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POLARIZABILITY OF THE IONIC CLOUD AROUND A CHARGED MEMBRANE SHEET

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The polarizability of the ionic cloud around a charged membrane sheet parallel to the surface is calculated. The membrane is modeled as an infinitely thin and long strip of width $2d'$. The Poisson-Boltzmann equation is solved with an external electric field as a perturbation. The polarizability is given in closed integral form, with numerical results. At higher salt concentration the polarizability varies approximately as κ^{-3}, where κ is the Debye-Hückel constant. The given theoretical result can account for the a.c. electrodichroism of purple membrane suspensions.

1. Introduction

If a charged object is placed in an ionic solution the charges will be compensated by an ionic cloud around the object. As a result, far away from the object, the system (charged object and the ionic cloud) will appear as electrically neutral. Not only the charges are compensated, but also the electric dipole moment of the whole system equals zero for a finite charged object. In other words, the multipole series expansion [1] for a charged object in ionic solution gives zero net charge and dipole moment. The distribution of the ions around the charged object is governed by the Poisson-Boltzmann equation [2]. If an external electric field is switched on this system there is an ionic current and the distribution of the ionic cloud around the object is distorted. This results in an induced dipole moment of the system and the effect of the external field can be characterized by a polarizability. If the charged object is not a sphere with spherical charge distribution the polarizability is anisotropic, i.e., it depends on the mutual orientation of the external field and the charged object. (The electric field interacts directly with the charges of the object resulting in an electrophoretic movement. This is not relevant in the following, so the object can be imagined as fixed in space.)

In principle, the polarizability can be determined by solving the Poisson-Boltzmann equation in an external field (with ionic conduction); in practice this can be done only in limited cases. In this paper we give the solution of this problem for a long, infinitely thin, charged strip. The interest in the solution of this problem arose in connection with the electric dichroism of the purple membrane. The electric dichroism of a purple membrane suspension in an alternating electric field can be explained by assuming a polarizability of the membrane fragments and the surrounding ionic cloud [3,4]. As our result shows, the ionic strength dependence of the polarizability of a purple membrane suspension can be adequately explained by our model calculations. In the following we formulate the problem, give the differential equations and solve them for the polarizability parallel to the strip. We would like to keep the problem as simple as possible to obtain an analytical solution. We shall neglect hydrodynamic drag forces (solvent flow) and dielectric loss effects, i.e., the polarizability will be given for the low-frequency (d.c.) response to the external perturbing electric field. Our measurements on purple membranes show that the polarizability is approximately frequency independent at $\nu \lesssim 10$ kHz. A more general treatment including drag forces and frequency response is given in refs. 5–8. A similar calculation was given by Rau and Charney [9] for a charged cylinder (but see also ref. 5 and 10 for the same problem).

2. Theory

We wish to calculate the ionic distribution around a thin, infinitely long, charged strip, whose width is $2d'$ (fig. 1). The strip has a smoothly distributed charge of Q per unit surface and is immersed in an ionic solution. For simplicity we assume monovalent ions with $N = N_+ = N_-$ concentration (number of ions per unit volume) far away from the strip. The external electric field, E', is directed along the x'-axis. The ion distribution $n_\pm$ and the electric potential ψ' are given by:

$$n_\pm = N\left(n^0_\pm + \delta_\pm\right) \tag{1}$$

$$\psi' = \phi' + \varphi' - E'x' \tag{2}$$

where $n^0_\pm$ and ϕ' describe the static distribution of the ions and potential when the external field is off. $\delta_\pm$ and φ' give the change caused by the electric field E', i.e.:

$$\delta_\pm, \varphi' \to 0 \text{ if } E' \to 0 \tag{3}$$

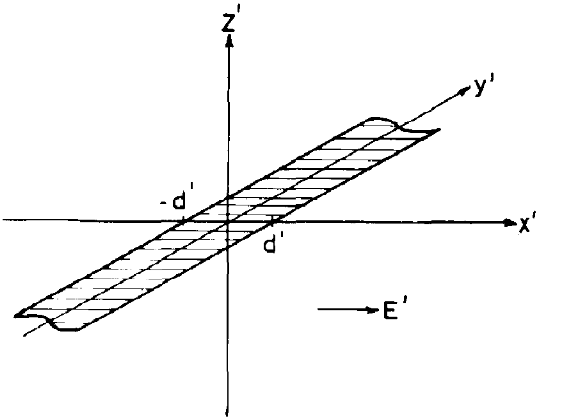

Fig. 1. The infinite membrane sheet for calculation of the polarizability parallel to the x' direction.

All functions depend on x' and z'.

When the external field is off, we apply the following Poisson-Boltzmann equations:

$$\Delta'\phi' = \kappa^2\phi' \tag{4a}$$

$$n^0_+ + n^0_- = 1 + \left(\frac{e}{kT}\right)^2(\phi')^2 \tag{4b}$$

$$n^0_+ - n^0_- = -\frac{2e}{kT}\phi' \tag{4c}$$

$$\kappa^2 = \frac{8\pi e^2 N}{kT} \tag{4d}$$

with the boundary conditions:

$$-\left.\frac{\partial\phi'}{\partial z'}\right|_{z'=0} = \begin{cases} \dfrac{2\pi}{\epsilon}Q & \text{if } |x'| \leq d' \\ 0 & \text{if } |x'| > d' \end{cases} \tag{5a}$$

$$\phi', n^0_\pm \to 0 \quad \text{if } |x'|,|z'| \to \infty \tag{5b}$$

where ϵ is the dielectric constant of the ionic solution, k and κ the Boltzmann and Debye-Hückel constants, T the absolute temperature and e the elementary charge.

The equations are much simpler if we measure the energy in kT and the distance in $1/\kappa$ units [11]. Then the potentials and the coordinates will be dimensionless quantities:

$$\psi = \frac{e\psi'}{kT} \qquad \phi = \frac{e\phi'}{kT}$$
$$\varphi = \frac{e\varphi'}{kT} \qquad E = \frac{1}{\kappa}\frac{eE'}{kT} \tag{6}$$
$$x = \kappa x' \qquad z = \kappa z'$$

With rescaled variables eqs. 4 transform to:

$$\Delta\phi = \phi \tag{7a}$$

$$n^0_+ + n^0_- = 2 + \phi^2 + \ldots \tag{7b}$$

$$n^0_+ - n^0_- = -2\phi + \ldots \tag{7c}$$

and eqs. 5:

$$-\left.\frac{\partial\phi}{\partial z}\right|_{z=0} = \begin{cases} \dfrac{2\pi eO}{\epsilon kT\kappa} & \text{if } |x| \leq d \\ 0 & \text{if } |x| > d \end{cases} \tag{8}$$

As ψ must fulfill the Poisson-Boltzmann equation, we obtain for φ:

$$\Delta\varphi = -\tfrac{1}{2}\kappa^2\rho_- \tag{9}$$

where

$$\rho_+ = \delta_+ + \delta_-$$
$$\rho_- = \delta_+ - \delta_- \tag{10}$$

The boundary conditions for φ, δ_+ and δ_-:

$$\left.\frac{\partial\varphi}{\partial z}\right|_{z=0} = 0 \tag{11a}$$

$$\varphi, \delta_\pm \to 0 \text{ if } |x|, |z| \to \infty \tag{11b}$$

The drift velocities of the ions in the external field E are given [11] in rescaled variables by:

$$\frac{f_\pm}{\kappa^2 kT}\boldsymbol{u}_\pm = \mp e\nabla\psi - \nabla \ln n_\pm \tag{12}$$

where $f_\pm$ are the frictional coefficients of the ions. For steady-state conditions [11]:

$$\nabla\cdot(n_\pm \boldsymbol{u}_\pm) = 0 \tag{13}$$

and from eq. 12 it follows that:

$$\nabla\cdot[\mp n_\pm \nabla\psi - \nabla n_\pm] = 0 \tag{14}$$

As eq. 14 is also valid for $n^0_\pm$ and ϕ, subtracting this from eq. 14 we obtain:

$$\nabla\cdot[\mp n^0_\pm \nabla(\varphi - Ex) \mp \delta_\pm \nabla\psi - \nabla\delta_\pm] = 0 \tag{15}$$

We would like to determine the effect of the external field on the ion distribution in the first order of E. All higher terms of E in eqs. 15 will be neglected (e.g., $\delta_\pm\varphi$):

$$\nabla\cdot[-n^0_+ \nabla(\varphi - Ex) - \delta_+ \nabla\phi - \nabla\delta_+] = 0 \tag{16a}$$

$$\nabla\cdot[n^0_- \nabla(\varphi - Ex) + \delta_- \nabla\phi - \nabla\delta_-] = 0 \tag{16b}$$

Adding and subtracting eqs. 16a and 16b and introducing the quantities in eqs. 10 we obtain:

$$\nabla\cdot[(n^0_+ + n^0_-)\nabla(\varphi - Ex) + \rho_+\nabla\phi + \nabla\rho_-] = 0 \tag{17a}$$

$$\nabla\cdot[(n^0_+ - n^0_-)\nabla(\varphi - Ex) + \rho_-\nabla\phi + \nabla\rho_+] = 0 \tag{17b}$$

The quantities $n^0_\pm$ and ϕ describe the static conditions of the ionic cloud and $\delta_\pm$ and φ the perturbations caused by the external field, E. The perturbations $\delta_\pm$ and φ depend on E and on the static distribution $n^0_\pm$ and ϕ. We have already linearized eqs. 15 in E, now the order dependence of the perturbation ($\delta_\pm$ and φ) on static conditions ($n^0_\pm$ and ϕ) is taken into account. Examination of eqs. 17a and 17b shows that ρ_+ depends on ϕ, but ρ_- and φ depend on ϕ^2 in the lower order (see also eqs. 4b and 4c). In other words, if we expand eqs. 17a and 17b in powers of ϕ and keeping only the lower order terms, we obtain:

$$\Delta\rho_+ = -2E\frac{\partial\phi}{\partial x} \tag{18a}$$

$$\Delta\rho_- - \rho_- = 2E\phi\frac{\partial\phi}{\partial x} - \nabla\rho_+\cdot\nabla\phi - \rho_+\Delta\phi \tag{18b}$$

Further boundary conditions for $\rho_\pm$ can be obtained from eqs. 11a and 17a and b by taking into account that:

$$u_z^\pm|_{z=0} = 0 \text{ if } |x| \leqslant d$$

In the same order of ϕ, we obtain:

$$\left.\frac{\partial\rho_+}{\partial z}\right|_{z=0} = 0 \tag{19a}$$

$$\left.\frac{\partial\rho_-}{\partial z}\right|_{z=0} = \begin{cases} \dfrac{2\pi eQ}{\epsilon kT}\rho_+(z=0) & \text{if } |x| \leqslant d \\ 0 & \text{if } |x| \geqslant d \end{cases} \tag{19b}$$

We notice that all functions are even in z, but that ϕ is even, and ρ_+ and ρ_- are odd in x.

The electric dipole moment m, induced by the external field E, for unit length y' (fig. 1) is given by

$$m = 2eN\int_0^\infty\int_{-\infty}^\infty(\delta_+ - \delta_-)x'\mathrm{d}x'\mathrm{d}z'$$
$$= \frac{2eN}{\kappa^3}\int_0^\infty\int_{-\infty}^\infty x\rho_-\mathrm{d}x\mathrm{d}z \tag{20}$$

To obtain the induced dipole moment, it is not necessary to solve eqs. 18a and b. By partial integration of eq. 20 and taking into account the boundary conditions, it can be shown that:

$$m = E\frac{2eN}{\kappa^3}\int_0^\infty\int_{-\infty}^\infty\phi^2\mathrm{d}x\mathrm{d}y$$

$$+\frac{2eN}{\kappa^3}\int_0^\infty\int_{-\infty}^\infty \phi\frac{\partial\rho_+}{\partial x}\mathrm{d}x\mathrm{d}z \tag{21}$$

According to eq. 21 we need only ϕ and ρ_+ to calculate the dipole moment.

2.1. Solutions of the differential equations

First we solve the differential equation, eq. 7a, with boundary conditions eqs. 5b and 8. We seek the solution in the Fourier integral of ϕ in x:

$$\phi(x, z) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^\infty f(k, z)e^{ikx}\mathrm{d}k$$

For $f(k, z)$, we obtain from eq. 7a:

$$\frac{\mathrm{d}^2 f}{\mathrm{d}k^2} - (k^2+1)f = 0$$

which has the solution:

$$f(k, z) = a_1 e^{\lambda z} + a_2 e^{-\lambda z}$$

with

$$\lambda = \sqrt{k^2+1}$$

As ϕ is a real function, a_1 and a_2 are also real and eq. 8 gives for $z \geqslant 0$:

$$a_1 = 0$$

$$a_2 = \frac{4\pi eQ}{\epsilon kT\kappa}$$

and

$$f(k, z) = \frac{4\pi eQ}{\epsilon kT\kappa}\cdot\frac{\sin(kd)}{k\sqrt{k^2+1}}e^{-\sqrt{k^2+1}\cdot z} \tag{22}$$

(It was taken into account that ϕ should be finite at $z \to \infty$.)

The final solution is:

$$\phi(x, z) = \frac{2\sqrt{\pi}eQ}{\epsilon kT\kappa}\int_{-\infty}^\infty \frac{\sin(kd)}{k\sqrt{k^2+1}} \cdot e^{-\sqrt{k^2+1}\cdot z}\cdot e^{ikx}\cdot\mathrm{d}k \tag{23}$$

In a similar way we seek the solution of eq. 18a in the form:

$$\rho_+(x, z) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^\infty r(k, z)e^{ikx}\mathrm{d}k$$

From eqs. 18a and 22 we obtain a differential equation for $r(k, z)$:

$$\frac{\mathrm{d}^2 r}{\mathrm{d}k^2} - k^2 r = -2ikEf \tag{24}$$

The general solution of eq. 24 has the form:

$$r = r_0 + r_1$$

where r_0 is the general solution for:

$$\frac{\mathrm{d}^2 r_0}{\mathrm{d}k^2} - kr_0 = 0$$

and r_1 is a special solution of eq. 24. It is easy to find r_1 with eq. 22:

$$r_1 = -4iE\frac{2\pi eQ}{kT}\cdot\frac{\sin(kd)}{\sqrt{k^2+1}}\cdot e^{-\sqrt{k^2+1}\cdot z}$$

With the boundary conditions eqs. 11b and 19a and taking into account that ρ_+ is real and an odd function in x, the solution for r_0 is:

$$r_0 = 4iE\frac{2\pi eQ}{\epsilon kT\kappa}\cdot\frac{\sin(kd)}{|k|}\cdot e^{-|k|z}$$

With these results we obtain for ρ_+:

$$\rho_+ = Ei\frac{4\sqrt{2\pi}eQ}{\epsilon kT\kappa}\int_{-\infty}^\infty \sin(kd) \times\left(\frac{e^{-|k|z}}{|k|} - \frac{e^{-\sqrt{k^2+1}\cdot z}}{\sqrt{k^2+1}}\right)e^{ikx}\mathrm{d}k \tag{25}$$

The solution shows that the perturbation ρ_+ is linear in the external field, E.

3. Results and discussion

With the solutions given by eqs. 23 and 25 and using eq. 21 we can calculate the induced dipole moment. The result is:

$$m = E\frac{2\pi eQ^2}{\epsilon kT\kappa^3}\int_{-\infty}^\infty \frac{\sin^2(kd)}{k^2\sqrt{k^2+1}} \times\left(1 + \frac{k^2}{k^2+1} - \frac{4k^2}{k^2+|k|\sqrt{k^2+1}}\right)\mathrm{d}k \tag{26}$$

The induced dipole moment is proportional to E,

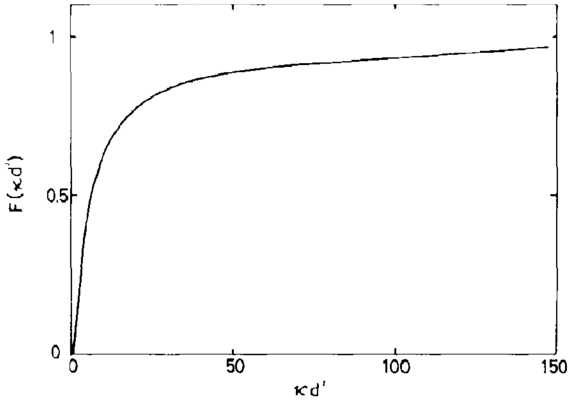

Fig. 2. The behavior of the function F in eq. 27.

with the proportionality factor giving the polarizability, α, of the ionic cloud around the membrane sheet (for unit length in the y' direction).

Returning to the conventional units in d' and E', the polarizability α, parallel to the sheet, can be given in the form:

$$\alpha = \frac{2}{\epsilon}\left(\frac{\pi e Q}{kT}\right)^2 \frac{d'}{\kappa^3} F(\kappa d') \tag{27}$$

where

$$F(\kappa d') = \frac{2}{\pi}\int_0^\infty \frac{\sin^2 x}{x^2} f[x/(\kappa d')]\,\mathrm{d}x \tag{28}$$

and

$$f(y) = \frac{1}{\sqrt{1+y^2}}\left[1 + \frac{y^2}{1+y^2} - \frac{4y^2}{y^2 + y\sqrt{1+y^2}}\right] \tag{29}$$

$$y = x/(\kappa d')$$

The integral in eq. 28 was calculated numerically and the result is shown in fig. 2. In the high salt concentration limit $d' \gg 1/\kappa$, the function $F(\kappa d')$ approaches 1. This behavior follows from the dependence of f on y. The function f under the integral in eq. 28 varies linearly at small values of its argument (fig. 3) and this is the main contribution to the integral at $\kappa d' \gg 1$. At lower values of $\kappa d'$ (below $\kappa d' \approx 20$) the rapid decrease and the change of sign in the function f (fig. 3) decrease the integral, eq. 28, more rapidly.

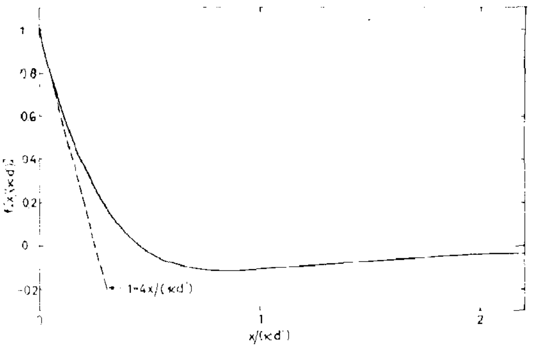

Fig. 3. A plot of the function f under the integral in eq. 28.

At high values of $\kappa d'$ the polarizability, α, varies approximately as κ^{-3}. In this case the ionic cloud approaches the charged strip,the interaction between the cloud and the charge on the strip is stronger, and the effect of the external field of polarizing the ionic cloud decreases rapidly. As eq. 27 shows, in that range of salt concentration the polarizability is approximately proportional to the surface of the membrane sheet.

It can be shown approximately that eq. 27 is consistent with the result given in ref. 9 for a rod. Let $\kappa d' \gg 1$. Take a piece of the strip of length κ^{-1} in the y' direction. Its polarizability is given by

$$\alpha \approx \left(\frac{eQ}{kT}\right)^2 \frac{d'}{\kappa^4}$$

Such a piece is very similar (but not completely identical) in behavior to a thin rod of length $L' = d'$ with double layer thickness κ^{-1}. $Q\kappa^{-1} = Q_R$ is the equivalent linear charge density. Hence

$$\alpha \approx \left(\frac{eQ_R}{kT}\right)^2 \frac{L'}{\kappa^2}$$

This is essentially eq. 41 of Rau and Charney [9].

The polarizability of purple membrane suspensions was measured by electrodichroism in ref. 4 as a function of salt concentration. At higher salt concentration (above approx. 1 mM KCl) a κ^{-3} dependence was found. Comparison of the experimental result with eq. 27 allowed the determination of the membrane surface charge density and separation of the inner membrane polarizability component.

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