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## To cite this version:

B. Simons. Stability of dipolar fluid membranes. Journal de Physique II, 1992, 2 (5), pp.1141-1148. 10.1051/jp2:1992192 . jpa-00247698

*J. Phys. II France* **2** (1992) 1141-1148 MAY **1992**, PAGE 1141

Classification
*Physics Abstracts*
68.10—87.10—02.40

# Stability of dipolar fluid membranes

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*(Received 29 October 1991, accepted 20 January 1992)*

**Abstract.** — We determine the electrostatic contribution to the elastic bending moduli of an insulating fluid membrane composed of either permanent, or field induced dipoles oriented along the normal directors of the surface. Using Debye-Hückel screening theory, we show that in contrast to the uniformly charged membrane the bending rigidity becomes softened by the electrostatic interaction.

## 1. Introduction.

Internal degrees of freedom can have a striking effect on the fluctuations of two-dimensional fluid membranes. Amongst cases recently studied include membranes with internal order parameters of both scalar [1-3], such as with concentration fluctuations, and vector degrees of freedom, such as molecular orientation [4].

In this paper we investigate the influence of dipolar interactions on the fluctuation of insulating fluid membranes immersed in an ionic solution. Existing theories of uniformly charged membranes suggest a stabilisation associated with an increase in the modulus of rigidity [5-8]. In contrast, we demonstrate that dipolar interactions can lead to a softening of the membrane rigidity which can ultimately cause the persistence length of the membrane to vanish. Restricting attention to moments oriented normal to the surface, we examine membranes in the presence of both permanent and field induced dipoles. The electrostatic interaction, screened by the surrounding solution, favours a locally curved orientation of the host membrane in which neighbouring dipoles are no longer parallel. This competes with the elastic bending energy, which favours a flat orientation, and serves to diminish the effective mean bending modulus.

Permanent dipoles can arise either by the constituent molecules possessing an intrinsic dipole moment, or by the existence of a potential difference across an insulating membrane. In the case of monolayers, it is reasonable to suppose that the asymmetry is capable of supporting an intrinsic molecular dipole moment that acts across the membrane. For bilayers of a single component only intrinsic quadrupoles appear feasible. However molecular asymmetry in two component bilayers do allow for the existence of permanent dipole moments. (Even in single component bilayers dipolar effects may become important if the screening length becomes comparable with the membrane thickness.) Finally, the application of a potential difference across an insulating membrane can be used to induce dipole moments across bilayers and monolayers. Indeed, biological systems contain numerous examples of membranes, such as neural axons, which display a potential difference of as much as 100 mV [9].

The free energy of an ideal fluid membrane without dipoles is dominated by the elastic bend energy [10, 11],

$$\mathcal{F}_{\mathrm{B}} = \int \mathrm{d}S \left[\frac{\kappa}{2}\,(\mathrm{Tr}\ \mathbf{K})^2 + \bar{\kappa}\ \det \mathbf{K}\right], \tag{1.1}$$

where $\kappa$ and $\bar{\kappa}$ denote the mean and Gaussian elastic moduli respectively, and the integral is performed over the entire two-dimensional surface of the membrane. Positions on the membrane are specified by a vector $\mathbf{X}(\sigma)$, with $\sigma$ denoting the parametric coordinates of the surface. The curvature tensor is related to the surface tangent vectors at $\sigma$, $\boldsymbol{\epsilon}_\alpha = \partial_\alpha \mathbf{X}$ by $K_{\alpha\beta} = \mathbf{n}\cdot\partial_\alpha \boldsymbol{\epsilon}_\beta$ with $\mathbf{n}$ denoting the outward pointing director of the surface, and where we have used the notation, $\partial_\alpha \equiv \partial/\partial\sigma^\alpha$. Finally, the element of surface area is given by, $\mathrm{d}S = \mathrm{d}\sigma^1 \mathrm{d}\sigma^2 \sqrt{\det \mathrm{g}}$ where the metric $g_{\alpha\beta} = \boldsymbol{\epsilon}_\alpha \cdot \boldsymbol{\epsilon}_\beta$. For simplicity we have assumed a membrane with zero spontaneous curvature.

The contribution of the electrostatic energy to the free energy of the membrane, $\mathcal{F}_{\mathrm{E}}$ can be determined from the thermodynamic relation [10, 12],

$$\mathcal{E} = \frac{\partial}{\partial\beta}(\beta\mathcal{F}_{\mathrm{E}}), \tag{1.2}$$

where $\mathcal{E}$ denotes the electrostatic field energy, $\beta = 1/kT$.

Throughout, we will suppose that the compressibility of the membrane is zero and that the area remains fixed. To sensibly compare the elastic bending energy with electrostatic energies it is necessary to compare the free energy *per unit area*. In this way we can formally eliminate the chemical potential of total area. However, in section 3, the breaking of symmetry by an external electric field requires the introduction of a "chemical potential of projected area [7]".

## 2. Permanent dipoles.

For fluid membranes composed of rod-like molecules, it is natural to suppose that permanent electric dipole moments are directed along the central axis of the molecule and parallel to the normal directors of the surface. For simplicity we will suppose the "dipole layer" to be ideal in having a negligible thickness whilst maintaining a finite dipole moment. In this way, we neglect the dielectric properties of the membrane itself as well as the position of the neutral surface with respect to the dipole layer. The ionic solution that surrounds the membrane screens the electrostatic interaction of the dipoles. The electric field on each side of the membrane is assumed to satisfy the linearised version of the Poisson-Boltzman equation, the Debye-Hückel equation,

$$\nabla^2\phi = \lambda^2\phi, \tag{2.1}$$

where $\lambda^{-1}$ denotes the Debye screening length.

In general, the solvents that surround the membrane will have different dielectric and screening properties. For simplicity we will suppose that both the screening length and dielectric constant are uniform above and below the membrane, as would be the case for bilayers. (A more careful investigation which accounts for the asymmetry would yield contributions to the electrostatic energy which are dependent on the spontaneous curvature.) For a monovalent solution of ionic concentration, $n_0$ with a dielectric constant $\epsilon = \epsilon_r \epsilon_0$, the screening length is determined by $\lambda^2 = 8\pi n_0 e^2/\epsilon kT$. For an isolated dipole of strength, $\mathbf{p}$ at position, $\mathbf{X} = 0$ the screened potential is given by,

$$\phi_d(\mathbf{r}) = \frac{1}{4\pi\epsilon} \frac{\mathbf{p}\cdot\mathbf{r}}{r^3} \exp[-\lambda r]. \tag{2.2}$$

The regime in which the linear approximation is valid can be estimated by requiring that the potential in the vicinity of the surface remains smaller than $kT/e$. This translates to the condition that $p \lesssim kT\epsilon/e$ giving an upper bound to the surface dipole density in aqueous solution ($\epsilon_r = 80$) of $p \sim 0.1\ \mathrm{D}/\text{Å}^2$. Above this dipole density the linear approximation of the Poisson-Boltzmann equation becomes unreliable.

The electrostatic energy of a surface of dipoles is given by,

$$\mathcal{E}_{\mathrm{d-d}} = \frac{1}{8\pi\epsilon} \int \mathrm{d}S\, \mathrm{d}S' \frac{\mathrm{e}^{-\lambda r}}{r^3} \left[\mathbf{p}\cdot\mathbf{p}' - \frac{3+\lambda r}{r^2} (\mathbf{p}\cdot\mathbf{r})\,(\mathbf{p}'\cdot\mathbf{r})\right], \tag{2.3}$$

where $\mathbf{r} = \mathbf{X}' - \mathbf{X}$, and the dipole surface density, $\mathbf{p} = p\,\mathbf{n}$, with $p$ uniform. As usual, the convergence of the integral is assured by a minimum wavelength cut-off at the length scale of the solvent size $a$. Moreover, the dipole-dipole interaction is made short-ranged by the screening enabling a controlled expansion of the electrostatic energy in powers of the curvature.

A comparison of the electrostatic energy with the elastic free energy of the membrane requires an expansion up to second order in the gradients of the deformation. The integration over the primed coordinates is performed with respect to each position vector $\mathbf{X}(\boldsymbol{\sigma})$ using the representation of the relative coordinates, $\mathbf{r}(\boldsymbol{\rho}) = (\rho_1, \rho_2, f(\boldsymbol{\rho}))$, where $\boldsymbol{\rho}$ denotes the relative parametric coordinate of the surface. It is convenient to work in the metric of the tangent plane at each $\mathbf{X}(\boldsymbol{\sigma})$, for which $g_{\alpha\beta}(\boldsymbol{\sigma}) = \delta_{\alpha\beta}$, and where both $\partial_\alpha f|_{\boldsymbol{\sigma}}$ and the affine connection, $\Gamma^\delta_{\alpha\gamma} = \boldsymbol{\epsilon}_\delta \cdot \partial_\alpha \boldsymbol{\epsilon}_\gamma$ vanish. Applying these conditions together with the identities,

$$\begin{aligned} \partial_\alpha \mathbf{n} &= K_{\alpha\beta} \boldsymbol{\epsilon}^\beta, \\ \partial_\alpha \partial_\beta \mathbf{n} &= \left(\partial_\alpha K^\delta_\beta + \Gamma^\delta_{\alpha\gamma} K^\gamma_\beta\right) \boldsymbol{\epsilon}_\delta + K_{\alpha\gamma}\ K^\gamma_\beta \mathbf{n}, \end{aligned} \tag{2.4}$$

which imply the following expansions about $\mathbf{X}(\boldsymbol{\sigma})$,

$$\begin{aligned} \mathbf{n}' &= (1 - \frac{1}{2}\rho^\alpha \rho^\beta K_{\alpha\gamma}\ K^\gamma_\beta)\,\mathbf{n} + (\rho^\alpha K^\gamma_\alpha + \frac{1}{2}\rho^\alpha\rho^\beta \partial_\alpha K^\gamma_\beta)\ \boldsymbol{\epsilon}_\gamma + \mathcal{O}(\rho^3), \\ \mathbf{r} &= \rho^\alpha \boldsymbol{\epsilon}_\alpha + \frac{1}{2}\rho^\alpha \rho^\beta\ K_{\alpha\beta}\mathbf{n}, \\ g'_{\alpha\beta} &= \delta_{\alpha\beta} + \rho^\gamma\ \rho^\delta\ K_{\gamma\alpha}\ K_{\delta\beta} + \mathcal{O}(\rho^3), \end{aligned} \tag{2.5}$$

we obtain the following expression for the electrostatic energy,

$$\mathcal{E}_{\mathrm{d-d}} = \frac{p^2}{8\pi\epsilon} \int \mathrm{d}S \int \mathrm{d}\rho_1 \mathrm{d}\rho_2\, \frac{\mathrm{e}^{-\lambda|\boldsymbol{\rho}|}}{|\boldsymbol{\rho}|^3} \left[1 - \frac{7}{8|\boldsymbol{\rho}|^2}(3 + \lambda|\boldsymbol{\rho}|)\ \rho^\alpha \rho^\beta \rho^\gamma \rho^\delta\ K_{\alpha\beta}\ K_{\gamma\delta}\right]. \tag{2.6}$$

At this level of approximation the integration over the relative coordinates can be performed when we find,

$$\mathcal{E}_{\mathrm{d-d}} = \frac{p^2}{4\epsilon}\Big[\lambda\Gamma[-1,\lambda a]\int \mathrm{d}S - \frac{7}{16\lambda}\int \mathrm{d}S\;[3(\mathrm{Tr}\;\mathbf{K})^2 - 4\det\,\mathbf{K}]\Big], \tag{2.7}$$

The first term denotes the positive shift in energy arising from the predominantly parallel dipoles while the remaining terms describe how the electrostatic energy is reduced by deformations. Since the first term scales in proportion to the surface area it has the effect of merely shifting the total energy per unit area of the membrane by a constant. The remaining two components contribute to the mean and Gaussian bending energy. The contribution of the electrostatic energy to the total free energy of the membrane can be estimated by integrating the thermodynamic relation (1.2).

$$\begin{aligned}\mathcal{F}_{\mathrm{d-d}} &= \frac{1}{\beta}\int \mathcal{E}_{\mathrm{d-d}}\mathrm{d}\beta,\\ &= \frac{p^2}{4\epsilon}\Big[\frac{1}{a}\int \mathrm{d}S - \frac{7}{8\lambda}\int \mathrm{d}S\;[3(\mathrm{Tr}\;\mathbf{K})^2 - 4\det\,\mathbf{K}]\Big],\end{aligned} \tag{2.8}$$

where we have assumed a Debye length much larger than the solvent size, $\lambda a \ll 1$ implying $\lambda\Gamma[-1,\lambda a] \sim 1/a$. The curvature independent part of the electrostatic free energy is of order $p^2/a\epsilon$, while the curvature dependent part can be combined with elastic free energy by defining the effective bending moduli,

$$\kappa_{\mathrm{eff}} = \kappa - \frac{21p^2}{16\epsilon\lambda}, \qquad \bar{\kappa}_{\mathrm{eff}} = \bar{\kappa} + \frac{7p^2}{8\epsilon\lambda}. \tag{2.9}$$

The decrease in the effective mean bending modulus from the bare value implies a softening of the membrane rigidity. Indeed for sufficiently large dipole moments the effective mean bending modulus can vanish implying a vanishing of the persistence length. The change in Gaussian bending modulus favours the creation of handles over components. This effect can be understood by recognising that the local dipole energy is lowered by a relative saddle splay deformation of neighbouring dipoles which changes their relative orientation whilst preserving an average separation comparable to that of the flat surface.

The permanent electric dipole moment of amphiphilic molecules will generally be of the order of 1D. However, exceptions include the zwitterions, such as the Poly(ammonium alkoxydicyanoethenolates) [13] where dipole moments of 26D or equivalently $90\times10^{-30}$Cm have been measured. The Debye screening length, $\lambda^{-1}$ varies from $10^3$Å for extremely pure water to just a few Å for ionic solvents. Typically each molelcule occupies an area of the order $a^2 \sim 50$ Å$^2$. Thus, a dipolar membrane immersed in an aqueous solution with a dielctric constant of $\epsilon_{\mathrm{r}} = 80$ has a reduction in mean bending modulus of order 50 $\mu$eV $(pa^2/\mathrm{D})^2$ $(\lambda^{-1}/\text{Å})$ corresponding to 2mkT $(pa^2/\mathrm{D})^2$ $(\lambda^{-1}/\text{Å})$ at room temperature. Thus, for a dipole moment per molecule of $pa^2 = 1\mathrm{D}$, and a typical screening length of $\lambda^{-1} = 10^2$Å, the reduction is an order of magnitude smaller than the bare elastic moduli of surfactants, for which $\kappa \sim kT$.

Permanent dipoles may also be induced by the creation of a voltage difference across a membrane. For a typical molecular polarisability of $\alpha \sim \epsilon_0 da^2$, where $d$ denotes the layer thickness, a potential difference $V$ across the layer gives rise to a surface dipole density, $p \sim \epsilon_0 V$. For a screening length of $\lambda^{-1} = 10^2$Å, the corresponding change in mean bending modulus is of order $0.4kT(V/\mathrm{Volt})^2$. Typically the effect of the renormalisation would be beyond resolution for biological systems where it is possible to find potential differences of at most 100 mV in bilayers with bend moduli of order $10kT$. However, as we will investigate in the next section, potential differences across membranes can also be created artificially by charging an insulating membrane in a conducting background by an external field when in principle voltages in excess of 100 mV can be produced in membranes of much smaller bend moduli.

Whilst the permanent dipole moment of an amphiliphile can be large, fluid membranes in polar solvents such as the zwitterionic lecthicins mentioned above, tend to form bilayers. The membrane then comprises two dipolar surfaces with opposite polarity. Then if the screening length is smaller than the membrane thickness, and the dipoles are well offset from the neutral surface of the membrane, the dipolar interactions on each side of the bilayer become approximately independent. Their behaviour becomes equivalent to two superposed monolayers and in the most simple approximation the electrostatic contribution to the bending moduli simply doubles [14]. On the other hand, if the Debye length is greater than the width of the membrane the bilayer behaves approximately as a quadrupolar surface. At leading order, dipoles on opposite sides of the bilayer impart an equal and opposite effect on the neighbouring dipoles and the modulus of rigidity remains approximately unchanged.

As mentioned above, the charge symmetry of the membrane can be broken by an external electric field. In the next section we will investigate the influence of dipole moments induced by a uniform electric field on the fluctuations of a fluid membrane.

## 3. Field induced dipoles.

In the previous section we demonstrated that the effect of permanent electric dipoles oriented along the normal directors of a membrane was to soften the modes of distortion. In this section, we will examine the influence of dipole moments induced by a uniform "external" electric field $\mathbf{E}$ maintained in the solution.

For simplicity we will again imagine the membrane to be composed of rod-shaped amphiphilic molecules but with a molecular polarisability, $\boldsymbol{\alpha}$. As before, the local rod axis will be assumed to define the normal director of the membrane. The action of the external field is to induce electric dipole moments along the axes of the molecules. The electrostatic interaction of the dipoles with the external field strongly favour a surface orientation of the membrane that remains normal to the applied field. However, as we have seen in the previous section the interaction of the dipoles within the layer favour curvature of the surface. We will demonstrate that the competition between these two requirements results in a short-wavelength softening of the membrane rigidity.

For a molecular polarisability, $\boldsymbol{\alpha} = \alpha\ \mathbf{n} : \mathbf{n}$, the induced surface dipole density is given by,

$$\mathbf{p}(\mathbf{X}) = \frac{1}{a^2}\boldsymbol{\alpha} \cdot \mathbf{E}_{\mathrm{L}}(\mathbf{X}), \tag{3.1}$$

where $\mathbf{E}_{\mathrm{L}}$ denotes the local electric field. The local field deviates from the value of the bare external field by the depolarising effect of the neighbouring dipoles. Summing over the all the neighbouring dipoles the local field can be related to the external field by $\mathbf{E}_{\mathrm{L}}(\mathbf{X}) = \boldsymbol{\Lambda}(\mathbf{X}) \cdot \mathbf{E}$, where

$$\Lambda_{ij}^{-1}(\mathbf{X}) = \left[\delta_{ij} + \frac{\alpha}{4\pi\epsilon a^2} \int \mathrm{d}S'\ \frac{\mathrm{e}^{-\lambda r}}{r^3}[n_i - \frac{1}{r^2}\ (3+\lambda r)\ (\mathbf{n}\cdot\mathbf{r})\ \mathbf{r}_i]\ n_j\right]. \tag{3.2}$$

Redefining the surface dipole density by $\mathbf{p} = \mathrm{d}\epsilon\boldsymbol{\chi}_{\mathrm{e}}\ \ \mathbf{E}$, the susceptibility is given by $\boldsymbol{\chi}_{\mathrm{e}} = \boldsymbol{\alpha}\cdot\boldsymbol{\Lambda}/da^2\epsilon$. The integration over the relative coordinates in (3.2) can be performed to the same level of approximation achieved in the previous section when we find, $\boldsymbol{\chi}_{\mathrm{e}} = \chi_{\mathrm{e}}(\mathbf{X})\ \mathbf{n} : \mathbf{n}$, where

$$\chi_{\mathrm{e}}(\mathbf{X}) = \frac{\alpha}{da^2\epsilon}\ \left[1 + \frac{\alpha}{2a^2\epsilon}(\lambda\Gamma[-1, \lambda a] - \frac{1}{16\lambda}(5\ (\mathrm{Tr}\ \mathbf{K})^2 - 4\ \det\ \mathbf{K}))\right]^{-1} \tag{3.3}$$

Then, for curvatures $\mathbf{K}_{\alpha\beta} \lesssim \sqrt{d/\lambda}$, the susceptibility is approximately given by,

$$\chi_\mathrm{e}(\mathbf{X}) = \left[1 + \frac{\chi_\mathrm{f} d}{32\lambda}(5\ (\mathrm{Tr}\ \mathbf{K})^2 - 4\ \det\ \mathbf{K})\right]\ \chi_\mathrm{f}, \tag{3.4}$$

where $\chi_\mathrm{f}$ is defined to be the susceptibilty of a flat surface found by setting $\mathbf{K} \equiv 0$.

Using the constituitive relations defined above, the total electrostatic energy of the membrane is given by, $\mathcal{E}_\mathrm{Dip} = \mathcal{E}_\mathrm{E-d} + \mathcal{E}_\mathrm{d-d}$ where the direct interaction of the dipoles with the external field is determined by,

$$\mathcal{E}_\mathrm{E-d} = -\frac{1}{2}\int \mathrm{d}S\ \mathbf{p}\cdot\mathbf{E} = -\frac{1}{2}\mathrm{d}\epsilon\ \int \mathrm{d}S\ \chi_\mathrm{e}(\mathbf{X})\ (\mathbf{n}\cdot\mathbf{E})^2, \tag{3.5}$$

and the dipole-dipole energy, $\mathcal{E}_\mathrm{d-d}$ is given by (2.3) but where the magnitude of the dipole density is allowed to fluctuate according to $\chi_\mathrm{e}(\mathbf{X})$. Using the same expansion of the primed coordinates as in the previous section, and integrating over the relative coordinates we obtain,

$$\begin{aligned}\mathcal{E}_\mathrm{d-d} = \frac{\mathrm{d}^2\epsilon}{4}\int \mathrm{d}S\ \chi_\mathrm{e}(\mathbf{X})^2\ (\mathbf{n}\cdot\mathbf{E})\bigg[\Big(\lambda\Gamma[-1,\lambda a] - \frac{1}{16\lambda}[29(\mathrm{Tr}\ \mathbf{K})^2 - 44\det\ \mathbf{K}]\Big)\ (\mathbf{n}\cdot\mathbf{E}) \\ + \frac{1}{4\lambda}\partial_\alpha(K_\alpha^\beta\ \boldsymbol{\epsilon}_\beta\cdot\mathbf{E})\bigg].\end{aligned} \tag{3.6}$$

Since the parameters which enter (3.5) and (3.6) are dependent on the orientation of the membrane with respect to the field it is not in general possible to find a simple reparameterisation in terms of elastic constants. However, since the direct interaction of the dipoles with the external field strongly favours an orientation of the membrane which is normal to the field direction we can proceed by examining perturbative deformations of a flat surface.

For an external field $\mathbf{E} = E\ \hat{\mathbf{x}}_3$ we will investigate a surface, $\mathbf{X} = (x_1, x_2, f(\mathbf{x}))$ where $\partial_\alpha f(\mathbf{x}) \ll 1$, and the mean and Gaussian curvatures are given by $\mathrm{Tr}\ \mathbf{K}/2 = \nabla^2 f/2$ and $\det\ \mathbf{K} = \det\ \partial_\alpha\partial_\beta f$ respectively. By reexpressing the Gaussian curvature as a total derivative, $-\epsilon_{im}\epsilon_{jn}\partial_m\partial n[(\partial_i f)(\partial_j f)]$ its contribution in the electrostatic energy for this geometry can be shown to vanish. Similarly, the total derivative that appears in the final term of (3.6) also integrates to zero.

Using this representation, the bare elastic free energy of the membrane, (1.1) is determined up to a constant factor by,

$$\mathcal{F} = \int \mathrm{d}x_1\mathrm{d}x_2\left[\frac{\kappa}{2}(\nabla^2 f)^2 - r\right], \tag{3.7}$$

where the symmetry breaking effect of the field requires the introducion of a "chemical potential" of projected area, $r$, taken to be zero for the unperturbed membrane. Similarly, in this representation the electrostatic energy is

$$\begin{aligned}\mathcal{E}_\mathrm{Dip} = \frac{1}{2}\mathrm{d}\chi_\mathrm{f}\epsilon E^2\bigg[\Big(1 - \frac{\mathrm{d}\chi_\mathrm{f}\lambda\Gamma[-1,\lambda a]}{2}\Big)\ \Big[\int \mathrm{d}S - 2\int \mathrm{d}x_1\mathrm{d}x_2\ \Big] \\ - \Big[\frac{\mathrm{d}\chi_\mathrm{f}}{32\lambda}\ \Big(34 - 5\mathrm{d}\chi_\mathrm{f}\lambda\Gamma[-1,\lambda a]\Big)\Big]\ \int \mathrm{d}x_1\mathrm{d}x_2(\nabla^2 f)^2\bigg].\end{aligned} \tag{3.8}$$

As before, the electrostatic contribution to the free energy can be determined by integrating the thermodynamic relation (1.2) when, using the same assumption that $\lambda a \ll 1$ we find,

$$\mathcal{F}_{\mathrm{Dip}} = \frac{1}{2}\mathrm{d}\chi_{\mathrm{f}}\epsilon E^2\left[\left(1-\frac{\mathrm{d}\chi_{\mathrm{f}}}{2a}\right)\left[\int \mathrm{d}S - 2\int \mathrm{d}x_1\mathrm{d}x_2\right]\right.$$
$$\left. - \left[\frac{\mathrm{d}\chi_{\mathrm{f}}}{16\lambda}\left(34-\frac{5\mathrm{d}\chi_{\mathrm{f}}}{a}\right)\right]\int \mathrm{d}x_1\mathrm{d}x_2(\nabla^2 f)^2\right]. \tag{3.9}$$

The electrostatic energy can then be combined with the unperturbed surface free energy by defining a chemical potential of projected area to account for the second term,

$$r_{\mathrm{eff}} = \mathrm{d}\chi_{\mathrm{f}}\epsilon E^2\left(1-\frac{\mathrm{d}\chi_{\mathrm{f}}}{2a}\right), \tag{3.10}$$

and an effective mean bending modulus,

$$\kappa_{\mathrm{eff}} = \kappa - \mathrm{d}\chi_{\mathrm{f}}\epsilon E^2\,\frac{\mathrm{d}\chi_{\mathrm{f}}}{16\lambda}\left(34-\frac{5\mathrm{d}\chi_{\mathrm{f}}}{a}\right). \tag{3.11}$$

The positive sign of the chemical potential, which favours a large projected area is natural since the dipole moment together with the corresponding direct interaction with the external field is maximised in this configuration. As for permanent dipoles, the mean bending modulus is generally reduced by the interaction indicating a softening of the membrane rigidity. Although the topology of the flat surface prevents a discussion of the Gaussian curvature, it is clear from (3.6) that the effect of the interaction is to increase the modulus as for permanent dipoles.

For typical molecular polarisabilities of $\alpha \sim da^2\epsilon_0$, and $d/a \lesssim 10$, the susceptibility is approximately $\chi_{\mathrm{f}} \sim 1/\epsilon_{\mathrm{r}}$. Then for $\lambda^{-1} \sim 10^2$ Å, a membrane thickness of $d \sim 30$ Å and an external electric field corresponding to $E = V/d$ the chemical potential is approximately, $r_{\mathrm{eff}} \sim 0.4\ (V/\mathrm{Volts})^2 kT$ per molecule, and the mean bending modulus is reduced by approximately $0.3\ (V/\mathrm{Volts})^2 kT$ from the bare value. Therefore, as in the case of the permanent dipoles, the renormalisation at high voltages is comparible to the bare mean bending modulus of surfactant membranes.

## 4. Discussion.

We have demonstrated that the effective membrane rigidity softens in the presence of both permanent and field induced dipoles. In the case of the latter, the gain in electrostatic energy from bending is diminished by the reduction in projected area. For $q^2 \gg q_{\mathrm{c}}^2 = r_{\mathrm{eff}}/\kappa_{\mathrm{eff}}$, where the bend modulus dominates, second order perturbation theory predicts a membrane persistence length of [15],

$$\xi_{\mathrm{p}} = a\exp\left[\frac{4\pi\kappa_{\mathrm{eff}}}{3kT}\right]. \tag{4.1}$$

Then, for increasing external field, and a corresponding decrease in effective bend modulus, the persistence length becomes rapidly reduced. In particular, we would expect a short- wavelength instability if the effective bend modulus changes sign. The estimates for the magnitude of the renormalisation indicate that these effects can realistically be observed. The crumpled state of the membrane in which the electrostatic energy dominates the elastic energy is much more complicated, and beyond the scope of this paper. However, one simple possibility is for the membrane to collapse into a compact structure in which the layers roll into a spiral and thereby minimise the dipolar energy.

In conclusion, we have focused attention on a simple model of dipoles in membranes showing their effects to be experimentally relevant. We have examined the behaviour of both permanent and field induced dipoles, where in both cases we have assumed the dipolar surface to be of negligible thickness. Moreover, we have made the implicit assuption that the dipoles lie on the neutral surface of the membrane. We have neglected the "non-local" interaction of the dipolar surfaces but rather focused attention on the perturbations of an approximately flat unilamella membrane. As mentioned in the text, these results could be extended to describe more accurately the behaviour of real membranes. In particular, the finite thickness, and internal dielectric and compositional properties of the membrane could be included. In addition, throughout this work we have assumed that the dipoles are aligned along the normal directors of the surface. More realistically, the moments could develop some component in the plane of the membrane. The influence of the electrostatic energy on the fluctuation of the membrane would then depend crucially on the degree of orientational order of the dipoles. This problem bares similarities to the role of molecular orientational order in smectic-A liquid crystals [16] recently discussed by MacKintosh and Lubensky [4].

## Acknowledgements.

I am grateful to D Andelman, M E Cates, T J Drye, M Schwarz, and D E Khmel'nitskii for valuable discussions. This work was supported in part by Gonville and Caius College, Cambridge

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