

# Effective Screening Length of Isotropic Liquid Samples Submitted to an Applied Voltage

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A cell of isotropic liquid in the shape of a slab of thickness  $d$  and containing ionic impurities is considered. It is shown that the screening effect produced by the ionic charges on the external field is characterized by an effective surface length,  $\lambda_s(U)$ , depending on the applied voltage  $U$ . The analysis indicates that  $\lambda_s(U) \ll \lambda_D$  when the applied voltage is very large, and  $\lambda_s(U) \rightarrow \lambda_D$  for very small values of the applied voltage, where  $\lambda_D$  is the Debye screening length. The presence of the ions is responsible also for a counterpotential,  $v$ , that for small  $U$  is such to cancel the effective electric field in the sample, whereas in the opposite limit it is inversely proportional to the applied difference of potential.

## 1. Introduction

The influence of the ionic charge on the electric potential distribution of an isotropic liquid containing ions, submitted to an external field, has been investigated in recent years by several authors.<sup>1–10</sup> The effective electric field distribution as well as the surface charge have been investigated in the framework of the Poisson–Boltzmann theory, by means of analytical models and numerical simulations.<sup>11–14</sup> The effective electric potential inside the sample is shown to be dependent on the presence of ionic charges, exhibiting a very strong variation near the surfaces. These surfaces can selectively adsorb one type of ion (usually positive charged) with an adsorption energy  $A$ . As is well-known in electrolyte theory, such an adsorption produces a counterion cloud over a depth  $\lambda_D$ , called the Debye screening length. When the sample is submitted to an external voltage, the surface layer in which the ions are confined is expected to depend on the external voltage.<sup>15</sup> Furthermore, this surface distribution of charges is responsible for a counterpotential. To have complete information about the field distribution in the cell, is necessary to know the thickness in which the ions are squeezed and the electric field of ionic origin.

In this paper we investigate the effective screening length and the counterpotential due to the ionic redistribution, when the cell of liquid is submitted to an external electric field. We first recall the fundamental equations governing the electric potential distribution in a sample of isotropic liquid containing ions, in the presence of an external field.<sup>15</sup> We consider the case in which the phenomenon of selective adsorption is absent, because the adsorption energies for positive and negative ions are the same. After that, by means of a numerical procedure, we determine the effective screening length as a function of the bias voltage. We obtain also the dependence of a counterpotential inside the sample on the applied voltage, which exhibits two distinct behaviors, according to the regimes of low and high voltage. This procedure permits us to obtain an effective solution

for the profile of the electrical potential across the sample. We notice that, if the liquid is an anisotropic fluid, as a nematic liquid crystal, in a first approximation the same results apply.

## 2. Effective Surface Screening Length

We consider a sample of isotropic liquid. The liquid is assumed dielectric, with dielectric coefficient  $\epsilon$ , but containing impurities able to give rise to ions by means of a chemical dissociation reaction. We assume that the actual electric field is so small that the chemical equilibrium relevant to the dissociation is independent of the external applied voltage.<sup>16</sup> The sample is supposed to be in the shape of a slab, with two uniform flat surfaces in the  $x$ – $y$  plane, separated by a distance  $d$ , located at  $z = \pm d/2$  where blocking electrodes are placed. It is supposed, for simplicity, that all the physical quantities entering in the calculation are only  $z$  dependent. The fundamental equations have been presented in ref 15, but they will be recalled here for clarity. In the absence of an external field, the liquid is globally and locally neutral such that the densities of positive and negative ions are equal to the initial density, i.e.,  $n^\pm(z) = n_0$ . In the presence of a difference of potential  $U$  (supplied by an external agent) such that  $V(\pm d/2) = \pm U/2$  the equilibrium distribution of charges is governed by classical statistics, i.e.

$$n_\pm(z) = ne^{-\psi(z)} \quad (1)$$

in which  $\psi(z) = qV(z)/k_B T$  is the electric potential in  $k_B T/q$  units and  $n$  is the density of ions where  $\psi = 0$ . This quantity has to be determined by imposing the conservation of the number of ions, i.e.

$$n_0 d = \int_{-d/2}^{d/2} n_+(z) dz \quad (2)$$

The spatial dependence of the electrical potential is governed by the Poisson equation, which can be put in the form

$$\frac{d^2 \psi}{dz^2} = \frac{1}{\lambda^2} \sinh \psi(z) \quad (3)$$

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where

$$\lambda^2 = \frac{n_0}{n} \lambda_D^2 \quad (4)$$

is a length depending on the applied voltage and connected with the Debye screening length  $\lambda_D^2 = \epsilon k_B T / (2q^2 n_0)$ .

Equation 3 has to be solved with the boundary conditions

$$\psi(\pm d/2) = \pm u = \pm \frac{1}{2} \frac{qU}{k_B T} \quad (5)$$

and can be integrated to give

$$\frac{d\psi}{dz} = \frac{\sqrt{2}}{\lambda} \sqrt{\cosh \psi + k} \quad (6)$$

where  $k$  can be determined by connecting it with the electric field at  $z = 0$ , i.e.

$$k = \frac{\lambda^2}{2} \left( \frac{d\psi}{dz} \right)_{z=0} - 1$$

The fundamental equations can be now obtained. First, we rewrite eq 2 in the form

$$\int_{-u}^u \frac{e^{-\psi}}{\sqrt{\cosh \psi + k}} d\psi = J(k, u) = \sqrt{2} \frac{\lambda d}{\lambda_D^2} \quad (7)$$

whereas eq 6 is rewritten as

$$\int_{-u}^u \frac{1}{\sqrt{\cosh \psi + k}} d\psi = I(k, u) = \sqrt{2} \frac{d}{\lambda} \quad (8)$$

which, together, imply that

$$I(k, u) J(k, u) = 2 \left( \frac{d}{\lambda_D} \right)^2 \quad (9)$$

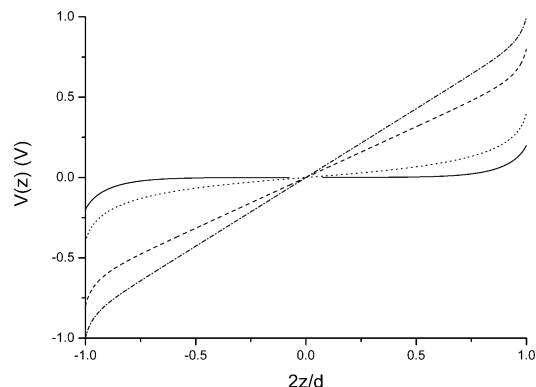
The procedure is now straightforward. For a given applied voltage  $U$ , one solves eq 9 to obtain  $k(U)$  for a sample of definite thickness  $d$  and a Debye screening length  $\lambda_D$ . Once this is done, eq 8 gives the effective (voltage dependent) Debye screening length, in the form

$$\lambda = \sqrt{2} \frac{d}{I(k, u)} \quad (10)$$

Finally, with these quantities determined as a function of  $U$ , one numerically integrates eq 6 to obtain  $\psi(z)$  at each  $z$ . The electric field profile is then easily obtained.

In Figure 1, the electrical potential is shown as a function of the reduced coordinate  $2z/d$  for different values of the applied voltage. The calculations were numerically performed as discussed above. The first salient feature of these curves is the strong variation of the electrical potential near the surfaces placed  $Z = 2z/d = \pm 1$  and a clear linear behavior in the major part of the sample. The second remarkable feature is that the distance over which the strong variation takes place changes with the applied voltage. For the cases illustrated in Figure 1 it is apparent that this length decreases for increasing  $U$ .

To proceed further, we can do a kind of “experimental” physics by considering numerical results as the “experimental” data to be analyzed. It is possible to use an analytical expression,



**Figure 1.** Electrical potential  $V(z)$  versus  $2z/d$ , for  $d = 10 \mu\text{m}$  and  $\lambda_D = 0.5 \mu\text{m}$ . Solid line corresponds to  $U = 0.2 \text{ V}$ , dotted line to  $U = 0.4 \text{ V}$ , dashed line to  $U = 0.8 \text{ V}$ , and dash dotted line  $U = 1.0 \text{ V}$ . The curves were depicted from the numerical solution of eq 3.

depending on two adjustable parameters, to fit these “experimental” data in a very good manner. The expression is

$$V(z) = \left( \frac{U}{2} - v \right) \frac{2z}{d} + v \frac{\sinh(z/\lambda_s)}{\sinh(d/2\lambda_s)} \quad (11)$$

where  $v$  and  $\lambda_s$  are the adjustable parameters.  $v$  plays the role of a counterpotential whereas  $\lambda_s$  is a length. It is the effective screening length where strong variations of the electrical potential are localized near the surfaces. It has been shown that the exact solution of eq 3, for the case of small applied voltage  $u \ll 1$ , is given by<sup>15</sup>

$$\psi(z) = u \frac{\sinh(z/\lambda_D)}{\sinh(d/2\lambda_D)} \quad (12)$$

showing that, in this limit,  $\lambda$  coincides with  $\lambda_D$  and  $v = U/2$ . In the same manner, by means of a perturbative calculation in the limit of large applied voltage  $u \gg 1$  the solution is

$$\psi(z) = 2u \frac{z}{d} \left[ 1 - \frac{\delta^2}{u^2} \right] + 2 \frac{e^{-u}}{u} \delta^2 \sinh \left( 2u \frac{z}{d} \right) \quad (13)$$

where  $\delta = d/2\lambda_D$  is a reduced length. The above expression represents a good solution for the problem when  $(\delta/u)^2 \ll 1$ , which is equivalent to consider that  $u \gg \delta$ . In this limit, eq 13 can be rewritten as

$$V(z) = \left[ \frac{U}{2} - \frac{2 \left( \frac{K_B T \delta}{q} \right)^2}{U} \right] \frac{2z}{d} + \frac{2 \left( \frac{K_B T \delta}{q} \right)^2}{U} \frac{\sinh(2uz/d)}{\sinh u} \quad (14)$$

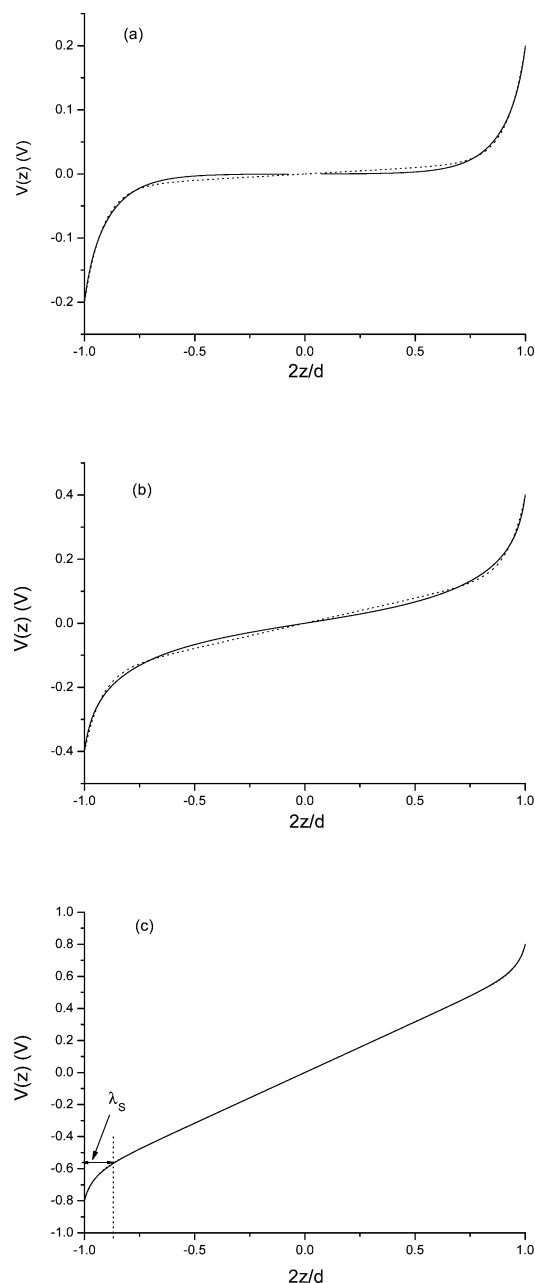
A comparison between (13) with (11) permits us to conclude that

$$\lambda_s = \frac{K_B T}{q} \frac{d}{U}$$

and

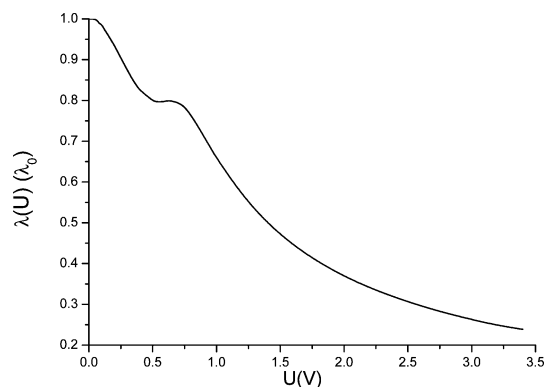
$$v = 2 \left( \frac{K_B T}{q} \right)^2 \frac{\delta^2}{U} \quad (15)$$

In this manner, the general solution proposed in (11) embodies the two limiting solutions, while leaving two parameters free to be adjusted. Some examples of the good agreement of the numerical solutions with the approximated one are given in Figure 2. In fact, the agreement is good in the entire range of applied voltage, ranging from very small to large values.

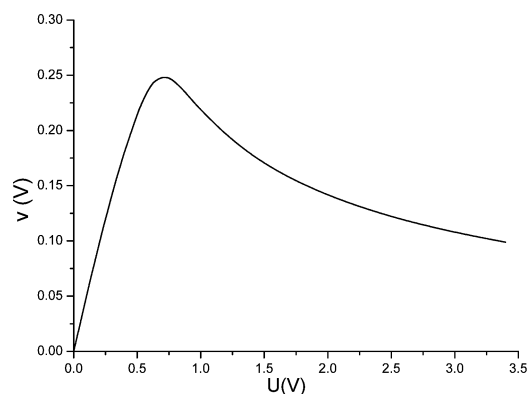


**Figure 2.** Electrical potential  $V(z)$  versus  $2z/d$ , for  $d = 10 \mu\text{m}$  and  $\lambda_D = 0.5 \mu\text{m}$ . Solid line corresponds to the numerical solution of eq 3; dotted line corresponds to the best fit obtained from solution 11. (a)  $U = 0.2 \text{ V}$ , (b)  $U = 0.4 \text{ V}$ , and (c)  $U = 0.8 \text{ V}$ . In curve c there is an illustration of the effective screening length introduced in eq 11.

To obtain the behavior of the adjustable parameters as a function of the applied voltage, we fix the thickness of the sample and the Debye screening length,  $\lambda_D$ . For each value of the applied voltage  $U$  a fit using (11) is performed in order to obtain the best fit. This gives the values of  $\lambda_s(U)$  and  $\nu(U)$  for that considered sample. Figure 3 shows the best fits giving the value of  $\lambda_s(U)$  in units of  $\lambda_D$ . For large applied voltage,  $\lambda_s(U)$  decreases but tends to zero only for very large voltage, as  $1/U$  according to eq 15; for small applied voltage  $\lambda_s(U) \rightarrow \lambda_D$ , as expected. There is a plateau separating the regions of small and large voltages. This behavior can be understood by considering that for small applied voltage, the ionic charges (of a given sign) present in the liquid move toward the electrode of opposite sign forming a charged surface layer of density  $\sigma$ , in such a manner that in the bulk the effective electric field vanishes. In this limit, the liquid behaves as a conductor. On the contrary, for large



**Figure 3.**  $\lambda_s/\lambda_D$  versus  $U$  for  $d = 10 \mu\text{m}$  and  $\lambda_D = 0.5 \mu\text{m}$  (solid line). The results correspond to the best fit using solution (11) to approximate the numerical result of eq 3.



**Figure 4.**  $\nu$  vs  $U$ , for  $d = 10 \mu\text{m}$  and  $\lambda_D = 0.5 \mu\text{m}$ . The curve was obtained by the same procedure as in Figure 3.

applied electric field, all the ions are pushed close to the limiting surface. In this limit, the liquid behaves as a true insulating material, but the actual field in the bulk is partially screened by the ionic charges collected at the surfaces. Therefore, the distribution of charges and fields in the sample is characterized by two regimes of low and high applied voltage.<sup>14,17</sup>

Figure 4 shows the best fits giving  $\nu(U)$ . In the low-voltage region  $\nu(U)$  is linear. It changes the behavior in a drastic manner in the region where  $\lambda_s(U)$  presents a plateau. After that, it tends to zero, as predicted by eq 15.

### 3. Conclusions

We have analyzed the influence of the ions on the effective field distribution of a cell of isotropic fluid of thickness  $d$  submitted to an applied voltage. The electric field distribution across the sample was determined by means of a complete electrostatic model, using numerical calculations. The exact results, analytically established for the limits of small and high applied voltage, were represented by an interpolating general solution in which two adjustable parameters are considered. One of these parameter is an effective screening length and the other a counterpotential. The behaviors of these parameters were numerically investigated as a function of the bias voltage. We have shown that this effective screening length reduces to the Debye screening length for small values of the applied field and becomes very small in the limit of high applied voltage. This approach permits us to quantify, by means of an effective screening length, the importance of surface effect on the bulk orientation and on the electric field distribution when the ionic charges are taking into account.

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