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Abstract

The dielectric constant of an electrolytic solution is known to decrease with increasing salt concentration. This effect, frequently called dielectric decrement, is experimentally found for many salts and solvents and shows an almost linear decrease up to a certain salt concentration. However, the actual origin of this concentration dependence is yet unclear, and many different theoretical approaches investigate this effect. Here I present an investigation based on microscopic Maxwell equations and periodic homogenization theory. The microscopic perception of anions and cations forming a pseudo lattice in the liquid solution is exploited by multi-scale asymptotic expansions, where the inverse Avogadro number arises as small scaling parameter. This leads to a homogenized Poisson equation on the continuum scale with an effective or homogenized dielectric constant that accounts for microscopic field effects in the pseudo lattice. Incomplete dissociation is further considered at higher salt concentrations due to solvation effects. The numerically computed homogenized dielectric constant is then compared to experimental data of NaCl and shows a remarkable qualitative and quantitative agreement in the concentration range of $(0-5)$mol L.

1 Introduction

In this letter we investigate the dielectric constant $\boldsymbol{\varepsilon}_{AC}$ of an electrolytic solution AC and its decrease with increasing salt concentration c. This effect is known as dielectric decrement or dielectric depression[1] and was first observed by Hasted *et al.* in 1948 [2] and verified for many electrolytic solutions, *e.g.* [3–11]. Up to a certain concentration c^{sat} a linear decrease was found, *i.e.*

$$\boldsymbol{\varepsilon}_{AC} = \varepsilon_0(1+\chi) - A_{AC}\cdot c \qquad c < c^{\mathsf{sat}} \;, \tag{1}$$

where ε_0 is the vacuum permittivity, χ the susceptibility of the solvent, and A_{AC} an electrolyte specific constant. At higher salt concentration, $c > c^{\mathsf{sat}}$, the relation becomes non-linear and flattens towards a plateau value (see Fig. 2b). Various theoretical approaches investigate this effect [12–21], mainly based on Possion–Boltzmann equations and recent extensions.

However, none actually exploits the periodicity of the quasi-lattice structure in terms of periodic homogenization theory and multi-scale asymptotic expansions. This mathematical tool [22–28] is frequently and very successfully used to model porous media, but seldomly applied to bridge the scale between atomistic and continuum descriptions. Based on a simple model for an electrolytic solution which relies only on Maxwells equations on the atomistic scale we use multi-scale periodic homogenization techniques to derive the Poisson equation on the continuum scale, *i.e.* with a continuous charge distribution function. Due to the homogenization procedure, the dielectric constant becomes dependent on the salt concentration c, which is shown in the following. The obtained concentration dependence of the homogenized dielectric constant is in remarkable agreement to measured data, and it is further shown that incomplete dissociation leads to an overall agreement for salt concentrations from $(0-5)$ mol L^{-1}.

Consider a salt AC which is dissolved and, up to a certain limit c^{sat} [30], completely dissociated in a liquid solvent S . The anions A^- and cations C^+ are assumed to form some quasi-crystalline structure in the liquid solution, *c.f.* Fig. 1. The distance between two adjacent ions is related to the bulk salt concentration c. The idea that ions in solution form a quasi-lattice in liquid electrolytes is widely employed nowadays [31–35]. Bahe [31], for example, derived on the basis of a face centered cubic pseudo-lattice an expression for the mean activity coefficient which shows a remarkable accordance to experimental data [34].

The electrolyte Ω is considered as periodic repetition of unit cells ω in all three space dimensions. In the unit cell ω, the cations C^+ form a fcc crystal lattice, with an interpenetrated fcc lattice of the anions A^- (NaCl -crystal structure). In total the unit cell captures 4 cations and 4 anions whereby it is charge neutral. The unit cell width is denoted by a and determined from the salt concentration c via

$$a = \left(\frac{1}{4}\cdot c\right)^{-\frac{1}{3}} \ . \tag{2}$$

For a salt concentration of 0.01mol L^{-1} the cell width is 8.72 nm and for a concentration of 1mol L^{-1} about 1.88nm. For comparison, solid NaCl has a lattice constant of $a_{\mathrm{NaCl}} = 0.54$ nm. Within each unit cell we consider a solvent phase ω_S, spherical anions ω_A and spherical cations ω_C with $\omega = \omega_S \cup \omega_A \cup \omega_C$. The respective interfaces within the unit cell are denoted by $\sigma_{i,j}, i,j = S,A,C$, where $\sigma_{S,S}$ denotes the boundary to the adjacent unit cells. Note that $\partial\omega_S = \sigma_{S,S} \cup \sigma_{A,S} \cup \sigma_{C,S}$.

Consider then the electrostatic Maxwell equation

$$\mathrm{div}\,\mathbf{D} = 0 \tag{3}$$

with boundary conditions

$$\mathbf{D}\cdot\mathbf{n} = \frac{e_0 z_\alpha}{4\pi r_\alpha^2} \qquad \text{on} \qquad \sigma_{S,\alpha} \ , \tag{4}$$

where e_0 is the elementary charge in Coulomb, z_α the charge number of the ion $\alpha = A, C$, and r_α the respective ionic radius. Note that we assume thus spherical symmetry of each ion as well as a homogenous surface charge distribution on the atomic scale. This is sufficient for the sake of this work, but not a necessary constraint.

We introduce the Faraday constant $F = e_0 N_A$ which yields

$$\mathbf{D}\cdot\mathbf{n} = \delta \cdot \underset{s}{q_\alpha} \quad \text{with} \quad \underset{s}{q_\alpha} = \frac{z_\alpha F}{4\pi r_\alpha^2} \quad \text{and} \quad \frac{1}{N_A} := \delta \ . \tag{5}$$

Note that δ is a small parameter for the periodic problem, and we can consider a multi-scale asymptotic expansion of $\mathbf{D}$ in this small parameter δ. Actually δ is the parameter bridging the scale from the atomistic to the continuum scale.

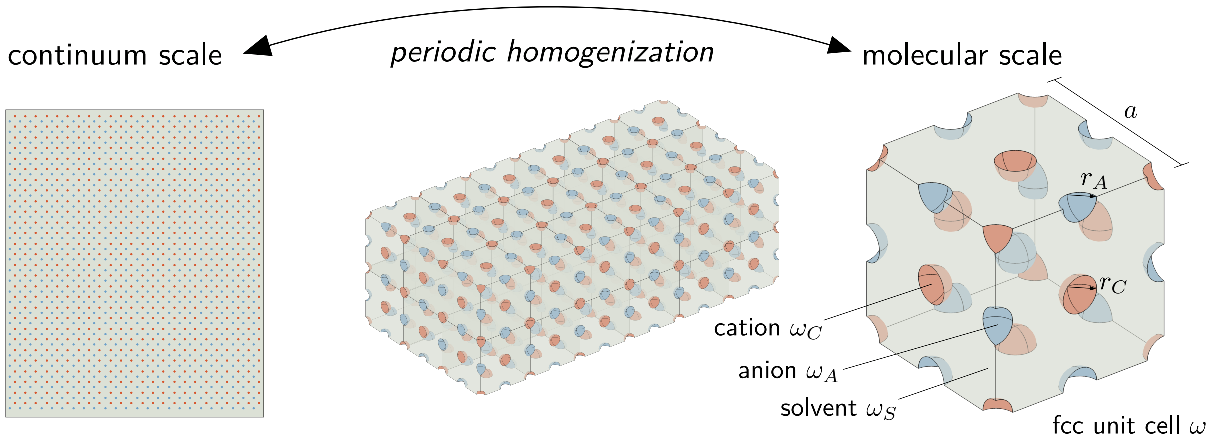

Figure 1: Sketch of a liquid electrolyte with quasi-lattice structure.

Consider now for the displacement field

$$\mathbf{D} = -\varepsilon \nabla \varphi \tag{6}$$

where $\varepsilon = \varepsilon_0(1+\chi)$ and χ is the susceptibility of the pure solvent. We consider the multi-scale expansion

$$\varphi(\mathbf{x}) = \varphi^0(\mathbf{x}, \frac{\mathbf{x}}{\delta}) + \delta^1 \cdot \varphi^1(\mathbf{x}, \frac{\mathbf{x}}{\delta}) + \mathcal{O}(\delta^2)\ . \tag{7}$$

and require φ^i to be periodic with respect to the unit cell ω. With $\mathbf{y} = \frac{\mathbf{x}}{\delta}$ being the micro-scale we have

$$\mathrm{div} = \mathrm{div}_x + \delta^{-1}\mathrm{div}_y \quad \text{and} \quad \nabla = \nabla_x + \delta^{-1}\nabla_y\ . \tag{8}$$

Hence we obtain for the Maxwell equation

$$\begin{aligned} \mathrm{div}\,\mathbf{D} = {} & \delta^{-2} \cdot \mathrm{div}_y(\varepsilon \nabla_y \varphi^0) + \delta^{-1} \cdot \Big(\mathrm{div}_x(\varepsilon \nabla_y \varphi^0) + \mathrm{div}_y(\varepsilon \nabla_x \varphi^0 + \varepsilon \nabla_y \varphi^1)\Big) \\ & + \delta^0 \Big(\mathrm{div}_x(\varepsilon \nabla_x \varphi^0 + \varepsilon \nabla_y \varphi^1) + \mathrm{div}_y \varepsilon \nabla_x \varphi^1\Big) = \mathcal{O}(\delta)\ . \end{aligned} \tag{9}$$

The corresponding boundary condition at $\sigma_{\alpha,S}$, $\alpha = A, C, S$ with $\underset{s}{q_S} = 0$ read

$$\mathbf{D} \cdot \mathbf{n} = \Big(\delta^{-1} \cdot (\varepsilon \nabla_y \varphi^0) + \delta^0 \cdot (\varepsilon \nabla_x \varphi^0 + \varepsilon \nabla_y \varphi^1) + \delta^1 \varepsilon \nabla_x \varphi^1 + \mathcal{O}(\delta^2)\Big) \cdot \mathbf{n} = \delta \cdot \underset{s}{q_\alpha}\ . \tag{10}$$

In the limit $\delta \to 0$ we obtain a sequence of PDEs in orders of the small parameter δ [22].

Order δ^{-2}: In leading order we have

$$\mathrm{div}_y \nabla_y \varphi^0 = 0 \qquad \text{for } \mathbf{y} \in \omega_i \tag{11}$$

together with

$$\nabla_y \varphi^0 \cdot \mathbf{n} = 0 \qquad \text{on} \quad \sigma_{i,j} \tag{12}$$

and the periodicity condition of $\varphi^0(\mathbf{x}, \mathbf{y})$ with respect to $\mathbf{y}$. Note that the maximum principle[23] yields

$$\varphi^0(\mathbf{x}, \mathbf{y}) = \varphi^0(\mathbf{x})\,,\ \nabla_y \varphi^0 = 0\ . \tag{13}$$

The leading order or macroscopic electrostatic potential φ^0 is thus independent of the micro-scale $\mathbf{y}$.

Order δ^{-1}: Since $\varphi^0(\mathbf{x},\mathbf{y}) = \varphi^0(\mathbf{x})$ we obtain from (9) the condition

$$0 = \mathrm{div}_y \nabla_y \varphi^1 \ , \tag{14}$$

together with the boundary condition

$$\nabla_x \varphi^0 \cdot \mathbf{n} = -\nabla_y \varphi^1 \cdot \mathbf{n} \quad \text{on} \quad \sigma_{i,j} \tag{15}$$

and the periodicity condition for φ^1. The solution $\varphi^1(\mathbf{x},\mathbf{y})$ can be written as

$$\varphi^1(\mathbf{x},\mathbf{y}) = -\boldsymbol{\xi}(\mathbf{y}) \cdot \nabla_x \varphi^0(\mathbf{x}) \tag{16}$$

where $\boldsymbol{\xi} = (\xi^1, \xi^2, \xi^3)$ satisfies the **cell problem** $(k = 1, 2, 3)$

$$(\mathbf{C1}) \qquad \begin{cases} \mathrm{div}_y \nabla_y \xi^k & = 0 \qquad \mathbf{y} \in \omega_S \\ \nabla \xi^k \cdot \mathbf{n} & = n_k \\ \quad \xi^k & \text{is periodic} \end{cases} \tag{17}$$

The geometric function $\boldsymbol{\xi}$ thus encodes the microstructure of the electrolyte since the cell problem ($\mathbf{C1}$) is dependent on the unit cell geometry ω. In order to determine the microscopic eletrostatic potential contribution φ^1, the cell problem ($\mathbf{C1}$) has to be solved (numerically).

Order δ^0: The δ^0-equation

$$\mathrm{div}_x(\varepsilon \nabla_x \varphi^0 + \varepsilon \nabla_y \varphi^1) + \mathrm{div}_y \varepsilon \nabla_x \varphi^1 = 0 \tag{18}$$

can be integrated with respect to ω_S which yields

$$\mathrm{div}_x \int\limits_{\omega_S} \varepsilon(\nabla_x \varphi^0 + \nabla_y \varphi^1)\, dV = 4 z_A F + 4 z_C F \ , \tag{19}$$

since

$$\int\limits_{\omega_S} \mathrm{div}_y \varepsilon \nabla_x \varphi^1 dV = \int\limits_{\sigma_{S,A} \cup \sigma_{S,C}} \varepsilon \nabla_x \varphi^1 \cdot \mathbf{n}\, dA = 4 \cdot 4\pi r_A^2 \underset{s}{q_A} + 4 \cdot 4\pi r_C^2 \underset{s}{q_C} \ . \tag{20}$$

The integral expression in (19) can be written, by re-considering $\varphi^1 = -\boldsymbol{\xi} \cdot \nabla_x \varphi^0$ whereby

$$\nabla_y \varphi^1 = -\boldsymbol{\nabla}_y \boldsymbol{\xi} \cdot \nabla_x \varphi^0 \ , \tag{21}$$

as

$$\int\limits_{\omega_S} (\nabla_x \varphi^0 - \boldsymbol{\nabla} \boldsymbol{\xi} \cdot \nabla_x \varphi^0)\, dV = \left(\int\limits_{\omega_S} (\mathbf{1} - \boldsymbol{\nabla}_y \boldsymbol{\xi})\, dV \right) \cdot \nabla_x \varphi^0 \ . \tag{22}$$

With

$$\boldsymbol{\pi} := \frac{1}{\mathrm{vol}(\omega)} \left(\int\limits_{\omega_S} (\mathbf{1} - \boldsymbol{\nabla}_{\mathbf{y}} \boldsymbol{\xi})\, dV \right) \tag{23}$$

and

$$q_i = 4Fz_i \frac{1}{\int\limits_\omega 1\,dV} = 4Fz_i a^{-3} = Fz_i c \qquad i = A, C \tag{24}$$

we obtain the *homogenized Poisson equation*

$$-\mathrm{div}_x \left(\boldsymbol{\varepsilon}_{AC} \cdot \nabla_x \varphi^0 \right) = q_A + q_C \ . \tag{25}$$

with **homogenized dielectric constant**

$$\boldsymbol{\varepsilon}_{AC} = \varepsilon_0(1+\chi) \cdot \boldsymbol{\pi} \tag{26}$$

of the electrolyte AC . We call the term $\boldsymbol{\pi}$ **dielectric homogenization factor** and emphasize that $\boldsymbol{\pi}$ can be calculated (numerically) from the **cell problem C1** for a specific unit cell ω. Note that $\boldsymbol{\pi}$ is actually dependent on the electrolyte concentration c via the lattice parameter a of cell problem. This is a very interesting result since it shows that the homogenization procedure actually impacts the dielectric constant $\boldsymbol{\varepsilon}_{AC}$ of the continuous Poisson equation (25).

In order to compare this result to experimental and theoretical work of others we consider explicitly the 3D unit cell ω of a NaCl structure (see Fig. 1) and solve numerically the cell problem **C1** with COMSOL® Multiphysics. For the numerical determination of $\boldsymbol{\pi}$ the only paramters are the ionic radii r_A and r_C since the unit cell width a is determined from eq. (2).

However, the radii r_α of ions in solutions are a difficile quantity[36, 37] and we discuss several values and their impact on the homogenized dielectric constant. As lower bounds for Na^+ and Cl^- we consider the values of the crystal ionic radii, *i.e.* $r_{\mathrm{Cl}^-} = 168\mathrm{pm}$ and $r_{\mathrm{Na}^+} = 116\mathrm{pm}$. For comparison, we consider also the soft ionic radii[38], which are $r_{\mathrm{Cl}^-} = 218\mathrm{pm}$ and $r^{\mathsf{soft}}_{\mathrm{Na}^+} = 150.$ Since solvation effects[1] occur in liquid solutions, r_α can also be understood as the radius of a (solvated) ion beyond which the solvent behaves as homogenous, continuous dielectrium[2]. Y. Marcus[39] proposes for water as solvent values of $r^{\mathsf{solv}}_{\mathrm{Cl}^-} = 224\mathrm{pm}$ and $r^{\mathsf{solv}}_{\mathrm{Na}^+} = 218\mathrm{pm}$ for radius of solvated ions where 2.0 solvent molecules are bound to Cl^- and 3.5 to Na^+ in the (first) solvation shell. Finally we consider $r_{\mathrm{Cl}^-} = r_{\mathrm{Na}^+} = [250, 300]\mathrm{pm}$ as free parameter of a solvated ion to show the general impact of the radius on the dielectric constant.

Figure 2 shows a comparison between the numerically computed homogenized dielectric constant $\frac{\varepsilon_{AC}}{\varepsilon_0}$ (dashed line) and measured values of Hasted *et. al*[2], for aqueous NaCl . First of all we find that $\frac{\varepsilon_{AC}}{\varepsilon_0}$ is indeed dependent on the salt concentration c via the periodic homogenization procedure. In the concentration range up to $c^{\mathsf{sat}} = 2\mathrm{mol}\,\mathsf{L}^{-1}$ we find that the qualitative concentration dependence of $\boldsymbol{\varepsilon}_{AC}$ is in well agreement to experimental data for a completely dissociated electrolyte. The crystal ionic radii $r_{\mathrm{Cl}^-} = 168\mathrm{pm}$ and $r_{\mathrm{Na}^+} = 116\mathrm{pm}$, and also the soft ionic radii, underestimate the influence of the microstructure on the homogenized dielectric constant. For ionic radii of $r_{\mathrm{C}^+} = r_{\mathrm{A}^-} = 0.22\mathrm{nm}$ we find a remarkable quantitative agreement to the measured values of Hasted *et. al.* These values correspond to the values proposed of Y. Marcus[39], and it is to emphasize that there is no additional fitting

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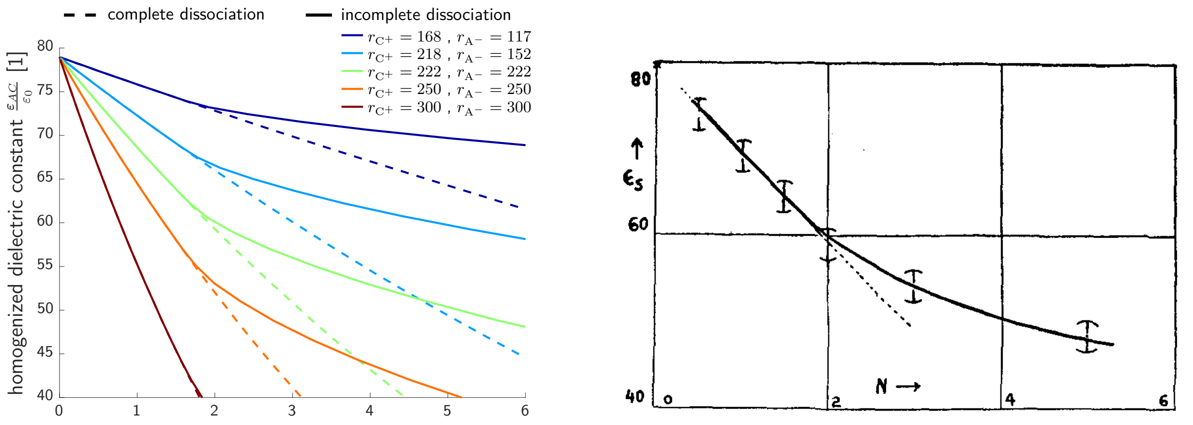
[1] Note that solvation occurs in two or more shells around the central ion. Since solvent molecules in the first solvation shell are rather strongly bound to the central ion, they will certainly influence the dielectrium due to their oriented dipole moment. Since solvent molecules are less bound in the second shell they are not permanently oriented towards the central ion and thus not incorporated in r_α.

[2] This is actually the implicit definition via the boundary condition (4).



(a) Computed dielectric constant based on the periodic homogenization procedure.

(b) Measured static dielectric constant of NaCl at 21°C (Fig. 2 from [2] Hasted *et. al.*, reprinted with permission of AIP.)

Figure 2: Comparison of the dielectric constant obtained from periodic homogenization and measured values.

parameter in the modeling procedure. Note that larger ionic radii overestimate the dielectric decrement.

Beyond a concentration of $c^{\mathsf{sat}} = 2$mol L^{-1} incomplete dissociation becomes important because of the solvation effect [30]. The solvation number $\kappa_{A,C}$ of solvated ions $\mathrm{A}-, \mathrm{C}^+$ covers the number of solvent molecules in the first **and** second solvation shell around the central ion [40–42]. The solvation effect binds $(\kappa_A + \kappa_C) \cdot c$ solvent molecules, whereby the number of free solvent molecules in solution is $n_S = n_S^B - (\kappa_A + \kappa_C) \cdot c$, where n_S^B is the number density of pure solvent. For water as solvent and solvation numbers of $\kappa_A = \kappa_C = 12$ this leads to $n_S = (55 - 24 \cdot c)$mol L^{-1}, whereby the number of free solvent molecules would become negative beyond a salt concentration of 2.3mol L^{-1}. This requires the introduction of ion pairs AC in solution. These ion pairs are part of the mixture[30] and in thermodynamic equilibrium to the solvated ions via the dissociation reaction

$$\mathrm{AC} + (\kappa_A + \kappa_C)\,\mathrm{S} \rightleftharpoons \mathrm{C}^+ + \mathrm{A}^- \,. \tag{27}$$

This yields a constraint

$$\mu_{AC} + (\kappa_A + \kappa_C)\mu_S = \mu_A + \mu_C \tag{28}$$

where μ_α is the chemical potential of the constituent A_α, *i.e.* $\mu_\alpha = g_\alpha + k_{\mathsf{B}}T \ln(y_\alpha) + v_\alpha(p - p^R)$[29]. Equation (28) is then an implicit equation between the dissociation degree δ, the salt concentration c, the solvation number $(\kappa_A + \kappa_C)$ and the dissociation energy $\Delta g = g_C + g_A - (\kappa_A + \kappa_C) g_S - g_{AC}$ (28). We employ a value of $\Delta g = 0.2$ eV which corresponds to a strong electrolyte and refer to [30] for details and a comparison to the classical Ostwald dilution law. Eq. (28) allows us then to determine the dissociation degree δ as function of the salt concentration c, *i.e.* $\delta = \hat{\delta}(c)$. The lattice constant a is then related to the electrolyte concentration c via $c = \delta \cdot 4a^{-\frac{1}{3}}$.

In Fig. 2a, the dashed line corresponds to complete dissociation while the solid line accounts for incomplete dissociation. The deviation beyond a concentration of $c^{\mathsf{sat}} = 2$mol L^{-1} arises from incomplete dissociations due to the solvation effect. For the ionic radii of Y. Marcus we obtain a remarkable qualitative and quantitative agreement of the homogenized dielectric constant ε_{AC} to experimental data in the whole concentration range of $(0-5)$mol L^{-1}. Reconsidering the rather simple model approach,*i.e.* a configuration of cations and anions in an fcc lattice, this is a surprising result. It seems that multi scale expansions and periodic homogenization are an effective tool to bridge the scale between atomistic and continuum descriptions of ionic systems. The described model approach is certainly not limited to monovalent ions in an fcc quasi lattice, but can also be applied to multivalent salts or even larger charged molecules.

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