ELECTROSTATIC STIFFNESS PROPERTIES OF CHARGED BILAYERS ☆

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We calculate the exact stiffness constants $\varkappa$, $\bar{\varkappa}$, c_0 of mean, Gaussian, and spontaneous curvature for a double layer of surface charges separated by a fixed distance $2d$ in an electrolyte with finite screening length l_0. This extends earlier studies of the limits of very small and very large d/l_{D}.

1. Fluctuating surfaces appear in many physical systems, ranging from magnets (domain walls), over alloys (phase separation boundaries), microemulsions (soap interfaces between oil and water), elementary particles (world sheets swept out by the string between quarks), to biophysics (cell walls). Most properties of such surfaces are dominated by surface tension. Specially interesting effects arise, however, when the tension happens to be very small. Then fluctuations are very large and the relevant material property to control them is the bending stiffness. In the limit of small bending it can be parametrized by the local energy density [1]

$$e(\xi)=\tfrac{1}{2}\varkappa(c_1+c_2-c_0)^2+\tfrac{1}{2}\bar{\varkappa}\times 2c_1c_2\,, \qquad (1)$$

with a total energy

$$E=\int \mathrm{d}^2\xi\,\sqrt{g(\xi)}\,e(\xi)\,, \qquad (2)$$

where c_i are the principal curvatures, the inverse of the principal radii $1/R_i$ and c_0 is the most favored curvature. We have parametrized the surface by $\xi=(\xi^1,\xi^2)$ and denoted the induced metric by $g_{ij}(\xi)$ and its determinant by $g(\xi)$. The ansatz (1) represents a purely phenomenological collection of many microscopic effects. First, there is in-plane elasticity. If the membrane were to consist of isotropic continous material with a thickness d, the opposite distortions of the surface regions generate a stiffness [2]. In the symmetric case, if E, μ denote the elastic and the shear modulus, respectively, $\nu=\frac{1}{2}E/\mu-1$ is the Poisson ratio, the constants $\varkappa$, $\bar{\varkappa}$ are given by

$$\varkappa=\frac{Ed^3}{12(1-\nu^2)},\quad \bar{\varkappa}=-\varkappa(1-\nu)\,. \qquad (3)$$

Certainly, for molecular layers the isotropy assumption is not applicable and the detailed relations between elasticity and stiffness constants will be modified. In the extreme anisotropic case of a lipid bilayer in which there is liquid behaviour in the horizontal direction and an incompressibility in the vertical direction, one finds [3]

$$\varkappa=d^2\frac{K_1K_2}{K_1+K_2}\,, \qquad (4)$$

where K_1, K_2 are the horizontal compressibilities. Notice that the power of d^3 in (3) is lowered to d^2, i.e. such a material is usually stiffer than an isotropic one. In addition the material is not homogeneous at the microscopic scale, the elastic forces being themselves a manifestation of even more fundamental molecular forces which could in principle be used to calculate $\varkappa$ but at the scale of many atoms at which we shall work here this will not concern us.

2. An important source of stiffness are the electric fields surrounding a membrane. For neutral membranes, the dispersive forces cause a stiffening which has recently been calculated [4].

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In general, since electrostatic forces are of long range, this stiffness will not be parametrizable in the form (1), (2). A non-local interaction will result, with the generic form [4]

$$E=\int d\xi\, d\xi' \sqrt{g(\xi)}\sqrt{g(\xi')}$$
$$\times [\tfrac{1}{2}\varkappa(\xi,\xi')(c_1+c_2-c_0)(\xi)(c_1+c_2-c_0)(\xi')$$
$$+\bar{\varkappa}(\xi,\xi')c_1(\xi)c_2(\xi')] . \qquad (5)$$

If, however, a membrane moves in a saline aqueous environment the electromagnetic forces are screened down to a finite length range, the Debye length

$$l_D \equiv m^{-1} = \left(\frac{\varepsilon_W k_B T}{n_0 e^2}\right)^{1/2} , \qquad (6)$$

where T=temperature, k_B=Boltzmann's constant, n_0=density of charge carriers in the environment, $\pm e$ the charge carried by them ($e^2=4\pi\alpha$ where $\alpha\equiv$fine structure constant), and ε the dielectric constant of the water. In this case it is possible to parametrize the curvature stiffness by a quasi local term of the form (1), (2) for curvature radii much larger than the Debye length.

In a recent note we have developed a simple theoretical framework for calculating the stiffness constants $\varkappa$, $\bar{\varkappa}$ due to various field effects [5]. The particular case of a screened electrostatic field was also given. If membranes carry a surface charge, the stiffness of the field lines emanating from the surface will generate a stiffness of the surface [5]. For an infinitely thin membrane of surface charge density σ we found

$$\varkappa=\tfrac{1}{16}\sigma_0^2 m ,$$
$$\bar{\varkappa}=-\tfrac{1}{8}\sigma_0^2 m , \qquad (7)$$

with σ measured in natural units $\sigma_0=em^2$. The purpose of this note is to extend the calculation to membranes of finite thickness by considering two surfaces carrying different charge density σ_+, σ_- at an arbitrary distance $2d$. We extend the previous theory and include also the case of a purely dispersive interior of the membrane with dielectric constant ε_M and $m_M=0$, $M=\infty$. Then there are two relevant dimensionless system parameters md and $(\varepsilon_W/\varepsilon_M)md$. The relative dielectric constant to be denoted by $\varepsilon_r\equiv\varepsilon_W/\varepsilon_M$, is in general quite large, usually around 40. Hence, we can easily be in a regime where md is small but $\varepsilon_r md$ is large. An example is a flickering biological cell in an environment of low salinity. The purpose of this note is to present exact expressions for the curvature elastic constants $\varkappa$, $\bar{\varkappa}$, c_0 valid for all md and $\varepsilon_r md$.

While this work was in process we received a paper by Winterhalter and Helfrich [6] who studied the same system but were able to give a solution only in the limit in which both md and $\varepsilon_r md$ are very large. Thus they do not cover the important regime of a large screening length (i.e. low salinity). Their paper should be consulted, however, for an evaluation of earlier work on this subject [7].

3. As in ref. [4], the calculation will be done in the Debye–Hückel approximation in which the electrostatic field in the neighborhood of the surface satisfies the linearized Poisson–Boltzmann equation

$$(\Delta-m^2)\varphi(\boldsymbol{x})$$
$$=\sigma\int d^2\xi \sqrt{g(\xi)}\,\delta^{(3)}(\boldsymbol{x}-\boldsymbol{x}(\xi)) , \qquad (8)$$

where σ is the charge density; we consider two surfaces of charge densities σ_+, σ_- positioned at the radii $R-d$ and $R+d$, respectively, and calculate the electrostatic energy once in a cylindrical and once in spherical configuration. Thereby we assume that the distance $2d$ does not change upon bending. This is certainly true if the compressional stiffness is much larger than the horizontal one. We then pick out the leading $1/R$, $1/R^2$ coefficients in the energy density e_c, e_s, to be denoted $e_{c,s}^{(1)}$, $e_{c,s}^{(2)}$, and identify

$$\varkappa=2e_c^{(2)}, \quad \bar{\varkappa}=e_s^{(2)}-4e_c^{(2)} ,$$
$$c_0=-e_c^{(1)}/e_c^{(2)} . \qquad (9)$$

Let r be the radial coordinate in either configuration. We shall denote the small-r solution by $I(r)$, the large-r solution by $K(r)$, and the interior solution by $f(r)$. Then the boundary condition at $r_\pm=R\pm d$ reads

$$DI(r_-)=C+Bf(r_-) , \qquad (10)$$

$$Bf(r_+)+C=AK(r_+) , \qquad (11)$$

$$\varepsilon_M B\partial_r f(r_+)-\varepsilon_W A\partial_r K(r_+)=\sigma_+ , \qquad (12)$$

$$\varepsilon_W D\partial_r I(r_-)-\varepsilon_M B\partial_r f(r_-)=\sigma_- . \qquad (13)$$

If ∂_r is abbreviated by a prime and $I(r_-)$, $K(r_+)$,

$f(r_\pm)$ by I, K, $f_\pm$, respectively, the solutions are

$$A=(\varepsilon_M Bf'_+ - \sigma_+)/\varepsilon_W K',$$

$$D=(\varepsilon_M Bf'_- + \sigma_+)/\varepsilon_W I',$$

$$B=(AK-DI)/(f_+ - f_-)$$
$$=\frac{\sigma_+ K/K' + \sigma_- I/I'}{\varepsilon_M(f'_+ K/K' - f'_- I/I') - \varepsilon_W(f_+ - f_-)}. \quad (14)$$

We now introduce the dimensionless functions $Q_+ \equiv -mK(r_+)/K'(r_+)$, $Q_- \equiv mI(r_-)/I'(r_-)$, $g_\pm \equiv f'(r_\pm)/f(r)$ and obtain the fields on the $\pm$ surfaces,

$$\phi(x_\pm)=(AK, DI)$$
$$\times \frac{Q_\pm}{m\varepsilon_W}\left(\sigma_\pm \mp \frac{g_\pm}{2}\frac{\sigma_+ Q_+ - \sigma_- Q_-}{1+\lambda+\alpha}\right), \quad (15)$$

with $\lambda \equiv \varepsilon_r md$ and

$$\alpha \equiv \frac{1}{2}\left(g_+ Q_+ + g_- Q_- + \frac{\lambda}{d}\frac{f_+ - f_-}{f'}\right) - 1 - \lambda. \quad (16)$$

The electrostatic energy density is then given by

$$e=\tfrac{1}{2}[\sigma_+\phi(r_+) + \sigma_-\phi(r_-)]$$
$$=\frac{1}{2m\varepsilon_W}\left(\sigma_+^2\frac{Q_+}{g_+} + \sigma_-^2\frac{Q_-}{g_-} - \frac{1}{2}\frac{(\sigma_+ Q_+ - \sigma_- Q_-)^2}{1+\lambda+\alpha}\right). \quad (17)$$

We now insert for specific solutions for cylindrical and spherical configurations $I^c = I_0(mr)$, $K^c = K_0(mr)$, $f^c(r) = \log r$ and $I^s = \mathrm{sh}(mr)/r$, $K^s = e^{-mr}/r$, $f^s = 1/r$, respectively. The associated functions

$$Q^c_\pm = \left(\frac{K_0(mR_+)}{K_1(mR_+)}, \frac{I_0(mR_-)}{I_1(mR_-)}\right),$$

$$Q^s_\pm = \left(\frac{mR_+}{mR_+ + 1}, \frac{mR_-}{mR_- \,\mathrm{cth}(mR_-) - 1}\right),$$

$$g^c_\pm = (1 \pm d/R)^{-1}, \quad g^s_\pm = (1 \pm d/R)^{-2} \quad (18)$$

are easily expanded in powers of $1/R$ up to $1/R^2$,

$$Q^c_\pm = 1 \mp \frac{1}{2mR}\left(1 \mp \frac{d}{R}\right) + \frac{3}{8(mR)^2},$$

$$Q^s_\pm = 1 \mp \frac{1}{mR}\left(1 \mp \frac{d}{R}\right) + \frac{1}{(mR)^2},$$

$$f^c_\pm = 1 \mp \frac{d}{R} + \frac{d^2}{R^2}, \quad f^s_\pm = 1 \mp \frac{2d}{R} + \frac{3d^2}{R^2},$$

$$\alpha^c = \frac{3}{8(mR)^2} + \frac{d}{mR^2} + \frac{d^2}{R^2} + \lambda\frac{d^2}{3R^2},$$

$$\alpha^s = \frac{1}{(mR)^2} + \frac{3d}{(mR)^2} + \frac{3d^2}{R^2} + \lambda\frac{d^2}{R^2}. \quad (19)$$

Collecting all $1/R$ and $1/R^2$ contributions and forming the combinations (9) we arrive at the following stiffness parameters,

$$\varkappa = \frac{\sigma^2 m}{16\varepsilon_W}\left[\frac{1}{1+\lambda} + 3\frac{\lambda}{1+\lambda}\left(1+\delta^2\frac{\lambda}{1+\lambda}\right) + \frac{16\delta^2}{(1+\lambda)^2}[\lambda d + (\tfrac{1}{3}\lambda - 1)d^2]\right],$$

$$\bar{\varkappa} = -\frac{\sigma^2 m}{8\varepsilon_W}\left[(1+2d-2d^2)\left(1+\delta^2\frac{\lambda^2}{(1+\lambda)^2}\right) - \frac{40}{3}\frac{\delta^2 d^2 \lambda}{(1+\lambda)^2}\right],$$

$$c_0 = 8m\delta(1+\lambda) \times \frac{\lambda - 2d(1+\lambda)}{1+4\lambda+3(1+\delta^2)\lambda^2 - 16\delta^2[\lambda d + (\tfrac{1}{3}\lambda - 1)d^2]}, \quad (20)$$

where d is measured in units of $1/m$ (and $\lambda = \varepsilon_r md$, $\sigma_\pm = \frac{1}{2}(1 \pm \delta)$ is used). This is an exact result valid for all md, $\varepsilon_r md$. In the limit $d \to 0$ it reduces to our previous result (7). In the limit of both md and $\lambda = \varepsilon_r md$ large, it gives the same result as Winterhalter and Helfrich's except that they have ignored the pure d^2 term in $\bar{\varkappa}$, which is quite important for $d > 1/m$, i.e. for high salinity.

The entire regime is displayed in fig. 1 for some typical dielectric constants $\varepsilon_r = \varepsilon_W/\varepsilon_M = 1$, 10, 40. The dashed curves indicate the previous two limits. For $\varkappa$, $\bar{\varkappa}$ we have plotted once the charge symmetric case $\delta = 0$ (denoted by $\varkappa_s$, $\bar{\varkappa}_s$), and once the extreme asymmetric case $\delta = \pm 1$ ($\varkappa_u$, $\bar{\varkappa}_u$). Instead of the spontaneous curvature c_0 we have plotted c_0/δ for the present two cases. The arbitrary case δ is obtained by forming the combination $\varkappa = \varkappa_s + \delta^2(\varkappa_u - \varkappa_s)$ (the same for $\bar{\varkappa}$), while c_0 can be deduced from

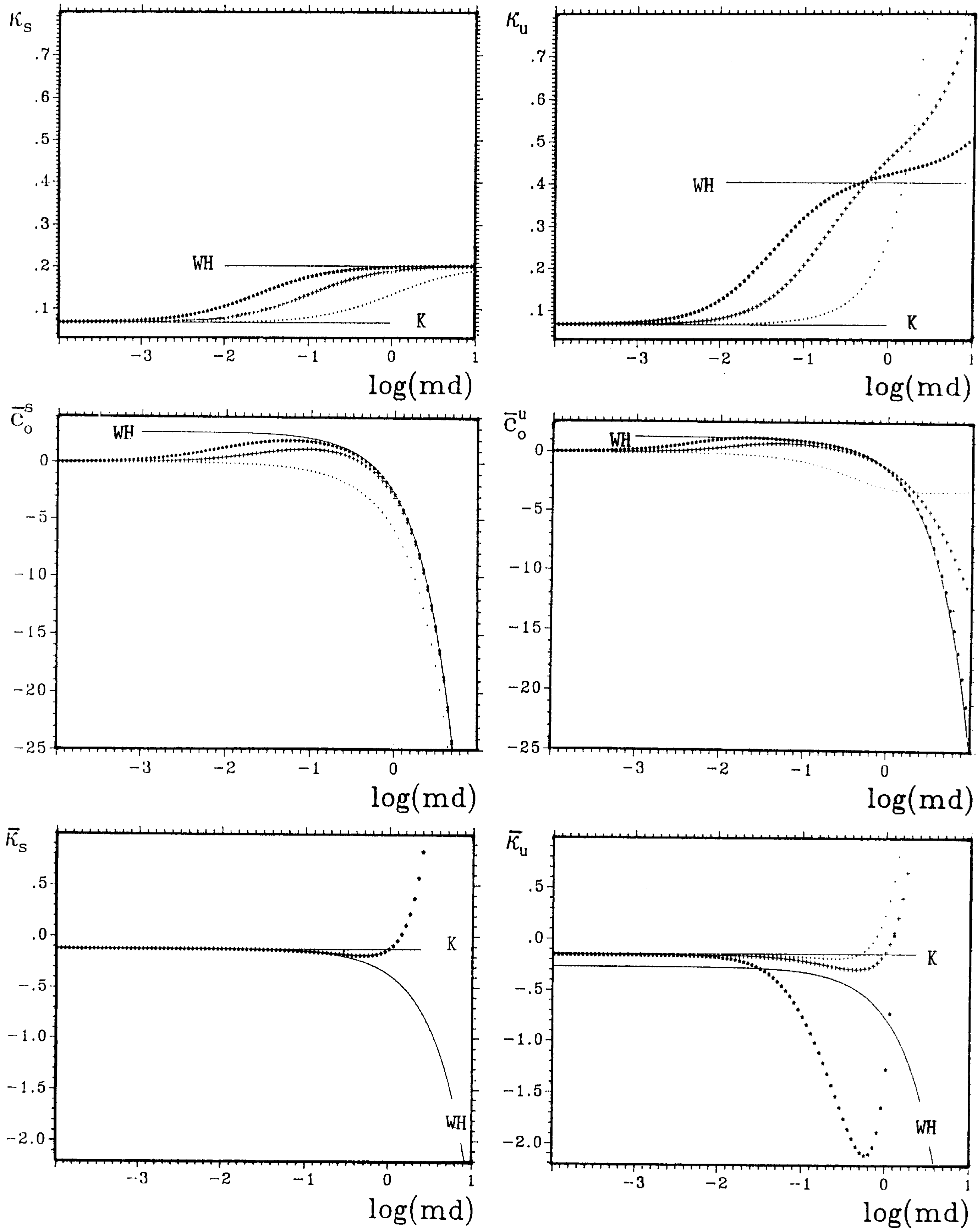

Fig. 1. The dependence of the curvature elastic constants $\varkappa$, $\bar{\varkappa}$, $\bar{c}_0=c_0/\delta$ on the reduced thickness measured in terms of the screening length, md, for a ratio of dielectric constants $\varepsilon_r=\varepsilon_W/\varepsilon_M=40$ (∗∗∗), 10 (+ + +), 1 (···). For $\varkappa$, $\bar{\varkappa}$ we plot the curves with which charge symmetry $\delta=\frac{1}{2}(\sigma_+-\sigma_-)/(\sigma_++\sigma_-)=0$ ($\varkappa_s$), and for $\delta=1$ ($\varkappa_u$). For arbitrary δ one has to compose $\varkappa_s+\delta^2(\varkappa_u-\varkappa_s)$ to obtain $\varkappa$ (the same for $\bar{\varkappa}$) or $1/c_{0,s}+\delta^2(1/c_{0,u}-1/c_{0,s})$ to obtain δ/c_0. We have indicated the previous limiting results by Winterhalter and Helfrich (WH) [6], $\varepsilon_r\to\infty$ and Kleinert (K) [5], $d\to 0$. Note that the (WH) curve for $\bar{\varkappa}_u$ is no good approximation anywhere.

$$\frac{1}{c_0}=\frac{1}{c_{0,s}}+\delta^2\left(\frac{1}{c_{0,u}}-\frac{1}{c_{0,s}}\right).$$

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