m}^{-2}\), \(h = 50 \text{ nm}\) and \(a = 25 \text{ nm}\).
Contrary to hydraulic permeability, evolution of $\frac{K_{\text{e},N}}{N_k}$ spreads on a large $L/a$ range. Nevertheless, the ratio tends asymptotically to 1, which is consistent to more and more isolated pores (and so to decreasing pore interactions). The normalized electric conductance is always lower than one, revealing a deleterious effect of pore interaction on electric transport efficiency, as already observed experimentally [25]. This effect decreases when $L/a$ rises but remain important even for very loosely porous membranes. Furthermore, we observe a strong influence of the number of pores on electric conductance. Contrary to hydraulic permeability, pore interactions are long-range since they scale as $(L/a)^{-1}$ whose infinite sum does not converge. Consequently, even if the influence of a distant pore is lower than for a neighbour one, the crescent number of interacting pores counterbalances the decrease of the interaction strength, for a fixed $L/a$. Finally, influence of the Dukhin length is noticeable. For a given $N$, the electric transport is larger when $I_{Dh}$ is short (corresponding to high salt concentration), with ratio up to $\sim 10$ at low $L/a$.

Similarly to hydraulic permeability, we do not observe influence of membrane spatial organisation on electrical transport, when plotted as a function of membrane porosity (not shown here).

C. Coupled transport

We now consider a hexagonal-lattice membrane. Fig. 5 shows $\frac{\mu_{\text{e},N}}{\mu_{\text{e},0}}$ as a function of $L/a$ ratio for different $N$. To compute this ratio, we use the same conditions as the ones used for fig. 4.

The evolution of the electroosmotic mobility is very close to the one of the electric conductance. The evolution of $\frac{\mu_{\text{e},N}}{\mu_{\text{e},0}}$ spreads on a large $L/a$ range but the ratio tends asymptotically to 1. The electroosmotic mobility is always lower than one, revealing a deleterious effect of pore interaction on coupled transport efficiency. This effect decreases when $L/a$ rises but remains important even for very loosely porous membranes. Furthermore, we observe a strong influence of the number of pores on coupled transport, similarly to electric conductance. Finally, the influence of the Dukhin length is also noticeable. For a given $N$, the electric transport is larger when $I_{Dh}$ is short (corresponding to high salt concentration), with ratio up to $\sim 10$ at low $L/a$.

Such similar behaviour between $\mu_{\text{e},N}$ and $K_{\text{e},N}$ can be explained from the expression obtained earlier for the electroosmotic mobility. We can observe that $\beta_{\text{e},N}^m = \beta_{\text{e},h}^m \beta_{\text{h},N}^m$. Yet, we observed that $K_{\text{e},N}/N_k h$ tends to one for $L/a \sim 10$ so $\beta_{\text{e},h}^m$ is asymptotically constant for $L/a \gg 1$. Thus, for large $L/a$, $\mu_{\text{e},N} \propto K_{\text{e},N}$. The electroosmotic transport (or streaming current) in a multi-pore membrane is thus largely driven by the electrical transport, and not by the hydrodynamic one, when the inter-pore distance is larger than few pore radii.

Fig. 6 shows a comparison of $\frac{\mu_{\text{e},N}}{\mu_{\text{e},0}}$ for three different membrane configurations: hexagonal lattice, square lattice and random lattice, as a function of the membrane porosity. We do not observe any noticeable differences when changing the pore spatial organisation. The porosity is again the only relevant parameter for coupled transport efficiency.

To strengthen that it is indeed the only relevant parame-
The spherical membrane we have considered allows to re-
produce drastically computation time when
only one computation of the \( \beta^n \) coefficients is necessary, in-
stead of one for each pore. If the study of pores placed on
a sphere is justified with potential applications, and natural
objects, flat membranes are also common in industry. We
performed then in this case the computation for a flat mem-
brane pierced with \( N = 10^5 \) pores. The values of the differ-
ent Onsager’s coefficients for a flat membrane do not exceed
20% more than the ones for a spherical membrane, and the
global trends with \( c_0 \) and \( L/a \) remain similar. Fig. 8 compares
these two situations for different salt concentrations, consid-
ering the electroosmotic mobility. One observes that the gap
between a flat and a spherical membrane decreases with \( L/a \).
Moreover, the difference drops faster when salt concentration
is increased. This computation justify to extend trends from
spherical membranes to flat membranes.

D. Energy conversion efficiency

The performance of a membrane for renewable energy re-
cover is evaluated by determining the theoretical maximum
power yield of the electrokinetic process \[11, 42\]. In the
framework presented here, hydraulic energy can be converted
to electricity (streaming current) or electric energy can be con-
verted to mechanical fluid displacement (electroosmosis). Let
us consider the second case. A membrane, of hydraulic per-
meability \( K_{h,N} \), is connected to a variable load pipe (analogous
to a variable load resistance) whose hydraulic permeability is
noted \( K_L \). A voltage difference is applied through the mem-
brane which leads to a flow rate \( Q = \mu_{eo,N} \Delta V \). Fig. 9 rep-
resents the equivalent hydraulic circuit. We follow the same
reasoning as van der Heyden et al. \[11\] for streaming current
recovery through a nanochannel. An electric analogy allows to
write:

\[
\Delta P = -\frac{\mu_{eo,N} \Delta V}{K_{h,N} + K_L}.
\]

The injected (electric) power is \( P_{in} = I \Delta V \) whereas the re-
covered (mechanical) power can be written as \( P_{out} = K_L \Delta P^2 \). Elec-
tric current \( I \) can be expressed as \( I = \mu_{eo,N} \Delta P + K_{e,N} \Delta V \). Con-
sequently, efficiency of energy conversion is defined as:

\[
\mathcal{E} = \frac{P_{out}}{P_{in}} = \frac{\mu_{eo,N}^2 K_L}{K_{e,N}(K_{h,N} + K_L)^2 - \mu_{eo,N}^2 (K_{h,N} + K_L)}. \]
We write out $\alpha = \mu_{eo,N}^2/(K_{h,N}K_e,N)$ and $\Theta = K_{h,N}/K_L$. The efficiency of energy conversion can be written as:

$$\varepsilon = \frac{\alpha \Theta}{1 + \Theta}(1 + \Theta - \alpha \Theta).$$

(48)

The maximal efficiency is obtained for $\Theta = 1/\sqrt{1-\alpha}$ (impedance matching). This leads to a maximal efficiency:

$$\varepsilon_{\text{max}} = \frac{\alpha}{\alpha + 2(\sqrt{1-\alpha} + 1 - \alpha)}.$$

(49)

Fig. [10] shows the maximal yield $\alpha_{\text{max}}$ as a function of $L/a$, in a semi-log scale, for a hexagonal-lattice membrane with same parameters as in fig. [5]. Numerical results are plotted for only one concentration, $c_0 = 10^{-2}$ M ($t_d/a = 0.26$). Results from previous sections show that there is no influence of the pore spatial organisation and that the main relevant parameter is again the porosity of the membrane $\varepsilon$. One notices however that efficiency increases with $L/a$, meaning that pore interactions decrease energy conversion yield. Consequently, addition of pores is deleterious for energy conversion efficiency.

A central phenomenon is the influence of the salt concentration. The effect of salt concentration shows up in surface conduction term, characterized in eq. [22] by the term depending on the Dukhin length $l_{Du}$. Indeed, as surface entrance effects have been shown to be important for the electric conductivity of one pore [22], we also considered them for pore interactions (eq. [35], figs. [4] and [5]). Fig. [11] shows the maximal efficiency as a function of salt concentration for $L/a = 200$. This efficiency is not monotonic, with a maximum around $5 \times 10^{-3}$ M. The values computed here reach asymptotically 0.1% for $c_0 \sim 10^{-2}$ M and $N = 10^3$, which seems to be near a maximal value in the case where pore interactions become negligible. Let’s note that such a dependency of the yield versus salt concentration was observed experimentally [42] for a single nanochannel, but of course in this case with a different origin. It is due to variations of surface charge density with respect to salt concentration [42]. A thorough study should take into account both contributions.

IV. DISCUSSION AND CONCLUSION

We have investigated electrokinetic coupled transport properties through a nanofluidic membrane drilled with a large number of nanopores, by taking into account entrance effects and then pair interactions between the pores. This study leads to various results, which are crucial when the design of membrane for renewable energy conversion is considered.

First, we have shown that the electroosmotic mobility scales as $\sqrt{N}$ where $N$ is the number of pore in the membrane. This sub-linear scaling is the same as the one obtained for electric transport in the membrane [23], the effect of interactions between pores in the hydraulic resistance being incidentally very small compared to the electrical case [27].

Second, we have shown for the first time that the different transport coefficients do not depend on the spatial organisation of the pores. When normalized by membrane porosity, all transport coefficients collapse whatever the membrane type (amorphous arrangement, hexagonal-lattice, square-lattice)
and the pore size distribution. A possible interpretation for this absence of effect is that the high number of pores \( N \geq 10^3 \) smooth the spatial organisation, provided the porosity is the same. This is a crucial result in the design of nanoporous membrane. Furthermore, whereas pore interactions are beneficial for hydrodynamic transport, up to \( L/a \sim 10 \), they are deleterious for electric transport, even for \( L/a \gg 10 \). In this case, the come-back to independent pores is very slow with \( L/a \). This is due to the \( (L_m/a)^{-3} \) (\( L_m \) is the distance between pore \( m \) and pore \( n \)) of the electric conductance of a given pore \( m \) in the membrane. The term \( \gamma^m \) looks like a harmonic series which does not converge. In our study, since the sum is finite, there is no convergence problem, but the variation is slower than the one of \( \lambda^m \) which is at maximum a sum of \( (L_m/a)^{-3} \) terms. Since we can write, for a spherical membrane where all pores have the same environment:

\[
\mu_{eo,N} = \frac{K_{ho,N}K_{e,N}}{K_h^o K_e} \mu_{eo}^i N,
\]

the behaviour of \( \mu_{eo,N} \) is the same as \( K_{e,N} \) for \( L/a \geq 10 \) (\( \mu_{eo,N} \approx \mu_{eo}^i K_{e,N}/K_{e} \)).

Third, we show that both the electric conductance and the electroosmotic mobility varies a lot with salt concentration. This can be explained by the origin of pore interactions. They are due to access resistance provoked, among others, by surface conduction effects \[22\] we have taken into account for the first time. They are directly related to the extension of the zone at which surface conduction effects dominate the bulk ones, i.e. the Dukhin length \( l_{Du} \approx \Sigma/c_0 \). A low salt concentration results in a large Dukhin length and enhanced entrance effects. Since pore interactions are deleterious for electric and electroosmotic transport, a drop in salt concentration results in decrease of related Onsager’s coefficients.

Fourth, we calculate energy conversion efficiency and we show it reveals an exotic behaviour. For a fixed surface charge density, it is not monotonic with salt concentration, with a maximum around \( c_0 = 5 \times 10^{-3} \) M, whereas \( K_{e,N} \) and \( \mu_{eo,N} \) are monotonic with \( c_0 \) for a fixed \( L/a \) ratio (as reported in Fig. 8). Theoretically, a plateau is expected for efficiency as a function of concentration \[11\]. It is due to surface-conduction-generated plateau in electric conductance versus salt concentration \[11\]. This plateau of efficiency is observed experimentally in a nanochannel \[42\] with a subtle peak when EDL overlap. In our case, we do not consider EDL overlapping and minimal concentration was chosen to avoid it. So we should expect a plateau. However, we can attribute the peak observed on \( \delta_{max} \) (fig. 11) to surface effects influence on pore interactions. In addition to electric resistance of the pores, two phenomena are in competition to explain energy conversion efficiency. (i) Surface effects, related to \( l_{Du} \), are deleterious for pore interactions and decrease the coupled transport amplitude (fig. 8). An increase of \( c_0 \) (decrease of \( l_{Du} \)) is good for coupled transports. (ii) Presence of co-ions in the pore, out of EDL, participates to power dissipation, but not to coupled transports \[11\]. Consequently, an increase of salt concentration, via the EDL thickness decrease, reduces \( \delta_{max} \). The first effect is more important when \( a \ll l_{Du} \) (low \( c_0 \)) whereas the second one is important when \( a \gg \Sigma^{-1} \) (high \( c_0 \)). This explains the appearance of such a peak of \( \delta_{max} \) in the intermediate zone of salt concentration. This work constitutes a first step to optimize the design of nanoporous membranes for energy harvesting. A trade-off between low porosity to reach larger yields and space constraints to add as many channels as possible in a membrane has to be reached. If primary energy is “free” (osmotic pressure for instance), recoverable power \( P_{out} \) is proportional to \( N \) for a large number of pores, provided that the hydrodynamic load is large. It means that the recoverable power per unit of membrane surface varies as \( 1/N \) or, if the porosity is constant, as \( 1/\sqrt{S} \) if \( S \) is the surface of the membrane. Larger membranes will be indeed more efficient than smaller ones, but the sublinear relationship shows that the quest to always larger membranes might not be the ultimate strategy. Specific design of small membrane patches can indeed be more efficient. Finally, a new effect of salt concentration due to access resistance has also to be considered and to be coupled to other concentration effects such as interface ionization. Future directions should concern (i) the experimental evidences of these predictions, (ii) the consideration of other types of EK transport or ways of nanofluidics energy harvesting (chemical or thermal energy harvesting for example) and (iii) the investigation of membranes with much more complex geometries, such as connected entangled channels.

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