



HAL
open science

Stability of charged membranes

D. Bensimon, F. David, S. Leibler, A. Pumir

► **To cite this version:**

D. Bensimon, F. David, S. Leibler, A. Pumir. Stability of charged membranes. *Journal de Physique*, 1990, 51 (8), pp.689-695. 10.1051/jphys:01990005108068900 . jpa-00212399

HAL Id: jpa-00212399

<https://hal.science/jpa-00212399>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

LE JOURNAL DE PHYSIQUE

J. Phys. France 51 (1990) 689–695

15 AVRIL 1990, PAGE 689

Classification
Physics Abstracts
87.10-87.20E

Short Communication

Stability of charged membranes

D. Bensimon⁽¹⁾, F. David⁽²⁾, S. Leibler⁽²⁾ and A. Pumir⁽¹⁾

⁽¹⁾ Laboratoire de Physique Statique, ENS, 24 rue Lhomond, Paris 75005, France

⁽²⁾ Service de Physique Théorique, CEN Saclay, 91191 Gif/Yvette Cedex, France

(Reçu le 18 janvier 1990, accepté le 9 février 1990)

Résumé. — La contribution électrostatique au module d'élasticité est calculée pour une bicouche phospholipide chargée en milieu ionique. Cette contribution, identique pour une membrane conductrice comme isolante, est toujours stabilisante. On montre que cette stabilité des membranes libres est une conséquence de l'absence de tension superficielles.

Abstract. — The electrostatic contribution to the bending elastic modulus of charged phospholipid bilayers in an ionic solution is computed. It is found to be the same for conducting and non-conducting membranes and is always stabilizing. This stability for free membranes is shown to be a simple consequence of the vanishing of the physical surface tension.

1. Introduction.

The physical properties and stability of phospholipid bilayers and the objects they form (cells and vesicles) is an important problem in biology and pharmacology. Various aspects of these properties have been studied over the years and some are by now well established, in particular the Van der Waals and electrostatic intermembrane forces which form the basis of the DLVO theory[1].

An artificial membrane consists of a bilayer of phospholipid molecules with a polar head (which may be charged) in contact with the aqueous medium and two hydrophobic tails which form the bulk of it. In absence of external stresses (e.g. osmotic pressures, film tension, etc.) the area per head of phospholipid molecules in a fluid membrane is optimized, i.e. the free energy is minimized [2, 3]. That results from a balance between hydrophilic and entropic interactions which

tend to increase the area per head and the hydrophobic interactions between the lipidic chains and the water which tend to reduce it. If the compressibility of the membrane is low the area per head will be fixed at this optimal value and does not fluctuate much. In the following we suppose that the compressibility is strictly zero; the total area of the membrane is thus fixed and the free energy \mathcal{F} is then essentially of elastic origin [4 – 6]:

$$\mathcal{F}_b = \frac{1}{2}\kappa \int dS \left(\frac{1}{R_1} + \frac{1}{R_2} - \frac{1}{R_0} \right)^2 + \bar{\kappa} \int dS \frac{1}{R_1 R_2} \quad (1)$$

Where R_1, R_2 are the principal radii of curvature, R_0 a possible spontaneous curvature and $\kappa, \bar{\kappa}$ the normal and Gaussian bending elastic moduli.

In the following, we will investigate the stability of a membrane with surface charge density σ_0 in an ionic solution characterized by a Debye screening length given by χ^{-1} . We shall be interested mostly in the long wavelength limit ($\chi \gg k = 2\pi/\lambda$), where the electrostatic contribution to the free energy amounts to a modification of some *local parameters*, such as the elastic moduli. In that limit the only relevant lengthscale is χ^{-1} and since κ and $\bar{\kappa}$ have units of energy (typically: $\kappa \approx 10^{-19}$ J [7 – 12]), by straightforward dimensional analysis [13] the electrostatic contribution to the elastic modulus κ is $\delta\kappa = C\sigma_0^2/\chi^3\epsilon$ with C a constant of $O(1)$ and ϵ the dielectric constant of the solution. There are two reasons one may want to go beyond this simple estimation. First, there are now some rather accurate measurements [7 – 12] of the bending rigidity, κ , for phospholipid membranes and it therefore becomes possible to make precise measurements of the electrostatic contribution to κ for charged phospholipid bilayers. The surface charge density can be controlled by changing the *pH* (which determines the degree of dissociation of the polar groups) and the Debye screening length by changing the ionic concentration. The second reason is to determine the *sign* of $\delta\kappa$. If it is positive the membrane is rigidified, but if it is negative the membrane may be destabilized at long wavelengths by the electrostatic interactions.

In the following we shall consider two cases: membranes for which the in-plane conductivity of charges is much smaller than the conductivity of charges through the solution (non-conducting or insulating membranes), or membranes for which the in-plane conductivity is much larger than the bulk ionic conductivity of the solution (conducting membranes). For insulating membranes the local charge is constant during a deformation, whereas for conducting membranes it is the surface potential (and possibly the total charge) which is constant during the deformation. For insulating membranes one expects a bending deformation to increase the free energy of the membrane and thus the sign of $\delta\kappa$ is expected to be positive: the membrane is rigidified by the electrostatic interactions. For a conducting membrane, however one may expect the existence of an electrostatic instability similar to the electrostatic instability of a charged surface [14]. This is however *not* the case, as the full calculation (to be described below) shows. In fact charged insulating and conducting membranes have identical *positive* $\delta\kappa$!

2. Electrostatic contribution to the free energy of a membrane.

Consider a charged infinite membrane of thickness d in contact with an ionic solution characterized by a Debye screening length: χ^{-1} . For conducting membranes and for insulating ones with equal charges on both sides, we may without loss of generality consider the limiting case: $d = 0$. We suppose that the electric fields ϕ_{\pm} on both sides of the membrane (+ above and – below) satisfy the Poisson-Boltzmann equation, or its linearized version: the Debye-Hückel equation [1] (for potentials: $\phi_{\pm} < k_B T/e \approx 25$ mV)

$$\nabla^2 \phi_{\pm} = \chi^2 \phi_{\pm} \quad (2)$$

For a monovalent solution of ionic concentration n_0 the screening length is given by: $\chi^2 = 8\pi n_0 e^2 / k_B T \epsilon W$, where ϵW is the relative dielectric constant of water ($\epsilon W \approx 80$). We shall consider two types of boundary conditions. If the membrane is insulating and incompressible with a constant surface charge density σ_0 , the fields on the membrane have to satisfy Gauss'law

$$\vec{\nabla}\phi_- - \vec{\nabla}\phi_+ = \frac{4\pi\sigma'_0}{\epsilon W} \mathbf{n} \tag{3a}$$

where \mathbf{n} is the normal to the interface. If the membrane is conducting its surface is an equipotential:

$$\phi_- = \phi_+ = \phi_0, \quad \text{on the surface of the membrane} \tag{3b}$$

Let $\zeta(x, y)$ be a small deformation of a flat membrane. Our purpose is to calculate the *net* change in the *free energy* $\delta\mathcal{F}$ of the membrane as a result of this deformation. The procedure is straightforward:

- 1) Solve perturbatively equations (2, 3) for the field ϕ_{\pm} up to $O(\zeta^3)$.
- 2) Compute the electrostatic energy[16]:

$$\mathcal{E} = \frac{\epsilon W}{8\pi} \int d^3\mathbf{r} \left| \vec{\nabla}\phi_{\pm} \right|^2 \tag{4}$$

And identify the change $\delta\mathcal{E}$ in the electrostatic energy due to the deformation.

3) Keeping the surface charge or the membrane potential constant (depending on the case considered) compute the electrostatic contribution to the *free energy* \mathcal{F}_e by integrating the thermodynamic relation[4, 17]:

$$\mathcal{E} = -T^2 \left(\frac{\partial \mathcal{F}_e}{\partial T} \right) \equiv \frac{\partial}{\partial \beta} (\beta \mathcal{F}_e), \quad \beta \equiv 1/k_B T \tag{5}$$

2.1 NON-CONDUCTING MEMBRANES. — Let $\zeta(x, y)$ be a small ($O(\epsilon)$) deformation of a flat membrane (Eq. $(x, y, z = \zeta(x, y))$) and $\zeta(k_x, k_y)$ its Fourier transform:

$$\zeta(x, y) = \int d^2k \bar{\zeta}(k_x, k_y) e^{i\mathbf{k} \cdot \boldsymbol{\rho}}, \quad \boldsymbol{\rho} \equiv (x, y) \tag{6}$$

We look for a perturbative solution of equation(2):

$$\begin{aligned} \phi_{\pm}(x, y, z) &= \phi_{\pm}^{(0)}(x, y, z) + \epsilon \phi_{\pm}^{(1)}(x, y, z) + \epsilon^2 \phi_{\pm}^{(2)}(x, y, z) + \dots \\ \phi_{\pm}^{(n)}(x, y, z) &= \int d^2k \tilde{\phi}_{\pm}^{(n)}(k_x, k_y) e^{i\mathbf{k} \cdot \boldsymbol{\rho} \pm qz}, \quad q^2 = \chi^2 + k^2 \end{aligned} \tag{7}$$

Inserting equations (6, 7) into the boundary condition equation (3a) and solving the resulting algebraic equations order by order in ϵ up to $O(\epsilon^3)$ yields:

$$\phi_{\pm}(x, y, z) = \frac{2\pi\sigma_0}{\epsilon W \chi} \left[e^{\mp \chi z} \pm \chi \int d^2k \left(\tilde{\zeta}_{\mathbf{k}} \pm \frac{\tilde{\psi}}{q} \right) e^{i\mathbf{k} \cdot \boldsymbol{\rho} \mp qz} \right] + O(\epsilon^3) \tag{8}$$

Where $\tilde{\psi}(k_x, k_y)$ is the Fourier transform of $\psi(x, y) = \chi^2 \zeta^2 / 2 - (\vec{\nabla} \zeta)^2 / 2 - \zeta \nabla^2 \zeta$. We may now compute the electrostatic energy \mathcal{E} , equation (4):

$$\begin{aligned} \mathcal{E} &= \frac{\varepsilon W}{8\pi} \int d^3 r \left| \vec{\nabla} \phi_{\pm} \right|^2 \\ &= \frac{\varepsilon W}{8\pi} \int d^2 \rho \left[\int_{-\infty}^{\zeta} dz \left| \vec{\nabla} \phi_{-} \right|^2 + \int_{\zeta}^{\infty} dz \left| \vec{\nabla} \phi_{+} \right|^2 \right] \\ &= \frac{\pi \sigma_0^2}{2\varepsilon W \chi} \int d^2 k \left[1 + (3\chi^2 - 3\chi q + \chi k^2 q^{-1} + k^2) \tilde{\zeta} k \tilde{\zeta} - k \right] \end{aligned} \quad (9)$$

In the case of a surface in contact with an electrolytic solution ($\chi \neq 0$), part of the electrostatic energy is “used” to lower the entropy of the solution by partially segregating the ions within the Debye screening layer. The relevant thermodynamic quantity is the *free energy* \mathcal{F}_e , equation (5), which is obtained by integrating equation (9):

$$\begin{aligned} \mathcal{F}_e &= \frac{1}{\beta} \int \mathcal{E} d\beta = \frac{1}{\chi^2} \int \mathcal{E} d\chi^2 \\ &= \frac{\pi \sigma_0^2}{\varepsilon W \chi} \int d^2 k \left(1 + \frac{1}{2} k^2 \tilde{\zeta} k \tilde{\zeta} - k \right) \\ &\quad + \frac{\pi \sigma_0^2 \chi}{\varepsilon W} \int d^2 k \left(1 + \frac{1}{2} (k/\chi)^2 - \sqrt{1 + (k/\chi)^2} \right) \tilde{\zeta} k \tilde{\zeta} - k \end{aligned} \quad (10)$$

Where we have used: $\chi^2 = (8\pi n_0 e^2 / \varepsilon W) \beta$.

2.2 CONDUCTING MEMBRANES — The case of conducting membranes held at constant potential ϕ_0 (or which total charge Q is constant) is similar to the case of insulating membranes treated previously. Inserting equations (6, 7) into the relevant boundary condition, equation (3b), yields:

$$\phi_{\pm}(x, y, z) = \phi_0 \left[e^{\mp \chi z} \pm \chi \int d^2 k \left(\tilde{\zeta} \pm \tilde{\psi} \right) e^{i\mathbf{k} \cdot \boldsymbol{\rho} \mp qz} \right] + O(\zeta^3) \quad (11)$$

Where $\tilde{\psi}(k_x, k_y)$ is the Fourier transform of $\psi(x, y) = -\chi \zeta^2 / 2 + \zeta \int d^2 k q \zeta_k e^{i\mathbf{k} \cdot \boldsymbol{\rho}}$. For a membrane held at a constant potential ϕ_0 (by patch clamp techniques, for example), the electrostatic energy is:

$$\mathcal{E} = \frac{\varepsilon W}{8\pi} \int d^3 r \left| \vec{\nabla} \phi_{\pm} \right|^2 - \phi_0 \int d^2 \rho \sigma \quad (12)$$

The second term represents the work done in order to keep the potential of the membrane constant [16], i.e. in order to bring a charge $Q = \int \sigma d^2 \rho$ from a “reservoir” at potential ϕ_0 . Using equation (11) in equation (12) one obtains:

$$\mathcal{E} = \frac{\varepsilon W \phi_0^2 \chi}{8\pi} \int d^2 k \left[-3 + (5\chi^2 - 5\chi q + \chi k^2 q^{-1}) \tilde{\zeta} k \tilde{\zeta} - k \right] \quad (13)$$

Let us note that in the limit $\chi \mapsto 0$ and $\sigma_0 = \varepsilon W \chi \phi_0 / 2\pi = \text{const.}$, we recover the result for the instability of a free charged conducting surface [14]:

$$\delta \mathcal{E} = -2 \frac{\pi \sigma_0^2}{\varepsilon W} \int d^2 k |k| \tilde{\zeta} k \tilde{\zeta} - k \quad (14)$$

In the case of electrolytic solutions $\chi \neq 0$, the free energy \mathcal{F}_e becomes:

$$\mathcal{F}_e = -\frac{\epsilon W \phi_0^2 \chi}{4\pi} \int d^2k \left(1 + \frac{1}{2} k^2 \tilde{\zeta}_k \tilde{\zeta}_{-k} \right) + \frac{\epsilon W \phi_0^2 \chi^3}{4\pi} \int d^2k \left(1 + \frac{1}{2} (k/\chi)^2 - \sqrt{1 + (k/\chi)^2} \right) \tilde{\zeta}_k \tilde{\zeta}_{-k} \tag{15}$$

3. Vanishing surface tension and stability of the membrane.

The k^2 terms present in equation (15) has a negative sign. This may naively suggest that the conducting charged membrane is unstable with respect to long-wavelength modes (in opposite to the insulating case, in which the k^2 term, Eq.(10), is positive). On the other hand the k^2 term is usually associated with the *surface tension* which, as we have mentioned in the introduction, is strictly zero for the free membrane. It is therefore necessary to reconsider the significance of the vanishing of the surface tension and its consequences in our problem.

The size of a fluctuating membrane can be in general described by two *distinct* variables: the total area A and the “projected” area A_p , i.e. the area of the projection of the membrane on the plane (x, y) . Whereas for the incompressible membrane, whose number of molecules does not vary, the total area A is *constant*, this is not the case for A_p . Indeed, for the *free* membrane there is no constraint on the value of A_p and it fluctuates around its mean value $\langle A_p \rangle$. As a consequence the intensive thermodynamical variable coupled to A_p - the physical surface tension r - vanishes identically [18]:

$$r = \left. \frac{\mathcal{F}}{A_p} \right|_{A_p = \langle A_p \rangle} = 0 \tag{16}$$

Here \mathcal{F} is the *total* free energy of the membrane, which is the sum of the three contributions: (i) the elastic energy (1), (ii) the electrostatic term (10) or (15) and (iii) the chemical potential term for the total area A :

$$\mathcal{F}_A = r_0 \int d^2S = r_0 \int d^2k \left(1 + \frac{1}{2} k^2 \tilde{\zeta}_k \tilde{\zeta}_{-k} + \dots \right). \tag{17}$$

r_0 is the chemical potential of the amphiphilic molecules. We have thus

$$\mathcal{F} = r \int d^2k \left(1 + \frac{1}{2} k^2 \tilde{\zeta}_k \tilde{\zeta}_{-k} \right) \times \int d^2k \left(\frac{\kappa}{2} k^4 + \frac{\epsilon W \phi_0^2 \chi^3}{4\pi} \left(1 + \frac{1}{2} \left(\frac{k}{\chi} \right)^2 - \sqrt{1 + (k/\chi)^2} \right) \right) \tilde{\zeta}_k \tilde{\zeta}_{-k} \tag{18}$$

where

$$r = r_0 - \frac{\epsilon \phi_0^2 \chi}{4\pi} \quad \text{for conducting membranes}$$

$$r_0 + \frac{\epsilon \phi_0^2 \chi}{4\pi} \quad \text{for insulating membranes}$$

Since we consider in this paper the case of free, unconstrained, membranes, the coefficient r_0 adjust itself so that equation (16) is satisfied. However, this also implies that the k^2 term in

equation (18) identically vanishes! Therefore there is *no instability* and the lowest term which contributes to the free energy of the charged membrane is the last term of equation (18). It is the *same* both for conducting and insulating membranes and is always positive.

The k^4 term gives the effective rigidity of the charged membrane κ_{eff} . It can thus be written as

$$\kappa_{\text{eff}} = \kappa + \delta\kappa \quad (19)$$

where

$$\begin{aligned} \delta\kappa &= \frac{\varepsilon_w \phi_0^2}{16\pi\chi} \\ &= \frac{\varepsilon_w \phi_0^2}{4\chi} \quad (\text{SI units}) \end{aligned} \quad (20)$$

where $\varepsilon_w \approx 7 \times 10^{-10}$ F/m is the dielectric constant of water.

Thus both insulating and conducting membranes are rigidified by electrostatic interactions. Our results equation (20) are in agreement, in the long wavelength limit, with a similar and independent perturbative analysis of reference [19] for conducting membranes, but they disagree with calculations of $\delta\kappa$ for the nonconducting case of reference [20]. We believe that the discrepancy is related to the fact that in reference [20] the membrane has a finite thickness and a much smaller attenuation length inside the membrane, so that the electric potentials on both sides of the membrane are decoupled. It is not clear to us whether such an assumption is valid for purely dielectric medium. We have checked that the procedure of reference [20], based on the comparison of the electrostatic energies per unit area for a charged sphere, a charged cylinder and an infinite plane, leads, both for insulating and conducting membranes, to the same results for the electrostatic contribution to the bending modulus of elasticity κ than our perturbative analysis.⁽¹⁾ It allows also to assess the electrostatic contribution to the Gaussian modulus of elasticity $\bar{\kappa}$ which is opposite to $\delta\kappa$.

4. discussion

Our result, equation (20), is only valid within the Debye-Hückel approximation, i.e. for values of the membrane potential $\phi_0 < 25$ mV. Since the values of the Debye screening length χ^{-1} vary between 10^{-6} m in pure water ($n_0 = 10^{-7}$ M) and 10^{-9} m in physiological conditions ($n_0 \approx 0.1$ M), for $\phi_0 \sim 10$ mV, $\delta\kappa$ may vary between 0.2×10^{-19} J in pure water (where it should be measurable) and 2×10^{-23} J in physiological conditions, where it is thus not expected to be relevant. We also remark that the “bare” electrostatic contribution to the surface tension (the coefficient of the first term in equation (15): $\delta\gamma = -\varepsilon_w \chi \phi_0^2$) is always very small ($7 \times 10^{-8} \leq -\delta\gamma \leq 7 \times 10^{-5}$ N/m). To measure $\delta\kappa$ one could extend the work of Safinya *et al* [11] to charged phospholipids (e.g. DMPG). In such a system by controlling the concentration of surfactants and ions, one should be able to achieve a situation where $\delta\kappa > \kappa$, i.e. where the electrostatic contribution to the bending rigidity is dominant.

⁽¹⁾ *Note added in proof:* This corrects a statement made in a preprint version of this letter. These results were independently found by several authors. See: P. Higgs and J.-F. Joanny (private communication); B. Duplantier, R.E. Goldstein, A.T. Pesci and V. Romero-Rochin (in preparation), B. Duplantier (Saclay preprint). See also D. Andelman, J.-F. Joanny and P. Pincus (to be published).

Acknowledgements.

We would like to acknowledge R.E. Goldstein and F.I.B. Williams for useful discussions. The work of D.B. was supported in part by the DRET under contract no.89/1327. D.B. acknowledges B. Duplantier for useful discussions.

References

- [1] ISRAELACHVILI J.N., Intermolecular and Surface Forces (Academic Press) 1985.
- [2] SCHULMAN J.H. and MONTAGNE J.B., *Ann. N.Y. Acad. Sci.* **92** (1961) 366.
- [3] BROCHARD F., de GENNES P.G. and PFEUTY P., *J. Phys. France* **37** (1976) 1099.
- [4] CANHAM P.B., *J. Theor. J. Biol.* **26** (1970) 61.
- [5] LANDAU L. and LIFCHITS E., Theory of Elasticity, (Pergamon) 1970.
- [6] HELFRICH W., *Z. Naturforsch.* **28c** (1973) 93.
- [7] SERVUSS R.M., HARBICH W. and HELFRICH W., *Biochim. Biophys. Acta* **436** (1976) 900.
- [8] EVANS E.A., *Biophys. J.* **43** (1983) 27.
- [9] SCHNEIDER M.B., JENKINS M.B. and WEBB W.W., *Biophys. J.* **45** (1984) 891; *J. Phys. France* **45** (1985) 1457.
- [10] BIVAS I., HANUSSE P., BOTHOREL P., LALANNE J. and AGUERRE-CLARIOL O., *J. Phys. France* **48** (1987) 855.
- [11] SAFINYA C.R., SIROTA E.B., ROUX D. and SMITH G.S., *Phys. Rev. Lett.* **62** (1989) 1134.
- [12] ZILKER A., ENGELHARDT H. and SACKMANN E., *J. Phys. France* **48** (1987) 2139.
- [13] KANTOR Y. and KARDAR M., *Europhys. Lett.* **9** (1989) 53.
- [14] SHIKIN V.B. and LEIDERER P., *Sov. Phys. JETP* **54** (1981) 92.
- [15] We do not consider here the influence of thermal fluctuations on the elastic constants κ and $\bar{\kappa}$. See for example, PELITI L. and LEIBLER S., *Phys. Rev. Lett.* **54** (1985) 1690.
- [16] LANDAU L. and LIFCHITZ E., *Electrodynamics of Continuous Media*, (Pergamon).
- [17] JAHNIG F., *Biophys. Chem.* **4** (1976) 309.
- [18] DAVID F. and LEIBLER S., in preparation.
- [19] GOLDSTEIN R.E., PESCI A.I. and Romero-Rochin V., preprint (1989).
- [20] WINTERHALTER M. and HELFRICH W., *J. Phys. Chem.* **92** (1988) 6865
MITCHELL D.J. and NIHAM B.W., *LANGMUIR* **5** (1989) 1121
LEKKERKERKER H.N.W., *Physica A* **159** (1989) 319
KIOMETZIS M. and KLEINERT H., *Phys. Lett.* **A140** (1989) 520.