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Independence of the effective dielectric constant of an electrolytic solution on the ionic distribution in the linear Poisson-Nernst-Planck model

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We consider the influence of the spatial dependence of the ions distribution on the effective dielectric constant of an electrolytic solution. We show that in the linear version of the Poisson-Nernst-Planck model, the effective dielectric constant of the solution has to be considered independent of any ionic distribution induced by the external field. This result follows from the fact that, in the linear approximation of the Poisson-Nernst-Planck model, the redistribution of the ions in the solvent due to the external field gives rise to a variation of the dielectric constant that is of the first order in the effective potential, and therefore it has to be neglected in the Poisson's equation that relates the actual electric potential across the electrolytic cell to the bulk density of ions. The analysis is performed in the case where the electrodes are perfectly blocking and the adsorption at the electrodes is negligible, and in the absence of any ion dissociation-recombination effect. © *2014 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4893712]

I. INTRODUCTION

The problem of the static effective dielectric constant of a solution containing ions has been extensively studied in the frame of various approximations and in conjunction with experimental data for a variety of physical systems. In the static case, the traditional approach that has been used is the Poisson-Boltzmann (PB) theory and its modifications and/or generalizations.[1–3] Alternative models have been developed in the frame of the field theory,[4] molecular hydrodynamic theory,[5] etc. Molecular dynamics has been performed.[6] The discreteness of the charge effects in the double layer has also been considered.[7] In this context, a well known problem is the dielectric decrement that describes the decrease of the static dielectric constant of a solution when the salt concentration increases.[9–11] If currents are present in the system, the PB model is generalized by the Poisson-Nernst-Planck (PNP) model.[8] The latter is usually employed in its linear version that can be analytically solved.

The classical PNP model proposed to take into account the influence of the ionic impurities on the effective dielectric constant of an insulating medium is based on a continuum description of the medium under investigation.[12–16] The dimensions of the ions are not considered, and hardcore potentials, taking into account the finite dimension of the ions and of the molecules forming the guest liquid are not introduced.[17] In this framework, the distribution of ions is responsible for a variation of the actual electric field acting on the ions themselves. The unknowns of the problem are the bulk densities of ions and the actual field across the sample[18–21] while the dielectric constant ε entering into the equations of the model is the one of the liquid free of ions. This simple model is

able to predict several results observed in the response of an electrolytic cell submitted to an external periodic voltage of small enough amplitude in order that the system remains in the linear regime.[22] In particular, the giant increasing of the real component of the dielectric constant of a liquid containing ionic impurities in the dc limit.[23] For an electrolytic cell with flat and perfectly blocking electrodes at a distance d apart, the dc effective dielectric constant is found to be $\varepsilon'(0) = \varepsilon d/(2\lambda)$, where λ is the Debye's length for the solution under investigation.[12, 16, 23] This result is due to the confinement of the ions in two surface layers whose thickness is comparable with λ.[24] In the dc limit, and in the case of small external voltage, the field vanishes in the cell, and it is localized just in the vicinity of the limiting electrodes. Hence in this limit the hypothesis of a uniform electric field across the sample does not work.[25]

When the density of ions is large and uniform, the dielectric constant of the solution depends on the density of the ions themselves. In the absence of an external electric field, the effective dielectric constant of the medium depends on the dielectric constant of the liquid and on that of the ions (if the latter are formed by polarizable molecules or if their presence modify the polarization of the solvent), that is, the solution has to be considered as a mixture of three different media and consequently treated as an effective medium.[26] In this framework, the description of the medium has to be done in terms of the densities of the liquid and of the ions, and of the actual potential across the sample.[27]

Finally, another problem that arrives when the ionic distribution is a function of the position and of the time, is the dependance of the effective dielectric constant on the distribution of the ions, that is $\varepsilon_{eff} = \varepsilon_{eff}(\mathbf{r}, t)$. In a first

approximation, one expects a linear correction to the effective dielectric constant. The aim of the present note is to investigate if the latter correction results to a position and/or time dependance of ε_{eff} in the linearized version of the PNP model as it has been recently suggested.[28]

II. POISSON-NERNST-PLANCK MODEL

Our aim is to show by means of a simple analysis that in the linear approximation of the PNP model, the dielectric constant has to be considered position and time independent. To this end, we remind that a possible interpretation of a position or time dependent dielectric constant, could be related to the assumption that the solution under investigation is a mixture of three components: the insulating liquid, the positive and negative ions, whose dielectric constants are ε_ℓ, ε_p, and ε_m, respectively. In this framework, the effective dielectric constant of the liquid, ε_{eff}, also depends on the concentration of the liquid and of the positive and negative ions, that we indicate by n_ℓ, n_p, and n_m, respectively, as discussed in Ref. 26, that is, $\varepsilon_{\text{eff}} = \varepsilon_{\text{eff}}(n_\ell, n_p, n_m)$. In the state of thermodynamic equilibrium, that corresponds to an unlimited sample in the absence of external electric field, the distribution of ions is position independent, and the system is locally and globally neutral. The bulk densities of positive and negative ions, in this reference state, are indicated by n_0. If the limiting surfaces, in the slab approximation of the sample under investigation, are not selectively adsorbing the bulk density of ions is n_0 even in a sample of finite thickness, d, when no external voltage is applied. In this state of reference, the dielectric constant is $\varepsilon_R = \varepsilon_{\text{eff}}(n_\ell, n_0, n_0)$. When the sample is submitted to an external voltage $\Delta V = \Delta V(t)$, the ions move under the effect of the electric field. If we use a Cartesian reference frame having the z-axis perpendicular to the limiting surfaces, located at $z = \pm d/2$, $n_p = n_p(z, t) = n_0 + \delta n_p(z, t)$, $n_m = n_m(z, t) = n_0 + \delta n_m(z, t)$, where $\delta n_p(z, t)$ and $\delta n_m(z, t)$ are the bulk variations of the ionic densities due to the presence of the external voltage. It follows that $\varepsilon_{\text{eff}} = \varepsilon_{\text{eff}}(z, t)$, i.e., the effective dielectric constant depends on time and on position, via δn_p and δn_m. In this framework, the equations of continuity for the positive and negative ions are

$$\frac{\partial(\delta n_p)}{\partial t} = D_p \frac{\partial}{\partial z} \left\{ \frac{\partial(\delta n_p)}{\partial z} + \frac{q}{K_B T}(n_0 + \delta n_p)\frac{\partial V}{\partial z} \right\}, \quad (1)$$

$$\frac{\partial(\delta n_m)}{\partial t} = D_m \frac{\partial}{\partial z} \left\{ \frac{\partial(\delta n_m)}{\partial z} - \frac{q}{K_B T}(n_0 + \delta n_m)\frac{\partial V}{\partial z} \right\}, \quad (2)$$

where D_p and D_m are the diffusion coefficients for the positive and negative ions, q is the electric charge of the ions, assumed monovalent, K_B is the constant of Boltzmann, T the absolute temperature, and we have taken into account the relation of Einstein relating the mobility to the diffusion coefficient.[27] Equations (1) and (2) are valid in the limit of full dissociation of the impurities responsible for the ionic contamination. They are valid in dilute solutions, where the recombination of ions can be neglected.[29, 30]

III. EFFECTIVE DIELECTRIC CONSTANT OF A DISPERSION

In the linear approximation of the PNP model, the applied voltage ΔV is assumed so small that $\delta n_p \ll n_0$, $\delta n_m \ll n_0$. Therefore, the z-derivative of $\delta n_p \, \partial V/\partial z$ and of $\delta n_m \, \partial V/\partial z$, in the continuity equations, can be neglected with respect to $n_0 \partial^2 V/\partial z^2$, where $V(z)$ is the actual electric potential across the sample.[12] In this case, the equation $\nabla \cdot \mathbf{D} = \rho$, where $\mathbf{D}$ is the electric displacement and ρ the bulk density of charge, takes the form

$$-\frac{\partial}{\partial z}\left(\varepsilon_{\text{eff}} \frac{\partial V}{\partial z}\right) = q(\delta n_p - \delta n_m). \quad (3)$$

From (3), we obtain

$$\frac{\partial \varepsilon_{\text{eff}}}{\partial z}\frac{\partial V}{\partial z} + \varepsilon_{\text{eff}}\frac{\partial^2 V}{\partial z^2} = -q(\delta n_p - \delta n_m). \quad (4)$$

Since ε_{eff} depends on z via δn_p and δn_m, we have

$$\frac{\partial \varepsilon_{\text{eff}}}{\partial z} = \left(\frac{\partial \varepsilon_{\text{eff}}}{\partial n_p}\right)_0 \frac{\partial(\delta n_p)}{\partial z} + \left(\frac{\partial \varepsilon_{\text{eff}}}{\partial n_m}\right)_0 \frac{\partial(\delta n_m)}{\partial z}, \quad (5)$$

from which $\partial \varepsilon_{\text{eff}}/\partial z$ is found to be a small quantity of the first order, as δn_p, δn_m, and V. From Eq. (4), we obtain that in the present case the equation of Poisson at the first order can be written as

$$\frac{\partial^2 V}{\partial z^2} = -\frac{q}{\varepsilon_{\text{eff}}}(\delta n_p - \delta n_m), \quad (6)$$

relating the effective potential to the ionic distribution, in the linear approximation of the PNP model.

IV. IONIC DISTRIBUTION AND EFFECTIVE DIELECTRIC CONSTANT

In the presence of an external voltage the effective dielectric constant of the medium is $\varepsilon_{\text{eff}}(n_\ell, n_p, n_m) = \varepsilon_{\text{eff}}(n_\ell, n_0 + \delta n_p, n_0 + \delta n_m)$, from which, taking into account that $\delta n_p \ll n_0$ and $\delta n_m \ll n_0$, we get

$$\varepsilon_{\text{eff}}(z, t) = \varepsilon_R + \left(\frac{\partial \varepsilon_{\text{eff}}}{\partial n_p}\right)_0 \delta n_p(z, t)$$
$$+ \left(\frac{\partial \varepsilon_{\text{eff}}}{\partial n_m}\right)_0 \delta n_m(z, t) + \mathcal{O}(2), \quad (7)$$

where, as before, $\varepsilon_R = \varepsilon_{\text{eff}}(n_\ell, n_0, n_0)$ is the effective dielectric constant of the reference state. By substituting Eq. (7) into Eq. (6), we have

$$\frac{\partial^2 V}{\partial z^2} = -\frac{q}{\varepsilon_R}\left\{1 - \frac{1}{\varepsilon_R}\left[\left(\frac{\partial \varepsilon_{\text{eff}}}{\partial n_p}\right)_0 \delta n_p + \left(\frac{\partial \varepsilon_{\text{eff}}}{\partial n_m}\right)_0 \delta n_m\right]\right\}$$
$$\times (\delta n_p - \delta n_m) \quad (8)$$

that at the first order in the variations induced by the external voltage reduces to

$$\frac{\partial^2 V}{\partial z^2} = -\frac{q}{\varepsilon_R}(\delta n_p - \delta n_m). \quad (9)$$

From Eq. (9), it is evident that in the linear approximation of the PNP model the dielectric constant of the medium in which

the ions are moving cannot be considered time or position dependent.[28]

The generalization of Eqs. (1) and (2) to the case of partial dissociation does not present any difficulty,[29,30] and the main conclusion of our analysis does not change.

V. CONCLUSION

We have analyzed the contribution of the ions to the effective dielectric constant of a solution in which the ions are dispersed. The effective dielectric constant of the solution depends on the concentration and on the distribution of the ions, that is, it depends on position and on time. However, in the framework of the linear version of the PNP model, the effective dielectric constant is independent of the redistribution of ions due to the presence of the external electric field. This conclusion follows from the observation that the electric field has to be considered as a small quantity, of the first order in the variation of the bulk densities of ions. Since the contribution due to the redistribution of ions to the effective dielectric constant is also of the first order in these quantities, its contribution to the dielectric displacement is of the second order and hence has to be dropped out in the linear version of the PNP model. From this observation it follows that recently proposed generalizations of the linear PNP model are not physically based,[28] despite the apparent good agreement with experimental data. Of course, in the nonlinear approximation of the PNP model the renormalization of the dielectric constant due to the ions distribution could be important.[3] However, in the case where the ionic concentration is a small quantity this renormalization is small, and linear in the ionic concentration, and hence usually negligible. In the opposite limit where the ionic concentration is large, the standard PNP model is no longer working, because the recombination has to be taken into account,[29,30] and the continuum approximation has to be changed along the lines discussed in Ref. 17.

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