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THE ELECTRIC CONTRIBUTION TO THE CURVATURE ELASTIC MODULI OF CHARGED FLUID INTERFACES

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The electric contributions to the bending moduli of a charged fluid interface are calculated from the transverse pressure profile in an electric double layer. The results are in complete agreement with the expressions obtained from the electrical free energy of curved double layers.

1. Introduction

Recently expressions for the electric contribution to the curvature elastic moduli of charged monolayers and membranes were obtained [1–3]. By expanding the electrical free energy for a spherical and cylindrical surface in inverse powers of the radius of curvature a, the bending elastic moduli were obtained from the $(1/a)^2$ coefficient in this expansion of the free energy.

In the theory of surface tension the mechanical expression for the surface tension [4], in which the surface tension is related to the surface excess value of the transverse pressure, plays an important role. For example Kirkwood and Buff [5], who initiated the statistical mechanical theory of the surface tension of the planar liquid–vapour interface about 40 years ago, based their theory on this mechanical concept of the surface tension. Also for the effect of an electric double layer on the surface tension it was noted by Frenkel [6] many years ago that a clearer insight into the nature and origin of the decrease of surface tension is obtained from a consideration of the tensions acting in the electrolyte solution near the interface.

About 10 years ago Helfrich [7] gave expressions relating the curvature elastic properties to the moments of the transverse pressure profile. The use of these relations has been discussed extensively in the review paper on curvature elastic properties by Petrov and Bivas [8]. Recently Szleifer [9] gave a new derivation of the expressions first given by Helfrich [7] and added an important new relation relating one of the curvature elastic constants to the curvature

dependence of the transverse stress profile. Here we show how the electric contribution to the curvature elasticity of charged interfaces can be obtained from the electric contribution to the transverse pressure profile. For the case of low surface charge densities where the electric double layer can be described by the linearized Poisson–Boltzmann equation this was already partially done by Winterhalter and Helfrich [1]. It turns out that also for the case of high surface charge densities where one has to use the full (non-linear) Poisson–Boltzmann equation, the calculations can still be carried out analytically. As a matter of fact, not only gives the calculation of the curvature elastic moduli from the transverse pressure profile a clearer insight into the nature and origin of the effect of the electric double layer, they actually turn out to be slightly simpler than starting from the curvature dependence of the free energy. Whereas in the latter method the free energy has to be calculated up to order $(1/a)^2$, the elastic bending moduli can be calculated from the transverse pressure profile to order $(1/a)$.

2. The transverse pressure profile in an electric double layer

2.1. *The planar double layer*

The lateral pressure profile $\Pi(z)$ in an electric double layer contains a contribution from the Maxwell pressure (i.e. minus the Maxwell stress) and the osmotic pressure due to the excess of ions in the electric double layer. Adding these contributions one obtains for the case of a 1–1 electrolyte

$$\Pi(z) = \tfrac{1}{2}\varepsilon_0\varepsilon_r\left(\frac{\mathrm{d}\psi^{(0)}}{\mathrm{d}z}\right)^2 + 2n_{el}k_BT\left[\cosh\left(\frac{e\psi^{(0)}}{k_BT}\right) - 1\right], \tag{1}$$

where $\psi^{(0)}$ is the electric potential in the planar double layer (the superscript 0 denotes that we are dealing with the planar double layer), k_B is Boltzmann's constant, T is the absolute temperature, n_{el} is the number of molecules of electrolyte per unit volume, ε_r is the dielectric constant of the aqueous medium and ε_0 is the permittivity of the vacuum. Changing to dimensionless potential

$$\Psi^{(0)} = \frac{e\psi^{(0)}}{k_BT} \tag{2}$$

and dimensionless distance

$$x = \kappa z\,, \tag{3}$$

where κ is the inverse Debye length

$$\kappa = \left(\frac{2e^2 n_{el}}{\varepsilon_0 \varepsilon_r k_B T} \right)^{1/2}, \tag{4}$$

the lateral pressure profile can be written as

$$\Pi(x) = \varepsilon_0 \varepsilon_r \left(\frac{k_B T}{e} \right)^2 \kappa^2 \left[\tfrac{1}{2} \left(\frac{d\Psi^{(0)}}{dx} \right)^2 + [\cosh(\Psi^{(0)}) - 1] \right]. \tag{5}$$

We assume that the potential $\Psi^{(0)}$ can be described by the Poisson–Boltzmann equation, which in terms of the dimensionless variables introduced in eqs. (2) and (3) can be written as

$$\frac{d^2\Psi^{(0)}}{dx^2} = \sinh(\Psi^{(0)}). \tag{6}$$

Integrating this equation once we obtain

$$\frac{d\Psi^{(0)}}{dx} = -2 \sinh(\tfrac{1}{2}\Psi^{(0)}). \tag{7}$$

Using this result in eq. (5) we can write

$$\Pi(x) = 4\varepsilon_0 \varepsilon_r \left(\frac{k_B T}{e} \right)^2 \kappa^2 [\sinh(\tfrac{1}{2}\Psi^{(0)})]^2. \tag{8}$$

The solution of the Poisson–Boltzmann equation for a flat double layer is well known and can be written as

$$\Psi^{(0)}(x) = 2 \ln \left(\frac{1 + t_0 e^{-x}}{1 - t_0 e^{-x}} \right), \tag{9}$$

where

$$t_0 = \tanh(\tfrac{1}{4}\Psi_0^{(0)}) \tag{10}$$

with $\Psi_0^{(0)}$ the value of the potential at the surface. The potential $\Psi^{(0)}(x)$ can also be related to the surface charge density σ. Inverting eq. (7) it follows that

$$\Psi_0^{(0)} = 2 \ln(p + q), \tag{11}$$

where

$$p = \frac{1}{2}\left|\left(\frac{\mathrm{d}\Psi^{(0)}}{\mathrm{d}x}\right)_{x=0}\right| = \sinh(\tfrac{1}{2}\Psi_0^{(0)})$$

and (12)

$$q = \sqrt{p^2+1} = \cosh(\tfrac{1}{2}\Psi_0^{(0)})\,.$$

(In writing down eq. (11) we have assumed that we are dealing with a situation where $\Psi_0^{(0)}$ is positive.) Through the equation of Gauss the quantity p is related to the surface charge density σ,

$$p = \frac{2\pi Q|\sigma|}{\kappa e}\,, \tag{13}$$

where Q is the Bjerrum length

$$Q = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r k_B T} \tag{14}$$

($Q = 0.714$ nm for aqueous solutions at 298 K).

Eq. (8) together with eq. (9) gives a complete description of the lateral pressure profile in an electric double layer on the level of the Poisson–Boltzmann equation.

2.2. *The spherical double layer*

As mentioned in the introduction, for the calculation of the curvature elastic moduli we need to know the transverse pressure profile up to order $(1/a)$. This means that we have to solve the Poisson–Boltzmann equation for a curved charged surface up to that order. Such a solution can be obtained by expanding the electrical potential Ψ in $1/\kappa a$,

$$\Psi = \Psi^{(0)} + \frac{1}{\kappa a}\Psi^{(1)} + \cdots\,. \tag{15}$$

Substituting this expansion in the Poisson–Boltzmann equation for a spherical double layer,

$$\frac{\mathrm{d}^2\Psi}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}\Psi}{\mathrm{d}r} = \kappa^2\sinh(\Psi)\,, \tag{16}$$

where r is the radial coordinate and Ψ is the dimensionless potential and making the coordinate transformation

$$r = a + \frac{x}{\kappa}\,, \tag{17}$$

one obtains

$$\frac{d^2}{dx^2}\left(\Psi^{(0)}+\frac{1}{\kappa a}\Psi^{(1)}+\cdots\right)+\frac{2/\kappa a}{1+x/\kappa a}\frac{d}{dx}\left(\Psi^{(0)}+\frac{1}{\kappa a}\Psi^{(1)}+\cdots\right)$$
$$=\sinh\left(\Psi^{(0)}+\frac{1}{\kappa a}\Psi^{(1)}+\cdots\right). \tag{18}$$

Equating terms of the same power of $1/\kappa a$ on both sides of eq. (18) gives the following equations:

$$\frac{d^2\Psi^{(0)}}{dx^2}=\sinh(\Psi^{(0)}),$$
$$\frac{d^2\Psi^{(1)}}{dx^2}-\Psi^{(1)}\cosh(\Psi^{(0)})=-2\frac{d}{dx}\Psi^{(0)}. \tag{19}$$

The first equation is again the Poisson–Boltzmann equation for a flat double layer and the second equation determines the first order modification of the electrical potential due to curvature. With the boundary condition that

$$\Psi^{(0)}=\Psi^{(1)}=\cdots=0 \qquad \text{as } x\to\infty, \tag{20}$$

one obtains from eq. (19)

$$\frac{d\Psi^{(1)}}{dx}+\Psi^{(1)}\cosh(\tfrac{1}{2}\Psi^{(0)})=-4\tanh(\tfrac{1}{4}\Psi^{(0)}). \tag{21}$$

This equation can be solved easily by writing

$$\Psi^{(1)}(x)=\sinh(\tfrac{1}{2}\Psi^{(0)})\,X(x). \tag{22}$$

Substituting this ansatz in eq. (21) one obtains

$$\frac{dX}{dx}=-\frac{4\tanh(\frac{1}{4}\Psi^{(0)})}{\sinh(\frac{1}{2}\Psi^{(0)})}. \tag{23}$$

In solving this simple equation one has to distinguish carefully between two boundary conditions:

i) constant surface potential, implying $\Psi_0^{(1)}=0$;

ii) constant surface charge, implying $(d\Psi^{(1)}/dx)_{x=0}=0$.

In the case of constant potential obviously $X(0)=0$ and we find

$$X(x)=t_0^2(1-e^{-2x})-2x. \tag{24}$$

This solution was first obtained by Dukhin et al. [10] (see also refs. [11–13]).

In the case of constant charge it follows directly from the differential equation for $\Psi^{(1)}(x)$ that

$$\Psi_0^{(1)} = -\frac{4t_0}{\cosh(\frac{1}{2}\Psi_0^{(0)})}\,, \tag{25}$$

and thus the solution for $X(x)$ now becomes

$$X(x) = -\frac{4t_0}{\cosh(\frac{1}{2}\Psi_0^{(0)})\sinh(\frac{1}{2}\Psi_0^{(0)})} + t_0^2(1-\mathrm{e}^{-2x}) - 2x\,. \tag{26}$$

Again adding the Maxwell pressure and the osmotic pressure due to the excess of ions in the double layer we find for the transverse pressure profile at a dimensionless distance x from the surface

$$\Pi(x) = \varepsilon_0\varepsilon_r\left(\frac{k_BT}{e}\right)^2\kappa^2\left\{4[\sinh(\tfrac{1}{2}\Psi^{(0)})]^2 + \frac{1}{\kappa a}\left[\left(\frac{\mathrm{d}\Psi^{(0)}}{\mathrm{d}x}\right)\left(\frac{\mathrm{d}\Psi^{(1)}}{\mathrm{d}x}\right) + \sinh(\Psi^{(0)})\,\Psi^{(1)}\right]\right\}. \tag{27}$$

Using eqs. (7) and (21) this result can be written as

$$\Pi(x) = \varepsilon_0\varepsilon_r\left(\frac{k_BT}{e}\right)^2\kappa^2\left\{4[\sinh(\tfrac{1}{2}\Psi^{(0)})]^2 + \frac{1}{\kappa a}\left[4\sinh(\tfrac{1}{2}\Psi^{(0)})\cosh(\tfrac{1}{2}\Psi^{(0)})\,\Psi^{(1)} + 8\sinh(\tfrac{1}{2}\Psi^{(0)})\tanh(\tfrac{1}{4}\Psi^{(0)})\right]\right\}. \tag{28}$$

As we will see in the next section, using this expression for the transverse pressure profile in a spherical double layer it is possible to calculate the electrical contribution to the bending elastic modulus.

3. Bending elastic moduli

The curvature free energy per unit area of a fluid layer can be written as [14]

$$f_c = \tfrac{1}{2}K(c_1 + c_2 - c_0)^2 + \bar{K}c_1c_2\,, \tag{29}$$

where c_1 and c_2 are the principal curvatures, c_0 is the spontaneous curvature, K

is the bending elastic modulus and $\bar{K}$ is the modulus of Gaussian curvature. Using mechanical arguments Helfrich [7] has shown that Kc_0 and $\bar{K}$ can be related to moments of the transverse pressure profile $\Pi(z)$ of a flat surface,

$$Kc_0 = \int_{-\infty}^{+\infty} z\Pi(z)\,\mathrm{d}z \tag{30}$$

and

$$\bar{K} = -\int_{-\infty}^{+\infty} z^2\Pi(z)\,\mathrm{d}z\,. \tag{31}$$

Recently Szleifer [9] has presented a new derivation of these relations and at the same time obtained an important new relating the bending elastic modulus to the curvature dependence of the transverse pressure profile

$$K = -\int_{-\infty}^{+\infty} z\left(\frac{\partial\Pi(z)}{\partial(2/a)}\right)_{2/a\to 0}\mathrm{d}z\,, \tag{32}$$

where now $\Pi(z)$ is the transverse pressure around a spherical surface with radius a.

Since, as we have seen in the previous section, the transverse pressure profile both for a flat and spherical double layer can be calculated being the Poisson–Boltzmann equation in a straightforward manner, the above expressions can be used to calculate the electric contribution to the curvature elastic moduli of charged interfaces. Using eqs. (8) and (30) we obtain

$$\begin{aligned} K^{\mathrm{el}}c_0^{\mathrm{el}} &= \frac{1}{\kappa^2}\int_0^{\infty} x\Pi(x)\,\mathrm{d}x \\ &= 4\varepsilon_0\varepsilon_{\mathrm{r}}\left(\frac{k_{\mathrm{B}}T}{e}\right)^2\int_0^{\infty}[\sinh(\tfrac{1}{2}\Psi^{(0)})]^2 x\,\mathrm{d}x\,. \end{aligned} \tag{33}$$

The integral that occurs on the right-hand side of eq. (33) can easily be evaluated by using the relation

$$\sinh(\tfrac{1}{2}\Psi^{(0)}) = \frac{2t_0\,\mathrm{e}^{-x}}{1 - t_0^2\,\mathrm{e}^{-2x}}\,. \tag{34}$$

Using this expression one obtains by elementary methods

$$\int_0^{\infty}[\sinh(\tfrac{1}{2}\Psi^{(0)})]^2 x\,\mathrm{d}x = -\ln(1 - t_0^2)\,. \tag{35}$$

This means that

$$K^{el}c_0^{el} = \frac{k_B T}{\pi Q}\left[-\ln(1-t_0^2)\right]. \tag{36}$$

In the above expression $K^{el}c_0^{el}$ is related to the surface potential $\Psi_0^{(0)}$ via t_0. Using the relation

$$1 - t_0^2 = \frac{2}{1+\cosh(\frac{1}{2}\Psi_0^{(0)})} = \frac{2}{1+q}, \tag{37}$$

we can also express $K^{el}c_0^{el}$ in terms of q, which is related to the surface charge density,

$$K^{el}c_0^{el} = \frac{k_B T}{\pi Q}\ln[\tfrac{1}{2}(q+1)]. \tag{38}$$

This is exactly the same result as follows from the comparison of the $(1/a)$ term in the phenomenological expression for the curvature free energy and the electrical free energy for a charged spherical surface [3].

We now consider the modulus of Gaussian curvature. Using eqs. (8) and (31) we obtain

$$\bar{K}^{el} = -\frac{1}{\kappa^3}\int_0^\infty x^2 \Pi(x)\,dx$$

$$= -4\varepsilon_0\varepsilon_r\left(\frac{k_B T}{e}\right)^2 \frac{1}{\kappa}\int_0^\infty [\sinh(\tfrac{1}{2}\Psi^{(0)})]^2 x^2\,dx. \tag{39}$$

Using the relation (35) the integral appearing on the right-hand side of eq. (39) can again be evaluated by elementary methods,

$$\int_0^\infty [\sinh(\tfrac{1}{2}\Psi^{(0)})]^2 x^2\,dx = \int_{1-t_0^2}^1 \frac{\ln(u)}{u-1}\,du. \tag{40}$$

The dilogarithm appearing on the right-hand side of eq. (40) can be expressed in terms of rapidly converging power series [15]. We now find

$$\bar{K}^{el} = -\frac{k_B T}{\pi Q\kappa}\int_{1-t_0^2}^1 \frac{\ln(u)}{u-1}\,du \tag{41}$$

$$= -\frac{k_B T}{\pi Q\kappa}\int_{2/(1+q)}^1 \frac{\ln(u)}{u-1}\,du, \tag{42}$$

where in eq. (41) $\bar{K}^{el}$ is related to the surface potential $\Psi_0^{(0)}$ via t_0 and in eq. (42) $\bar{K}^{el}$ depends on the surface charge density in terms of q. The expression obtained here for $\bar{K}^{el}$ from the transverse pressure profile agrees exactly with the result obtained from the $(1/a)^2$ term in the electrical free energy [3].

We finally consider the calculation of the bending elastic modulus from the curvature dependence of the transverse pressure profile. Combining eqs. (28) and (32) we find

$$K^{el} = -\varepsilon_0\varepsilon_r\left(\frac{k_B T}{e}\right)^2 \frac{1}{\kappa}\int_0^\infty [2\sinh(\tfrac{1}{2}\Psi^{(0)})\cosh(\tfrac{1}{2}\Psi^{(0)})\,\Psi^{(1)} + 4\sinh(\tfrac{1}{2}\Psi^{(0)})\tanh(\tfrac{1}{4}\Psi^{(0)})]x\,dx\,. \tag{43}$$

Using the differential equation (21) in combination with partial integration one obtains

$$K^{el} = -\varepsilon_0\varepsilon_r\left(\frac{k_B T}{e}\right)^2 \frac{1}{\kappa}\int_0^\infty \sinh(\tfrac{1}{2}\Psi^{(0)})\,\Psi^{(1)}\,dx\,. \tag{44}$$

With the expressions obtained for $\Psi^{(1)}$ in section 2.2 we get for a constant surface potential

$$\int_0^\infty \sinh(\tfrac{1}{2}\Psi^{(0)})\,\Psi^{(1)}\,dx = -2t_0^2 \qquad \text{(constant surface potential)} \tag{45}$$

and in the case of a constant surface charge we get

$$\int_0^\infty \sinh(\tfrac{1}{2}\Psi^{(0)})\,\Psi^{(1)}\,dx = -2t_0^2 - \frac{4t_0^2}{\cosh(\tfrac{1}{2}\Psi_0^{(0)})} = -2\frac{(q-1)(q+2)}{(q+1)q}$$

(constant surface charge)\,. \tag{46}

Combining the above results with eq. (44), we obtain for the constant surface potential

$$K^{el} = \frac{k_B T}{2\pi Q\kappa}\,t_0^2 \qquad \text{(constant surface potential)} \tag{47}$$

and for the constant surface charge

$$K^{el} = \frac{k_B T}{2\pi Q\kappa}\,\frac{(q-1)(q-2)}{(q+1)q} \qquad \text{(constant surface charge)}\,. \tag{48}$$

Again the result at constant surface charge obtained here for K^{el} from the curvature dependence of the transverse pressure profile agrees exactly with the result obtained from the $(1/a)^2$ term in the electrical free energy [3]. The result for K^{el} at constant surface potential has as far as I know not been presented before. Notice that contrary to the case for $K^{el}c_0^{el}$ and $\bar{K}^{el}$, in the case of K^{el} the transition from constant surface potential to constant surface charge cannot be made by simply expressing t_0 in terms of q. The reason for this is that $\Psi^{(1)}$ changes in a non-trivial manner depending on whether we are dealing with constant surface charge or with constant surface potential.

4. Concluding remarks

I have shown how to calculate the electric contribution to the curvature elastic moduli of charged interfaces from the transverse pressure profile. The results are in complete agreement with the expressions obtained from the free energy. It is interesting to compare the two methods to calculate the curvature elastic moduli. In the case of the calculation starting from the free energy one needs to know the dependence of the surface potential on the surface charge up to $(1/a)^2$. On the other hand, in the case one uses the transverse pressure profile one only has to go to terms of order $(1/a)$. So the calculation of the curvature elastic properties from the pressure profile apears to be simpler than the free energy method. But it should be realized that one has to know the pressure profile as a function of the distance from the surface, whereas in the case of the free energy method only the surface potential as a function of the surface charge is required.

In the case of a charged amphiphilic monolayer at an oil–water interface one has in the aqueous phase the electric double layer and in the oil phase the "brush" formed by the tails of the surfactants. Szleifer et al. [9, 16, 17] presented detailed statistical mechanical calculations of the contribution of the tials of the curvature elastic moduli. By combining the approach of Szleifer et al. and the considerations presented here it should be possible to calculate the complete transverse pressure profile, i.e. both in the oil and in the water phase. From that information it is possible to calculate the full curvature elastic moduli of a charged amphiphilic monolayer at an oil–water interface.

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