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Extensions to Study Electrochemical Interfaces, A Contribution to the Theory of Ions

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ABSTRACT. In the present study an alternative model allows the extension of the Debye-Hückel Theory (DHT) considering time dependence explicitly. From the Electro-Quasistatic approach (EQS) done in earlier studies time dependent potentials are suitable to describe several phenomena especially conducting media as well as the behaviour of charged particles in arbitrary solutions acting as electrolytes.

This leads to a new formulation of the meaning of the nonlinear Poisson-Boltzmann Equation (PBE). If a concentration and/or flux gradient of particles is considered the original structure of the mPBE will be modified leading to a new nonlinear partial differential equation (nPDE) of the third order. It is shown how one can derive classes of solutions for the potential function analytically by application of an algebraic method. The benefit of the mathematical tools used here is the fact that closed-form solutions can be calculated without any numerical approximations.

Keywords: Nonlinear partial differential equations, Debye–Hückel theory, Poisson–Boltzmann equation.

1. PRELIMINARIES

We summarize some known ideas and give a short overview whereby the remarks are far from being complete. We restrict us as short as possible however some important notes should indicate a historical point of view. There is a good historical reason to deal the subject. When the developments of interefacial electrochemistry along modern lines became restricted by the overthermodynamics attidude of its adherents in the pre-1950 days, much attention was diverted to what had seemed previously to some extent the accompanying side issues, i.e. the physical chemistry of the bulk solution adjoining the

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double layer. This had concentrated upon an interest in the deviations in the behaviour of solutions from laws derived on the assumption that interaction between particles in them was negligible. It is known that the properties of electrolyte solutions can significantly deviate from the laws used to derive the chemical potential of solutions. In non-electrolyte solutions the intermolecular forces are mostly comprised of weak Van der Waals interactions, which have a $\propto r^{-7}$ dependence (in principle), and for practical purposes this can be considered as ideal. In ionic solutions, however, there are significant electrostatic interactions between solute-solvent as well as solute-solute molecules. These electrostatic forces are governed by Coulomb's law which has a $\propto r^{-2}$ dependence. Consequently, the behaviour of an electrolyte solution deviates considerably from that an ideal solution. Thus, the famous DHT of such interactions attracted the attention of electrochemists away from the blocked interface studies [1]. The DHT was proposed as a theoretical explanation for departures from ideality in solutions of electrolytes [2]. Thus from about 1920 to 1950 the majority of research in this domain were occupied with determining activity coefficients of salts in dilute aqueous solutions , the electrical conductance of molten salts, or electrostatic effects of the dissociation constant of acids or bases in aqueous solutions [3], [4]. Note, that by applying the DHT restrictions have taken into account, such like much diluted solutions, completely dissociation and more [5]. Contemporaneously, Helmholtz considered a double-layer model wherein he proposed a simple charge separation at the interface [6]. Gouy [7], [8] developed an electric double-layer model that includes the effects both of the electric potential and ionic concentration with the aid of the Boltzmann distribution [7], [9]. A further contribution was done by Chapman [10]. He established the steady-state governing equation for the diffuse layer, the Poisson-Boltzmann equation [7]. This equation is based upon the combination of the electrostatic basic equation, the Poisson Equation [11], and the Boltzmann distribution [12]. The model is referred to as the Gouy-Chapman model. Further, Stern [13] improved the Gouy-Chapman model by assuming a finite ion size and by dividing the electrolyte into two layers, specified to as the Stern layer and the diffuse layer. Later on Grahame [14] revised the Stern model using three layers: the inner Helmholtz layer (IHL), the outer Helmholtz layer (OHL) and the diffuse layer. The difference between the Grahame model and the Stern model is due to the existence of specific adsorption [7]. A transient version of the model [7] is referred to as the Nernst-Planck-Poisson-modified Stern model or simply the Nernst-Planck-Poisson (NPP) model if there is no modified Stern layer. During the past 80 decades several well-known scientists did their contributions in this domain. Unfortunately only a few numbers is mentioned like Bjerrum [15], Gronwall, La Mer, Sandved [16], Onsager [17], Kirkwood [18], Falkenhagen [2], [5], Ghosh [19], Smoluchowski [20], Parker [21], Walden [22], Planck [23], Fuoss [24], Kortüm [25], [26], and extensive developments are not finalized up to now.

1. 1. ELECTROMAGNETICS FROM A QUASISTATIC PERSPECTIVE

General theory can be found in [27], [28], and [29]. Here only the essentials are cited. The quasistatic limit of the Maxwell Equations (MEs) is a kind of $c \to \infty$ limit (the fields propagate at once) obtained by neglecting time retardation. EQS has important applications modelling transient phenomena in approximating theories for materials with low conductivity (or low-frequency approximation). The crucial step is the fact that the time-dependent electric field may derived from a scalar potential which is, in our case the solution of a certain nPDE of the third-order [30]. Transient electrodynamical problems are not easy to solve in general, e.g. by occurring solutions depending on roots we have to take into account branch points. In media with a finite conductivity a static field is not possible and the pertinent relaxations time is given by $\tau = \varepsilon_0 \varepsilon / \sigma$ [28], where ε is the relative permittivity and σ the conductivity.

For metals (e.g. copper) the relaxation time is in the range of 10^{-18} s. Otherwise, new developments on the material sector produces materials with a relative dielectric constant in the range $2 < \varepsilon < 4$ and a conductivity of about 10^{-9} S/m. Then the decay rate is approximately $\tau \approx 10^{-3}$ s and this is long compared to other time constants of the system (e.g. an electromagnetic field passes through a panel). This is exactly the field where EQS can be applied [28], [29] and only pure capacitive effects are of interest. In further studies considering both capacitive and inductive effects the Darwin model will be used. Note that statics is just a particular case of the general MEs but quasistatics is an approximation.

2. DERIVATION OF THE MODEL EQUATION

It is stressed that the basic assumption of the DHT is the connection between the electrostatic Poisson equation and the Boltzmann distribution. However, this needs some assumptions: **(i)** the forces are short–ranged, **(ii)** only Coulomb forces are undertaken (no dispersion forces), **(iii)** the involved particles are assumed to be point-like and unpolarized, **(iv)** the dielectric constant of the solution is assumed to be the same as the solvent and **(v)** electrolytes are dissociated completely. To derive the new model equation one starts from the MEs [11]:

$$rot\vec{E} = -\frac{\partial \vec{B}}{\partial t}, \; rot\vec{H} = \vec{j} + \frac{\partial \vec{D}}{\partial t} = \sigma \vec{E} + \varepsilon_0 \varepsilon \frac{\partial \vec{E}}{\partial t} + \vec{j}_e,$$

$$div\vec{B} = 0, \; div\vec{D} = div\left(\varepsilon_0 \varepsilon \vec{E}\right) = \rho. \tag{2.1}$$

Note: The fields $\vec{E},\vec{B},\vec{D}$ and $\vec{H}$ are assumed time-dependent explicitly. Also the impressed current density and the charge density are functions of both arguments. However in this study the material constants are assumed as scalar quantities, that means $\sigma \neq \sigma(t)$ and $\varepsilon \neq \varepsilon(t)$.

It is assumed that there is both a weak current density due to the electric field and an impressed current density $\vec{j}_e$. The EQS assumption now means that the sources act slowly so that the fields change slowly and the conductivity σ is rather small. Therefore the magnetic fields (the solenoidal part of the electric field) are negligibly small. From the EQS assumption one sets $\frac{\partial \vec{B}}{\partial t} \approx 0$ or $\frac{\partial \vec{D}}{\partial t} \approx \frac{\partial \vec{E}}{\partial t} \neq 0$. For that reason the electric field is derived from a scalar potential, so that one has the conclusion that the rotation of the magnetic part vanishes: $-rot\,\vec{E} = \frac{\partial \vec{B}}{\partial t} \approx 0 \Rightarrow \vec{E} = -grad\,u$. Taking the divergence of the second equation of (2.1) one derives at an equation containing the unknown potential function $u = u(x,t)$ depending upon their time derivative:

$$\sigma \Delta u + \varepsilon_0 \varepsilon \frac{\partial}{\partial t} \Delta u - div\,\vec{j}_e = -\frac{\partial \rho_e}{\partial t}. \tag{2.2}$$

Then the concentration of particles due to diffusion will be considered. In general diffusion requires a gradient of the concentration of the particles. Under 'balanced' conditions the situation may be regarded as tantamount to equilibrium because there is no net flux or transport of ions. Hence, the Boltzmann law can be used. The argument is, that, since the field varies along the x-direction, the concentration of the ions at any distance $\vec{x}$ is given by

$$c_i = c_0 \exp\left[-\frac{z_i e_0 u}{kT}\right], \tag{2.3}$$

where $u(\vec{x},t)$ is the potential energy of an ion in the applied field and c_0 is the concentration in a region where the potential energy is zero (as $\vec{x} \to \infty$). Differentiating one obtains

$$\frac{dc_i}{dx} = -c_0 \exp\left[-\frac{z_i e_0 u}{kT}\right] \frac{1}{kT} \frac{du}{dx} = -\frac{c_i}{kT} \vec{\nabla} u. \tag{2.4}$$

Otherwise, from Fick's law one has a contribution to the current density of the form

$$j_D = -z_i F D \frac{dc_i}{dx} = -z_i F D \frac{c_i}{kT} \vec{\nabla} u, \tag{2.5}$$

and finally, the relation to the total charge density is therefore given by

$$div j_D = -\frac{\partial \overline{\rho}}{\partial t} = -\frac{\partial}{\partial t}\left(z_i FD \frac{c_0}{kT} \overset{\rho}{\nabla} u \right). \tag{2.6}$$

For the second contribution it is obvious from the DHT that

$$\overline{\rho}_e = \sum_{i=1}^{N} z_i e_0 N_i^0 \exp\left[-\frac{z_i e_0 \Delta u}{kT} \right], \quad \Delta u = u_0 - u_L . \tag{2.7}$$

u_0 is the potential at any surfaces and u_L is the potential in the electrolyte far away from a reference ion (for further discussion we set $u_L = 0$, hence $u_0 = u$); z_i is the charge number, e_0 the elementary charge, k the Boltzmann constant, T is the temperature and N_i^0 is the particle number in the bulk, F the Faraday's constant and D means the diffusion coefficient. So one has both contributions of the r.h.s. of eq.(2.2) and the new model equation reads as

$$\sigma \Delta u + \varepsilon_0 \varepsilon \frac{\partial}{\partial t} \Delta u + \frac{\partial}{\partial t}\left(- z_i FD \frac{c}{kT} \overset{\rho}{\nabla} u \right) - \frac{\partial}{\partial t}\left(\sum_{i=1}^{N} z_i e_0 N_i^0 \exp\left[-\frac{z_i e_0 u}{kT} \right] \right) = 0 . \tag{2.8}$$

Note: Precisely for the charge density a mean value is used in eq.(2.7) and Δ is the Laplacian. For further considerations one-valued ions are assumed so that $z_i = z = 1$. Both the arguments of the potential function $u(\overset{\rho}{x},t)$ will be suppressed, that means simply $u(\overset{\rho}{x},t) \equiv u$. The potential function $u(\overset{\rho}{x},t) \equiv u$ represents the ion's potential surrounded by the 'ion cloud'. In further meaning this function describes the time-dependent potential of an arbitrary metal electrode (due to the restrictions underlying by the EQS not all metals can be considered) dipping in a liquid electrolyte. Note that a standard concentration of $c = 0{,}01\, mol/l$, resp. c_i for the concentration of the i-th ion at a standard temperature of $T = 293{,}15\, K$ is assumed ($T = 20^o C$).

For the following we take the conversion for the concentration: Let $N_i^0 \times 1000 = N_A c_i$, where c_i is the molar concentration and considering the ion strength by $I = \frac{1}{2}\sum_i c_i z_i^2$ we introduce

$$\beta^2 = \frac{e_0^2 N_A}{1000\, \sigma\, kT} \frac{1}{2} \sum_i c_i z_i^2 \rightarrow \beta^2 = \frac{2 e_0^2 N_A}{1000\, \sigma\, kT} I \quad , \tag{2.9}$$

which is more useful in practical calculations later as well as by interpreting double layer devices. It is convenient to introduce the following abbreviations:

$$\eta = \frac{ze_0}{kT}, \quad \alpha^2 = \frac{Dc}{kT}. \tag{2.9a}$$

Finally one derives at the following nPDE of the third-order for the unknown time-depending potential function $u = u(x,t)$:

$$\frac{\partial^3 u}{\partial x^2 \partial t} + \frac{\partial^2 u}{\partial x^2} + \alpha^2 \frac{\partial^2 u}{\partial x \partial t} - \beta^2 \frac{\partial u}{\partial t} e^{-\eta u} = 0. \tag{2.10}$$

At this stage let us impose formally boundary conditions so that $\lim_{x \to \infty} u_0 = u_L$ and $\lim_{x \to \infty} \frac{du}{dx} = 0$ holds; they are necessary conditions later for the function $u = u(x,t)$. We seek for solutions for the nPDE, eq.(2.10) for which $u = F(x,t)$, $F \in C^3(D)$, $D \subset R^2$ is an open set and further we exclude $D := \{(u(x,t)) \in \widetilde{D} : u = 0, u_x = 0, u_t = 0, ...\}$ and a positive time $t > 0$. Suitable classes of solutions are $u \in I$, I an interval so that $I \subseteq D$ and $u : I \to R^2$. Since it is always not an easy task to solve nPDEs analytically we wish to solve the nPDE, eq.(2.10) analytically by use of an algebraic method. In the following note we summarize the basic facts of the hyperbolic tangent method [31], [32] which is used below (only the basic steps are proposed).

Note: Consider a given nPDE in its two independent variables x and t

$$P\left(u, \frac{\partial u}{\partial x}, \frac{\partial u}{\partial t}, \frac{\partial^2 u}{\partial x^2}, \frac{\partial u}{\partial x}\frac{\partial u}{\partial t}, ..., \frac{\partial^{n-1} u}{\partial x^{n-1}}, \frac{\partial^n u}{\partial x^n}\right) = 0. \tag{a}$$

Firstly the nPDE converts into a nonlinear ordinary differential equation (nODE) by using a frame of reference $u(x,t) = f(\xi)$, $\xi = x - \lambda t$ and λ is a constant to be determined. Thus one has

$$Q\left(f(\xi), f'(\xi), f''(\xi), ...\right) = 0. \tag{b}$$

The next step is that the solution can be expressed in terms of the following series representation by using an auxiliary variable $\omega = \omega(\xi)$ such that

$$u(x,t) = f(\xi) = \sum_{i=0}^{n} a_i \, \omega^i(\xi). \tag{c}$$

Now one assumes that $\omega(\xi)$ satisfies a Riccati Equation of the form

$$\omega'(\xi) = \frac{d\,\omega}{d\,\xi} = k_1\left(1-\omega^2(\xi)\right) \tag{d}$$

and k_1 means a constant. The parameter n in eq.(c) is found by balancing the highest derivative with the nonlinear terms in the reduced nODE eq.(b). Moreover, this parameter must be a positive integer since it represents the number of terms in the series (c). In the case of fractions one can take transformations as shown later. Substituting (c) and (d) into the relevant nODE will yield a system of nonlinear polynomial equations with respect to a_0, a_1 , ... , k_1 and λ.Solutions of the Riccati Equation can be expressed depending upon the constant k_1

$$w(\xi) = -\sqrt{-k_1}\tanh\left(\sqrt{-k_1}\,\xi\right),\ w(\xi) = -\sqrt{-k_1}\coth\left(\sqrt{-k_1}\,\xi\right), \qquad \text{for } k_1 < 0, \tag{e}$$

$$w(\xi) = \sqrt{k_1}\tan\left(\sqrt{k_1}\,\xi\right) - \sqrt{k_1}\cot\left(\sqrt{k_1}\,\xi\right). \qquad \text{for } k_1 > 0. \tag{f}$$

Remark: The case $k_1 = 0$ will be excluded here although a solution exists [31]. It represents a useless solution for our purposes. To prevent confusions with the Boltzmann constant the character k is marked.

2. 1. THE APPLICATION OF THE HYPERBOLIC TANGENT METHOD – SOLUTION PROCEDURE

We convert the eq.(2.10) by $u(x,t) = f(\xi)$, $\xi = x - \lambda t$ to derive the nODE of the third-order

$$\lambda\frac{d^3 f}{d\xi^3} - \frac{d^2 f}{d\xi^2} + \alpha^2\lambda\frac{d^2 f}{d\xi^2} - \beta^2\lambda\frac{df}{d\xi}\exp[-\eta f] = 0,\ f = f(\xi),\ -\infty < \xi < \infty. \tag{2.11}$$

Note: The similarity transformation is called the traveling wave reduction describing any wave propagation and λ means the velocity. However if we assume the EQS model solutions of electromagnetic field problems can not represent traveling waves.

We seek for solutions for which $v = F(\xi)$, where $F \in R^3$ and $D \subset R^2$ is an open set and further we exclude $D := \left\{(f,\xi) \in \widetilde{D} : f(\xi) = 0\right\}$. Suitable solutions are $v \in I$, I an interval so that $I \subseteq D$ and $v : I \to R^2$. Since the l.h.s of eq.(2.11) is a continuous function we ensure at least existence locally and due to the lemmas both from Peano and Picard-Lindelöf we assume uniqueness (also at least locally) in a given domain.

The question is: Can we integrate the nODE so that we can write the nODE, Eq. (2.11) in a complete differential form? Indeed, one has

$$\frac{d}{d\xi}\left\{\frac{df}{d\xi}-\lambda\frac{d^2f}{d\xi^2}-\alpha\lambda\frac{df}{d\xi}\right\}+\frac{d}{d\xi}\left\{\beta\lambda e^{-\eta f}\right\}=0. \tag{2.12}$$

Integrating once with C as an arbitrary constant of integration gives a second-order nODE

$$\lambda\frac{d^2f}{d\xi^2}+\alpha^2\lambda\frac{df}{d\xi}-\frac{df}{d\xi}--\beta^2\lambda e^{-\eta f}-C=0. \tag{2.13}$$

Note: During calculations it could have been shown that one can set the integration constant equal to zero without loss of generality. Here this constant will act as an arbitrary calculation quantity without any relation to the problem.

The transformation $f(\xi)=\frac{1}{\eta}\ln[w(\xi)]$ will remove the exponential function yielding a further second-order nODE for the new dependent variable $w(\xi)$:

$$\lambda w\frac{d^2w}{d\xi^2}-\lambda\left(\frac{dw}{d\xi}\right)^2+\alpha^2\lambda w\frac{dw}{d\xi}-w\frac{dw}{d\xi}-\beta^2\eta\lambda w=0, \quad w=w(\xi). \tag{2.14}$$

To apply the algorithm performed in the note above it is necessary to know the quantity n in the series representation of eq.(c). It can be shown that two values exists: $n_1=-1$ and $n_2=-2$. This is not possible since this quantity must be $n\in\wedge^{+}$. Introducing further a new dependent variable $p(\xi)$ by the transformations $w_1(\xi)=p(\xi)^{-1}$and $w_2(\xi)=p(\xi)^{-2}$ will give a second-order nODE for the function $p(\xi)$:

$$\lambda p\frac{d^2p}{d\xi^2}-\lambda\left(\frac{dp}{d\xi}\right)^2+\alpha^2\lambda p\frac{dp}{d\xi}-p\frac{dp}{d\xi}+\beta^2\eta\lambda p^3=0. \tag{2.15}$$

Note: Further analysis has shown that the inverse quadratic transformation only led to trivial solutions. We stress that $p=0$ is the singular point of this nODE.

The balancing procedure will result into two cases: **(i)** $n_1=1$ and **(ii)** $n_2=2$. Case **(i)** results into trivial solutions thus the quadratic form $p(\xi)=a_0+a_1v+a_2v^2$ is suitable. Using this, considering eq.(d) and inserting into the relevant nODE eq.(2.15) a nonlinear homogeneous algebraic system of equations for the unknown coefficients have to be solved consistently. In total seven equations exist; for saving space we stress the first and the last equations

$$\begin{aligned} &2k_1^2 + a_2\beta^2\eta\lambda = 0 \\ &\cdots\cdots\cdots\cdots\cdots\cdots \\ &\cdots\cdots\cdots\cdots\cdots\cdots \\ &a_0 a_1 k_1 + a_1^2 k_1^2\lambda + 2a_0 a_2^2 k_1^2\lambda + a_0 a_1 k_1 \alpha^2\lambda + a_0^3\beta^2\eta\lambda = 0. \end{aligned} \tag{2.16}$$

From the seven solutions totally the only non-trivial solution yields

$$a_0 = \frac{2k_1^2}{\beta^2\eta}, \quad a_1 = 0, \quad a_2 = -\frac{2k_1^2}{\beta^2\eta}, \quad \lambda = \frac{1}{\alpha^2}, \quad k_1 \neq 0, \quad \alpha \neq 0, \; \beta \neq 0, \; \eta \neq 0. \tag{2.17}$$

Transforming back a compact written form for the potential function is given by

$$u(x,t) = f(\xi) = -\frac{1}{\eta}\ln\left[2\left(1 + \tanh^2\sqrt{\xi}\right)\right] + const., \quad \xi = x - \lambda t = x - t\alpha^{-2}, \; \xi > 0. \tag{2.18}$$

or explicitly in terms of time and space variables

$$u(x,t) = -\frac{kT}{z e_0}\ln\left[2\left(1 + \tanh^2\sqrt{x - \frac{kTt}{Dc}}\right)\right] + const.. \tag{2.18a}$$

For further calculations the exponential form may be preferred; so we have

$$f(\xi) = const. - \frac{1}{\eta}\ln\left[2\left(1 + \frac{A^2}{B^2}\right)\right] = const. - \frac{1}{\eta}\ln\left[\frac{4\left(1 + \exp\left[4\sqrt{\xi}\right]\right)}{\left(1 + \exp\left[2\sqrt{\xi}\right]\right)^2}\right], \tag{2.18b}$$

with $A = e^{\sqrt{\xi}} - e^{-\sqrt{\xi}}$ and $B = e^{\sqrt{\xi}} + e^{-\sqrt{\xi}}$.

Note: In order to realize real-valued solutions the constant k_1 must be $k_1 < 0$ and the root terms become positive (during analysis we assume $k_1 = -1$). Moreover eq.(2.18) is the only appropriate solution for the chemical problem since the second solution of eq.(e) becomes singular. To ensure non-vanishing solutions the argument of the logarithm function must be greater than identity (that means that the relation $2\left(1 + \tanh^2\sqrt{\xi}\right) > 1$ holds).

From the laws of logarithms it follows that $const = \eta^{-1}\ln\left(\eta\beta^2\right)$. This contribution will act as a shift for the (f, ξ) curve. For imagination a concrete example is given: Consider the values for KCl in water [33] and inserting the relevant quantities ones derived at $const. = -1{,}95$. A sketch of the functions is given in Figure 1.

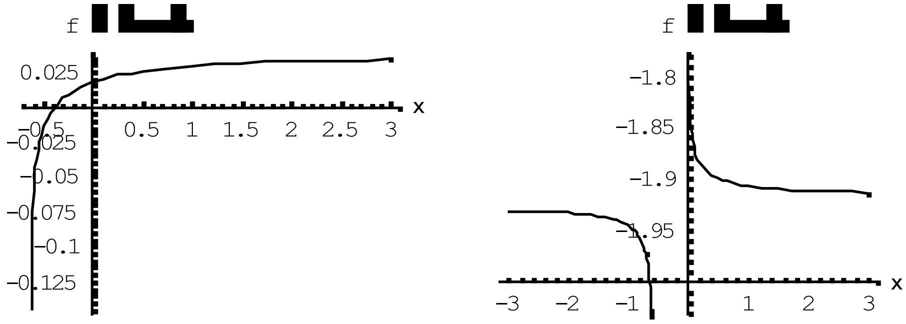

Figure 1. Comparison Between the Regular Solution Eq. 2.18.

Left containing the hyperbolic tangent function and the singular solution containing the hyperbolic cotangent,

Right. The regular solution covers the boundary condition so that the solution tends to a finite value. Taking a limit analysis one can prove $\lim_{\xi \to \infty} f(\xi) = 0{,}035$. This finite value can be interpreted as a finite potential value in any electrolytes. The first derivative exists (meant as the second boundary condition) and vanishes as $\xi \to \infty$ as to be required. The positive branch of the singular solution may be considered as a potential starting on a conducting surface leading into a constant value in any liquids.

2. 2. A NUMERICAL STATEMENT

As mentioned above the highly nPDE eq.(2.11) and all nODEs derived from it, especially the nODE eq.(2.15) can only be solved under special circumstances, e.g. any similarity transformations. It is clear that by applying numerical standard procedures a closed-form solution is always obtained (considering suitable boundary and/or initial conditions). One of these standard procedures is the representation in ascending power series which is useful in numerical calculations. At the regular point $\xi = 0$ of the nODE eq.(2.15) one can assume a series representation up to order four in the form (here we set the constants η, β equal to identity and $\lambda = 2$ since they do not influence the result necessarily):

$$p(\xi) = a_0 + a_1\xi - \frac{1}{4}\left(2a_0^2 + a_1 + \frac{2a_1^2}{a_0}\right)\xi^2 + \frac{1}{24}\left(2a_0^2 + a_1 + \frac{6a_1^2}{a_0} + \frac{12a_1^3}{a_0^2}\right)\xi^3 + O[\xi]^4 \qquad (2.19)$$

with arbitrary chosen coefficients a_0, a_1 but $a_0 \neq 0$ .In figure 2 some integral curves are shown.

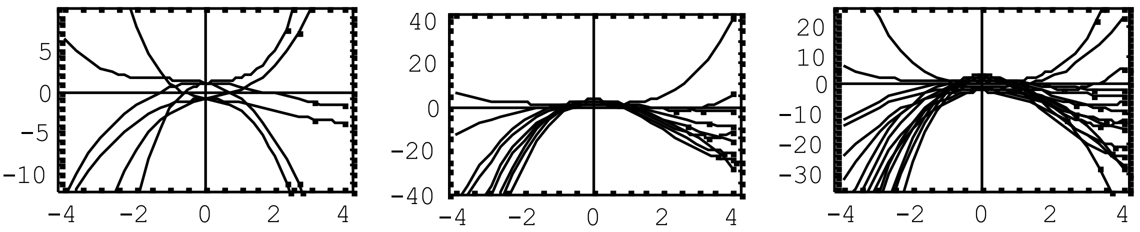

Figure 2. Some integral curves of the nonlinear nODE, eq.(2.15) generated by the series representation eq.(2.19).

Different values of the coefficients a_i are used. Left the domain $(-1,1) \le (a_0, a_1) \le (-1,1)$, middle the domain $(1,3) \le (a_0, a_1) \le (-1,1)$ and right the domain $(-2,3) \le (a_0, a_1) \le (-1,1)$. Parabolic forms of the potential function and behaviour of the order three is evident in the positive as well as negative directions.

3. ANALYSIS

Let us summarize in short: Our main task was to solve the nPDE, eq.(2.10) in an analytical way dispensing any numerical approaches. This can be done by keeping in mind the special function methods. Although the eq.(2.10) is highly nonlinear, algebraic methods can therefore be applied successfully. A closed-form solution was then derived by the explicit formula for the time-dependent solution function eq.(2.18). By taking a limiting analysis it was shown that the potential function eq.(2.18) satisfies the required boundary conditions. Now we are interested in further quantities. The electric field can then derived from the potential (we further use the variable ξ) by application of the gradient operator ($\vec{E} = -\nabla\phi$) to give

$$\vec{E}(\xi) = \frac{\sec h\left(2\sqrt{\xi}\right)\tanh\left(\sqrt{\xi}\right)}{\eta\sqrt{\xi}} = \frac{2\exp\left(2\sqrt{\xi}\right)\left\{\exp\left(2\sqrt{\xi}\right)-1\right\}}{\eta\sqrt{\xi}\left\{1+\exp\left(2\sqrt{\xi}\right)\left(1+\exp\left(4\sqrt{\xi}\right)\right)\right\}}, \quad \xi \neq 0, \tag{3.1}$$

where we have converted the hyperbolic functions into an exponential representation and $\xi = x - \lambda t = x - t\alpha^{-2}$ holds. In figure 3 the electric field distribution is seen. This field distribution may be considered around a point-like charge in the centre (by assuming $\eta = 1$) symmetrically. To derive the charge density one has to apply the divergence operator upon the electric field (ξ also acts as the local coordinate):

$$\rho(\xi)=\frac{1}{8\pi\xi}\left(\left\{\sec h^{2}\left(\sqrt{\xi}\right)-2\sec h^{2}\left(2\sqrt{\xi}\right)\right\}+\sec h\,\left(\sqrt{2\xi}\right)\tanh\,\left(\sqrt{\xi}\right)\right),\quad \xi\neq 0\,. \tag{3.2}$$

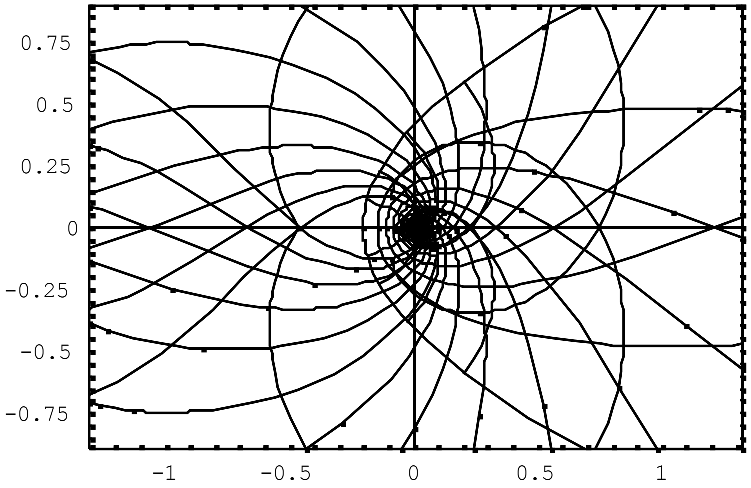

Figure 3. The electrical field distribution derived from eq.(3.1). It can be shown that the field is of conservative character since by considering Cartesian coordinates, e.g. $\xi=(\xi_x,\xi_y,\xi_z)$ the relation $rot\,\vec{E}=0$ holds (it means that the field is irrotational or equivalently, the existence of the potential is secured since the curl of the field vanishes).

To show that the field is really solenoidal one introduces Cartesian coordinates for the electric field, eq.(3.1) so that $\vec{E}=(E_x,E_y,E_z)$. Then we have per definition with a unit vector $\vec{e}_i$: $rot\vec{E}=\nabla\times\vec{E}=\begin{vmatrix}\vec{e}_x & \vec{e}_y & \vec{e}_z\\ \partial_x & \partial_y & \partial_z\\ E_x & E_y & E_z\end{vmatrix}=\vec{e}_x\begin{vmatrix}\partial_x & \partial_y\\ E_x & E_y\end{vmatrix}+\vec{e}_y\begin{vmatrix}\partial_x & \partial_z\\ E_x & E_z\end{vmatrix}+\vec{e}_z\begin{vmatrix}\partial_y & \partial_z\\ E_y & E_z\end{vmatrix}$. (3.1.a)

Now it follows that (only the first component E_x is considered)

$$rot\vec{E}=\left|\partial_x\frac{\cosh\sqrt{2y}\tan\sqrt{y}}{\sqrt{y}}-\partial_y\frac{\cosh\sqrt{2x}\tan\sqrt{x}}{\sqrt{x}}\right|+|........|+|.......|=0,\ x\neq 0,\ y\neq 0\,. \tag{3.1.b}$$

The charge density represents an analytical function except as $\xi=0$ where the function is singular. From a limiting analysis it can be shown that the charge density vanishes as $\xi\to\infty$, that is $\lim_{\xi\to\infty}\rho(\xi)=0$. Also it can be shown that for small values of the charge density, that is $\xi\to 0$, the charge density will take a finite value such that $\lim_{\xi\to 0}\rho(\xi)=7/12\pi$ holds.

That means by considering an arbitrary surface this surface will be charged by the given amount of charges of $7/12\pi$.

Let a be a specific distance (e.g. from the electrode surface to the centre of the hydrated ions in the OHL, the **O**uter **H**elmholtz **L**ayer). The total charge q_{tot} contained in the OHL is obtained by integrating the charge density $\rho(\xi)$ from the electrode surface with the reference point taken at infinity. Therefore we have from eq.(3.2):

$$q_{tot} = \int_{a}^{\infty} \rho(\xi)\,d\xi = \frac{Exp\left(2\sqrt{a}\right)\left\{Exp\left(2\sqrt{a}\right)-1\right\}}{2\pi\left(1+Exp\left(2\sqrt{a}\right)\right)\left(1+Exp\left(4\sqrt{a}\right)\right)}, \tag{3.3}$$

and q_{tot} takes a function of the distance a.To avoid singularities one has to exclude special values of the denominator, e.g. $a = \left\{0, -9\pi^2/16, -\pi^2/4, -\pi^2/16\right\}$, and, for completeness some complex numbers $a = \left(\log^2\left(-(-1)^{1/4}\right), \log^2\left(-(-1)^{3/4}\right)\right)$.

Let us study two limit cases: **(i)** for small distances, say, $a \to 0$, the total charge tends to a constant factor: $q_{tot} = 1/4\pi$ (this may be interpreted as the square of the first spherical harmonics Y_{00}^2); **(ii)** for large distances it is shown that $q_{tot} \to 0$ as $a \to \infty$. This is also in agreement with the boundary conditions assumed earlier and matches our expectation exactly. In the following figures we show the charge density derived from the eq.(3.2) compared with the total charge density from the eq.(3.3).

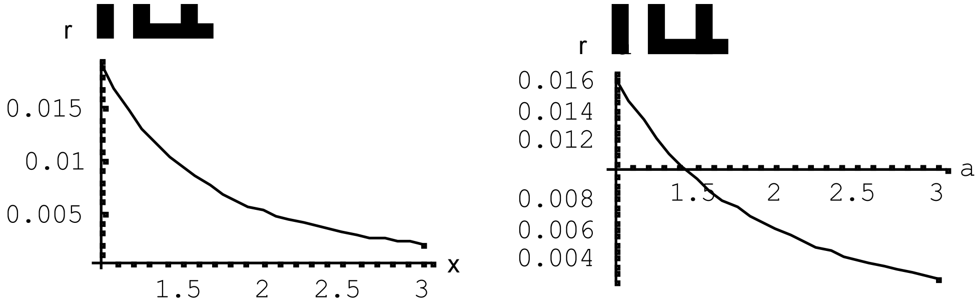

Figure 4. Comparison between the charge density from eq.(3.2) as a function of the dependent variable ξ left and the total charge density as a function of the distance a calculated from eq.(3.3).

3. 1. FURTHER PROPERTIES OF THE INVOLVED QUANTITIES

For practical numerical calculation some series representations both of the potential and the electrical field is useful. Since the function eq.(2.18) is a continous differentiable function one can calculate an alternating representation as $\xi = 0$ (but the series diverges). Thus a convergent series as $\xi = 1$ is given by

$$f(\xi) = A + \frac{1}{\eta}\left\{0{,}202(\xi-1) - 0{,}120\,(\xi-1)^2 + 0{,}064(\xi-1)^3 - 0{,}032(\xi-1)^4\right\} + O[\xi-1]^5, \tag{3.4}$$

where we have used the abbreviation $A = \left\{const. - \frac{1{,}151}{\eta}\right\}$ and *const.* from above.

The convergence is relatively slow but in first order approximation a linear dependence is a good compromise. In the same manner for the electrical field it follows from, Eq. (3.1)

$$\vec{E}(\xi) = \frac{1}{\eta}\left\{0{,}202 + 0{,}2405(\xi-1) - 0{,}1922(\xi-1)^2 + 0{,}1330(\xi-1)^3\right\} + O[\xi-1]^4 \ . \tag{3.5}$$

Since the function takes singular as $\xi = 0$ the series is taken up from the point $\xi = 1$.

Note: One can asks if the potential function eq.(2.18) is a square-integrable function. That means one has to find a real, finite constant M so that the relation $\int_{-\infty}^{\infty} |f(\xi)|^2 d\xi < M$ holds. Taking into account the laws of logarithm one can transform eq.(2.18) into a sum of logarithmic parts. The integration shows that all these sums diverge and the latter relation is not satisfied (thus $f(\xi) \notin L^2(R^n)$). Consider appropriate domains, e.g. $0 < \xi \le 1$, the existence of the constant M is given and a normalization is feasible. This may be important by representing the potential function in terms of orthonormalizations and closure relations related with different basis sets.

4. SUMMARY

Let us summarize in short: Due to our special model one is able to show that a special form of the PBE could solved exactly without any numerical calculations. However some restrictions (due to the EQS assumption) have been taken into account. For this special model, four important quantities could derive: **(i)** The potential of an electrode and/or the potential distribution of some charged particles, **(ii)** the electric field around an electrode and/or the field distribution inside a medium, **(iii)** the charge density, **(iv)** the charge density in the OHL.

In this paper we extended our model equation to cases in which concentration and diffusion play a further role. A further possible extension of this time-depending model will be the case if ions and/or charged particles will move in electric and/or magnetic fields.

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