

## The Space Charge Model. A new analytical approximation solution of Poisson–Boltzmann equation: the extended homogeneous approximation

Jalal Dweik<sup>a</sup>, Hassan Farhat<sup>b</sup>, Joumana Younis<sup>c</sup>

Jinan University, Tripoli, Lebanon

<sup>a</sup>jalal.douwayk@jinan.edu.lb, <sup>b</sup>hassan.farhat@jinan.edu.lb, <sup>c</sup>joumana.younis@jinan.edu.lb

Corresponding author: Jalal Dweik, jalal.douwayk@jinan.edu.lb

**ABSTRACT** The validity of different analytical approximations solution is studied using the classical Poisson–Boltzmann (PB) equation based on a mean-field description of ions as ideal point charges in combination with the assumption of fully overlapped electrical double layers in the membrane pores. The electrical conductivity is calculated by numerical and approximate analytical methods in order to explain the process of ion transport. In this paper, a new analytical approximation named the extended homogeneous approximation (EH) is presented, which provides better results than the homogeneous approximation based on Donnan theory. Also, the results show that the electrical conductivity calculated by the EH, is coherent with the numerical method within specific limits.

**KEYWORDS** space charge model, Poisson–Boltzmann (PB) equation, electrical conductivity, extended homogeneous (EH) approximation

**FOR CITATION** Dweik J., Farhat H., Younis J. The Space Charge Model. A new analytical approximation solution of Poisson–Boltzmann equation: the extended homogeneous approximation. *Nanosystems: Phys. Chem. Math.*, 2023, **14** (4), 428–437.

### 1. Introduction

Nanofiltration membranes (NF) are particularly relevant for industrial applications because of their valuable features, such as pore diameters smaller than 2 nm [1–3]. NF has several advantages over other filtration processes, including lower energy consumption, lower operating pressures, and the ability to selectively remove specific components. One of the most interesting applications of these membranes is the separation of ions [4, 5]. The separation of ions in NF occurs due to a combination of size exclusion, charge repulsion, and electrostatic attraction. The selectivity of NF membranes can be further enhanced by adjusting the pH of the solution or using different membrane materials with specific surface charges. However, the mechanism of transport through NF membranes is not yet well-established. To shed light on this topic, numerous researchers have utilized different macro and mesoscopic approaches [6–10] to elucidate the physical and chemical mechanisms underlying membrane transport. The space charge (SC) model, which is based on the Poisson–Boltzmann (PB) equation [11], describes ions as ideal point charges and assumes fully overlapped electrical double layers in the membrane pores. This model is well-suited for studying ion transport through charged nanopores membrane. However, the accuracy of the SC model and other approximations, such as Donnan's theory or the homogeneous theory based on the electroneutrality in the pore, is challenged when applied to NF. In this paper, the SC model is applied to study the limit of effectiveness of different areas that provide a physical idea about the behavior of the salt-nanopore system using analytical approximations (homogeneous approximation, good exclusion of co-ions, and plane approximation) and numerical calculations obtained from the PB equation. In this paper, a new analytical approximation solution, named the extended homogeneous approximation (EH) is presented. This approximation allows the researchers to use only one approximation instead of all other approximations mentioned above within specific limits. Finally, the validity of the EH approximation is studied by calculating the electrical conductivity and depends on three main parameters: pore radius, concentration of ions in the bulk, and surface charge density of the pore. These three parameters play a significant role in the transport through the pores. The remainder of this paper is organized as follows. The description of the models is given in section 2. The results and discussion are presented in section 3. The conclusions and suggestions are given in section 4.

### 2. Space charge model

The space charge model was developed by Osterle and colleagues [12–14]. It is a theoretical framework used to describe the behaviour of charged solutes near charged surfaces, such as nanofiltration membranes. It considers the electrostatic interactions between the charged solutes and the charged membrane surface. This model considers axial and radial variations in pressure, electric potential, and concentration. Assume a simple cylindrical pore of radius  $r_p$  and length  $d \gg r_p$ , filled with an aqueous solution with two ionic species [ $i = 1$  (counter-ion), 2 (co-ion)]. The pore's

electrical properties are defined by an assumed uniform surface charge density that depends on the ionic concentrations and the pore surface pH (Fig. 1).

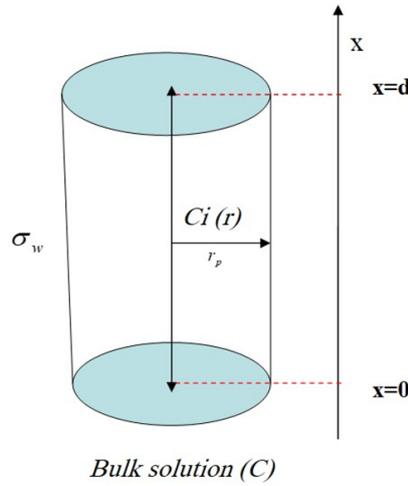


FIG. 1. Description of the model with the important parameters

Suppose that the ionic transport is at the steady state, so that there is no time function in the governing equations. The continuity equation for each ion can be expressed as

$$\nabla \cdot \vec{j}_i = 0, \quad (1)$$

where  $\vec{j}_i$  is the molar flux density of ion  $i$ , described by the extended Nernst–Planck equation

$$\vec{j}_i = -D_i \nabla c_i - \frac{F}{RT} z_i D_i c_i \nabla \Phi + c_i \vec{u}, \quad (2)$$

where  $D_i$  is the local diffusion coefficient of the ion  $i$ ,  $c_i$  is the local concentration of the species considered,  $z_i$  is the ion valence,  $\Phi$  is the total local electric potential,  $F$  is the Faraday constant.

The flow velocity is obtained by the Navier–Stokes equation. Neglecting all inertial terms (“creeping flow approximation”) and the inclusion of electrical forces, the Navier–Stokes equation is expressed by

$$\eta \nabla^2 \vec{u} = \rho \nabla \Phi + \nabla p, \quad (3)$$

where  $p$  is the local pressure applied to the fluid,  $\eta$  is the dynamic viscosity of the solution,  $\rho$  is the ionic charge density, which is defined by the following formula

$$\rho = F \sum_{i=1}^2 z_i c_i. \quad (4)$$

When the density of the fluid is constant, there is, in addition, the incompressibility condition

$$\nabla \cdot \vec{u} = 0. \quad (5)$$

The key of the space charge model is the Poisson–Boltzmann (PB) equation for electric potential and ionic concentration

$$\nabla^2 \Phi = \frac{\rho}{\varepsilon}, \quad (6)$$

$$\nabla^2 \Phi = \frac{\partial^2 \Phi}{\partial x^2} + \frac{1}{r} \frac{\partial \Phi}{\partial r} + \frac{\partial^2 \Phi}{\partial r^2}, \quad (7)$$

where  $\varepsilon = \varepsilon_0 \varepsilon_r$  is the absolute dielectric constant of the solution,  $\varepsilon_0$  is the dielectric constant in vacuum ( $\varepsilon_0 = 8.85 PF/m$ ),  $\varepsilon_r$  is the relative dielectric constant for water ( $\varepsilon_r = 78.54$ ).

The normal component of the molar flux density and velocity is equal to zero at the surface. Thus the boundary condition for Eq. (6) takes the following form:

$$\vec{j}_{i,r} \Big|_{r=r_p} = \frac{\partial c_i}{\partial r} \Big|_{r=r_p} + \frac{z_i F}{RT} c_i \frac{\partial \Phi}{\partial r} \Big|_{r=r_p} = 0. \quad (8)$$

By symmetry, another boundary condition of Eq. (6) which corresponds to the concentration and electric potential at the pore center is fined:

$$\frac{\partial c_i}{\partial r} \Big|_{r=0} = 0, \quad \frac{\partial \Phi}{\partial r} \Big|_{r=0} = 0, \quad (9)$$

and so

$$j_{i,r} \Big|_{r=0} = 0. \quad (10)$$

The global surface charge  $\sigma_w$  is related to the gradient of the potential *via* the Gaussian equation:

$$\frac{\partial \Phi}{\partial r} \Big|_{r=r_p} = \frac{\sigma_w}{\varepsilon}. \quad (11)$$

If the tangential component of the velocity at the pore surface is zero (no slip), then we can write the boundary condition of the Navier–Stokes equation

$$u_x \Big|_{r=r_p} = 0. \quad (12)$$

By symmetry,

$$\frac{\partial u_x}{\partial r} \Big|_{r=0} = 0. \quad (13)$$

The total local electric potential  $\Phi(x, r)$  can be divided into two parts:

$$\Phi(x, r) = \psi(r) + \varphi(x), \quad (14)$$

where  $\psi(r)$  is the potential due to the electrical double layer at the surface on the radial direction and the potential  $\varphi(x)$  is due to the bulk (outside the pore) along the  $x$  axis. Assume that the variation of  $\varphi(x)$  along  $x$  axis is negligible compared to the variation of the radial component, then Eq. (7) becomes as follows

$$\nabla^2 \Phi \approx \frac{1}{r} \frac{\partial \psi}{\partial r} + \frac{\partial^2 \psi}{\partial r^2}. \quad (15)$$

Assuming that Eqs. (8) and (10) allow the approximation  $j_i(r) = 0$  to be used for any  $r$ , then this equation can be integrated between  $0 < r < r_p$  to find the “radial equilibrium” approximation which gives one the concentration  $c_i(r)$  (Boltzmann distribution)

$$c_i(r) \approx k_i(r) v_i C, \quad (16)$$

where

$$k_i(r) = \exp \left[ -\frac{z_i F \psi(r)}{RT} \right], \quad (17)$$

$C$  is the electrolyte concentration equivalent to the concentration of a bulk solution in equilibrium with the pore at position  $x$  and  $v_i$  (the stoichiometric coefficient) represents the number of ions coming from the dissociated electrolytes. In the case of two ionic species  $i = 1, 2$ , the condition of electroneutrality is described by  $v_1 z_1 + v_2 z_2 = 0$  or  $v_1 |z_1| = v_2 |z_2|$ :

$$(\text{Counter-ion})_{z_1}^{\nu_1} (\text{Co-ion})_{z_2}^{\nu_2} \longrightarrow \nu_1 (\text{Counter-ion})^{z_1} + \nu_2 (\text{Co-ion})^{z_2}$$

The index ( $i = 1$ ) represents the counter ions and the index ( $i = 2$ ) represents the co-ions.

After substitution of Eqs. (15) and (16) in (6), the Poisson–Boltzmann equation which determines the electric potential inside the pore is obtained. It is presented in dimensionless form [14] by the following relation:

$$\frac{2}{\tilde{r}} \frac{\partial}{\partial \tilde{r}} \left( r \frac{\partial \tilde{\psi}}{\partial \tilde{r}} \right) \approx \left( \frac{r_p}{\lambda_c} \right)^2 \left( e^{+\tilde{\psi}} - e^{-\tau \tilde{\psi}} \right), \quad (18)$$

where

$$\tilde{\psi} = -\frac{z_1 F \psi(x, \tilde{r})}{RT} \geq 0, \quad \tilde{r} = \frac{r}{r_p}, \quad \tau = \frac{|z_2|}{|z_1|}, \quad (19)$$

$\lambda_c$  is the Debye length associated with the concentration  $C$  given by:

$$\lambda_c = \left( \frac{RT\varepsilon}{2v_1 z_1^2 F^2 C} \right) \propto C^{-1/2}. \quad (20)$$

The boundary conditions at the center and surface of the pore can be presented in dimensionless form [11–14]:

$$\frac{\partial \tilde{\psi}}{\partial \tilde{r}} \Big|_{\tilde{r}=1} = 4\sigma^*, \quad \frac{\partial \tilde{\psi}}{\partial \tilde{r}} \Big|_{\tilde{r}=0} = 0, \quad (21)$$

where

$$\sigma^* = \frac{1}{4} \left( \frac{r_p}{\lambda_m} \right)^2, \quad (22)$$

$\lambda_m$  is the Debye length associated with the membrane charge density

$$\lambda_m = \left( \frac{2\varepsilon RT}{|z_1| F^2 |X_m|} \right)^{1/2} \propto |X_m|^{-1/2}, \quad (23)$$

and  $R$  is the constant of the ideal gas and  $X_m$  is defined by

$$X_m = \frac{2\sigma_w}{F r_p}. \quad (24)$$

The membrane charge density  $|X_m|$  is expressed in moles per unit volume of the pore. It is proportional to  $|\sigma_w|$  and inversely proportional to the radius of the pore  $r_p$ . The average flux density in the pore can be calculated by integrating the local flux using the formula:

$$\bar{j}_{i,x} = \frac{2}{r_p^2} \int_0^{r_p} j_{i,x} r dr. \quad (25)$$

The average electrolyte flow density is denoted by  $J$ , the volume flow density – by  $J_v$  and the current density – by  $\bar{I}$ . It should be noted that the volume flow rate  $J_v$  is a very good approximation to the barycentric velocity  $U_m$  [13].

$$J = \sum_{i=1}^2 \bar{j}_i, \quad J_v = \bar{u}_x, \quad (26)$$

with the current density given by

$$\bar{I} = F \sum_{i=1}^2 z_i \bar{j}_i. \quad (27)$$

From Eq. (3), using Eqs. (8) and (13) for  $u_x$  and component  $x$  from Eq.(2) and averaging the fluxes over the pore cross-section by Eq. (27), the following system of transport equations is obtained:

$$\begin{aligned} J_v &= -L_{11} \left( \frac{\partial P_0}{\partial x} \right) - L_{12} \left( \frac{\partial \mu}{\partial x} \right) - L_{13} \left( \frac{\partial \varphi}{\partial x} \right), \\ J &= -L_{21} \left( \frac{\partial P_0}{\partial x} \right) - L_{22} \left( \frac{\partial \mu}{\partial x} \right) - L_{23} \left( \frac{\partial \varphi}{\partial x} \right), \\ \bar{I} &= -L_{31} \left( \frac{\partial P_0}{\partial x} \right) - L_{32} \left( \frac{\partial \mu}{\partial x} \right) - L_{33} \left( \frac{\partial \varphi}{\partial x} \right), \end{aligned} \quad (28)$$

where  $\mu$  is the chemical potential given by

$$\mu = RT \ln(C), \quad (29)$$

and  $P_0$  is the effective pressure

$$P_0 = P - \Pi, \quad (30)$$

with  $\Pi$  the osmotic pressure defined according to:

$$\Pi = RT(v_1 + v_2)C. \quad (31)$$

The term of conductivity is given by

$$\kappa = L_{33} = \bar{I} \left( \frac{\partial \varphi}{\partial x} \right)^{-1}, \quad (32)$$

where

$$L_{33} = L'_{33} + L''_{33}, \quad (33)$$

$L_{33} = [\text{diffusive conductivity}] + [\text{convective conductivity}]$  such as

$$\kappa_D = L'_{33} = \left( \frac{C v_1 z_1 F^2}{RT} \right) [D_1 z_1 \bar{k}_1 - D_2 z_2 \bar{k}_2], \quad (34)$$

$$\kappa_c = L''_{33} = \left( (C v_1 z_1 F r_p)^2 \eta^{-1} \right) [\bar{k}_1 g - \bar{k}_2 g]. \quad (35)$$

Using the definition

$$\bar{y} = 2 \int_0^1 y \tilde{r} d\tilde{r}, \quad (36)$$

$\bar{k}_i$  and  $\bar{k}_i g$  can be calculated with the function which is defined [12, 13] by

$$g = \int_{\tilde{r}}^1 \frac{1}{\tilde{r}''} \int_0^{\tilde{r}''} (k_1 - k_2) \tilde{r}' d\tilde{r}' d\tilde{r}'' . \quad (37)$$

The function defined above can be simplified by using the PB equation and Green's theorem to find

$$g(\tilde{r}) = 2 (r_p / \lambda_c)^{-2} [\tilde{\psi}(\tilde{r}) - \tilde{\psi}_w]. \quad (38)$$

The conductivity can therefore be calculated from the electrostatic potential  $\tilde{\psi}(\tilde{r})$  inside the pore. So, in this case, it is necessary to solve the PB equation in dimensionless form to evaluate  $\tilde{\psi}(\tilde{r})$  ( $\tilde{\psi}_w = \tilde{\psi}(\tilde{r}_p)$ ). This potential is a function of the dimensionless parameters  $r_p/\lambda_m$  and  $r_p/\lambda_c$ , which are proportional, respectively, to  $|\sigma_w|^{1/2}$  and  $C_s^{1/2}$

$$\frac{r_p}{\lambda_m} = 7.485 (z_1 r_p \sigma_w)^{1/2}, \quad \frac{r_p}{\lambda_c} = 3.288 (\nu_1 z_1^2 C r_p^2)^{1/2}, \quad (39)$$

with the surface charge density  $\sigma_w$  in  $C/m^2$ , the pore radius  $r_p$  in nm and the bulk concentration  $C$  in moles/l.

### 2.1. Homogeneous analytical approximation (H)

The homogeneous approximation is used to analyze the behaviour of ions inside a cylindrical pore. In a charged pore, ions move through the pore driven by electrostatic forces due to the presence of a fixed charge distribution on the pore surface. The homogeneous approximation assumes that the charge density along the length of the pore is uniformly distributed. By making this approximation, the problem of ion transport in the cylindrical pore can be simplified. This simplification greatly facilitates the mathematical analysis. The homogeneous theory, which assumes a uniform potential, is valid when the pore radius is small and the surface charge density is lower, according to the space charge model [15]. Within the membrane pore, the macroscopic Donnan equilibrium theory can be used in combination with global charge electroneutrality then

$$\sum_{i=1}^2 z_i \bar{c}_i + X_m = 0, \quad (40)$$

with

$$\bar{c}_i = k_i \nu_i C, \quad (41)$$

where

$$k_i = \exp \left[ \frac{z_i}{|z_1|} \tilde{\psi}_0 \right]. \quad (42)$$

The value of the potential  $\tilde{\psi}_0$  is given by Eq. (42) which also allows one to write down:

$$\xi = k_h - k_h^{-\tau} = \frac{|X_m|}{|z_1| \nu_1 C}, \quad (43)$$

with

$$k_h = e^{\tilde{\psi}_0} \quad (44)$$

and  $\xi$  is the normalized membrane charge density in dimensionless form given in terms of  $(r_p/\lambda_m)$  and  $(r_p/\lambda_c)$  by

$$\xi = 4 \frac{(r_p/\lambda_m)^2}{(r_p/\lambda_c)^2}. \quad (45)$$

In the case of the symmetric salt ( $\tau = 1$ ), the solution of the quadratic equation  $k_h^2 - \xi k_h - 1 = 0$  is given by the formula

$$k_h = \frac{1}{2} \left( \xi + \sqrt{\xi^2 + 4} \right). \quad (46)$$

### 2.2. The approximate solutions of the Poisson–Boltzmann equation

**2.2.1. Numerical method.** The simplified Poisson–Boltzmann Eq. (18) is a non-linear partial differential equation and a fundamental equation used to find the electrostatic potential in porous systems [14]. In this work, a numerical approach uses the finite difference method to approximate solutions in one dimension. The proposed numerical method involves discretizing the spatial coordinate, applying suitable boundary conditions, and iteratively updating the electrostatic potential until convergence.

**2.2.2. Analytical solution.** Additionally, the article explores analytical approximations solution for specific scenarios with simplified charge distributions and boundary conditions, providing insights into the behavior of simple systems (*Good Co-Exclusion Approximation, Plane approximation, and Debye–Hückel approximation*). By comparing the numerical and analytical approaches, researchers gain valuable tools to efficiently analyze charged systems in radial direction and better understand their electrostatic behaviour in porous system. However, the validity of the analytical approximations depends on the value of the dimensional electrostatic potential  $\tilde{\psi}(\tilde{r})$ . Therefore, the ranges of validity of different types of analytical approximations vary in function of the parameters  $(r_p/\lambda_m, r_p/\lambda_c)$ .

2.2.3. *Good Co-Exclusion Approximation (GCE).* The concept of ‘‘Co-Exclusion’’ arises from the fact that ions of the same charge have a strong tendency to repel each other, leading to an excluded volume effect. The ‘‘Good Co-Exclusion Approximation’’ is an approach used to simplify the PBE solution by incorporating this excluded volume effect, particularly, for ionic solutions with concentrated charges. In the Good Co-Exclusion Approximation, the ions are treated as hard spheres, and their excluded volume effects are taken into account by modifying the boundary conditions in the PBE. Instead of considering the actual physical boundaries of the ions, the boundary conditions are adjusted to reflect the presence of neighboring ions and their excluded volumes. This approximation assumes that the ions cannot penetrate each other’s excluded volumes and considers their spatial arrangement to account for the effect of ionic crowding. By using the Good Co-Exclusion Approximation, the PBE can be simplified, and the computational cost can be significantly reduced while still providing reasonably accurate results for systems with concentrated ionic solutions. However, it is important to note that this approximation is most applicable to systems with relatively low ion concentration. It is valid for high potential values  $\tilde{\psi} > 1$ , because the second term on the right of Eq. (18) becomes negligible. In this limit, the solution of PB equation [13, 14] between  $0 \leq \tilde{r} \leq 1$  is given by

$$\tilde{\psi}(\tilde{r}) = 2 \ln \left( \frac{\lambda_c}{r_p} \right) + f(\tilde{r}; \sigma^*), \quad (47)$$

with

$$f(\tilde{r}; \sigma^*) = \ln \left[ \frac{16\sigma^*(1 + \sigma^*)}{(1 + \sigma^* - \sigma^*\tilde{r}^2)^2} \right]. \quad (48)$$

By combining Eq. (22) and Eq. (47), the GEC approximation is valid when  $\tilde{\psi}(0) \geq 1$  (minimum value of  $\tilde{\psi}$  at the origin)

$$\left( \frac{r_p}{\lambda_c} \right) \leq 2.426 \left( \frac{r_p}{\lambda_m} \right) \left[ 4 + \left( \frac{r_p}{\lambda_m} \right)^2 \right]^{-1/2}. \quad (49)$$

Staying within the range of validity of the GEC approximation, when the value of  $\sigma^*$  becomes small, the function appearing in Eq. (47) can be simplified. In this case, the homogeneous approximation for the electrostatic potential is valid in the whole range  $0 < \tilde{r} < 1$  with

$$e^{\tilde{\psi}(\tilde{r})} \approx \frac{|X_m|}{|z_1|v_1 C f} = \frac{16\sigma^*}{(r_p/\lambda_c)^2}. \quad (50)$$

The homogeneous GEC approximation is valid when  $(r_p/\lambda_m) < 2$  and inequality (49) simplifies to  $(r_p/\lambda_c) < 1.21 (r_p/\lambda_m)$ .

2.2.4. *Plane and Debye–Hückel approximation.* Solving the Poisson–Boltzmann equation directly in three dimensions can be challenging, especially for complex systems. In some cases, it is possible to simplify the equation and make approximations to make the problem more tractable. One such approximation is the plane approximation or the Debye–Hückel (DH) approximation. The plane approximation assumes that the charge distribution is confined to a single plane, and the system’s behaviour is effectively two-dimensional. This approximation is valid for situations where the charged species are confined to a surface. Solving this simplified one-dimensional Poisson–Boltzmann equation can provide valuable insights into the electrostatic behaviour near the charged plane, making it easier to study systems like charged membranes. The DH approximation is a method to simplify the PB equation under specific conditions related to dilute solutions and weak electrostatic interactions between ions. For a solution containing a symmetric salt at a concentration  $C$ , the nonlinear PB equation can be solved analytically, where the potential  $\tilde{\psi}$  is different from zero only at the pore surface. In this case one has:

$$\frac{1}{\tilde{r}} \frac{\partial \tilde{\psi}}{\partial \tilde{r}} \ll \frac{\partial^2 \tilde{\psi}}{\partial \tilde{r}^2}. \quad (51)$$

Apply the change of variable  $\tilde{r} = 1 - \tilde{t}$ , and consider a uniform potential  $\psi_w$  at the surface, the variation of the potential becomes strong near the surface of the pore, as opposed to inside the pore where its value is close to zero. In this approximation [14], the electrostatic potential at a distance  $\tilde{t}$  from the surface satisfies the plane approximation of the PB equation.

$$\frac{\partial^2 \tilde{\psi}}{\partial \tilde{t}^2} \cong \left( \frac{r_p}{\lambda_c} \right)^2 \sinh(\tilde{\psi}). \quad (52)$$

After integration, the solution of this equation can be found using the boundary condition at the pore surface:

$$\tilde{\psi}(\tilde{t}) = 2 \ln \left[ \frac{1 + u(\tilde{t})}{1 - u(\tilde{t})} \right], \quad (53)$$

where

$$u = \tanh(h) e^{-(r_p/\lambda_c)\tilde{t}}, \quad h = \frac{1}{2} \operatorname{arsinh} \left[ \frac{(r_p/\lambda_m)^2}{2(r_p/\lambda_c)} \right]. \quad (54)$$

At the limit, for a low potential and dilute solution, the solution takes the form of the plane DH approximation.

$$\tilde{\psi}(\tilde{t}) \cong \frac{(r_p/\lambda_m)^2}{(r_p/\lambda_c)} e^{-(r_p/\lambda_c)\tilde{t}}. \quad (55)$$

We observe that the plane approximation is valid when  $r_p/\lambda_c > 11$ . It's important to note that the plane approximation is valid only when the charged particles are distributed primarily along the x-axis and when the distance between the charged particles and the plane is much larger than the characteristic size of the charged particles themselves. In cases where the system deviates significantly from these conditions, the plane approximation may not be accurate.

### 3. Results and discussion

#### 3.1. Extended homogeneous approximation (EH)

EH is a new analytical approximation solution based on the Donnan theory (homogeneous approximation in the pore). It can be studied by adding a small radial variation  $\tilde{\psi}_1(\tilde{r}) \leq 1$ . The potential can be expressed as  $\tilde{\psi}(\tilde{r}) = \tilde{\psi}_0 + \alpha\tilde{\psi}_1(\tilde{r})$ , an approximate analytical solution to Eq. (18) with a development parameter,  $\alpha$ , which depends on  $|\sigma_w|$  and takes the value 1 at the end of the calculation. The expansion of the PB equation to the first order of  $\alpha$  according to the boundary condition given by:

$$2\nabla^2(\tilde{\psi}_1) - W\tilde{\psi}_1 = R, \quad (56)$$

$$\left. \frac{\partial \tilde{\psi}_1}{\partial \tilde{r}} \right|_{\tilde{r}=1} = \left( \frac{r_p}{\lambda_m} \right)^2, \quad (57)$$

$$\left. \frac{\partial \tilde{\psi}_1}{\partial \tilde{r}} \right|_{\tilde{r}=0} = 0, \quad (58)$$

with

$$W = \left( \frac{r_p}{\lambda_c} \right)^2 [k_h + \tau k_h^{-\tau}], \quad R = \left( \frac{r_p}{\lambda_c} \right)^2 [k_h - k_h^{-\tau}]. \quad (59)$$

For a given value of  $\tilde{\psi}_0$ , the analytical solution to Eq. (73) is as follows

$$\tilde{\psi}_1(\tilde{r}) = \frac{(r_p/\lambda_m)^2}{m} \left[ \frac{I_0(m\tilde{r})}{I_1(m)} \right] - 2 \left( \frac{r_p/\lambda_m}{m} \right)^2, \quad (60)$$

with

$$m = (W/2)^{1/2}, \quad (61)$$

$I_0$  and  $I_1$  are the modified Bessel functions of order 0 and 1, respectively.

When the value of  $\tilde{\psi}_0$  is zero, we fall on the Debye–Hückel approximation, for which the approximation is valid if  $\tilde{\psi}_1(1) < 1$  then

$$V > \left( \frac{r_p}{\lambda_m} \right)^2 \left[ \frac{I_0(V)}{I_1(V)} \right], \quad (62)$$

with

$$V = \left( \frac{1 + \tau}{2} \right)^{1/2} \left( \frac{r_p}{\lambda_c} \right). \quad (63)$$

The EH approximation can be represented in the plane ( $r_p/\lambda_m, r_p/\lambda_c$ ) by the inequality  $\tilde{\psi}_1(1) < 1$ . If this radial function tends to 0, it moves to the domain of validity of the homogeneous approximation ( $r_p/\lambda_m < 2$ ). For the GEC zone, the extended homogeneous approximation is valid for  $r_p/\lambda_m < 2.4$ , while outside the GEC zone, the EH zone includes and extends the homogeneous and the Debye–Hückel (DH) zones. Fig. 2 summaries the validity domains of different analytical approximations solution [16].

#### 3.2. Electrical conductivity

The electrical conductivity in charged nanopores is determined by various factors, including the size of the nanopore, the surface charge density (Table 1), the concentration and type of ions presented in the pore (Table 2), and the properties of the surrounding medium. However, the behaviour of electrical conductivity in charged nanopores can be complex and dependent on many factors, and may require detailed computational studies to fully understand. The conductivity is computed by numerical approach using equation (33) and compared to the conductivity calculated by homogeneous and extended homogeneous analytical approximations. Using the EH approximation, the conductivity  $\kappa$  can be calculated analytically and is given by:

$$\kappa = L_{33}^H + \delta L_{33}, \quad (64)$$

where the homogeneous conductivity is given by

$$L_{33}^H = (C\nu_1|z_1|F^2/RT) (D_1|z_1|k_h + D_2|z_2|k_h^{-\tau}) + ((C\nu_1z_1F)^2 L_P^0) \xi^2. \quad (65)$$

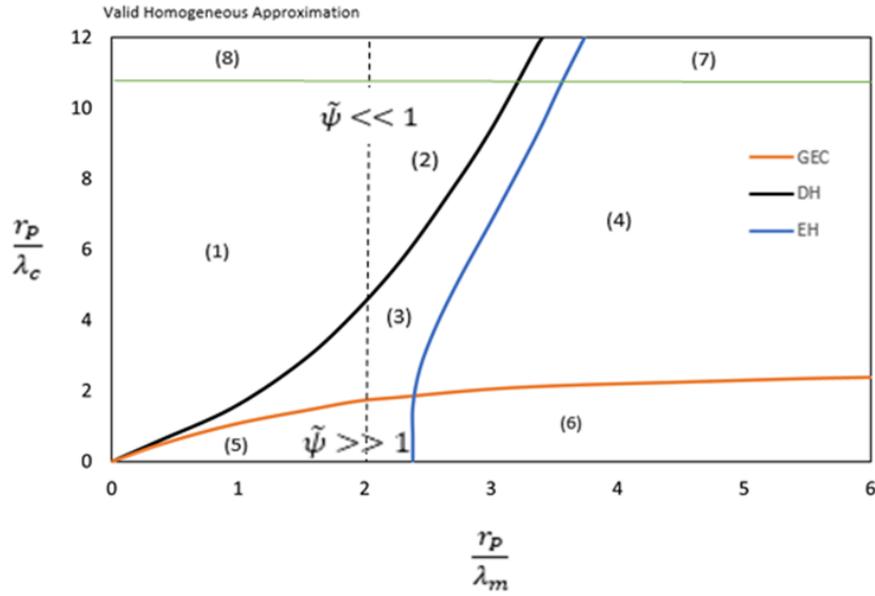


FIG. 2. Representation of the validity domains of different analytical solution approximations [16]. Representation of different zones: (1) and (2) – Validity of the Homogeneous and Debye–Hückel (DH) zone; (1), (2) and (3) – Validity of EH zone; (5) and (6) – Validity of the Homogeneous zone and inhomogeneous GEC; (4) – Intermediate zone; (7) – Validity of the plane approximation; (8) – Validity of the plane Debye–Hückel approximation. The blue curve delimits the area of EH and the dashed line delimits the H area.

The hydraulic permeability of the membrane is given by the following formula

$$L_P^0 = r_p^2/8\eta \tag{66}$$

and the correction term of the homogeneous approximation of order 1 is given by

$$\delta L_{33} = \frac{(C\nu_1 z_1 F r_p)^2 \xi^2}{2\eta} \left[ \frac{1}{4} + \frac{1}{m} \frac{I_0(m)}{I_1(m)} - \frac{1}{2} \left( \frac{I_0(m)}{I_1(m)} \right)^2 \right]. \tag{67}$$

TABLE 1. The Parameter  $r_p/\lambda_m$ , the surface charge density and membrane charge density  $X_m$  for  $r_p = 2$  nm

$r_p/\lambda_m$	$\sigma_w$ (C/m <sup>2</sup> )	$X_m$ (mol/l)
0.18	0.0003	0.0031
4	0.15	1.55
6.4	0.37	3.83
8	0.58	6.01
10.4	0.97	10.05

TABLE 2. Parameter  $r_p/\lambda_c$  and concentration in the bulk for  $r_p = 2$  nm

$r_p/\lambda_c$	$C$ (M)
0.2	$10^{-3}$
0.6	$10^{-1}$
6.5	1
11.4	3

When  $\xi$  tends to 0, then the correction term  $\delta L_{33}$  tends to 0. In this case, the conductivity in the homogeneous zone is attained. Fig. 3 shows that at low surface charge densities, the electrical conductivity is dominated by the properties of the electrolyte solution, and the conductivity decreases as the size of the nanopore decreases due to increased surface effects. At higher surface charge densities, the electrical conductivity may increase due to the formation of ion transport channels or ion hopping mechanisms. At low surface charge density, Fig. 3 shows that the conductivity in a charged pore is proportional to the ionic concentration of the counter ions compensated by the volume charge density of the membrane (contribution of the electrical double layer). It turns out that the SC model predicts very well the experimentally observed conductivity in cylindrical nanopores of radius  $r_p > 3$  nm [16]. This indicates that the model captures the relevant physical phenomena and properties of the nanopores accurately. In this context, the homogeneous approximation is coherent with the numerical method up to  $r_p/\lambda_m \approx 3$ , while the EH remains coherent until  $r_p/\lambda_m \approx 6$ . Indeed, the EH approximations can be valuable analytical methods to calculate physical quantities of certain systems, including membranes for low and high surface charge density  $\sigma_w$ . The issue of the validity of this model for small pore radius  $r_p < 2$  nm remains an open question.

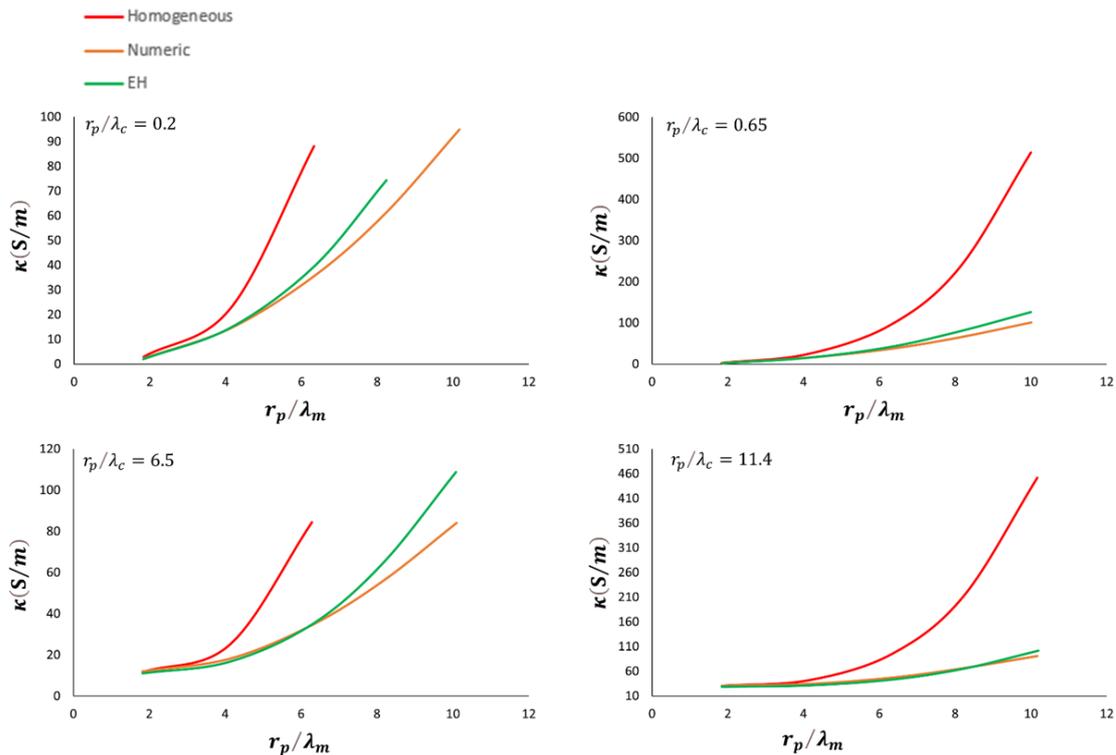


FIG. 3. Conductivity  $\kappa$  as a function of parameter  $r_p/\lambda_m$  in a nanopore of radius  $r_p = 2$  nm containing KCl salt. The conductivity is calculated by numerical, Homogeneous and extended homogeneous approximation

#### 4. Conclusion and perspective

The aim of this paper was to highlight the influence of physical parameters on the ionic transfer, especially the concentration of the bulk and the surface charge density  $\sigma_w$ . Different analytical approximations based on the space charge (SC) model (Homogeneous, Good Co-Ion Exclusion and Planar approximation) is described in this paper. A new analytical approximation named the extended homogeneous approximation is presented. The behavior of the salt-porous system depends mainly on the surface charge density and the concentration in the bulk. The calculation of the conductivity by numerical and approximate analytical methods shows that the Extended Homogeneous approximation (EH) is coherent with the numerical method up to a limit value of  $r_p/\lambda_m \approx 6$ , corresponding to 0.37 value of surface charge density. Then, without going through a heavy numerical method, the EH approximations can be used as simple analytical methods to calculate the physical quantities of the membrane such as electrical conductivity and flow potential within specific limits, help the development of new applications in water treatment, food processing, and the recovery of valuable materials from industrial waste streams.

## References

- [1] Feng X., Peng D., Zhu J., Wang Y., Zhang Y. Recent advances of loose nanofiltration membranes for dye/salt separation. *Separation and Purification Technology*, 2022, **285**, P. 120–228.
- [2] Filippov A.N., Shkirkaya S.A. Theoretical and experimental study of joint osmotic and electroosmotic water transfer through a cation-exchange membrane. *Int. J. of Molecular Sciences*, 2022, **23**, P. 127–178.
- [3] Chen W., Gu Z., Ran G., Li Q. Application of membrane separation technology in the treatment of Leachate in china: A review. *Waste Management*, 2021, **121**, 127.
- [4] Rautenbach R., Groschl A. Separation potential of nanofiltration membranes. *Desalination*, 1990, **77**, P. 73–84.
- [5] Tsuru T., Urairi M., Nakao S., Kimura S. Negative rejection of anions in the loose reverse osmosis separation of mono-and divalent ion mixtures. *Desalination*, 1991, **81**, P. 219–227.
- [6] Yaroshchuk A.E. Osmosis and reverse osmosis in fine-porous charged diaphragms and membranes. *Advances in Colloid and Interface Science*, 1995, **60**, P. 1–93.
- [7] Lefebvre X., Palmeri J., David P. Nanofiltration theory: An analytic approach for single salts. *J. of Physical Chemistry B*, 2004, **108**, P. 16811–16824.
- [8] Lefebvre X., Palmeri J. Nanofiltration (Transport Phenomena). *J. of Physical Chemistry B*, 2005, **109**, P. 5525–5540.
- [9] Szymczyk A., Fievet P. Investigating transport properties of nanofiltration membranes by means of a steric, electric and dielectric exclusion model. *J. of Membrane Science*, 2005, **252**, P. 77–88.
- [10] Chmiel H., Lefebvre X., Mavrov V., Noronha M., Palmeri J. Computer simulation of nanofiltration, membranes and processes. In *Handbook of Theoretical and Computational Nanotechnology – American Scientific Publishers*, 2006, **5**, P. 93–214.
- [11] Peters P.B., van Roij R., Bazant M.Z., Biesheuvel M. Analysis of electrolyte transport through charged nanopores. *Physical Review E*, 2016, **93**, 052801.
- [12] Morrison F.A. Jr., Osterle J.F. Electrokinetic energy conversion in ultrafine capillaries. *J. of Chemical Physics*, 1965, **43**, P. 2111–2115.
- [13] Gross R.J., Osterle J.F. Membrane transport characteristics of ultrafine capillaries. *J. of Chemical Physics*, 1968, **49**, P. 228–234.
- [14] Fair J.C., Osterle J.F. Reverse electrodialysis in charged capillary membranes. *J. of Chemical Physics*, 1971, **54**, P. 3307–3316.
- [15] Dweik J., Koabaz M. Study of ion partitioning in nanoporous materials by analytical approach and molecular modeling. *Nanosystems: Phys. Chem. Math.*, 2023, **14**, P. 172–177.
- [16] Cwirko H.E., Carbonell R.G. Transport of electrolytes in charged pores: Analysis using the method of spatial averaging. *J. of Colloid and Interface Science*, 1989, **129**, P. 513–531.

---

*Submitted 4 July 2023; revised 25 July 2023; accepted 28 July 2023*

### *Information about the authors:*

*Jalal Dweik* – Jinan university, Tripoli Lebanon – Main Campus: Zaytoun Abi-Samra, P. O. Box: 818;  
ORCID 0009-004-2988-0918; jalal.douwayk@jinan.edu.lb

*Hassan Farhat* – Jinan university, Tripoli Lebanon – Main Campus: Zaytoun Abi-Samra, P. O. Box: 818;  
ORCID 0009-0005-4696-9786; hassan.farhat@jinan.edu.lb

*Joumana Younis* – Jinan university, Tripoli Lebanon – Main Campus: Zaytoun Abi-Samra, P. O. Box: 818;  
ORCID 0000-0003-0576-4264; joumana.younis@jinan.edu.lb

*Conflict of interest:* the authors declare no conflict of interest.