

Effect of Surface Charge on the Curvature Elasticity of Membranes

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Within the Debye-Hückel approximation we calculate the energy of the diffuse double layer of a charged membrane for planar, cylindrical, and spherical geometry. Comparing the three energies with the phenomenological formula for the curvature-elastic energy of fluid membranes, we find the electrical contributions to the bending rigidity, the elastic modulus of Gaussian curvature, and the spontaneous curvature. The same value for the modulus of Gaussian curvature is obtained from the stress profile of the flat membrane.

Curvature elasticity is a useful concept to understand and predict the shapes of lipid bilayers, also called membranes,^{1,2} and surfactant monolayers^{3,4} if the radii of curvature are much larger than the constituent molecules. The phenomenological formula for the bending energy per unit area may be written in the usual quadratic approximation⁵

$$g_{\text{bend}} = \frac{1}{2}k_c(c_1 + c_2 - c_0)^2 + \bar{k}_c c_1 c_2 \quad (1)$$

Here c_1 and c_2 are the principal curvatures (inverse radii of curvature), c_0 is the spontaneous curvature, k_c is the bending rigidity, and \bar{k}_c is the elastic modulus of Gaussian curvature $c_1 c_2$.

Some years ago Israelachvili et al.⁶ proposed a condenser model to account for the bending energy of fluid membranes. It assumes surface charge and electrolytic countercharge of each monolayer to form a condenser of fixed spacing which is held together by the interfacial tension at the water/oil boundary. The condenser model is complete in the sense that it gives nonvanishing values for both k_c and \bar{k}_c and, with asymmetric bilayers, also for c_0 .⁷ However, it is rather special and of interest mainly in its generalized version in which the origin of repulsion need not be electrostatic.

More recently, Ljunggren and Eriksson⁸ asserted that the curvature-elastic energy of membranes is solely due to electrostatic double layers. Comparing their results for cylindrical and spherical geometry, they distinguished and calculated both elastic moduli. However, their theory is incomplete as they use an ansatz for the bending energy of the monolayer which is strictly linear in $c_1 + c_2$. This should lead to a vanishing bending rigidity also for the bilayer. (They escape this conclusion by overlooking the difference between the monolayers in the number of molecules per unit area of membrane middle surface.) A formula for the energy of the electric double layer of spheres which contains a linear and quadratic term was recently given by Overbeek et al.⁹

In the present note we calculate the electrical contribution to the curvature-elastic energy of membranes in the framework of the Debye-Hückel approximation. Considering plane, cylinder, and sphere, we obtain a nonzero bending rigidity, an elastic modulus of Gaussian curvature, and a spontaneous curvature. The same value of the Gaussian modulus is obtained from the stress profile of the flat membrane. We point out the intricate dependence of the latter modulus on the mechanical properties of the

membrane. The spontaneous curvature associated with asymmetrically charged membranes is also calculated.

The usual starting point to derive the electrostatic potential ϕ within the Debye-Hückel approximation is the linearized Poisson-Boltzmann equation

$$\Delta\phi = \chi^2\phi \quad (2)$$

where Δ is the Laplacian. Because of the symmetries ϕ is a function of the distance from the charged surface only. The quantity

$$\chi = \left(\frac{2n_0 e^2}{\epsilon_w k T} \right)^{1/2} \quad (3)$$

denotes the inverse Debye length. Here n_0 is the density of (monovalent) ions of one sign in the electrolyte far from the membrane, e is the elementary charge, ϵ_w the dielectric constant of water, k Boltzmann's constant, and T temperature.

We assume in the following calculations that the field emanating from the surface charges goes only into the water, thus neglecting any electrical coupling of the monolayers. This simplification is justified for Debye lengths up to $(\epsilon_w/\epsilon_L)d$, where d is the membrane thickness and ϵ_L the dielectric constant of the lipid, e.g., up to 160 nm for $\epsilon_w/\epsilon_L \approx 40$ and $d = 4$ nm. The surface charge density on the inner interface of a curved membrane (sphere or cylinder) at radius $r = a$ is denoted by σ_a and that on the outer one at $r = b$ by σ_b . The charge densities are thought to remain unchanged when the membrane is bent. In other words, the neutral surfaces of the monolayers are taken to coincide with the oil/water interfaces.

The solutions of the linearized Poisson-Boltzmann equation for the three geometries may be found in textbooks.¹⁰ For planar symmetry they are

$$\begin{aligned} \phi^{(\text{in})}(z) &= \frac{\sigma_a}{\epsilon_w} \frac{\exp(-\chi d/2)}{\chi} \exp(\chi z) & \text{for } z \leq -\frac{d}{2} \\ \phi^{(\text{out})}(z) &= \frac{\sigma_b}{\epsilon_w} \frac{\exp(\chi d/2)}{\chi} \exp(-\chi z) & \text{for } z \geq \frac{d}{2} \end{aligned} \quad (4)$$

if we define inside and outside and have the xy plane coincide with the middle surface of the membrane. With cylindrical symmetry one has

$$\begin{aligned} \phi^{(\text{in})}(r) &= \frac{\sigma_a}{\epsilon_w \chi I_1(\chi a)} I_0(\chi r) & \text{for } r \leq a \\ \phi^{(\text{out})}(r) &= \frac{\sigma_b}{\epsilon_w \chi K_1(\chi b)} K_0(\chi r) & \text{for } r \geq b \end{aligned} \quad (5)$$

where r is the radial coordinate and I_i and K_i are the modified

(1) Harbich, W.; Deuling, H. J.; Helfrich, W. *J. Phys. (Paris)* **1977**, *38*, 727.

(2) Deuling, H. J.; Helfrich, W. *J. Phys. (Paris)* **1976**, *37*, 1335.

(3) De Gennes, P. G.; Taupin, C. *J. Phys. Chem.* **1982**, *86*, 2294.

(4) Safran, S. A.; Turkevich, L. A. *Phys. Rev. Lett.* **1983**, *50*, 1930.

(5) Helfrich, W. *Z. Naturforsch.* **1973**, *28C*, 693.

(6) Israelachvili, J. N.; Mitchell, D. J.; Ninham, B. W. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1525.

(7) Helfrich, W., unpublished.

(8) Ljunggren, S.; Eriksson, J. C. *J. Colloid Interface Sci.* **1985**, *107*, 138.

(9) Overbeek, J. T. G.; Verhoeckx, G. J.; De Bruyn, P. L.; Lekkerkerker, H. N. W. *J. Colloid Interface Sci.* **1987**, *119*, 422.

(10) Hunter, R. J. *Foundation of Colloid Science*; Clarendon Press: Oxford, U.K., 1987; Vol. I, p 358.

Bessel functions of i th order. Finally, with spherical symmetry one has

$$\begin{aligned}\phi^{(in)}(r) &= \frac{\sigma_a}{\epsilon_\omega \cosh(\chi a)} \frac{a^2}{(\chi a - 1)} \frac{\sinh(\chi r)}{r} \quad \text{for } r \leq a \\ \phi^{(out)}(r) &= \frac{\sigma_b}{\epsilon_\omega} \frac{b^2}{\exp(\chi b)(1 + \chi b)} \frac{\exp(-\chi r)}{r} \quad \text{for } r \geq b\end{aligned}\quad (6)$$

In the Debye-Hückel approximation the free energy per unit area g of the electrostatic double layer is easily obtained from the potentials and the surface charge. For example, the inner double layer has the energy

$$g^{(in)} = \int_0^{\sigma_a} \phi^{(in)}(a, \sigma) d\sigma = \frac{1}{2} \phi^{(in)}(a, \sigma_a) \sigma_a$$

Denoting by 2δ the difference in surface charges between the inner and outer monolayer, we can write $\sigma_b = \sigma(1 + \delta)$ and $\sigma_a = \sigma(1 - \delta)$. The total electric energy per unit area of membrane is in the case of planar symmetry

$$\begin{aligned}g_{el}^{plane} &= g^{(in)} + g^{(out)} \\ &= \frac{\sigma^2}{\epsilon_\omega \chi} (1 + \delta^2)\end{aligned}\quad (7)$$

In the case of cylindrical geometry we require the central surface of the membrane to conserve its area A_c , which means that the outer monolayer gains as much material as the inner one loses. Keeping only terms up to second order in $1/R$, where R is the radius of the central surface, we obtain for the total energy per unit area of membrane

$$\begin{aligned}g_{el}^{cyl} &= g^{(in)} \frac{A^{(in)}}{A_c} + g^{(out)} \frac{A^{(out)}}{A_c} \\ &= \frac{\sigma^2}{\epsilon_\omega \chi} (1 + \delta^2) \left[1 + \frac{1}{R^2} \left(\frac{3}{8\chi^2} \right) \right] + \frac{\sigma^2}{\epsilon_\omega \chi} \delta \left[\frac{1}{R} \left(d - \frac{1}{\chi} \right) \right]\end{aligned}\quad (8)$$

where $A^{(in)} = A_c(1 - d/(2R))$ and $A^{(out)} = A_c(1 + d/(2R))$ are the areas of the inner and outer interfaces, respectively, and d the thickness of the membrane. We proceed in a similar way in the case of spherical curvature. Assuming again the total membrane surface to be constant yields for spherical surfaces a different partition, the inside area becoming $A^{(in)} = A_c(1 - d/R)$ and the outer one $A^{(out)} = A_c(1 + d/R)$. (This implies a decrease of the central surface area proportional to d^2/R^2 which is irrelevant.) The result is

$$\begin{aligned}g_{el}^{sphere} &= g^{(in)} \frac{A^{(in)}}{A_c} + g^{(out)} \frac{A^{(out)}}{A_c} \\ &= \frac{\sigma^2}{\epsilon_\omega \chi} (1 + \delta^2) \left[1 + \frac{1}{R^2} \left(\frac{1}{\chi^2} - \frac{d}{2\chi} \right) \right] + \frac{\sigma^2}{\epsilon_\omega \chi} \delta \left[\frac{2}{R} \left(d - \frac{1}{\chi} \right) \right]\end{aligned}\quad (9)$$

If the principal curvatures are expressed by the radius R of the cylinder or sphere, eq 1 becomes, for the respective symmetries

$$g_{bend}^{plane} = \frac{1}{2} k_c (c_0)^2 \quad (10)$$

$$g_{bend}^{cyl} = \frac{1}{2} k_c \left(\frac{1}{R} - c_0 \right)^2 \quad (11)$$

$$g_{bend}^{sphere} = \frac{1}{2} k_c \left(\frac{2}{R} - c_0 \right)^2 + \bar{k}_c \frac{1}{R^2} \quad (12)$$

apart from a constant term which is omitted. Adopting these dependences, we obtain from (11) the electric contribution to the bending rigidity

$$k_c^{el} = \frac{\sigma^2(1 + \delta^2)}{\epsilon_\omega \chi} \frac{3}{4\chi^2} \quad (13)$$

and from (11) and (12) that to the modulus of Gaussian curvature

$$\bar{k}_c^{el} = -\frac{\sigma^2(1 + \delta^2)}{\epsilon_\omega \chi} \left(\frac{1}{2\chi^2} + \frac{d}{2\chi} \right) \quad (14)$$

The electric contribution to the spontaneous curvature is found to be

$$c_0^{el} = \delta \frac{4\chi}{3} \frac{(1 - \chi d)}{(1 + \delta^2)} \quad (15)$$

equally from the cylinder and the sphere.

It is interesting to derive \bar{k}_c^{el} by a further completely different method. The modulus of Gaussian curvature has been shown to be the second moment of the stress profile $s(z)$ of the flat membrane;¹¹ i.e.

$$\bar{k}_c = \int s(z) z^2 dz \quad (16)$$

Here $s(z)$ is the three-dimensional stress (normal force per unit area) along a vertical cut through the membrane, z being the coordinate normal to the layer. The relationship is valid if the zeroth and first moments vanish and, therefore, for symmetric membranes at zero lateral tension. In order to calculate the electric contributions we need the Maxwell stresses normal to the z axis

$$T_{xx} = T_{yy} = -\frac{1}{2} \epsilon_\omega E_z^2 \quad (17)$$

and the electric contribution to the osmotic pressure. The latter is calculated from the ion concentrations

$$n_i = n_i^0 \exp(-z_i e \phi / kT)$$

where n_i^0 are the concentrations far from the membrane and z_i the charge numbers of the ions. For a 1:1 electrolyte we have $n_1^0 = n_2^0$ and $z_1 = -z_2$. Expanding the exponential and keeping terms up to second order yields for the electrically induced osmotic pressure

$$\Pi_{osm}^{el} = \frac{1}{2} \chi^2 \epsilon_\omega \phi^2 \quad (18)$$

if the inverse Debye length χ is used to eliminate n_0 . Insertion of the Debye-Hückel potential of the flat membrane, eq 4, shows that the osmotic pressure is equal to the negative Maxwell stress $-T_{xx} = -T_{yy}$.

The integral of the two pressures over z must be balanced by a positive force if the lateral tension of each monolayer is to remain zero. The natural position of this force is at the oil/water interface at $z = \pm d/2$, since the interface was specified in our model as the neutral surface of the monolayer. Accordingly, we may write

$$\bar{k}_c^{el} = 2 \left(\int \Pi_{osm}^{el} z^2 dz - \int \Pi_{osm}^{el} dz (d/2)^2 \right)$$

which, with $z^2 = (z - (d/2))^2 + (z - (d/2))d + (d/2)^2$ for $z > 0$ and the corresponding transformation for $z < 0$, is readily seen to result again in eq 14.

Let us now estimate the electric contribution to the bending rigidity which can be obtained in the range of validity of the Debye-Hückel approximation. The Debye length of very pure water, $\chi^{-1} = 10^{-6}$ m, permits a surface charge density up to about $\sigma = 10^{-5}$ A s m⁻². This is seen by inserting σ into (4) which leads to the surface potential $\phi \approx 0.014$ V and thus $e\phi \approx \frac{1}{2} kT$. Inserting χ and σ into (13) yields $k_c^{el} = 10^{-19}$ J. The maximum surface charge density allowed within the Debye-Hückel approximation is inversely proportional to the Debye length. Inspection of eq 13 for k_c^{el} shows, however, that the increase in surface charge is more than compensated by the decrease of the Debye length. In fact, the maximum k_c^{el} compatible with the Debye-Hückel approximation is proportional to the Debye length. The bending rigidity of lecithin membranes has been measured¹² to be of the order of 10^{-19} J. With the more typical Debye length

(11) Helfrich, W. In *Physics of Defects*; Balian, R., et al., Eds.; North-Holland: Amsterdam, 1981; p 716.

(12) Beblík, G.; Servuss, R. M.; Helfrich, W. *J. Phys. (Paris)* **1985**, *46*, 1773 and references cited therein.

of distilled water, $\chi^{-1} = 10^{-7}$ m, it would be increased by ca. 10% to the maximum allowable surface charge density which is now 10^{-4} A s m⁻². The new limit corresponds to 6×10^{14} elementary charges per m² and to a fraction of 0.036% of singly charged molecules if the molecular cross section is 6×10^{-19} m². The effect of this charge density should be measurable with lecithin membranes and even more so with more flexible bilayers.

The electric part of the bending rigidity does not depend on the membrane thickness d in our approximation which is quadratic in the curvatures. Therefore, it is also independent of the position of the neutral surface of the monolayer. In contrast, the electric contribution to the modulus of Gaussian curvature contains a second term which is proportional to d . We have seen that the position of the neutral surface enters into the derivation of this term. The actual situation is even more complicated than our model since the mechanical force balancing both the pressure due to the Maxwell stresses and the electrical part of the ion gas pressure will be balanced not by a δ -function-like force but by a change of the whole mechanical stress profile similar to that occurring under lateral tension. (This may have an effect on the bending rigidity which we ignore.) The second term dominates for $\chi^{-1} < d$. While this condition is easily satisfied, a strongly negative \bar{k}_c^{el} may be expected only for surface charge densities

far beyond the limit of the Debye-Hückel approximation. It is conceivable that in favorable cases the total energy of a spherical vesicle

$$G_{\text{sphere}} = 8\pi k_c + 4\pi \bar{k}_c$$

also becomes negative. That might result in the spontaneous vesiculation which has been observed with certain membranes when their surface charge density was made very large.^{13,14} Further theoretical work is needed to check and quantify our expectation.

It should also be noted that the quasi one-dimensional Debye-Hückel approximation breaks down for very small surface charge densities, i.e., if the mean spacing of the charged lipid molecules is much larger than the Debye length. We are below this limit for $\sigma = 10^{-4}$ A s m⁻² and $\chi^{-1} = 10^{-7}$ m, but cross it when σ is increased and χ^{-1} decreased by a factor of 10. However, we feel that the use of the quasi-one-dimensional Debye-Hückel approximation is justified as a first step toward understanding the effect of the electrostatic double layer on the curvature elasticity of membranes.

- (13) Hauser, H.; Gains, N.; Müller, M. *Biochemistry* **1983**, 22, 4775.
 (14) Talmon, Y.; Evans, D. F.; Ninham, B. W. *Science* **1983**, 221, 1047.

Ice Ionization from Vibrational Excitation

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The dissociative ionization of cubic ice, induced by 488-nm radiation from a CW argon ion laser, has been monitored through the conversion of intact D₂O molecules isolated in protiated ice films to neighbor-coupled (HOD)₂ units at ~90 K. By coupling the laser beam to the 3- μ m-thick ice films using an interference-enhanced internal-reflection approach, the photon density was sufficiently enhanced that isotopic exchange was extensive after a few hours. The absorption of the blue light, and therefore the dissociative ionization, presumably depends on single-photon excitation of the vibrational overtones of the water molecules as has been reported for liquid water.

The dissociative ionization of pure liquid water induced by single-photon vibrational excitation was first reported over a decade ago¹ and has been the basis for other more recent studies.² The single-photon nature of the ionization was deduced from an observed correlation of the frequency dependence of the ionization efficiency with the features of the overtone spectrum and an observed linear dependence of the effect on the laser beam intensity (1.5–50 MW cm⁻²). Because the quantum efficiency for such ionization tends to increase with increasing photon energy, while the absorption coefficient of water decreases with a similar rate, the extent of induced ionization is *relatively* insensitive to photon energy for frequencies ranging from 10 000 to 20 000 cm⁻¹. A similar single-photon-induced ionization of ice has been anticipated but several attempts to observe this phenomenon in *pure* ice at wavelengths greater than 200 nm have been unsuccessful.³ However, in this Letter we report conclusive evidence for the dissociative ionization of ice for a single frequency, namely the

20 050 cm⁻¹ (488 nm) radiation of a CW argon ion laser.

The successful observation of vibrationally induced ionization of ice has depended on (a) the availability of a sensitive probe of the presence of nonthermal mobile protons in ice, and (b) the generation of exceptionally large CW electric field intensities within the ice samples. A sensitive probe that measures integrated proton activity for unlimited time periods is available from recent studies of ionic defect activities in cubic ice.^{4–6} These studies have been based on (a) the growth of thin films of cubic ice containing ~2% intact D₂O using vapor-beam epitaxial cocondensation techniques at 125 K and (b) the recognition that proton hopping converts D₂O molecules into (HOD)₂ units while the subsequent conversion to isolated HOD molecules requires the passage of mobile Bjerrum defects. Since there are no thermally generated mobile protons or Bjerrum defects in *pure* ice at temperatures below 130 K, D₂O remains intact indefinitely in H₂O-ice films.⁴ However, mobile protons, generated by using either high-energy electrons or UV radiation, convert isolated D₂O molecules to (HOD)₂ units, which accumulate to an equilibrium saturation limit for temperatures less than 130 K.^{5,6} Since the vibrational spectra of isolated D₂O, (HOD)₂ and isolated HOD are known, the

(1) (a) Goodall, D. M.; Greenhow, R. C. *Chem. Phys. Lett.* **1971**, 9, 583.
 (b) Knight, B.; Goodall, D. M.; Greenhow, R. C. *J. Chem. Soc., Faraday Trans. 1* **1979**, 75, 841.

(2) (a) Natze, W. C.; Moore, C. B.; Goodall, D. M.; Frisch, W.; Holzwarth, J. F. *J. Phys. Chem.* **1981**, 85, 2882. (b) Natze, W. C.; Moore, C. B. *J. Phys. Chem.* **1985**, 89, 2605.

(3) This comment reflects negative results from this laboratory as well as information communicated privately by V. F. Petrenko of the Institute of Solid State Physics, Academy of Sciences of the USSR.

(4) Collier, W. B.; Ritzhaupt, G.; Devlin, J. P. *J. Phys. Chem.* **1984**, 88, 363.

(5) Devlin, J. P.; Richardson, H. H. *J. Chem. Phys.* **1984**, 81, 3250.

(6) Wooldridge, P. J.; Devlin, J. P. *J. Chem. Phys.* **1988**, 88, 3086.