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Electromechanics of a membrane with spatially distributed fixed charges: Flexoelectricity and elastic parameters

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We investigate the electrostatic contribution to the lipid membrane mechanical parameters: tension, bending rigidity, spontaneous curvature, and flexocoefficient, using an approach where stress in the membrane is explicitly balanced. Our model includes an applied electrostatic potential as well as a charge distribution in the membrane. We apply our theory to membranes having surface charges and electric dipoles at the surface.

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I. INTRODUCTION

In nature various molecules have different charge distributions. For example, the main constituent of the membrane, the lipids, can carry an effective charge, and even if they are not charged the lipid head groups often carry a net dipole moment [1]. In cells and artificial vesicles various proteins can be included which can also bear charges or dipole moments. The membrane can then have a very complex charge distribution. These charge distributions will interact among themselves and with the charges in the surrounding bulk fluids possibly creating an osmotic pressure. Cells in particular often bear a negative charge on the cytoplasmic side of the membrane as well as maintaining a potential difference between the two sides of the membrane [2,3].

A number of papers have treated various electrostatic properties of the membrane including bending moduli [4–10], free-energy contributions [7,11–14], interactions of the membrane with macroions [15], and possible domain formation in charged lipid membranes [16]. In this rich literature, however, the electrostatic contribution to the membrane elastic parameters is usually calculated numerically and the few works that do give analytical expressions do so for a specific symmetrical charge distribution and/or an electrically decoupled bilayer. The aim of this paper is hence to perform an analytical calculation of the electrostatic contribution to the tension, bending rigidity, and spontaneous curvature for a more general charge distribution and including the possibility of a membrane potential. Furthermore, we explicitly take into consideration the local balancing of mechanical force in the membrane. In doing so we expand on the work of [5], where this was done globally. From the expression of the spontaneous curvature we will deduce an expression for the membrane flexocoefficient.

We are interested in how the electrostatic interactions renormalize the membrane mechanical parameters. In order to describe the mechanical properties of the membrane we will use the well-known Helfrich effective Hamiltonian [17]

$$\mathcal{H} = \int dA \left(\frac{\kappa_{\mathrm{b}}}{2} (2H - C_0)^2 + \kappa_{\mathrm{G}} K + \sigma \right), \tag{1}$$

where H is the local mean curvature, K is the local Gaussian curvature, and the integral is over the membrane area. κ_{b} is the bending rigidity. It measures the energy cost of bending the membrane around its preferred curvature C_0 also called spontaneous curvature. Lastly, σ is the tension of the membrane, which can also be seen as minus the lateral pressure in the membrane. We will not be concerned with the electrostatic contribution to the Gaussian bending constant, κ_{G}, since we assume that the membrane does not change its topology so that the integral over the membrane area of the local Gaussian curvature does not change (Gauss-Bonnet theorem).

Our approach explicitly takes into account the electrical coupling between the two sides of the membrane by explicitly solving Poisson's equation in the membrane. We also include the possibility of having a charge distribution in the membrane as this could give a significant contribution to the stress and force in the membrane due to the low dielectric permittivity of the membrane region. We are interested in the membrane equilibrium properties and as such we have to make sure that there is no excess force in the system due to the charge distribution we introduced; we will therefore assume that the normal electrostatic stress in the whole system is balanced by a local pressure in the membrane and the surrounding bulk fluids [18]. Note that the membrane could very well change its thickness in response to a change of normal stress but we will not consider this possibility here. The carbon tails of the lipids actually account for most of the dielectric permittivity inside the membrane; it is on the order of $2\varepsilon_0$. We will therefore model the membrane as a dielectric slab of permittivity $\epsilon_{\mathrm{m}} \approx 2\varepsilon_0$ surrounded by two dielectrics media with the permittivity of water $\epsilon \approx 80\varepsilon_0$. In the region corresponding to the water we will include free ions and we will assume them to be distributed according to the Poisson-Boltzmann theory such that the chemical potential change due to the electrostatic potential is exactly compensated by the change due to the gradient of the concentration of the charged species (taken as an ideal solution). In particular, we will take the linearized form of the Poisson-Boltzmann equation, the Debye-Hückel equation.

In Sec. II we set up and solve the model we sketched in this Introduction and we then calculate the equilibrium stress for a flat membrane as well as the restoring force on a slightly bent membrane. In Sec. III we give the expressions for the electrostatic contributions to the tension, spontaneous curvature, and bending rigidity in terms of integrals of the charge distribution in the membrane. We compare our results to the literature in Sec. IV, where we also give order of magnitude estimates. We finally conclude this work in Sec. V.

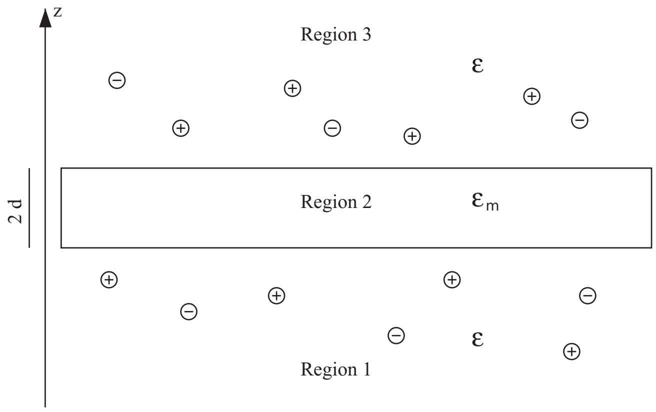

FIG. 1. Theoretical model: An infinite flat membrane (region 2) with a fixed charge distribution and a dielectric permittivity $\epsilon_{\rm m}$ is embedded between two symmetrical bulk fluids of permittivity ϵ (regions 1 and 3) containing free Boltzmann distributed charges (see text).

II. THEORY

We will first set up the equations for an infinite planar membrane with an internal density of charge which is uniform in the lateral direction but unspecified in the transverse direction. We will present the potential in all space for this setup. We will then calculate the equilibrium stress through the whole system, including the interior of the membrane. We will then proceed to calculate the restoring force for a slightly deformed membrane.

A. Electrostatic potential of a flat membrane

The situation we consider is summarized in Fig. 1. We model the membrane as a dielectric slab of finite thickness $2d$ and of dielectric permittivity $\epsilon_{\rm m}$. The membrane is normal to the z axis of a Cartesian coordinate system (x,y,z) with its center located at $z=0$. The membrane contains a charge distribution coming from its different constituents, e.g., the lipid polar head groups or some charged proteins. The charge distribution in the interior of the membrane, $\rho_{\rm m}(z)$, is considered fixed and uniform on the lateral directions x and y as if the charge distribution had been averaged in these directions. The membrane is embedded in a fluid of dielectric permittivity ϵ, e.g., water, which contains ions. The distribution of the ions outside the membrane depends on the electric field created by the charge inside the membrane as well as a possible applied potential difference, $V_{\rm m}$, between the two sides of the membrane. We label the three regions of the system as region 1 ($z<-d$) and region 3 ($z>d$) for the bulk fluid regions and region 2 ($-d<z<d$) for the membrane region.

The bulk fluid regions contain free Boltzmann distributed ions. The charge distributions in the bulk fluids read [19]

$$\rho_\gamma(z)=\sum_i q^i c^i \exp\big(-\beta q^i\big[\phi_\gamma(z)-\phi_\gamma^0\big]\big), \tag{2}$$

where the $\gamma=1$ or 3 indicate the region considered, q^i and c^i are the charge and overall concentration of ionic species i in the solution, the c^i are taken to be identical in both bulk fluid regions, $\phi_\gamma(z)$ is the potential in the region γ, ϕ_γ^0 is the potential at infinity in the given region, and $\beta=1/(k_BT)$, with k_B the Boltzmann constant and T the temperature. The equation that we have to solve in the bulk fluid regions is Poisson's equation

$$\epsilon\Delta\phi_\gamma=-\rho_\gamma, \tag{3}$$

where Δ is the Laplacian. If we use Eq. (2) directly in Eq. (3) we get the Poisson-Boltzmann equation [20–22]. However, we will assume the linear limit of this equation where the term in the exponential of Eq. (2) is small. The resulting equation is called the Debye-Hückel equation [23,24]. It reads

$$\frac{\partial^2\phi_\gamma}{\partial z^2}=\kappa_{\rm D}^2\big(\phi_\gamma-\phi_\gamma^0\big),\quad \gamma=1,3, \tag{4}$$

where $\kappa_{\rm D}$ is the inverse Debye screening length for the two bulk fluids and is defined as

$$\kappa_{\rm D}^2=\frac{\beta}{\epsilon}\sum_i[q^i]^2c^i. \tag{5}$$

In the membrane we have the charge distribution $\rho_{\rm m}(z)$ that depends on the z coordinate but is laterally uniform. The equation satisfied by the potential ϕ_2 in the membrane is then

$$\epsilon_{\rm m}\frac{\partial^2\phi_2}{\partial z^2}=-\rho_{\rm m}(z), \tag{6}$$

which is just Poisson's equation. The equation for the potential Eqs. (4) and (6) must be supplemented by boundary conditions [25,26]: the continuity of the potential at the dielectric interfaces

$$\phi_1(-d)=\phi_2(-d), \tag{7a}$$

$$\phi_3(d)=\phi_2(d), \tag{7b}$$

and the continuity of the normal component of the electric displacement field

$$\epsilon\left.\frac{\partial\phi_1}{\partial z}\right|_{z=-d}=\epsilon_{\rm m}\left.\frac{\partial\phi_2}{\partial z}\right|_{z=-d}, \tag{8a}$$

$$\epsilon\left.\frac{\partial\phi_3}{\partial z}\right|_{z=d}=\epsilon_{\rm m}\left.\frac{\partial\phi_2}{\partial z}\right|_{z=d}. \tag{8b}$$

Finally, we need the boundary conditions at infinity. We choose

$$\phi_1(-\infty)=\frac{V_{\rm m}}{2}=\phi_1^0\quad\text{and}\quad\phi_3(+\infty)=-\frac{V_{\rm m}}{2}=\phi_2^0, \tag{9}$$

where $V_{\rm m}$ is the potential difference between the two sides of our system.

We will now write down the solution for the equations, Eqs. (4) and (6), using the boundary conditions, Eqs. (7), (8), and (9).

The solutions for the potential in the regions 1 and 3 are

$$\phi_1(z)=A_1e^{\kappa_{\rm D}(z+d)}+\frac{V_{\rm m}}{2}, \tag{10a}$$

$$\phi_3(z)=A_3e^{-\kappa_{\rm D}(z-d)}-\frac{V_{\rm m}}{2}, \tag{10b}$$

where the A_γ are integration constants. They read

$$A_1 = \frac{1}{2\epsilon\kappa_{\mathrm{D}}}M_0 - \frac{1}{2}\frac{M_1}{\epsilon\kappa_{\mathrm{D}}d + \epsilon_{\mathrm{m}}} - \frac{\epsilon_{\mathrm{m}}}{\epsilon\kappa_{\mathrm{D}}d + \epsilon_{\mathrm{m}}}\frac{V_{\mathrm{m}}}{2}, \tag{11}$$

$$A_3 = \frac{1}{2\epsilon\kappa_{\mathrm{D}}}M_0 + \frac{1}{2}\frac{M_1}{\epsilon\kappa_{\mathrm{D}}d + \epsilon_{\mathrm{m}}} + \frac{\epsilon_{\mathrm{m}}}{\epsilon\kappa_{\mathrm{D}}d + \epsilon_{\mathrm{m}}}\frac{V_{\mathrm{m}}}{2}, \tag{12}$$

where we have introduced the moments of the charge distribution inside the membrane

$$M_n \equiv \int_{-d}^{d} z^n \rho_{\mathrm{m}}(z)dz. \tag{13}$$

Equations (10) give the solutions for the potential in the bulk fluid regions as a function of the membrane charge distribution and the applied potential. We note that the solutions in the bulk fluids depend only on the first two moments of the charge distribution inside the membrane (and the applied potential). This means that the solutions in the bulk fluids are insensitive to the details of the charge distribution in the membrane as expected from Gauss law. They are sensitive only to the membrane total charge (M_0) and its (electrical) dipole moment (M_1).

Inside the membrane the potential reads

$$\begin{aligned}\phi_2(z) = {} & M_0\frac{\epsilon\kappa_{\mathrm{D}}d + \epsilon_{\mathrm{m}}}{2\epsilon_{\mathrm{m}}\epsilon\kappa_{\mathrm{D}}} + M_1\frac{1}{2\epsilon_{\mathrm{m}}} - \frac{1}{\epsilon_{\mathrm{m}}}\int_z^d z'\rho_{\mathrm{m}}(z')dz' \\ & + z\left(-\kappa_{\mathrm{D}}\frac{\epsilon}{\epsilon_{\mathrm{m}}}A_3 + \frac{1}{\epsilon_{\mathrm{m}}}\int_z^d \rho_{\mathrm{m}}(z')dz'\right).\end{aligned} \tag{14}$$

The expression for the potential in the membrane depends on the details of the charge distribution inside the membrane. For an arbitrary charge distribution it cannot be expressed as a function of the first few moments of the charge distribution only. Hence the remaining integrals in Eq. (14).

B. Equilibrium stress

We first establish the conditions for the membrane to be in mechanical equilibrium. In order to do so we introduce the total force per unit volume acting at any point in the system, $\tilde{\boldsymbol{f}}_{\mathrm{el}}(x,y,z)$. In the following we will take the convention that the tilde denotes a force per unit volume and a force without the tilde denotes a force per unit area. The total stress tensor of the system is related to $\tilde{\boldsymbol{f}}_{\mathrm{el}}$ as

$$\tilde{\boldsymbol{f}}_{\mathrm{el}}(x,y,z) = \boldsymbol{\nabla}\cdot T_{\mathrm{eq}}(x,y,z), \tag{15}$$

where T_{eq} is the total equilibrium stress tensor of the system. Its components are

$$\begin{aligned}T_{\mathrm{eq},ij}(x,y,z) = {} & \Theta(-z-d)T_{1,ij} + \Theta(z-d)T_{3,ij} \\ & + [\Theta(z+d) - \Theta(z-d)]T_{2,ij},\end{aligned} \tag{16}$$

where

$$\Theta(z) = \begin{cases} 0 & \text{if} \quad z < 0, \\ 1 & \text{if} \quad z \geqslant 0 \end{cases} \tag{17}$$

is the Heaviside step function and $T_{\gamma,ij}$ are the ij component of the stress tensor of region γ. Using Eq. (16) in Eq. (15) we get

$$\begin{aligned}(\tilde{\boldsymbol{f}}_{\mathrm{el}})_i = {} & \partial_j T_{\mathrm{eq},ij} = \partial_j T_{1,ij}\Theta(-z-d) + \partial_j T_{3,ij}\Theta(z-d) \\ & + \partial_j T_{2,ij}[\Theta(z+d) - \Theta(z-d)] \\ & + (T_{2,iz} - T_{1,iz})\delta(z+d) + (T_{3,iz} - T_{2,iz})\delta(z-d),\end{aligned} \tag{18}$$

where a summation over repeated subscripts is implied. The equilibrium condition $\tilde{\boldsymbol{f}}_{\mathrm{el}} = 0$ then implies the conservation of stress in all regions γ of the system $\partial_j T_{\gamma,ij} = 0$ and the balance of the force at the boundaries of the membrane

$$(\boldsymbol{f}_{1,2})_i \equiv T_{2,iz}(x,y,-d) - T_{1,iz}(x,y,-d) = 0 \tag{19}$$

and

$$(\boldsymbol{f}_{2,3})_i \equiv T_{3,iz}(x,y,d) - T_{2,iz}(x,y,d) = 0. \tag{20}$$

Note that $\boldsymbol{f}_{1,2}$ and $\boldsymbol{f}_{2,3}$ have the unit of force per unit area. We will use these equations in the following in order to derive the equilibrium stress tensor:

$$T_{\gamma,ij} = T_{\gamma,ij}^{\mathrm{Maxwell}} + T_{\gamma,ij}^{\mathrm{pressure}}. \tag{21}$$

$T_{\gamma,ij}^{\mathrm{Maxwell}}$ is the electrical stress in region γ and can be calculated from the potential of region γ as

$$T_{\gamma,ij}^{\mathrm{Maxwell}} = \epsilon_\gamma\left(\partial_i\phi_\gamma\partial_j\phi_\gamma - \frac{1}{2}\delta_{ij}\sum_k \partial_k\phi_\gamma\partial_k\phi_\gamma\right), \tag{22}$$

where we assumed $\epsilon_1 = \epsilon_3 = \epsilon$ and $\epsilon_2 = \epsilon_{\mathrm{m}}$. $T_{\gamma,ij}^{\mathrm{pressure}}(x,y,z) \equiv -\delta_{ij}p_\gamma(x,y,z)$, where p_γ is the pressure of region γ. We will calculate these pressures by assuming that the membrane is at equilibrium. Or, said in other words, the electrostatic stress due to the charges present in the system is compensated by a local pressure such that the resulting force is zero. In our model, which is translationally invariant in the x and y direction, the total stress tensor is diagonal and its components are

$$T_{\gamma,zz} = \epsilon_\gamma\tfrac{1}{2}(\partial_z\phi_\gamma)^2 - p_\gamma(z), \tag{23}$$

$$T_{\gamma,xx} = T_{\gamma,yy} = -\epsilon_\gamma\tfrac{1}{2}(\partial_z\phi_\gamma)^2 - p_\gamma(z). \tag{24}$$

The conservation of stress reads (using Poisson's equation)

$$\rho_\gamma\boldsymbol{\nabla}\phi_\gamma + \boldsymbol{\nabla}p_\gamma = (\rho_\gamma\partial_z\phi_\gamma + \partial_z p_\gamma)\boldsymbol{e}_z = 0. \tag{25}$$

In the bulk fluid regions we can deduce the equilibrium pressures using Eq. (10) in Eq. (25) and integrating. We obtain

$$p_\gamma(z) = \epsilon_\gamma\frac{\kappa_{\mathrm{D}}^2}{2}\left(\phi_\gamma - \phi_\gamma^0\right)^2 + p^0, \quad \gamma = 1,3, \tag{26}$$

where p^0 is the pressure at infinity. This equation tells us that there is an osmotic pressure due to the distribution of free ions around the membrane. This osmotic pressure balances the electrical stress normal to the membrane and the resulting stress in the bulk fluid regions is

$$T_{\gamma,zz}(z) = -p^0, \quad \gamma = 1 \text{ or } 3, \tag{27}$$

$$T_{1,xx}(z) = T_{1,yy}(z) = -\epsilon\kappa_{\mathrm{D}}^2 A_1^2 e^{2\kappa_{\mathrm{D}}(z+d)} - p^0, \tag{28}$$

$$T_{3,xx}(z) = T_{3,yy}(z) = -\epsilon\kappa_{\mathrm{D}}^2 A_3^2 e^{-2\kappa_{\mathrm{D}}(z-d)} - p^0. \tag{29}$$

To obtain the equilibrium pressure in the membrane we need a boundary condition which can be obtained by calculating the force on the membrane interfaces, Eqs. (19) and (20). We have

$$\boldsymbol{f}_{1,2} = [T_{2,zz}(-d) - T_{1,zz}(-d)]\boldsymbol{e}_z = [T_{2,zz}(-d) + p^0]\boldsymbol{e}_z, \quad (30)$$

$$\boldsymbol{f}_{2,3} = [T_{3,zz}(d) - T_{2,zz}(d)]\boldsymbol{e}_z = [-p^0 - T_{2,zz}(d)]\boldsymbol{e}_z. \quad (31)$$

At equilibrium, where $\boldsymbol{f}_{2,3} = 0$ and $\boldsymbol{f}_{1,2} = 0$, we get two equations [using Eqs. (8)],

$$p_2(d) = p^0 + \frac{\epsilon_{\rm m}}{2}\kappa_{\rm D}^2 A_3^2\left(\frac{\epsilon}{\epsilon_{\rm m}}\right)^2 \quad (32)$$

and

$$p_2(-d) = p^0 + \frac{\epsilon_{\rm m}}{2}\kappa_{\rm D}^2 A_1^2\left(\frac{\epsilon}{\epsilon_{\rm m}}\right)^2. \quad (33)$$

We can now calculate $p_2(z)$ from Eq. (25) as

$$\left.\frac{\partial p_2}{\partial z}\right|_z = -\rho_{\rm m}(z)\left.\frac{\partial \phi_2}{\partial z}\right|_z. \quad (34)$$

This equation can be integrated using either Eq. (32) or (33) to give

$$p_2(z) = p^0 + \frac{\epsilon_{\rm m}}{2}[\partial_z\phi_2(z)]^2. \quad (35)$$

Finally, the stress tensor in the membrane at equilibrium reads

$$T_{2,zz}(z) = -p^0, \quad (36)$$

$$T_{2,xx}(z) = T_{2,yy}(z) = -\epsilon_{\rm m}[\partial_z\phi_2(z)]^2 - p^0. \quad (37)$$

From the stress tensor we calculate both the electrostatic contributions to the tension and the spontaneous curvature in Sec. III.

C. Electrostatics of a weakly deformed membrane, with a slightly nonuniform charge distribution

In order to calculate the renormalization of the bending rigidity, $\kappa_{\rm el}$, we can calculate the electrical force that is applied on the membrane when it is slightly deformed. In order to do so we choose a Monge representation where the center of the membrane is characterized by a height field $h(x,y)$. We then calculate the first-order correction to the potential due to the small deviation $h(x,y)$. In addition, we will consider a slightly nonuniform charge distribution inside the membrane which could be due to the deformation of the membrane as it bends.

In this subsection we use a slightly different notation than in the previous ones. We will denote the zeroth-order solution for the planar case derived previously as $\phi_\gamma^{(0)} \equiv \phi_\gamma$ in order to distinguish it from the potential to first order in the deviation from a flat and laterally uniform case, $\phi_\gamma^{(1)}$. The total potential, $\phi_\gamma^{\rm tot}$, is defined as

$$\begin{aligned}\phi_\gamma^{\rm tot}(x,y,z) &\equiv \phi_\gamma^{(0)}[z - h(x,y)] + \phi_\gamma^{(1)}(x,y,z)\\ &\approx \phi_\gamma^{(0)}(z) - h(x,y)\partial_z\phi_\gamma^{(0)}(z) + \phi_\gamma^{(1)}(x,y,z). \quad (38)\end{aligned}$$

$\phi_\gamma^{\rm tot}$ obeys the Debye-Hückel equation, Eq. (4), in the bulk fluid regions of the system

$$\Delta\phi_\gamma^{\rm tot} - \kappa_{\rm D}^2\left(\phi_\gamma^{\rm tot} - \phi_\gamma^0\right) = 0, \quad \gamma = 1,3, \quad (39)$$

and Poisson's equation

$$\epsilon_{\rm m}\Delta\phi_2^{\rm tot} = -\rho(x,y,z) \quad (40)$$

inside the membrane. $\rho(x,y,z)$ is defined as

$$\rho(x,y,z) = \rho^{(0)}(z) + \rho^{(1)}(x,y,z), \quad (41)$$

where $\rho^{(0)}(z) \equiv \rho_{\rm m}(z)$ is the zeroth-order laterally uniform charge density, while $\rho^{(1)}(x,y,z)$ is its first-order counterpart. We will take

$$\rho^{(1)}(x,y,z) = -h(x,y)\left.\frac{\partial\rho^{(0)}}{\partial z}\right|_z + \rho^{(1)}_{\rm add}(x,y,z). \quad (42)$$

The first term is the contribution to the charge density due to the displacement along the z coordinate of the uniform charge distribution. The second term $\rho^{(1)}_{\rm add}(x,y,z)$ is the additional first-order charge distribution which we leave arbitrary for now. Using that the zeroth-order potential obeys Eqs. (3) and (4) in Eqs. (39) and (40) we get the equations for $\phi_\gamma^{(1)}$ as

$$\Delta\phi_\gamma^{(1)} - \kappa_{\rm D}^2\phi_\gamma^{(1)} = 0, \quad \gamma = 1,3, \quad (43)$$

$$\epsilon_{\rm m}\Delta\phi_2^{(1)} = -\rho^{(1)}(x,y,z). \quad (44)$$

We define the Fourier transform of a function of (x,y), say $f(x,y,z)$, as

$$\bar f(q_x,q_y,z) = \int dx\,dy\,e^{ixq_x+iyq_y}f(x,y,z) \quad (45)$$

and its inverse

$$f(x,y,z) = \frac{1}{(2\pi)^2}\int dq_x dq_y e^{-ixq_x-iyq_y}\bar f(q_x,q_y,z). \quad (46)$$

We then rewrite Eqs. (43) and (44) in Fourier space as

$$-\bar q^2\bar\phi_\gamma^{(1)} + \frac{\partial^2\bar\phi_\gamma^{(1)}}{\partial z^2} = 0, \quad \gamma = 1,3, \quad \text{(47a)}$$

$$\epsilon_{\rm m}\left(-q^2\bar\phi_2^{(1)} + \frac{\partial^2\bar\phi_2^{(1)}}{\partial z^2}\right) = -\bar\rho^{(1)}(q_x,q_y,z), \quad \text{(47b)}$$

where $q = \sqrt{q_x^2 + q_y^2}$, $\bar q = \sqrt{q_x^2 + q_y^2 + \kappa_{\rm D}^2}$, and

$$\bar\rho^{(1)}(q_x,q_y,z) = -\bar h(q_x,q_y)\left.\frac{\partial\rho^{(0)}}{\partial z}\right|_z + \bar\rho^{(1)}_{\rm add}(q_x,q_y,z). \quad (48)$$

Also the boundary conditions for $\phi_\gamma^{\rm tot}$ are

$$\phi_1^{\rm tot}(-\infty) = \frac{V_m}{2}, \quad \phi_3^{\rm tot}(+\infty) = -\frac{V_m}{2}, \quad (49)$$

$$\phi_1^{\rm tot}(-d) = \phi_2^{\rm tot}(-d), \quad \phi_3^{\rm tot}(d) = \phi_2^{\rm tot}(d), \quad (50)$$

$$\epsilon\left.\frac{\partial\phi_1^{\rm tot}}{\partial z}\right|_{z=-d} = \epsilon_{\rm m}\left.\frac{\partial\phi_2^{\rm tot}}{\partial z}\right|_{z=-d}, \quad \text{(51a)}$$

$$\epsilon\left.\frac{\partial\phi_3^{\rm tot}}{\partial z}\right|_{z=d} = \epsilon_{\rm m}\left.\frac{\partial\phi_2^{\rm tot}}{\partial z}\right|_{z=d}. \quad \text{(51b)}$$

For $\bar{\phi}_\gamma^{(1)}$ the boundary conditions of $\phi_\gamma^{(0)}$ imply

$$\bar{\phi}_1^{(1)}(q_x,q_y,-\infty)=0,\quad \bar{\phi}_3^{(1)}(q_x,q_y,+\infty)=0, \tag{52}$$

$$\bar{h}\frac{\partial\phi_1^{(0)}}{\partial z}\bigg|_{-d}+\bar{\phi}_1^{(1)}(-d)=\bar{h}\frac{\partial\phi_2^{(0)}}{\partial z}\bigg|_{-d}+\bar{\phi}_2^{(1)}(-d), \tag{53a}$$

$$\bar{h}\frac{\partial\phi_3^{(0)}}{\partial z}\bigg|_{d}+\bar{\phi}_3^{(1)}(d)=\bar{h}\frac{\partial\phi_2^{(0)}}{\partial z}\bigg|_{d}+\bar{\phi}_2^{(1)}(d), \tag{53b}$$

$$\epsilon\left(\frac{\partial\bar{\phi}_1^{(1)}}{\partial z}+\bar{h}\frac{\partial^2\phi_1^{(0)}}{\partial z^2}\right)\Bigg|_{-d}=\epsilon_{\mathrm{m}}\left(\frac{\partial\bar{\phi}_2^{(1)}}{\partial z}+\bar{h}\frac{\partial^2\phi_2^{(0)}}{\partial z^2}\right)\Bigg|_{-d}, \tag{54a}$$

$$\epsilon\left(\frac{\partial\bar{\phi}_3^{(1)}}{\partial z}+\bar{h}\frac{\partial^2\phi_3^{(0)}}{\partial z^2}\right)\Bigg|_{d}=\epsilon_{\mathrm{m}}\left(\frac{\partial\bar{\phi}_2^{(1)}}{\partial z}+\bar{h}\frac{\partial^2\phi_2^{(0)}}{\partial z^2}\right)\Bigg|_{d}. \tag{54b}$$

Equation (47) with the boundary conditions, Eqs. (52), (53), and (54), can be solved to give

$$\begin{aligned}\bar{\phi}_2^{(1)}(z,q)=&\frac{2}{\epsilon_{\mathrm{m}}q(b^2-a^2)}\Bigg\{\sinh[q(z+d)]\int_{-d}^{d}dz'\bar{\rho}^{(1)}(z')\sinh[q(d-z')]-\sinh[2qd]\int_{-d}^{z}dz'\bar{\rho}^{(1)}(z')\sinh[q(z-z')]\\&+\frac{\epsilon_{\mathrm{m}}q}{\epsilon\bar{q}}\left[\int_{-d}^{d}dz'\bar{\rho}^{(1)}(z')\sinh[q(2d-z'+z)]-2\cosh[2dq]\int_{-d}^{z}dz'\bar{\rho}^{(1)}(z')\sinh[q(z-z')]\right]\\&+\left(\frac{\epsilon_{\mathrm{m}}q}{\epsilon\bar{q}}\right)^2\left[\cosh[q(z+d)]\int_{-d}^{d}dz'\bar{\rho}^{(1)}(z')\cosh[q(d-z')]-\sinh[2qd]\int_{-d}^{z}dz'\bar{\rho}^{(1)}(z')\sinh[q(z-z')]\right]\Bigg\}\\&+\frac{2\bar{h}}{\epsilon_{\mathrm{m}}(b^2-a^2)}\left[A\,\sinh[q(d+z)]+B\,\sinh[q(z-d)]+\frac{\epsilon_{\mathrm{m}}q}{\epsilon\bar{q}}\{A\,\cosh[q(d+z)]-B\,\cosh[q(z-d)]\}\right],\end{aligned} \tag{55}$$

$$\begin{aligned}\bar{\phi}_1^{(1)}(z,q)=&e^{\bar{q}(z+d)}\frac{2}{\epsilon_{\mathrm{m}}q(b^2-a^2)}\left\{\frac{\epsilon_{\mathrm{m}}q}{\epsilon\bar{q}}\int_{-d}^{d}dz'\bar{\rho}^{(1)}(z')\sinh[q(d-z')]+\left(\frac{\epsilon_{\mathrm{m}}q}{\epsilon\bar{q}}\right)^2\int_{-d}^{d}dz'\bar{\rho}^{(1)}(z')\cosh[q(z'-d)]\right\}\\&+\frac{\bar{h}}{\epsilon_{\mathrm{m}}}e^{\bar{q}(z+d)}\left\{a_1\left(1-\frac{\epsilon_{\mathrm{m}}}{\epsilon}\right)+A\frac{2}{(b^2-a^2)}\frac{\epsilon_{\mathrm{m}}q}{\epsilon\bar{q}}-B\frac{2}{(b^2-a^2)}\left(\sinh[2qd]+\frac{\epsilon_{\mathrm{m}}q}{\epsilon\bar{q}}\cosh[2qd]\right)\right\},\end{aligned} \tag{56}$$

$$\begin{aligned}\bar{\phi}_3^{(1)}(z,q)=&e^{-\bar{q}(z-d)}\frac{2}{\epsilon_{\mathrm{m}}q(b^2-a^2)}\left\{\frac{\epsilon_{\mathrm{m}}q}{\epsilon\bar{q}}\int_{-d}^{d}dz'\bar{\rho}^{(1)}(z')\sinh[q(d+z')]+\left(\frac{\epsilon_{\mathrm{m}}q}{\epsilon\bar{q}}\right)^2\int_{-d}^{d}dz'\bar{\rho}^{(1)}(z')\cosh[q(d+z')]\right\}\\&+\frac{\bar{h}}{\epsilon_{\mathrm{m}}}e^{-\bar{q}(z-d)}\left\{-a_3\left(1-\frac{\epsilon_{\mathrm{m}}}{\epsilon}\right)-B\frac{2}{(b^2-a^2)}\frac{\epsilon_{\mathrm{m}}q}{\epsilon\bar{q}}+A\frac{2}{(b^2-a^2)}\left(\sinh[2qd]+\frac{\epsilon_{\mathrm{m}}q}{\epsilon\bar{q}}\cosh[2qd]\right)\right\},\end{aligned} \tag{57}$$

where we have introduced

$$a=e^{-qd}\left(1-\frac{\epsilon_{\mathrm{m}}}{\epsilon}\frac{q}{\bar{q}}\right),\quad b=e^{qd}\left(1+\frac{\epsilon_{\mathrm{m}}}{\epsilon}\frac{q}{\bar{q}}\right), \tag{58}$$

$$A=\frac{\epsilon_{\mathrm{m}}}{\epsilon\bar{q}}\left(\kappa_{\mathrm{D}}a_3+\rho^{(0)}(d)\right)+\left(1-\frac{\epsilon_{\mathrm{m}}}{\epsilon}\right)a_3, \tag{59}$$

$$B=\frac{\epsilon_{\mathrm{m}}}{\epsilon\bar{q}}\left(\kappa_{\mathrm{D}}a_1+\rho^{(0)}(-d)\right)+\left(1-\frac{\epsilon_{\mathrm{m}}}{\epsilon}\right)a_1, \tag{60}$$

and

$$a_1=\kappa_{\mathrm{D}}\epsilon A_1=\frac{M_0}{2}-\gamma\frac{M_1}{2d}-\gamma\frac{\epsilon_{\mathrm{m}}V_m}{2d}, \tag{61}$$

$$a_3=\kappa_{\mathrm{D}}\epsilon A_3=\frac{M_0}{2}+\gamma\frac{M_1}{2d}+\gamma\frac{\epsilon_{\mathrm{m}}V_m}{2d}, \tag{62}$$

$$\gamma=\frac{1}{1+\frac{\epsilon_{\mathrm{m}}}{\epsilon}\frac{1}{\kappa_{\mathrm{D}}d}}. \tag{63}$$

Next we will calculate the force on the membrane.

D. Forces on a thin membrane sheet

When the membrane is bent a force will arise to restore the planar (equilibrium) configuration. Note that in order to obtain the electrostatic contribution to the bending rigidity (and the tension) we only need to know the electrostatic part of this restoring force. In this section we will therefore calculate the electrostatic force on the membrane when it is bent. The free energy of Eq. (1) is the free energy per unit area of an infinitely thin surface. However, the model we developed so far takes into account explicitly the thickness of the membrane. The membrane is therefore a three-dimensional (3D) object. In order to find a relation between the two descriptions one should integrate over the normal component of the 3D membrane in such a way that the total physical quantities integrated over a volume that span the membrane be the same in the 2D and 3D descriptions. The theory for this was developed in [27–29] and we will use the results found in these papers in order to relate the force we found in the 3D model, $\tilde{\boldsymbol{f}}_{\mathrm{el}}$, to the effective force on the 2D surface, $\boldsymbol{f}_{\mathrm{el}}$, which in this context is due to electrostatic force. It reads

$$\boldsymbol{f}_{\mathrm{el}} = \int d\tilde{z}(1 - 2\tilde{z}H + \tilde{z}^2 K)\tilde{\boldsymbol{f}}_{\mathrm{el}}^{\mathrm{tot}}, \tag{64}$$

where $\tilde{z}$ is the coordinate along the normal of the surface and we recall that H and K are the mean and Gaussian curvature, respectively. In this section we are searching for the force to first order in h and $\rho^{(1)}$ such that $\boldsymbol{f}_{\mathrm{el}} = \boldsymbol{f}_{\mathrm{el}}^{(0)} + \boldsymbol{f}_{\mathrm{el}}^{(1)}$ and $\tilde{\boldsymbol{f}}_{\mathrm{el}}^{\mathrm{tot}} = \tilde{\boldsymbol{f}}_{\mathrm{el}}^{(0)} + \tilde{\boldsymbol{f}}_{\mathrm{el}}^{(1)}$. In our flat and uniform, zero-order case this reduces to

$$\boldsymbol{f}_{\mathrm{el}}^{(0)} = \int dz\, \tilde{\boldsymbol{f}}_{\mathrm{el}}^{(0)} = 0, \tag{65}$$

where $\tilde{\boldsymbol{f}}_{\mathrm{el}}^{(0)}$ is the total force for the flat laterally uniform case as previously calculated. This implies that the term $(-2\tilde{z}H + \tilde{z}^2 K)\tilde{\boldsymbol{f}}_{\mathrm{el}}^{\mathrm{tot}}$ in Eq. (64) is of second order in h and we have

$$\boldsymbol{f}_{\mathrm{el}}^{(1)} = \int_{-d}^{d} dz\, \tilde{\boldsymbol{f}}_{\mathrm{el}}^{(1)}. \tag{66}$$

Next we define the stress tensor $T_{\gamma,ij}^{\mathrm{tot}} \equiv T_{\gamma,ij}^{(0)} + T_{\gamma,ij}^{(1)}$, where $T_{\gamma,ij}^{(0)} = T_{\gamma,ij}$ as previously calculated in Sec. II B and $T_{\gamma,ij}^{(1)}$ is the first-order tensor resulting from replacing ϕ_γ by $\phi_\gamma^{\mathrm{tot}}$ in Eq. (21), and taking the first-order part. $\tilde{\boldsymbol{f}}_{\mathrm{el}}^{(1)}$ then reads

$$\begin{aligned}\left(\tilde{\boldsymbol{f}}_{\mathrm{el}}^{(1)}\right)_i &= \partial_j T_{1,ij}^{(1)}\Theta(-z-d) + \partial_j T_{3,ij}^{(1)}\Theta(z-d)\\ &\quad + \partial_j T_{2,ij}^{(1)}[\Theta(z+d) - \Theta(z-d)]\\ &\quad + \sum_{j=x,y} -\partial_j h\big[-T_{1,ij}^{(0)}\delta(-z-d) + T_{3,ij}^{(0)}\delta(z-d)\\ &\quad + T_{2,ij}^{(0)}[\delta(z+d) - \delta(z-d)]\big] - T_{1,iz}^{(1)}\delta(-z-d)\\ &\quad + T_{3,iz}^{(1)}\delta(z-d) + T_{2,iz}^{(1)}[\delta(z+d) - \delta(z-d)].\end{aligned} \tag{67}$$

We are interested in the z component of the force Eq. (67). Using that

$$\partial_j T_{2,zj}^{(1)} = -\rho^{(1)}\partial_z\phi_2^{(0)} - \rho^{(0)}\partial_z\phi_2^{(1)} - \partial_z p_2^{(1)}, \tag{68}$$

and that

$$T_{2,ij}^{(1)} = T_{2,ij}^{\mathrm{Maxwell},(1)} - p_2^{(1)}, \tag{69}$$

where the superscript (1) in $T_{2,ij}^{\mathrm{Maxwell},(1)}$ and $p_2^{(1)}$ denotes first-order quantities, we calculate $\mathbf{f}_{\mathrm{el}}^{(1)}$ as

$$\begin{aligned}\boldsymbol{f}_{\mathrm{el}}^{(1)}\cdot\boldsymbol{e}_z &= T_{2,zz}^{\mathrm{Maxwell},(1)}(x,y,-d) - T_{1,zz}^{(1)}(x,y,-d)\\ &\quad + T_{3,zz}^{(1)}(x,y,d) - T_{2,zz}^{\mathrm{Maxwell},(1)}(x,y,d)\\ &\quad - \int_{-d}^{d} dz\, \rho^{(0)}\partial_z\phi_2^{\mathrm{tot}(1)} - \int_{-d}^{d} dz\, \rho^{(1)}\partial_z\phi_2^{(0)}.\end{aligned} \tag{70}$$

The pressure $p_2^{(1)}$ cancels in this expression. Finally, using the boundary conditions for both $\phi^{(0)}$ and $\phi^{(1)}$, we calculate the boundary forces

$$\begin{aligned}&T_{2,zz}^{\mathrm{Maxwell},(1)}(x,y,-d) - T_{1,zz}^{(1)}(x,y,-d)\\ &\quad = -\epsilon\left(1 - \frac{\epsilon}{\epsilon_{\mathrm{m}}}\right)\partial_z\phi_1^{(0)}\big(h\partial_z^2\phi_1^{(0)} + \partial_z\phi_1^{(1)}\big)\\ &\qquad + \epsilon\kappa_{\mathrm{D}}^2\big(\phi_1^{(0)} - \phi_1^0\big)\big(\phi_1^{(1)} + h\partial_z\phi_1^{(0)}\big),\end{aligned} \tag{71}$$

$$\begin{aligned}&T_{3,zz}^{(1)}(x,y,d) - T_{2,zz}^{\mathrm{Maxwell},(1)}(x,y,d)\\ &\quad = \epsilon\left(1 - \frac{\epsilon}{\epsilon_{\mathrm{m}}}\right)\partial_z\phi_3^{(0)}\big(h\partial_z^2\phi_3^{(0)} + \partial_z\phi_3^{(1)}\big)\\ &\qquad - \epsilon\kappa_{\mathrm{D}}^2\big(\phi_3^{(0)} - \phi_3^0\big)\big(\phi_3^{(1)} + h\partial_z\phi_3^{(0)}\big),\end{aligned} \tag{72}$$

where the first equation is evaluated in $z = -d$ and the second one is evaluated in $z = d$. We will use Eq. (70) to derive an expression of the bending rigidity in Sec. III.

III. RESULTS

In this section we apply the results of Sec. II in order to give an expression for the tension and spontaneous curvature from the equilibrium stress and for the bending rigidity from the force calculation.

A. Tension

The tension can be written as the integral of the lateral component of the stress tensor, see Eq. (A4),

$$\sigma_{\mathrm{el}} = \int_{-\infty}^{+\infty} [T_{xx}(z) - (-p^0)]dz. \tag{73}$$

By inserting Eqs. (28), (29), and (37) into Eq. (73) we obtain

$$\sigma_{\mathrm{el}} = -\frac{\epsilon}{2}\kappa_{\mathrm{D}}A_1^2 - \frac{\epsilon}{2}\kappa_{\mathrm{D}}A_3^2 - \epsilon_{\mathrm{m}}\int_{-d}^{d}\left(\left.\frac{\partial\phi_2}{\partial z}\right|_z\right)^2 dz. \tag{74}$$

This equation shows that σ_{el} is always negative. This can be explained as follows. The Debye layers of ions can only squeeze the membrane either because there is an applied potential or because the ions are attracted by the charges in the membrane. We have taken a charge distribution in the membrane which is uniform over the lateral direction which means that the lateral interactions in the membrane are necessarily repulsive. Both contributions will then tend to expand the membrane laterally and hence lower the tension. The first two terms in Eq. (74) are the contributions to the tension at the membrane boundaries while the last one is the internal contribution. Using that

$$\begin{aligned}\left.\frac{\partial\phi_2}{\partial z}\right|_z &= -\frac{\kappa_{\mathrm{D}}}{2}(A_3 - A_1)\frac{\epsilon}{\epsilon_{\mathrm{m}}}\\ &\quad + \frac{1}{2\epsilon_{\mathrm{m}}}\left(\int_z^d \rho_{\mathrm{m}}(z')dz' - \int_{-d}^{z}\rho_{\mathrm{m}}(z')dz'\right),\end{aligned} \tag{75}$$

we rewrite $\sigma_{\rm el}$ so that we get the terms dependent on $V_{\rm m}$ and $\kappa_{\rm D}$,

$$\sigma_{\rm el} = \frac{1}{2d}\frac{u}{(1+u)^2}M_1V_{\rm m} - \frac{\epsilon_{\rm m}}{4d}\frac{2+u}{(1+u)^2}V_{\rm m}^2 - \frac{1}{4\epsilon\kappa_{\rm D}}M_0^2 + \frac{1}{4\epsilon_{\rm m}d}\frac{2+3u}{(1+u)^2}M_1^2 - \frac{\tilde{I}[\rho_{\rm m}]}{4\epsilon_{\rm m}}, \tag{76}$$

where $u \equiv \epsilon_{\rm m}/(\epsilon\kappa_{\rm D}d)$ is a dimensionless constant that quantifies the coupling between the two sides of the membrane. This parameter is equal to the one called H in [5]. $\tilde{I}[\rho_{\rm m}]$ depends on the details of the charge distribution. It reads

$$\begin{aligned}\tilde{I}[\rho_{\rm m}] &= \int_{-d}^{d} dz\left(\int_z^d \rho_{\rm m}(z')dz' - \int_{-d}^{z}\rho_{\rm m}(z')dz'\right)^2\\ &= 2dM_0^2 + 4\int_{-d}^{d}dz'\int_{z'}^{d}dz''(z'-z'')\rho(z')\rho(z''). \end{aligned}\tag{77}$$

The first two terms in Eq. (76) give the dependence of the tension as a function of the applied potential. The first one couples the applied potential to the total dipole moment of the charge distribution inside the membrane, while the second one is the contribution to the tension due to the Debye layers of ions created by the applied potential. All the terms in the tension must stay the same upon inversion of the z axis. This means that terms which would be odd in the inversion (i.e., change sign), like terms proportional to M_0M_1 or $V_{\rm m}M_0$, for example, are not present in the expression. The terms that do not depend on $V_{\rm m}$ are the contributions to the membrane tension of the interactions of the charges inside the membrane with each other and with the charges in the Debye layers. $\tilde{I}[\rho_{\rm m}]$ does not depend on the inverse Debye length and only represents mutual interactions of the charges in the membrane.

B. Spontaneous curvature

The spontaneous curvature $C_{\rm el}$ can be calculated as the first moment of the lateral stress tensor, see Eq. (A7),

$$\kappa_{\rm b}C_{\rm el} = \int_{-\infty}^{+\infty} dz\, z\left[T_{xx}^0 - (-p^0)\right], \tag{78}$$

where $\kappa_{\rm b}$ is the total bending rigidity (including the electrical contribution). Using Eqs. (28), (29), and (37), we get

$$\kappa_{\rm b}C_{\rm el} = \frac{\epsilon}{4}(1+2d\kappa_{\rm D})\left(A_1^2 - A_3^2\right) - \epsilon_{\rm m}\int_{-d}^{d} z\left(\left.\frac{\partial\phi_2}{\partial z}\right|_z\right)^2 dz. \tag{79}$$

$C_{\rm el}$ can be positive or negative depending on the imbalance of stress between the two sides of the membrane. Rewriting this equation in order to make apparent the terms dependent on $V_{\rm m}$, we get

$$\kappa_{\rm b}C_{\rm el} = \frac{1}{2d}\frac{1}{1+u}\left(\frac{M_1}{\epsilon_{\rm m}} + V_{\rm m}\right) \times\left[-M_0d^2\left(\frac{u}{2\kappa_{\rm D}d} + u + 1\right) + M_2\right] - \frac{\hat{I}[\rho]}{4\epsilon_{\rm m}}, \tag{80}$$

where

$$\hat{I}[\rho_{\rm m}] = \int_{-d}^{d} dz\, z\left(\int_z^d \rho_{\rm m}(z')dz' - \int_{-d}^{z}\rho_{\rm m}(z')dz'\right)^2. \tag{81}$$

Under a reversal of both the applied potential and the charge distribution the spontaneous curvature changes sign as it should. Note that with respect to the spontaneous curvature the total dipole moment of the membrane, M_1, acts like an applied potential. As an interesting application we can identify the converse flexoelectric coefficient f as in [30],

$$C_{\rm el} = \frac{f}{\kappa_{\rm b}}E_{\rm m}, \tag{82}$$

where $E_{\rm m}$ is the electric field applied on the membrane. If we take $E_{\rm m}$ to be the contribution of the applied potential alone we get

$$E_{\rm m} = -\left.\frac{\phi_2(d) - \phi_2(-d)}{2d}\right|_{\rho_{\rm m}(z)=0} = \frac{1}{1+u}\frac{V_{\rm m}}{2d}. \tag{83}$$

The identification of the flexocoefficient follows:

$$f = -M_0d^2\left(\frac{u}{2\kappa_{\rm D}d} + u + 1\right) + M_2. \tag{84}$$

The flexocoefficient only depends on the total charge and the quadrupole moment of the charge distribution inside the membrane. Note that the choice of $E_{\rm m}$ is somewhat arbitrary and one could have defined it as $E_{\rm m} = V_{\rm m}/(2d)$, for example, in which case the factor in front of $V_{\rm m}/(2d)$ in Eq. (83) enters in the definition of the flexocoefficient.

C. Bending rigidity

At low Reynolds number where inertia can be discarded the force on the membrane must vanish. The electrical force is then compensated by an equal and opposite contribution coming from the membrane mechanical free energy or/and from membrane elastic force or friction force. One can then identify the electrical tension and bending rigidity contributions by looking at the electrical force after expanding to first order in $\bar{h}$ and to fourth order in q. More precisely, it reads

$$\bar{\boldsymbol{f}}_{\rm el}^{(1)}\cdot\boldsymbol{e}_z = -[\sigma_{\rm el}q^2 + \kappa_{\rm el}q^4]\bar{h}, \tag{85}$$

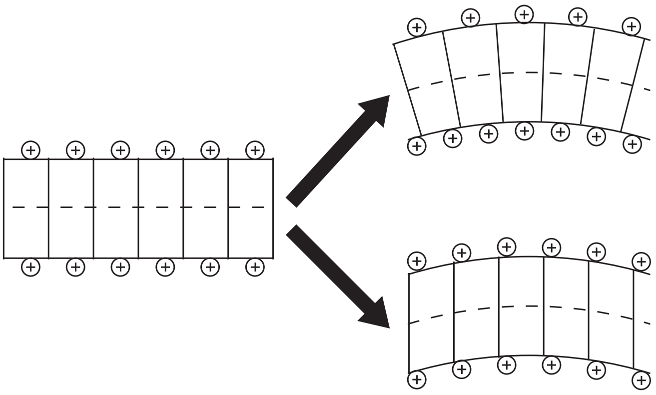

FIG. 2. Membrane bends and the charge distribution deforms. The surface pictured as a dashed line is the neutral surface, for which the area does not change upon bending. The region above this neutral surface expands and the one below compresses. On the right the charge distribution either follows the trend of the area (top) or it stays constant (bottom).

where $\sigma_{\rm el}$ and $\kappa_{\rm el}$ are the electrical contribution to the tension and the bending rigidity, respectively. We then expand $\bar{f}_{\rm el}$, from Eq. (70), using the potentials Eqs. (55), (56), and (57) (assisted by Mathematica). However, the final result will depend on the q dependence of $\bar{\rho}^{(1)}_{\rm add}$, which accounts for the effect of the deformation of the membrane on the charge distribution. Indeed when the membrane bends outward the inner part of the membrane contracts, while the outer part expands. One can imagine that the charge distribution in the membrane will follow the same trend; see Fig. 2. This is taken into account by multiplying the charge density $\rho^{(0)}(z)$ by a factor $(1 + 2zH)$ to first order in the curvature; see Eq. (64). We then take $\bar{\rho}^{(1)}_{\rm add} = -\alpha z q^2 \bar{h} \rho^{(0)}(z)$, where the neutral surface, i.e., the surface that does not stretch when the membrane bends, is considered to be in the middle of the membrane. This term is parametrized by the unitless constant $0 \leqslant \alpha \leqslant 1$. When $\alpha = 0$ the charge distribution does not stretch when the membrane bends i.e., the charge density stays the same but it is still translated vertically; see Eq. (42). The $\alpha = 0$ case actually corresponds to a membrane that conserves its area per lipid and thickness to first order in the deviation h. When $\alpha = 1$ the charge distribution follows the deformation of the membrane. An example of this term would be if the charges are carried by lipids in the membrane. The case $\alpha = 0$ could arise if there are fast lipid exchanges between the two monolayers forming the bilayer, also called flip-flop. Then $\alpha = 1$ would correspond to the absence of flip-flop. We finally get for the bending rigidity contribution

$$
\begin{aligned}
\kappa_{\rm el} = {}& +V_{\rm m}\left(M_1^0\frac{2d\kappa_{\rm D}(3\alpha-2)+3u\big(2d\kappa_{\rm D}(3\alpha-2)+2(\alpha+2)+\frac{3}{d\kappa_{\rm D}}\big)+6u^2(\alpha-2)(2d\kappa_{\rm D}+1)}{24\kappa_{\rm D}(1+u)^2}-M_3^0\frac{3\alpha-2}{12d(1+u)}\right)\\
&+V_{\rm m}^2\frac{\epsilon_{\rm m}}{d\kappa_{\rm D}^2}\frac{8d^2\kappa_{\rm D}^2+3u\big(8d^2\kappa_{\rm D}^2+8d\kappa_{\rm D}+3\big)}{48(1+u)^2}+\big(M_0^0\big)^2\frac{d}{\epsilon_{\rm m}\kappa_{\rm D}^2}\frac{2d^2\kappa_{\rm D}^2+u\big(8d^2\kappa_{\rm D}^2+12d\kappa_{\rm D}+9\big)+3u^2}{48(1+u)}\\
&+\big(M_1^0\big)^2\frac{d}{\epsilon_{\rm m}}\left(\frac{8+3u\big(8+\frac{3}{d^2\kappa_{\rm D}^2}\big)+24u^2\big(1-\frac{1}{d\kappa_{\rm D}}\big)+24u^3}{48(1+u)^2}\right)-\alpha\big(M_1^0\big)^2\frac{d}{\epsilon_{\rm m}}\left(\frac{1+u\big(2-\frac{1}{d\kappa_{\rm D}}\big)+2u^2}{4(1+u)}\right)\\
&+\big(M_2^0\big)^2\frac{2\alpha-1}{8d\epsilon_{\rm m}(1+u)}+M_0^0M_2^0(\alpha-1)\frac{d\kappa_{\rm D}+u(2d\kappa_{\rm D}+1)}{4\epsilon_{\rm m}\kappa_{\rm D}(1+u)}-M_1^0M_3^0\frac{3\alpha-2}{12d\epsilon_{\rm m}(1+u)}+\frac{\tilde{\tilde{I}}[\rho]}{6\epsilon_{\rm m}},
\end{aligned}
\tag{86}
$$

where

$$
\tilde{\tilde{I}}[\rho] = \int_{-d}^{d} dz \int_{-d}^{z} d\tilde{z}\, \bar{\rho}^{(0)}(z)\bar{\rho}^{(0)}(\tilde{z})(z-\tilde{z})^3\left(1-\frac{3}{2}\alpha\right). \tag{87}
$$

We also recover the same expression for the tension as in Eq. (74) for the term proportional to q^2 by expanding the force (not shown). The tension does not depend on the parameter α. The bending rigidity does depend on α and is separated, like the tension in Eq. (76), into terms that depend on the applied potential, and terms that do not. There is also an internal contribution that depends on the details of the charge distribution inside the membrane and not on the Debye length (the last term in the equation). The up-down symmetry is respected such that the bending rigidity stays the same upon inversion of the z axis. We note here that we do obtain the same contribution to the tension as [31–33] for the potential dependent part, but the bending rigidity we find has a few numerical factors different from these references. However, we recover the result of [18,34]. The difference between our result and the result of [31–33] can be explained by their use of the Robin type boundary conditions which are different from the boundaries conditions we used, Eqs. (53) and (54), for a slightly deformed membrane.

IV. DISCUSSION

A. Free energy and stress balance

In this subsection we comment on how our calculations compare to previous calculations of the membrane bending moduli through the calculation of the electrostatic free energy for planar and curved geometry. This approach is in contrast to the method employed here as we have calculated the force and stress on a planar and a slightly deformed surface. It has been shown that the two approaches should give the same result for the bending moduli of a stack of membranes [35,36]. However, the additional condition of balance of the stress we have enforced introduces a difference with previous works [4,5,8,11,37].

In the literature [5] the usual way of handling the stress balance in the membrane consists of adding a δ-function contribution to the lateral stress such that its zeroth moment vanishes. This relaxes the membrane to a state of zero tension. The location of this balancing stress in the membrane is somewhat arbitrary and is often chosen for convenience in the calculation. The calculation based on the electrostatic free energy of the membrane, including an osmotic contribution from the mobile ions (see [38]) implicitly assumes that the balancing stress is located at the monolayer interface [5]. Another choice would be to put the balancing force in the midplane of the membrane; the stress balance then contributes only to the zeroth moment of the stress profile. In our approach we have locally balanced the stress in the membrane by a continuous pressure tensor; see Sec. II B. Note that this idea was already discussed in [5] as a better way to handle the stress balance. However, we explicitly employ this balancing stress with a fixed charge distribution in the membrane.

To what extent does the balance of the stress make our results different from those previously published? If one identifies the free energy per unit area calculated for a planar membrane in [4,5,8,11,37] with the tension we calculated one has

$$\sigma_{\rm el} - \sigma_{\rm ub} = -\int dz[p_2(z) - p_0] \tag{88}$$

$$= -\frac{1}{2}\epsilon_{\rm m}\int_{-d}^{d} dz[\partial_z\phi_2(z)]^2, \tag{89}$$

where $\sigma_{\rm ub}$ is the tension when the stress is locally unbalanced in the membrane and p_2 is defined in Eq. (35). Similarly, the contribution to the spontaneous curvature reads

$$\kappa_{\rm b}(C_{\rm el} - C_{\rm ub}) = -\int dz\, z[p_2(z) - p_0] \tag{90}$$

$$= -\frac{1}{2}\epsilon_{\rm m}\int_{-d}^{d} dz\, z[\partial_z\phi_2(z)]^2. \tag{91}$$

Next we give an explicit expression for $\sigma_{\rm ub}$ and $\kappa_{\rm b}C_{\rm ub}$ using Eqs. (74), (79), (88), and (90),

$$\sigma_{\rm ub} = -\frac{\epsilon}{2}\kappa_{\rm D}A_1^2 - \frac{\epsilon}{2}\kappa_{\rm D}A_3^2 - \frac{1}{2}\epsilon_{\rm m}\int_{-d}^{d}\left(\frac{\partial\phi_2}{\partial z}\bigg|_z\right)^2 dz \tag{92}$$

and

$$\kappa_{\rm b}C_{\rm ub} = \frac{\epsilon}{4}(1 + 2d\kappa_{\rm D})\big(A_1^2 - A_3^2\big) - \frac{1}{2}\epsilon_{\rm m}\int_{-d}^{d} z\left(\frac{\partial\phi_2}{\partial z}\bigg|_z\right)^2 dz. \tag{93}$$

The difference between Eqs. (74) and (92), and (79) and (93) is only the $1/2$ factor in front of the integral of the last terms, the moments of the stress in the membrane. For completeness we give the expression for the flexocoefficient without stress balance in the membrane, $f_{\rm ub}$,

$$f_{\rm ub} = -M_0 d^2\left(\frac{u}{2\kappa_{\rm D}d} + u + \frac{1}{2}\right) + \frac{1}{2}M_2, \tag{94}$$

where $u \equiv \epsilon_{\rm m}/(\epsilon\kappa_{\rm D}d)$. The strength of the effect of the detailed balance of stress depends on the strength of the electric field inside the membrane. If there is no field inside the membrane, there is no electrostatic stress and there is no need to balance the stress inside the membrane. The effect will therefore be more apparent for a highly asymmetric charge distribution or with a strong applied electric field. It is interesting to note that this is the case for the plasma membrane where a negative surface charge is present on the intracellular side of the membrane and there is a negative potential (with respect to the extracellular side): the two effects add to each other and to the electric field inside the membrane. However, we will show in the next section that for a realistic estimate the relative difference between $\sigma_{\rm ub}$ and $\sigma_{\rm el}$ is small in this case. For a decoupled membrane, where the electric field in the membrane vanishes (taking $V_{\rm m} = 0$ and the limit $u \to 0$ such that $d \to \infty$, for example), the correction due to the stress balance vanishes. The detailed balance of the stress will change the expression of the bending rigidity because it changes the force in the membrane. Note that we did not explicitly calculate this effect. However, we still expect the bending rigidity to be the same as the one calculated from the free energy of a bent surface (sphere or cylinder) in the decoupled-membrane limit.

B. Surface charges

In this section we investigate the case of surface charges present at the dielectric interfaces between the membrane and the bulk fluids. This case is an important case as it is believed that the charges present in the bulk fluid adsorb on the surface of the membrane and that the head group of some lipids can be charged, creating a surface charge in addition to the Debye layers of ions. For surface charges at the boundaries between the dielectrics the boundary conditions of Eq. (8) should, in principle, be changed to

$$\epsilon\frac{\partial\phi_1}{\partial z}\bigg|_{z=-d} = \epsilon_{\rm m}\frac{\partial\phi_2}{\partial z}\bigg|_{z=-d} + \sigma_-, \tag{95a}$$

$$\epsilon\frac{\partial\phi_3}{\partial z}\bigg|_{z=d} = \epsilon_{\rm m}\frac{\partial\phi_2}{\partial z}\bigg|_{z=d} - \sigma_+. \tag{95b}$$

σ_+ and σ_- are the charges per area of the outer and the inner surface, respectively. An alternative and easier way of calculating this contribution from our Eqs. (76), (80), and (86) is by taking a charge distribution $\rho_{\rm m}(z) = \sigma_+\delta[z - (d - l)] + \sigma_-\delta[z - (-d + l)]$ and then taking the limit $l \to 0$. Note that for all the results of this subsection we have checked explicitly that we obtain the same results in both approaches. We first give our results for the case of prescribed surface charges, giving results for the tension, spontaneous curvature, and bending rigidity. Then we will comment on them. For the tension, using Eq. (76), we find

$$\sigma_{\rm el} = \frac{u}{(1+u)^2}\frac{V_{\rm m}}{2}(\sigma_+ - \sigma_-) - V_{\rm m}^2\frac{\epsilon_{\rm m}}{4d}\frac{2+u}{(1+u)^2} - \frac{(\sigma_- + \sigma_+)^2}{4\epsilon\kappa_{\rm D}} - \frac{(\sigma_+ - \sigma_-)^2}{4\epsilon\kappa_{\rm D}}\frac{1+2u}{(1+u)^2}. \tag{96}$$

From Eq. (80) we get for the spontaneous curvature, with no applied potential,

$$\kappa_{\rm b}C_{\rm el} = -\frac{d^2}{2\epsilon_{\rm m}}(\sigma_+^2 - \sigma_-^2)\frac{u}{1+u}\left(\frac{1}{2\kappa_{\rm D}d} + 1\right). \tag{97}$$

The contribution from the potential is included in the flexocoefficient Eq. (84),

$$f = -ud^2(\sigma_+ + \sigma_-)\left(\frac{1}{2\kappa_{\rm D}d} + 1\right). \tag{98}$$

We found the bending rigidity from Eq. (86) as

$$\kappa_{\rm el} = V_{\rm m}^2\frac{\epsilon_{\rm m}}{d\kappa_{\rm D}^2}\frac{8d^2\kappa_{\rm D}^2 + 3u\big(8d^2\kappa_{\rm D}^2 + 8d\kappa_{\rm D} + 3\big)}{48(1+u)^2}$$
$$+ V_{\rm m}(\sigma_+ - \sigma_-)\frac{\epsilon_{\rm m}}{\epsilon\kappa_{\rm D}^2}\frac{\frac{9}{d\kappa_{\rm D}} + 12 - 8\kappa_{\rm D}d - 12u(1 + 2\kappa_{\rm D}d)}{24(1+u)^2}$$
$$+ \alpha V_{\rm m}(\sigma_+ - \sigma_-)\frac{\epsilon_{\rm m}}{\epsilon\kappa_{\rm D}^2}\frac{1 + 2\kappa_{\rm D}d}{4(1+u)}$$
$$+ (\sigma_- + \sigma_+)^2\frac{1}{\kappa_{\rm D}^3\epsilon}\frac{3 + 4\alpha\kappa_{\rm D}d + u}{16(1+u)}$$

$$+\frac{d^2}{\epsilon\kappa_{\rm D}}(\sigma_+-\sigma_-)^2\,\frac{\frac{9}{(d\kappa_{\rm D})^2}+8u\left(1-\frac{3}{d\kappa_{\rm D}}\right)+24u^2}{48(1+u)^2}$$
$$+\alpha\frac{d^2}{\epsilon\kappa_{\rm D}}(\sigma_+-\sigma_-)^2\,\frac{\frac{1}{d\kappa_{\rm D}}-2u}{4(1+u)}. \qquad (99)$$

As explained in the previous section, there are some similarities and differences between the expressions we give and the expressions given previously in the literature [5,8,11,37].

The expression given in the Debye-Hückel regime for the bending rigidity in [5,8] agrees with our results to first order in the coupling parameter between the two sides of the membrane, u. This is due to the approximate handling of the coupling, specifically Eq. (2) in [5]. They also give an expression for the spontaneous curvature to zeroth order in u, i.e., for no coupling, which agrees with the corresponding expansion of Eq. (97).

In [11] another calculation has been performed for which the coupling between the two leaflets of the membrane has been taken care of explicitly, at least to the lowest order in the curvature expansion. However, in this reference the stress is not balanced and our results only agree to zeroth order in u for the tension and bending rigidity and do not agree for the spontaneous curvature.

The electrostatic contribution to the bending rigidity was calculated taking into account explicitly the coupling between the two sides of the bilayer as well as a different surface charge distribution for the two sides of the membrane in [37]. For the bending rigidity our calculations agree with theirs for a symmetrical surface charge and for a decoupled membrane, i.e., for $u = 0$. However, we have a different numerical factor in front of the terms proportional to the square of the surface charge difference in the coupled case.

In [39] the flexocoefficient was calculated without taking into account the dielectric difference between the membrane and the water ($\epsilon_{\rm m} = \epsilon$). In this limit we obtain the same analytical expression for the flexocoefficient. Note that for the case of having surface charge only it is important to take into account the coupling between the two bilayer sides to have a nonzero flexocoefficient.

In Fig. 3 we plotted the contributions we have obtained for surface charge $\sigma_+ = 0$ and σ_- ranging from 0 to -120 mC m^{-2}, which corresponds roughly to half a charge per lipid. The bending rigidity we obtain is on the order of $k_{\rm B}T$ in an appreciable range of the charge density and is substantially larger if we take into account the deformation of the charge by setting $\alpha = 1$. Electrostatic renormalization of the bending rigidity on the order of $k_{\rm B}T$ has indeed been observed [40] and predicted before. On the same figure we can see that a negative electrostatic tension contribution on the order of 1 mN m^{-1} is possible. Note that the actual total membrane tension (the electrostatic contribution plus the elastic one) can be moderated if the membrane slightly changes its area, as proposed by two of us in [41]. The spontaneous curvature we obtained is

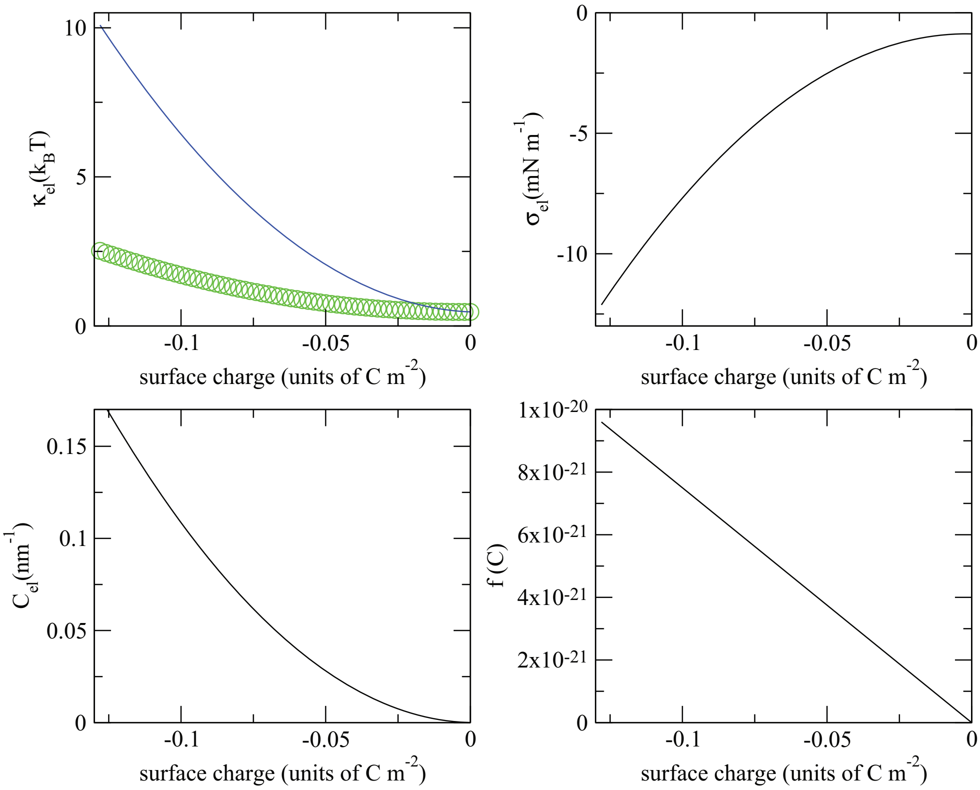

FIG. 3. (Color online) Electrostatic contribution to the bending rigidity, tension, spontaneous curvature, and flexocoefficient with no applied potential. For the bending rigidity we have plotted both the case with no charge deformation ($\alpha = 0$ circle) and the case with full deformation ($\alpha = 1$ continuous line). The parameters we used are $d = 2.5$ nm, $\epsilon = 80\epsilon_0$, $\epsilon_{\rm m} = 2\epsilon_0$, $V_{\rm m} = 0$, a salt concentration of 100 mM, which corresponds to $\kappa_{\rm D} \simeq 1$ nm^{-1}, and $\kappa_{\rm b} = 50k_{\rm B}T$.

qualitatively and quantitatively very close to the ones obtained from a recent study [42,43] in which a numerical calculation of the membrane stress due to a surface charge density was performed. Note that in those papers the electrostatic stress normal to the membrane is automatically balanced by the elastic properties of the membrane and is found to be very small compared to the lateral contribution. This justifies our zero normal stress and constant thickness approach. Finally, the value of the flexocoefficient we obtained with surface charges only is lower than the experimental values obtained in [30,44], which are on the order of 10^{-19}–10^{-18} C. Only for $\sigma_- \simeq -0.25$ C m^{-2} does the flexocoefficient reach -1.9×10^{-20} C, which corresponds roughly to a membrane with one charge per lipid. The bending rigidity, tension, and spontaneous curvature contributions we find all have a quadratic dependence on the charge distribution without an applied potential. If in addition to the surface charge a potential is applied, then a term quadratic in the potential will be added but also a coupling term linear in both the potential and the charge distribution will appear. With the approach we used we were unable to obtain the analytical expressions of the spontaneous curvature and the flexocoefficient from a deformation of the charge density, but this contribution (a nonzero α) is likely to change both the spontaneous curvature and the flexocoefficient. Finally, let us discuss the quantitative difference due to the detailed balance of the stress we imposed induces on the quantities we calculate. If we take the parameters of Fig. 3 and $\sigma_- \simeq -0.12$ C m^{-2} as well as an applied potential of 500 mV we get, using Eqs. (74) and (92), $\sigma_{\rm el} \simeq -3.3$ mN/m and $\sigma_{\rm el} - \sigma_{\rm ub} \simeq -0.3$ mN/m. There is no difference between $C_{\rm ub}$, Eq. (93), and $C_{\rm el}$, Eq. (79), in the surface charge case.

C. Dipole moment

In this section we will consider the impact of the electrostatic contribution coming from the dipolar lipid head groups. We take the charge density

$$\rho_{\rm m}(z) = \frac{\mu_+}{2l}[\delta(z-d+j-l) - \delta(z-d+j+l)] + \frac{\mu_-}{2l}[\delta(z+d-j-l) - \delta(z+d-j+l)], \quad (100)$$

where μ_+ (μ_-) are the dipole moments per area associated with the head groups in the upper (lower) monolayer, $\pm\tilde{d} = \pm(d-j)$ is the distance between the center of the membrane and the dipoles center, and $2l$ is the spacing between the two charges of the dipole. From this charge distribution we can calculate the moments and integrals we introduced in Sec. III:

$$M_0 = 0, \quad (101)$$

$$M_1 = \mu_+ + \mu_-, \quad (102)$$

$$M_2 = 2\tilde{d}(\mu_+ - \mu_-), \quad (103)$$

$$M_3 = 3\tilde{d}^2(\mu_+ + \mu_-), \quad (104)$$

$$\tilde{I}[\rho_{\rm m}] = 2\frac{1}{l}(\mu_+^2 + \mu_-^2), \quad (105)$$

$$\hat{I}[\rho_{\rm m}] = 2\frac{d}{l}(\mu_+^2 - \mu_-^2), \quad (106)$$

$$\tilde{\tilde{I}}[\rho_{\rm m}] = -2l(\mu_+^2 + \mu_-^2) - 12\tilde{d}\mu_+\mu_-. \quad (107)$$

In order to give a numerical estimate of the electrostatic contribution to the dipole moment of lipids one could simply evaluate the dipole moments as $\mu \sim 2le/a$, where e is the elementary charge and a is the area occupied by one lipid. However, this would be neglecting the contribution of water which actually overcompensates for the dipole moment of the lipids [45,46]. Based on the total charge distribution obtained from various numerical simulations [47,48], we will take $2l \sim 0.5$ nm, $j \sim 0.25$ nm, and $\mu_- = -\mu_+ \sim 3$ D nm^{-2}. We do not take the limit $l \to 0$ as our Debye length is on the order of 1 nm in our system. Note that here the internal charge $\rho_{\rm m}$ is seen to represent the charge of the lipid head groups as well as the polarized water molecules close to them. The dipole moment we take has contributions from the water molecules in the interfacial region and the lipid head groups. The dipole moment we use gives a potential in the middle of the membrane, without an applied potential, of 60 mV (the so-called dipole potential). Using these numbers and the same parameters as in Fig. 3 we obtain the following values: $\sigma_{\rm el} \sim -2.2 \times 10^{-2}$ N m^{-1}, $C_{\rm el} = 0$, $\kappa_{\rm el}(\alpha = 0) \sim 0.1\ k_{\rm B}T$, $\kappa_{\rm el}(\alpha = 1) \sim 3.3\, k_{\rm B}T$, and $f \sim -0.9 \times 10^{-20}$ C. We obtained a very high value for the electrostatic contribution to the tension but one has to keep in mind that this is the contribution from the electrostatics only; the total tension of the membrane includes the contribution from all the other interactions. Because we choose to have a symmetrical dipole distribution (by choosing $\mu_+ = -\mu_-$) the spontaneous curvature is zero due to symmetry. We can see that, at least in the case where the charge density stretches with the membrane, the dipole moment should contribute a few $k_{\rm B}T$ to the bending rigidity. Finally, we obtain a flexocoefficient 10 times higher than in the surface charge case, which accounts better for the experimental data [30,44]. Note that the charge distribution we use in this section could be modified to take into account adsorption of the ions on the membrane surface, by modifying the charge density we used.

V. CONCLUSION

In this paper we have given the electrostatic contribution to the membrane mechanical parameters explicitly taking into account the electrostatic coupling between the two sides of the membrane in the Debye-Hückel regime including an applied potential. This potential could either be applied by electrodes or generated as a result of pumping activity imposing a charge imbalance across the membrane. In addition, we explicitly treated the balance of stress in the membrane by applying a local pressure tensor. The contributions from any laterally uniform charge distribution in the membrane can be deduced from our calculations. This is useful as an analytical tool as one can use it to easily calculate the contributions by plugging in a specific charge distribution, but it can also be useful in numerical simulations where the average charge distribution is readily available. Note that our equations use the Poisson-Boltzmann approach, which is a mean-field approximation and as such does not take into account ion correlations. In addition, we have used its linear counterpart, the Debye-Hückel equations, which limits the maximum difference of potential between the bilayer and the surrounding fluid. However, we have solved Poisson's equation in the membrane region for any laterally uniform charge distribution. This extends the validity of our calculation to the case where the contribution of the Debye layer is small (i.e., a small Debye length); then the main electrostatic contribution to the bending moduli should come from the force and stress in the membrane that we calculated explicitly. We believe our approach to be a good starting point to evaluate what would be the impact of changing the membrane charge distribution, for example, by changing the membrane composition, and we have shown that a semiquantitative agreement with experimental results is possible.

APPENDIX: LATERAL STRESS INTEGRAL, TENSION, AND SPONTANEOUS CURVATURE

In this Appendix we derive the relation between the moments of the stress profile and the tension and the spontaneous curvature. The derivation we use is based on the approach of [29]. In this reference the relations between an ideal infinitely thin membrane and its equivalent three-dimensional description are derived in terms of integrals of excess quantities. These excess quantities represent the "real" 3D quantities minus the values of the quantities far from the membrane. The integral of the excess quantities are associated with the ideal 2D membrane. According to [29], Eq. (24) in this reference, the relation between the 2D linear stress associated with the ideal membrane, T^α, and its excess quantities $\bar{T}_{\text{excess}}$ is

$$\boldsymbol{t}_\beta \cdot T^\alpha = \int dh[g^{\alpha\gamma} - h(2Hg^{\alpha\gamma} - K^{\alpha\gamma})]\boldsymbol{t}_\beta \cdot (\bar{T}_{\text{excess}} \cdot \boldsymbol{t}_\gamma), \tag{A1}$$

and h is the normal coordinate to the surface. $\boldsymbol{t}_\beta$ are the two tangential vectors entering the definition of the metric g. The $\cdot$ denotes the operation between a 3D vector v_i and a 3×3 tensor T_{ij} such that $(\boldsymbol{v} \cdot T)_i = v_j T_{ij}$; between two vectors the $\cdot$ denotes the scalar product. The stress tensor T^α can also be calculated from a free energy f associated with the 2D membrane; see [29]. If we take the free energy to be

$$f = 2\kappa_{\text{b}}H^2 - 2\kappa_{\text{b}}C_0H + \sigma + \kappa_{\text{G}}K, \tag{A2}$$

we get, from Eq. (111) of [29],

$$\boldsymbol{t}_\beta \cdot T^\alpha = g^\alpha_\beta(2\kappa_{\text{b}}H^2 - 2\kappa_{\text{b}}C_0H + \sigma) - \kappa_{\text{b}}(2H - C_0)K^\alpha_\beta. \tag{A3}$$

Combining Eqs. (A1) and (A3) for a planar case ($g_{\alpha\beta} = \delta_{\alpha\beta}$, $H = 0$, and $K_{\alpha\beta} = 0$), we get

$$\sigma = \int dz\, \boldsymbol{t}_\gamma(\boldsymbol{t}_\gamma \cdot \bar{T}_{\text{excess}}), \tag{A4}$$

without sum over γ and in the planar case $\boldsymbol{t}_\gamma = \boldsymbol{t}^\gamma$, or expressed in words: the integral of the lateral stress is equal to the tension, in the planar case. This is the equation used in the text.

The spontaneous curvature is related to another quantity, the internal excess angular stress or bending moment $\boldsymbol{N}^\alpha$ of [29], but the demonstration follows the same way as the one for the tension. We express $\boldsymbol{N}^\alpha$ in the function of the excess stress tensor, Eq. (40) of [29],

$$\boldsymbol{N}^\alpha = -\int dh\, h[g^{\alpha\beta} - h(2Hg^{\alpha\beta} - K^{\alpha\beta})] \times \boldsymbol{t}_\gamma \varepsilon^{\gamma\delta}(\boldsymbol{t}_\beta \cdot \bar{T}_{\text{excess}} \cdot \boldsymbol{t}_\delta), \tag{A5}$$

where $\varepsilon_{\alpha\beta}$ is the second-order Levi-Civita symbol. Then we express it using the free energy Eq. (A2) from Eq. (117) of [29],

$$\boldsymbol{N}^\alpha = -[\kappa_{\text{b}}(2H - C_0)g^{\alpha\beta} + \kappa_{\text{G}}(2Hg^{\alpha\beta} - K^{\alpha\beta})]\varepsilon_{\beta\gamma}\boldsymbol{t}^\gamma. \tag{A6}$$

Putting these two equations together for the planar case we get the desired equation:

$$\kappa_{\text{b}}C_0 = \int dz\, z\boldsymbol{t}_\gamma \cdot (\boldsymbol{t}_\gamma \cdot \bar{T}_{\text{excess}}), \tag{A7}$$

without sum over γ. Both derivations are based on the assumption that there is no deformation of the membrane and no internal torque.

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[1] M. Langner and K. Kubica, Chem. Phys. Lipids **101**, 3 (1999).

[2] B. Alberts, A. Johnson, J. Lewis, M. Raff, K. Roberts, and P. Walter, *Molecular Biology of the Cell*, 4th ed. (Garland, New York, 2002).

[3] T. Yeung, G. E. Gilbert, J. Shi, J. Silvius, A. Kapus, and S. Grinstein, Science **319**, 210 (2008).

[4] M. Winterhalter and W. Helfrich, J. Phys. Chem. **92**, 6865 (1988).

[5] M. Winterhalter and W. Helfrich, J. Phys. Chem. **96**, 327 (1992).

[6] H. N. W. Lekkerkerker, Physica A **159**, 319 (1989).

[7] P. A. Barneveld, D. E. Hesselink, F. A. M. Leermakers, J. Lyklema, and J. M. H. M. Scheutjens, Langmuir **10**, 1084 (1994).

[8] S. May, J. Chem. Phys. **105**, 8314 (1996).

[9] L. M. Bergstrom, Langmuir **22**, 3678 (2006).

[10] A. Shafir and D. Andelman, Soft Matter **3**, 644 (2007).

[11] T. Chou, M. Jaric, and E. Siggia, Biophys. J. **72**, 2042 (1997).

[12] Y. Li and B.-Y. Ha, Europhys. Lett. **3**, 411 (2005).

[13] B. Harland, W. E. Brownell, A. A. Spector, and S. X. Sun, Phys. Rev. E **81**, 031907 (2010).

[14] D. Mengistu and S. May, Eur. Phys. J. **26**, 251 (2008).

[15] A. J. Wagner and S. May, Eur. Biophys. J. **36**, 293 (2007).

[16] I. Bivas, Colloid Surf. A **282-283**, 423 (2006).

[17] W. Helfrich, Z. Naturforsch. **28c**, 693 (1973).

[18] T. Ambjörnsson, M. A. Lomholt, and P. L. Hansen, Phys. Rev. E **75**, 051916 (2007).

[19] D. Andelman, in *Handbook of Biological Physics*, edited by R. Lipowsky and E. Sackmann (Elsevier Science B.V., Amsterdam, 1995), Vol. 1, p. 605.

[20] G. Gouy, J. Phys. (France) **9**, 457 (1910).

[21] G. Gouy, Ann. Phys. (Leipzig) **7**, 129 (1917).

[22] D. L. Chapman, Philos. Mag. **25**, 475 (1913).

[23] P. Debye and E. Hückel, Phyzik Z **24**, 185 (1923).

[24] P. Debye and E. Hückel, Phyzik Z **25**, 97 (1923).

[25] J. D. Jackson, *Classical Electrodynamics*, 3rd ed. (Wiley, New York, 1998).

[26] J. R. Reitz, F. J. Milford, and R. W. Christy, *Foundations of Electromagnetic Theory*, 4th ed. (Addison-Wesley, Redwood City, CA, 1993).

[27] P. A. Kralchevsky, J. C. Eriksson, and S. Ljunggren, Adv. Colloid. Interface. Sci. **48**, 19 (1994).

[28] M. A. Lomholt, P. L. Hansen, and L. Miao, Eur. Phys. J. E **16**, 439 (2005).

[29] M. A. Lomholt and L. Miao, J. Phys. A: Math. Gen. **39**, 10323 (2006).

[30] A. G. Petrov, *The Lyotropic State of Matter. Molecular Physics and Living Matter Physics* (Gordon and Breach Science, New York, 1999).

[31] D. Lacoste, G. I. Menon, M. Z. Bazant, and J.-F. Joanny, Eur. Phys. J. E **28**, 243 (2009).

[32] F. Ziebert, M. Z. Bazant, and D. Lacoste, Phys. Rev. E **81**, 031912 (2010).

[33] F. Ziebert and D. Lacoste, New J. Phys. **12**, 095002 (2010).

[34] S. Chatkaew and M. Leonetti, Eur. Phys. J. E **17**, 203 (2005); see also **22**, 353 (2007).

[35] A. Fogden, J. Daicic, D. Mitchell, and B. Ninham, Physica A **234**, 167 (1996).

[36] J. Harden, C. Marques, J. F. Joanny, and D. Andelman, Langmuir **8**, 1170 (1992).

[37] M. Kiometzis and H. Kleinert, Phys. Lett. A **140**, 520 (1989).

[38] K. Sharp and B. Honig, J. Phys. Chem. **94**, 7684 (1990).

[39] K. Hristova, I. Bivas, A. G. Petrov, and A. Derzhanski, Mol. Cryst. Liq. Cryst. **200**, 71 (1991).

[40] A. C. Rowat, P. L. Hansen, and J. H. Ipsen, Europhys. Lett. **67**, 144 (2004).

[41] M. A. Lomholt, B. Loubet, and J. H. Ipsen, Phys. Rev. E **83**, 011913 (2011).

[42] M. Tajparast and M. Glavinovi, Biochim. Biophys. Acta **1818**, 411 (2012).

[43] M. Tajparast and M. Glavinovi, Biochim. Biophys. Acta **1818**, 829 (2012).

[44] A. G. Petrov, Biochim. Biophys. Acta **1561**, 1 (2002).

[45] C. Zheng and G. Vanderkooi, Biophys. J. **63**, 935 (1992).

[46] M. L. Berkowitz, D. L. Bostick, and S. Pandit, Chem. Rev. **106**, 1527 (2006).

[47] A. A. Gurtovenko and I. Vattulainen, J. Phys. Chem. B **112**, 4629 (2008).

[48] C. J. Hogberg and A. P. Lyubartsev, Biophys. J. **94**, 525 (2008).