

# Applying a potential across a biomembrane: Electrostatic contribution to the bending rigidity and membrane instability

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We investigate the effect on biomembrane mechanical properties due to the presence of an external potential for a nonconductive incompressible membrane surrounded by different electrolytes. By solving the Debye-Hückel and Laplace equations for the electrostatic potential and using the relevant stress-tensor we find (1) in the small screening length limit, where the Debye screening length is smaller than the distance between the electrodes, the screening certifies that all electrostatic interactions are short range and the major effect of the applied potential is to decrease the membrane tension and increase the bending rigidity; explicit expressions for electrostatic contribution to the tension and bending rigidity are derived as a function of the applied potential, the Debye screening lengths, and the dielectric constants of the membrane and the solvents. For sufficiently large voltages the negative contribution to the tension is expected to cause a membrane stretching instability. (2) For the dielectric limit, i.e., no salt (and small wave vectors compared to the distance between the electrodes), when the dielectric constant on the two sides are different the applied potential induces an effective (unscreened) membrane charge density, whose long-range interaction is expected to lead to a membrane undulation instability.

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## I. INTRODUCTION

Biomembranes are thin fluid films composed mostly of lipids. In cells they help separate different cellular environments and compartments. Biomembranes are typically “soft,” i.e., the typical energy required to bend them is of the order the thermal energy and membrane tension is often quite small. Softness implies that membrane geometry can become sensitive to different perturbations, such as alteration of the electrostatic configuration. Much effort has, for instance, been devoted to calculation of the electrostatic contribution to tension and bending rigidity for membranes with fixed charges or surface potentials in an electrolyte solution, see Ref. [1] for a review; in general, the presence of fixed (and screened due to the electrolyte) charges tend to increase bending rigidity and hence make the membrane stiffer. However, it has also been found that when the membrane charges are not fixed but free to rearrange themselves on the surface and no electrolyte solution is present to screen the interaction, a long-wavelength undulation instability can occur [2], somewhat similar to DNA condensation [3]. Electric fields can also be present across intrinsically neutral membranes. An example would be a nerve cell, where ion pumps create a potential difference between the two sides of the nerve cell membrane [4]. Another example is provided in laboratories

by the routine formation of liposomes in a process known as electroformation [5], during which lipid membranes swell from electrodes under the application of electric fields.

In this study we investigate the electromechanical coupling of a membrane and an applied potential. In particular, we solve the Debye-Hückel and Laplace equations for the electrostatic potential for a nonconductive, incompressible membrane between two flat electrodes (kept at fixed potentials). On either side the membrane is surrounded by different electrolyte solutions. From the solutions for the potential we quantify how the corresponding induced membrane charges change the free energy for the membrane and identify electrostatic contributions to membrane mechanical parameters. In the presence of an electrolyte (in the small screening length limit, see below) we find that the electrostatic contribution to membrane bending rigidity is positive. In the absence of added salt (the dielectric limit) the membrane becomes unstable against long wavelength undulations (in a somewhat similar fashion to the behavior of the interface between two immiscible fluids, see Ref. [6]) if the two fluids surrounding the membrane have different dielectric constants. For the symmetric dielectric case, as well as for the small screening length limit, the membrane tension receives a negative contribution; for a sufficiently large applied potential this contribution would lead to a membrane stretching instability.

Several studies (see Ref. [1], and references therein) have investigated the electrostatic contributions to tension and bending rigidity for membranes having a fixed surface charge density or fixed potential at the membrane. However, less work has been dedicated to the effect of induced charges due to an applied potential, as considered in the present

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study. The results found here complement previous results given in Ref. [7] [using coupled hydrodynamical-electric field equations, similar to Ref. [8]] for the symmetric case of a membrane surrounded by identical electrolytes (in the small screening length limit), to the asymmetric case and by giving an explicit expression for the bending rigidity; in the limit of identical electrolytes on the two sides of the membrane our expression for the tension agrees with that derived in Ref. [7]. Also, our formulation allows us to investigate the dielectric (no salt) limit, which was not considered in Ref. [7]. However, unlike Ref. [7] we do not consider any dynamical effects. In contrast to the study [9] based on electrolyte conductivities, our approach through the Debye-Hückel equation allow us to study the effect of a finite Debye screening length. In Ref. [9] a nonzero membrane conductivity was considered, whereas we consider nonconductive membranes. Similar to the results in Ref. [9] we find a negative contribution to the membrane tension in the presence of an electrolyte, although the two results are difficult to compare because of the different mathematical formulations.

This work is organized as follows. In Sec. II we give the general equations governing the electrostatic response of a nonconductive membrane of any shape; the membrane region is described by the Laplace equation and the electrolyte solutions on either side satisfy the Debye-Hückel equations. In a standard fashion, the boundary conditions are that the potential and the displacement fields should be continuous. In Sec. III these equations are solved for the case of a flat membrane in an external potential. In Sec. IV corrections to the flat case solutions are derived for a weakly curved incompressible membrane. In Sec. V the forces acting on the membrane, as well as the corresponding electrostatic contribution to the membrane free energy, are obtained. Assuming that membrane fluctuations occur on a time scale slower than the relaxation time for the electrostatic potential we use the expressions for the forces for the weakly curved membrane in order to obtain the renormalized membrane mechanical parameters, such as tension and bending rigidity (in terms of a power series expansion in the wave vector) as a function of the applied potential, the salt concentrations (entering through the Debye screening lengths), and the dielectric constants of the membrane and the solvents. We investigate three different limits: (1) the small screening length limit, where the Debye screening length is smaller than the distance between the electrodes, (2) the dielectric limit, i.e., no salt, (3) the symmetric case, where the salt concentration and dielectric constants on the two sides of membrane are equal. The results for the membrane mechanical parameters in the three limits above (the main results in this study) are given in Eqs. (41)–(51). Finally, in Sec. VI a summary and discussion are given.

## II. GENERAL FORMULATION

We are interested in how biomembrane mechanical parameters (and thereby, for instance, membrane fluctuations) are effected by an applied potential. Two parameters characterizing a membrane in the absence of an applied potential are the tension  $\sigma$  and the bending stiffness  $K$  [10,11]. As an

external potential is applied there will in general be electrostatic contributions ( $\sigma_{el}$  and  $K_{el}$ ) to both of these quantities so that  $\sigma \rightarrow \sigma + \sigma_{el}$  and  $K \rightarrow K + K_{el}$  in the presence of the applied potential. An aim of this paper is to calculate  $\sigma_{el}$  and  $K_{el}$ . In a standard fashion we consider a small perturbation from a flat membrane, characterized by a height undulation  $h(x, y)$  (where  $x$  and  $y$  are coordinates in the plane of the flat membrane) and solve the electrostatic equations (via a Fourier transformation in the  $x$  and  $y$  coordinates) for this weakly perturbed geometry. Through a power series expansion in wave vector  $q$  ( $q = \sqrt{q_x^2 + q_y^2}$ , where  $q_x$  and  $q_y$  are the Fourier-transform variables of  $x$  and  $y$ , respectively) of the free energy  $G$  one may identify  $\sigma_{el}$  and  $K_{el}$  (see Chap. 2 in Ref. [11]). We find it convenient to, rather than utilize the free energy directly, consider the electrostatic contribution to the “restoring” force, from which we identify  $\sigma_{el}$  ( $K_{el}$ ) as the prefactor in front of the  $-q^2 \bar{h}$  ( $-q^4 \bar{h}$ ) term in a small  $q$  expansion of the force, where  $\bar{h} = \bar{h}(q_x, q_y)$  is the Fourier transform of  $h(x, y)$ . Notice that for obtaining the tension and bending rigidity it suffices to keep terms linear in  $\bar{h}$  in the restoring force expression. In general there may be other terms in the power series expansion in  $q$ . For instance, as noted in the Introduction, for the asymmetric dielectric case there is a membrane undulation instability which mathematically arises due to the presence of a negative term linear in  $q$  in the series expansion.

The approach described above relies on a “quasistatic” approximation, i.e., we assume that membrane fluctuations occur on a time scale  $t_{mem}$  slower than the time scale  $t_{el}$  over which the electrostatic configuration adjusts itself ( $t_{el} \ll t_{mem}$ ). This assumption allows us to solve the electrostatic problem for a fixed, weakly curved (but otherwise arbitrary) geometry. Let us estimate the time scales  $t_{el}$  and  $t_{mem}$ : To estimate  $t_{el}$  for an electrolyte we assume that this time scale equals the time for an ion to diffuse the distance of the order the Debye screening length, i.e.,  $t_{el} \approx \kappa^{-2}/D$ , where  $D$  is the ion diffusion constant and  $\kappa$  is the inverse Debye screening length introduced below (one may more realistically assume that  $t_{el} = \min\{\kappa^{-2}, q^{-2}\}/D$ , since for a wavelength perturbation of the order  $1/q$  the ions need only diffuse a distance  $1/q$  for the ion cloud to relax). From the Einstein relation and Stoke’s law, we have  $D = k_B T / (6\pi\eta R)$ , where  $\eta$  is the viscosity,  $k_B$  is the Boltzmann constant,  $T$  the temperature, and  $R$  the ion Stoke’s radius, using  $k_B T = 4 \times 10^{-21}$  J,  $\eta = 10^{-3}$  N s/m<sup>2</sup> and  $R \approx 0.1$ – $0.3$  nm [12], we find  $D \approx 10^{-9}$  m<sup>2</sup>/s. Furthermore, taking  $\kappa^{-1} = 10$  nm we obtain  $t_{el} \approx 10^{-7}$  s. For the membrane relaxation time we estimate [13]  $t_{mem} \approx \eta / (q^3 K)$ , and assuming  $q^{-1} > 100$  nm,  $K = 10^{-19}$  J we find  $t_{mem} \gtrsim 10^{-5}$  s. Therefore, indeed, we have  $t_{el} \ll t_{mem}$  in general. We note from the expressions above that the longer the wavelength perturbation (smaller  $q$ ) the better justified is our quasistatic approximation. In the dielectric limit there are no ions and the relevant relaxation time  $t_{el}$  is instead that of water relaxation (hydrogen-bond rearrangement time), which typically is of the order  $10^{-12}$  s (see Ref. [14]) at room temperature, again certifying that  $t_{el} \ll t_{mem}$ .

We are now set to consider the effect of an applied potential on the mechanical properties of a biomembrane within

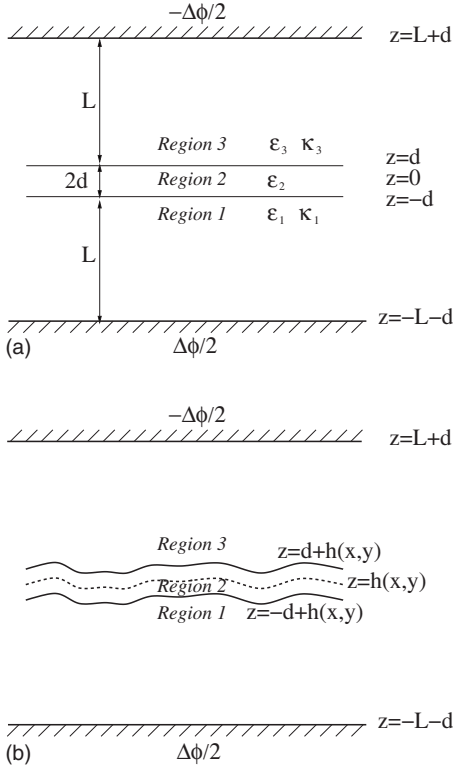


FIG. 1. Cartoon of the problems considered in this study: a membrane of width  $2d$  is placed between two electrodes. Regions 1 and 3 are characterized by dielectric constant  $\epsilon_1$  and  $\epsilon_3$  and Debye screening lengths  $\kappa_1$  and  $\kappa_3$ , respectively. The membrane is assumed nonconductive (and incompressible) and characterized by a dielectric constant  $\epsilon_2$ . Solving for the electrostatic potential  $\Phi(\vec{x})$  for (a) a flat membrane and (b) a weakly curved membrane (and utilizing the stress tensor) allows us to obtain the electrostatic contribution to the membrane mechanical parameters.

the quasistatic approximation. The explicit problem we consider is depicted in Fig. 1: an incompressible membrane of thickness  $2d$  is placed with its center-of-mass at positions  $z=0$  between two flat electrodes [at  $z=\pm(L+d)$ ] which are kept at potentials  $\mp\Delta\phi/2$ ; the distance between the membrane surface (for a flat membrane) and the electrodes are hence  $L$ . Regions 1 and 3 are electrolyte solutions, and in general these two regions are of different composition (different concentration of ions and different dielectric constants). As noted above the first stage towards calculating electrostatic forces on the membrane and thereby the membrane free energy in the presence of the applied potential is to obtain the electrostatic potential  $\Phi(\vec{x})$ . In this section we give general equations determining  $\Phi(\vec{x})$  for any membrane shape. In the subsequent sections we analyze in detail: (i) the flat membrane case, see Fig. 1(a); all quantities for this case carry a superscript (0), (ii) for the weakly curved situation (since we assume the membrane to be incompressible we only consider undulation deformation modes), illustrated in Fig. 1(b), there will be corrections of all quantities compared with the flat case; all such corrections carry the superscript (1).

For all three regions the electrostatic potential satisfies the Poisson equation (using SI units [15])

$$\epsilon_0 \epsilon_\gamma \nabla^2 \Phi_\gamma(\vec{x}) = -\rho_\gamma(\vec{x}). \quad (1)$$

We will henceforth use a subscript  $\gamma$  ( $=1, 2$ , or  $3$ ) to distinguish quantities in the three different regions. Above  $\epsilon_0$  is the permittivity of vacuum,  $\epsilon_\gamma$  is the dielectric constant for region  $\gamma$ , and  $\rho_\gamma(\vec{x})$  is the free charge density (the bound charges are, in a standard fashion, taken into account through  $\epsilon_\gamma$ ). We require

$$\int_{\text{region } \gamma} \rho_\gamma(\vec{x}) d^3x = 0, \quad (2)$$

i.e., that in each region we have charge neutrality (the membrane is assumed to be impermeable to ions). Let us now consider the explicit expression for the charge density in each of the three regions.

*Region 2.* In region 2 we assume

$$\rho_2(\vec{x}) = 0, \quad (3)$$

i.e., there are no free charges in this region.

*Region 1.* In region 1 we assume that there are ions of two types (positively and negatively charged) which are taken to be Boltzmann distributed, i.e. ( $i$  distinguishes the different ionic species),  $\rho_1(\vec{x}) = \sum_i q^i c_{\text{bulk},1}^i \exp\{-\beta q^i [\Phi_1(\vec{x}) - \phi_1^0]\}$ , where  $q^i$  is the charge of ionic species  $i$ ,  $c_{\text{bulk},1}^i$  is the concentration of ions in region 1, and  $\beta = 1/(k_B T)$ , with  $k_B$  the Boltzmann constant and  $T$  the temperature, as before. The constant  $\phi_1^0$  is determined through the charge neutrality condition (see also Appendix A). Making a linear approximation, i.e., assuming  $\beta q^i [\Phi_1(\vec{x}) - \phi_1^0] \ll 1$ , and using the charge neutrality condition in the absence of the external potential  $\sum_i q^i c_{\text{bulk},1}^i = 0$  we find that the charge density can be written

$$\rho_1(\vec{x}) = -\epsilon_0 \epsilon_1 \kappa_1^2 [\Phi_1(\vec{x}) - \phi_1^0], \quad (4)$$

with

$$\kappa_1^2 = \frac{\beta}{\epsilon_0 \epsilon_1} \sum_i [q^i]^2 c_{\text{bulk},1}^i, \quad (5)$$

where  $\kappa_1$  is the inverse Debye screening length for region 1.

*Region 3.* For region 3, with the same approximations as above, the charge density becomes

$$\rho_3(\vec{x}) = -\epsilon_0 \epsilon_3 \kappa_3^2 [\Phi_3(\vec{x}) - \phi_3^0], \quad (6)$$

where

$$\kappa_3^2 = \frac{\beta}{\epsilon_0 \epsilon_3} \sum_i [q^i]^2 c_{\text{bulk},3}^i \quad (7)$$

is the square of the inverse Debye screening length and  $c_{\text{bulk},3}^i$  is the concentration of ions in region 3.

Inserting Eq. (3) into Eq. (1) yields the Laplace equation

$$\nabla^2 \Phi_2(\vec{x}) = 0 \quad (8)$$

for the potential in region 2. Inserting Eqs. (4) and (6) into Eq. (1) gives the Debye-Hückel equation ( $\gamma=1, 3$ )

$$\nabla^2 \Phi_\gamma(\vec{x}) - \kappa_\gamma^2 [\Phi_\gamma(\vec{x}) - \phi_\gamma^0] = 0 \quad (9)$$

for regions 1 and 3. The charge neutrality condition (2) for region 1 and 3 becomes

$$\int_{\text{region } \gamma} [\Phi_\gamma(\vec{x}) - \phi_\gamma^0] d^3x = 0. \quad (10)$$

Note that we have trivial charge neutrality in region 2 [see Eq. (3)].

Let us now consider the boundary conditions supplementing the equations above. At the electrodes we have

$$\begin{aligned} \Phi_1(\vec{x})|_{z=-L-d} &= \frac{\Delta\phi}{2}, \\ \Phi_3(\vec{x})|_{z=L+d} &= -\frac{\Delta\phi}{2}. \end{aligned} \quad (11)$$

In addition we have that the potential and the normal component of the displacement fields are continuous across the region-1–region-2 and region-2–region-3 boundaries, i.e. [15],

$$\begin{aligned} \Phi_1(\vec{x}) &= \Phi_2(\vec{x}) \text{ at the region 1–2 boundary,} \\ \Phi_2(\vec{x}) &= \Phi_3(\vec{x}) \text{ at the region 2–3 boundary} \end{aligned} \quad (12)$$

and

$$\begin{aligned} \epsilon_1 \hat{n} \cdot \vec{\nabla} \Phi_1(\vec{x}) &= \epsilon_2 \hat{n} \cdot \vec{\nabla} \Phi_2(\vec{x}) \text{ at region 1–2 boundary,} \\ \epsilon_2 \hat{n} \cdot \vec{\nabla} \Phi_2(\vec{x}) &= \epsilon_3 \hat{n} \cdot \vec{\nabla} \Phi_3(\vec{x}) \text{ at region 2–3 boundary,} \end{aligned} \quad (13)$$

where  $\hat{n}$  is the normal to the respective interface. Equations (8)–(10), together with the boundary conditions (11)–(13) completely determine the electrostatic potential  $\Phi(\vec{x})$ .

From the solutions for  $\Phi(\vec{x})$  one can calculate other quantities. For instance, one may obtain the induced potential defined through  $\Phi_{\text{ind}}(\vec{x}) = \Phi(\vec{x}) - \Phi_{\text{appl}}(\vec{x})$ , where the applied potential is  $\Phi_{\text{appl}}(\vec{x}) = -\Delta\phi z / [2(L+d)]$ . The total electric field is given by  $\vec{E}(\vec{x}) = -\vec{\nabla}\Phi(\vec{x})$ , the applied electric field is  $\vec{E}_{\text{appl}} = -\vec{\nabla}\Phi_{\text{appl}}$ , and the induced field is  $\vec{E}_{\text{ind}} = -\vec{\nabla}\Phi_{\text{ind}} = \vec{E} - \vec{E}_{\text{appl}}$ . In the next section we solve the equations given in this section for the case of a flat membrane. In the section after we find corrections to the flat case solutions for a weakly curved membrane.

### III. POTENTIAL FOR A FLAT MEMBRANE

Below we obtain the electrostatic potential in and around a flat membrane. We use a superscript (0) to indicate the flat case quantities.

For a flat membrane the solutions depend only on  $z$ , and explicitly the solutions to Eqs. (8) and (9) are

$$\Phi_2^{(0)}(z) = \phi_2^0 + A_2 z, \quad (14)$$

where  $\phi_2^0$  and  $A_2$  are constants determined by the boundary conditions below. Also,

$$\Phi_1^{(0)}(z) = \phi_1^0 + A_1(e^{\kappa_1(z+d)} - e^{-\kappa_1(L+d+z)}) \quad (15)$$

and

$$\Phi_3^{(0)}(z) = \phi_3^0 + A_3(e^{-\kappa_3(z-d)} - e^{-\kappa_3(L+d-z)}), \quad (16)$$

where  $\phi_1^0$ ,  $\phi_3^0$ ,  $A_1$ , and  $A_3$  are constants, and we used the charge neutrality condition (10).

We now use the boundary conditions [together with the fact that the boundary surfaces are at  $z = \pm d$  for the flat case considered here, see Fig. 1(a)] in order to determine the unknown constants above. From Eq. (11), the condition that the potential is continuous [Eq. (12)] and the fact that the displacement field is continuous [Eq. (13)], we get six equations for the six constants  $\phi_\gamma^0$  and  $A_\gamma$  ( $\gamma=1,2,3$ ). Solving these equations leads to

$$\begin{aligned} A_1 &= -\frac{\Delta\phi}{2(1+e^{-\kappa_1 L})} l_1 \Gamma, \\ A_2 &= -\frac{\Delta\phi}{2\epsilon_2} \Gamma, \\ A_3 &= \frac{\Delta\phi}{2(1+e^{-\kappa_3 L})} l_3 \Gamma \end{aligned} \quad (17)$$

and

$$\begin{aligned} \phi_1^0 &= \frac{\Delta\phi}{2} [1 - g(\kappa_1) l_1 \Gamma], \\ \phi_2^0 &= -\frac{\Delta\phi}{2} [g(\kappa_1) l_1 - g(\kappa_3) l_3] \Gamma, \\ \phi_3^0 &= -\frac{\Delta\phi}{2} [1 - g(\kappa_3) l_3 \Gamma], \end{aligned} \quad (18)$$

where

$$g(q) = \frac{1 - e^{-qL}}{1 + e^{-qL}} = \tanh\left(\frac{qL}{2}\right) \quad (19)$$

and  $\Gamma = 1/[g(\kappa_1)l_1 + g(\kappa_3)l_3 + d/\epsilon_2]$ , and we introduced the “rescaled” Debye screening lengths  $l_1 = (\epsilon_1 \kappa_1)^{-1}$  and  $l_3 = (\epsilon_3 \kappa_3)^{-1}$ .

There are three limits of particular interest.

(1) “*Small*” screening length,  $\kappa_1 L, \kappa_3 L \gg 1$ . For this case we have  $g(q) \rightarrow 1$  in Eqs. (17) and (18). Also the prefactors for  $A_1$  and  $A_3$  simplify.

(2) We define the dielectric limit as the limit of no salt, i.e.,  $c_{\text{bulk},1}^i, c_{\text{bulk},3}^i \rightarrow 0$ ; within the Debye-Hückel approximation this is the equivalent to  $\kappa_1, \kappa_3 \rightarrow 0$ . Expanding the exponentials in Eqs. (15) and (16), and using the explicit form for  $A_1$  and  $A_3$  above one straightforwardly show that the solutions in all three regions take the form  $\Phi(\vec{x}) = az + b$  where  $a$  and  $b$  are constants independent of  $\kappa_1$  and  $\kappa_3$ , as it should since in the dielectric limit the potential satisfies Laplace equation  $\nabla^2 \Phi(\vec{x}) = 0$ , see Eq. (9).

(3) *The symmetric case*,  $\epsilon_1 = \epsilon_3$  and  $\kappa_1 = \kappa_3$ . In this limit we find that  $A_1 = -A_3$ ,  $\phi_1^0 = -\phi_3^0$  and  $\phi_2^0 = 0$ .

The potential and charge densities are illustrated in Fig. 2, using the flat membrane results in Eqs. (14)–(16). The electric field in the  $z$  direction (the electric field components in the  $x$  and  $y$  direction are zero for a flat membrane) is also illustrated. We notice that the potential is continuous as it should and that the free charges tend to build up close to the membrane and electrodes (for  $\kappa_1, \kappa_3 \neq 0$ ). Since the normal component of the displacement field is continuous across the boundaries, the relative jump in the electric field as the boundary between region 1-2 (region 2-3) is crossed equals  $\varepsilon_2/\varepsilon_1$  ( $\varepsilon_2/\varepsilon_3$ ), see Fig. 2 (bottom).

#### IV. POTENTIAL FOR A WEAKLY CURVED MEMBRANE

We now consider a weakly curved membrane, see Fig. 1(b): The center of the membrane is slightly displaced from the flat ( $z=0$ ) case, according to  $z=h(x,y)$  with membrane surfaces at  $z=\pm d+h(x,y)$  [16]. We write the solution for the electrostatic potential according to ( $\gamma=1,2,3$  as before)

$$\Phi_\gamma(\vec{x}) = \Phi_\gamma^{(0)}(z) + \Phi_\gamma^{(1)}(\vec{x}), \quad (20)$$

where  $\Phi_\gamma^{(0)}(z)$  is the potential for region  $\gamma$  for the flat case given in the previous section and  $\Phi_\gamma^{(1)}(\vec{x})$  is a correction to the potential due to the perturbed geometry. In this section we will calculate  $\Phi_\gamma^{(1)}$  only to first order in the perturbation  $h(x,y)$ ; this suffices for obtaining membrane mechanical parameters such as tension and bending rigidity (see discussion at the beginning of Sec. II). In each of the regions Eqs. (8) and (9) has to be satisfied.  $\Phi_\gamma^{(0)}(\vec{x})$  satisfies these equations for  $h(x,y) \equiv 0$ , and we therefore require that the corrections satisfy

$$\nabla^2 \Phi_\gamma^{(1)}(\vec{x}) = 0 \quad (21)$$

and ( $\gamma=1,3$ )

$$\nabla^2 \Phi_\gamma^{(1)}(\vec{x}) - \kappa_\gamma^2 \Phi_\gamma^{(1)}(\vec{x}) = 0. \quad (22)$$

Let us now consider the boundary conditions [the boundary surfaces are at  $z=\pm d+h(x,y)$  for the curved membrane considered here]. Since  $\Phi_\gamma^{(0)}(z)$  satisfies Eq. (11) we require for the perturbation

$$\begin{aligned} \Phi_1^{(1)}(\vec{x})|_{z=-L-d} &= 0, \\ \Phi_3^{(1)}(\vec{x})|_{z=L+d} &= 0. \end{aligned} \quad (23)$$

Before imposing the conditions that the potential and the displacement fields are continuous, Eqs. (12) and (13), we note that for “small”  $h$  any scalar quantity  $g(\vec{x})$  may be expanded, to first order in  $h$ , according to:

$$\begin{aligned} g(\vec{x}) &= g^{(0)}(\vec{x})|_{z=\pm d+h} + g^{(1)}(\vec{x})|_{z=\pm d+h} \\ &\approx \left( g^{(0)}(\vec{x}) + h \frac{\partial g^{(0)}(\vec{x})}{\partial z} + g^{(1)}(\vec{x}) \right) \Big|_{z=\pm d}, \end{aligned}$$

we briefly discuss the quantitative meaning of “small”  $h$  at the end of this section. Equations (12) and (13) can then be written

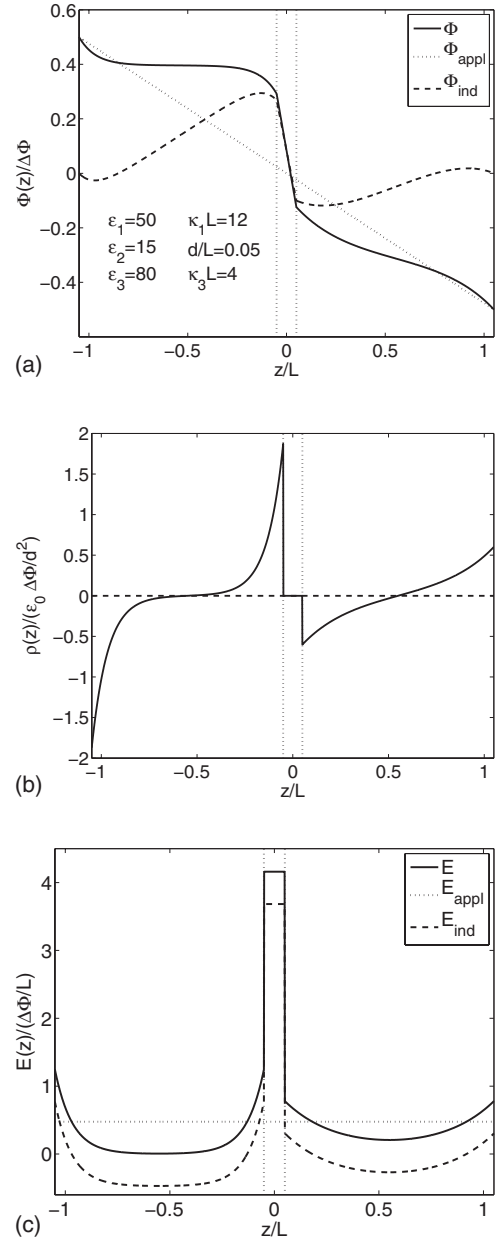


FIG. 2. Illustration of the response of a flat membrane, surrounded by different electrolyte solutions, to an applied potential. (a) Electrostatic potential  $\Phi(\vec{x})=\Phi^{(0)}(z)$  for a flat membrane (solid curve) as a function of position  $z$ . Illustrated are also the applied potential  $\Phi_{\text{appl}}(z)$  (dotted curve) and the induced potential  $\Phi_{\text{ind}}(z)$  (dashed curve). (b) Free charge density  $\rho(z)$  (solid curve) as a function of position  $z$ . The dashed curve at  $\rho=0$  corresponds to the free charge density in the absence of the applied potential ( $\Delta\phi=0$ ). (c) The electric field  $E=-\partial\Phi/\partial z$  in the  $z$  direction for different positions  $z$ . Illustrated are also the applied field  $E_{\text{appl}}=-\partial\Phi_{\text{appl}}/\partial z$  and the induced field  $E_{\text{ind}}=-\partial\Phi_{\text{ind}}/\partial z$ . The vertical lines in each figure corresponds to the membrane surfaces. The chosen parameter values are the same for all three graphs, and are listed in the top graph (we chose the somewhat unrealistically large value  $\varepsilon_2=15$  in order to be able to better visualize the Debye screening layers, a more reasonable value would be  $\varepsilon_2 \approx 2$ ). Note that the potential is continuous, whereas the free charge density and the  $z$  component of the electric field are not continuous, as it should.

$$\left( h \frac{\partial \Phi_1^{(0)}}{\partial z} + \Phi_1^{(1)} \right) \Big|_{z=-d} = \left( h \frac{\partial \Phi_2^{(0)}}{\partial z} + \Phi_2^{(1)} \right) \Big|_{z=-d},$$

$$\left( h \frac{\partial \Phi_2^{(0)}}{\partial z} + \Phi_2^{(1)} \right) \Big|_{z=d} = \left( h \frac{\partial \Phi_3^{(0)}}{\partial z} + \Phi_3^{(1)} \right) \Big|_{z=d} \quad (24)$$

and

$$\varepsilon_1 \left( h \frac{\partial^2 \Phi_1^{(0)}}{\partial z^2} + \frac{\partial \Phi_1^{(1)}}{\partial z} \right) \Big|_{z=-d} = \varepsilon_2 \left( h \frac{\partial^2 \Phi_2^{(0)}}{\partial z^2} + \frac{\partial \Phi_2^{(1)}}{\partial z} \right) \Big|_{z=-d},$$

$$\varepsilon_2 \left( h \frac{\partial^2 \Phi_2^{(0)}}{\partial z^2} + \frac{\partial \Phi_2^{(1)}}{\partial z} \right) \Big|_{z=d} = \varepsilon_3 \left( h \frac{\partial^2 \Phi_3^{(0)}}{\partial z^2} + \frac{\partial \Phi_3^{(1)}}{\partial z} \right) \Big|_{z=d}, \quad (25)$$

where we used the fact that  $\Phi_\gamma^{(0)}$  satisfies the boundary conditions for  $h=0$ . Equations (21) and (22) together with the boundary conditions (23)–(25) completely determine the correction  $\Phi_\gamma^{(1)}(\vec{x})$ .

We proceed by introducing the Fourier transform in the  $x$  and  $y$  direction (not for  $z$  direction) of  $\Phi_\gamma^{(1)}(\vec{x})$ :

$$\bar{\Phi}_\gamma^{(1)}(q_x, q_y, z) = \int dx dy e^{iq_x x + iq_y y} \Phi_\gamma^{(1)}(\vec{x}), \quad (26)$$

and similarly we denote by  $\bar{h}(q_x, q_y)$  the Fourier transform of  $h(x, y)$ . Equations (21) and (22) can then be written

---


$$D_2(q) = -\bar{h} \times \frac{e^{qd} k_3^+ [p_1 + \varepsilon_1 \bar{q}_1 r(\bar{q}_1) m_1^-] - e^{-qd} k_1^- [p_3 - \varepsilon_3 \bar{q}_3 r(\bar{q}_3) m_3^+]}{e^{2qd} k_1^+ k_3^+ - e^{-2qd} k_1^- k_3^-}, \quad (33)$$

where we introduced the short-hand notations ( $\gamma=1, 3$ )

$$k_\gamma^\pm = k_\gamma^\pm(q) = \varepsilon_2 q \pm \varepsilon_\gamma \bar{q}_\gamma r(\bar{q}_\gamma),$$

$$m_\gamma^\pm = A_2 \pm A_\gamma \kappa_\gamma (1 + e^{-\kappa_\gamma L}),$$

$$p_\gamma = \varepsilon_\gamma A_\gamma \kappa_\gamma^2 (1 - e^{-\kappa_\gamma L}),$$

$$r(q) = \frac{1 + e^{-2qL}}{1 - e^{-2qL}}, \quad (34)$$

with  $A_\gamma$  given in Eq. (17). The remaining coefficients are

$$C_2(q) = \frac{e^{qd}}{k_1^-} [D_2(q) e^{qd} k_1^+ + \bar{h} p_1 + \bar{h} \varepsilon_1 \bar{q}_1 r(\bar{q}_1) m_1^-],$$

$$D_1(q) = \frac{1}{1 - e^{-2\bar{q}_1 L}} [\bar{h} m_1^- + C_2(q) e^{-qd} + D_2(q) e^{qd}],$$

$$\frac{\partial \bar{\Phi}_2^{(1)}}{\partial z^2} - q^2 \bar{\Phi}_2^{(1)} = 0 \quad (27)$$

and ( $\gamma=1, 3$ )

$$\frac{\partial \bar{\Phi}_\gamma^{(1)}}{\partial z^2} - \bar{q}_\gamma^2 \bar{\Phi}_\gamma^{(1)} = 0, \quad (28)$$

where  $q = \sqrt{q_x^2 + q_y^2}$  and

$$\bar{q}_\gamma = \sqrt{q^2 + \kappa_\gamma^2}. \quad (29)$$

The boundary conditions (23)–(25) remains the same in Fourier space (using the fact that  $\Phi_\gamma^{(0)}$  is independent of  $x$  and  $y$ ), with the sole replacement  $\Phi_\gamma^{(1)} \rightarrow \bar{\Phi}_\gamma^{(1)}$  and  $h \rightarrow \bar{h}$ . The solution of Eq. (27) is

$$\bar{\Phi}_2^{(1)}(q, z) = C_2(q) e^{qz} + D_2(q) e^{-qz}, \quad (30)$$

with  $q$ -dependent coefficients  $C_2(q)$  and  $D_2(q)$ . Using the boundary condition (23) we find that the solutions to Eq. (28) are

$$\bar{\Phi}_1^{(1)}(q, z) = D_1(q) (e^{\bar{q}_1(z+d)} - e^{-\bar{q}_1(z+d+2L)}) \quad (31)$$

and

$$\bar{\Phi}_3^{(1)}(q, z) = D_3(q) (e^{-\bar{q}_3(z-d)} - e^{\bar{q}_3(z-d-2L)}). \quad (32)$$

The unknown coefficients  $C_2(q)$ ,  $D_1(q)$ ,  $D_2(q)$ , and  $D_3(q)$  are determined through the boundary conditions (24) and (25). We find

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$$D_3(q) = \frac{1}{1 - e^{-2\bar{q}_3 L}} [\bar{h} m_3^+ + C_2(q) e^{qd} + D_2(q) e^{-qd}]. \quad (35)$$

We notice that  $C_1(q)$ ,  $D_1(q)$ ,  $D_2(q)$ , and  $D_3(q)$  are all proportional to  $\bar{h}$  as they should be. The full solution for the electrostatic potentials  $\Phi_\gamma(\vec{x})$  for a weakly curved membrane is given by Eq. (20), where  $\Phi_\gamma^{(0)}(z)$  were given in the previous section and the Fourier transform of  $\Phi_\gamma^{(1)}(\vec{x})$  are given by Eqs. (30)–(32) together with Eqs. (33)–(35).

Again, we point out that in order to obtain membrane mechanical parameters, such as tension and bending rigidity, it suffices to know the restoring force (calculated in the next section) to first order in  $\bar{h}$ , i.e., it is enough to consider “small” fluctuation amplitudes. Therefore, even though the results given above formally assume that  $h$  is smaller than all other length scales in the problem ( $d$ ,  $\kappa_\gamma^{-1}$ ,  $q^{-1}$ , and  $L$ ), they are sufficient for the purpose of calculating the tension and bending rigidity. A different matter is whether the Helfrich

form of the electrostatic contribution to the restoring force (in terms of tension and bending rigidity), derived in the next section, describe well “large” membrane fluctuations in the presence of an applied potential. To address this question we must clarify the meaning of “small”  $h$ , i.e., make clear what is the relevant dimensionless expansion parameter, in the context of calculating the electrostatic contribution to the membrane restoring force or membrane free energy. The electrostatic contribution to the membrane free energy is determined by the interactions between induced charges at or in the vicinity of the membrane, with characteristic interaction distances of the order  $d$  and  $\kappa_\gamma^{-1}$  (here we consider the small screening length limit, where  $\kappa_\gamma$  is nonzero). Therefore, whenever  $dq \ll 1$ ,  $\kappa_\gamma^{-1}q \ll 1$  and  $hq \ll 1$  all interactions are effectively local on a locally flat membrane and the free energy must take the Helfrich form [10]. Note that this argument is valid independent of particular values of  $h\kappa_\gamma$  and  $h/d$ , and the free energy expansions given in the next section (in the small screening length limit) is therefore an expansion in the (small) parameters  $hq$ ,  $dq$ ,  $\kappa_\gamma^{-1}q$ , but when these parameters are small there is no restriction on the values of  $h\kappa_\gamma$  and  $h/d$ . In consistency with the discussion above, we point out that in Ref. [17] a method that formally avoids the assumptions  $h\kappa_\gamma \ll 1$  and  $h/d \ll 1$ , by utilizing the geometrical transformation  $z' = z - h(x, y)$ , was found to give results consistent with results obtained by the flat membrane perturbative approach (of the kind used in this paper) for a charged membrane in an electrolyte.

## V. FORCES, FREE ENERGY AND ELECTROSTATIC CONTRIBUTION TO MEMBRANE MECHANICAL PARAMETERS

In this section we derive general expressions for the membrane forces (within the quasistatic approximation) and the corresponding electrostatic contribution to the membrane free energy, using the results from the previous two sections. In particular, we obtain the electrostatic contribution to the membrane free energy for three cases: (1) the small screening length limit, where the Debye screening length is smaller than the distance between the electrodes, (2) the dielectric limit, i.e., no salt, and, (3) the symmetric case, where the salt concentrations and dielectric constants on the two sides of the membrane are equal.

### A. Membrane forces via a stress-tensor calculation

The forces acting on the membrane are obtained using the relevant stress tensor  $T_{ij}$ . Following the derivation in Appendix A we have (in the Debye-Hückel regime considered here)

$$T_{ij} = \varepsilon_0 \varepsilon_\gamma \left( \frac{\partial \Phi_\gamma}{\partial x_i} \frac{\partial \Phi_\gamma}{\partial x_j} - \frac{1}{2} \delta_{ij} \sum_k \frac{\partial \Phi_\gamma}{\partial x_k} \frac{\partial \Phi_\gamma}{\partial x_k} - \delta_{ij} \frac{\kappa_\gamma^2}{2} (\Phi_\gamma - \phi_\gamma^0)^2 \right) - p_\gamma^0 \delta_{ij}, \quad (36)$$

where  $x_1 = x$ ,  $x_2 = y$ , and  $x_3 = z$ . The first two terms are the usual Maxwell stress-tensor [15, 18], the third term is an osmotic contribution for the ions being “confined” by the elec-

tric potential (see Appendix A), and the last term incorporates pressures  $p_\gamma^0$  for each of the three regions ( $\gamma = 1, 2, 3$ ). The discontinuities of  $T_{ij}$  at the region boundaries will produce forces on the membrane which will have to be balanced by other forces in the system, such as, for example, viscous forces within the membrane or from the surrounding bulk fluids. We are only interested in calculating the electromechanical contribution at a given  $(x, y)$  to this total force balance here. To do this we note that the force (per unit area) in the  $i$  direction on a region boundary from the stress in a given region is  $\pm \sum_j n_j T_{ji}$  evaluated at the boundary, where the membrane normal  $n_j$  is taken to point towards positive  $z$  and the plus (minus) sign applies when the region is at larger (smaller)  $z$  than the boundary. Defining

$$f_\gamma = f_\gamma^{(0)} + f_\gamma^{(1)},$$

$$f_\gamma^{(0)} = \frac{1}{2} \varepsilon_0 \varepsilon_\gamma \left[ \left( \frac{\partial \Phi_\gamma^{(0)}}{\partial z} \right)^2 - \kappa_\gamma^2 (\Phi_\gamma^{(0)} - \phi_\gamma^0)^2 \right] \Big|_{z=\pm d} - p_\gamma^0,$$

$$f_\gamma^{(1)} = \varepsilon_0 \varepsilon_\gamma \left[ \frac{\partial \Phi_\gamma^{(0)}}{\partial z} \left( h \frac{\partial^2 \Phi_\gamma^{(0)}}{\partial z^2} + \frac{\partial \Phi_\gamma^{(1)}}{\partial z} \right) - \kappa_\gamma^2 (\Phi_\gamma^{(0)} - \phi_\gamma^0) \times \left( h \frac{\partial \Phi_\gamma^{(0)}}{\partial z} + \Phi_\gamma^{(1)} \right) \right] \Big|_{z=\pm d}, \quad (37)$$

where  $z = -d$  ( $z = d$ ) is to be used for forces acting on the interface separating region 1 and 2 (region 2 and 3), and using that to first order in  $h$ :  $n_z = 1$ ,  $n_j = -\partial_j h$  ( $j = x, y$ ), we find that the  $z$  component of the total force acting on the surface separating regions 1 and 2 is  $f_{1-2} = f_2 - f_1$ . Using the explicit expressions for the potentials from the previous two sections we find

$$f_{1-2} = f_{1-2}^{(0)} + f_{1-2}^{(1)},$$

$$f_{1-2}^{(0)} = -\varepsilon_0 \left( 2\varepsilon_1 A_1^2 \kappa_1^2 e^{-\kappa_1 L} - \frac{\varepsilon_2 A_2^2}{2} \right) + p_1^0 - p_2^0,$$

$$\begin{aligned} \bar{f}_{1-2}^{(1)} = & -\varepsilon_0 \{ D_1(q) \varepsilon_1 A_1 \kappa_1 [\bar{q}_1 (1 + e^{-\kappa_1 L}) (1 + e^{-2\bar{q}_1 L}) - \kappa_1 (1 \\ & - e^{-\kappa_1 L}) (1 - e^{-2\bar{q}_1 L})] - \varepsilon_2 A_2 q [C_2(q) e^{-qd} - D_2(q) e^{qd}] \}, \end{aligned} \quad (38)$$

where  $f_{1-2}^{(0)}$  is the force on a flat membrane interface and  $f_{1-2}^{(1)}$  is the first order correction for a weakly curved membrane, here expressed explicitly in terms of its Fourier transform  $\bar{f}_{1-2}^{(1)}$ ; note that  $\bar{f}_{1-2}^{(1)}$  is proportional to  $\bar{h}$  (via  $D_1$ ,  $C_2$ , and  $D_2$ ), as it should. Similarly, the  $z$  component of the force acting on the surface separating regions 2 and 3 is  $f_{2-3} = f_3 - f_2$  and we find

$$f_{2-3} = f_{2-3}^{(0)} + f_{2-3}^{(1)},$$

$$f_{2-3}^{(0)} = \varepsilon_0 \left( 2\varepsilon_3 A_3^2 \kappa_3^2 e^{-\kappa_3 L} - \frac{\varepsilon_2 A_2^2}{2} \right) + p_2^0 - p_3^0,$$

$$\begin{aligned} \bar{f}_{2-3}^{(1)} = & \varepsilon_0 \{ D_3(q) \varepsilon_3 A_3 \kappa_3 [\bar{q}_3 (1 + e^{-\kappa_3 L}) (1 + e^{-2\bar{q}_3 L}) - \kappa_3 (1 \\ & - e^{-\kappa_3 L}) (1 - e^{-2\bar{q}_3 L})] - \varepsilon_2 A_2 q [C_2(q) e^{qd} - D_2(q) e^{-qd}] \}, \end{aligned} \quad (39)$$

where  $A_\gamma$  are given in Eq. (17) and  $C_2(q)$ ,  $D_\gamma(q)$  are given in Eqs. (33) and (35). The results given in Eqs. (38) and (39) completes the calculation of the forces acting on the membrane interfaces. In Appendix B we utilize these results in order obtain results for the total net force on a flat membrane in some detail. In the next subsection the membrane free energy and the electrostatic contribution to the membrane mechanical parameters in different limits are investigated.

### B. Contribution to the free energy of the membrane

Let us now investigate the electrostatic contribution to the membrane free energy. We first note that if the fluids surrounding the membrane are incompressible, then the pressures  $p_\gamma^0$  [occurring in the zero order terms in Eqs. (38) and (39)] adjust such that there is no net force (and hence no net movement of the membrane) in the  $z$  direction; we will here consider such incompressible fluids and also assume the membrane to be incompressible. Nevertheless the investigation of the net force  $f^{(0)} = f_{1-2}^{(0)} + f_{2-3}^{(0)}$  on a membrane provides some insights into the electrostatic problem under consideration here, and is given in Appendix B.

Let us now proceed by considering the  $z$  component of first order correction to the forces  $\bar{f}^{(1)} = \bar{f}_{1-2}^{(1)} + \bar{f}_{2-3}^{(1)}$ ; from  $\bar{f}^{(1)}$  one can obtain the work on the membrane under an undulation deformation of the shape, and thereby the free energy and electrostatic contribution to membrane mechanical parameters (through a power series in  $q$ , i.e., a long wavelength expansion). In particular we want to compare the results of such an expansion to the corresponding result for a “free” membrane: the free energy  $G$  for a membrane is described by the Helfrich form [10,11]  $G = \int dA (2KH^2 + \sigma)$ , where  $H$  is the mean curvature,  $dA$  the area element on the membrane,  $\sigma$  is the tension, and  $K$  is the bending rigidity. The restoring force is then obtained as  $f_{rs} = -\delta G / \delta h$  giving in  $q$  space

$$\bar{f}_{rs}(q) = -[\sigma q^2 + Kq^4] \bar{h} + O(\bar{h}^2). \quad (40)$$

This type of expansion requires only that the expectation value of  $[\nabla h(x,y)]^2$  is small [11], i.e., that the characteristic fluctuation amplitude is small compared to  $1/q$ . In the presence of an applied potential there will be electrostatic contributions  $\sigma_{el}$  and  $K_{el}$  to the tension and bending rigidity, so that  $\sigma \rightarrow \sigma + \sigma_{el}$  and  $K \rightarrow K + K_{el}$ . Below we proceed by expanding  $\bar{f}^{(1)}$ , using the results in Eqs. (38) and (39), in a power series in  $q$  for different limits in order to obtain  $\sigma_{el}$  and  $K_{el}$  (note, however, in the expansion for the dielectric limit, for  $qL \gg 1$ , we also find terms odd in  $q$ ). Note that since the tension and bending rigidities are identified through terms in the restoring force expansion which are proportional to  $\bar{h}$ , second and higher order terms in  $\bar{h}$  (see discussion at the end of the previous section) do not contribute to  $\sigma_{el}$  and  $K_{el}$ .

(1) In the “small” screening length limit  $\kappa_1 L, \kappa_3 L \gg 1$ , a straightforward but lengthy expansion of  $\bar{f}^{(1)}$  in a power series in  $q$  assuming that the wavelength of the perturbation ( $= 2\pi/q$ ) is larger than the membrane thickness and the Debye screening lengths  $qd, q/\kappa_1, q/\kappa_3 \ll 1$ , gives

$$\bar{f}^{(1)} = -[\sigma_{el} q^2 + K_{el} q^4 + O(q^6)] \bar{h}. \quad (41)$$

The explicit expression for the electrostatic contribution to the tension is

$$\sigma_{el} = -\frac{\varepsilon_0 \Delta \phi_m^2}{2} \frac{l_1 + l_3 + 4d/\varepsilon_2}{(l_1 + l_3 + 2d/\varepsilon_2)^2}, \quad (42)$$

where, as before, the “rescaled” Debye screening lengths are  $l_1 = (\varepsilon_1 \kappa_1)^{-1}$  and  $l_3 = (\varepsilon_3 \kappa_3)^{-1}$ . We also introduced

$$\Delta \phi_m = \phi_1^0 - \phi_3^0 = \frac{\Delta \phi}{2} \frac{l_1 + l_3 + 2d/\varepsilon_2}{l_1 + l_3 + d/\varepsilon_2} \quad (43)$$

being the potential difference between the main parts of the two bulk fluids. Notice that  $\sigma_{el}$  gives a negative contribution to the tension. The fact that  $\sigma_{el} < 0$  originates from the fact that the applied potential creates a net charge density on either side of the membrane surfaces, see Fig. 2; since ions of equal charge repel each other the system would, for a compressible membrane, be able to decrease the free energy by separating the charges through a stretching of the membrane (i.e., by increasing the membrane area). For an incompressible membrane (as assumed here) the membrane is likely to respond to the electrostatically induced negative tension by an opposite increase in the membrane elastic contribution to the tension. If the magnitude of  $\sigma_{el}$  exceeds the membrane elastic strength (tensile strength) a stretching instability occur. For the symmetric case ( $\kappa = \kappa_1 = \kappa_3$  and  $\varepsilon = \varepsilon_1 = \varepsilon_3$ ) Eq. (42) becomes

$$\begin{aligned} \sigma_{el} = & \sigma_{el}^0 \frac{1 + \tilde{\varepsilon}_m (\kappa d)^{-1/2}}{[1 + \tilde{\varepsilon}_m (\kappa d)^{-1}]^2}, \\ \sigma_{el}^0 = & -\frac{\varepsilon_0 \varepsilon_2 (\Delta \phi_m)^2}{2d}, \end{aligned} \quad (44)$$

where we introduced the ratio  $\tilde{\varepsilon}_m \equiv \varepsilon_2 / \varepsilon$  between the membrane and surrounding medium dielectric constant (typically  $\tilde{\varepsilon}_m \approx 1/40$ , see Refs. [1] and [7]). We notice that when  $s = \tilde{\varepsilon}_m (\kappa d)^{-1} \ll 1$ , i.e., for an effectively small screening length compared to the membrane width, the tension approaches  $\sigma_{el}^0$ ; the dimensionless parameter  $s$  is commonly appearing in membrane electromechanical problems, see Refs. [1] and [7]. From Eq. (42) we notice that for the asymmetric case we similarly have  $\sigma_{el} \approx \sigma_{el}^0$  for  $s_\gamma = (\varepsilon_2 / \varepsilon_\gamma) (\kappa d)^{-1} \ll 1$ , where  $\gamma = 1, 3$ . Since  $\sigma_{el}^0$  only depend on the membrane dielectric constant, membrane width, and the applied potential,  $\sigma_{el}$  is for large salt concentration independent on the properties of the surrounding medium (i.e., independent on  $\kappa_1, \kappa_3, \varepsilon_1$ , and  $\varepsilon_3$ ). The origin of this result is discussed below.

The electrostatic contribution to the bending rigidity is



$$K_{\text{el}} = \varepsilon_0 \Delta \phi_m^2 \frac{b_0 + b_1 d + b_2 d^2 + b_3 d^3 + b_4 d^4}{(l_1 + l_3 + 2d/\varepsilon_2)^3} \quad (45)$$

with coefficients

$$b_0 = \frac{1}{8} [(l_1 \kappa_1^{-2} + l_3 \kappa_3^{-2})(l_1 + l_3) + 2l_1 l_3 (\kappa_1^{-1} + \kappa_3^{-1})^2],$$

$$b_1 = \frac{1}{4} \left( \frac{3}{\varepsilon_2} (l_1 \kappa_1^{-2} + l_3 \kappa_3^{-2}) + 8l_1 l_3 (\kappa_1^{-1} + \kappa_3^{-1}) \right),$$

$$b_2 = 2 \left( \frac{1}{\varepsilon_2} (l_1 \kappa_1^{-1} + l_3 \kappa_3^{-1}) + 2l_1 l_3 \right),$$

$$b_3 = \frac{8}{3} \frac{1}{\varepsilon_2} (l_1 + l_3),$$

$$b_4 = \frac{4}{3} \frac{1}{\varepsilon_2^2}. \quad (46)$$

We point out that  $K_{\text{el}} > 0$ , i.e., the applied potential tends to make the membrane more rigid towards bending. During a bending deformation the induced charge density on one side of the membrane gets compressed, whereas the charge density on the opposite side gets expanded. The free energy changes of compression and expansion has different signs, but are in general of different magnitude. It is only for the case that all Debye screening charges are collapsed onto the surfaces ( $\kappa \rightarrow \infty$ ) and zero membrane thickness  $d \rightarrow 0$  that the expansion and compression free energies are identical and  $K_{\text{el}} = 0$  [see Eq. (45)]. Thus, loosely speaking, the smaller the “effective” membrane thickness (the membrane thickness including the Debye screening layer thicknesses) the smaller is the bending rigidity. For the symmetric case ( $\kappa = \kappa_1 = \kappa_3$  and  $\varepsilon = \varepsilon_1 = \varepsilon_3$ ) we write Eq. (45) according to

$$K_{\text{el}} = K_{\text{el}}^0 [1 + \tilde{\varepsilon}_m (\kappa d)^{-1}]^{-3} [1 + 4\tilde{\varepsilon}_m (\kappa d)^{-1} + 3\tilde{\varepsilon}_m (1 + \tilde{\varepsilon}_m) (\kappa d)^{-2} + \tilde{\varepsilon}_m (9/8 + 3\tilde{\varepsilon}_m) (\kappa d)^{-3} + (9/8) \tilde{\varepsilon}_m^2 (\kappa d)^{-4}],$$

$$K_{\text{el}}^0 = \frac{1}{6} \varepsilon_0 \varepsilon_2 d (\Delta \phi_m)^2. \quad (47)$$

We note that in the limit of small relative membrane dielectric constant  $\tilde{\varepsilon}_m \rightarrow 0$  as well as for small screening length compared to the membrane thickness  $(\kappa d)^{-1} \rightarrow 0$ , we have  $K_{\text{el}} \rightarrow K_{\text{el}}^0$ . Notice that, in practice,  $\tilde{\varepsilon}_m$  is always small  $\approx 1/40$ , and therefore we have  $K_{\text{el}} \rightarrow K_{\text{el}}^0$  also for “not too small” values for  $(\kappa d)^{-1}$ . Similarly, we note from Eq. (45) that for the asymmetric case we have  $K_{\text{el}} \rightarrow K_{\text{el}}^0$  in the  $\varepsilon_2/\varepsilon_\gamma \rightarrow 0$  and in the  $(\kappa_\gamma d)^{-1} \rightarrow 0$  ( $\gamma = 1, 3$ ) limits. For the above considered limits the major part of the potential drop is across the membrane [since  $\varepsilon_2/\varepsilon_\gamma$  or  $(\kappa d)^{-1}$  is small], and hence the electric field is essentially zero everywhere except for the membrane region. Therefore, the membrane parameters play the dominant role in the expression for  $K_{\text{el}}$  and  $\sigma_{\text{el}}$  (notice that  $K_{\text{el}}^0$  and  $\sigma_{\text{el}}^0$  depend only on  $\varepsilon_0 \varepsilon_2$ ,  $d$ , and  $\Delta \phi_m$ ), provided that the interactions of the induced surface charges do not occur through the surrounding medium [again, certified if  $\varepsilon_2/\varepsilon_\gamma$  or

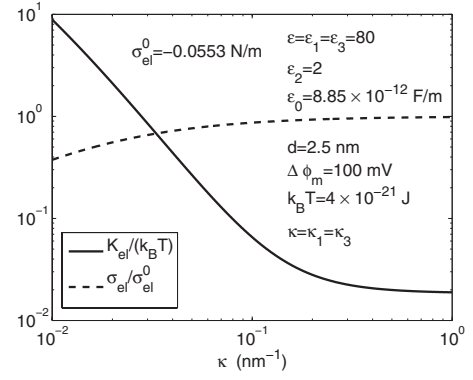


FIG. 3. The electrostatic contributions  $\sigma_{\text{el}}$  and  $K_{\text{el}}$  to the tension and the bending rigidity and as a function of Debye screening in the small screening length limit (symmetric case), using Eqs. (44) and (47). We express  $K_{\text{el}}$  in terms of the (room temperature) thermal energy  $k_B T$  and  $\sigma_{\text{el}}$  in terms of its infinite  $\kappa$  value  $\sigma_{\text{el}}^0$ . The parameters used are listed in the figure. Notice that increasing salt concentration, i.e., increased  $\kappa$ , leads to a decrease in the electrostatic contribution to the bending rigidity. In contrast, for increasing  $\kappa$  the magnitude of the electrostatic contribution to the tension increases.

( $\kappa d$ )<sup>-1</sup> is small]. Given that  $K_{\text{el}}$  and  $\sigma_{\text{el}}$  can only depend on  $\varepsilon_0 \varepsilon_2$ ,  $d$ , and  $\Delta \phi_m$  in the limits considered above one may use dimensional arguments to argue that the limiting results  $K_{\text{el}}^0$  and  $\sigma_{\text{el}}^0$  for the bending rigidity and tension must (up to a constant prefactor) take the forms given in Eqs. (44) and (47). Figure 3 illustrates the electrostatic contribution to the tension and membrane bending rigidity and its dependence on salt concentration (Debye screening) for the symmetric case for simplicity. We see that the absolute value of electrostatic contribution to the membrane tension increases with increasing salt concentration, i.e., for increasing  $\kappa$ . We attribute this to an increase of screening charges (in a layer of decreased thickness) next to the membrane; the increased amount of charges will result in larger electrostatic repulsion between ions in the screening clouds [see discussion following Eq. (43)]. In contrast to the effect on tension the electrostatic contribution to the bending rigidity decreases with increasing salt concentration (with  $K_{\text{el}}$  approaching  $K_{\text{el}}^0$  as  $\kappa \rightarrow \infty$ ). The reason behind this is that for bending properties the thickness of the Debye screening layers plays a role—a larger “effective” membrane thickness gives a higher bending rigidity [see discussion following Eq. (45), and the spontaneous curvature calculation in Appendix C]. If we choose the potential difference between the membrane sides  $\Delta \phi_m = 100$  mV,  $\varepsilon_2 = 2$ , and  $d = 2.5$  nm we find that  $K_{\text{el}}^0 = 0.018 k_B T$  (for room temperature,  $k_B T = 4 \times 10^{-21}$ ). From Fig. 3 we see that  $K_{\text{el}}/K_{\text{el}}^0$  can become quite large for small  $\kappa$  and, therefore, for sufficiently small salt concentration the bending rigidity  $K_{\text{el}}$  can exceed the thermal energy  $k_B T$ ; we therefore expect that the increase of the bending rigidity in the presence of an applied electrostatic potential predicted in this study can indeed be experimentally observed for sufficiently large  $\Delta \phi_m$  and small salt concentrations (note, however, the below restriction on salt concentration due to assumptions in the Debye-Hückel approximation).

Let us compare the results above for the symmetric case to the results obtained in Ref. [7]. We find that the result for

$\sigma_{el}$  given in Eq. (44) agrees with the finite bilayer thickness, nonconductive membrane tension (there denoted by  $\Sigma_{in} + \Sigma_{out}$ ) obtained in Ref. [7] (Note that in Ref. [7] the membrane thickness is denoted by  $d$ , whereas we denote by  $d$  the size of a lipid monolayer, so that in our case the membrane thickness is  $2d$ ). Also note that, due to different boundary conditions at the electrodes, the  $V$  in Ref. [7] should be equated with our  $\Delta\phi_m$ . Concerning the bending rigidity result, we note that no explicit expression for  $K_{el}$  was given in Ref. [7], only a numerical value for a specific set of parameter values. We choose the same parameter values ( $\Delta\phi_m = 50$  mV,  $d = 2.5$  nm,  $\tilde{\epsilon}_m = 1/40$ , and  $2d\kappa = 7.4$ ), but note that in order to get the expression for  $K_{el}$  one must also choose the actual value of  $\epsilon_2$  (not just the ratio  $\epsilon_2/\epsilon$ ), which was not specified in Ref. [7]. We choose the standard value  $\epsilon_2 = 2$  [1,9] and then find that  $K_{el} = 0.00467k_B T$ , which is a bit less than half the value found in Ref. [7]. Since no explicit expression for  $K_{el}$  was given in Ref. [7] it is difficult to comment on the nature of this discrepancy. Finally, using the approximate expression  $K_{el} \approx K_{el}^0$  for the parameters above we find that this approximation underestimates  $K_{el}$  by merely 1%.

Here, a few words on the validity of the Debye-Hückel approximation, used throughout this study, are in place. This approximation should work when the quantity  $I = \beta q^i [\Phi_\gamma(\vec{x}) - \phi_\gamma^0]$ , where  $\gamma = 1, 3$ , is very small, i.e.,  $I \ll 1$  (see Sec. II), but in practice the Debye-Hückel approximation works well whenever  $I < 1$ , see Ref. [19]. The maximum of  $I$  occurs at the membrane surfaces, see Eqs. (15), (16) and Fig. 2, and we find that for the  $\kappa_\gamma L \gg 1$  limit considered here we have  $I = \beta q^i \Delta\phi_\gamma / [2(l_1 + l_3 + d/\epsilon_2)]$ . Using  $d \approx 2.5$  nm,  $\epsilon_2 \approx 2$ , and  $\epsilon_\gamma \approx 80$ , the denominator in the expression for  $I$  above is dominated by the  $d/\epsilon_2$  term whenever  $\kappa_\gamma^{-1} < 50$  nm (in this limit also  $\Delta\phi \approx \Delta\phi_m$ ); for such ion concentrations we have the following criterion for the validity of the Debye-Hückel approximation

$$I = \frac{1}{2} \beta q^i \Delta\phi_m s_\gamma < 1 \quad (48)$$

again involving the parameter  $s_\gamma = (\epsilon_2/\epsilon_\gamma)(\kappa_\gamma d)^{-1}$ . For a large potential difference  $\Delta\phi_m = 100$  mV we find that  $I < 1$  when  $\kappa_\gamma^{-1} < 50$  nm (using  $q^i = 1.6 \times 10^{-19}$  C and assuming room temperature). This means that the Debye-Hückel approximation, which was made in Sec. II in the main text, works surprisingly well, in general; the reason for this is the small value of  $\epsilon_2/\epsilon_\gamma$  ( $\approx 1/40$ ) guaranteeing that the major part of the potential drop occurs across the membrane and that, therefore, the potential drop across the electrolytes, for which we applied the Debye-Hückel approximation, is modest, see Fig. 2. We point out that the dielectric limit  $c_{bulk,\gamma}^i \rightarrow 0$  does not rely on a Debye-Hückel approximation and results to be given below are therefore valid for any value of the applied potential. We have shown above that our results for the small screening length limit (with the above explicit restriction) and in the dielectric limit are usually valid. We note, however, that there is in general an intermediate salt regime where the Debye-Hückel approximation breaks down (for sufficiently large applied potentials). We leave the investiga-

tion of this intermediate regime for future studies.

We finally point out that there are alternative ways of computing the membrane mechanical parameters. For instance, one can calculate the tension by finding the integral of the deviation of the pressure profile from the value of the pressure far from the membrane. This approach is demonstrated in Appendix C, giving the same result as Eq. (42) for the tension. In that appendix the same type of approach is also used in order to obtain the electrostatic contribution to the membrane spontaneous curvature, see Eq. (C7).

(2) In the dielectric limit  $\kappa_1, \kappa_3 \rightarrow 0$ , one can again perform a power series expansion in  $q$  using Eqs. (38) and (39) and assuming  $qd \ll 1$ . In addition, there are two limits of interest depending on whether the wavelength perturbation is smaller or larger than  $L$ .

For (i)  $qL \gg 1$  we find that

$$\bar{f}^{(1)} = -[aq + \sigma_{el}q^2 + bq^3 + K_{el}q^4 + O(q^5)]\bar{h}, \quad (49)$$

where

$$a = -\epsilon_0 \left( \frac{\Delta\phi}{L} \right)^2 \frac{(\epsilon_1^{-1} - \epsilon_3^{-1})^2}{(\epsilon_1^{-1} + \epsilon_3^{-1})^3} \quad (50)$$

and

$$\sigma_{el} = -8d\epsilon_0\epsilon_2 \left( \frac{\Delta\phi}{L} \right)^2 \frac{\epsilon_1^{-1}\epsilon_3^{-1}}{(\epsilon_1^{-1} + \epsilon_3^{-1})^4} (\epsilon_1^{-1} - \epsilon_2^{-1})(\epsilon_3^{-1} - \epsilon_2^{-1}), \quad (51)$$

and the higher order terms in  $q$  are more complicated functions of the dielectric constants and  $d$ . The term linear in  $q$  is negative and is expected to cause an instability for long wavelengths [20]. We notice that the prefactor  $a$  [see Eq. (50)] is proportional to the membrane polarization charge density (for a flat membrane) squared  $a \propto (\rho^s)^2$ , see Eq. (B4). The linear, nonanalytic,  $q$  term may be interpreted as follows: for the asymmetric dielectric case the external potential induces an effective net membrane polarization charge density  $\rho^s$ . The membrane charges interact via the unscreened (there are no ions in the present limit) Coulomb interaction, giving rise to the  $(\rho^s)^2$  proportionality for  $a$ ; the nonanalyticity of the free energy arises due to the long-range character of the Coulomb interaction (which decays as  $1/r$ , where  $r$  is the distance between charges). We point out that the linear  $q$  term does not depend on the membrane parameters  $d$  and  $\epsilon_2$  which means that this instability should exist for any interface between coexisting fluids (fluid interface instabilities of a rather similar nature has been investigated previously, see, for instance, Ref. [6]). For the symmetric case  $\epsilon_1 = \epsilon_3$  we see that  $a = 0$ , but the third order term above is still present  $b \neq 0$ , in general (see discussion below).

For the case (ii)  $qL \ll 1$ , i.e., the wavelength perturbation is longer than the distance between the electrodes, the first order force takes the form  $\bar{f}^{(1)} = -[c + \sigma_{el}q^2 + K_{el}q^4 + O(q^6)]\bar{h}$ . In this limit the interactions between the membrane polarization charges become short range due to effectively small (compared to the wavelength of the perturbation) distance of the membrane to the electrodes. In this limit we thus do not have any odd  $q$  terms the effect of the applied potential is

simply to give an electrostatic contribution to the tension and bending rigidity. The explicit expressions become somewhat complicated, but can be produced straightforwardly by a small  $q$  expansion using a symbolic mathematical software such as MATHEMATICA or MAPLE together with the expressions for  $\bar{f}_{1-2}$  and  $\bar{f}_{2-3}$  given in Eqs. (38) and (39).

(3) For the symmetric case ( $\varepsilon=\varepsilon_1=\varepsilon_3$ ,  $\kappa=\kappa_1=\kappa_3$ ) the lowest order term in the  $q$  expansion is the tension term ( $q^2$  term), both in the small screening length limit and for the dielectric limit. For both these limits we have that the electrostatic contribution to the tension  $\sigma_{el}$  is negative. Thus when  $|\sigma_{el}|$  becomes sufficiently large, i.e., large applied potential, a membrane stretching instability can occur. We also find that in the symmetric dielectric limit there is a  $q^3$  term present (for  $qL \gg 1$ ), where explicitly we find [see Eq. (49)]

$$b = 2\varepsilon_0\varepsilon\varepsilon_2^2 \left( \frac{\Delta\phi}{2L} \right)^2 (\varepsilon^{-1} - \varepsilon_2^{-1})^2 d^2. \quad (52)$$

We notice that  $b \propto P_z^2$ , where  $P_z$  is the membrane polarization per unit area, see Eq. (B8). For the symmetric dielectric case the effect of the applied potential is to polarize the membrane and the  $q^3$  term is expected to originate from induced, unscreened, dipole-dipole interactions (which decays as  $1/r^3$ , where  $r$  is the distance between the dipoles [15]) within the membrane.

## VI. SUMMARY AND DISCUSSION

We have in this paper derived expressions for the electrostatic contributions to biomembrane mechanical parameters (such as tension and bending rigidity) in the presence of an static applied potential across a membrane. The membrane was assumed incompressible, nonconductive (membrane region described by Laplace equation), and surrounded by electrolyte solutions (described by the Debye-Hückel equation). By solving the equations for the electrostatic potential and using the stress tensor the forces acting on the membrane were obtained, which in turn were used to obtain the free energy and the electrostatic contribution to the membrane mechanical parameters as a function of the applied potential, the salt concentrations (entering through the Debye screening lengths) and the dielectric constants of the membrane and the solvents. Results of particular interest, that are found in this study, include for (1) the small screening length limit, where the Debye screening length is smaller than the distance between the electrodes, the screening certifies that all electrostatic interactions are short range, leading to a free energy expansion of the form  $\sim \sigma_{el}q^2 + K_{el}q^4 + O(q^6)$  (where  $q$  is the wave vectors), the main effects of the applied potential are to decrease the membrane tension and increase the bending rigidity; explicit expression are given in Eqs. (42) and (45). Our expression for the tension for the symmetric case reproduces the result in Ref. [7]. In Ref. [9] it was also found that an applied electric field gives a negative contribution to the tension. However, in that study the medium surrounding the membrane was characterized by conductivities rather than Debye screening lengths, and it is therefore difficult to directly compare our results to theirs. For sufficiently large

applied potentials the magnitude of the electrostatic contribution to the tension will exceed the maximum tension the membrane can sustain, leading to a membrane stretching instability. Possibly, this instability can result in the formation of pores and flow of ions through the membrane (in fact, the membrane tension is one of the key parameters in the modeling of membrane electroporation dynamics [21]). For (2) the dielectric limit, i.e., no salt (for small wave vectors  $q$  compared to the distance between the electrodes), when the dielectric constants on the two sides are different, the applied potential induces an effective (unscreened) membrane charge density, whose long-range interaction causes a membrane undulation instability if the dielectric constants of the two bulk fluids are different; this effect is characterized by a negative term linear in  $q$  in the free energy expansion, see Eqs (49) and (50), i.e., this term is of lower order in  $q$  than the tension term. Previous similar results include the following: In Ref. [6] the interface between two immiscible fluids of different dielectric constants was found to be unstable in the presence of a perpendicular electric field. The case of stiff (charged) DNA with bound, but mobile, counter ions was investigated in Ref. [3] and a shape instability found (supposedly leading to a DNA condensation). If the two dielectrics on each side of the membrane are identical, we found that then the applied electric field will give a negative contribution to the tension. Hence, if the applied potential is sufficiently large a membrane instability occurs also for the (dielectric) symmetric case.

We quantified the validity of the Debye-Hückel approximation (used throughout this study) and showed that our results are in general valid in the small screening length limit as well as in the dielectric limit. However, for “small,” but nonzero, salt concentration and large applied potential the Debye-Hückel approximation is no longer valid and one needs to consider the full Poisson-Boltzmann equation. It remains a future challenge to solve the full Poisson-Boltzmann problem in order to find expressions for the free energy for arbitrary salt concentration and, in particular, to investigate in more detail the nature of the onset of the predicted membrane instability (via the negative term linear in  $q$  in the free energy) as salt concentration is lowered.

Possible applications of the result for the small screening length limit above would be to lipid membranes where a potential difference across the membrane is enforced by ion pumps incorporated in the membrane. Changes in membrane rigidity might then be observed in micropipette or video microscopy experiments, if the screening length and the membrane potential are large, see Fig. 3. Another possible experiment would be to observe the structural change of domains in a multicomponent membrane using fluorescence correlation spectroscopy (FCS) as the membrane potential in a patch clamp experiment is altered; one might be able to observe a change from a phase with caps to one with stripes or buds as the effective bending rigidity is changed by the applied potential [22].

For the cases discussed above where a membrane instability occurs, the system is expected to be driven from the quasiflat shape into a new equilibrium configuration. Our perturbation analysis cannot, in general, say anything about this new configuration. However, for the small screening

length limit we above speculated that the negative electrostatic contribution to the tension (for large applied potentials) could lead to electroporation and a corresponding flux of ions through the membrane. It may also be speculated (similar to the studies in Refs. [2] and [9]) that the electrostatically induced new equilibrium configuration under certain conditions could be a spherical membrane (a vesicle); it is known that vesicles can be created in laboratories in a process known as electroformation [5] under the application of electric fields. We hope that the present theory will stimulate further work directed towards the controlled estimation of vesicle sizes as a function of electrostatic parameters, e.g., potential differences and electrolyte concentration.

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### APPENDIX A: DERIVATION OF BULK EQUATIONS

In this appendix we show how the electrostatic equations and the stress tensor used in the main text can be derived as Euler-Lagrange equations from a free energy. Suppressing the region index  $\gamma$  for convenience we can write the appropriate free energy as

$$G = \int d^3x \left\{ -\frac{1}{2} \epsilon_0 \epsilon |\vec{\nabla} \Phi(\vec{x})|^2 + \rho \Phi - p + \sum_i c^i \left[ k_B T \left( \ln \frac{c^i}{c_{\text{total}}} - 1 \right) + \mu^i \right] \right\}. \quad (\text{A1})$$

Here  $p = p(\vec{x})$  is the local pressure,  $c^i = c^i(\vec{x})$  are the local concentrations of the ions,  $c_{\text{total}} = c_{\text{total}}(\vec{x})$  is the total concentration of molecules of all kinds (including water) and  $\mu^i$  are (constant) chemical potentials for the ions. The logarithmic term corresponds to the entropy of mixing. Some of the Euler-Lagrange equations of this free energy can be found by demanding stationarity when varying the ion concentrations

$$0 = \left. \frac{\delta G}{\delta c^i} \right|_{c_{\text{total}}} = \Phi q^i + k_B T \ln \frac{c^i}{c_{\text{total}}} + \mu^i. \quad (\text{A2})$$

Solving for the ion concentrations we find

$$c^i = c_{\text{total}} \exp\left(-\frac{q^i \Phi + \mu^i}{k_B T}\right). \quad (\text{A3})$$

Inspection of the expression for the charge density  $\rho = \sum_i q^i c^i$  with  $c^i$  given by Eq. (A3) reveals that there is a unique value of  $\Phi$  for which  $\rho$  vanishes. We define  $\phi^0$  to be this ‘‘equilibrium value,’’ i.e.,

$$\rho|_{\Phi=\phi^0} = 0. \quad (\text{A4})$$

The ion concentrations at ‘‘equilibrium’’ is labeled by

$$c_{\text{bulk}}^i = c^i|_{\Phi=\phi^0}. \quad (\text{A5})$$

The Euler-Lagrange equation for  $\Phi$  is

$$0 = \frac{\delta G}{\delta \Phi} = \epsilon_0 \epsilon \vec{\nabla}^2 \Phi + \rho, \quad (\text{A6})$$

which is simply the Poisson equation. Insertion of Eqs. (A3) and (A5) gives the Poisson-Boltzmann equation

$$\epsilon_0 \epsilon \vec{\nabla}^2 \Phi + \sum_i q^i c_{\text{bulk}}^i \exp\left(-\frac{q^i(\Phi - \phi^0)}{k_B T}\right) = 0, \quad (\text{A7})$$

which when linearized gives the Debye-Hückel equation (9) in the main text.

The force balance in the bulk regions can be found by demanding that  $G$  should be stationary with respect to moving all fluid elements, particles and fields by an infinitesimal position dependent distance  $\delta \vec{x} = \delta \vec{x}(\vec{x})$ . Denoting fields after the move by a prime one has the new fields

$$\Phi'(\vec{x}') = \Phi(x), \quad (\text{A8})$$

$$p'(\vec{x}') = p(x), \quad (\text{A9})$$

$$c^{i'}(\vec{x}') = (1 - \vec{\nabla} \cdot \delta \vec{x}) c^i(\vec{x}), \quad (\text{A10})$$

where  $\vec{x}' = \vec{x} + \delta \vec{x}$ . The free energy after the move is

$$G' = \int d^3x' \left\{ -\frac{1}{2} \epsilon_0 \epsilon |\vec{\nabla}' \Phi'(\vec{x}')|^2 + \rho' \Phi' - p' + \sum_i c^{i'} \left[ k_B T \left( \ln \frac{c^{i'}}{c'_{\text{total}}} - 1 \right) + \mu^i \right] \right\}, \quad (\text{A11})$$

and using

$$d^3x' = (1 + \vec{\nabla} \cdot \delta \vec{x}) d^3x, \quad (\text{A12})$$

$$\frac{\partial}{\partial x_i'} = \sum_j \left( \delta_{ij} - \frac{\partial \delta x_j}{\partial x_i} \right) \frac{\partial}{\partial x_j}, \quad (\text{A13})$$

one finds that the change in free energy is

$$\delta G = G' - G = \int d^3x \sum_{ij} T_{ij} \frac{\partial \delta x_i}{\partial x_j}, \quad (\text{A14})$$

where  $T_{ij}$  is the stress tensor for the system

$$T_{ij} = \epsilon_0 \epsilon \left( \frac{\partial \Phi}{\partial x_i} \frac{\partial \Phi}{\partial x_j} - \frac{1}{2} \delta_{ij} \sum_k \frac{\partial \Phi}{\partial x_k} \frac{\partial \Phi}{\partial x_k} \right) - p \delta_{ij}. \quad (\text{A15})$$

Note that the first two terms on the right hand side of Eq. (A15) are simply the classic Maxwell stress tensor. Performing a partial integration in Eq. (A14) one can see that the condition of stationarity of  $G$  implies the conservation of stress

$$\sum_i \frac{\partial T_{ij}}{\partial x_i} = 0. \quad (\text{A16})$$

Combing this with Eq. (A6) one arrives at the more physically revealing form

$$-\rho \vec{\nabla} \Phi - \vec{\nabla} p = 0, \quad (\text{A17})$$

i.e., electric forces should be balanced by changes in hydrostatic pressure. Finally, since we know the behavior of the charge density  $\rho$  as a function of  $\Phi$  from Eq. (A3) we can integrate Eq. (A17) to find the pressure as a function of  $\Phi$

$$p = p^0 + k_B T \sum_i c_{\text{bulk}}^i \left[ \exp\left(-\frac{q^i(\Phi - \phi^0)}{k_B T}\right) - 1 \right]. \quad (\text{A18})$$

The quadratic version of Eq. (A15) with Eq. (A18) inserted is Eq. (36) of the main text. Note that the pressure can also be written  $p = p^0 + k_B T \sum_i (c^i - c_{\text{bulk}}^i)$ , i.e., there is an osmotic contribution to the pressure when ions are ‘‘confined’’ by the electric potential (see, for instance, Ref. [23]).

## APPENDIX B: TOTAL NET FORCE ON A FLAT MEMBRANE

In this appendix we investigate the total force acting on a flat membrane in some detail. From Eqs. (38) and (39), and Eq. (17) we obtain the following explicit expression for the total force (per unit area) acting on a flat membrane:

$$f^{(0)} = f_{1-2}^{(0)} + f_{2-3}^{(0)} = p_1^0 - p_3^0 - \frac{\varepsilon_0}{2} (\Delta\phi)^2 \left( \frac{\varepsilon_1^{-1} e^{-\kappa_1 L}}{(1 + e^{-\kappa_1 L})^2} - \frac{\varepsilon_3^{-1} e^{-\kappa_3 L}}{(1 + e^{-\kappa_3 L})^2} \right) \Gamma^2 \quad (\text{B1})$$

and  $\Gamma = 1/[g(\kappa_1)l_1 + g(\kappa_3)l_3 + d/\varepsilon_2]$ , and  $l_1 = (\varepsilon_1 \kappa_1)^{-1}$  and  $l_3 = (\varepsilon_3 \kappa_3)^{-1}$  as before [the function  $g(q)$  is defined in Eq. (19)]. If the fluids surrounding the membrane are incompressible, then the pressures  $p_\gamma^0$  adjust such that the above force vanishes. In fact, in this study we assume that both the membrane and the surrounding fluids are incompressible. Let us, however, in order to gain some physical insights, investigate different limits of the nonpressure part of the above force (i.e., we take  $p_1^0 = p_3^0$ ).

(1) In the ‘‘small’’ screening length limit  $\kappa_1 L, \kappa_3 L \gg 1$ , the nonpressure part of Eq. (B1) becomes

$$f^{(0)} \approx 0. \quad (\text{B2})$$

The force is zero whenever the screening length is small compared to the distance between the electrodes. Thus it is not possible to get a net force on the membrane solely by having different concentration of ions (free charges) on the two sides. That there is no net force on the membrane can be related to the fact that there is no net free charge around the membrane, which can be understood from Gauss’ law  $\int \vec{D} \cdot \hat{n} dS = Q_{\text{free}}$ , where  $\vec{D}$  is the displacement field and  $Q_{\text{free}}$  is the enclosed free charge: since far from the membrane on both sides the electric field is zero [in the here considered limit, see Eqs. (15) and (16), and Fig. 2] so is the displacement field, and applying Gauss law (for a large ‘‘pillbox’’ enclosing the membrane and the Debye screening layers) one finds that  $Q_{\text{free}} = 0$ , as well as no net charge due to changes in polarization of the dielectric media. The effective net charge for the membrane and the Debye screening layers is hence

zero and there will be no net force due to these charges.

(2) In the dielectric limit  $\kappa_1, \kappa_3 \rightarrow 0$ , we find

$$f^{(0)} = -2\varepsilon_0 \left( \frac{\Delta\phi}{2L} \right)^2 \frac{\varepsilon_1^{-1} - \varepsilon_3^{-1}}{[\varepsilon_1^{-1} + \varepsilon_3^{-1} + 2(d/L)\varepsilon_2^{-1}]^2} \quad (\text{B3})$$

for the nonpressure part of the force. When there are no free charges, as considered here, the Gauss law argument above does not apply. One then needs to also take into account the bound charges, which create a polarization surface charge density  $\rho_{1-2}^s = -(\vec{P}_2 - \vec{P}_1) \cdot \hat{z}$  (see Ref. [15], Chap. 4) on the region 1-2 interface. Similarly, for the region 2-3 interface we have a polarization surface charge density  $\rho_{2-3}^s = (\vec{P}_2 - \vec{P}_3) \cdot \hat{z}$ . From the fact that  $\vec{P} = \vec{D} - \varepsilon_0 \vec{E}$  and that the normal component of the  $\vec{D}$  field is continuous we find that  $\rho_{1-2}^s = \varepsilon_0(\vec{E}_2 - \vec{E}_1) \cdot \hat{z}$  and  $\rho_{2-3}^s = -\varepsilon_0(\vec{E}_2 - \vec{E}_3) \cdot \hat{z}$ , i.e., the polarization surface charge density is determined by the jump in the electric field at the interface. Using the explicit expressions for the potential  $\Phi(z)$  given in Sec. III and that  $z$  component of the electric field is  $E_z = -\partial\Phi/\partial z$  we find  $\rho_{1-2}^s \approx -\varepsilon_0 E_{z,\text{appl}}(\varepsilon_1^{-1} - \varepsilon_2^{-1})/(\varepsilon_1^{-1} + \varepsilon_3^{-1})$  and  $\rho_{2-3}^s \approx \varepsilon_0 E_{z,\text{appl}}(\varepsilon_3^{-1} - \varepsilon_2^{-1})/(\varepsilon_1^{-1} + \varepsilon_3^{-1})$ , with the applied field being  $E_{z,\text{appl}} = \Delta\phi/(2L)$ , where we assumed a small membrane thickness  $d/L \ll 1$ . The effective membrane charge density  $\rho^s = \rho_{1-2}^s + \rho_{2-3}^s$  then becomes proportional to the dielectric asymmetry between regions 1 and 3, explicitly

$$\rho^s \approx \varepsilon_0 E_{z,\text{appl}} \frac{\varepsilon_3^{-1} - \varepsilon_1^{-1}}{\varepsilon_1^{-1} + \varepsilon_3^{-1}}, \quad (\text{B4})$$

where the proportionality  $\rho^s \propto \varepsilon_3^{-1} - \varepsilon_1^{-1}$  follows directly from the fact that the jump in the electric field is proportional to  $\varepsilon_2/\varepsilon_1$  ( $\varepsilon_2/\varepsilon_3$ ) for the region 1-2 (region 2-3) interface (see discussion at the end of Sec. III and Fig. 2). Thus, whenever  $\varepsilon_1 \neq \varepsilon_3$  we have that the membrane has an effective net charge of induced bound charges, which when put into the applied electric field  $E_{z,\text{appl}}$  gives rise to the force above; note that the force is proportional to  $\rho^s$  as it should (for  $d/L \ll 1$ ). We also note that Eq. (B3) for  $d \rightarrow 0$  can be written

$$f^{(0)} = \frac{1}{2} \left( \frac{\varepsilon_1}{\varepsilon_3} - 1 \right) \varepsilon_0 \varepsilon_1 (\hat{z} \cdot \vec{E}_1)^2, \quad (\text{B5})$$

which can be compared with, for instance, the formula in Ref. [18] for the pressure decrease in a fluid at the fluid-air interface due to a normal electric field

$$\hat{z} \cdot \vec{E}_1 = \frac{\Delta\phi}{2L} \frac{2\varepsilon_1^{-1}}{\varepsilon_1^{-1} - \varepsilon_3^{-1}} \quad (\text{B6})$$

on the fluid side.

(3) For the symmetric case ( $\varepsilon_1 = \varepsilon_3 = \varepsilon$ ,  $\kappa_1 = \kappa_3$ , and  $p_1^0 = p_3^0$ ) the nonpressure part of Eq. (B1) is zero,

$$f^{(0)} = 0, \quad (\text{B7})$$

since for the symmetric case there is no net surface charge, and hence no net force on the flat membrane. We point out, however, that the membrane gets polarized. In particular, the polarization per unit area in the  $z$  direction (using the results above) is

$$P_z = (-d)\rho_{1-2}^s + d\rho_{2-3}^s = \varepsilon_0 \varepsilon E_{z,\text{appl}}(\varepsilon^{-1} - \varepsilon_2^{-1})d \quad (\text{B8})$$

in the dielectric limit.

### APPENDIX C: ALTERNATIVE APPROACH TO TENSION AND SPONTANEOUS CURVATURE

In this appendix we will demonstrate an alternative approach to deriving the tension in the membrane, which can also be used to obtain the spontaneous curvature induced by the electric field. This approach consists of calculating moments of the deviation of the pressure profile from the value of the pressure far from the membrane. We will therefore in this appendix only study the small screening length limit, where effectively  $L \rightarrow \infty$ , such that the pressure approaches a well defined pressure away from the membrane.

The tension is obtained as the integral of the lateral pressure profile deviation or, equivalently, the excess lateral stress, of the planar membrane [24]. Choosing the diagonal  $x$  component of the stress tensor to represent the lateral stress one has the precise formula [24]

$$\sigma = \int_{-\infty}^{\infty} dz [T_{xx}^{(0)} - (-p^0)], \quad (\text{C1})$$

where we have used that the pressure on the two sides of the membrane should be identical  $p^0 = p_1^0 = p_3^0$ , since the zeroth order force in the small screening length limit (B2) vanishes. In terms of the zeroth order solution given in Eqs. (14)–(16), we obtain

$$\sigma = -\frac{\varepsilon_0}{2} \varepsilon_1 \kappa_1 A_1^2 - \frac{\varepsilon_0}{2} \varepsilon_3 \kappa_3 A_3^2 - \varepsilon_0 \varepsilon_2 d A_2^2 - 2d(p_2^0 - p^0). \quad (\text{C2})$$

To obtain the final result we need to find  $p_2^0$ . To do this we note that in a flat equilibrium configuration the force on the two region boundaries should vanish,  $f_{1-2}^{(0)} = 0$  and  $f_{2-3}^{(0)} = 0$  [or, equivalently,  $T_{zz}^{(0)}(z) = -p^0$  for all  $z$ ]. From either Eq. (38) or Eq. (39) one finds

$$p_2^0 = p^0 + \frac{1}{2} \varepsilon_0 \varepsilon_2 A_2^2. \quad (\text{C3})$$

This gives

$$\sigma = -\frac{\varepsilon_0}{2} \varepsilon_1 \kappa_1 A_1^2 - \frac{\varepsilon_0}{2} \varepsilon_3 \kappa_3 A_3^2 - 2\varepsilon_0 \varepsilon_2 d A_2^2. \quad (\text{C4})$$

This expression is identical to the tension given by Eq. (42) in the main text.

An advantage of the approach of integrating the stress profile is that we can obtain the change in spontaneous curvature  $C_0$  induced by the electric potential. If we include a spontaneous curvature in the Helfrich free energy  $G$  given at the beginning of Sec. V B, writing it as

$$G = \int dA \left[ \frac{1}{2} K (2H)^2 - K C_0 2H + \sigma \right] \quad (\text{C5})$$

and, as before, calculate the force  $f_{rs} = -\delta G / \delta h$ , then the spontaneous curvature will drop out at linear order in  $h$  and we would end up with our previous expression for the force where  $C_0$  is not present; thus it is not possible to obtain the spontaneous curvature using the approach of the main text. However, just as for the tension, the spontaneous curvature can be obtained from the lateral stress profile, namely, as the negative first moment of the lateral stress profile, sometimes also called the bending moment. The formula is [24]

$$K C_0 = \int_{-\infty}^{\infty} dz z [T_{xx}^{(0)} - (-p^0)], \quad (\text{C6})$$

and insertion of the zeroth order solution gives

$$K C_0 = \frac{\varepsilon_0 \varepsilon_1}{4} A_1^2 (1 - 2\kappa_1 d) - \frac{\varepsilon_0 \varepsilon_3}{4} A_3^2 (1 - 2\kappa_3 d)$$

or, explicitly,

$$K C_0 = \frac{\varepsilon_0}{4} \left( \frac{\Delta \phi}{2} \right)^2 [\varepsilon_1 l_1^2 (1 - 2\kappa_1 d) - \varepsilon_3 l_3^2 (1 - 2\kappa_3 d)] \Gamma^2, \quad (\text{C7})$$

where  $\Gamma = 1/[l_1 + l_3 + d/\varepsilon_2]$ ,  $l_1 = (\varepsilon_1 \kappa_1)^{-1}$ , and  $l_3 = (\varepsilon_3 \kappa_3)^{-1}$ . Note that  $C_0$  vanishes in the symmetric case where  $\kappa_1 = \kappa_3$  and  $\varepsilon_1 = \varepsilon_3$  as it should.

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