HOMOGENIZATION OF ELECTROKINETIC FLOWS IN POROUS MEDIA: THE ROLE OF NON-IDEALITY.

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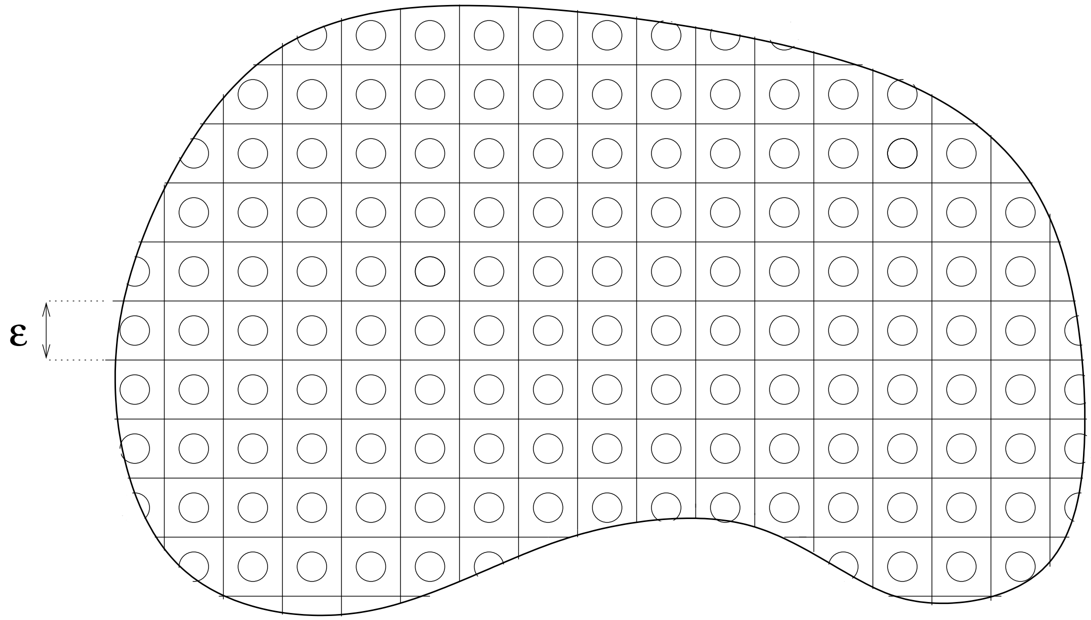
-I- INTRODUCTION

We consider ion transport in a charged porous medium.

- Coupled model:
  - **Poisson equation** for the electrostatic potential Ψ^ϵ,
  - **Stokes equations** for the fluid velocity and pressure $(\mathbf{u}^\epsilon, p^\epsilon)$,
  - **Nernst-Planck (convection-diffusion) equations** for the N species concentrations n_j^ϵ.
- Non-ideal model for the ion diffusion: activity coefficients given by the MSA model.
- Our goal is to homogenize this model and compare the effective properties in the ideal and MSA cases.
- Small pores: Debye length of the order of the pore size.
- We choose a scaling of the model for which all unknowns are varying at the pore scale (similar to Looker and Carnie 2006).

Assumptions and notations

- Rigid solid part of the porous medium.
- Saturated incompressible single phase flow containing N dilute charged species with valence z_j and same ion radius σ.
- For each species: diffusion coefficient D_j^0, Péclet number Pe_j, diffusive flux $\mathbf{j}_j^\epsilon$.
- Surface charge $-\Sigma^*$ on the pore walls.
- Small hydrostatic force $\mathbf{f}^*$ and external potential $\Psi^{ext,*}$.



Ω

Small parameter ϵ = ratio between the period and a macroscopic lengthscale.

Periodic porous medium Ω: fluid part Ω^ϵ, solid part $\Omega \setminus \Omega^\epsilon$.

Adimensionalized equations (Poisson + Stokes + Nernst-Planck):

$$-\epsilon^2 \Delta \Psi^\epsilon = \beta \sum_{j=1}^N z_j n_j^\epsilon \quad \text{in} \quad \Omega^\epsilon,$$

$$\epsilon^2 \Delta \mathbf{u}^\epsilon - \nabla p^\epsilon = \mathbf{f}^* + \sum_{j=1}^N z_j n_j^\epsilon \nabla \Psi^\epsilon \quad \text{in} \quad \Omega^\epsilon,$$

$$\mathrm{div}\mathbf{u}^\epsilon = 0 \quad \text{in} \quad \Omega^\epsilon,$$

$$\mathrm{div}\left(\mathbf{j}_i^\epsilon + \mathrm{Pe}_i n_i^\epsilon \mathbf{u}^\epsilon\right) = 0 \quad \text{in} \quad \Omega^\epsilon, \quad i = 1, \dots, N,$$

$$\mathbf{j}_i^\epsilon = -\sum_{j=1}^N L_{ij}^\epsilon \nabla M_j^\epsilon \quad \text{and} \quad M_j^\epsilon = \ln\left(n_j^\epsilon \gamma_j^\epsilon e^{z_j \Psi^\epsilon}\right),$$

$$L_{ij}^\epsilon = n_i^\epsilon \left(\delta_{ij} + \frac{k_B T}{D_i^0} \mathbf{\Omega}_{ij}\right)\left(1 + \mathcal{R}_{ij}\right) \quad i, j = 1, \dots, N,$$

Boundary conditions on the pore walls:

$$\epsilon \nabla \Psi^\epsilon \cdot \nu = -\Sigma^*, \quad \mathbf{u}^\epsilon = 0\,, \quad \mathbf{j}_i^\epsilon \cdot \nu = 0 \quad \text{on} \quad \partial\Omega^\epsilon, \quad i = 1, \dots, N.$$

Non-ideality: MSA model

γ_j^ϵ = activity coefficient

Ideal case: $\gamma_j^\epsilon = 1$, $\mathbf{\Omega}_{ij} = 0$ and $\mathcal{R}_{ij} = 0$ ($\Rightarrow L_{ij}^\epsilon = n_i^\epsilon \delta_{ij}$).

Non-ideal case:

$$\gamma_j^\epsilon = \gamma^{HS} \exp\{-\frac{L_B \Gamma^\epsilon \Gamma_c z_j^2}{(1+\Gamma^\epsilon \Gamma_c \sigma)}\} \quad \text{and} \quad (\Gamma^\epsilon)^2 = \sum_{k=1}^N \frac{n_k^\epsilon z_k^2}{(1+\Gamma_c \Gamma^\epsilon \sigma)^2}$$

where Γ^ϵ is the screening parameter and γ^{HS} is the hard-sphere term

$$\gamma^{HS} = \exp\{p(\xi)\} \quad \text{with} \quad p(\xi) = \xi \frac{8 - 9\xi + 3\xi^2}{(1-\xi)^3} \quad \text{and} \quad \xi = \frac{\pi n_c}{6} \sum_{k=1}^N n_k^\epsilon \sigma^3$$

Complicated formulas for $\mathbf{\Omega}_{ij}$ and $\mathcal{R}_{ij}$ (but the Onsager tensor L_{ij}^ϵ is symmetric).

External boundary conditions

For simplicity we choose a cube domain $\Omega = (0, L)^d$ with $d = 2, 3$.

On the outer boundary $\partial\Omega^\epsilon \cap \partial\Omega$ we can thus impose periodic boundary conditions.

- The fluid velocity and pressure $(\mathbf{u}^\epsilon, p^\epsilon)$ and the concentrations n_j^ϵ are L-periodic.
- Given an external potential $\Psi^{ext,*}(x)$, the total electrokinetic potential $\Psi^\epsilon + \Psi^{ext,*}$ is L-periodic.

The forcing is caused by $\Psi^{ext,*}$, the surface charge density $-\Sigma^*$ and the hydrodynamic force $\mathbf{f}^*$.

Strategy for the homogenization process

- Find so-called equilibrium solutions in the absence of exterior forcing. In the ideal case it yields the (non-linear) Poisson-Boltzmann equation.
- For small exterior forcing $\mathbf{f}^*$ and $\Psi^{ext,*}$ (but large surface charge Σ^*), linearize the transport model.
- Homogenize the linear model on a non-linear electrostatic background.

Bibliography

- ✍ Reference book on the model: Karniadakis-Beskok-Aluru, Microflows and Nanoflows. Fundamentals and Simulation. Interdisciplinary Applied Mathematics, Vol. 29, Springer, New York, (2005).
- ✍ Many numerical works on the upscaling: Adler, Coelho, Marino, Shapiro, Smith...
- ✍ Linearization process: O'Brien and White (1978).
- ✍ Formal two-scale asymptotic expansions: Auriault-Strzelecki (1981), Moyne-Murad (2002, 2003, 2006), Looker and Carnie (2006).
- ✍ Homogenization: Schmuck (2010), Ray (2011)...
- ✍ Our own work in the ideal case: Journal of Mathematical Physics, 51, 123103 (2010). MSA case: Physica D, 282, 39-60 (2014)

-II- PARTIAL LINEARIZATION OF THE MODEL

- Following the lead of O'Brien and White (1978) we perform a (partial) linearization.
- In the ideal case, this is the same as in Looker and Carnie (2006).
- We assume that the forcing terms $\Psi^{ext,*}$ and $\mathbf{f}^*$ are small, but not the surface charge density Σ^* which can still be large.
- We denote by $n_i^{0,\epsilon}, \Psi^{0,\epsilon}, \mathbf{u}^{0,\epsilon}, p^{0,\epsilon}$ the equilibrium quantities for $\mathbf{f}^* = 0$ and $\Psi^{ext,*} = 0$.
- At equilibrium we look for a solution with vanishing fluxes

$$\mathbf{u}^{0,\epsilon} = 0 \quad \text{and} \quad \mathbf{j}_i^{0,\epsilon} = 0$$

and an ϵ-periodic electrostatic potential

$$\Psi^{0,\epsilon}(x) = \Psi^0(\frac{x}{\epsilon})$$

Equilibrium solution

Consequence of the zero ionic flux $\mathbf{j}_i^{0,\epsilon} = 0$:

$$\nabla M_j^\epsilon = 0 \quad \text{with} \quad M_j^\epsilon = \ln\left(n_j^\epsilon \gamma_j^\epsilon e^{z_j \Psi^\epsilon}\right)$$

Thus

$$n_j^{0,\epsilon}(x) = n_j^0(\infty)\gamma_j^0(\infty)\frac{\exp\left\{-z_j\Psi^{0,\epsilon}(x)\right\}}{\gamma_j^{0,\epsilon}(x)}$$

where $n_j^0(\infty)$ are constants (called infinite dilution concentrations) and $\gamma_j^0(\infty)$ are the constant activity coefficients for zero potential.

Poisson-Boltzmann equation at equilibrium

$$
\left\{
\begin{array}{ll}
-\Delta_y \Psi^0(y) = \beta \sum_{j=1}^{N} z_j n_j^0(y) & \text{in } Y_F, \\
\nabla_y \Psi^0 \cdot \nu = -\Sigma^* & \text{on } \partial Y_F \setminus \partial Y, \\
y \to \Psi^0(y) \ \text{ is } 1-\text{periodic}, & \\
n_j^0(y) = n_j^0(\infty)\gamma_j^0(\infty) \dfrac{\exp\left\{-z_j \Psi^0(y)\right\}}{\gamma_j^0(y)}, &
\end{array}
\right.
$$

with the activity coefficient defined by

$$
\gamma_j^0(y) = \gamma^{HS}(y) \exp\{-\frac{L_B \Gamma^0(y) \Gamma_c z_j^2}{(1+\Gamma^0(y)\Gamma_c \sigma)}\} \quad \text{and} \quad (\Gamma^0(y))^2 = \sum_{k=1}^{N} \frac{n_k^0(y) z_k^2}{(1+\Gamma_c \Gamma^0(y)\sigma)^2},
$$

$$
\gamma^{HS} = \exp\{p(\xi)\} \quad \text{with} \quad p(\xi) = \xi \frac{8-9\xi+3\xi^2}{(1-\xi)^3} \quad \text{and} \quad \xi(y) = \frac{\pi n_c}{6} \sum_{k=1}^{N} n_k^0(y)\sigma^3.
$$

Poisson-Boltzmann equation at equilibrium

We impose the bulk electroneutrality condition, i.e., for $\Psi^0 = 0$,

$$\sum_{j=1}^{N} z_j n_j^0(\infty) = 0.$$

Theorem. Assuming that the ion radius σ is not too small and that the characteristic concentration n_c is not too large, there exists a solution Ψ^0 of the Poisson-Boltzmann equation.

Remark. In the ideal case, $\gamma_j^0(y) = 1$, the Poisson-Boltzmann equation has always a unique solution since it corresponds to the minimization of a convex energy. The MSA model destroys this convexity property.

Linearization

$$n_i^\epsilon(x) = n_i^{0,\epsilon}(x) + \delta n_i^\epsilon(x), \quad \Psi^\epsilon(x) = \Psi^{0,\epsilon}(x) + \delta\Psi^\epsilon(x),$$

$$\mathbf{u}^\epsilon(x) = \mathbf{u}^{0,\epsilon}(x) + \delta\mathbf{u}^\epsilon(x), \quad p^\epsilon(x) = p^{0,\epsilon}(x) + \delta p^\epsilon(x),$$

Trick (O'Brien and White): introduce the ionic potential Φ_i^ϵ defined by

$$n_i^\epsilon(x)\gamma_i^\epsilon(x) = n_i^0(\infty)\exp\{-z_i(\Psi^\epsilon(x) + \Phi_i^\epsilon(x) + \Psi^{ext,*}(x))\}.$$

In the ideal case, this trick is useful because it yields the following change of variables

$$\delta n_i^\epsilon(x) = -z_i n_i^{0,\epsilon}(x)\Big(\delta\Psi^\epsilon(x) + \Phi_i^\epsilon(x) + \Psi^{ext,*}(x)\Big)$$

However, in the non-ideal case the algebra is much more complex !

In particular, each δn_i^ϵ involves all Φ_k^ϵ.

After linearization (and some algebra !) we obtain the problem we want to homogenize:

$$\left\{\begin{array}{l}
\epsilon^2\Delta\mathbf{u}^\epsilon - \nabla P^\epsilon = \mathbf{f}^* - \sum_{j=1}^N z_j n_j^{0,\epsilon}\nabla\left(\Phi_j^\epsilon + \Psi^{ext,*}\right) \text{ in } \Omega^\epsilon, \\
\operatorname{div}\mathbf{u}^\epsilon = 0 \quad \text{in } \Omega^\epsilon, \quad \mathbf{u}^\epsilon = 0 \text{ on } \partial\Omega^\epsilon\setminus\partial\Omega, \\
\operatorname{div} n_i^{0,\epsilon}\left(\sum_{j=1}^N K_{ij}^\epsilon z_j \nabla(\Phi_j^\epsilon + \Psi^{ext,*}) + \mathrm{Pe}_i\mathbf{u}^\epsilon\right) = 0 \quad \text{in } \Omega_\epsilon,\ i = 1,\dots,N, \\
K_{ij}^\epsilon = \left(\delta_{ij} + \frac{k_B T}{D_i^0}\mathbf{\Omega}_{ij}\right)\left(1 + \mathcal{R}_{ij}\right),\ i,j = 1,\dots,N, \\
\sum_{j=1}^N K_{ij}^\epsilon z_j \nabla(\Phi_j^\epsilon + \Psi^{ext,*})\cdot\nu = 0 \text{ on } \partial\Omega^\epsilon\setminus\partial\Omega, \\
\mathbf{u}^\epsilon,\ P^\epsilon,\ \Phi_j^\epsilon \text{ are L-periodic.}
\end{array}\right.$$

In the previous equations, $n_j^{0,\epsilon}$ and K_{ij}^{ϵ} are ϵ-periodic coefficients evaluated at equilibrium (by solving the **non-linear** Poisson-Boltzmann equation).

$$\Psi^{0,\epsilon}(x) = \Psi^0(\frac{x}{\epsilon}), \quad n_j^{0,\epsilon}(x) = n_j^0(\frac{x}{\epsilon}), \quad K_{ij}^{\epsilon}(x) = K_{ij}(\frac{x}{\epsilon}).$$

The linearization is thus **partial** because Ψ^0 is solution of a (highly) non-linear equation.

Lemma. The linearized problem admits a unique solution.

Remark. It is a crucial assumption that all ions have the same diameter.

-III- HOMOGENIZATION AND TWO-SCALE LIMIT

- ✗ We assume that the porous medium is periodic.
- ✗ Periodic unit cell $Y = (0,1)^n = Y_F \cup \Sigma^0$ with fluid part Y_F.
- ✗ Fast variable $y = \dfrac{x}{\epsilon}$.
- ✗ Two-scale asymptotic expansions:

$$\left\{ \begin{array}{l} \mathbf{u}^\epsilon(x) = \mathbf{u}^0(x, x/\epsilon) + \epsilon \mathbf{u}^1(x, x/\epsilon) + \ldots, \\ P^\epsilon(x) = p^0(x) + \epsilon p^1(x, x/\epsilon) + \ldots, \\ \Phi_j^\epsilon(x) = \Phi_j^0(x) + \epsilon \Phi_j^1(x, x/\epsilon) + \ldots. \end{array} \right.$$

Theorem.

The solution satisfies

$$\mathbf{u}^\epsilon(x) \approx \mathbf{u}^0(x, \frac{x}{\epsilon}), \quad P^\epsilon(x) \approx p^0(x) + \epsilon p^1(x, \frac{x}{\epsilon}), \quad \Phi_j^\epsilon(x) \approx \Phi_j^0(x) + \epsilon \Phi_j^1(x, \frac{x}{\epsilon}),$$

where $(\mathbf{u}^0, p^0, p^1, \{\Phi_j^0, \Phi_j^1\})$ is the solution of the two-scale homogenized problem (which admits a unique solution).

Remark.

The difficulty is to extract from the two-scale homogenized problem a macroscopic homogenized model and to study its Onsager properties.

Remark.

The (oscillating) concentrations are recovered from the ionic potentials by

$$n_i^\epsilon(x) \approx \frac{n_i^0(\infty)\gamma_i^0(\infty)}{\gamma_i^0(\frac{x}{\epsilon})} \exp\{-z_i(\Psi^0(\frac{x}{\epsilon}) + \Phi_i^0(x) + \Psi^{ext,*}(x))\}.$$

Two-scale homogenized problem

$$-\Delta_y \mathbf{u}^0(x,y) + \nabla_y p^1(x,y) = -\nabla_x p^0(x) - \mathbf{f}^*(x)$$
$$+ \sum_{j=1}^{N} z_j n_j^0(y)\left(\nabla_y \Phi_j^1(x,y) + \nabla_x \Phi_j^0(x) + \mathbf{E}^*(x)\right) \text{ in } \Omega \times Y_F,$$

$$\operatorname{div}_y \mathbf{u}^0(x,y) = 0 \text{ in } \Omega \times Y_F, \quad \operatorname{div}_x \left(\int_{Y_F} \mathbf{u}^0 \, dy \right) = 0 \text{ in } \Omega,$$

$$-\operatorname{div}_y n_i^0(y) \left(\sum_{j=1}^{N} K_{ij} z_j \left(\nabla_y \Phi_j^1(x,y) + \nabla_x \Phi_j^0(x) + \mathbf{E}^*(x)\right) + \mathrm{Pe}_i \mathbf{u}^0(x,y) \right) = 0$$

$$-\operatorname{div}_x \int_{Y_F} n_i^0(y) \left(\sum_{j=1}^{N} K_{ij} z_j \left(\nabla_y \Phi_j^1(x,y) + \nabla_x \Phi_j^0(x) + \mathbf{E}^*(x)\right) + \mathrm{Pe}_i \mathbf{u}^0(x,y) \right) dy = 0$$

$$\mathbf{u}^0(x,y) = 0 \text{ on } \Omega \times \partial Y_F, \quad \sum_{j=1}^{N} K_{ij} z_j \left(\nabla_y \Phi_j^1 + \nabla_x \Phi_j^0 + \mathbf{E}^*\right) \cdot \nu = 0 \text{ on } \Omega \times \partial Y_F.$$

The macroscopic forcing terms are in red and blue.

Factorization of the two-scale functions

We want to separate the slow x and fast y variables. Our approach is different from that of Looker and Carnie.

We decompose

$$\mathbf{u}^0(x,y) = \sum_{k=1}^{d} \left(-\mathbf{v}^{0,k}(y) \left(\frac{\partial p^0}{\partial x_k} + f_k^* \right)(x) + \sum_{i=1}^{N} \mathbf{v}^{i,k}(y) \left(E_k^* + \frac{\partial \Phi_i^0}{\partial x_k} \right)(x) \right)$$

$$p^1(x,y) = \sum_{k=1}^{d} \left(-\pi^{0,k}(y) \left(\frac{\partial p^0}{\partial x_k} + f_k^* \right)(x) + \sum_{i=1}^{N} \pi^{i,k}(y) \left(E_k^* + \frac{\partial \Phi_i^0}{\partial x_k} \right)(x) \right)$$

$$\Phi_j^1(x,y) = \sum_{k=1}^{d} \left(-\theta_j^{0,k}(y) \left(\frac{\partial p^0}{\partial x_k} + f_k^* \right)(x) + \sum_{i=1}^{N} \theta_j^{i,k}(y) \left(E_k^* + \frac{\partial \Phi_i^0}{\partial x_k} \right)(x) \right)$$

where $(\mathbf{v}^{i,k}, \pi^{i,k}, \theta_j^{i,k})$, for $0 \le i \le N$, are solutions of cell problems.

Definition of effective (or homogenized) quantities

We define the following effective hydrodynamic velocity:

$$\mathbf{u}(x) = \frac{1}{|Y_F|} \int_{Y_F} \mathbf{u}^0(x,y)\, dy.$$

We also introduce the effective electrochemical potential of the jth species

$$\mu_j(x) = -z_j \Big(\Phi_j^0(x) + \Psi^{ext,*}(x) \Big),$$

and the effective ionic flux of the jth species

$$\mathbf{j}_j(x) = \frac{1}{|Y_F|} \int_{Y_F} n_j^0(y) \left(\sum_{l=1}^{N} K_{jl} \frac{z_l}{\mathrm{Pe}_j} \big(\nabla_y \Phi_l^1(x,y) + \nabla_x \Phi_l^0(x) + \mathbf{E}^*(x) \big) + \mathbf{u}^0 \right) dy$$

We are now able to write the homogenized equations for the above effective fields.

Theorem (homogenized equations)

The macroscopic equations in Ω are

$$\operatorname{div}_x \mathbf{u} = 0 \quad \text{and} \quad \operatorname{div}_x \mathbf{j}_i = 0, \text{ for } i = 1, \dots, N, \quad \text{with}$$

$$\begin{pmatrix} \mathbf{u} \\ \{\mathbf{j}_i\} \end{pmatrix} = -\mathcal{M} \begin{pmatrix} \nabla p^0 + \mathbf{f}^* \\ \{\nabla \mu_i\} \end{pmatrix} \text{ and } \mathcal{M} = \begin{pmatrix} \mathbb{K} & \frac{\mathbb{J}_1}{z_1} & \dots & \frac{\mathbb{J}_N}{z_N} \\ \mathbb{L}_1 & \frac{\mathbb{D}_{11}}{z_1} & \dots & \frac{\mathbb{D}_{1N}}{z_N} \\ \vdots & \vdots & \ddots & \vdots \\ \mathbb{L}_N & \frac{\mathbb{D}_{N1}}{z_1} & \dots & \frac{\mathbb{D}_{NN}}{z_N} \end{pmatrix}$$

Furthermore the tensor $\mathcal{M}$ is symmetric positive definite (Onsager properties).

The matrices $\mathbb{J}_i$, $\mathbb{K}$, $\mathbb{D}_{ji}$ and $\mathbb{L}_j$ are defined by their entries

$$\{\mathbb{J}_i\}_{lk} = \frac{1}{|Y_F|}\int_{Y_F} \mathbf{v}^{i,k}(y)\cdot\mathbf{e}^l\,dy, \quad \{\mathbb{K}\}_{lk} = \frac{1}{|Y_F|}\int_{Y_F} \mathbf{v}^{0,k}(y)\cdot\mathbf{e}^l\,dy,$$

$$\{\mathbb{D}_{ji}\}_{lk} = \frac{1}{|Y_F|}\int_{Y_F} n_j^0(y)\Big(\mathbf{v}^{i,k}(y) + \sum_{m=1}^{N} K_{jm}\frac{z_m}{\mathrm{Pe}_j}\left(\delta_{im}\mathbf{e}^k + \nabla_y\theta_m^{i,k}(y)\right)\Big)\cdot\mathbf{e}^l\,dy,$$

$$\{\mathbb{L}_j\}_{lk} = \frac{1}{|Y_F|}\int_{Y_F} n_j^0(y)\Big(\mathbf{v}^{0,k}(y) + \sum_{m=1}^{N} K_{jm}\frac{z_m}{\mathrm{Pe}_j}\nabla_y\theta_m^{0,k}(y)\Big)\cdot\mathbf{e}^l\,dy.$$

First cell problem: imposed pressure gradient

$$\begin{cases} -\Delta_y \mathbf{v}^{0,k}(y) + \nabla_y \pi^{0,k}(y) = \mathbf{e}^k + \displaystyle\sum_{j=1}^N z_j n_j^0(y) \nabla_y \theta_j^{0,k}(y) \quad \text{in } Y_F \\ \operatorname{div}_y \mathbf{v}^{0,k}(y) = 0 \quad \text{in } Y_F, \quad \mathbf{v}^{0,k}(y) = 0 \quad \text{on } \partial Y_F, \\ -\operatorname{div}_y n_i^0(y) \left(\displaystyle\sum_{j=1}^N K_{ij}(y) z_j \nabla_y \theta_j^{0,k}(y) + \mathrm{Pe}_i \mathbf{v}^{0,k}(y) \right) = 0 \quad \text{in } Y_F \\ \displaystyle\sum_{j=1}^N K_{ij}(y) z_j \nabla_y \theta_j^{0,k}(y) \cdot \nu = 0 \quad \text{on } \partial Y_F. \end{cases}$$

Second cell problem: imposed electrostatic field

$$
\begin{cases}
-\Delta_y \mathbf{v}^{l,k}(y) + \nabla_y \pi^{l,k}(y) = \displaystyle\sum_{j=1}^{N} z_j n_j^0(y)(\delta_{lj}\mathbf{e}^k + \nabla_y \theta_j^{l,k}(y)) \ \text{ in } Y_F, \\
\operatorname{div}_y \mathbf{v}^{i,k}(y) = 0 \quad \text{in } Y_F, \quad \mathbf{v}^{i,k}(y) = 0 \quad \text{on } \partial Y_F, \\
-\operatorname{div}_y n_i^0(y) \left(\displaystyle\sum_{j=1}^{N} K_{ij}(y) z_j \big(\delta_{lj}\mathbf{e}^k + \nabla_y \theta_j^{l,k}(y)\big) + \mathrm{Pe}_i \mathbf{v}^{l,k}(y) \right) = 0 \ \text{ in } Y_F, \\
\displaystyle\sum_{j=1}^{N} K_{ij}(y) z_j \big(\delta_{lj}\mathbf{e}^k + \nabla_y \theta_j^{l,k}(y)\big) \cdot \nu = 0 \ \text{ on } \partial Y_F.
\end{cases}
$$

-IV- NUMERICAL RESULTS

All computations are done with FreeFem++.

Aqueous solution of $NaCl$ at $298^\circ K$.

Cation Na^+ with diffusivity $D_1^0 = 13.33\text{e}{-}10\, m^2/s$.

Anion Cl^- with diffusivity $D_2^0 = 20.32\text{e}{-}10\, m^2/s$.

The concentrations of the species in the bulk are considered equal : $n_1^0(\infty) = n_2^0(\infty) = 0.1 mole/l$.

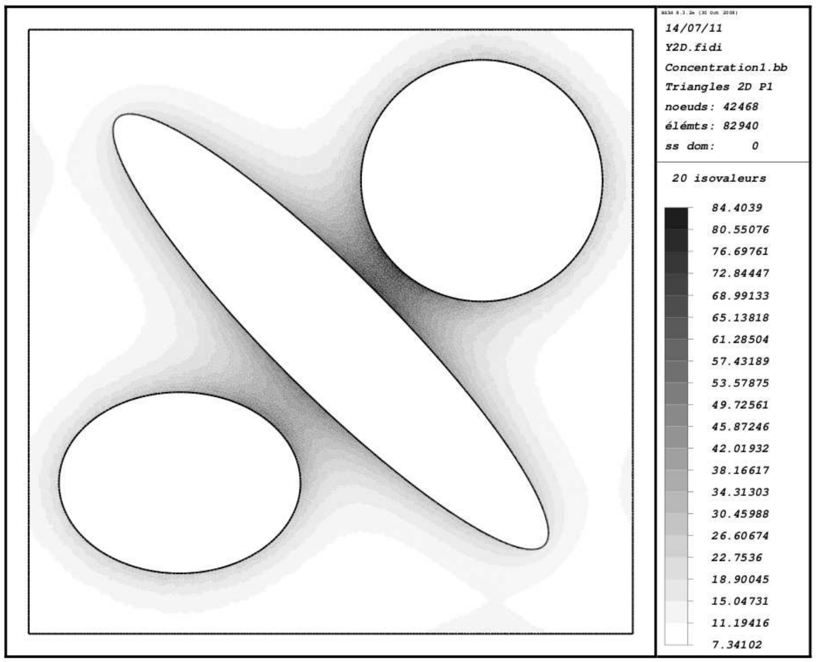
The dynamic viscosity η is equal to $0.89\text{e}{-}3\, kg/(m\, sec)$.

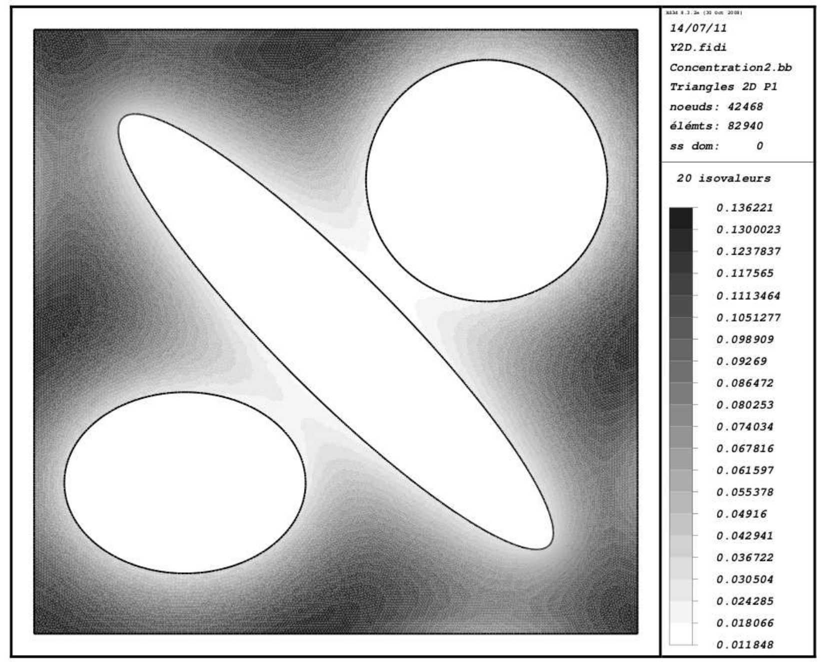
The pore size is $\ell = 5.e - 8m = 50nm$.

The ion radius is $\sigma = 2nm$.

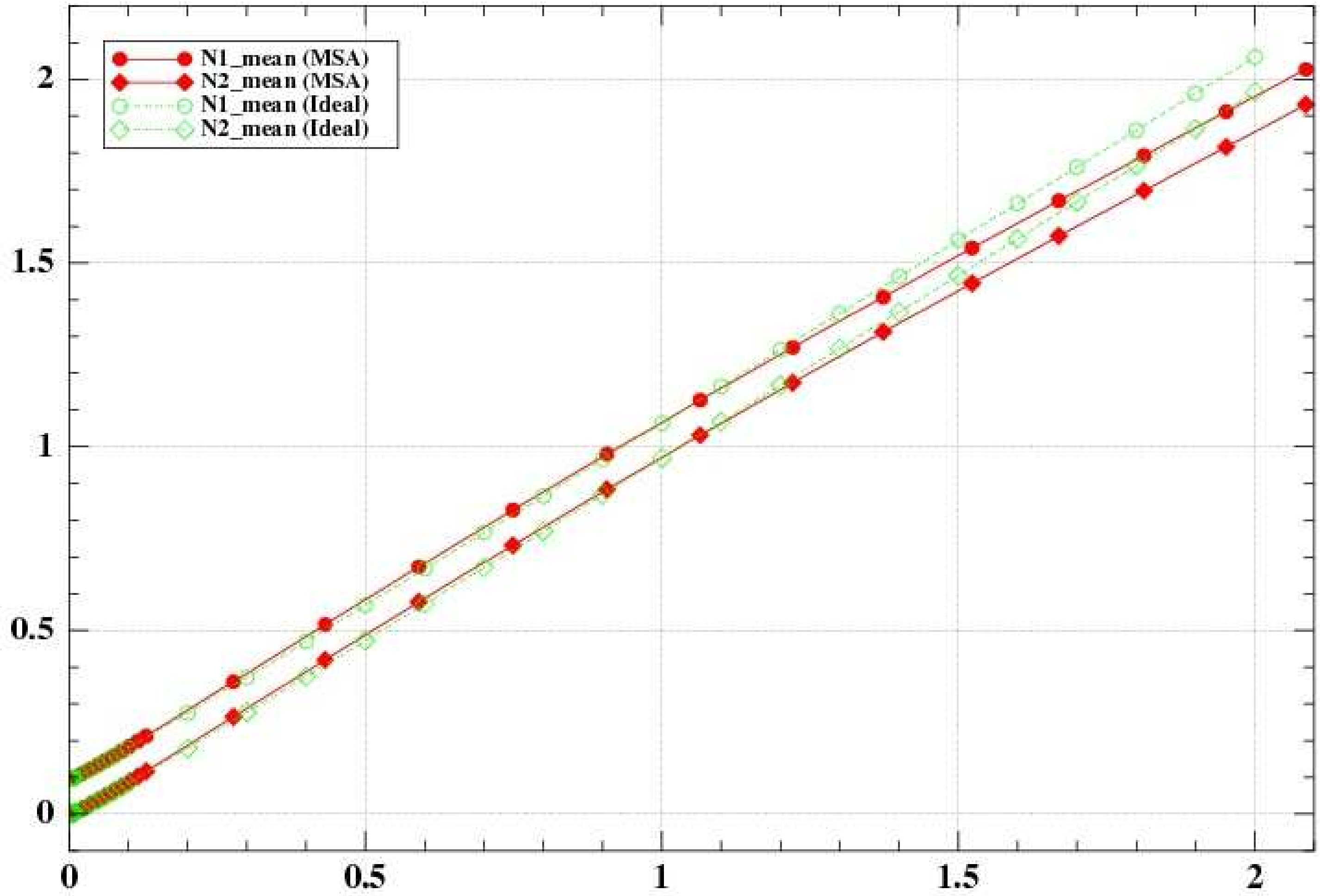
The surface charge density is (minus) $\Sigma^* = 0.129 C/m^2$.

Ideal case: cation concentration (left), anion concentration (right)

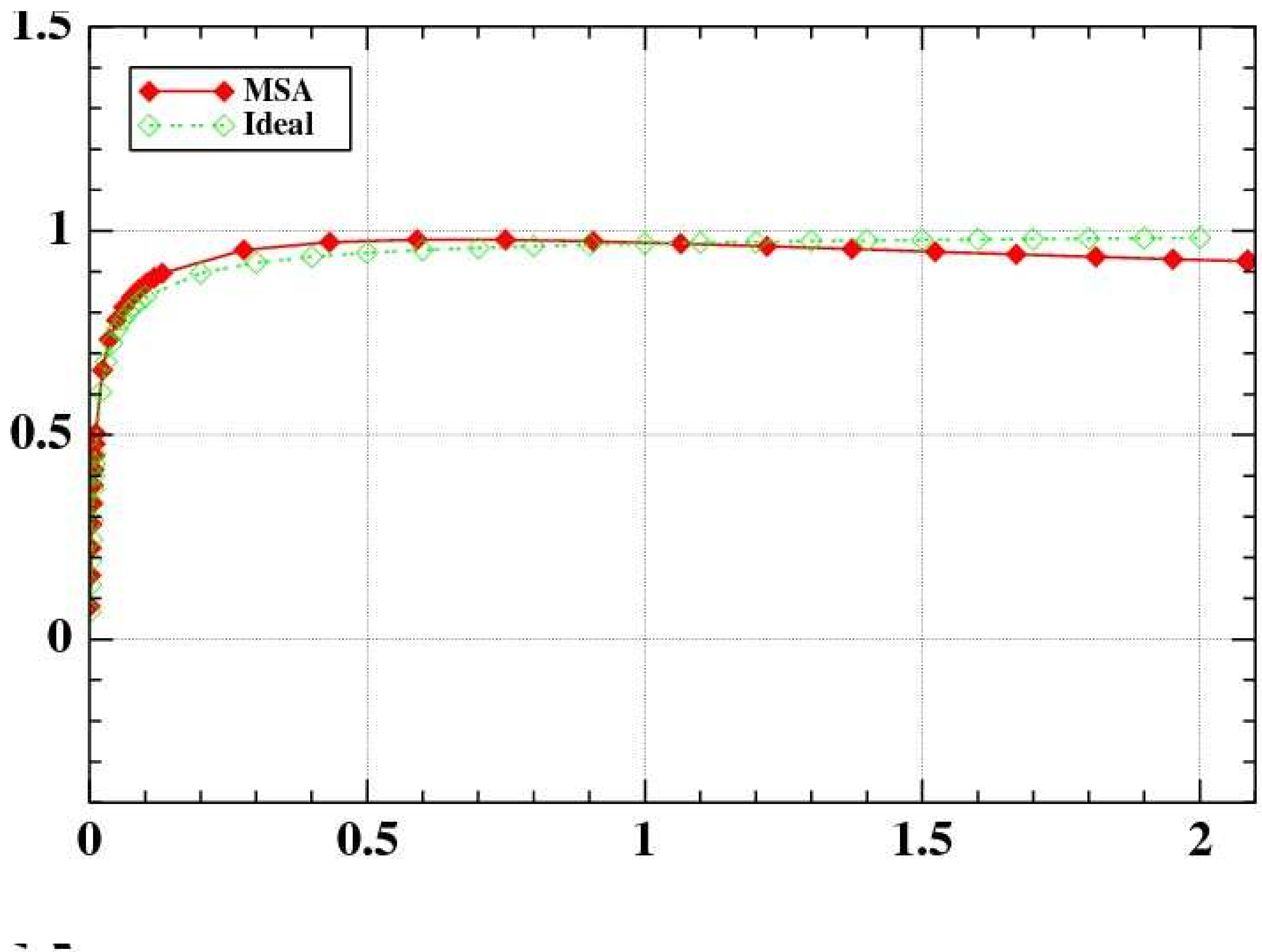




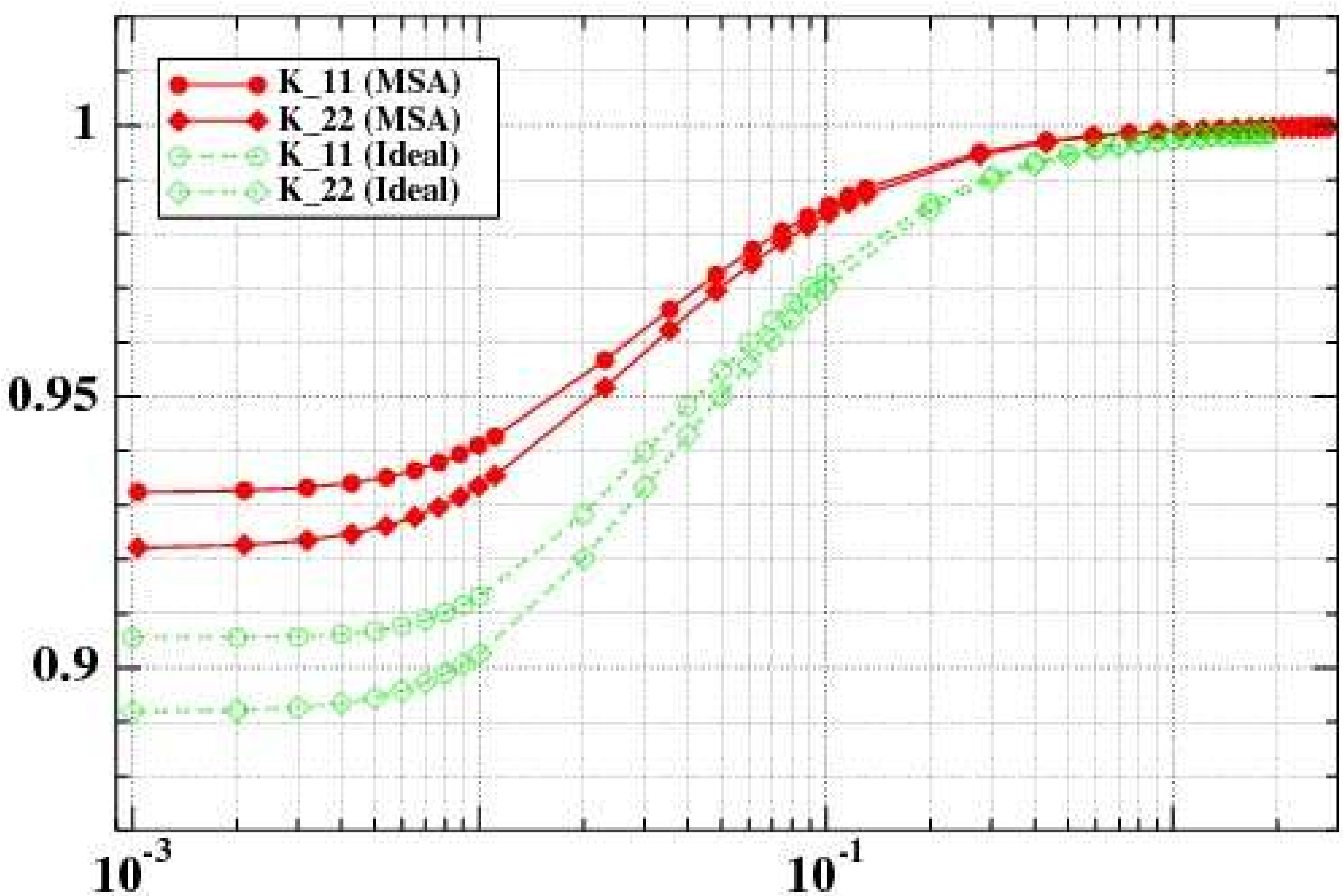
Averaged ion concentration as a function of $n_1^0(\infty) = n_2^0(\infty)$



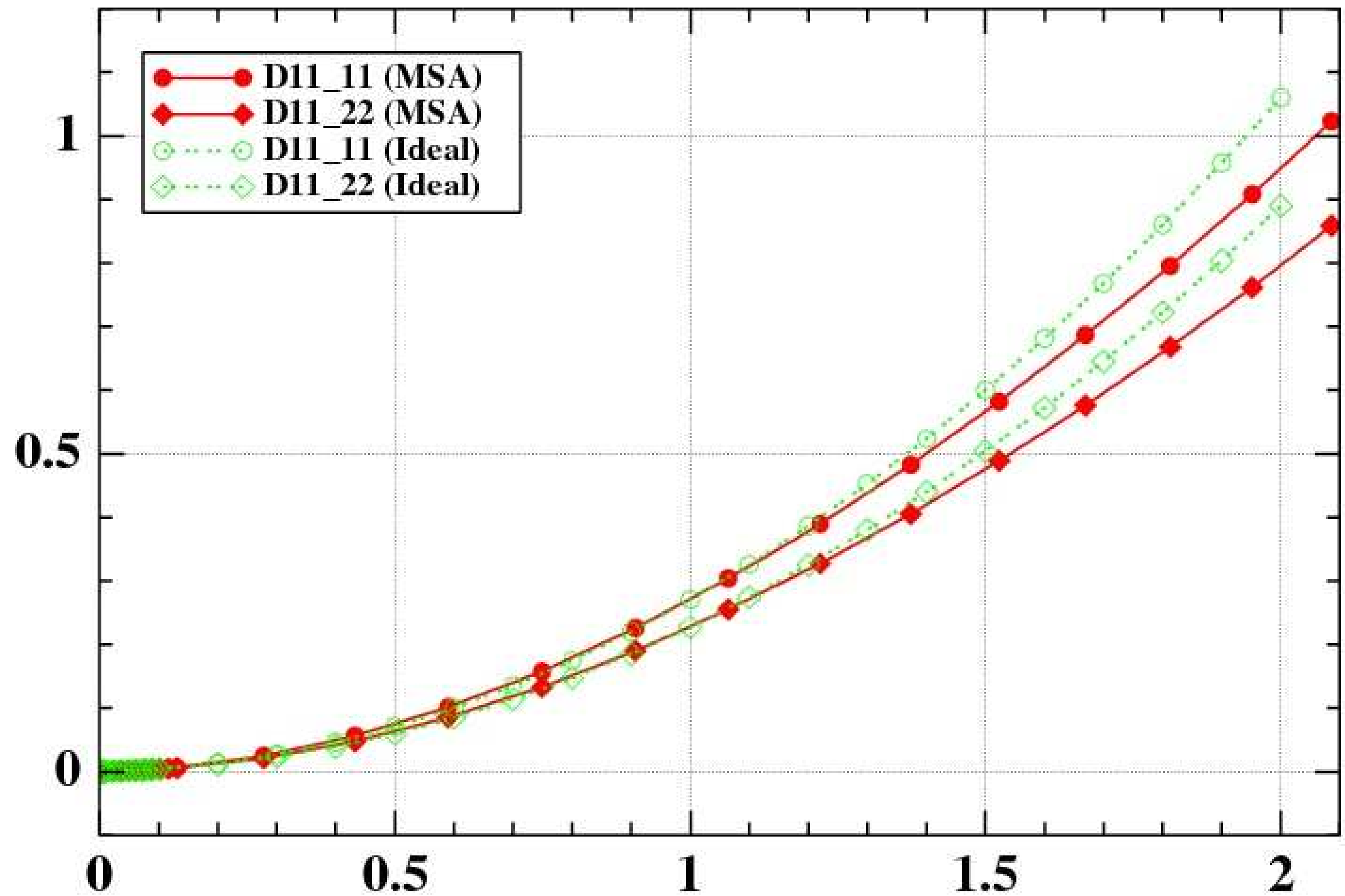
Rescaled anion concentration $N2mean/n_2^0(\infty)$ as a function of $n_1^0(\infty) = n_2^0(\infty)$



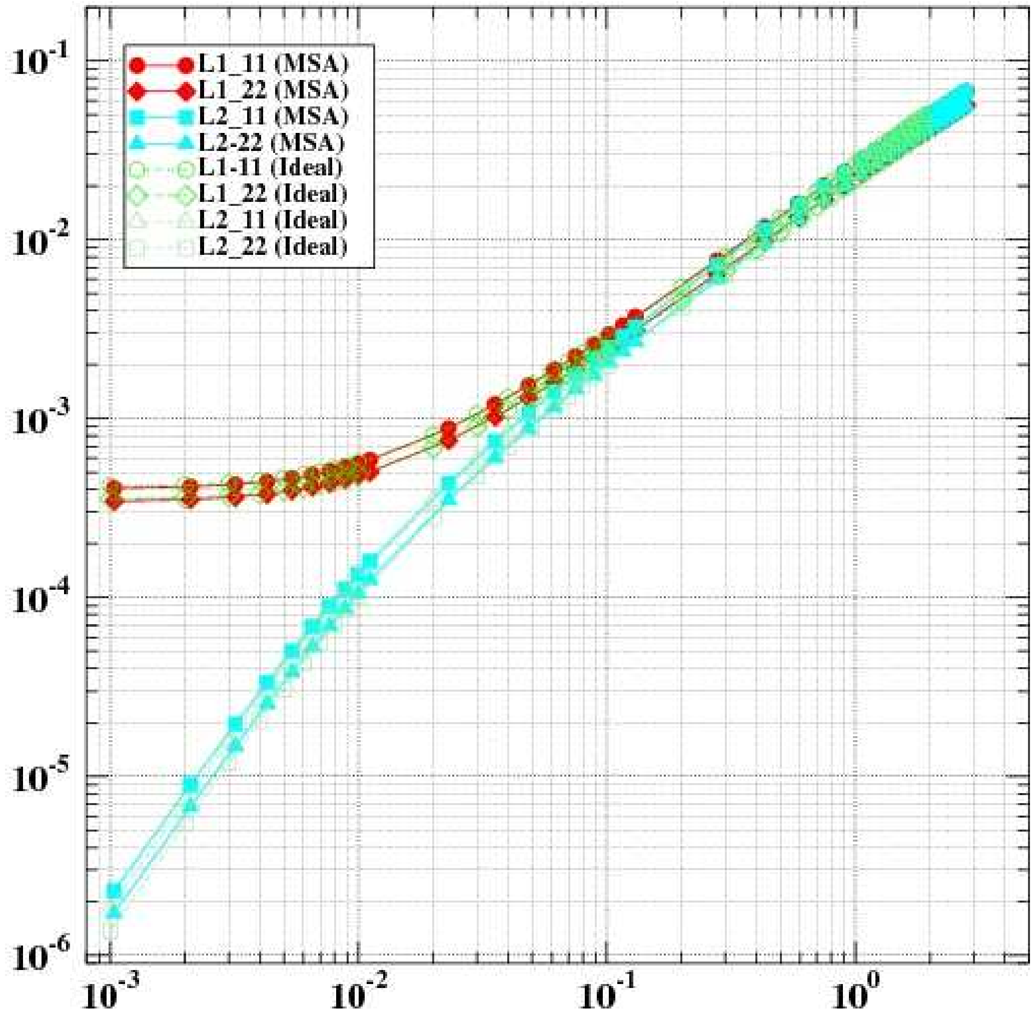
Permeability tensor (rescaled): variation of $n_1^0(\infty) = n_2^0(\infty)$



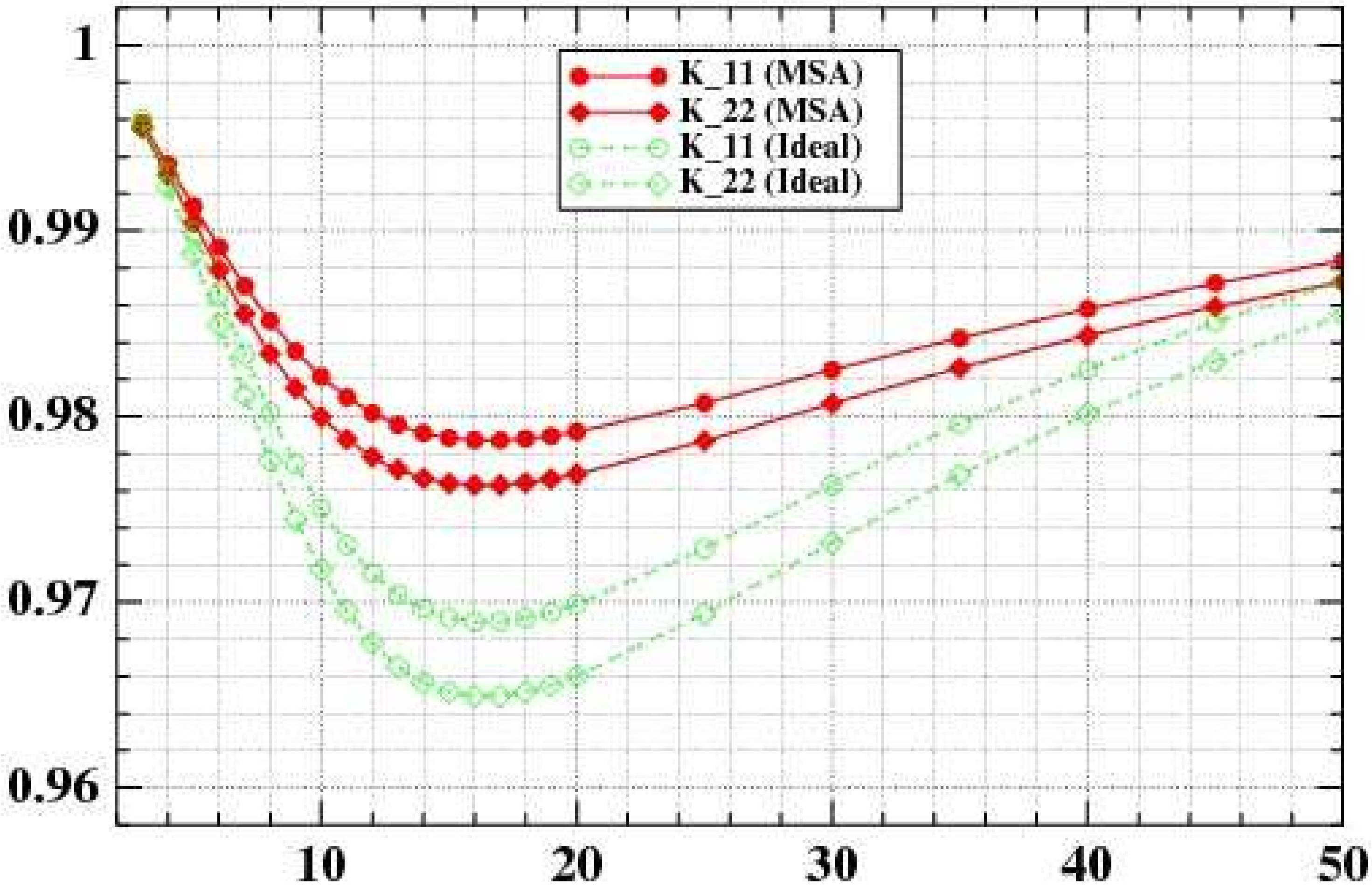
Diffusion tensor for the cation: variation of $n_1^0(\infty) = n_2^0(\infty)$



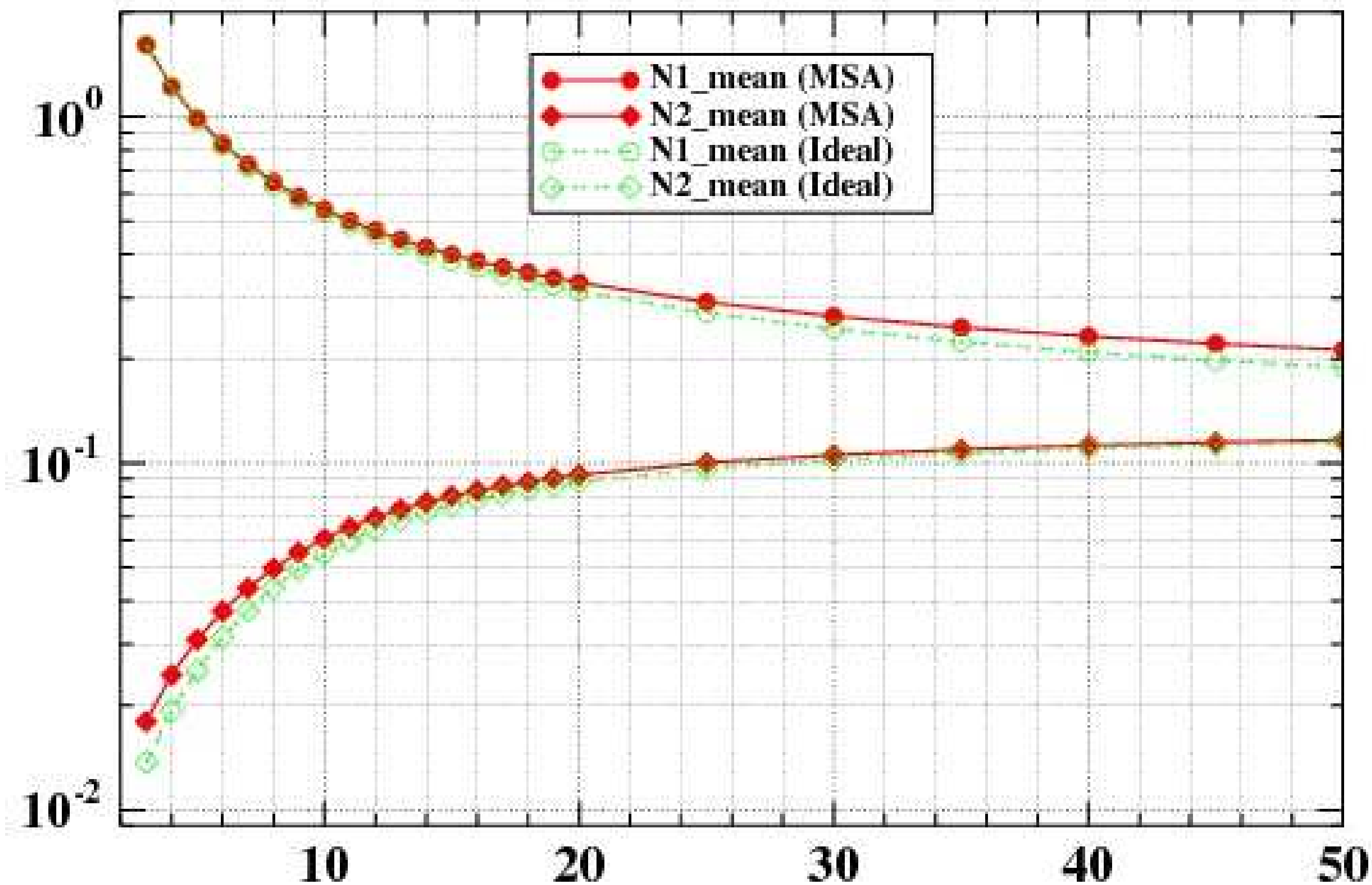
Coupling tensors $\mathbb{L}_i$: variation of $n_1^0(\infty) = n_2^0(\infty)$



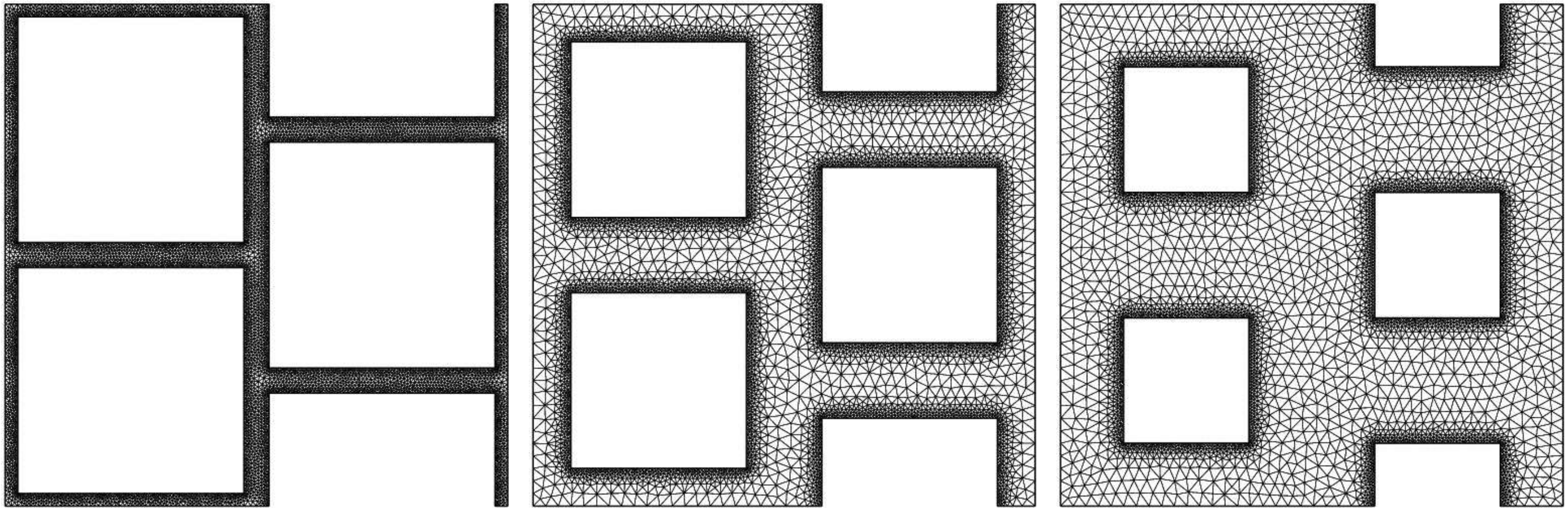
Permeability tensor : variation of the pore size (nm)



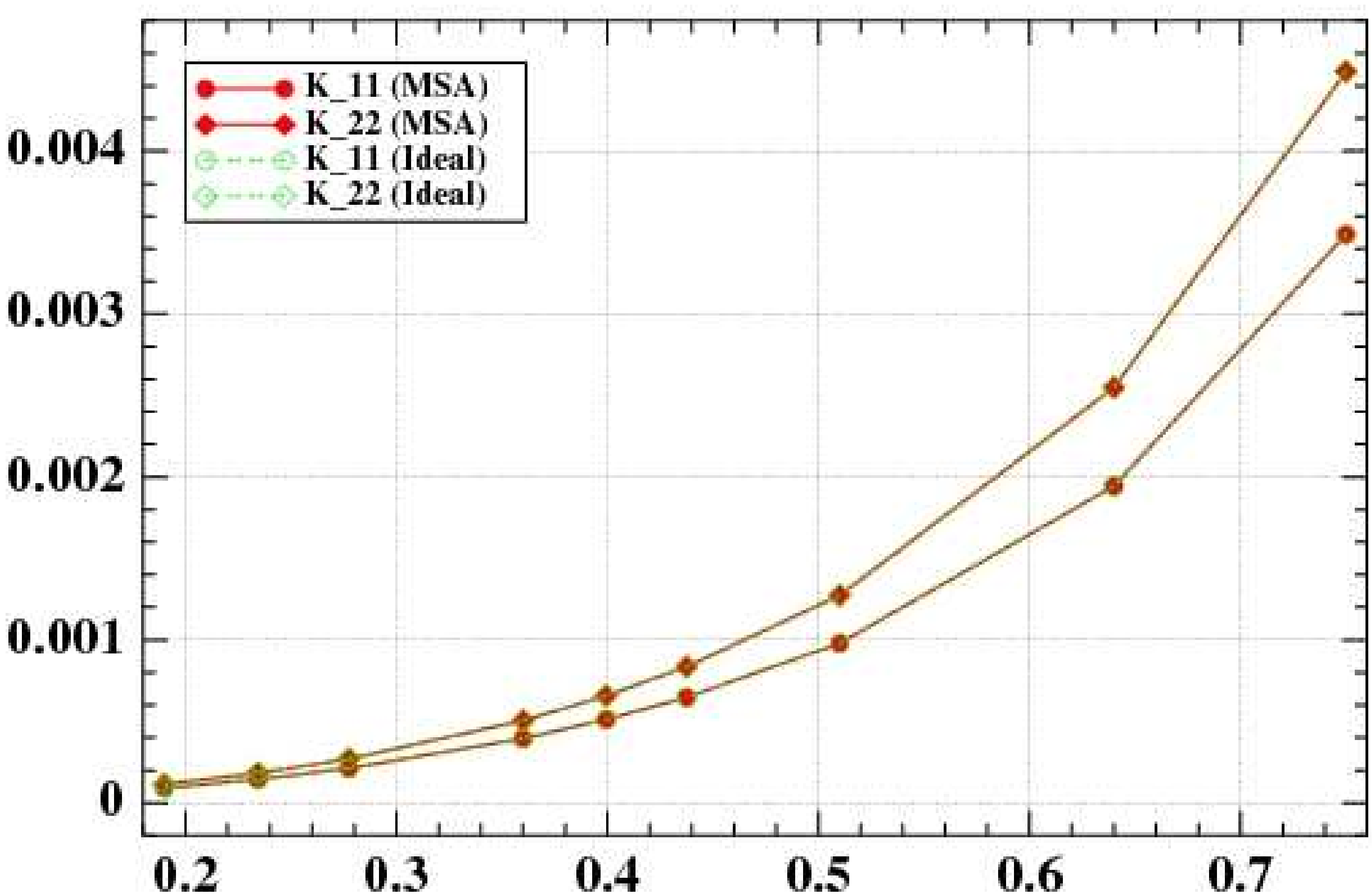
Averaged cell concentration : variation of the pore size (nm). Donnan effect



Variation of porosity: 0.19, 0.51 and 0.75



Variation of porosity: permeability



Diffusion versus porosity: cation (left), anion (right)