

Electrostatic interaction of neutral semi-permeable membranes

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We consider an osmotic equilibrium between bulk solutions of polyelectrolyte bounded by semi-permeable membranes and separated by a thin film of salt-free liquid. Although the membranes are neutral, the counter-ions of the polyelectrolyte molecules permeate into the gap and lead to a steric charge separation. This gives rise to a distance-dependent membrane potential, which translates into a repulsive electrostatic disjoining pressure. From the solution of the nonlinear Poisson–Boltzmann equation, we obtain the distribution of the potential and of ions. We then derive an explicit formula for the pressure exerted on the membranes and show that it deviates from the classical van't Hoff expression for the osmotic pressure. This difference is interpreted in terms of a repulsive electrostatic disjoining pressure originating from the overlap of counterion clouds inside the gap. We also develop a simplified theory based on a linearized Poisson–Boltzmann approach. A comparison with simulation of a primitive model for the electrolyte is provided and does confirm the validity of the theoretical predictions. Beyond the fundamental result that the neutral surfaces can repel, this mechanism not only helps to control the adhesion and long-range interactions of living cells, bacteria, and vesicles, but also allows us to argue that electrostatic interactions should play enormous role in determining behavior and functions of systems bounded by semi-permeable membranes.

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I. INTRODUCTION

It is hard to overestimate the role semi-permeable membranes and osmotic equilibria associated with them play in our everyday life. The best-known examples are the natural biological membranes, which are highly impermeable to ions due to their phospholipid bilayer structure, but become semi-permeable when ion channels are open. Such lipid membranes with channel proteins surround all biological (eukaryotic and prokaryotic) cells.¹ Many synthetic membranes used in electrochemical fuel cells² and dialysis³ take advantage of the semi-permeability of their materials. The same concerns various types of synthetic vesicles,^{4–6} the promising gene and drug carriers, as well as other systems used to mimic biological objects. Being in contact with ionic solutions, such as gels, polyelectrolytes (including DNA, proteins, dendrimers), micelles, or colloids, a semi-permeable membrane maintains an unequal distribution of ionic solute concentrations, which leads to an ion density gradient across the membrane, determines its actual potential, and generates an osmotic pressure difference that the membrane has to sustain. This situation is traditionally referred to as a Donnan equilibrium.^{7,8}

A great deal of research has been devoted to understanding the Donnan equilibria and the pressure exerted on semi-

permeable membranes. Although the problem was treated at various levels of sophistication, traditionally the reservoirs separated by a semi-permeable wall are assumed to be sufficiently large, so that both solutions contain a phase with the bulk properties. Our paper deals with another situation, when two ionic electrolyte solutions consisting of large ions and small ions (referred below to as counter-ions) are in equilibrium with a thin film bounded by the semi-permeable membranes. As some mobile counter-ions will inevitably escape from electrolyte solutions, at some separation their clouds will begin to overlap and give rise the effect similar to the celebrated Derjaguin disjoining pressure⁹ and will change dramatically the Donnan equilibrium⁷ in the system. Some experimental observations¹⁰ support this idea. However, to our surprise, such a scenario, which represents enormous interests for many biological and materials science problems associated with the membrane adhesion and long-range interactions,^{11–13} and are also relevant to modern micro- and nanofluidics,^{14,15} has never been addressed before.¹⁶

In our previous papers, we made an attempt to calculate an excess pressure on a semi-permeable shell in contact with an inner¹⁷ or outer¹⁸ solution of polyions. Since a nonlinear Poisson–Boltzmann (NLPB) equation cannot be solved analytically for spherical geometry,¹⁹ linearized Poisson–Boltzmann equation (LPB) has been used. Our present paper solves a pressure problem for a flat geometry of two

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interacting semi-permeable membranes. We first solve semi-analytically a NLPB equation to evaluate the distribution of electrostatic potential in the system. We then derive an explicit expression for a pressure on the membranes and a disjoining pressure in the gap between them. Our mean-field approach is verified for monovalent salts by molecular dynamics (MD) simulations. Simulation data fully support our theory.

Our paper is organized as follows. In Sec. II, some general consideration concerning a theoretical description of an interaction between two semi-permeable membranes are presented. Here we also describe a simplified linearized version of the theory. Section III contains a description of our MD simulation approach. In Sec. IV, simulation results are presented to validate the predictions of the theory.

II. THEORY

The geometry of the system under consideration is shown in Fig. 1. A semi-permeable membrane is in contact with a solution of polyelectrolyte composed of cations with an effective charge Z and concentration C , anions with charge z and concentration c . We assume here that the polyelectrolyte (here cations) cannot permeate through the semi-permeable membrane, while their counter-ions (here anions) are free to pass through it. The membrane is at distance h from another membrane.

To make the formulas as transparent as possible, we keep our analysis at the mean-field level by using the Poisson–Boltzmann approach. This means that we treat ions as point-like and neglect their correlations. In particular, while the results of the Poisson–Boltzmann theory to be discussed below can be computed for any valence Z of the macromolecules, correlations between macro-ions should be taken into account in the limit of large charges Z in order to obtain quantitative predictions. However, based on earlier results,¹⁸ one does not expect the main physical picture to be altered in this case, and we leave the study of this regime for a future work.

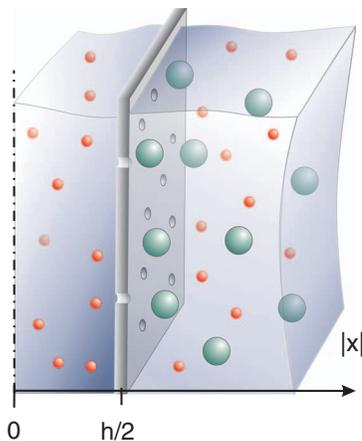


FIG. 1. An electrolyte solution in equilibrium with a thin liquid film of thickness h bounded by neutral semi-permeable membranes. They are permeable for small counterions only (here anions), while the larger solute (here cations) are bounded to the region $|x| > h/2$. The membranes have to support an excess osmotic pressure $\Delta p(h)$ which is the sum of the bulk Donnan pressure and an electrostatic disjoining pressure $\Pi(h)$ in the interlayer.

We consider a hypothetical case of an infinitesimally thin and rigid membrane. We further assume that both membranes are neutral, and axis x is directed normally to the surfaces with $x = 0$ at the midplane of the gap. The membranes are located at $|x| = h/2$. Our description thus essentially follows that of the classical nonlinear Poisson–Boltzmann theory, except for the fact that there is no charge *per se* on the membranes and the membrane surface potential builds up self-consistently: accordingly, the distribution of the charged species is a consequence of the semi-permeable character of the membrane, which leads to a steric charge separation.

A. Nonlinear theory

1. Potential

We first introduce the dimensionless electrostatic potentials,

$$\phi_{i,o} = \frac{ze\varphi_{i,o}}{k_B T}, \quad (1)$$

with the index $\{i, o\}$ standing for “in” ($|x| < h/2$) and “out” ($|x| > h/2$) of the confined slab.

The NLPB equation then reads as

$$\Delta\phi_o = -\kappa_i^2(e^{-\phi_o} - e^{-\tilde{Z}\phi_o}), \quad (2)$$

$$\Delta\phi_i = -\kappa_i^2 e^{-\phi_i}, \quad (3)$$

where the inner inverse Debye screening length, κ_i , is defined as $\kappa_i^2 = 4\pi\ell_B c_\infty$ with $\ell_B = z^2 e^2 / (4\pi\epsilon\epsilon_0 k_B T)$, the Bjerrum length, $\tilde{Z} = Z/z$ (< 0), is the valence ratio of large and small ions, and c_∞ is the concentration of small ions far from the membrane. The outer inverse Debye screening length, κ_o , can be defined as $\kappa_o^2 = 4\pi\ell_B(\tilde{Z}^2 C_\infty + c_\infty)$, where C_∞ is the concentration of large ions far from the membrane. Obviously, it represents the inverse Debye length of the bulk electrolyte solution. Since the electroneutrality condition $ZC_\infty + zc_\infty = 0$ is employed, $\kappa_o = \kappa_i\sqrt{1 - \tilde{Z}}$. We stress, however, that for this particular problem, the main reference length scale that determines the behavior of the system is κ_i^{-1} , and this is reflected in the analysis below.

The first integration gives a differential equation for ϕ_o ,

$$\frac{1}{2\kappa_i^2} \left(\frac{\partial\phi_o}{\partial x} \right)^2 = e^{-\phi_o} - \frac{1}{\tilde{Z}} e^{-\tilde{Z}\phi_o} + A_0, \quad (4)$$

where the integration constant A_0 is determined by the boundary conditions at infinity: $\phi_o \rightarrow 0$ and $\partial_x\phi_o \rightarrow 0$. Imposing them on Eq. (4) yields $A_0 = \frac{1}{\tilde{Z}} - 1$. Thus, the outer solution ϕ_o can be obtained in terms of the membrane “surface” potential $\phi_s = \phi(h/2)$,

$$\int_{\phi_s}^{\phi_o} \frac{d\phi}{\sqrt{2(\exp[-\phi] - 1 - \frac{1}{\tilde{Z}}(\exp(-\tilde{Z}\phi) - 1))}} = -\kappa_i \left(x - \frac{h}{2} \right). \quad (5)$$

For the inner compartment, ϕ_i , the first integration of the NLPB equation yields

$$\frac{1}{2\kappa_i^2} \left(\frac{\partial \phi_i}{\partial x} \right)^2 = e^{-\phi_i} - e^{-\phi_m}. \quad (6)$$

Here we used $\partial_x \phi(x=0) = 0$ implied by symmetry. This leads to

$$\int_{\phi_m}^{\phi_i} \frac{d\phi}{\sqrt{2(\exp[-\phi] - \exp[-\phi_m])}} = -\kappa_i x, \quad (7)$$

with ϕ_m , the (dimensionless) potential at the center of the film between membranes. This integral can be evaluated exactly as

$$2 \arctan \left[\sqrt{\exp[-(\phi_i - \phi_m)] - 1} \right] \exp \left[\frac{\phi_m}{2} \right] = \sqrt{2} \kappa_i x, \quad (8)$$

leading to the Gouy-type expression

$$\phi_i(x) = \phi_m + \ln \left[\cos^2 \left(\frac{\sqrt{2}}{2} e^{-\phi_m/2} \kappa_i x \right) \right]. \quad (9)$$

The continuity of the electric field at the membrane surface, Eqs. (4)–(6) (no surface charge) leads to

$$e^{-\phi_s} - \frac{1}{\tilde{Z}} e^{-\tilde{Z}\phi_s} + \frac{1}{\tilde{Z}} - 1 = e^{-\phi_s} - e^{-\phi_m}. \quad (10)$$

Altogether, the membrane potential ϕ_s and mid-plane potential ϕ_m are thus given by the self-consistent equations,

$$\phi_s = \phi_m + \ln \left[\cos^2 \left(\frac{\sqrt{2}}{2} e^{-\phi_m/2} \kappa_i \frac{h}{2} \right) \right], \quad (11)$$

and

$$\phi_m = -\ln \left[1 + \frac{1}{\tilde{Z}} (e^{-\tilde{Z}\phi_s} - 1) \right]. \quad (12)$$

In the general case, the derived equations should be solved numerically while in the limits of large and small $\kappa_i h$, we can also find the asymptotic analytical expressions. In the thick gap limit, $\kappa_i h \gg 1$, the midplane potential diverges, $\phi_m \rightarrow \infty$, and the equation for ϕ_s , Eq. (12), can be simplified to give

$$\phi_s \simeq -\frac{1}{\tilde{Z}} \ln(1 - \tilde{Z}). \quad (13)$$

This value represents the bulk Donnan potential.

Similarly, the asymptotic behavior for ϕ_m can be obtained from Eq. (11). Since ϕ_s is bounded by a constant, the condition $\phi_m \gg 1$ as $\kappa_i h \gg 1$ imposes that $\frac{\sqrt{2}}{2} e^{-\phi_m/2} \kappa_i \frac{h}{2} \simeq \pi/2$. This leads to

$$\phi_m \simeq 2 \ln \left[\frac{\sqrt{2}}{2\pi} \kappa_i h \right]. \quad (14)$$

In the thin gap limit, $\kappa_i h \ll 1$, where the inner ionic clouds strongly overlap, both ϕ_m and ϕ_s vanish. Such a situation would be realistic for very dilute polyelectrolyte solutions and/or very thin gap. One can easily verify that $\phi_m \simeq \phi_s \propto \kappa_i h$.

Thus, the convergence of two semi-permeable membranes is necessarily accompanied by the decrease in the absolute value of their potential. The idea that the constant

potential condition is not appropriate for fully permeable charged membranes has been suggested before.^{20,21} Now we have shown that the potential of neutral semi-permeable surfaces should inevitably change and can even vanish as a result of their approach. Such a finding might be especially important for biomembranes, where an alteration of a surface potential can lead to a characteristic biological response.

2. Osmotic and disjoining pressure

The force balance in each part of the membrane (in and out) can be written as

$$-\nabla p + \rho_c E = 0, \quad (15)$$

with ρ_c , the charge density and $E = -\partial_x \phi$, the local electric field. Using the Boltzmann expressions for the charge densities in terms of the local electrostatic potentials allows to integrate this equation once.

In midspace between the membranes ($|x| < h/2$), this leads to

$$p_i(x) = k_B T c(x) + p_0, \quad (16)$$

with $c(x) = c_\infty \exp[-\phi(x)]$, the counter-ion concentration and p_0 a constant.

In the outer space ($|x| < h/2$) one gets

$$p_o(x) = k_B T c(x) + k_B T C(x) + p_L, \quad (17)$$

with $C(x) = C_\infty \exp[-\tilde{Z}\phi(x)]$, the concentration of large ions and p_L the pressure of pure solvent.

At the membrane, there is a pressure drop due to the repulsion force acting on the polyelectrolyte by the membrane (and proportional to the difference of polyelectrolyte concentration on the two sides of the membrane), i.e.,

$$p_o \left(\frac{h^+}{2} \right) - p_i \left(\frac{h^-}{2} \right) = k_B T C \left(\frac{h^+}{2} \right). \quad (18)$$

This imposes $p_0 = p_L$, i.e., the solvent pressure, as expected.

The force acting on the membrane (osmotic pressure) can be found from the Maxwell tensor $\mathbb{T} = (P + \frac{\epsilon}{2} E^2) \mathbb{I} - \epsilon E \otimes E$. Using $\nabla \cdot \mathbb{T} = 0$, we find the force per unit surface on the membrane as $\Delta p = \mathbb{T}(x=0) - \mathbb{T}(x=\infty)$,

$$\begin{aligned} \Delta p &= \mathbb{T}(x=0) - \mathbb{T}(x=\infty) \\ &= k_B T c_\infty (1 - e^{-\phi_m}) + k_B T C_\infty. \end{aligned} \quad (19)$$

Note that by using Eq. (12), one can demonstrate that expression given in Eq. (19) is fully equivalent to Eq. (18). Therefore, since the disjoining pressure, Π , is defined via

$$\Delta p = k_B T (c_\infty + C_\infty) - \Pi, \quad (20)$$

it can be expressed through the concentration (or potential) at the mid-plane as

$$\Pi = k_B T c_m = k_B T c_\infty e^{-\phi_m}. \quad (21)$$

In other words, the whole effect can be expressed through the osmotic pressure of small ions in the mid-plane of the gap where the electric field vanishes. Note that the similar physical interpretation of the disjoining pressure between flat solid surfaces was given long ago in the famous work

by Langmuir.²² Note that the disjoining pressure is always positive indicating an electrostatic repulsion between neutral semi-permeable membranes separating the similar electrolyte solutions.

By using the expression of the disjoining pressure, Eq. (21), we get in thick gap limit

$$\Pi \simeq k_B T c_\infty \frac{2\pi^2}{(\kappa_i h)^2}, \quad (22)$$

i.e., $\Pi \propto h^{-2}$. This is very similar to the famous Langmuir result, but here for an *a priori* uncharged semi-permeable membrane.

In contrast, at small $\kappa_i h$,

$$\Pi \approx k_B T c_\infty. \quad (23)$$

This suggests that the osmotic pressure in the gap is dramatically reduced compared to the value expected in the bulk,

$$\Delta p = k_B T C_\infty = \frac{1}{1 - \tilde{Z}} p_{id}, \quad (24)$$

with $p_{id} = k_B T (C_\infty + c_\infty)$, the “ideal” (bulk) osmotic pressure. Accordingly, $\Pi = -\tilde{Z}/(1 - \tilde{Z}) p_{id}$ in this limit. This is one of the key results of our work.

B. Linearized theory

At low charge densities and low values of the electric potential, the description of the problem can be simplified by linearization of the Poisson–Boltzmann approach. The linear approximation for the local concentrations reads: $c_{i,o}(x) = c_\infty(1 - \phi_{i,o}(x))$, and $C_o(x) = C_\infty(1 - \tilde{Z}\phi_o(x))$. Substituting them into Eq. (3), we get its linearized version with the straightforward solutions,

$$\phi_o = \phi_s \exp[\kappa_o(h/2 - |x|)], \quad (25)$$

$$\phi_i = 1 + (\phi_s - 1) \frac{\cosh(\kappa_i x)}{\cosh(\kappa_i h/2)}. \quad (26)$$

The electroneutrality of the membrane allows us to deduce

$$\phi_s = \frac{\kappa_i}{\kappa_i + \kappa_o \coth(\kappa_i h/2)}, \quad (27)$$

$$\phi_m = 1 - \frac{\kappa_o}{\kappa_o \cosh(\kappa_i h/2) + \kappa_i \sinh(\kappa_i h/2)}. \quad (28)$$

In the thin gap limit, the membrane potential vanishes similarly to the nonlinear case. For large gaps, we get

$$\phi_s \simeq \frac{\kappa_i}{\kappa_i + \kappa_o} = \frac{1}{1 + \sqrt{1 - \tilde{Z}}}. \quad (29)$$

The value of this bulk Donnan potential is different from predicted by NLPB theory, Eq. (13).

We also note that the potential in the midplane at large $\kappa_i h$ saturates, asymptotically approaching 1 (in contrast to its divergence in the NLPB theory, cf. Eq. (14)). This is an evidence of a failure of the linear theory in calculation of potentials (and relevant ion profiles in the system).

Motivated by recent analysis,^{18,23,24} we then obtain the following expression for the pressure,

$$p_o = p_L + k_B T (C_\infty + c_\infty) + \frac{\epsilon_0 \epsilon \kappa_o^2 \phi_o^2}{2}, \quad (30)$$

$$p_i = p_L + k_B T c_m - z e c_\infty (\phi_i - \phi_m) + \frac{\epsilon_0 \epsilon \kappa_i^2 (\phi_i^2 - \phi_m^2)}{2}, \quad (31)$$

which contains quadratic terms to provide thermodynamic self-consistency of the linear theory.

Using these expressions, one can calculate the pressure difference on both sides of the membrane to obtain²⁵

$$\Delta p = p_{id} - k_B T c_m. \quad (32)$$

As one can easily see, all the electrostatic terms cancel and the whole effect is expressed by the osmotic pressure of small ions in the mid-plane of the gap. In other words, physically we have arrived to the same result as in the NLPB case. Clearly, in the LPB case, $c_m = c_i(x=0)$ is very different, so that the disjoining pressure takes the form

$$\Pi = k_B T C_\infty \frac{\kappa_o}{\kappa_o \cosh(\kappa_i h/2) + \kappa_i \sinh(\kappa_i h/2)}. \quad (33)$$

For large $\kappa_i h$, one can note some similarity to a repulsion of solids,^{9,26} which exponentially decays to zero as

$$\Pi \simeq k_B T C_\infty \frac{2\kappa_o}{\kappa_o + \kappa_i} \exp\left(-\frac{\kappa_i h}{2}\right), \quad (34)$$

which obviously differs from NLPB result, Eq. (22). For small $\kappa_i h$, we again get Eq. (23).

III. SIMULATIONS

The Langevin dynamics simulations were performed on the level of the primitive model with explicit large and small ions using the ESPResSo simulation package.²⁷ We constructed a 1D-periodic setup with two membranes fixed perpendicular to the x axis. The membranes were made impermeable for cations, but “invisible” for anions.²⁸

For an initial illustration of our approach, we here use a monovalent electrolyte, and ionic species were represented by Lennard–Jones (LJ) spheres with a central charge $Z = 1$ or $z = -1$. We used the repulsive Lennard–Jones potential with the cut-off distance $r_c = 2^{1/6}\sigma$:

$$U_{LJ}(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 + \frac{1}{4} \right], & r \leq r_c; \\ 0, & r > r_c, \end{cases} \quad (35)$$

where r is the distance between centers of two particles. The energy parameter ϵ controls the strength of the interaction, and its value was fixed to $\epsilon = 1.0 k_B T$. The units of length and energy in all presented data were set by σ and ϵ , respectively (LJ units). The bead sizes were set as $\sigma_{pp} = \sigma_{cc} = \sigma_{pc} = 1.0$.

The interaction of ions with the membrane was set by

$$U_{LJ}(x) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{x}\right)^{12} - \left(\frac{\sigma}{x}\right)^6 - \left(\frac{\sigma}{x_c}\right)^{12} + \left(\frac{\sigma}{x_c}\right)^6 \right], & x \leq x_c; \\ 0, & x > x_c, \end{cases} \quad (36)$$

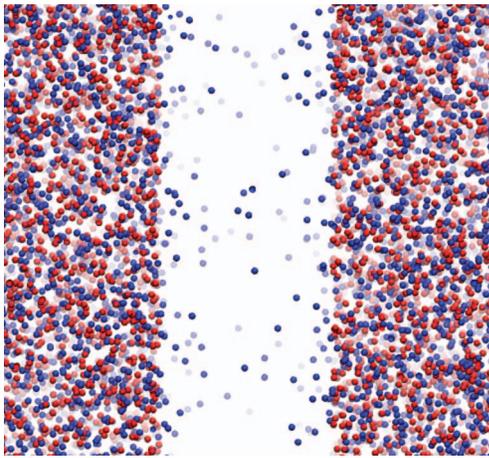


FIG. 2. Side view of the film confined between two semi-permeable membranes. Cations are shown by blue spheres and anions by the red spheres. One can see that anions leak out into the gap between the membranes.

with the cut-off distance $x_c = 2^{1/6}\sigma$.

The solvent was treated as a homogeneous medium with a dielectric permittivity set through the Bjerrum length. The electrostatic interaction between the ionic species was modeled by the Coulomb potential,

$$U_{\text{Coul}}(r_{ij}) = k_B T \frac{\ell_B q_i q_j}{r_{ij}}, \quad (37)$$

where $q_i = \pm 1$. In all simulations, we used $\ell_B = 1$.

We modeled the systems in a rectangular cell with side L ranging from 100 to 700 for different electrolyte concentrations. The number of ions in the cell was varied from $N_p = 500$ to 15 000, and an equivalent number of counterions was added. The number of ions in each simulation was chosen to keep the ionic concentration in center of the membrane fixed at $C_\infty = 0.03$ and to vary the value of $\kappa_i h$ in a very large range, from 0.7 to 30.

Three-dimensional periodic boundary conditions were used. For Coulomb interactions we used the P3M algorithm with maximum relative accuracy of 10^{-5} . A snapshot of the system is presented in Fig. 2.

Pressure has been evaluated via integration of the LJ force of cations, acting on the membrane walls,

$$F(x) = 4\epsilon \left(\frac{12\sigma^{12}}{(x - \frac{h}{2})^{13}} - \frac{6\sigma^6}{(x - \frac{h}{2})^7} \right). \quad (38)$$

Using this force expression, we calculated the pressure as

$$p = \int_{h/2}^{h+2^{1/6}\sigma} C(x)F(x)dx. \quad (39)$$

IV. RESULTS AND DISCUSSION

In this section, we present results of MD computer simulations and some example calculations based on the general NLPB theory as well as the analytical LPB results.

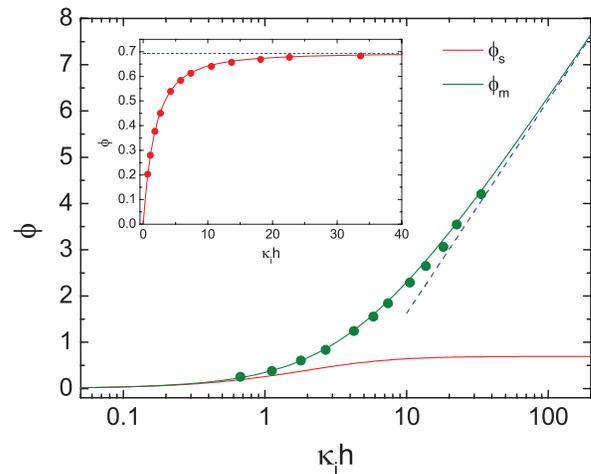


FIG. 3. Midplane and surface potentials, ϕ_m (top curve), ϕ_s (bottom curve), as a function of $\kappa_i h$. The dashed line is the asymptotic behavior for ϕ_m in the large $\kappa_i h$ regime according to Eq. (14): $\phi_m \approx 2 \log[\kappa_i h \sqrt{2/2\pi}]$. Inset shows zoom on the behavior of the surface potential versus $\kappa_i h$. The dashed line here is the asymptotic behavior for ϕ_s in the large $\kappa_i h$ regime according to Eq. (13): $\phi_s \approx -\frac{1}{Z} \log(1 - \bar{Z})$. In these plots, we use $\bar{Z} = 1$.

The distribution of the electrostatic potentials, ϕ_s and ϕ_m , is shown in Fig. 3 versus $\kappa_i h$ (symbols). Also included are the exact theoretical curve, calculated with Eqs. (11) and (12) (solid curves). The agreement is excellent for all $\kappa_i h$, even for very large values, confirming the validity of the mean-field approach for our system. Asymptotic results are in agreement with the numerical calculations presented in Fig. 3. At $\kappa_i h \ll 1$ (strong overlap of an inner double layer), the membrane potential vanishes. Such a situation would be realistic for very dilute solutions and/or very thin gap. Another asymptotic limit of large films and/or concentrated solutions, $\kappa_i h \gg 1$ (no overlap of the inner ionic layers) gives Eq. (13), which is fully supported by the simulation results.

These pressure trends are illustrated in Fig. 4. Simulations show that at large $\kappa_i h$, the pressure, $\Delta p/p_{id}$, supported by the membrane, is close to the osmotic pressure of the corresponding bulk solution $\Delta p/p_{id} \approx 1$, and we deal with the standard bulk Donnan equilibrium. In this situation, the disjoining pressure is negligibly small. At smaller $\kappa_i h$, the pressure exerted on the semi-permeable wall is much less than that in the bulk, and at very small $\kappa_i h$, it approaches a constant, which is equal to the bulk osmotic pressure of large ions, Eq. (24). This is accompanied by an increase in the value of a disjoining pressure in the gap. The results for the pressure and the disjoining pressure obtained in the NLPB theory and simulations coincide confirming the validity of the mean-field approach for our system. Figure 4 also includes the theoretical curves calculated within LPB theory. The agreement is quite good at very small and very large $\kappa_i h$, but at intermediate values of $\kappa_i h$, there is some discrepancy. The discrepancy is always in the direction of the pressure on membrane is larger than than “measured” in simulations and predicted by the NLPB theory. Correspondingly, the disjoining pressure is smaller. Still, LPB and simulation pressures are in surprisingly good harmony, especially taking into account the simplicity of the model and the complexity of the system. Obviously, the effects are

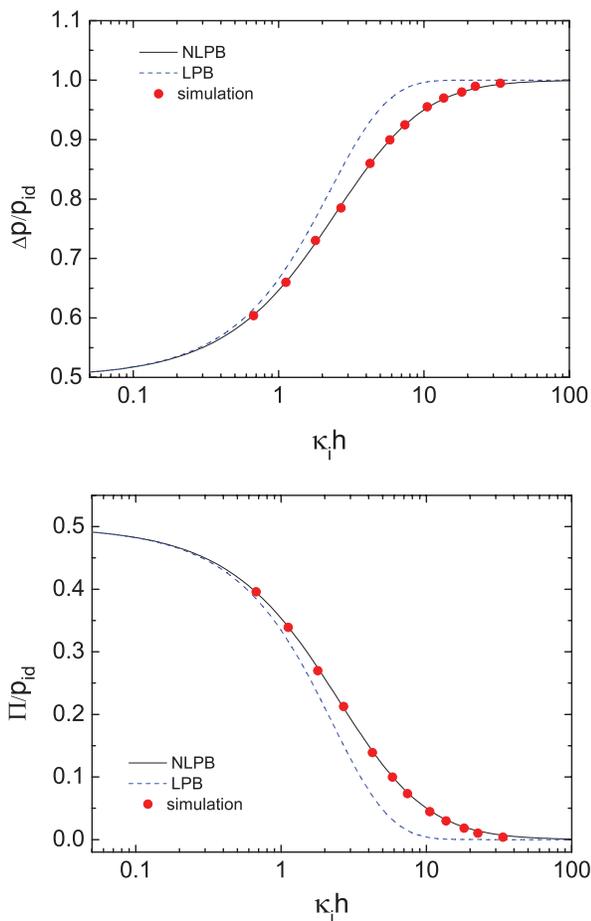


FIG. 4. Pressure acting on a membrane and a disjoining pressure normalized by the ideal osmotic pressure, $p_{id} = k_B T(c_\infty + C_\infty)$. Solid curves show NLPB predictions, dashed curve shows LPB theory predictions, and symbols present simulation results.

somehow included in the quadratic term of the expression for a pressure which provided a self-consistency of the LPB theory. These questions, however, deserve further investigation and remain subject of a future work.

Finally, we note that all the results derived above hold also for the case of a membrane placed at a distance $h/2$ from the neutral wall suggesting that the tight adhesion of semi-permeable membrane to the neutral wall is impossible within our scenario. In general, for more complex systems, where the membrane adhesion is controlled by the competition of several effects, the physical mechanism we considered here should reduce the attractive interactions by orders of magnitude similarly to what was predicted for other types of electrostatic interactions in the membrane systems.^{29,30} It would be also worthwhile to emphasize that our derivation can easily be modified for the situation where a thin film separates the reservoirs with oppositely charged polyelectrolytes. In this case, however, no attraction between semi-permeable membranes takes place as it would be tempting to expect. The point is that only solution for such a configuration is $\phi = 0$. Hence, all phases are homogeneous and neutral. This result can, however, still be of help when new synthetic delivery systems are designed. For example, to avoid repulsion from the cell mem-

brane, a semi-permeable neutral container should contain positively charged molecules of drugs or proteins.

To summarize, we have examined theoretically the situation of an interaction of two neutral semi-permeable membranes separated by a thin film. Our mechanism predicts an alteration of the membrane potential during the approach, a decrease in osmotic pressure on membranes when they are in a close proximity, and an electrostatic repulsion between them. Our analysis also allows one to express a disjoining pressure in the film through the osmotic pressure of counter-ions in the midplane.

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