Electrostatic Interactions and Electro-osmotic Properties of Semipermeable Surfaces.

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(Dated: January 5, 2018)

We consider two charged semipermeable membranes, which bound bulk electrolyte solutions and are separated by a thin film of salt-free liquid. Small counter-ions permeate into the gap, which leads to a steric charge separation in the system. To quantify the problem, we define an effective surface charge density of imaginary impermeable surface, which mimics an actual semipermeable membrane and greatly simplify analysis. The effective charge depends on separation, generally differ from the real one, and could even be of the opposite sign. From the exact and asymptotic solutions of the nonlinear Poisson-Boltzmann equation, we obtain the distribution of the potential and of counter-ions in the system. We then derive explicit formulae for the disjoining pressure in the gap and electro-osmotic velocity, and show that both are controlled by the effective surface charge.

I. INTRODUCTION

Electrostatic Diffuse Layer (EDL) is usually defined as the region where the surface charge is balanced by the cloud of counterions and local electro-neutrality is not obeyed. It determines both static and dynamic properties of charged objects and results in a variety of phenomena, important for both fundamental and practical applications. Extending over hundreds molecular diameters it results in long-range electrostatic forces between surfaces \cite{1-3}, which control coagulation stability \cite{4-7} and open many opportunities for electrostatic self-assembly \cite{8-11}. EDL also responds to external electric field, leading to various kinds of electrokinetic phenomena \cite{12-16}. The majority of previous work on colloidal forces and electrokinetics has assumed that surfaces are impermeable, so that the EDL profile is determined by the surface charge density and the Debye length of bulk electrolyte solution \cite{17, 18}.

The assumption that surfaces are impermeable for ions becomes unrealistic in colloidal systems where membranes are involved. In such cases another factor, surface permeability, comes into play and strongly affects EDLs, so it becomes a very important consideration in interactions involving membranes or determining electrokinetic phenomena. The body of work investigating EDLs near permeable charged surfaces is much less than that for impermeable objects, although there is a growing literature in this area \cite{19, 21}.

Here we explore what happens when surfaces are semi-permeable, i.e. impermeable for large ions, but allow free diffusion of small counterions. Examples of such surfaces abound in our everyday life. They include bacterial and cell membranes \cite{22}, viral capsids \cite{23}, liposomes with ion channels \cite{24-26}, polymersomes \cite{20, 27}, free-standing polyelectrolyte multilayer films \cite{28-31}. In efforts to understand the connection between EDLs and semipermeability, their formation near membranes has been studied over several years and by several groups \cite{23, 24, 25, 51}.

These investigations so far have been limited by the simplest case of electro-neutral membranes and have shown that a steric charge separation in such a system gives rise to a finite surface potential \cite{35}. This means that due to semi-permeability electro-neutral surfaces demonstrate properties of charged systems \cite{32, 34, 36, 57}. In reality, the majority of semipermeable surfaces are charged. For example, the polyelectrolyte multilayers take a charge of the last deposited polyelectrolyte layer and the channel proteins determine a charge of biological membranes. However, we are unaware of any previous work that has...
II. GENERAL THEORY

A. Model

Consider a solvent confined between two parallel semipermeable membranes at a separation \( h \), both are in contact with an electrolyte reservoir. Small (here positive with a charge \( z \)) ions are free to pass through membranes and leak out from the salt reservoir into the gap, but large (here negative with a charge \( Z \), \( |Z| > |z| \)) ions cannot permeate through it. This gives rise to the steric charge separation and inhomogeneous equilibrium distribution of ions as sketched in Fig. [1]. Similar system with neutral membranes has been considered before [33]. Now we assume that membranes have a surface charge density, \( \tilde{\sigma} \), which could be either due to dissociation of functional surface groups, or due to the adsorption of ions from solution to the surface [1].

As before, we use continuum mean-field description by assuming point-like ions and neglecting ionic correlations. Non-uniform averaged ionic profiles can then be described by using non-zero electrostatic potential \( \phi(x) \equiv z e \psi / k_B T \) and Boltzmann distribution:

\[
c_i(x) = c_{\infty,i,o} \exp(-\phi_{i,o})
\]

\[
C_i(x) = C_{\infty,i,o} \exp(-\tilde{\phi}_{i,o})
\]

Here \( \phi_{i,o} = z e \psi_{i,o} / k_B T \) are the dimensionless electrostatic potentials, and \( c_{i,o}, C_{i,o} \) are concentrations of small and large ions respectively, where indices \( \{i,o\} \) indicate inner \( (|x| < h/2) \) and outer \( (|x| > h/2) \) solutions.

The NLPB equation for the dimensionless electrostatic potential \( \phi \) is then given by

\[
\Delta \phi_o = -\kappa_o^2 \left( e^{-\phi_o} - e^{-\tilde{\phi}_o} \right) \quad (1)
\]

\[
\Delta \phi_i = -\kappa_i^2 e^{-\phi_i} \quad (2)
\]

where the inner inverse screening length, \( \kappa_i \), is defined as \( \kappa_i^2 = 4 \pi \ell_B e \) with \( \ell_B = z e^2 / \left( 4 \pi \epsilon_0 \epsilon_k k_B T \right) \) the Bjerrum length, \( \tilde{Z} = Z / z \) \((< 0)\) is the valence ratio of large and small ions, and \( c_{\infty} \) is the concentration of large ions at \( |x| \rightarrow \infty \). The outer inverse screening length, \( \kappa_o \), which represents the inverse Debye length of the bulk electrolyte solution, can be defined as \( \kappa_o^2 = 4 \pi \ell_B (Z^2 C_{\infty} + c_{\infty}) \), where \( C_{\infty} \) is the concentration of large ions at infinity. Since the electroneutrality condition \( ZC_{\infty} + zc_{\infty} = 0 \) is employed, \( \kappa_0 = \kappa_i \sqrt{1 - \tilde{Z}} \). We recall that the NLPB has been proven to adequately describe a semipermeable membrane system even at a high valence ratio, \( \tilde{Z} = -5 \).

To solve Eqs. (1) and (2) at the membrane surface, \( \phi_o(h/2) - \phi_i(h/2) = \kappa \sigma \),

\[
\phi_i(h/2) = 0,
\]

where \( \sigma = 4 \pi \ell_B \tilde{\sigma} / \kappa \) is the dimensionless surface charge density. At the midplane, \( x = 0 \), the electric field vanishes due to symmetry, \( \phi'_i = 0 \). Finally, we set \( \phi_o \rightarrow 0 \) at infinity.

Now it is convenient to define inner and outer diffuse layer charges:

\[
\tilde{\sigma}_i^D = \int_0^{h/2} z e c(x) dx, \quad \tilde{\sigma}_o^D = \int_{h/2}^{\infty} [z e c(x) - Z e C(x)] dx.
\]

which satisfy a global electroneutrality condition:

\[
\sigma + \tilde{\sigma}_i^D + \tilde{\sigma}_o^D = 0.
\]

It follows from Gauss’s theorem that

\[
\kappa_i \sigma_o^D = \phi'_i(h/2), \quad \kappa_o \sigma_o^D = -\phi'_o(h/2),
\]

which suggests that Eq. (3) is equivalent to Eq. (5). It is therefore always possible to construct imaginary impermeable surfaces with an effective surface charge density \( \sigma_{eff} \), which induce the same potential and, therefore, mimic actual semipermeable membranes. Such an effective charge is equal to \( -\sigma_o^D \) for an inner area, and to \( -\sigma_o^D \) for an outer reservoir, and fully characterizes electroosmotic equilibria in the system of real membranes.

B. Concentration profiles and electrostatic potential

To illustrate the approach, we begin by studying concentration profiles of small ions obtained by solving numerically Eqs. (1) and (2) for different values of membrane surface charge \( \sigma \). Calculation results are shown in Fig. [2]. We see that away from membranes \( (|x - h/2| \gg \kappa_i^{-1}) \) density profiles turn to \( c_{\infty} \). However, in the vicinity of membranes they are generally non-uniform due to EDL formation in both inner and outer regions. When membranes are close to each other, \( \kappa_i h = 1 \) (see Fig. [2(a)]), inner EDLs strongly overlap. When the surface charge is negative, the counter-ion density, \( c_m \), at the mid-plane
is finite, and for large negative charges it can be larger than \( c_\infty \). In other words we observe a counter-ion enrichment in the thin film. Since only counter-ions penetrate the gap, so that the inner region can be only positively charged or nearly neutral (if membranes are strongly positively charged as discussed above), \( \sigma_o^D \geq 0 \). A vanishing \( \sigma_o^D \) indicates that inner EDLs disappear and practically all diffuse charges are outside the slit, \( \sigma_o^D \simeq -\sigma \). Eq. (5) implies that the outer EDL is negatively charged if \( \sigma > 0 \). However, for negatively charged membranes the situation can be more complicated than the usual picture. For a relatively small negative surface charge we observe \( \sigma_o^D < 0 \), but for higher negative surface charges \( \sigma_o^D \) becomes positive. Therefore, at a certain surface charge, \( \sigma = \sigma_o < 0 \), the outer double layer should fully disappear since all diffuse charges are confined in the slit, \( \sigma_o^D = -\sigma \).

The distribution of a potential calculated for a fixed thick film, \( \kappa_i h = 10 \), and different values of \( \sigma \) is shown in Fig. 3. We first remark that in the case of neutral membranes, \( \sigma = 0 \), the surface potential, \( \phi_s \), is positive, and the distribution of a potential in the system is inhomogeneous. This observation has been reported before [33]. The surface potential is always of the same sign as the surface charge for large \( |\sigma| \), but at low values of negative surface charge \( \phi_s \) could vanish or become positive.

Let us now use Eq. (2) to obtain exact expressions for concentration and potential profiles in the slit. This leads to a Gouy-type expression [33]:

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

(7)

where \( \phi_m \) is the (dimensionless) potential at the midplane. By comparing the Gouy solution [1] for impermeable surfaces with Eq. (7) we can define the effective surface charge as \( \phi'_i(h/2) = \kappa \sigma_{\text{eff},i} \) (cf. Eq. (8)). The dimensionless inner effective surface charge is then:

\[
\sigma_{\text{eff},i} = -\sqrt{2} e^{-\phi_m/2} \tan \left( \frac{\sqrt{2}}{2} e^{-\phi_m/2\kappa_i h/2} \right),
\]

(8)

and the outer effective charge always differs from the inner and is given by \( \sigma_{\text{eff},o} = \sigma - \sigma_{\text{eff},i} \). We note that Eq. (8) indicates that effective charges depend on separation between membranes.

In many cases properties of the system can be related to \( \phi_s \) or \( \phi_m \). Therefore, below we focus on their analysis. First we rewrite the differential equations for a potential, \( \phi \), into self-consistent algebraic equations for \( \phi_s \) and \( \phi_m \).
The equation for $\phi_s$ follows immediately from Eq. (7) by setting $x = h/2$

$$\phi_s = \phi_m + \ln \left[ \cos^2 \left( \frac{\sqrt{2}}{2} e^{-\phi_m / 2 \kappa_h h} \right) \right]$$ (9)

The derivation of the equation for $\phi_m$ requires integration of Eqs. (11) and (2), which gives:

$$\frac{1}{2 \kappa_h^2} \left( \frac{\partial \phi_o}{\partial x} \right)^2 = e^{-\phi_o} - 1 - \frac{1}{Z} (e^{-\tilde{Z} \phi_o} - 1)$$ (10)

$$\frac{1}{2 \kappa_h^2} \left( \frac{\partial \phi_i}{\partial x} \right)^2 = e^{-\phi_i} - e^{-\phi_m}$$ (11)

By setting $x = h/2$ and applying the boundary condition for $\phi^i$, Eq. (13), and the condition of continuity of $\phi$ we derive the second relation between $\phi_s$ and $\phi_m$:

$$e^{-\tilde{Z} \phi_s} = 1 - \tilde{Z} \left( \frac{\sigma}{2} - \sigma_{eff,i} \sigma + 1 - e^{-\phi_m} \right)$$ (12)

C. Asymptotic analysis

In the general case, the system of Eqs. (9) and (12) should be solved numerically, but in some limits we can derive asymptotic analytical expressions, which relate $\phi_s$ and $\phi_m$ with $\sigma$ and parameters of the system. Below we focus on limits of large and small $\kappa_h h$ and on situations of strong and weak $\sigma$.

1. Large $\kappa_h h$

In a regime, $\kappa_h h \gg 1$, typical for concentrated solutions and/or very thick gap, it is convenient to introduce a new variable $\xi$ by using Eq. (11) as:

$$\frac{\sqrt{2}}{2} e^{-\phi_m / 2 \kappa_h h / 2} = \frac{\pi}{2} (1 - \xi)$$ (13)

Hence the surface potential in Eq. (9) can be expressed as:

$$\phi_s = 2 \ln \left[ \frac{\kappa_h h \sin(\xi \pi / 2)}{\sqrt{2 \pi} (1 - \xi)} \right]$$ (14)

One can easily prove that $\xi$ decays from 1 to 0 with the increase in $\kappa_h h$ from 0 to $\infty$, so that it is small, when $\kappa_h h$ is large. Since $\phi_s$ is bounded by a constant, $\xi$ decays with $\kappa_h h$ as:

$$\xi \simeq \frac{e^{\phi_s / 2} \sqrt{2}}{2 \sqrt{2} e^{\phi_s / 2} + \kappa_h h},$$ (15)

and the midplane potential reads

$$\phi_m \simeq 2 \ln \left[ \frac{\sqrt{2}}{2 \pi (1 - \xi)} \kappa_h h \right] \propto \ln(\kappa_h h)^2$$ (16)

Since in this limit $\xi \ll 1$, it can be neglected in the first-order approximation. Then Eq. (10) reduces to the known result for neutral membranes [33]. This suggests that at large $\kappa_h$ the midplane potential, $\phi_m$, is insensitive to $\sigma$ being controlled mostly by $\kappa_h$.

When $\phi_m$ is large, we can derive relation between surface charge and surface potential:

$$e^{-\tilde{Z} \phi_s} + \tilde{Z} \sqrt{2} e^{-\phi_s / 2} \sigma \simeq 1 - \tilde{Z} - \tilde{Z} \sigma^2 / 2.$$ (17)

and allows us to construct then the asymptotic solutions for strongly charged surfaces, $\sigma \gg 1$. For negative surface charges $\phi_s$ is also negative, $e^{-\tilde{Z} \phi_s} \ll 1$ and $e^{-\phi_s / 2} \gg 1$, which leads to

$$\phi_s \simeq -2 \ln \left[ \frac{2(1 - 1/\tilde{Z}) + \sigma^2}{2 \sqrt{2} \sigma} \right] \propto -\ln \sigma^2$$ (18)

For large positive charges and hence positive $\phi_s$ we can use $e^{-\tilde{Z} \phi_s} \gg 1$ and $e^{-\phi_s / 2} \ll 1$ to derive

$$\phi_s \simeq -\frac{1}{\tilde{Z}} \ln \left[ 1 - \tilde{Z} - \tilde{Z} \sigma^2 / 2 \right] \propto \frac{1}{|\tilde{Z}|} \ln \sigma^2$$ (19)

In the case of weak charges, $\sigma \ll 1$, one can construct first-order correction to the surface potential of neutral membranes, $\phi_s^0 = -\frac{1}{\tilde{Z}} \ln(1 - \tilde{Z})$ [33], which takes the form

$$\phi_s = \phi_s^0 + \sqrt{2} e^{\chi} \phi_s^0 \sigma \propto \sigma$$ (20)

We remark and stress that in all cases above $\phi_s$ does not depend on $\kappa_h$ being a function of only $\sigma$ and $\tilde{Z}$.

These expressions for $\phi_s$ together with Eq. (5) can be used to calculate the inner effective charge

$$\sigma_{eff,i} \simeq -\sqrt{2} e^{-\phi_s / 2},$$ (21)

and the outer effective charge is then

$$\sigma_{eff,o} \simeq \sigma + \sqrt{2} e^{-\phi_s / 2}$$ (22)

An important point to note that $\sigma_{eff,i}$ and $\sigma_{eff,o}$ differ from $\sigma$, but do not depend on $\kappa_h$. For neutral surfaces inner and outer effective charges have the same absolute value, but are of the opposite sign.

2. Small $\kappa_h h$

Now we investigate the system at $\kappa_h h \ll 1$. Such a situation would be realistic for a very dilute solutions and/or very thin gap. The asymptotic analysis can be performed with the procedure described above, although now $1 - \xi$ should be taken as a small parameter. However, in this limit another, a simper analysis can be used. Since inner diffuse layers strongly overlap, one can easily verify that $\phi_m \simeq \phi_s$ (a difference between these two potentials,
\( \propto (\kappa_i h)^2 / 8 \), which can be shown by series expansion of Eq. (9). Eq. (22) then allows us to obtain the relation between the surface charge and potential

\[
\sigma^2 / 2 + e^{-\phi_i h} \kappa_i h \sigma / 2 = e^{-\phi_e} - 1 - \frac{1}{Z} \left( e^{-\tilde{Z} \phi} - 1 \right) \tag{23}
\]

For strongly positively charged surfaces \( \phi_s \) is positive. This implies \( e^{-\phi_e} \ll 1 \) and Eq. (23) reduces then to Eq. (19), so that \( \phi_s \) does not depend on \( \kappa_i h \).

For strong negative charges \( e^{-\tilde{Z} \phi} \ll 1 \) and we get

\[
\phi_s \simeq - \ln \left[ \frac{2 (1 - 1/Z) + \sigma^2}{2 - \kappa_i h \sigma} \right] \propto - \ln \sigma^2 \tag{24}
\]

In the case of weakly charged surfaces the expansion in the vicinity of the solution for neutral membranes gives

\[
\phi_s \simeq \frac{\kappa_i h + 2 \sigma}{2 \sqrt{1 - Z}} \propto \kappa_i h + 2 \sigma \tag{25}
\]

Finally, by combining the expressions for \( \phi_s \) with Eq. (3) we evaluate inner effective charge, which in this limit depends on \( \kappa_i h \)

\[
\sigma_{\text{eff},i} \simeq - \frac{e^{-\phi_e} \kappa_i h}{2} \tag{26}
\]

Whence an outer effective charge is

\[
\sigma_{\text{eff},o} \simeq \sigma + \frac{e^{-\phi_e \kappa_i h}}{2} \tag{27}
\]

We emphasize that \( \sigma_{\text{eff},i} \) and \( \sigma_{\text{eff},o} \) are now becoming dependent on \( \kappa_i h \). However, since \( \kappa_i h \ll 1 \), one can conclude that one can roughly consider \( \sigma_{\text{eff},i} \simeq 0 \), and \( \sigma_{\text{eff},o} \simeq \sigma \).

III. RESULTS AND DISCUSSION

Here we present the results of numerical solution of Eqs. (1) and (2) and compare them with the above asymptotic expressions.

We begin by discussing \( \phi_s \), which has been predicted in general case to be controlled by \( \sigma \) and \( \kappa_i h \), and which determines at a given \( \kappa_i h \) the effective inner and outer surface charge. Let us first investigate the effect of \( \sigma \) on \( \phi_s \) at different values of \( \kappa_i h \), which is important for calculating electrostatic interaction energy as \( \int \bar{V}(\sigma) d\sigma \). In all calculations we use \( \tilde{Z} = -1 \), and vary \( \kappa_i h \) from 0.3 to 10. The calculation results are shown in Fig. 1. Also included are numerical results for conventional impermeable walls. We see that \( \phi_s \) of membranes significantly differs from the surface potential of impermeable plates of the same \( \sigma \), which confirms the important role of semi-permeability. In both cases \( \phi_s \) increases with \( \sigma \), but the values of \( \phi_s \) of membranes are quantitatively, and even qualitatively different. The only exception is the case of large positive \( \sigma \), where numerical calculations show that results obtained at all \( \kappa_i h \) converge to a single curve expected for an impermeable wall. We have compared these numerical results with predictions of asymptotic Eq. (19), and can conclude that the agreement between numerical results is excellent for all \( \kappa_i h \). Remarkably, our results show that Eq. (19) is very accurate when \( \sigma \geq 2.5 \), i.e. its range of applicability is much larger than expected initially. At large negative charge the surface potential increases with \( \kappa_i h \). A comparison of asymptotic Eqs. (18) and (21) with numerical data shows that they are surprisingly accurate when \( \sigma \leq -2.5 \). Now we recall that all asymptotic expressions for the potential of strongly charged membranes at a given \( \tilde{Z} \) scales as

\[
\phi_s \propto \pm \ln \sigma^2 \tag{28}
\]

This scaling expression is similar to known for impermeable surfaces. The calculations made with Eq. (28) are included in Fig. 4 and we conclude that they are in agreement with exact numerical results. Eqs. (20) and (24), obtained for small charges, are in good agreement with numerical results when \( |\sigma| \leq 2 \).

Fig. 3 represents a contour plot of \( \phi_s \) as a function of \( \sigma \) and \( \kappa_i h \). We see that for semi-permeable membranes the curve of \( \phi_s = 0 \) generally does not correspond to \( \sigma = 0 \), as it would be expected for impermeable surfaces (except some specific and more complex than considered here cases \( |\sigma| \geq 10 \)). The (negative) charge of zero surface potential decreases from \( \sigma \sim -\kappa_i h \) at small \( \kappa_i h \) down to \( \sigma \sim -\sqrt{2} \) in the limit of large \( \kappa_i h \), which can be easily obtained by using Eqs. (23) and (17). We emphasize that as follows from Eqs. (21), (22) and (20), (27) at \( \phi_s = 0 \) the inner effective charge is equal to \( \sigma \), and the outer effective charge vanishes. In other words, only inner diffuse
layers are formed. This conclusion is valid for any $\kappa_i h$ as validated by numerical calculations (now shown).

We now turn to the midplane potential. The numerical results for $\phi_m$ as a function of $\kappa_i h$ obtained at several $\sigma$ and predictions of asymptotic theory are given in Fig. 6 and are again in a good agreement. We note that at a given $\kappa_i h$ the midplane potential, $\phi_m$, monotonously grows with $\sigma$, which in particular imply that the midplane potential for neutral surfaces exceeds that for negatively charged membranes. At large $\kappa_i h$ the midplane potential, $\phi_m$, diverges as $\ln(\kappa_i h)^2$ as predicted by Eq. (16), and we see that indeed the curves are only slightly affected by small parameter $\xi$ (and by $\sigma$) in this equation. The numerical calculations validate asymptotic results at small $\kappa_i h$ and confirm that in this limit $\phi_m$ depends very strongly on $\sigma$. In this limit $\phi_m \approx \phi_s$ vanishes for neutral surface, but it is positive for positively charged and negative for negatively charged membranes. The concentration of (positive) small ions in the slit is uniform and equal to $c_\infty e^{-\phi_m}$. Therefore, in the limit of $\kappa_i h \ll 1$ for neutral surfaces the concentration of small ions in the gap coincides with $c_\infty$. However, if surfaces are positively charged, this concentration becomes smaller than $c_\infty$, i.e. the gap between membranes represents a depletion layer of small ions in the system. Note that in this case $\sigma_{\text{eff}, i} \simeq 0$, and $\sigma_{\text{eff}, o} \simeq \sigma$ similarly to neutral surfaces. In contrast, in the case of negatively charged surface small ions tend to accumulate in the gap, and their concentration can significantly exceed that in the bulk electrolyte solution.

IV. IMPLICATIONS OF RESULTS

In this section we briefly discuss the implications of the above results to interaction of semi-permeable membranes and electro-osmotic flows near them.

A. Interaction of charged semipermeable surfaces

Since membrane potential depends on $\kappa_i h$, this gives rise to a repulsive electrostatic disjoining pressure in the gap defined as $\Pi \equiv k_B T(c_\infty + c_\infty) - \Delta p$, where $\Delta p$ is the force per unit surface on the membrane. We refer the reader to the detailed analysis of $\Delta p$ given in \[9\], which led to a conclusion that the disjoining pressure can be expressed through the midplane potential as

$$\Pi = k_B T c_\infty e^{-\phi_m}$$  \hspace{1cm} (29)

We can therefore immediately calculate the disjoining pressure as a function of $\kappa_i h$ numerically. The results for different $\sigma$ are shown in Fig. 7. As expected, the electrostatic disjoining pressure always decreases with $\kappa_i h$. A startling result is that $\Pi$ decreases with the increase of $\sigma$. This implies, for example, that the electrostatic repulsion of positively charged membranes is always weaker than that of negatively charged and of even neutral membranes. This somewhat counter-intuitive result is a consequence of the behavior of $\phi_m$ discussed above and reflects that small ions accumulate in the gap at a negative surface charge, and strongly deplete when it is positive.

The typical disjoining pressure curve for the impermeable surfaces calculated using $\sigma = -1$ is included in Fig. 7. It can be seen that the calculations for semi-permeable membranes of the same charge give smaller $\Pi$ at intermediate and especially small $\kappa_i h$. The disjoining pressure does not diverge with a decrease in $\kappa_i h$ \[1, 2, 39\] by approaching the constant values, which can be easily evaluated using ideal gas approximation and the concept
slightly affects results at intermediate \( \kappa h \) where the exponential term depends weakly on \( \sigma \) splitting the no-slip boundary conditions to Eq. (34) one

\[
\Pi/k_B T c_\infty \propto 2\sigma_{\text{eff},i}/\kappa_i h:
\]

\[
\Pi/k_B T c_\infty \propto 1 - \frac{\kappa_i h + \sigma}{\sqrt{1 - Z}} \approx 1, \sigma \approx 0
\]

Calculations with these equations are shown in Fig. 7 and are again in excellent agreement with the exact numerical data up to \( \kappa_i h \approx 1 \).

At large \( \kappa_i h \) the decay of \( \Pi \) is not very sensitive to the value of \( \sigma \) (see Fig. 7). By using asymptotic expression for \( \kappa h \gg 1 \), Eq. (10), we derive:

\[
\Pi/k_B T c_\infty \propto \left( 2\sqrt{2} e^{\phi_s/2} + \kappa_i h \right)^{-2}
\]

B. Electroosmosis

If a tangent electric field, \( E \), is applied, the body force in the diffuse layers induces the liquid flow. Now our aim is to relate the velocity, \( u \), of this electro-osmotic flow to \( \phi_s \) and \( \phi_m \). The liquid flow satisfies Stokes equation:

\[
\eta \Delta u_{i,o} + \rho_i g E = 0,
\]

where \( \eta \) is dynamic viscosity and \( \rho = -\epsilon E/k_B T \). By applying the no-slip boundary conditions to Eq. (34) one can relate \( u \) to a potential:

\[
u_i(x) = \frac{\varepsilon Ek_B T/e}{4\pi\eta} (\phi_{i,o}(x) - \phi_s) = u_0(\phi_{i,o}(x) - \phi_s)
\]

Here \( u_0 = \frac{\varepsilon Ek_B T/e}{4\pi\eta} \) represents the Smoluchowski electro-osmotic velocity, which would be expected for impermeable surfaces with surface potential \( \phi_s = 1 \).

Fig. 8 allows one to calculate electro-osmotic velocity profiles by using the solution for a potential discussed above. The calculation results are shown in Fig. 8. A first result emerging from this is that in the outer region the electro-osmotic velocity outside of the EDL tends to a constant, which depends on \( \sigma \). Its value, \( u_\infty \approx -\phi_s u_0 \), can be easily found from Eq. (35). We recall that \( \phi_s \) is strongly affected by semi-permeability of membranes, and that it can vanish or even become positive in the case of weakly negatively charged membranes. We see, in particular, that surfaces of \( \sigma = -0.5 \) (where \( \sigma^D \) is also negative) induce an outer electro-osmotic flow in the direction opposite to the applied field as it would be for positively charged impermeable surfaces. This example illustrates that the electro-osmotic velocity in the outer region is determined by effective outer charge density of membranes, but not by their intrinsic charge. Inside the gap the EDL charge, \( \sigma^D \), is always positive, so that the flow is always in the direction of applied field. Its velocity augments with a decrease in \( \sigma \) from 5 (counter-ion depletion) to -5 (counter-ion enrichment). Finally, we note that the mid-plane (\( x = 0 \)) velocity can be expressed as \( u = u_0(\phi_m - \phi_s) \), and that at small \( \kappa_i h \) it is negligibly small, but at large gap it increases as \( u \approx 2u_0 \ln(\kappa_i h) \).

V. CONCLUSION

We have examined theoretically electro-osmotic equilibria in a system of two charged semi-permeable membranes separated by a thin film of salt-free liquid. We
have shown that these equilibria are fully characterized by an effective surface charge density of membranes we have introduced, which differs from the real surface charge density, and could even be of the opposite sign. Moreover, our model has predicted an alteration of the effective charge density during the approach. By using NLPB theory we have obtained accurate asymptotic formulae for surface and midplane potentials, which have been used to calculate the effective membrane charge and to interpret a distribution of counter-ions in the system. Finally, we have derived explicit formulae for the disjoining pressure in the gap and electro-osmotic velocity in the system, and have demonstrated that they both are determined by the effective surface charge density of membranes.

ACKNOWLEDGEMENTS

This research was partly supported by the Russian Foundation for Basic Research (grant 16-33-00861).

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