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Applicability of Donnan equilibrium theory at nanochannel-reservoir interfaces



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ABSTRACT

Understanding ionic transport in nanochannels has attracted broad attention from various areas in energy and environmental fields. In most pervious research, Donnan equilibrium has been applied widely to nanofluidic systems to obtain ionic concentration and electrical potential at channel-reservoir interfaces; however, as well known that Donnan equilibrium is derived from classical thermodynamic theories with equilibrium assumptions. Therefore the applicability of the Donnan equilibrium may be questionable when the transport at nanochannel-reservoir interface is strongly non-equilibrium. In this work, the Poisson-Nernst-Planck model for ion transport is numerically solved to obtain the exact distributions of ionic concentration and electrical potential. The numerical results are quantitatively compared with the Donnan equilibrium predictions. The applicability of Donnan equilibrium is therefore justified by changing channel length, reservoir ionic concentration, surface charge density and channel height. The results indicate that the Donnan equilibrium is not applicable for short nanochannels, large concentration difference and wide openings. A non-dimensional parameter, Q factor, is proposed to measure the non-equilibrium extent and the relation between Q and the working conditions is studied in detail.

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1. Introduction

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http://dx.doi.org/10.1016/j.jcis.2015.03.064 0021-9797/© 2015 Elsevier Inc. All rights reserved. Nanochannels are generally defined as channels with a characteristic size below 100 nm in at least one dimension. To date numerous fabrication technologies for nanochannels have been







developed, allowing construction of nanofluidic devices. The devices consist of nanochannels which connect larger channels or reservoirs, are used to control ionic and molecular transport. The applications of nanofluidic devices are broad, such as nanofluidic diodes and transistors, routing, preconcentration and separation of ions and biomolecules, micro total analysis systems (μ TAS) [1–5].

A typical diagram of the nanochannel network is referred to Fig. 1. The surfaces of nanochannels are automatically charged due to ionization of the surface groups, ions adsorption and other possible mechanisms [6-10]. The electrostatic force on ions by the surface charge rectifies the electrical field and therefore the ion distribution in nanochannels. This brings some specific functions and applications using these nanochannels [11]. Meanwhile, the existence of surface charge will change the ionic concentrations and electrical potentials at the nanochannel-reservoir interfaces from the bulk ones, so that the electrical potential difference and the ionic concentration difference actually acting on the ions in the nanochannels differ from those between reservoirs, as shown in Fig. 1. The bulk concentrations and electrical potentials in both reservoirs are known, whereas we need the real boundary conditions to refine the ion transport through the nanochannels. In previous studies, the Donnan equilibrium is commonly used to quantify such an interfacial drop of electrical potential [5,12–19]. As shown in Section 2, Donnan equilibrium is derived from the classical thermodynamic theories with an equilibrium assumption, and gives a succinct relationship of the quantities between the bulk solution and nanochannel-reservoir interface.

Donnan theory is very simple, but not the only interface theory. Besides it, there are two more major models for interfacial potentials. Mauro [20] used two Poisson equations (one for the bulk solution and the other for the aqueous phase in membrane) connected with continuous conditions to derive the continuous distribution of the electrical potential at the interfaces. This model is referred to as continuous Donnan model, though it is quite different from the original Donnan theory. However, the model has no explicit analytical solution, resulting in its difficulty to be used. The surface potential model is based on Poisson-Boltzmann equation, whose idea is similar to the electrical double layer theory [21]. The surface potential model assumes that the membrane surface has a uniform distribution of surface charge. It is clear that this assumption brings many doubts and challenges. Therefore, after a long time of developments the traditional Donnan equilibrium theory is still the most popular one in the literature [5,15,17– 19,22]. However, the nanofluidic system may be in a strongly non-equilibrium state. The applicability of the classical Donnan equilibrium for its interfacial condition may be questionable, and has not been systematically studied.

There are many theoretical studies on Donnan equilibrium. MacGillivray [16] used perturbation theory to study Poisson-Nernst-Plank equations which describe ion transport in charged membrane. He found that when the ratio of a Debye length and the membrane thickness is small, the electroneutrality assumption is a consequence of Poisson equation and Donnan equilibrium is a consequence of Nernst-Plank equations. Generally speaking, PNP model gives relatively accurate description of the ion transport. However, without numerical simulation, PNP model is hard to solve, therefore MacGillivary's theory can only provide qualitative analysis but not quantitative limit for the applicability of Donnan equilibrium. Besides MacGillivray's fundamental work, most of other researches on Donnan theory are more related to its applications [23,24], and readers can refer to them for extended comprehension. Measurement methods have been developed for the Donnan potential at a charged membrane/salt solution interface [25]. The measurement is available to provide effective membrane charge, which is an important parameter for ion transport. Nevertheless, the measurement is restricted to special conditions, making it hard to offer a large enough range of experiment data for applicability study.

Although the Donnan equilibrium theory has been used to determine boundary conditions for modeling ion transport in a single nanochannel in the previous research [15,19,22], its applicability has not been clarified yet. Since both theory analysis and experiments meet difficulties, numerical modeling may be the best way to quantitatively study the applicability of Donnan equilibrium at interfaces. Therefore, in this work the applicability of the Donnan equilibrium theory will be examined numerically in a reservoir–nanochannel–reservoir system as shown in Fig. 1(b). The original governing equations for ion transport without equilibrium assumptions will be solved by a high-efficiency lattice Boltzmann method (LBM), and the results are compared with predictions of Donnan equilibrium at interfaces.

In the rest parts of this paper, we first introduce the Donnan equilibrium theory in membrane science and at nanochannel-reservoir interfaces in Section 2. The mathematical model and the numerical algorithm of LBM are introduced in Section 3. Especially, a factor Q to measure the non-equilibrium effect is theoretically described in Section 3.3. The comparisons of Donnan equilibrium and the modeling results are summarized and the applicability of Donnan equilibrium is examined in Section 4. Finally the conclusions will be drawn in Section 5.



Fig. 1. A diagram of nanochannel assembly. (a) The nanochannel network. (b) The details of one channel, forming a typical reservoir–nanochannel–reservoir system. The left is inlet (I) and the other is outlet (O) of the channel.

2. Donnan equilibrium

2.1. Donnan equilibrium theory in membrane science

Donnan equilibrium was first derived by Donnan [12] to study semi-permeable membrane separating two salt solutions with different concentration or composition. Donnan analyzed several cases for membranes with different permeable properties and different solution systems, and gave the equilibrium concentration in the two solutions and equilibrium membrane electrical potential with the application of thermodynamic theories [12]. Alexander and Johnson [26] gave a systematic and explicit derivation for Donnan equilibrium; readers can refer to this book for further comprehension. Here in this paper, we only introduce the main idea for the Donnan equilibrium.

The classical thermodynamics gives [27]:

$$dG = Vdp - SdT + \sum_{i} \mu_{i} dn_{i}, \tag{1}$$

where *G* is the Gibbs free energy, *V* is the volume, *p* is the pressure, *S* is the entropy and *T* is the temperature; here consider dn_i moles of free ions transfer from one side of the membrane to the other; μ_i is the electrochemical potential for component ion *i*, and its expression for component ions in strong electrolyte is:

$$\mu_i = \mu_i^0 + RT \ln(f_i c_i) + z_i F \phi, \qquad (2)$$

where μ_i^0 is the standard electrochemical potential, *R* is the thermodynamic constant, f_i is the activity coefficient for *i*-th ion which is unity for ideal solutions, z_i is the valence and c_i is the molar concentration of *i*-th ion, *F* is the Faraday constant, and ϕ is the local electrical potential.

Gibbs free energy is a general criteria of equilibrium for a constant-pressure and constant-temperature system. For an equilibrium membrane system at given pressure and temperature, there is:

$$dG = \sum_{i} \mu_{i} dn_{i} = \sum_{i} (\mu_{i}' dn_{i}' + \mu_{i}'' dn_{i}'') \ge 0, \qquad (3)$$

where μ'_i represents the electrochemical potential in the bulk solution on one side of the membrane, and μ''_i is that on the other side. dn'_i and dn''_i are the slight changes of ion amount on either side, and they satisfy $dn'_i = -dn''_i = dn_i$ due to conservation of mass. Thus Eq. (3) becomes:

$$\mathbf{d}G = \sum_{i} (\mu'_i - \mu''_i) \mathbf{d}n_i \ge \mathbf{0}.$$
(4)

Since dn_i can be positive or negative, Eq. (4) is true for any *i*-th ion only if

$$\mu_i' = \mu_i''. \tag{5}$$

With assuming $(\mu_i^0)' = (\mu_i^0)''$, substituting of Eq. (2) into Eq. (5) leads to the general form of Donnan equilibrium in membrane science:

$$\phi'' - \phi' = \frac{RT}{z_i F} \ln\left(\frac{f'_i C'_i}{f''_i C''_i}\right).$$
 (6)

The physical significance of Eq. (6) is the balance between diffusion and electrical forces. If the electrolyte is simplified as binary and symmetric, that is $z_p = -z_n = z$ where i = p represents for positive ion and i = n represents for negative ion. Thus the Eq. (6) is re-written as:

$$\phi'' - \phi' = \frac{RT}{zF} \ln\left(\frac{f'_p c'_p}{f''_p c''_p}\right) = -\frac{RT}{zF} \ln\left(\frac{f'_n c'_n}{f''_n c''_n}\right).$$
(7)

A simple concentration relationship can be derived from Eq. (7):

$$c'_{p}c'_{n} = \frac{f''_{p}f''_{n}}{f'_{p}f'_{n}}c''_{p}c''_{n}.$$
(8)

However, the assumption $(\mu_i^0)' = (\mu_i^0)''$ is not always acknowledged. Therefore Q_i^0 parameter is introduced as a correction factor to describe the deviation [18,25,28]:

$$Q_{i}^{0} = \frac{f_{i}''}{f_{i}'} \exp\left(\left(\left(\mu_{i}^{0}\right)'' - \left(\mu_{i}^{0}\right)'\right)/RT\right).$$
(9)

As a result, Eq. (6) is modified as:

$$\phi'' - \phi' = \frac{RT}{z_i F} \ln\left(\frac{c_i'}{Q_i^0 c_i''}\right).$$
(10)

Define $Q^0 = Q_p^0 Q_n^0$, and Eq. (8) converts to:

$$c'_p c'_n = Q^0 c''_p c''_n \tag{11}$$

Eq. (10) is much less popular than Eq. (6), because it is hard or even impossible to calculate μ_i^0 in practice and Q^0 is a correction factor for non-ideal conditions due to the electrostatic forces unbalance between the fixed charge and the free ions in the membrane phase [18]. Note that the standard electrochemical potential is defined at a standard state and is independent of concentration and electric potential for dilute solution, therefore Q⁰ will also not change with these parameters. For the study of asymmetrical membrane consisting of a cation-exchange layer and an anionexchange layer, a contact factor ξ is multiplied with Q^0 to compensate the error of Donnan equilibrium due to different materials' characteristics [18,28]. By choosing an appropriate ξ , the experimental data showed well consistence with modified Donnan theory. Inspired by this process, we propose a new O factor to measure the non-equilibrium effect, as described in Section 3.3. Note that the original Donnan equilibrium is a membrane theory, and takes no considerations of geometrical and scale effects of the non-equilibrium cases.

Though the original Donnan equilibrium theory is proposed on the two sides of the membrane, the developed Donnan theory is available as well at the interface between the membrane and the bulk solution. Teorell, Meyer and Sievers developed a fixed-charge model (known as the TMS model) to describe the ion transport in charged membrane [25,29,30]. In TMS model, the membrane potential is divided into three parts:

$$\Delta \phi = \Delta \phi_{\text{Don}}^{\text{L}} + \Delta \phi_{\text{diff}}^{\text{R}} + \Delta \phi_{\text{Don}}^{\text{R}}, \qquad (12)$$

where $\Delta \phi_{\text{Don}}^{\text{L}}$ and $\Delta \phi_{\text{Don}}^{\text{R}}$ are the Donnan potential drops at the left and right surfaces of the membrane (or at the inlet and outlet of a nanochannel); $\Delta \phi_{\text{diff}}$ is the diffusion potential, which drives the ion transport in the membrane. Charged membrane exists in various processes such as electrodialysis, reverse electrodialysis and nanofiltration. The TMS model also obtains broad applications in these areas. Though Teorell's theory focuses on membrane, the analysis method is quite similar to that of nanochannel. The calculations for the two Donnan potentials of a nanochannel will be introduced in Section 2.2.

2.2. Donnan equilibrium theory at nanochannel-reservoir interfaces

As shown in Fig. 1, below we use subscript L to present the left bulk solution and subscript R to present the right bulk solution. The subscript I and O are used to mark the inlet and the outlet of nanochannel respectively; l is the channel length and H is the channel height. Here the Donnan equilibrium theory is applied to the reservoir–nanochannel interface in the reservoir–nanochannel– reservoir system as shown in Fig. 1(b). That is, the electrochemical equilibrium is assumed between the left bulk solution and the inlet of nanochannel and between the right bulk solution and the outlet of nanochannel. Here we first explore the relationship between the left bulk and the inlet quantities. Due to equilibrium, there is:

$$\phi_I - \phi_L = \frac{RT}{z_i F} \ln\left(\frac{f_{i,L} c_{i,L}}{f_{i,I} c_{i,I}}\right). \tag{13}$$

Notice that there is no membrane considered here between the left bulk solution and the left inlet of nanochannel. The Donnan equilibrium is essentially electrochemical equilibrium which is available for any equilibrium system with or without membrane. Eq. (13) means the balance between the electrical field and diffusion. However, if the bulk concentrations in the two reservoirs are given and unequal, the system can hardly reach equilibrium because the electrical potential cannot balance the concentration gradient of both the cations and anions, leading to the doubt of the applicability of Donnan equilibrium. The question will be discussed later. To use and test the Donnan theory, here we still suppose the quasi-equilibrium assumption is satisfied.

To facilitate the analysis, we assume a uniform negative surface charge on wall surfaces with a surface charge density σ . The electrolyte is simplified as binary and symmetric, and the solution is dilute, that is $z_p = -z_n = z$, $f_p = f_n = 1$. Thus Eq. (13) is re-written as:

$$\phi_{I} - \phi_{L} = \frac{RT}{zF} \ln\left(\frac{c_{p,L}}{c_{p,I}}\right) = -\frac{RT}{zF} \ln\left(\frac{c_{n,L}}{c_{n,I}}\right),\tag{14}$$

and the relationship of the concentrations are:

$$c_{p,L}c_{n,L} = c_{p,l}c_{n,l}. \tag{15}$$

The electroneutrality condition has to be ensured:

$$c_{p,L} = c_{n,L} = c_L, \tag{16}$$

$$c_{p,l} - c_{n,l} = -\frac{2\sigma}{zFH}.$$
(17)

Eq. (17) is derived from the charge compensation between the surface charge and solution charge, which are 2σ and $zFH(c_{p,I} - c_{n,I})$ per unit area respectively under the assumption of negligible concentration variation along the channel height direction. The combination of Eqs. (15)–(17) leads to the most common form of Donnan equilibrium for interface concentrations:

$$c_{p,l} = \sqrt{\left(\frac{\sigma}{zFH}\right)^2 + \left(c_L\right)^2} - \frac{\sigma}{zFH},$$
(18)

$$c_{n,l} = \sqrt{\left(\frac{\sigma}{zFH}\right)^2 + \left(c_L\right)^2} + \frac{\sigma}{zFH}.$$
(19)

The electrical potential drop at the interface can be obtained from Eq. (13). This derivation can be applied to both the left and right interface. The boundary conditions of both ends of the nanochannel can be obtained by the combination of Donnan equilibrium and electroneutrality assumption:

$$c_{i,l} = \sqrt{\left(\frac{\sigma}{zFH}\right)^2 + c_L^2} - \frac{\sigma}{z_i FH},$$
(20)

$$c_{i,0} = \sqrt{\left(\frac{\sigma}{zFH}\right)^2 + c_R^2} - \frac{\sigma}{z_iFH},$$
(21)

$$\phi_{I} = \phi_{L} + \frac{RT}{zF} \ln\left(\left(\sqrt{\left(\frac{\sigma}{zFH}\right)^{2} + c_{L}^{2}} + \frac{\sigma}{zFH}\right) \middle/ c_{L}\right),$$
(22)



Fig. 2. Electrochemical potential distributions along the *x* direction. μ p and μ n represent for electrochemical potential of the positive ion and negative ion, respectively. The dotted lines mark the entrance and exit of the nanochannel, and the dash-dot lines mark the electroneutrality location ($c_p - c_n = (-2\sigma/zFH) \times 99\%$). Simulation parameters are: $c_L = 5 \times 10^{-4}$ mol/L, $c_R = 1 \times 10^{-4}$ mol/L, $\phi_L = \phi_R = 0$ V, $\sigma = -0.001$ C/m², H = 100 nm, L = 1250 nm.

$$\phi_{0} = \phi_{R} + \frac{RT}{zF} \ln\left(\left(\sqrt{\left(\frac{\sigma}{zFH}\right)^{2} + c_{R}^{2}} + \frac{\sigma}{zFH}\right) \middle/ c_{R}\right).$$
(23)

In fact, since we take no special consideration of nanochannel geometry, Eqs. 20–23 are applicable also for membranes. Along the derivation of Eqs. 20–23, all the assumptions mentioned above summarized as: (a) ideal solution and symmetrical electrolyte; (b) uniform surface charge density; (c) uniform concentration at the inlet and outlet; (d) electroneutrality assumption; (e) equilibrium assumption. Eqs. 20–23 will become more complicated without the assumptions (a) and (b). The assumption (c) is natural because Donnan equilibrium is a simplified one-dimensional theory. The electroneutrality assumption (d) is unconvinced and the equilibrium assumption (e) is more critical and significant because most nanofluidic systems may be not in an equilibrium state. Thus we will compare Eqs. 20–23 with the PNP numerical results to explore the applicability of Donnan equilibrium. To facilitate the calculation, we choose a straight nanochannel for calculation and analysis.

3. Mathematical models and numerical methods

3.1. Poisson-Nernst-Plank model

We use the PNP model to solve the ion transport in a planer nanochannel (channel height is nano-sized and much smaller than the other two dimensions) which connects reservoirs, as shown in Fig. 1(b). Due to the symmetry of geometry, only a half is calculated. The side walls of the nanochannel framework are assumed to be negatively charged with the same surface charge density as the channel walls.

For simplicity, we assume: (a) dispersion and advection neglected (the convection is very weak in the conditions we studied because no pressure drop or electrical potential drop is applied to the system); (b) no chemical reaction considered; (c) the solution ideal or dilute. In this case, the steady-state Nernst–Plank equations are

$$\mathbf{J}_{p} = -\frac{ez_{p}D_{p}}{kT}c_{p}\nabla\phi - D_{p}\nabla c_{p}, \qquad (24)$$

$$\mathbf{J}_{n} = -\frac{ez_{n}D_{n}}{kT}c_{n}\nabla\phi - D_{n}\nabla c_{n}, \qquad (25)$$



Fig. 3. The variation of (a) concentrations and (b) electrical potential along the x axis. The dotted lines mark the entrance and exit of the nanochannel, and the dash-dot lines mark the electroneutrality location ($c_p - c_n = (-2\sigma/zFH) \times 99\%$). Calculation parameters: $c_L = 5 \times 10^{-4} \text{ mol/L}$, $c_R = 1 \times 10^{-4} \text{ mol/L}$, $\phi_L = \phi_R = 0 \text{ V}$, $\sigma = -0.001 \text{ C/m}^2$, H = 100 nm, L = 1250 nm.



Fig. 4. Comparison between Donnan theory and LBM results for inlet and outlet (a) cation concentration, (b) anion concentration and (c) electrical potential along with the variation of the channel length. The upper blue lines represent the inlet quantities, and the lower red lines represent the outlet quantities. Calculation parameters: $c_L = 5 \times 10^{-4} \text{ mol}/L$, $c_R = 1 \times 10^{-4} \text{ mol}/L$, $\phi_L = \phi_R = 0 \text{ V}$, $\sigma = -0.001 \text{ C/m}^2$, H = 100 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

where D_p and D_n are the diffusion coefficient of the cations and anions; e is the unit charge; k is the Boltzmann constant; \mathbf{J}_p and \mathbf{J}_n are the ion flux per unit area, and satisfy

$$\nabla \cdot \mathbf{J}_{\mathbf{i}} = \mathbf{0} \quad (\mathbf{i} = \mathbf{p}, \mathbf{n}). \tag{26}$$

The Poisson equation:

$$\nabla^2 \phi = -\frac{\rho_e}{\varepsilon_0 \varepsilon},\tag{27}$$

where ρ_e is the local volume charge density, and $\rho_e = \sum z_i e N_A c_i$ in the solution (N_A is the Avogadro constant); ε_0 is the permittivity of free space, ε is the dielectric constant.

The reservoir boundary conditions ϕ_L , ϕ_R , $c_{i,L}$, $c_{i,R}$ are given. All the walls are assumed to be homogeneously charged and have a uniform surface charge density σ .

In this work, all the parameters are given as follows: T = 300 K; $z_p = -z_n = 1$; $D_p = D_n = 1 \times 10^{-9}$; $\varepsilon = 6.95 \times 10^{-10}$ (take no account of the variation of ε). To make full use of the computing resources, instead of giving a large enough reservoir for all the cases, we use a parameter w to control the area of the reservoir:

$$w = \frac{\left(\frac{n_p - n_n}{2}\right)_{nanochannel}}{\left(\frac{n_p + n_n}{2}\right)_{reservoir+nanochannel}} \approx \frac{\frac{\sigma}{2H}Hl}{\frac{c_L + c_R}{2}Hl + H_{res}l_{res}(c_L + c_R)}$$
$$= \frac{\sigma l}{ZF(c_L + c_R)\left(\frac{Hl}{2} + H_{res}l_{res}\right)},$$
(28)

where n_p and n_n is the moles of positive ion and negative ion respectively; H_{res} and l_{res} are the size of the reservoir. w measures the variation of the concentration distribution induced by the surface charge of the reservoir. After numerical checks, we choose w = 0.05 to give the large enough reservoir, and $(H_{res} - H)/l_{res} = 2$ to give the shape of the reservoirs, since in this condition the concentration field and potential field become almost changeless with the reservoir size (generally the variation is less than 3%).

3.2. Lattice Boltzmann method

Lattice Boltzmann method is a promising numerical method for simulating fluid flows and modeling multiphysical transports in fluid [31]. Originally proposed to solve the Navier–Stokes (NS) equation, LBM has extended to solve other partial differential equations like convection–diffusion equation and Poisson equation. Previously, a multiple LB model has been established by Wang and Kang [32] and modified by Yoshida et al. [33] to maintain the locality of the algorithm. It is proved to be capable of simulating electrokinetic transport of ionic species by recovering the full PNP model.

Generally, the evolution equations for ion transport and electrical potential are written as

$$g_{\alpha}(\mathbf{r} + \mathbf{e}_{\alpha}\delta_{t,D_{i}}, t + \delta_{t,D_{i}}) - g_{\alpha}(\mathbf{r}, t) = -\frac{1}{\tau_{D_{i}}} \left[g_{\alpha}(\mathbf{r}, t) - g_{\alpha}^{eq}(\mathbf{r}, t) \right] + \omega_{\alpha}\delta_{t,D_{i}} \left(1 - \frac{0.5}{\tau_{D_{i}}} \right) \frac{ez_{i}D_{i}}{kT} \nabla \cdot (c_{i}\nabla\phi), \quad (29)$$



Fig. 5. Comparison between Donnan theory and LBM results for inlet and outlet (a) cation concentration, (b) anion concentration and (c) electrical potential along with the variation of concentration. The upper blue lines represent the inlet quantities, and the lower red lines represent the outlet quantities. Calculation parameters: $c_R = 1 \times 10^{-4}$ mol/L, $\phi_L = \phi_R = 0$ V, $\sigma = -0.001$ C/m², H = 100 nm, L = 1250 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$$h_{\alpha}(\mathbf{r} + \Delta \mathbf{r}, t + \delta_{t,\phi}) - h_{\alpha}(\mathbf{r}, t) = -\frac{1}{\tau_{\phi}} \left[h_{\alpha}(\mathbf{r}, t) - h_{\alpha}^{eq}(\mathbf{r}, t) \right] + \omega_{\alpha} \delta_{t,\phi} \left(1 - \frac{0.5}{\tau_{\phi}} \right) \frac{\rho_{e}}{\varepsilon_{r} \varepsilon_{0}},$$
(30)

respectively. g_{α} , h_{α} represent the distribution functions for ionic concentration and electrical potential, which depend on the position vector **r** and the time *t*. The τ_{D_i} , δ_{tD_i} and τ_{ϕ} , $\delta_{t,\phi}$ are the corresponding dimensionless relaxation time and time step. For higher efficiency, we employ the D2Q5 models with the discrete velocities

$$\mathbf{e}_{\alpha} = \begin{cases} (0,0) & \alpha = 1\\ (\cos \theta_{\alpha}, \sin \theta_{\alpha}), & \theta_{\alpha} = (\alpha - 2)\pi/2 & \alpha = 2 - 5 \end{cases},$$
(31)

and the distribution coefficients $\omega_{\alpha} = \frac{1}{3}$, $\alpha = 1$; $\omega_{\alpha} = \frac{1}{6}$, $\alpha = 2 - 5$. The macroscopic quantities, i.e., the ionic concentration and the electrical potential can be calculated as $c_i = \sum_{\alpha} g_{\alpha}$, $\phi = \sum_{\alpha} h_{\alpha}$.

Because of the explicit coupling of the governing equations, Eqs. (29) and (30) have to be solved iteratively. Detailed information for the numerical procedure can be found in Ref. [32].

3.3. Q factor for measuring Donnan theory

Before exploring the applicability of Donnan theory, we used our LBM simulations for intuitional understanding of the ion transport phenomenon in the system shown in Fig. 1(b). If μ_i^0 is negligible, the electrochemical potential can be calculated from the PNP numerical results, and its cross-sectional averaged value along the *x* direction for one case is shown in Fig. 2. It is known that Donnan equilibrium assumes the equality of the electrochemical potential for each ion species at the reservoir–nanochannel interface. However, as shown in Fig. 2, the electrochemical potentials (positive ion, negative ion and net charge) vary along the *x* axis, smoothly in the reservoir area and sharply in the channel region, especially for the electrochemical potential of net charge. This rationalizes Donnan equilibrium in some extent. The variation of the electrochemical potential at the reservoir–inlet interface is much smaller than that in the nanochannel, leading to good approximate equilibrium between the reservoir and the channel ends. Meanwhile the approximation results in the overestimated results at the inlet and underestimated ones at the outlet.

Therefore, we propose a *Q* factor in this study to measure the integrated non-equilibrium extent, which can estimate the theoretical deflection of the Donnan equilibrium for prediction of the concentrations. In consideration of inequality of the electrochemical potential under non-equilibrium conditions, we define:

$$Q_{i,in} = \frac{f_{i,l}}{f_{i,L}} \exp\left((\mu_{i,L} - \mu_{i,l})/RT\right).$$
(32)

Note the difference between Eqs. (9) and (32) that $Q_{i,in}$ is variable with concentration and electrical potential of the solution but Q_i^0 is not. As a result, $Q_{i,in}$ is available to reflect the non-equilibrium effect at the inlet interface of the nanochannel.



Fig. 6. Comparison between Donnan theory and LBM results for inlet and outlet (a) cation concentration, (b) anion concentration and (c) electrical potential along with the variation of surface charge density. The upper blue lines represent the inlet quantities, and the lower red lines represent the outlet quantities. Calculation parameters: $c_L = 5 \times 10^{-4} \text{ mol/L}$, $c_R = 1 \times 10^{-4} \text{ mol/L}$, $\phi_L = \phi_R = 0 \text{ V}$, H = 50 nm, L = 625 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

For simplicity, we assume $(\mu_i^0)_L = (\mu_i^0)_l$, and thus Eq. (14) converts to:

$$\phi_{I} - \phi_{L} = \frac{RT}{zF} \ln\left(\frac{c_{p,L}}{Q_{p,in}c_{p,l}}\right) = -\frac{RT}{zF} \ln\left(\frac{c_{n,L}}{Q_{n,in}c_{n,l}}\right).$$
(33)
Define $Q_{in} = Q_{n,in}Q_{n,in}$, Eq. (8) converts to:

$$c_{p,L}c_{n,L} = Q_{in}c_{p,l}c_{n,l}, \qquad (34)$$

and Q_{out} can be similarly defined. Eqs. (20) and (21) convert to:

$$c_{i,l} = \sqrt{\left(\frac{\sigma}{zFH}\right)^2 + \frac{c_L^2}{Q_{in}} - \frac{\sigma}{z_iFH}},$$
(35)

$$c_{i,0} = \sqrt{\left(\frac{\sigma}{zFH}\right)^2 + \frac{c_R^2}{Q_{out}} - \frac{\sigma}{z_iFH}}.$$
(36)

Here Q_{in} and Q_{out} represents for the integrated non-equilibrium effect caused by both cations and anions at the inlet and outlet interface of the nanochannel respectively. The calculated Q by Eq. (34) from the numerical results describes the theoretical deflection of Donnan equilibrium prediction for concentrations. In Section 4.2, we use Q to analyze non-equilibrium effect on concentrations.

4. Results and discussion

Fig. 3 shows the variation of ionic concentrations and electrical potential along the x direction, and all the values are averaged across the channel.

As shown in Fig. 3, the electroneutrality assumption is true in most part of the channel. Since Eqs. 20–23 are derived from combination of the Donnan equilibrium and the electroneutrality assumption, the check of Donnan equilibrium by comparing boundary conditions must be based on the truth of the electroneutrality assumption. Therefore, we can take $c_{p,l}$, $c_{n,l}$, ϕ_l , $c_{p,0}$, $c_{n,0}$, ϕ_0 at the electroneutrality location ($c_p - c_n = \left(-\frac{2\sigma}{2H}\right) \times 99\%$) as the real boundary conditions, as the dash-dot lines show in Fig. 4a and b.

However, the above method leads to shrinking of the channel length. For all cases the paper focuses on, under the condition of weak electrical field, the ionic concentration is linear along the channel except for the inlet and outlet regions, as shown in Fig. 3. This has been reported in previous literature [34,35]. In fact, the concentration gradient and electrical field were always assumed to be constant in the simplest approach of this problem [5]. Therefore the corrected boundary conditions rationalized as shown in Fig. 3. With acknowledgement of the electroneutrality assumption, we are able to explore the applicability of the Donnan equilibrium.

Note that in the following discussion, the effect from external electrical potential is not considered. If the external/applied potential is high, the potential profile and concentration profile will



Fig. 7. Comparison between Donnan theory and LBM results for inlet and outlet (a) cation concentration, (b) anion concentration and (c) electrical potential along with the variation of channel height. The upper blue lines represent the inlet quantities, and the lower red lines represent the outlet quantities. Calculation parameters: $c_L = 5 \times 10^{-4} \text{ mol}/L$, $c_R = 1 \times 10^{-4} \text{ mol}/L$, $\phi_L = \phi_R = 0 \text{ V}$, $\sigma/H = -1 \times 10^4 \text{ C/m}^3$, L = 1250 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

become non-linear, and the determination at the interfaces is not valid any more, which means the comparison between the Donnan equilibrium and the PNP results will make no sense.

4.1. Comparison between theoretical and numerical results

(1) Channel length effect

The comparisons between Donnan theory prediction and LBM numerical results for ionic concentrations and electrical potential distribution at inlet and outlet interfaces changing with the channel length are shown in Fig. 4. The figure show that when the channel is long enough, the predicted ionic concentrations by both the Donnan equilibrium theory and the LBM modeling agree well with each other. The deviation becomes significant when the channel length is low (approximately L/H < 10). The Donnan theory overrates the concentrations at the inlet and underrates that at the outlet. The electrical potential is more sensitive to the channel length because the deviation for the electrical potential prediction is much larger, especially at the outlet. When we switch the channel height, H = 50 nm, or the higher ionic concentration, $c_L = 1 \times 10^{-3}$ mol/L, the similar results are found. The figures for these two cases are not listed here, yet the data is used in the Q factor analysis in Section 4.2.

(2) Concentration effect

When $c_R = 1 \times 10^{-4}$ mol/L and c_L is increased, the comparison between Donnan theory and LBM results are shown in Fig. 5. The system is exactly at the equilibrium state when $c_L = c_R$ and $\phi_L = \phi_R$, and the Donnan equilibrium is accurate for this case. This is confirmed by the numerical results in Fig. 5. When the concentration gradient increases, the non-equilibrium effect becomes significant, and Donnan equilibrium deviates from the numerical results, as shown in Fig. 5. Since the channel length is not long enough, the electrical potential shows significant divergences at outlet. The concentration difference effect here together with the channel length effect above may lead to a hypothesis of simplified joint factor of the concentration gradient ($\Delta c/L$), which will be examined by the Q factor analysis in Section 4.2.

(3) Surface charge density effect

The comparison between Donnan equilibrium predictions and LBM results for different surface charge densities is shown in Fig. 6. Under the assumption of homogeneous charge of walls, the results indicate that surface charge density effects on the capability of Donnan theory in this nanochannel–reservoir system are slight. As has been known that the surface charge density may



Fig. 8. Q factor along with the change of (a) the channel length, (b) concentration, (c) surface charge density, and (d) channel height. All the relevant parameters can be referred to Section 4.1.

depend on the local solution properties [9,10], such as ionic concentration and temperature, more complicated surface complexity may be introduced to consider the real variable surface charge density effect in our future work.

(4) Channel height effect

To consider the channel height effect on the capability of Donnan theory, we select a large channel length, L = 1250 nm for a given moderate concentration difference to decouple with other effects discussed above. The comparisons between the Donnan theory and the numerical results are shown in Fig. 7. Basically as long as the channel height is much larger than the molecular size of solution so that the continuum assumption still holds [36,37], the channel height can hardly influence the local equilibrium of ion distribution in the nanochannel. This is confirmed by the results in Fig. 7, and it seems that Donnan equilibrium is more applicable for a narrower nanochannel. Note please such a conclusion is based on the homogeneous charge of walls and the long enough channel. For a given channel length, the wider is the channel, the more significant is the inlet and outlet effect and therefore the non-equilibrium effect.

4.2. Q factor analysis

The Donnan equilibrium applicability has been illustrated qualitatively by Figs. 5–8. For an accurate quantitative description, we adopt the Q factor analysis. In this work, the Q factor is calculated by Eq. (34) from the LBM modeling results. The variations of Q factor with the channel length, concentration difference, surface charge density and channel height are plotted in Fig. 8.

Fig. 8(a) confirms that for the given concentrations, the LBM results agree quite well with the predictions of Donnan equilibrium theory when the channel length is long enough. Furthermore, it indicates that $(Q_{in} - 1)$ or $(1/Q_{out} - 1)$ may have a power law relation with the channel length. The fitting power and the correlation coefficients are listed in Table 1. The correlation coefficients are pretty close to unity, which proves the power law relationship.

Similarly, influences from concentration, surface charge, and channel size on the applicability of Donnan equilibrium are analyzed by the Q factor in Fig. 8(b-d). Fig. 8(b) shows that if we keep $c_R = const$ and increase c_L , the theoretical deflection of Donnan theory increases with the concentration difference, and the relationship between Q and concentration difference seems nearly linear. However since the power exponents in Table 1 are not around unity, Q may not simply increase linearly with the concentration gradient. The Q factor versus the surface charge density is shown in Fig. 8(c). The relatively small variation indicates that the surface charge density may have limited influence on the non-equilibrium effect. Fig. 8(d) shows that Q factor increases with the channel height, but the change is relative small, especially at the inlet. The result means that the Donnan theory can predict accurately the interfacial electrical boundary conditions at the channel ends for very small channel height as long as the channel is long enough.

Table 1

Power relationship calculation.

	Group 1	Group 2	Group 3
Power expone	ent n		
Qin	-1.831	-1.344	-1.331
Qout	-1.415	-1.573	-1.362
Correlation co	pefficient R ²		
Qin	0.9972	0.9959	0.9799
Qout	0.9754	0.9933	0.9891



Fig. 9. *Q* factor along with the change of θ .

To summarize, we have known that the Q factor is available to measure the parameter influence of non-equilibrium effect on applicability of Donnan theory. Note that Q reflects the relative error instead of the absolute error, so that in spite of $(1/Q_{out} - 1) \gg (Q_{in} - 1)$, the absolute theoretical errors at inlet and outlet of Donnan theory are at the same level (Figs. 4–7). Yet the more distinct variation of $1/Q_{out}$ makes it much easier to analysis the applicability of Donnan theory.

One more step, a dimensionless parameter θ is defined to represent the integrated all influences from the channel length, concentration difference, surface charge density and channel size:

$$\theta = \frac{\Delta c}{c^*} \left(\frac{H}{L}\right)^{1/2} \frac{\lambda_D}{L},\tag{37}$$

where $c^* = c_L$ for calculations at inlet and $c^* = c_R$ for outlet; Δc is the concentration drop along the nanochannel:

$$\Delta c = c_{i,0} - c_{i,l} = \sqrt{\left(\frac{\sigma}{zFH}\right)^2 + c_R^2} - \sqrt{\left(\frac{\sigma}{zFH}\right)^2 + c_L^2},$$
(38)

and λ_D is the Debye length calculated by c^* :

$$\lambda_D = \sqrt{\frac{\varepsilon \varepsilon_0 RT}{2z^2 F^2 c^*}}.$$
(39)

The relationship between θ and Q for all the calculated cases in this paper is shown in Fig. 9. The results indicate that the Q factor increases approximately linearly with θ . Both Q_{in} and $1/Q_{out}$ are plotted in the same figure and the Q factor at outlet seems more sensitive. Therefore, the value of θ at the outlet interface is available as a criterion to evaluate the applicability of Donnan equilibrium theory. Donnan equilibrium is more accurate for a smaller θ .

5. Conclusions

In this work, the applicability of the Donnan equilibrium theory is studied by comparing the theoretical predictions with the numerical results of the Poisson–Nernst–Planck model solved by lattice Boltzmann methods at the nanochannel–reservoir interfaces. The results indicate that:

(i) For equilibrium or near-equilibrium conditions, such as long enough channels, Donnan equilibrium is available to provide accurate predictions of electrical potential and ionic concentration drops at the interfaces. The non-equilibrium conditions may lead to theoretical deflection of Donnan theory, and the predicted electrical potential at interfaces is more sensitive than the concentration to the non-equilibrium effects.

- (ii) The non-equilibrium factors in nanofluidic systems enhance the deflection of predictions by the Donnan theory at nanochannel-reservoir interfaces. The Donnan equilibrium underestimates electrokinetic quantities at inlet and overestimates those at outlet. The Donnan theory works poorly for short nanochannels, large concentration difference and wide openings, but its applicability is not sensitive to the surface charge of walls when a homogeneous charge is assumed;
- (iii) A non-dimensional parameter, Q factor, is proposed to measure the non-equilibrium extent quantitatively. Q increases significantly when the channel becomes shorter or the ionic concentration difference between reservoirs gets larger, yet Q is not sensitive to the surface charge of channel walls, for homogeneous charge assumption, and to the channel height. Furthermore, another dimensionless parameter θ is proposed to describe the integrated non-equilibrium influences from all working conditions. Donnan equilibrium is more accurate for a smaller θ .

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