REVIEW ARTICLE

Asymmetric Finite Size of Ions and Orientational Ordering of Water in Electric Double Layer Theory Within Lattice Model

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Abstract: In the present review, a brief historical survey of the mean-field theoretical description of electric double layer (EDL) is presented. Special attention is devoted to asymmetric finite size of ions and orientational ordering of water dipoles. A model of Wicke and Eigen, who were first to explicitly derive the ion distribution functions for finite size of ions, is discussed. Arguments are given in favour of changing the recently adopted name of the mean-field EDL model for finite size of ions from Bikerman model to Bikerman-Wicke-Eigen model. Theoretically predicted asymmetric and symmetric camel-like shape of the voltage dependence of the differential capacitance is also discussed.

Keywords: Electric double layer, Wicke-Eigen model, Bikerman model, finite volumes, water dipoles.

1. INTRODUCTION

In the interface between a charged surface and electrolyte solution, there are strong interactions between the charged surface and ions/molecules in the solution, which result in the formation of EDL [1, 2]. In EDL, the counterions are accumulated close to the charged surface and the coions are depleted from the surface (Fig. **1**). This non-homogeneous distribution of ions and water molecules and orientation of water molecules in EDL screen the electric potential. EDL is a convenient model for capturing the electrostatic properties of biological membranes, phospholipid bilayers and also metals and semiconductors in contact with electrolyte solution. Based on EDL theory, different physiological processes, such as transport of charged molecules across biological membranes or binding of charged molecules to biological membranes [1, 2], can be better understood.

EDL has been firstly modelled by Helmholtz [3, 4]. The model assumed that the charged surface attracts the surrounding counterions and a single layer is formed to balance the charge. Later, these ions (but still point-like) have been described following the Boltzmann distribution [5, 6]. The finite size has been incorporated by Stern [7] with the so-called distance of closest approach and later developed further [8-11]. Their work was carried out by numerous advanced studies [12-29], among them Outhwaite and Lamperski [12, 14, 25-27] and Kornyshev [30] who significantly contributed to the development of the field also gave its correct historical overview.

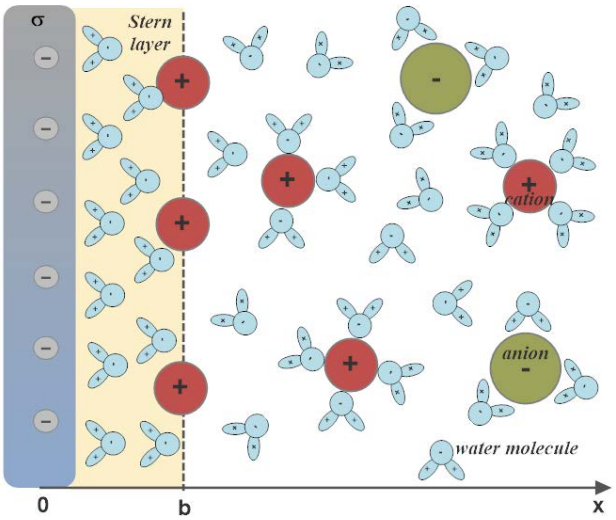

Fig. (1). A schematic figure of electric double layer showing an electrolyte solution in contact with a negatively charged planar surface ($\sigma < 0$). The symbol *b* denotes the distance of closest approach approximately equal to the thickness of Stern layer.

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Particularly, the orientational ordering of the water dipoles near the charged surface (Fig. **1**) proved to be beneficial for the local decrement of the relative permittivity [31-42]. Following the ideas of some studies [8, 11, 43], a modification and generalization of their EDL models were performed within, in this paper referred to as GI model, which considers both the orientational ordering of water dipoles and finite size of anions and cations. The water molecules in the GI model are described within the modified Kirkwood approach [44] as point-like dipoles at the centres of finite sized spheres with permittivity equal to the square of the optical refractive index of water [34]. Unlike the Bikerman approach, where the local polarisation is not a function of spatial dependent orientational ordering of water dipoles [8], the GI model may describe the decrement of the relative permittivity in the vicinity of the charged surface due to the saturation in average orientational ordering [34]. The decrement of the relative permittivity in the electrolyte solution near the charged surface is influenced also by the excluded volume effect due to the competition between counterions and water molecules [35]. To consider different size of positive and negative ions, the generalisation of GI model [34] was first performed by Sin et al. [45], assuming small volume shares of ions everywhere in electrolyte solution only, where the number densities of ions and water molecules were obtained implicitly.

Recently, the GI model [34] was generalized also without assuming small volume shares of ions everywhere in electrolyte solution [46]. The modified GI model [46], as a generalisation of the models of Bikerman [8], Wicke and Eigen [9, 10] and Freise [11], simultaneously takes into account the asymmetry of the anion and cation finite sizes and the spatial dependence of the polarisation along with the relative permittivity due to orientational ordering of water molecules. The modified GI model considering the asymmetry in the ion size and orientational ordering of water molecules is shortly described in the following section.

2. ASYMMETRY OF THE FINITE SIZE OF ANIONS AND CATIONS WITHIN MODIFIED GI MODEL

Taking into account the finite and asymmetric size of ions, the expressions for the spatial distribution of the monovalent cations ($n_+(x)$), anions ($n_-(x)$) and water ($n_w(x)$) in the electric double layer near a charged surface can be derived using the method of lattice statistics with Boltzmann correction factors [46] which has been proven to be equivalent to the method of minimization of the free energy of the system.

In the model [46], the parameters α_+ and α_- are the number of lattice sites occupied by a single positive and negative ion respectively [46] (Fig. **2**). A single water molecule occupies just one lattice site, therefore n_s/N_A = 55 mol/1 is equal to the concentration of pure water. In our model [46] (Fig. **2**), a single ion surrounded with strongly interacting water molecules (in the first hydration layer) is assumed not to contribute to the orientational ordering/polarization in the solution because the orientations of the water dipoles aroumd the ions are predominantly determined by the ion. This assumption is in accordance with the model of [47] who assumed that each ion *together* with the strongly interacting surrounding water molecules does *not* contribute to the orientational polarization in the electrolyte solution and is considered to be a sphere consisting of a homogeneous dielectric medium with permittivity equal to 2. In our model [46], we do not assume that the hydrated ion is a dielectric sphere (Fig. **2**). However, the used permittivity of 2 is very close to our contribution of the electronic polarizability of the hydrated ions to the relative permittivity (see Eqs.(7) and (8)), which is equal to the square of refractive index ($n^2 \cong 1.8$, where $n = 1.33$).

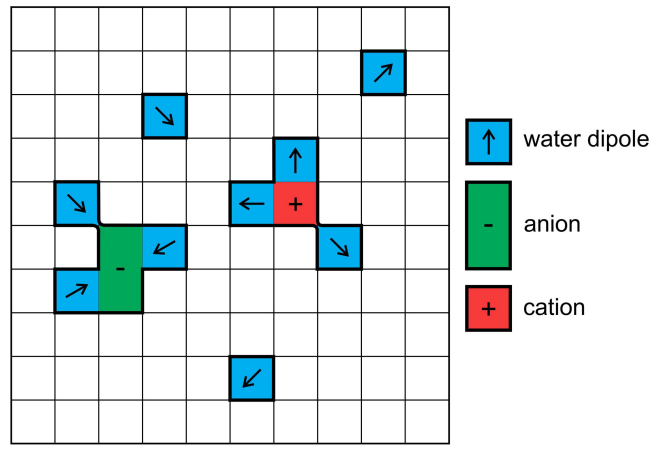

Fig. (2). In the modified GI lattice model [46] the single positive ion and the single negative ion, each of them together with the surrounding water molecules, which do not contribute to the orientational ordering/polarization in the solution, occupy α_+ and α_- lattice sites, respectively. In the model, the water molecules (and ions) which contribute to α_+ and α_- give rise to electronic polarization only, captured by the term n^2 in the expression for the relative permittivity (Eq.(7)). In the schematic figure α_+ = 4 and α_- = 5. A single water molecule occupies just one lattice site.

The number of densities $n_+(x)$, $n_-(x)$ and $n_w(x)$ can be derived by calculating the corresponding probabilities that a single lattice site in the bulk solution is occupied by one of the three particles (i.e. cations, anions or water molecules) [46]:

$$n_+(x) = n_0 e^{-e_0\phi\beta} \frac{n_s}{\mathcal{D}_A(\phi,E)} \quad (1)$$

$$n_-(x) = n_0 e^{e_0\phi\beta} \frac{n_s}{\mathcal{D}_A(\phi,E)} \quad (2)$$

$$n_w(x) = \frac{n_{0w} n_s}{\mathcal{D}_A(\phi,E)} \frac{\sinh(\gamma p_0 E\beta)}{\gamma p_0 E\beta} \quad (3)$$

corrected by the corresponding Boltzmann factors, with [46]:

$$\mathcal{D}_A(\Phi) = \alpha_+ n_0 e^{-e_0\phi\beta} + \alpha_- n_0 e^{+e_0\phi\beta} + \frac{n_{0w}}{\gamma p_0 E\beta}\sinh(\gamma p_0 E\beta), \quad (4)$$

where it is assumed that all lattice sites are occupied $n_s = \alpha_+ n_+(x) + \alpha_- n_-(x) + n_w(x)$.

Here n_{0w} is the bulk number density of water molecules, n_0 is the bulk number density of anions and cations, n_s is the number density of lattice sites, β = 1/kT, k is the Boltzmann

constant, T is the absolute temperature, e_0 is the unit charge, ϕ is the electric potential, p_0 is the magnitude of the external water dipole moment, E is the magnitude of electric field strength, x is the distance from the negatively charged planar surface, γ is given by [34, 46]: $\gamma = (2 + n^2)/2$ and n is the optical refractive index of water. In the bulk $n_s = \alpha_+ n_0 + \alpha_- n_0 + n_{0w}$.

The macroscopic volume charge density in the solution is [46]:

$$\rho(x) = e_0\, n_+(x) - e_0\, n_-(x) = -2e_0 n_s n_0 \frac{\sinh(e_0\phi\beta)}{\mathcal{D}_A(\phi,E)} \quad (5)$$

which then appears in the corresponding Poisson's equation:

$$\frac{d}{dx}\left[\varepsilon_0\varepsilon_r(x)\frac{d\phi}{dx}\right] = 2e_0 n_s n_0 \frac{\sinh(e_0\phi\beta)}{\mathcal{D}_A(\phi,E)} \quad (6)$$

where ε_0 is the permittivity of free space. The spatial dependence of the relative permittivity $\varepsilon_r(x)$ is:

$$\varepsilon_r(x) = n^2 + n_{0w} n_s \frac{p_0}{\varepsilon_0}\left(\frac{2+n^2}{3}\right)\left(\frac{\mathcal{F}(\gamma p_0 E\beta)}{\mathcal{D}_A(\phi,E)E}\right) \quad (7)$$

where the function $\mathcal{F}(u)$ is defined as $\mathcal{F}(u) = \mathcal{L}(u)(\sinh u/u)$, where $\mathcal{L}(u)$ is the Langevin function.

In the limit of vanishing electric field strength (E→0) and zero potential (ϕ→0), Eq.(7) for the relative permittivity gives the limit expression for bulk relative permittivity:

$$\varepsilon_{r,b} = n^2 + \frac{[n_s - (\alpha_+ + \alpha_-)n_0]\beta p_0^2}{2\varepsilon_0}\left(\frac{2+n^2}{3}\right)^2 \quad (8)$$

where we took into account that in the bulk solution $n_{0w} = n_s - (\alpha_+ + \alpha_-)n_0$. Eq.(8) predicts the linear decrement of the relative permitivitty in the bulk solution with salt concentration (Fig. **3**) and gives the value of $\varepsilon_{r,b} \cong 78.5$ for zero bulk salt concentration. The fitted value of $(\alpha_+ + \alpha_-) \cong 7$ from Fig. (**3**) gives reasonable hydration numbers of sodium cations and chloride anions in NaCl electrolyte solution. Hence, reflecting the fact that alkali metals like sodium cations are weakly hydrated and they have a tendency to disrupt the aqueous bulk structure *without strongly ordering the water molecules* as highly charged metal ions do through strong hydration [48]. Mähler and Persson [48] suggested for sodium ion a hydration number of around four. Since the hydration number of chloride is even smaller, the estimated value of $(\alpha_+ + \alpha_-) \cong 7$ in Fig. (**3**) (following from Eq.(8)) for bulk NaCl electrolyte seems to be very reasonable.

Hydration numbers of ions must diminish as their concentration increases beyond dilute solutions [49]. In EDL, the concentration of counterions is very high, therefore the hydration number of counterions should be diminished relative to the values in the bulk, meaning that in our cas $(\alpha_+ + \alpha_-)$ in EDL close to the charged surface is decreased relative to its bulk value.

The described modified GI model [46] may include Helmholtz/Stern layer and the distance of closest approach [51] (Fig. **1**) which in general can vary for cations and anions (see for example [52-55]). In Stern layer (Fig. **1**), there are no ions closed to the charged surface, i.e. $n_+(x) = n_-(x) = 0$ (chemisorbed or adsorbed ions are considered in the surface charge density σ). Therefore, in the Stern layer the general expression for the relative permittivity, $\varepsilon_r(x)$, (Eq.7) transforms into (see also [54, 55]:

$$\varepsilon_s = n^2 + n_s \frac{p_0}{\varepsilon_0}\left(\frac{2+n^2}{3}\right)\frac{\mathcal{L}(\gamma p_0 E\beta)}{E} \quad (9)$$

Combining the boundary condition $d\phi/dx(x=0) = -\sigma/\varepsilon_0\varepsilon_s$ (see Fig. **1**) and Eq.(9) results into the non-linear equation for the magnitude of electric field, E, in Stern layer [54, 55]:

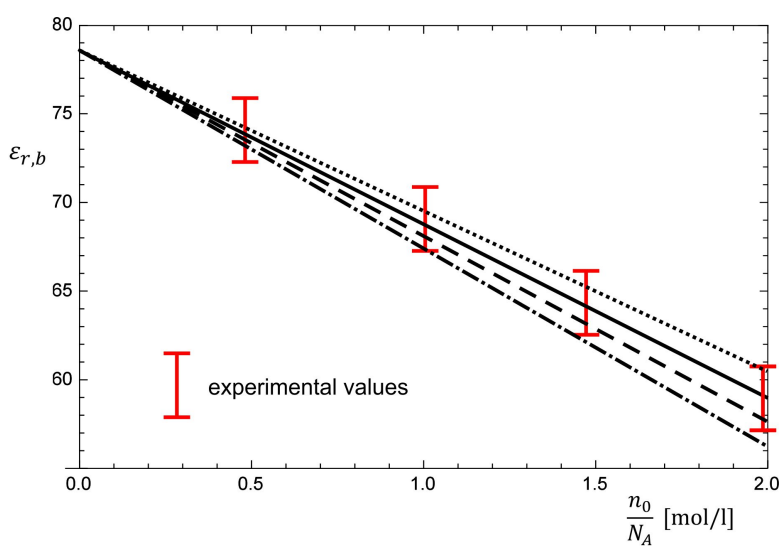

Fig. (3). Calculated dependence of $\varepsilon_{r,b}$ (using Eq.(8)) on the bulk salt (NaCl) concentration n_0/N_A. Model parameters are : $(\alpha_+ + \alpha_-) = 6.5$ (dotted line), 7.0 (full line), 7.5 (dashed line), 8.0 (dashed-dotted line), optical refractive index n =1.33, p_0 = 3.1 D [46], T = 298 K and $n_s/NA = 55$ mol/l. The experimental values are taken from [50].

$$\varepsilon_0 E\left(n^2 + n_s \frac{p_0}{\varepsilon_0}\left(\frac{2+n^2}{3}\right)\frac{\mathcal{L}(\gamma p_0 E\beta)}{E}\right) = |\sigma| \quad (10)$$

Inserting the calculated value of E in Eq.(9) gives the value of the relative permittivity in Stern layer (ε_s) for a given surface charge density σ (see also Fig. **4**). It can be clearly seen from Fig. (**4**) that strongly decreases with the increasing magnitude of σ , which can be explained by the saturation of the orientational ordering of water dipoles in strong electric field at large values of σ [34, 46, 54, 55].

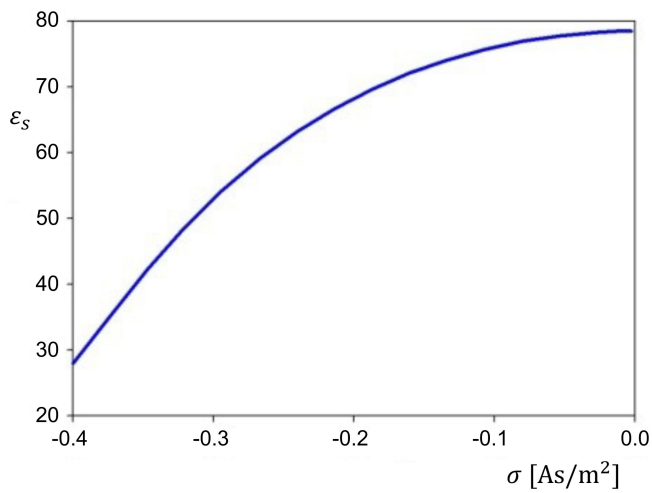

Fig. (4). Calculated relative permittivity ε_s in Stern layer (see Fig. 1) as a function of the magnitude of the surface charge density of an electrode surface σ. The values of the model parameters are: n =1.33, p_0 = 3.1 D [46], T = 298 K and $n_s/N_A = 55$ mol/l.

3. SYMMETRICAL CASE: EQUAL SIZE OF ANIONS AND CATIONS

Assuming equal size of the hydrated anions and cations and water molecules, i.e. $\alpha_+ = \alpha_- = 1$, Eq.(4) for asymmetric size of ions $\mathcal{D}_A(\Phi)$ of the modified GI model transforms into the corresponding equation of the GI model [34]:

$$\mathcal{D}_S(\phi, E) = 2n_0 \cosh(e_0\phi\beta) + \frac{n_{0w}}{\gamma p_0 E\beta}\sinh(\gamma p_0 E\beta) \quad (11)$$

Following with the rest of the general equations of the GI model in [34]:

$$n_+(x) = n_0 e^{-e_0\phi\beta}\frac{n_s}{\mathcal{D}_S(\phi,E)}, \quad (12)$$

$$n_-(x) = n_0 e^{e_0\phi\beta}\frac{n_s}{\mathcal{D}_S(\phi,E)}, \quad (13)$$

$$n_w(x) = \frac{n_{0w}n_s}{\mathcal{D}_S(\phi,E)}\frac{\sinh(\gamma p_0 E\beta)}{\gamma p_0 E\beta}, \quad (14)$$

$$\frac{d}{dx}\left[\varepsilon_0\varepsilon_r(x)\frac{d\phi}{dx}\right] = 2e_0 n_s n_0 \frac{\sinh(e_0\phi\beta)}{\mathcal{D}_S(\phi,E)}, \quad (15)$$

$$\varepsilon_r(x) = n^2 + n_{0w}n_s\frac{p_0}{\varepsilon_0}\left(\frac{2+n^2}{3}\right)\left(\frac{\mathcal{F}(\gamma p_0 E\beta)}{\mathcal{D}_S(\phi,E)E}\right) \quad (16)$$

As already mentioned above, the decrement of the relative permittivity in an electrolyte solution near a charged surface (electrode) is partially the consequence of orientational ordering of water dipoles close to or in saturation regime of orientational ordering [31-42, 45-46, 51, 56]. This fact was completely neglected in some phenomenological macroscopic models of EDL, as for example in [57]. Namely, simulations of the EDL clearly showed that orientational ordering of water molecules in an electrolyte solution is increased in direction towards the charged (electrode) surface, including the Stern and diffuse layers [56], accounting for the decrement in the relative permittivity in this direction, which is also in accordance with theoretical predictions (see [35, 51] and references therein). Therefore, the phenomenological approach in [57], applying the 19th century Maxwell's mixture formula and describing the ions as dielectric spheres within an oversimplified macroscopic thermodynamic phenomenological model, which totally neglects the orientational ordering of water dipoles, cannot contribute to better understanding of the physics of EDL, since the basic physical mechanism of decrease of relative permittivity, i.e. the orientational ordering of water molecules in Stern and diffuse layer [35, 51, 56], is neglected. As a consequence, the model [57] involves many unjustified and oversimplified assumptions, as for example the assumption of constant relative permittivity in the inner (Stern) layer which is clearly not in agreement with the results of simulations [56]. Namely, due to orientational ordering of water dipoles, the relative permittivity of the Stern layer depends on the electric field strength, i.e. on the surface charge density of the electrode [51, 54, 56]. Fitting of the model curves with many free model parameters to the experimental points [57] can not prove that the inner (Stern) layer capacitance and permittivity are constant.

As shown in [56], addition of NaCl, even at high concentrations (0.5 M), affects the spatial and orientational arrangement adopted by the water molecules only for high magnitudes of the surface charge density. Lower magnitudes of the surface charge densities, which still allow for the mean-field approach, barely affect the ordering of the water layers. A stronger salt effect on the orientation angle of the water molecules was predicted for higher magnitudes of the surface charge density [56]. However, for low enough surface charge densities the average orientation angle of water dipoles profile is not qualitatively changed after addition of NaCl even at concentration of 0.5 mol/l [56]. For example, for the surface charge density 0.16 As/m^2 there is only a very small quantitative difference in the water average orientation profile between the two cases with and without NaCl [56]. Even at the magnitude of the surface charge density 0.48 As/m^2 (which is too high for the mean-field approximation approach), the shape of the average orientation angle profile is not changed substantially after addition of NaCl, but only decreased in values [56]. Based on these results, we can conclude that considering the orientational ordering of water dipoles in Stern and diffuse layers [31-42, 45-46, 51, 56] is essential to realistically capture the basic physical properties of EDL and cannot be neglected as it was done in some oversimplified macroscopic phenomenological models of

EDL [57]. Accordingly, the suggestions/conclusions that close to the charged surface (electrode), almost all water molecules in electrolyte solution belong to water shells around the ions, while free water molecules are excluded [57], is against the results of simulations which clearly show the increased water ordering in the direction towards the charged surface (including the region close to the charged surface) [56] even for high salt concentrations, which is in agreement with theoretical predictions (compare Fig. (**6**) in [56] and Fig. (**4**) in [35]). For example, for surface charge density magnitude of 0.16 As/m^2, there is practically no difference in orientational ordering and space distribution of water dipoles close to the charged surface between the water with and without NaCl [56].

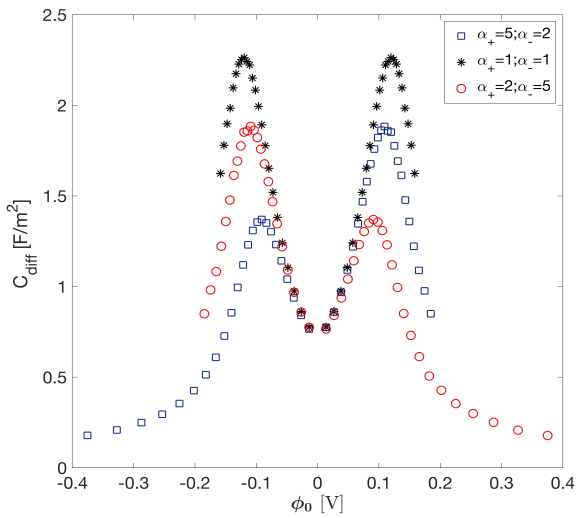

Fig. (5). Differential capacitance as a function of the surface potential calculated within modified GI model for bulk concentration of ions $n_0/N_A = 0.1$ mol/l and different combinations of the values of parameters α_+ and α_- (for definition of α_+ and α_- see Fig.2). The values of the other model parameters are : are: $b = 0$, $n = 1.33$, $p_0 = 3.1$ D [46], T = 298 K.

The finite ion size problem accounts for changes in macroscopic parameters on the scale of nanometers and below. It is therefore relevant to revisit the effects concerning eigenfunctions and eigenenergies of the nanoparticles composing the electric double layer, as well as limitations of the symmetry of the respective wave functions. Considering limitations of the symmetry of the wave functions means that the particles can no longer be treated as independent. The simplest treatment of these effects is introduction of quantum statistics while assuming the solutions of the Schrödinger equation independent of the local electric field. Such approach was recently applied to two oposed electric double layers composed by positively charged surfaces and electrons between them. It was shown that due to the limitations on the symmetry of the electron wave functions, a diffuse layer forms in the vicinity of the charged surface also at absolute zero temperature where there are no entropic effects tending to uniform distribution of particles [58]. It was shown that quantum effects can be important in nano sized electric double layers [58] and that they can be described by upgrading the existing methods based on the elaboration of the free energy of the system by the Euler-Lagrange minimization with respect to the relevant functions.

Such approach (which is also a subject of this work) [13, 40, 60-62] is due to its possibility to include quantum mechanics and quantum statistics superior to the acknowledged phenomenological Landau approach, as it addresses the reasons and mechanisms and does not stay with simplified relations expressed by polynomial term expressions. The simple approach based on the minimization of the free energy in EDL theory at relevant constraints and yielding at the same time the equilibrium distributions of the fields in the most transparent manner was derived with the purpose to implement different models [13] but included in its first presentation the simplest interaction - the hard core interaction of the particles composing the system within the lattice model. As briefly reviewed in this work, it was then extended and upgraded by considering spatially distributed charge within the rod-like [59] and spherical [60-62] nanoparticles. Introduction of the spatially distributed charge in the particles outlined the decrease of the free energy of the system due to orientational and spatial ordering of constituent particles, which was previously encountered in membranous systems subject to curvature field [63]. Recent introduction of the Pauli exclusion principle [58] indicates that there are many other relevant features that could be expressed in the descriptions of the fields, eigenenergies, eigenstates and energy distribution functions. These problems are awaiting for the future work on electric double layer to exhibit the power of probability-based quantities, as considered by Schrödinger and Boltzmann and the elegance of the Euler-Lagrange method in solving the variational problems. The major contributions in the theory of the electric double layer should outline also the Stirling approximation which enables simple and transparent consideration of probabilities. In addition, also quadrupole moment of water molecules should be taken into account [64].

4. BIKERMAN-WICKE-EIGEN MODEL

In the following, the Wicke-Eigen model of EDL, where the finite size of ions are taken into account, is derived as a limit case of the GI model [34] (Eqs.(11)-(16)). In the limit of vanishing electric field strength and zero potential, the relative permittivity gives the Onsager expression for the permittivity (Eq.(8)) [65] and for $p_0 = 3.1$ D the value of $\varepsilon_{r,b} \cong 78.5$ for bulk permittivity.

In order to derive the Wicke-Eigen model from GI model, we assume that the permittivity on the lhs of Eq.(15) is constant everywhere in the electrolyte solution and equal to its bulk value, i.e. $\varepsilon_{r,b} \cong 78.5$. In this way, the rotational ordering of water dipoles is completely neglected. Further, we neglect the energy of water dipoles in the electric field ($p_0E \to 0$), so Eqs.(12)- (14) transform into:

$$n_+(x) = n_0 e^{-e_0\phi\beta} \frac{n_s}{\mathcal{W}(\phi)} \quad , \tag{17}$$

$$n_-(x) = n_0 e^{e_0\phi\beta} \frac{n_s}{\mathcal{W}(\phi)} \quad , \tag{18}$$

$$n_w(x) = \frac{n_{0w} n_s}{\mathcal{W}(\phi)} \quad (19)$$

Correspondingly, Eqs.(15) and (11) turn into

$$\varepsilon_{r,b}\varepsilon_0 \frac{d^2\phi(x)}{dx^2} = 2e_0 n_s n_0 \frac{\sinh(e_0\phi\beta)}{\mathcal{W}(\phi)} \quad (20)$$

$$\mathcal{W}(\phi) = n_0 e^{e_0\phi\beta} + n_0 e^{-e_0\phi\beta} + n_{0w} = n_{0w} + 2n_0 \cosh(e_0\phi\beta) \quad (21)$$

where the macroscopic (net) volume charge density of co-ions and counterions, $\rho_{free}(x)$, is [9]:

$$\rho_{free}(x) = e_0 n_+(x) - e_0 n_-(x) = -2e_0 n_s n_0 \frac{\sinh(e_0\phi\beta)}{\mathcal{W}(\phi)} \quad (22)$$

The boundary condition at the charged plate is:

$$\frac{d\phi}{dx} = -\frac{\sigma}{\varepsilon_0\varepsilon_{r,b}} \quad (23)$$

5. DISCUSSION AND CONCLUSION

In this mini review, a short overview of the mean-field theoretical description of electric double layer (EDL) is presented with special emphasis on asymmetric finite size of ions and orientational ordering of water dipoles reflecting in the spatial variability of the relative permittivity in EDL. We have shown that in the saturation regime close to the charged surface, water dipole ordering may result in a strong local decrease of permittivity. The effect is modified by the size of the ions and the size asymmetry between the anions and cations. Analytical expressions for the space dependence of relative permittivity are derived in the model for finite and asymmetric size of anions and cations in monovalent electrolyte solution. Our approach, thus, provides a distinct and analytical description of the interplay between the steric effect of the molecules and orientational ordering of water dipoles in EDL.

According to the literature data, the hydration number of Na^+ in water at room temperature is between 3.2 and 4 and of Cl^- around 2 [48, 66-68], corresponding to the number of lattice sites occupied by both hydrated Na^+ and Cl^- ions (i.e. $\alpha_+ + \alpha_-$) between 7 and 8 (see also Fig. **2**). The experimentally estimated range of $\alpha_+ + \alpha_-$ is between 7 and 8 proving to be in a very good agreement with our predicted value of $\alpha_+ + \alpha_-$ of around 7.5 (see Fig. **3**). Namely, by using Eq.(8) the value of $\alpha_+ + \alpha_-$ of around 7.5 enables us to fit the experimentally determined dependence of the bulk relative permittivity on the salt concentration in the linear regime [50], i.e. at salt concentrations below 2 mol/l (see Fig. **3**). Note that in our model (GI), we take into account in the hydrated shell around the single ion only those strongly interacted water molecules whose dipole orientation is predominantly determined by its interaction with this ion (see Fig. **2**) and not by the mean field in the system. This means that $\alpha_+ + \alpha_-$ values close to the charged surface (but outside of the Stern layer) are smaller than the bulk value due to two main reasons, i.e. increased number density of counterions [49] and a very high magnitude of electric field strength in the region closed to charged surface.

We derived Bikerman-Wicke-Eigen model of EDL as a limit case of the more general GI model of EDL [34]. The Wicke-Eigen equation (Eq.(20)), taking into account finite size of ions, was in some publications named after Bikerman (see for example [33, 35]) in the honour of J. Bikerman who was first to study the influence of finite size of ions and water polarization on the properties of electric double layer within the mean-field approach [8]. However, cation and anion distribution functions (Eqs.(17)-(18)) and the corresponding volume charge density (Eq.(22)) were first derived by Wicke and Eigen in 1952 [9] (also cited by Freise in his subsequently printed article [11]), while in the Bikerman's paper [8] they did not appear at all. Therefore, it seems appropriate to give to Eq.(20) the name Wicke-Eigen equation, to Eqs.(17)-(19) Eigen-Wicke distribution functions and to the corresponding model Bikerman-Wicke-Eigen model.

We took into account the orientational ordering of water and asymmetric finite size of ions in the prediction of an asymmetric camel-like (saddle-like) shape of the voltage dependence of the differential capacitance [45, 46] (Fig. **5**). Asymmetric camel-like shape of the voltage dependence of the differential capacitance was also predicted by Monte-Carlo simulations [69-71] and by molecular dynamic simulations [69]. The asymmetric camel-like double layer differential capacitance can be theoretically predicted also within a simple Stern model by taking into account the decrease of permittivity in Stern layer (Fig. **4**) and varying the distance of closest approach for co-ions and counter-ions [55]. Symmetric camel-like dependence of the differential capacitance was calculated by considering the finite symmetric size of ions [30] and within the Bikerman-Wicke-Eigen (BWE) model [33, 35], which assumes an equal size of the anions, cations and water molecules (i.e. $\alpha_+ = \alpha_- = 1$). The predicted dependence of differential capacitance within BWE model was qualitatively supported by density functional studies (DFT) [72] and simulations [73, 74,72].

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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