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A Poisson–Boltzmann approach for a lipid membrane in an electric field

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Abstract. The behavior of a non-conductive quasi-planar lipid membrane in an electrolyte and in a static (dc) electric field is investigated theoretically in the nonlinear (Poisson–Boltzmann) regime. Electrostatic effects due to charges in the membrane lipids and in the double layers lead to corrections to the membrane elastic moduli, which are analyzed here. We show that, especially in the low salt limit, (i) the electrostatic contribution to the membrane's surface tension due to the Debye layers crosses over from a quadratic behavior in the externally applied voltage to a linear voltage regime, and (ii) the contribution to the membrane's bending modulus due to the Debye layers saturates for high voltages. Nevertheless, the membrane undulation instability due to an effectively negative surface tension predicted by the linear Debye–Hückel theory is shown to persist in the nonlinear, high-voltage regime.

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1. Introduction

Bilayers formed from lipid molecules are an essential component of the membranes of biological cells. The mechanical properties of membranes at equilibrium are characterized by two elastic moduli: the surface tension and the bending modulus [1]. These moduli typically depend on electrostatic properties, and their modifications in the case of charged membranes/surfaces in an electrolyte have been examined theoretically in the 1980s and 1990s, as reviewed in e.g. [2]: they were first derived by Winterhalter and Helfrich [3] within the linearized Debye–Hückel (DH) approximation, then by Lekkerkerker [4] in the nonlinear Poisson–Boltzmann (PB) regime for charged monolayers and by Ninham *et al* [5] for charged symmetric bilayers. Later, Helfrich and co-workers [6] revisited the question of the electrostatic corrections to the bending modulus of charged symmetric bilayers. The spontaneous curvature and the membrane moduli have also been derived for charged asymmetric bilayers (with unequal Debye lengths on both sides of the membrane) within the PB regime [7]. In addition, this reference investigated the effect on the elastic properties of imposing exact charge conservation within the interior of a vesicle.

The study of deformations of membranes or vesicles in electric fields is currently an active field of research linked to many biotechnological applications. For instance, the application of electric fields is used to produce artificial vesicles from lipid films (electroformation) and to create pores in vesicles (electroporation), which is an important route for drug delivery. Both processes are widely used experimentally, although they are not well understood theoretically. The effects of electric fields on giant unilamellar vesicles have been reviewed recently in [8]. This system shows a rich panel of possible behaviors and morphological transitions depending on experimental conditions—electric field frequency, conductivities of the medium and of the membrane, salt concentration, etc. These observations are supported to a large extent by theoretical modeling [9].

It was Helfrich and co-workers [10] who originally pointed out that the deformation of lipid vesicles in electric fields can serve as a means of determining the electrostatic corrections to the membrane elastic moduli. Besides this observation on the macroscopic scale, other techniques can provide valuable insights into the moduli corrections such as AFM, impedance spectroscopy [11], neutron reflectivity [12] and x-ray scattering [13]. Recently [13], x-ray scattering experiments were carried out on a system of two superposed lipid membranes in an ac electric field. In trying to analyze these data, we noted that these experiments have been carried out at relatively high voltages, in a regime where the linearized DH approach may not be applicable. In order to describe such a situation theoretically, we extend previous work [14]–[16] based on the DH approach to the nonlinear PB regime, which is more suitable for realistic situations in which the induced surface charges on the membrane are large.

In this paper, we present a simple approach to calculate electrostatic corrections in the elastic moduli of a quasi-planar lipid membrane. The membrane is assumed to be non-conductive to ions, non-permeable to water and electrically neutral; it is subjected to a normal dc electric field and embedded in an electrolyte described by the PB equation. In this situation, the electric field leads to an accumulation of charges on both sides of the membrane, which affect the mechanical properties of the membrane. The electrostatic corrections to the elastic moduli can be used to analyze the instability of a lipid membrane in an applied dc electric field. In contrast to previous works based on a free energy approach [4, 6, 17], our method is based on a calculation of the stress (or force) balance at the membrane surface using electrokinetic equations [18]. This method is related to the work of Kumaran [19], who used a similar approach in the context of equilibrium charged membranes. Two points are worth mentioning. Firstly, our approach is able to describe the capacitive effects of the membrane and of the Debye layers, while keeping the simplicity of the zero thickness approximation on which most of the literature on lipid membranes is based. Secondly, our approach can include non-equilibrium effects that cannot be described within the free energy approach. For instance, in [14]–[16] we investigated the effects of ionic currents flowing through the membrane, which in turn affect the fluid flow near the membrane. Other types of non-equilibrium effects that could be included in that framework are those arising from the stochasticity of ion channels.

2. Model equations

We consider a steady (dc) voltage V between two electrodes at a fixed distance $z = \pm L/2$, applied to an initially flat membrane located at $z = 0$. The membrane is embedded in an electrolyte of monovalent ions with densities n^+ and n^- . The membrane is treated as non-conductive for both ion species and is (effectively) uncharged; thus we focus solely on capacitive effects. A point on the membrane is characterized within the Monge representation by a height function $h(\mathbf{r}_\perp)$, where \mathbf{r}_\perp is a two-dimensional in-plane vector in the membrane.

In the electrolyte, the electric potential ϕ obeys Poisson's equation,

$$\nabla^2 \phi = -\frac{1}{\epsilon} (en^+ - en^-) = -\frac{2}{\epsilon} \rho. \quad (1)$$

Here, e is the elementary charge, ϵ is the dielectric constant of the electrolyte and we have introduced half of the charge density,

$$\rho = e \frac{n^+ - n^-}{2}. \quad (2)$$

For the sake of simplicity, we assume a symmetric 1:1 electrolyte, so that far away from the membrane $n^+ = n^- = n^*$, and the total system is electrically neutral.

The densities of the ion species obey the Poisson–Nernst–Planck equations,

$$\partial_t n^\pm + \nabla \cdot \mathbf{j}^\pm = 0, \quad (3)$$

with ionic current densities

$$\mathbf{j}^\pm = D \left(-\nabla n^\pm \mp n^\pm \frac{e}{k_B T} \nabla \phi \right), \quad (4)$$

where $k_B T$ is the thermal energy. For simplicity, we consider the case where both ion types have the same diffusion coefficient D and neglect various corrections for concentrated solutions [20].

As boundary conditions (BC), the potential at the electrodes is externally held at

$$\phi \left(z = \pm \frac{L}{2} \right) = \pm \frac{V}{2}. \quad (5)$$

This BC is oversimplified for real electrodes, but captures the main effects of the electric field; see the discussion in [16]. The distance between the electrodes is assumed to be much larger than the Debye length, $L \gg \lambda_D = \kappa^{-1}$. In that case, the bulk electrolyte is quasi-neutral, $n^+ = n^- = n^*$, with negligible charge density (compared to the total salt concentration), so that far from the membrane

$$\rho \left(z = \pm \frac{L}{2} \right) = 0. \quad (6)$$

The BC at the membrane is crucial for recovering the correct physical behavior. Let \mathbf{n} be the unit vector normal to the membrane. We use the Robin-type BC,

$$\lambda_m (\mathbf{n} \cdot \nabla) \phi|_{z=h^+} = \lambda_m (\mathbf{n} \cdot \nabla) \phi|_{z=h^-} = \phi(h^+) - \phi(h^-), \quad (7)$$

where

$$\lambda_m = \frac{\epsilon}{\epsilon_m} d \quad (8)$$

is a length scale that contains the membrane thickness d and the ratio of the dielectric constant of the electrolyte, ϵ , to that of the membrane, ϵ_m . This BC was originally developed for electrodes sustaining Faradaic current [21, 22] or charging capacitively [23]. In [15, 16, 24], this BC was derived and was shown to properly account for the jump in the charge distribution that occurs near the membrane as a result of the dielectric mismatch between the membrane and the surrounding electrolyte.

In brief, this BC can be motivated for a flat membrane as follows. Since the membrane bears no fixed charges, the normal components of the electric displacement are continuous at the two interfaces between the membrane and the electrolyte,

$$\epsilon \partial_z \phi(z = \pm d/2) = \epsilon_m \partial_z \phi_m(z = \pm d/2), \quad (9)$$

where ϕ_m is the electric potential inside the membrane. Since the electric field $E_m = -\partial_z \phi_m$ is constant (to leading order) inside the membrane, the integral of the inside field can be written in the following way:

$$E_m d = \int_{-d/2}^{d/2} E_m dz = -[\phi_m(d/2) - \phi_m(-d/2)] = -[\phi(d/2) - \phi(-d/2)], \quad (10)$$

where in the last step we used the continuity of the potential at the membrane surface. Together with equation (9), this yields

$$\lambda_m \partial_z \phi(z = \pm d/2) = \phi(d/2) - \phi(-d/2). \quad (11)$$

If one takes the limit $d \rightarrow 0$ while keeping $\lambda_m = \frac{\epsilon}{\epsilon_m} d$ constant, one obtains equation (7) in the particular case of $h = 0$ and $\mathbf{n} = \hat{z}$. The same derivation holds for the case of a slightly perturbed membrane surface $h(\mathbf{r}_\perp)$.

3. The Poisson–Boltzmann approach for a membrane in an external potential

Here, we show how the well-known solution of the PB equation for a single charged plate in an electrolyte can be used to describe the present situation of a capacitive membrane with induced Debye layers in an external potential.

In a steady state situation and when there is no electric current through the membrane, one obtains from equations (3) and (4)

$$-\nabla n^\pm \mp n^\pm \frac{e}{k_B T} \nabla \phi = 0. \quad (12)$$

After a direct integration using the BCs from above, one obtains

$$n^\pm = n^* e^{\mp(e/k_B T)(\phi(z) - (V/2))}, \quad (13)$$

and insertion in Poisson's equation then yields the PB equation

$$\nabla^2 \phi = \frac{2n^* e}{\epsilon} \sinh \left[\frac{e}{k_B T} \left(\phi(z) - \frac{V}{2} \right) \right]. \quad (14)$$

Linearization (for $\phi - \frac{V}{2} \ll 1$) leads to the well-known DH equation,

$$\nabla^2 \phi = \kappa^2 \left(\phi(z) - \frac{V}{2} \right), \quad (15)$$

where

$$\kappa^2 = \frac{2e^2 n^*}{\epsilon k_B T} \quad (16)$$

and $\kappa^{-1} = \lambda_D$ is the Debye length that defines the characteristic length scale for charge relaxation in the electrolyte.

The nonlinear PB equation (14) for the planar case can be integrated analytically [2], leading to

$$\phi(z) = -\frac{2k_B T}{e} \ln \left(\frac{1 + c e^{-\kappa z}}{1 - c e^{-\kappa z}} \right) + \frac{V}{2}, \quad (17)$$

$$n^\pm(z) = n^* \left(\frac{1 \pm c e^{-\kappa z}}{1 \mp c e^{-\kappa z}} \right)^2, \quad (18)$$

for $z > 0$. The expressions for $z < 0$ can be obtained using the symmetry of the system: $\phi(-z) = -\phi(z)$, $n^\pm(-z) = -n^\pm(z)$.

Just as in the classical PB solution for a single charged plate in contact with an electrolyte, the non-dimensional parameter c is determined by the BC for the potential at the membrane.

For a flat charged surface surrounded by an electrolyte [2], c is given by a simple quadratic equation and can be expressed in terms of the ratio of the two characteristic length scales: the Gouy–Chapman length $b = 2\epsilon k_B T / e |\sigma|$ (with $|\sigma|$ being the charge density of the surface) and the Debye length $\lambda_D = \kappa^{-1}$. In contrast, in the case of a membrane in an electric field, we obtain from equation (7) the following nonlinear equation:

$$4\kappa\lambda_m \frac{c}{c^2 - 1} + \frac{eV}{k_B T} = 4 \ln \left(\frac{1+c}{1-c} \right). \quad (19)$$

Note that two dimensionless parameters enter this equation: the ratio of electrostatic energy to thermal energy,

$$\bar{V} = \frac{eV}{k_B T}, \quad (20)$$

and the dimensionless parameter [22],

$$\bar{\lambda}_m = \kappa\lambda_m = \frac{\lambda_m}{\lambda_D} = \frac{\epsilon\kappa}{\epsilon_m/d} = \frac{C_D}{C_m}, \quad (21)$$

which quantifies the electrical coupling between the membrane and the Debye layers. More precisely, depending on whether this parameter is large or small with respect to one, the capacitance of the diffuse part of the double layer, $C_D = \epsilon\kappa$, or the capacitance of the membrane, $C_m = \epsilon_m/d$, dominates the overall voltage drop.

The non-dimensional parameter $c = c(\bar{\lambda}_m, \bar{V})$ that is determined by equation (19) is related to the potential at the membrane, $\phi(0^+)$, and to the charge density at the membrane, $\rho(0^+)$, by the following relations:

$$\phi(0^+) = -\frac{4k_B T}{e} \operatorname{artanh}(c) + \frac{V}{2}, \quad (22)$$

$$\rho(0^+) = en^* \sinh [4 \operatorname{artanh}(c)]. \quad (23)$$

From equation (22), one can see that the values of c must be restricted to the interval $[0, 1]$. In the limit of small voltages, $\bar{V} \ll 1$, there is a linear relation between c and the charge distribution at the membrane, since $c = \frac{\rho(0^+)}{4en^*} = \frac{\epsilon\kappa^2 V}{8en^*(2+\kappa\lambda_m)}$, in accordance with the calculations based on the DH approximation of [16].

Figure 1(a) shows the solution c of equation (19) as a function of external voltage for various values of κ , which corresponds to varying the amount of salt since $\kappa \propto \sqrt{n^*}$. Clearly, for low salt, the linear approximation remains valid only for quite small voltages (for instance, it holds only for $V \lesssim 0.1$ V in pure water), whereas, as for high salt, $V = 5$ V is still in the linear regime. Figure 1(b) shows a comparison of the charge distribution for the nonlinear PB (blue) and the linear DH solution (green). As expected, the figure shows that the DH approximation underestimates the surface charge on the membrane layers as compared to the PB calculation. The figure also shows the distribution of the positive and negative ions, which both tend to n^* far from the interface as a result of electroneutrality.

Although the present situation differs from the case of a single charged plate in an PB electrolyte, the structure of the solutions, equations (17) and (18), is very similar in both problems. Because of this, there is an equivalent to the *Contact theorem* [2], which relates, in the single charged plate problem, the surface charge density to the limiting value of the potential/ionic density at the plate: namely, one can give the effective surface charge σ_{eff} for

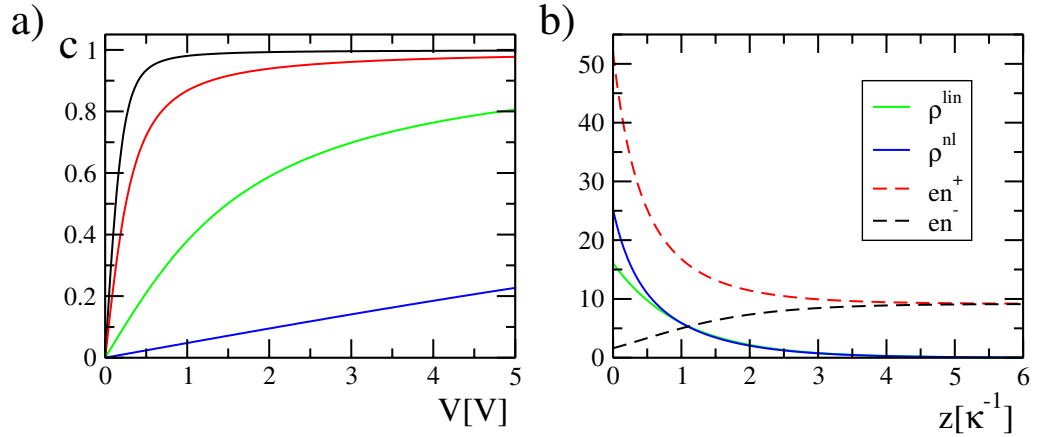


Figure 1. (a) Solution of equation (19) for different amounts of salt: $\kappa = 10^6 \text{ m}^{-1}$ (pure water; black), $\kappa = 10^7 \text{ m}^{-1}$ (red), $\kappa = 10^8 \text{ m}^{-1}$ (green) and $\kappa = 10^9 \text{ m}^{-1}$ (blue). (b) Charge distribution (in units of C m^{-3}) for $z > 0$: comparison of the nonlinear solution (blue) with the linearized DH solution (green). The asymmetric distribution of positive (red dashed line) and negative charges (black dashed line) for the nonlinear solution is also shown. Parameters used: $\epsilon = 80\epsilon_0$ (water) and $\epsilon_m = 2\epsilon_0$ for the membrane. As the membrane thickness is typically $d = 5 \text{ nm}$, this leads to $\lambda_m = (\epsilon/\epsilon_m)d = 200 \text{ nm}$. For (b), we used $\kappa = 10^6 \text{ m}^{-1}$, corresponding to $en^* \simeq 9.16 \text{ C m}^{-3}$, and $V = 0.1 \text{ V}$.

the charged plate problem that creates the same voltage/charge distributions as the capacitive membrane in the external field. This effective surface charge reads

$$\sigma_{\text{eff}}^2 = 4\epsilon n^* k_B T \left[\cosh \left(\frac{e}{k_B T} (\phi(0^+) - V/2) \right) - 1 \right]. \quad (24)$$

4. Corrections to membrane elastic moduli

4.1. Surface tension

The electrostatic corrections to the surface tension can be calculated directly from the stresses acting on the membrane in the flat configuration (also called the base state), as explained in [16, 25]. The total stress tensor reads

$$\tau_{ij} = -p\delta_{ij} + \eta (\partial_i v_j + \partial_j v_i) + \epsilon (E_i E_j - \frac{1}{2} \delta_{ij} E^2), \quad (25)$$

which contains the pressure, the viscous stresses in the surrounding fluid (the electrolyte) and the Maxwell stress due to the electrostatic field. η is the viscosity of the electrolyte and \mathbf{v} its velocity field. The electric field is given by $\mathbf{E} = -\nabla\phi$.

In the base state, the electric field is oriented in the z -direction, and the condition $\nabla \cdot \tau = 0$ implies that $\partial_z p = \frac{\epsilon}{2} \partial_z ((\partial_z \phi)^2) = -2\rho \partial_z \phi$. Using equations (17) and (18) and imposing $p(z \rightarrow \infty) = 0$, this is readily solved by

$$p(z > 0) = 16n^* k_B T c^2 \frac{e^{2\kappa z}}{(c + e^{\kappa z})^2 (c - e^{\kappa z})^2}, \quad (26)$$

and similarly with $z \rightarrow -z$ for $z < 0$.

Let us call S a closed surface enclosing the membrane with the normal vector field \mathbf{n} . The force acting on the surface S in the \mathbf{x} -direction (chosen to be the direction of the lateral stress) can be calculated from the stress tensor as $F_x = \int_S \mathbf{x} \cdot \boldsymbol{\tau} \cdot \mathbf{n} dS$. Since $\boldsymbol{\tau}$ is divergence free, the surface S can be deformed, for convenience, to a cube of size L , and it is easy to see that the integral is non-zero only on the faces of the cube with the normal along $\pm \mathbf{x}$. With $dS = L dz$ and $\Delta \Sigma = F_x/L$ for $\mathbf{n} = +\mathbf{x}$, we arrive at

$$\Delta \Sigma = \int_{-L/2}^{L/2} \tau_{xx}(z) dz. \quad (27)$$

From equation (25), one has $\tau_{xx}(z) = -p(z) - \frac{\epsilon}{2}(\partial_z \phi)^2$, where $\phi(z)$ and $p(z)$ are the potential and the pressure in the base state given above. Upon integration (using $L\kappa \gg 1$), one obtains the corrections to the surface tension as a sum of two terms.

Firstly, there is the *external contribution* due to the Debye layers,

$$\Delta \Sigma_\kappa = -\frac{32n^*k_B T}{\kappa} \frac{c^2}{1-c^2}. \quad (28)$$

Secondly, there is the *internal contribution* due to the electric field inside the membrane (cf [16]), which is given by $E_0^m = -\frac{1}{d}(\phi(0^+) - \phi(0^-))$. That correction to the surface tension is $\Delta \Sigma_m = -\epsilon_m d (E_0^m)^2$, or explicitly

$$\Delta \Sigma_m = -\frac{\epsilon_m}{d} \left[-\frac{4k_B T}{e} \ln \left(\frac{1+c}{1-c} \right) + V \right]^2. \quad (29)$$

Note that both corrections to the surface tension are *negative*, which means that these corrections can lead to an instability as soon as the total surface tension $\Sigma_{\text{tot}} = \Sigma_0 + \Delta \Sigma_\kappa + \Delta \Sigma_m$ (which is the sum of the bare tension Σ_0 plus the above corrections) becomes negative [26].

4.2. Bending modulus

To obtain the correction to the bending modulus, we perform, as detailed in [16] for the DH case, a calculation of the potential at first order in the membrane height. Then, by solving the hydrodynamics problem of the electrolyte around the membrane (in Stokes approximation), one determines the pressure and obtains the total stress tensor. The growth rate of membrane fluctuations, $s(k_\perp)$, where \mathbf{k}_\perp is the wave vector in the membrane plane, is then determined by imposing that the discontinuity of the normal–normal component of the total stress tensor at the membrane has to equal the membrane restoring force:

$$- \left[(\tau_{zz,1}(z=0^+) - \tau_{zz,1}(z=0^-)) \right] = -\frac{\partial F_H}{\partial h(\mathbf{r}_\perp)}. \quad (30)$$

Here, F_H is the standard Helfrich free energy,

$$F_H = \frac{1}{2} \int d^2 \mathbf{r}_\perp [\Sigma_0 (\nabla h)^2 + K_0 (\nabla^2 h)^2], \quad (31)$$

and Σ_0 and K_0 are the bare surface tension and the bare bending modulus of the membrane, respectively. With the contributions (from the pressure, the flow and the electric field) to the stress tensor, one evaluates the jump of the normal–normal component at the membrane, yielding the left-hand side of equations (30). Finally, one expands in powers of \mathbf{k}_\perp and isolates the growth rate $s(k_\perp)$ of membrane fluctuations, which has the form

$$\eta k_\perp s(k_\perp) = -\frac{1}{4} (\Sigma_0 + \Delta \Sigma_\kappa + \Delta \Sigma_m) k_\perp^2 - \frac{1}{4} (K_0 + \Delta K_\kappa + \Delta K_m) k_\perp^4. \quad (32)$$

Details of the calculations can be found in the [appendix](#). The surface tension corrections calculated above in equations (28) and (29) can be recovered by this method, which provides a self-consistency check. For the bending modulus, one obtains

$$\Delta K_\kappa = \frac{8n^*k_B T c^2(3-c^2)}{\kappa^3(1+c^2)}, \quad (33)$$

$$\Delta K_m = -\epsilon_m (E_m^0)^2 \left[-\frac{d^3}{12} + \frac{2k_B T c(1-c^2)}{E_m^0 e \kappa} d \right], \quad (34)$$

for the *external contribution* due to the Debye layers and the *internal contribution* due to the voltage drop at the membrane, respectively. The field inside the membrane is given by $E_0^m = -\frac{1}{d}[-\frac{4k_B T}{e} \ln(\frac{1+c}{1-c}) + V]$.

5. Discussion

Let us now discuss the nonlinear electrostatic effects on the membrane elastic moduli in the limits of low and high applied voltages.

5.1. The low-voltage regime

In the low voltage limit, $\bar{V} \ll 1$, a solution of equation (19) to linear order in c yields

$$c = \frac{\bar{V}}{4(2 + \bar{\lambda}_m)} = \frac{1}{4(2 + \lambda_m \kappa)} \frac{eV}{k_B T} = \frac{\rho(0^+)}{4en^*}. \quad (35)$$

Here, $\rho(0^+)$ is half the charge density at the membrane, corresponding to the quantity called ρ_m in [16] for the DH case. Expanding $\phi(z)$ and $\rho(z)$, as well as the corrections to the moduli $\Delta \Sigma_\kappa$, $\Delta \Sigma_m$, ΔK_κ and ΔK_m for small c , one exactly recovers all of the results given in [16]. Specifically, all corrections to the moduli scale quadratically with the external voltage, $\propto V^2$. This is due to the fact that both the potential and the induced charge are proportional to the applied voltage.

5.2. The high-voltage regime

In the opposite limit, $\bar{V} \gg 1$ implies $c \rightarrow 1$. Introducing $\alpha = 1 - c$ and expanding equation (19) for small α , one gets $-\frac{2\bar{\lambda}_m}{\alpha} + 4 \ln \alpha + \bar{V} + \bar{\lambda}_m - 4 \ln 2 = 0$. For high values of \bar{V} , one can neglect the last two (constant) terms and obtain

$$c = 1 - \frac{\frac{1}{2}\bar{\lambda}_m}{W(\frac{1}{2}\bar{\lambda}_m e^{\bar{V}/4})} \simeq 1 - \frac{\frac{1}{2}\bar{\lambda}_m}{\bar{V}/4}, \quad (36)$$

where $W(x)$ is Lambert's function, i.e. $y = W(x)$ is the solution of $y e^y = x$. As a result, the nonlinear electrostatics strongly affects the corrections to the moduli from the Debye layers. In fact, the external contribution to the surface tension scales as

$$\Delta \Sigma_\kappa(\bar{V} \gg 1) \propto -\frac{c^2}{1-c^2} \rightarrow -\frac{\bar{V}}{4\bar{\lambda}_m}, \quad (37)$$

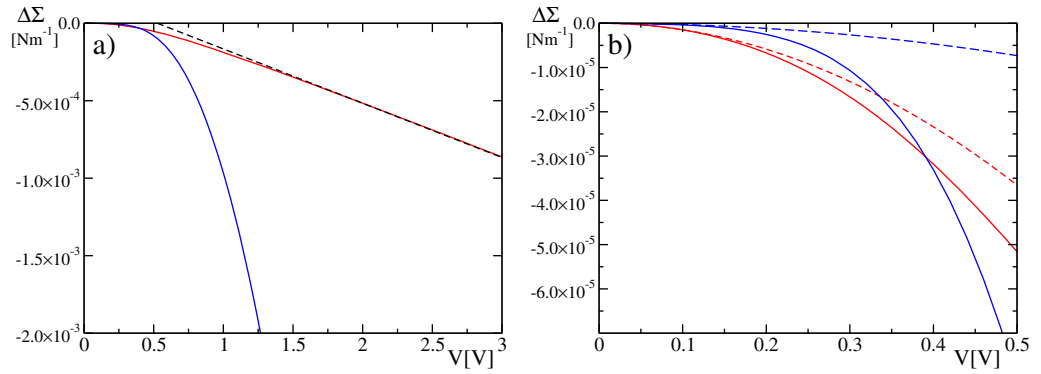


Figure 2. Corrections to the surface tension for $\kappa = 10^6 \text{ m}^{-1}$ (pure water) as a function of voltage. Corrections from the Debye layer are in red, corrections due to the voltage drop at the membrane are shown in blue. (a) Nonlinear PB result. One sees that the correction due to the Debye layer scales linearly in the voltage for high voltages (cf the black dashed straight line), while the contribution from inside the membrane scales quadratically in the voltage. (b) Comparison of the nonlinear PB result (solid lines) with the linear DH result (dashed lines).

instead of $\Delta\Sigma_\kappa(\bar{V} \ll 1) \propto -\frac{\bar{V}^2}{(2+\bar{\lambda}_m)^2}$: in the high voltage regime, the external surface tension correction scales linearly with the voltage instead of quadratically. The crossover from \bar{V}^2 to \bar{V} is salt dependent, i.e. depends on the value of $\bar{\lambda}_m = \lambda_m \kappa$, cf figure 1. In contrast, the external surface tension correction $\Delta\Sigma_m$ remains a quadratic function of the applied voltage.

Figure 2 displays both corrections to the surface tension as a function of voltage for low salt (pure water). Figure 2(a) shows that due to the crossover to a linear voltage dependence for the external surface tension correction, $\Delta\Sigma_m$ (blue curve) rapidly dominates and $\Delta\Sigma_\kappa$ (red curve) becomes negligible for $V \gtrsim 1.5$ V. Figure 2(b) shows a comparison of the nonlinear PB result (solid lines) with the linear DH result (dashed lines). For $V \lesssim 0.2$ V, there is agreement and the external contribution dominates. However, for higher voltages, the linearized DH solution becomes completely misleading: it predicts that $|\Delta\Sigma_\kappa| > |\Delta\Sigma_m|$ for all voltages (and both proportional to V^2), while already above $V \gtrsim 0.4$ V the internal contribution exceeds the external contribution.

For the bending modulus corrections, the differences between the DH and PB models are even more striking: as a function of the applied voltage, the external contribution levels off at a constant value,

$$\Delta K_\kappa(\bar{V} \gg 1) = \frac{8n^*k_B T}{\kappa^3} \frac{c^2(3-c^2)}{1+c^2} \rightarrow \frac{8n^*k_B T}{\kappa^3}. \quad (38)$$

In contrast, the internal contribution ΔK_m continues to grow quadratically in the high voltage limit. Figures 3(a) and (b) show comparisons of the nonlinear PB solutions (solid) and the linear DH solutions (dashed) for both contributions to the bending modulus. Note, however, the different scales: although the external contribution saturates (see figure 3(a)) this value is larger by two orders of magnitude than the still growing value from the internal contribution, cf figure 3(b). In conclusion, for pure water and voltages $\simeq 0.2$ –5 V, the total correction to the bending modulus will appear constant within this voltage interval. Only for still higher voltages, the quadratic growth due to the internal contribution ΔK_m will dominate.

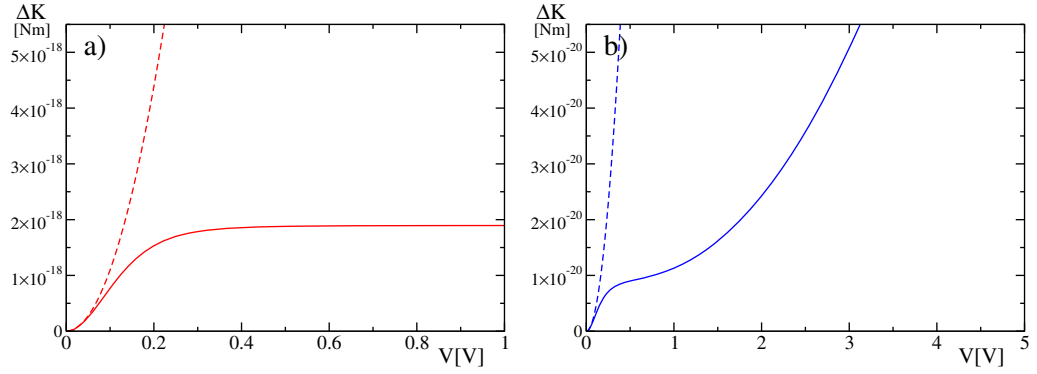


Figure 3. Corrections to the bending modulus for $\kappa = 10^6 \text{ m}^{-1}$ (pure water) as a function of voltage. (a) Corrections from the Debye layer. (b) Corrections due to voltage drop at the membrane. Nonlinear PB calculations are shown as solid lines and linearized DH calculations are shown as dashed lines (note the different scales on the left and right panels).

5.3. Membrane instability

Let us briefly discuss the consequences for the membrane undulation instability. As mentioned above, an instability develops in this system when the total surface tension, the sum of the bare value and the electrostatic corrections, becomes negative. The threshold value for the voltage, V_c , has been calculated in [16] within linearized DH theory and reads (in the case of a non-conductive membrane)

$$V_c^2 = \frac{\Sigma_0 d (2 + \kappa \lambda_m)}{\kappa (\kappa \epsilon_m \lambda_m^2 + \epsilon d)}. \quad (39)$$

This curve is shown in figure 4 as a blue line. The red line, in contrast, shows the nonlinear PB result given by the numerical solution of $0 = \Sigma_{\text{tot}} = \Sigma_0 + \Delta \Sigma_\kappa + \Delta \Sigma_m$ with equations (28) and (29) for the surface tension corrections and $c(\lambda_m, \bar{V})$ calculated from equation (19). In the high salt limit, the Debye layers shrink to zero and as a result the external contribution vanishes. For the internal contribution, the inside field is exactly calculated from the DH approach, as can be seen from the behavior of the parameter c in figure 1(a). Thus, both curves merge and attain the limiting value given by equation (39), $V_c(\kappa \rightarrow \infty) = \sqrt{\Sigma_0 d / \epsilon_m}$. In contrast, for low salt, the linear result overestimates the threshold value, since it underestimates the induced charges at the membrane, as shown in figure 1(b).

In addition to the threshold voltage for the instability, the most unstable wave number associated with the instability will be affected by the electrostatic nonlinearities of the PB equation. This wavevector corresponds to the maximum of the growth rate given by equation (32) with respect to k_\perp . In the low salt regime, since the system is more unstable in the presence of electrostatic nonlinearities, cf figure 4, in general the wave vector will be increased as compared to the predictions from the DH approach.

6. Conclusion

We have investigated the nonlinear electrostatic effects of an external dc electric field on a *purely capacitive* membrane, which is non-conductive for the ions and bears no fixed charges, in an

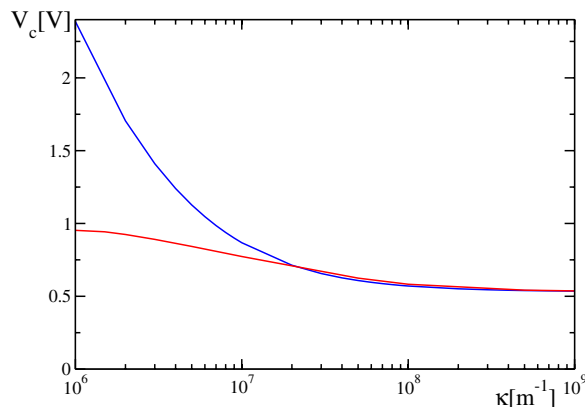


Figure 4. Threshold voltage V_c for the membrane undulation instability as a function of salt (i.e. κ). Nonlinear PB result (red curve) versus linear DH result (blue curve). Parameters: $\kappa = 10^6 \text{ m}^{-1}$ (pure water); bare surface tension $\Sigma_0 = 10^{-3} \text{ N m}^{-1}$; $\lambda_m = 200 \text{ nm}$.

electrolyte. We have calculated in the nonlinear PB regime the corrections to the membrane elastic moduli—both the external ones due to the Debye layers surrounding the membrane and the internal corrections due to the electric field inside the membrane. Strong deviations from the linear DH behavior have been found in the low salt regime already at quite moderate voltages. In particular, we have shown that the external contribution to the surface tension crosses over from a quadratic dependence on the externally applied voltage, as predicted by the linearized theory to a linear voltage dependence. In contrast, the internal contribution remains quadratic and becomes dominant at high voltages. The external contribution to the bending modulus even saturates for high voltages, while the internal contribution remains quadratic in voltage.

In addition, our present work confirms that surface tension still grows in absolute value with voltage, which means that the membrane undulation instability present in the DH theory (due to an effectively negative surface tension) persists in the nonlinear PB regime. The nonlinearities affect the threshold in voltage and the characteristic wavelength of the instability.

The method presented here can serve as a starting point for further extensions. One example would be to include fixed charges in addition to induced charges, similar to what was done in [27]. Another possible direction would be to improve the description of the membrane, cf the recent work [28], where thickness fluctuations of the membrane and fluctuations of the lipid dipole orientations within the membrane are accounted for in a comprehensive continuum model for a membrane in a normal dc electric field. Other possible extensions could include other types of nonlinear effects, for example due to membrane elasticity, due to the inclusion of proteins such as ion channels or pumps in the membrane [29], and also various relevant non-equilibrium effects, coupling electrostatics and hydrodynamics as in induced charge electro-osmosis [30]. Finally, in the biological context, the heterogeneity of the bilayer composition is another feature that is beyond the present model and that is likely to be important.

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Appendix. Calculation details for the bending modulus

Since this is an extension to nonlinear electrostatics of our earlier work [16], we only provide details of the calculation in this appendix. To solve the electrostatics problem to first order in the membrane height, one linearizes in h by writing

$$\begin{aligned}\phi(\mathbf{k}_\perp, z) &= \phi_0(z) + \phi_1(\mathbf{k}_\perp, z), \\ \rho(\mathbf{k}_\perp, z) &= \rho_0(z) + \rho_1(\mathbf{k}_\perp, z), \\ n^\pm(\mathbf{k}_\perp, z) &= n_0^\pm(z) + n_1^\pm(\mathbf{k}_\perp, z),\end{aligned}$$

where ϕ_0 and n_0^\pm are the base state solutions (flat membrane), as given in the main part and $\rho_0 = \frac{\epsilon}{2}(n_0^+ - n_0^-)$. Quantities with subscript 1 are of the order of h . We used the definition of the Fourier transform for the in-plane vector \mathbf{r}_\perp , $f(\mathbf{k}_\perp, z) = \int d\mathbf{r}_\perp e^{-i\mathbf{k}_\perp \cdot \mathbf{r}_\perp} f(\mathbf{r}_\perp, z)$.

Assuming zero current through the membrane, the Poisson–Nernst–Planck equation linearized in h has solutions $n_1^+ = -n_0^+ \phi_1$ and $n_1^- = n_0^- \phi_1$. Insertion of them into the PB equation yields, to linear order in h ,

$$(\partial_z^2 - k_\perp^2) \phi_1 = \kappa^2 \frac{(1 + 6c^2 e^{-2\kappa z} + c^4 e^{-4\kappa z})}{(1 - c^2 e^{-2\kappa z})^2} \phi_1, \quad (\text{A.1})$$

which is solved (with BC $\phi_1(z \rightarrow \infty) = 0$) by

$$\phi_1 = A \sqrt{\left(1 - 4 \frac{\kappa^2}{k_\perp^2} \frac{c^2 e^{2\kappa z}}{(e^{2\kappa z} - c^2)^2}\right) \frac{e^{2\kappa z} - \frac{(l-\kappa)^2}{k_\perp^2} c^2}{e^{2\kappa z} - \frac{(l+\kappa)^2}{k_\perp^2} c^2}} e^{-lz}, \quad (\text{A.2})$$

where we have introduced $l^2 = k_\perp^2 + \kappa^2$ (note that for $c \ll 1$ one regains a simple exponential, $\phi_1 = A'e^{-lz}$, as in [16]). The constant A can be obtained from the BC, equation (7), at order h

$$\lambda_m \left[(\partial_z^2 \phi_0)_{|z=0} \cdot h + (\partial_z \phi_1)_{|z=0} \right] = \phi_1(0^+) - \phi_1(0^-). \quad (\text{A.3})$$

As by symmetry $\phi(z) = -\phi(-z)$ and $\phi_1 \propto h$, one has $\phi_1(z) = \phi_1(-z)$ and equation (A.3) simplifies to $(\partial_z \phi_1)_{|z=0} = -(\partial_z^2 \phi_0)_{|z=0} \cdot h$. Thus A is independent of λ_m . The full expression for A is not needed, since later on we expand in k_\perp .

Since we study the case without ionic current through the membrane, the hydrodynamics problem (cf [16]) around the membrane is trivial and one obtains

$$v_z = h(\mathbf{k}_\perp) s(k_\perp) (1 + k_\perp z) e^{-k_\perp z} \quad (\text{A.4})$$

for the normal component of the velocity, as induced by a pure membrane bending mode [31]. Here $s(k_\perp)$ is the growth rate of the membrane fluctuations. The pressure is given by (in incompressible Stokes approximation)

$$p = -\eta \partial_z v_z + \frac{\mathbf{k}_\perp \cdot \mathbf{f}_\perp}{ik_\perp^2} + \frac{\eta}{k_\perp^2} \partial_z^3 v_z. \quad (\text{A.5})$$

Herein enters the bulk force due to the electric field acting on the charge distribution, which reads $\mathbf{f} = -2\rho \nabla \phi = -2\rho_0 \nabla \phi_1 - 2\rho_1 \nabla \phi_0 + \mathcal{O}(h^2)$ with the perpendicular component

$$\mathbf{f}_\perp = -2\rho_0(z) i\mathbf{k}_\perp \phi_1(\mathbf{k}_\perp, z). \quad (\text{A.6})$$

The total normal stress at the membrane is

$$\tau_{zz,1} = -p + 2\eta \partial_z v_z + \frac{\epsilon}{2} (\partial_z \phi)^2 - \frac{\epsilon_m}{2} (\partial_z \phi^m)^2. \quad (\text{A.7})$$

We now have to calculate the normal stress discontinuity at the membrane to linear order in h and to balance it with the membrane restoring force. With the abbreviation $[f]_0 = f(0^+) - f(0^-)$ the stress discontinuity can be written as

$$[\tau_{zz,1}]_{z=0} = -[p]_{z=0} + 2\eta[\partial_z v_z]_{z=0} + \epsilon [(\partial_z \phi_0)(\partial_z \phi_1)]_{z=0} - \epsilon_m \left((\partial_z \phi_0^m)(\partial_z \phi_1^m)|_{z=d/2} - (\partial_z \phi_0^m)(\partial_z \phi_1^m)|_{z=-d/2} \right). \quad (\text{A.8})$$

The contributions to the stress discontinuity from pressure and the velocity are easily obtained from equations (A.5) and (A.4), and the latter vanishes due to symmetry. The contribution from outside the membrane, $\epsilon[(\partial_z \phi_0)(\partial_z \phi_1)]_{z=0}$, is also straightforward to obtain from the ϕ_0 given by equation (17) and the ϕ_1 given by equation (A.2). The calculation of the contribution from inside the membrane is detailed below. The force balance at the membrane reads

$$-[\tau_{zz,1}]_{z=0} = -\frac{\partial F_H}{\partial h(\mathbf{r}_\perp)} = (-\Sigma_0 k_\perp^2 - K_0 k_\perp^4) h(\mathbf{k}_\perp), \quad (\text{A.9})$$

where the growth rate of membrane fluctuations $s(k_\perp)$ enters the left-hand side via the pressure. Expanding the left-hand side of equation (A.9) in powers of k_\perp and isolating $s(k_\perp)$ yields

$$\eta k_\perp s(k_\perp) = -\frac{1}{4} (\Sigma_0 + \Delta \Sigma_\kappa + \Delta \Sigma_m) k_\perp^2 - \frac{1}{4} (K_0 + \Delta K_\kappa + \Delta K_m) k_\perp^4, \quad (\text{A.10})$$

which is the same as equation (32). Here, we have separated the contributions from outside (index κ) and inside (index m) the membrane that are given by equations (28), (29), (33) and (34).

We now detail the calculation of the correction due to the inside field [16]. For this term, the last one in the rhs of equation (A.8), one has to keep the membrane thickness d finite. Since the internal field $E_{0,m}$ is constant, due to symmetry,

$$\epsilon_m \left((\partial_z \phi_0^m)(\partial_z \phi_1^m)|_{z=d/2} - (\partial_z \phi_0^m)(\partial_z \phi_1^m)|_{z=-d/2} \right) = -2\epsilon_m E_{0,m} (\partial_z \phi_1^m)|_{z=+d/2}. \quad (\text{A.11})$$

The potential inside the membrane can be written (using again the symmetry, as well as $\rho = 0$ inside; cf also [15] for details) as

$$\phi_1^m(k_\perp, z) = \phi_1^m \left(k_\perp, \frac{d}{2} \right) \frac{e^{k_\perp d/2}}{e^{k_\perp d} + 1} (e^{k_\perp z} + e^{-k_\perp z}). \quad (\text{A.12})$$

one can calculate $\phi_1^m(k_\perp, \frac{d}{2})$ approximately by using the outside solution, equation (A.2), and imposing the BC at the membrane, equation (7), leading to

$$\phi_1^m \left(k_\perp, \frac{d}{2} \right) = \phi_1 \left(k_\perp, \frac{d}{2} \right) - h(k_\perp) (\partial_z \phi_0^m - \partial_z \phi_0)|_{z=d/2}. \quad (\text{A.13})$$

On the right-hand side, now all quantities are known, and the contribution to equation (A.8) can be evaluated.

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