

Planar Membranes Interaction

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The system of two parallel planar, arbitrarily charged surfaces immersed in a solution containing only one ionic species, the counterions, is completely analyzed under a mean field Poisson–Boltzmann approach. Results for the pressure, reduced potential, and counterionic concentration are graphically displayed for two dissociating membranes and for a dissociating and an adsorbing membrane. The results indicate that the system of two planar parallel dissociating membranes acts as a buffer for pressure values and for counterionic concentration values in regions interior to and far from the membranes. The results are related to properties of planar or quasiplanar structures in biological cells.

I. Introduction

The ionic distribution in thermodynamic equilibrium around electrically charged surfaces in aqueous solution is a determinant factor on the properties and behavior of biological membranes, colloidal particles, charged molecular aggregates, and other systems. The problem has been theoretically addressed by Monte Carlo simulation or by a mean field Poisson–Boltzmann approach. The solution of the Poisson–Boltzmann equation for the system of two parallel charged surfaces with the same surficial charge density value, and containing only a counterion in the intervening solution, was already analyzed.¹ A comparison between results from the Monte Carlo simulation and from the results of the Poisson–Boltzmann equation was done for the system of two parallel, identically charged surfaces.² Measurement of repulsive forces between charged phospholipid bilayers shows that electrostatic repulsion forces are prevalent at large separation and in agreement with the result derived from a Poisson–Boltzmann description. The system of two rigid membranes with different surface charge densities of opposite sign in aqueous solution without added salt was also studied.⁴

In this work, the system consisting of two parallel planar uniformly charged surfaces, with arbitrary surface charge densities values, confining a solution with the dissociated ions as the unique ionic species present in the medium, is addressed under the mean field Poisson–Boltzmann formalism. The interest in this model system stems from its theoretical simplicity, allowing a complete analysis and from its close relationship to the experimental lamellar liquid system. The model system is also a first step in the description and understanding of biological structures such as in the mutual disposition of mitochondria inner and outer membranes. The theoretical model and results obtained apply to any system with the same boundary conditions, i.e., an electrically neutral system consisting of two parallel surfaces, with only the counterions inside and having fixed surficial charge density, independently of the nature of the surfaces.

II. The Mean Electrostatic Potential

The Poisson–Boltzmann equation for a system with planar symmetry, containing only one ionic species, is written as:

$$\frac{d^2\psi}{dx^2} = -\frac{nze}{\epsilon} \exp\left(\frac{-ze\psi}{kT}\right) \quad (1)$$

In the equation above, the symbol ψ stands for the mean electric potential. x is the coordinate perpendicular to the surfaces, ranging from the value zero, where the first surface is, with charge density σ_1 to the value L . L represents the distance between the two planar surfaces. The second charged surface has a charge density represented by σ_2 . The symbol z stands for the valence of the dissociated ion. The symbol e represents the electron charge modulus. The medium permittivity, the product of the dielectric constant value with the vacuum permittivity value ϵ , is represented by ϵ_0 . The symbol n stands for the ionic number density, k is the Boltzmann constant, and T is the absolute temperature. Figure 1 schematically shows the geometry of the system under consideration.

We define $\phi = ze\psi/kT$ as the reduced potential and a length λ by the relation $\lambda^2 = \epsilon kT/[2(ze)^2 n_u N_A]$, where $n_u N_A$ is the number density in the international unit system, n_u is the millimolar density, and N_A is Avogadro's number. The use of

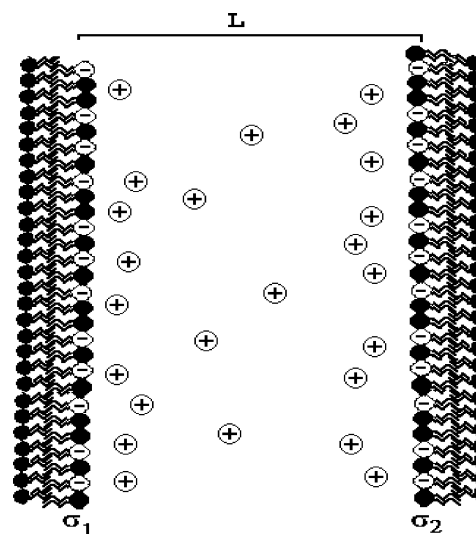


Figure 1. Schematic representation of the geometry of two interacting planar membranes.

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the variable $\xi = x/\lambda$ with the parameters above gives the Poisson–Boltzmann equation the form:

$$\frac{d^2\phi}{d\xi^2} = -\frac{n_0}{2} \exp(-\phi) \quad (2)$$

In eq 2, $n_0 = n/n_A N_A$ is the number corresponding to the milimolar density of ions.

By multiplying eq 2 by the factor $d\phi/d\xi$ and rearranging the terms, a first integral value comes from the resulting expression:

$$\frac{d}{d\xi} \left\{ \frac{1}{2} \left(\frac{d\phi}{d\xi} \right)^2 - \frac{n_0}{2} \exp(-\phi) \right\} = 0 \quad (3)$$

or

$$\frac{1}{2} \left(\frac{d\phi}{d\xi} \right)^2 - \frac{n_0}{2} \exp(-\phi) = \frac{-a^2}{2} \quad (4)$$

a^2 is an integration constant related to the ionic partial pressure, as will be shown in another section.

The hypothesis of neutrality condition, meaning that the total amount of charges in the surfaces and in the solution is zero, implies that the electric field outside the system is zero. The use of the Gauss theorem for electrostatics gives the value for the first derivative at the two extreme coordinates as:

$$\frac{d\phi}{d\xi} = -\frac{ze\sigma_1\lambda}{\epsilon kT} \quad \text{at } \xi = 0 \quad (5)$$

and

$$\frac{d\phi}{d\xi} = \frac{ze\sigma_2\lambda}{\epsilon kT} \quad \text{at } \xi = L/\lambda \quad (6)$$

The integration constant a^2 in eq 4 is related to the values given by the boundary conditions above as:

$$a^2 = -\left(\frac{ze\sigma_1\lambda}{\epsilon kT} \right)^2 + n_0 \exp(-\phi(0)) = -\left(\frac{ze\sigma_2\lambda}{\epsilon kT} \right)^2 + n_0 \exp(-\phi(L/\lambda)) \quad (7)$$

If $a^2 > 0$, the integration of eq 4 gives the following expression for the reduced potential:

$$\phi = \ln \left[\frac{\sqrt{n_0}}{a} \sin \left(\frac{a}{2} (\xi + \xi_0) \right) \right]^2 \quad (8)$$

for $a^2 = 0$, one gets:

$$\phi = \ln \left[\frac{\sqrt{n_0}}{2} (\xi + \xi_0) \right]^2 \quad (9)$$

and for $a^2 < 0$, with $a = ic$, the reduced potential is written as

$$\phi = \ln \left[\frac{\sqrt{n_0}}{c} \sinh \left(\frac{c}{2} (\xi + \xi_0) \right) \right]^2 \quad (10)$$

The relations 8–10 above apply to any charge density value in the surfaces. In particular, they can be used in the description of a system composed by surfaces with opposite charge sign, as done in ref 4.

The derivative of $\phi(\xi)$ in eq 8 ($a^2 > 0$) or eq 10 ($a^2 < 0$) and relations 5 and 6 lead to a set of two coupled algebraic transcendental equations. The equations are:

$$c \coth \left(\frac{c}{2} \xi_0 \right) = -\frac{ze\sigma_1\lambda}{\epsilon kT} \quad (11a)$$

$$a \cot \left(\frac{a}{2} \xi_0 \right) = -\frac{ze\sigma_1\lambda}{\epsilon kT} \quad (11b)$$

and

$$c \coth \left(\frac{c}{2} \left(\frac{L}{\lambda} + \xi_0 \right) \right) = \frac{ze\sigma_2\lambda}{\epsilon kT} \quad (12a)$$

$$a \cot \left(\frac{a}{2} \left(\frac{L}{\lambda} + \xi_0 \right) \right) = \frac{ze\sigma_2\lambda}{\epsilon kT} \quad (12b)$$

The equations above, 11 and 12, relate the integration constants, c or a , and ξ_0 , with the parameters σ_1 , σ_2 , and L . These equations can be decoupled using properties of the hyperbolic cotangent function.

By writing the hyperbolic function in eq 12 in terms of the hyperbolic cotangent of each of the parcels, a transcendental equation involving only the integration constant c is obtained. The equation is:

$$\coth \left(\frac{c}{2} \frac{L}{\lambda} \right) \frac{ze\lambda}{c\epsilon kT} (\sigma_1 + \sigma_2) = 1 + \left(\frac{ze\lambda}{c\epsilon kT} \right)^2 \sigma_1 \sigma_2 \quad (13)$$

If the parameters σ_1 and σ_2 have the same sign, both positive or both negative, there is no real solution for eq 13 because the product ze (the charge of dissociated counterions) and the surficial charges ($\sigma_1 + \sigma_2$) is negative. The right-hand term of eq 13 is, for c real, always positive. Then, when both membranes are dissociating ones, the possible solution can be found only if c is a pure imaginary number.

The substitution of c by ia in eq 13 corresponds to the value $a^2 > 0$. In this case, eq 8 is the relation for the reduced potential values, and the transcendental equation is expressed in terms of a trigonometric function:

$$\cot \left(\frac{a}{2} \frac{L}{\lambda} \right) \frac{ze\lambda}{a\epsilon kT} (\sigma_1 + \sigma_2) = \left(\frac{ze\lambda}{a\epsilon kT} \right)^2 \sigma_1 \sigma_2 - 1 \quad (14)$$

The resulting eq 14 can also be obtained directly starting from eq 8 by using the trigonometric forms in eqs 11 and 12 and using the same procedure used to get eq 13.

The reduced potential values described by eq 9 implies the following relation among the parameters σ_1 , σ_2 , and L :

$$\frac{\sigma_1 + \sigma_2}{\sigma_1 \sigma_2} = \frac{Lze}{2\epsilon kT} \quad (15)$$

Equation 15 can be obtained by a limiting procedure: c tending to zero in eq 13, or a tending to zero in eq 14. It must be emphasized that relations 15 and 9 are valid only for the values $c^2 = 0$ or $a^2 = 0$. In the other cases, $a^2 \neq 0$, the reduced potential is described by eqs 8 or 10.

Equation 15 corresponding to the value $c^2 = 0$ or $a^2 = 0$ for the integration constant implies the form given by relation 9 for the reduced potential. If, for the parameters in eq 15 ($\sigma_1 + \sigma_2$)/ $\sigma_1 \sigma_2 > (Lze/2\epsilon kT)$, the form describing the reduced potential is given by eq 8. Equation 10 is the appropriate form for the reduced potential when $(\sigma_1 + \sigma_2)/\sigma_1 \sigma_2 < (Lze/2\epsilon kT)$.

III. Ionic Partial Pressure

The partial pressure, the force per unit area, is evaluated by calculating the force in the first membrane. There are two contributions to this force, the first, $n_0 N_A n_0 \exp(-\phi(0))kT =$

ρkT , is associated with momentum transport, and the second, $-\sigma_1^2/2\epsilon$, with the electrostatic interaction. The value $-\sigma_1^2/2\epsilon$ is obtained as the product of the charge density value on the first membrane with the value of the electric field $-\sigma_1/2\epsilon$; see ref 6, for instance.

Because the momentum distribution is independent of the existence of intermolecular forces, the contribution of momentum transport to the pressure is the same as in an ideal gas at the same density and temperature, that is, ρkT . The pressure units, in the IU system, is the pascal.

The force per unit value of area due to the dissociated ions in solution, the osmotic pressure, can be written as:

$$p = \rho kT - \frac{\sigma_1^2}{2\epsilon} \quad (16)$$

By substituting ρ by $n_0 n_u N_A \exp(-\phi(0))$ and σ_1 according to eq 5, the osmotic pressure, eq 16, becomes:

$$\frac{p}{N_A n_u kT} = n_0 \exp(-\phi(0)) - \left(\frac{d\phi}{d\xi}\right)^2 \quad (17)$$

The derivative in the expression above is evaluated at the boundary of the first membrane, i.e., at $\xi = 0$.

The relation 17 when compared with eq 7 led to the identification of the first integration constant a^2 with the partial pressure. Because a^2 does not depend on ξ , the partial pressure has the same value for a planar system in thermodynamic equilibrium. This property of equal pressure is due to the planar symmetry of the system. Systems with cylindrical or spherical symmetry do not have a constant value for the partial pressure in the whole volume.

Rewriting eqs 13 and 14 in terms of the parameters $w = cL/2\lambda$ and $w = aL/2\lambda$, respectively, and $\beta = ze\sigma L/2\epsilon kT$, the transcendental eq 13 takes the form:

$$(\beta_1 + \beta_2)w \coth(w) = w^2 + \beta_1\beta_2 \quad (18)$$

and eq 14

$$(\beta_1 + \beta_2)w \cot(w) = \beta_1\beta_2 - w^2 \quad (19)$$

Equation 18, related to an attractive force between the membranes, does not have a limiting value for the parameter w that solves the equation, as eq 19 has. On the other hand, $w = \pi$ is the limiting value for the parameter in eq 19. It is implied by eq 19, related to two parallel dissociating membranes with repulsive interaction, that it does not matter what the value of the surficial charge density on the dissociating membranes is, the value of the osmotic pressure does not exceed the value $p = \pi^2(2\lambda\eta/L)^2 N_A n_u kT = \pi^2(2\lambda/L)^2 RT$, and it is equal to 2.44×10^4 Pa or about $1/4$ of one atmosphere for the temperature value around 300 K and $L = 2\lambda$; the symbol R stands for the ideal gas constant.

According to eq 4, there is also a limiting value for n_0 , the ionic density value where the reduced potential is zero. For a system consisting of two dissociating membranes, choosing the value $\phi = 0$ where $d\phi/d\xi = 0$, which corresponds to a plane between the membranes, the value of the counterion density in the plane has the limiting value given by $n_0 = \pi^2(2\lambda/L)^2$ mM. Such results suggest a kind of "condensation" phenomenon analogous to the counterion condensation proposed by Manning.⁵

The dependence of the force per unit area, the pressure, on parameters β_1 and β_2 , is inferred through eqs 18 and 19. Given

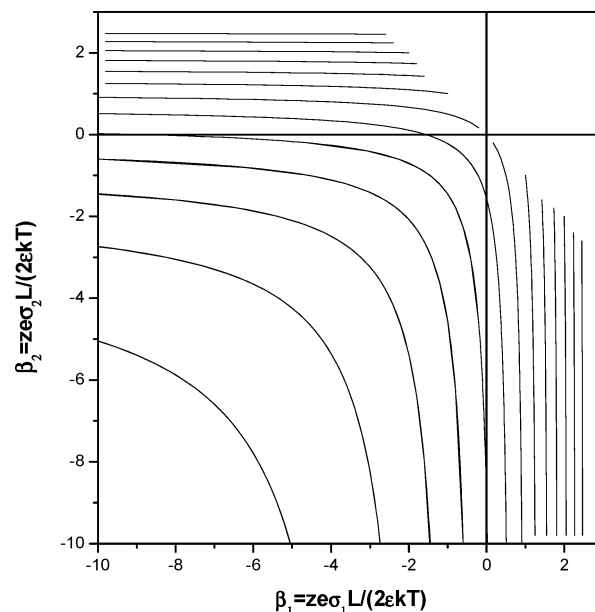


Figure 2. Constant pressure value curves. The pressure values for each curve are $p = 6, 5, 4, 3, 2, 1, 0, -1, -2, -3, -4, -5, -6$ in units of $N_A n_u kT = RT/m^3$ starting from the curve in the left side. The parameters β are related to the surficial charge density and the distance between the membranes by $\beta = ze\sigma L/(2\epsilon kT)$.

a value for the pressure, the value of the integration constant c or a is determined by relation 4, and with the corresponding value for w , the range of the parameters β is defined by eq 18 for negative pressure values, and by eq 19 for positive values. The curves, hyperbolas, obtained for pressure value in the interval from +6 to -6, in unit steps, are shown in Figure 2. The curve passing through the point $\beta_1 = \beta_2 = 0$ is the limiting curve between positive and negative pressure values and can be obtained either by eq 18 or 19. The discontinuity in the curves above the limiting curve is due to the fact that the surficial charge density value on an adsorbing membrane ($\beta > 0$) cannot exceed the absolute value of the surficial charge density absolute value on the dissociating membrane ($\beta < 0$).

The value of the force between the membranes as a function of their separation distance, considering fixed densities on the membranes, were calculated using the procedure described below.

Given the values of charge densities, counterion valence, temperature, the medium permittivity value, and the distance between the membranes, the values of the parameters β are calculated; for the value of the relation $(\beta_1 + \beta_2)/\beta_1\beta_2 < 1$, the transcendental eq 19 must be solved to get the value of the parameter w , and the pressure is given by $p = N_A n_u kT(2\lambda\omega/L)^2$. The solution of the transcendental eq 19 is obtained by defining a function $f(x) = x - \mu[(\beta_1 + \beta_2)x \cot(x) - \beta_1\beta_2 + x^2]$ with $\mu \neq 0$. The equation $x = f(x)$ is iteratively solved, i.e., with an initial value for x , calculating the $f(x)$ value gives a new value for x , the substitution of the last value gives a new one, and so forth, until the two last values are equal, according some criterion, for instance, the first five or six figures coincide. It is not difficult to choose the parameter μ value in order to have convergence.

If the β parameter values satisfy the relation $(\beta_1 + \beta_2)/\beta_1\beta_2 > 1$, the transcendental equation to be solved is eq 18, and the same procedure described above is used to obtain the result. If the condition in the system is such that $\beta_1 + \beta_2 = \beta_1\beta_2$, the solution is $x = 0$ and corresponds to zero value for the pressure.

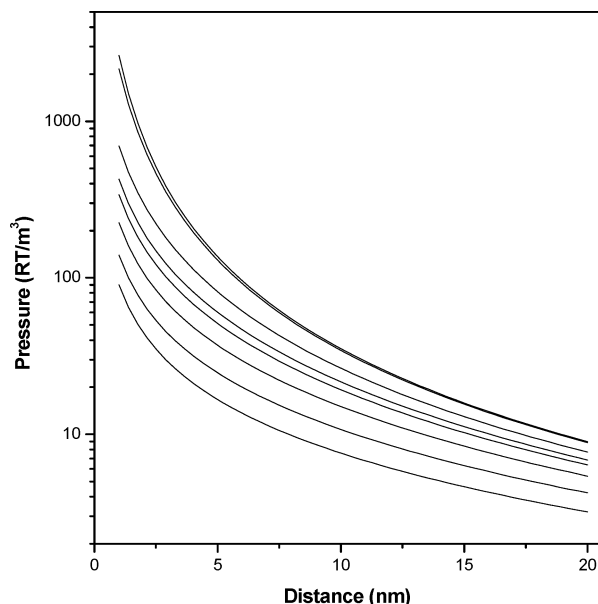


Figure 3. Pressure values, in units of RT/m^3 for a system consisting of two equally charged surfaces as a function of the distance between them. For the two almost coincident upper curves, the surficial charge density values are -0.40 and -0.229 C/m^2 . The curves below have density values of -0.04 , -0.0229 , -0.0178 , -0.0114 , -0.0070 , and -0.0045 C/m^2 .

Figure 3 shows the calculated values of the pressure as a function of the distance between two parallel planar surfaces with equal surficial charge density values. The values of the density on the membranes used to obtain the results shown in Figure 3 were chosen to compare with previously published values.³ A conclusion in this last reference is that, for distances greater than or around 30 Å, the calculated values, using Poisson–Boltzmann equation, account quite well for the experimentally determined values. The values displayed in Figure 3 agree with the results presented in ref 3 as far as electrostatic interaction is concerned.

The upper curve in Figure 3 corresponding to a charge density of -0.40 C/m^2 is almost the double of the value for the nearer curve, corresponding to a charge density value of -0.229 C/m^2 , which is equivalent to an electronic charge on a 70 Å² area.

It is observed that the curves describing the force as a function of the distance for the two values of surficial charge densities, -0.40 C/m^2 and -0.229 C/m^2 , almost coincide. This feature is interpreted as another manifestation of the “counterionic condensation”.

The surficial charge density values used to calculate the results shown in Figure 3 are the same as the values presented in ref 3, compared with experimental results, except the value of charge density, which is -0.40 C/m^2 . The same behavior is observed for the force between dissociating membranes with different values for surficial charge density, as shown in Figure 4. The surficial charge density values used to calculate the curves displayed in Figure 4 from the upper curve to the lower one, are: -0.20 , -0.10 C/m^2 ; -0.20 , -0.05 C/m^2 ; 0.20 , -0.02 C/m^2 ; -0.10 , -0.04 C/m^2 ; -0.10 , -0.01 C/m^2 .

For a system constituted by a dissociating membrane and another adsorbing, the surficial charge densities in the membranes have opposite signs. The calculations in this case were done for a set of values, and the results are shown in Figure 5. The values of charge density on one of the membranes, the dissociating one, for all the curves in Figure 5, was -0.20 C/m^2 , and the values for the surficial charge density on the other

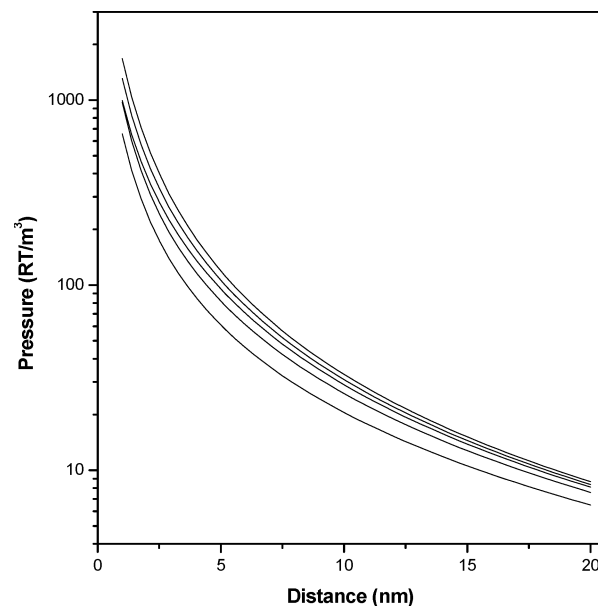


Figure 4. Pressure values in RT/m^3 units for two dissociating membranes with different surficial charge density values as a function of the distance between the membranes. The surficial charge density values used in the calculations are, for each pair of values, starting from the upper curve: -0.20 , -0.10 C/m^2 ; -0.20 , -0.05 C/m^2 ; -0.20 , -0.02 C/m^2 ; -0.10 , -0.04 C/m^2 ; -0.10 , -0.01 C/m^2 .

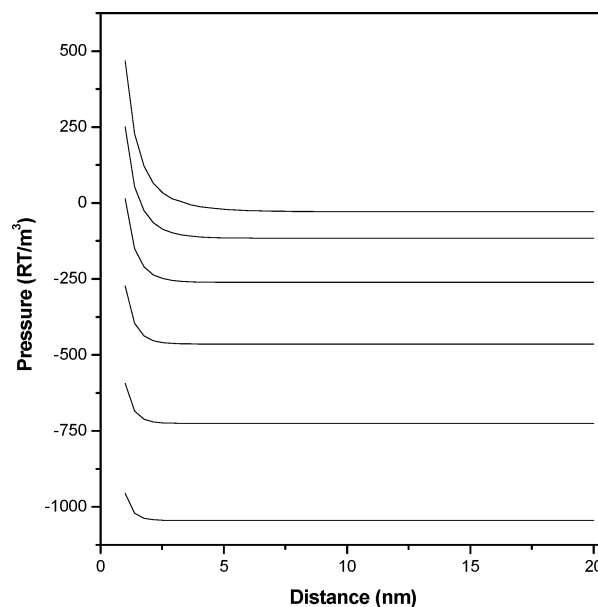


Figure 5. Pressure values expressed in terms of RT/m^3 for a system consisting of one dissociating membrane and another adsorbing. The value of the surficial charge density for the dissociating membrane is -0.20 C/m^2 for all the curves displayed. The surficial charge density values for the adsorbing membrane are, starting from above, $+0.01$, $+0.02$, $+0.03$, $+0.04$, $+0.05$, and $+0.06$ C/m^2 .

membrane, the adsorbing membrane, were 0.01 , 0.02 , 0.03 , 0.04 , 0.05 , and 0.06 C/m^2 from up to down in the figure. It can be seen that the force between the membranes is attractive and has a constant value for almost all the range of prevalence of the electrostatic attractive interaction between the membranes over the repulsive momentum transfer contribution due to the counterions in solution. The repulsive contribution to the pressure is effective only for membranes that are near to each other.

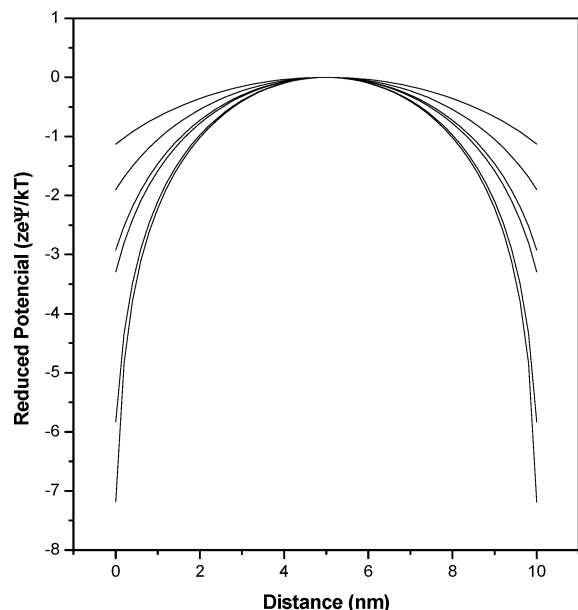


Figure 6. Reduced potential values $ze\Psi/kT$, as a function of position for a system consisting of two equally charged membranes separated by a distance of 10 nm. The surficial charge density values are, starting from the lower curve: -0.40 , -0.20 , -0.05 , -0.02 , and -0.01 C/m^2 .

IV. Reduced Potential

The values for the reduced potential calculated by eqs 8–10 are displayed in Figures 6, 7, and 8. Given the values of surficial charge density σ_1 and σ_2 and the distance L between the planar surfaces, the value of the constant a and c is inferred by solving the transcendental eqs 13 and 14, respectively, and ξ_0 is calculated by solving eq 11. The value zero for the reduced potential is attributed to a plane, parallel to the surfaces, where the derivative of ϕ , related to the electric field, is zero. This situation occurs for two dissociating membranes. by using eq 4, one gets $a^2 = n_0$. In the case of one dissociating membrane and another that absorbs the dissociated ions, the value $\phi = 0$ is taken in the second membrane, the adsorbing one. The value of the parameter n_0 is calculated with eq 7, with the result $n_0 = a^2 + (ze\sigma_2\lambda/\epsilon kT)^2 = -c^2 + (ze\sigma_2\lambda/\epsilon kT)^2$.

In Figure 6, it can be noted the manifestation of the “condensation”. The two lower curves associated to the values for the surficial charge density of -0.40 and -0.20 C/m^2 , respectively, show a minor difference between the reduced potential values in almost all the range of the position between the membranes.

The value of the charge density on the first surface is -0.20 C/m^2 for all the curves displayed in Figure 7. Referring to the right side of the figure, the lower curve corresponds to a surficial charge density of -0.10 C/m^2 , and in the sequence, from bottom to top, the values are -0.05 , -0.02 , -0.01 , and 0.00 C/m^2 . The reduced potential value near the first membrane, about -6.0 , is fairly independent of the surficial charge density value in the other membrane.

All the curves displayed in Figure 8 are calculated using the value of -0.20 C/m^2 for the charge density in the first membrane. The other lines in the figure correspond, starting from the lower one, to the values $+0.05$, $+0.04$, $+0.03$, $+0.02$, and $+0.01$ C/m^2 for the charge density value in the surface of the adsorbing membrane. The values of the reduced potential on the first membrane are, in absolute value, greater than the values obtained in the case of the system constituted by two dissociating membranes. It can be observed that the reduced potential values have a linear dependence with the distance,

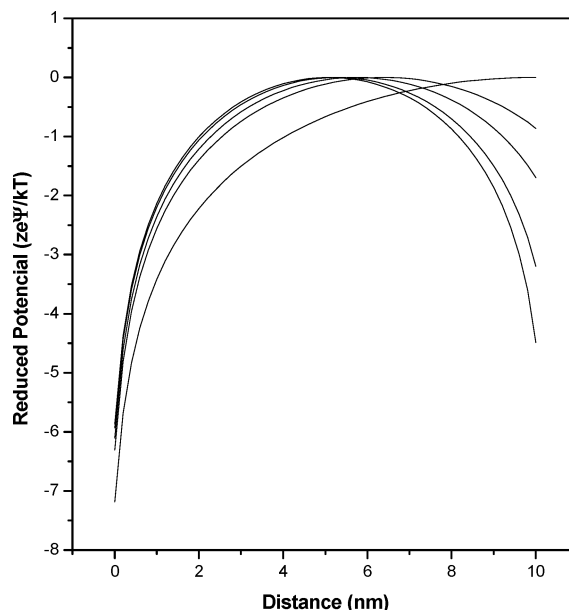


Figure 7. Reduced potential values, $ze\Psi/kT$, as a function of position for a system consisting of two plane parallel dissociating membranes with different charge density values and with a distance of 10 nm between them. The value of the surficial charge density on the first membrane is -0.20 C/m^2 for all the curves displayed. The surficial charge density values on the second membrane are -0.10 , -0.05 , -0.02 , -0.01 , and 0.00 C/m^2 from the bottom to above in the left side of the figure.

except for the region near the first membrane. This behavior is due to the higher counterion concentration values near the first membrane, and in the remaining region, the lower values of the counterions concentration practically do not affect the reduced potential value.

V. Ionic Concentration

The ionic concentration values can be calculated using the relation:

$$n(\xi) = n_0 \exp(-\phi)$$

If $a^2 > 0$, the use of eq 8 gives

$$n(\xi) = n_0 \csc^2 \left[\frac{a(\xi + \xi_0)}{2} \right] \quad (20)$$

If $a^2 = -c^2 < 0$, eq 10 leads to the following expression for the ionic density values:

$$n(\xi) = n_0 \operatorname{csch}^2 \left[\frac{c(\xi + \xi_0)}{2} \right] \quad (21)$$

The ionic concentration, when $a^2 = c^2 = 0$, corresponding to the case when the value of the pressure is equal to zero, can be obtained as a limit of eqs 20 or 21 and is expressed by:

$$n(\xi) = \frac{4}{(\xi + \xi_0)^2} \quad (22)$$

By applying relation 15, the value of the constant ξ_0 can be calculated using eqs 11a or 11b, and ξ_0 has the value:

$$\xi_0 = - \left(\frac{2\epsilon kT}{ze\sigma_1\lambda} \right) \quad (23)$$

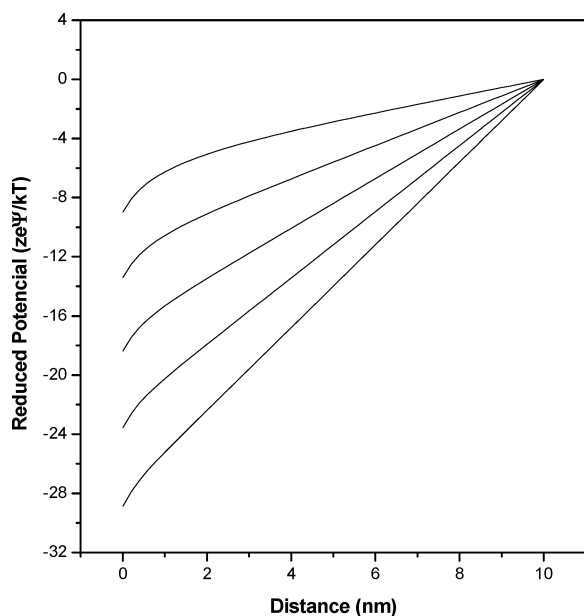


Figure 8. Position dependence of the reduced potential values, $ze\Psi/kT$, for a system of one dissociating membrane and another adsorbing. The surficial charge density value for the dissociating membrane is -0.20 C/m^2 for all the curves. The values of surficial charge density for the adsorbing membrane are, starting at the upper line: $+0.01$, $+0.02$, $+0.03$, $+0.04$, and $+0.05 \text{ C/m}^2$.

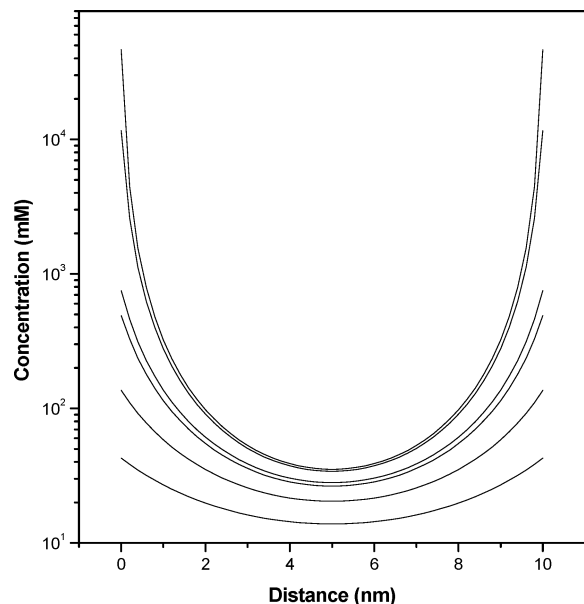


Figure 9. Concentration values in the inner region of two dissociating and equally charged membranes separated by a distance of 10 nm. From the top curve to the bottom, the surficial charge density values are: -0.40 , -0.20 , -0.05 , -0.04 , -0.02 , and -0.01 C/m^2 .

ξ_0 is always a positive number due to the fact that σ_1 , the surficial charge density of the dissociating membrane, has the charge sign contrary to that of the dissociated counterion with valence z .

The relation 22 shows that the ionic charge density is a monotonic decreasing function of ξ having a maximum value $n(0) = (z^2\sigma_1^2/\epsilon kTN_A) \text{ mM}$ near the dissociating membrane and a minimum value $n(L/\lambda) = (z^2\sigma_2^2/\epsilon kTN_A) \text{ mM}$ near the adsorbing membrane.

Figure 9 displays the millimolar concentration values for a system consisting of two dissociating membranes separated by a distance of 10 nm. The lines are a graphical representation of

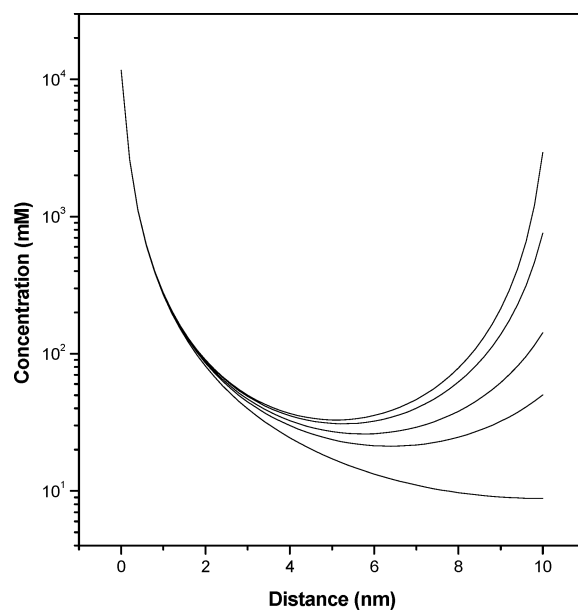


Figure 10. Ionic concentration values in the interior region of two dissociating membranes with different charge density values. The distance between the surfaces is 10 nm. The surficial charge density value for the first surface is -0.20 C/m^2 . The surficial charge density values for the second, from the upper curve to the lower, are: -0.10 , -0.05 , -0.02 , -0.01 , and 0.00 C/m^2 .

the function given by eq 20, with the parameters n_0 , a , and ξ_0 obtained by the same procedure described in the process of calculating the reduced potential values (Section IV). The curves in the figure correspond, starting from the lower one, to the values -0.01 , -0.02 , -0.04 , -0.05 , -0.20 , and -0.40 C/m^2 for the surficial charge density in both membranes. The two upper curves show the “condensation” effect: it can be noted that the similar results for the ionic density when the membranes have high values of surficial charge density. It can be noted that, in the interval from 2 to 8 nm, the ionic concentration values are of the same order of magnitude for surficial charge density values varying about three orders of magnitude. The system consisting of two dissociating membranes acts as a buffer for ionic concentration in the space inner to the membranes.

Results from the analysis of a system consisting of two dissociating membranes with different values of de surficial charge density, with a distance of 10 nm between them, are shown in Figure 10.

The surficial charge density in the first membrane is the same for all the curves displayed in the figure and is equal to $\sigma_1 = -0.20 \text{ C/m}^2$, the values of σ_2 are, starting from the lower one on the right side of the figure, 0.00 , -0.01 , -0.02 , -0.05 , and -0.10 C/m^2 . The curves are obtained using the same procedure used to obtain the lines in Figure 9. It is interesting to note that, near the membrane with a high value for the surficial charge density, the ionic concentration is practically unaffected by the dissociation degree of the other membrane.

The ionic density values for a system composed of one dissociating membrane and another adsorbing, are shown in Figure 11. The distance between the membranes is 10 nm. The surficial charge density values on the adsorbing membrane are: $+0.05$, $+0.04$, $+0.03$, $+0.02$, and $+0.01 \text{ C/m}^2$ starting from the lower curve. The value of -0.20 C/m^2 , the same for all the lines displayed in the figure, is the surficial charge density of the dissociating membrane. The curves are plots of relation 21. The parameters related to the integration constants were determined with the procedure already discussed. The results for the system show a different behavior when compared with

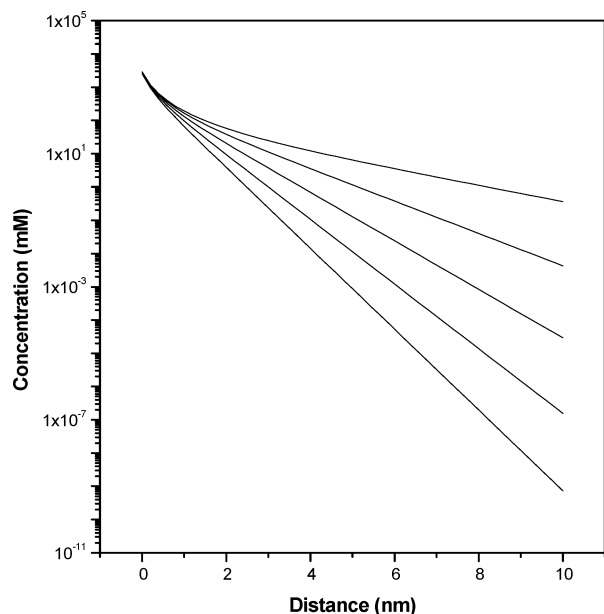


Figure 11. Concentration values in the interior region of two membranes separated by a distance of 10 nm. The dissociating membrane has a surficial charge density value of -0.20 C/m^2 . The adsorbing membrane surficial charge density values are, from top to bottom: $+0.01$, $+0.02$, $+0.03$, $+0.04$, and $+0.05 \text{ C/m}^2$.

a system composed of two dissociating membranes. The ionic concentration values show a variation of orders of magnitude along the space between the membranes. In the particular case with $\sigma_1 = -0.20 \text{ C/m}^2$ and $\sigma_2 = +0.05 \text{ C/m}^2$, there is a relation of $\sim 10^{12}$ for the values of the ionic concentration in the vicinity of the first membrane, the dissociating one, and in the regions near the second membrane, the absorbing membrane.

V. Discussion and Conclusion

The system of two planar parallel charged surfaces with counterions as the unique ionic species present was analyzed under a mean field Poisson–Boltzmann perspective. The approach used, in a particular situation, gives the same result as in a Monte Carlo description. Also, the calculated values of pressure are in agreement with experimentally determined values according to the work quoted as ref 3.

The Poisson–Boltzmann analysis shows that there is a maximum value for the counterion density between the membranes and a superior limiting value for the pressure, the pressure value being the same in the whole internal region. The limiting value for the pressure, independent of the surficial charge density of the dissociating membranes, is $p = \pi^2(2\lambda/L)^2 RT$. The limiting value for the ionic density in the region where the electric field vanishes is $n_0 = \pi^2 \text{ mM}$. These results imply that the system of two parallel dissociating membranes acts as a buffer for the pressure and ionic density in the central region of the membranes.

It is immediate to interpret some characteristics of membranes of cellular organelles as being related to the features discussed: The planar or quasiplanar structures provide a medium with a stable and limited value for internal pressure, and the almost equally spaced internal and external mitochondrial membranes structure must be related to the uniform pressure value in the internal volume, a property of parallel planar membranes. The bulged disk-like section of the Golgi apparatus may get its conformation due to a greater abundance of dissociating amphiphilic molecules in the interior layer of the membrane than in the external one, the additional dissociated ions in the inner region being trapped by the electric field. To sum up, the solution of the problem of two planar parallel dissociating membranes gives ground to formulate a sound hypothesis concerning cellular structures.

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