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An Algebraic Calculation Method for Describing Time–Dependent Processes in Electrochemistry – Expansion of Existing Procedures

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ARTICLE INFO	ABSTRACT
	In this paper an alternative model allowing the extension of the Debye-Hückel Theory (DHT) considering time dependence explicitly is presented. From the Electro-Quasistatic approach (EQS) introduced in earlier studies time dependent potentials are suitable to describe several phenomena especially conducting media as well as the behaviour of charged particles (ions) in electrolytes. This leads to a reformulation 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 PBE will be modified leading to a 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 pure algebraic steps. The benefit of the mathematical tools used here is the fact that closed-form solutions can be calculated and thus, numerical methods are not necessary. The important outcome of the present study is meaningful twofold: **(i)** The model equation allows the description of time dependent problems in the theory of ions, and **(ii)** the mathematical procedure can be used to derive classes of solutions of arbitrary nPDEs, especially those of higher order.

1   INTRODUCTION

Many problems of physical/chemical interest are described by nPDEs with appropriate side conditions. These can be suitable chosen initial and/or boundary

conditions. If the equations are linear, widely used methods for solving PDEs are known (e.g. the Fourier and/or Green's method) and the superposition principle generates further solutions by known of a pair of solutions. For nPDEs, however, the linear superposition principle can not be applied to generate new classes of solutions.

> **Note:** We stress the existence of a nonlinear superposition principle known as the Bäcklund transformation which means a special contact transformation [1]. The nPDE under consideration is not of Painlevé type, e.g. [2], [3], [4] and therefore a suitable Bäcklund system can not be associated. Apart from this a Bäcklund system is only (in the most cases) derivable for 'simple strutured' nPDEs. Thus this fact justifies the use of algebraic methods for deriving analytical solutions and often represents the only suitable way for a successful solution procedure.

Because most of the of solution methods for linear equations fail, there is no general method of finding analytical classes of solutions for nPDEs and numerical techniques are usually required. Sometimes special transformations can be done to transform a nPDE into a linear PDE, or some other 'ad hoc' methods (and/or assumptions) can be used to derive classes of solutions of a particular nonlinear equation.

> **Note:** We arrange that we suppress the item 'classes of solutions', so we will simply understood 'solutions' instead of classes of solutions (although classes of solutions is the correct notation). Since time occurs in the derivation(s) explicitly such types of nPDEs are called evolution equations (EVEs) since they allow the study of time-dependent processes. Any nPDE may not have the outer form $u_t = K[u, u_x, u_{xx}, \dots]$ necessarily being an EVE where $u_t = K[u, u_x, u_{xx}, \dots]$ is a nonlinear operator in general. Equations containing mixed higher derivations like $u_{xt} = K[u]$ and/or $u_{xxt} = K[u]$ are also called EVEs.

Techniques of finding solutions represent only one aspect in dealing with nPDEs. Like linear equations, questions of existence, uniqueness, and stability of solutions are also of fundamental importance.

1.1. HISTORICAL DEVELOPMENTS – A SHORT OVERVIEW

There is a good historical reason to deal the subject. When the developments of interfacial electrochemistry along modern lines became restricted by the over thermodynamics attitude 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 double layer.

This had concentrated upon an interest in the deviations in the behaviour of solutions from laws derived upon the assumption that interactions between particles are negligible. 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 $\propto r^{-7}$ dependence. Consequently, the behaviour of an electrolyte solution deviates considerably from that an ideal solution. Thus the DHT of such interactions attracted the attention of electrochemists away from the blocked interface studies [5]. The DHT was proposed as a theoretical explanation for departures from ideality in solutions of electrolytes [6]. 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 [7], [8]. Note that by applying the DHT restrictions have taken into account, like much diluted solutions, completely dissociation and more [9]. Contemporaneously, Helmholtz considered a double-layer model wherein he proposed a simple charge separation at the interface [10].

Gouy [11], [12] 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 [13]. He established the steady-state governing equation for the diffuse layer, the Poisson-Boltzmann Equation [11]. This equation is based upon the combination of the electrostatic basic equation, the Poisson Equation [14], and the Boltzmann distribution [15]. The model is referred to as the Gouy-Chapman model.

Further, Stern [16] 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 [17] revised the Stern model using three layers: The **I**nner Helmholtz layer (IHL), the **O**uter Helmholtz layer (OHL) and the diffuse layer. The difference between the Grahame model and the Stern model is due to the existence of a specific adsorption [11].

A transient version [11] is referred to as the Nernst-Planck-Poisson-modified Stern model or simply the Nernst-Planck-Poisson model (NPP) if there is no modified Stern layer.

During the past 90 decades several well-known scientists did their contributions in this domain, and, unfortunately only a small number are mentioned here like Bjerrum [18], Gronwall/La Mer/Sandved [19], Onsager [20], Kirkwood [21], Falkenhagen [6], [9], Ghosh [22], Smoluchowski [23], Parker [24], Walden [25], Planck [26], Fuoss [27], Kortüm [28], [29], and extensive developments are not finalized up to now.

1.2. ELECTROMAGNETICS FROM A QUASISTATIC PERSPECTIVE

The general theoretical considerations can be found in [30−32]. 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 the low-frequency approximation). The crucial step is the fact that a 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 [33−37]. General transient electrodynamical problems are not easy to solve, e.g. by occurring solutions depending upon roots one has 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 $\tau = \varepsilon_0 \varepsilon \sigma^{-1}$ [38], where ε is the relative permittivity (of the material) and σ is the conductivity. For the most metals (e.g. copper) the relaxation time is in the range of 10^{-18}s. New developments in material sciences produce materials with a relative dielectric constant in the range of $2 < \varepsilon < 4$ and a conductivity of about $10^{-9} sm^{-1}$. 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. if an electromagnetic field passes through a panel).

This is exactly the case where EQS can be applied [32], [38] 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 works as an approximation.

1.3. THE MODEL EQUATION UNDER CONSIDERATION

The starting point is an expanded version of the PBE, a special nPDE of the third order

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

where F is the Faraday constant, D the diffusion constant and k is the Boltzmann constant.

One assumes the conversion: Let $N_i^0 \times 1000 = N_A c_i$, c_i is the molar concentration and the ion strength is defined by $I = 1/2 \sum_i c_i z_i^2$. Introducing further per definition

$$\beta^2 = \frac{e_0^2 N_A}{1000 \, kT} \frac{1}{2} \sum_i c_i z_i^2 \;\rightarrow\; \beta^2 = \frac{2 \, e_0^2 N_A}{1000 \, kT} I \;\;, \; \eta = \frac{z_i e_0}{kT}, \; \alpha^2 = \frac{DFc}{kT}, \tag{2}$$

one derives a third-order nPDE for the time-dependent potential function $u = u(x,t)$:

$$\varepsilon \, \varepsilon_0 \frac{\partial^3 u}{\partial x^2 \partial t} + \sigma \frac{\partial^2 u}{\partial x^2} - \alpha^2 \frac{\partial^2 u}{\partial x \partial t} - \beta^2 \frac{\partial u}{\partial t} e^{-\eta \, u} = 0. \tag{3}$$

At this stage one formally imposes boundary conditions (BCs) 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 $u = u(x,t)$. Note that BCs may depend upon actual problems. We find it useful to split up the potential so that u_0 is the potential at any surfaces and u_L is the potential in the electrolyte far away from a reference ion, thus $\Delta u = u_0 - u_L$ (not to be changed with the Laplacian).

One seek solutions for the nPDE, Equation (3) for which $u = F(x,t)$, $F \in C^3(D)$, $D \subset R^2$ is an open set and

$$D := \left\{ u(x,t) \in \tilde{D} : u = 0, \, u_x = 0, \, u_t = 0, ... \right\}$$

is excluded with $t > 0$. Suitable solutions are $u \in I$, I an interval so that $I \subseteq D$ and $u : I \to R^2$. It is not an easy task to solve nPDEs (especially of higher order) exactly but here we wish to solve the Equation (3) analytically by using algebraic methods without numeric's. A mean value for the charge density is used in Equation (3) and one-valued ions are assumed so that $z_i = z = 1$. In later considerations the case of many-valued ions will be considered. The potential function $u(\vec{x},t) \equiv u$ 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 dipping in an (liquid) electrolyte (due to the restrictions imposed by EQS not all metals can be considered). 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. In the following we shortly present the basics.

1.4. THE ALGEBRAIC SOLUTION PROCEDURE

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

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

Firstly the nPDE converts into a nODE by using a frame of reference $u(x,t) = f(\xi)$, where $\xi = \delta x - \lambda t$; δ and λ are constants to be determined. Thus one has

$$Q\left(f(\xi), f'(\xi), f''(\xi), \dots\right) = 0.$$ (b)

The next step is that the solutions we are looking for can be expressed in terms of a finite series representation such that

$$u(x,t) = f(\xi) = \sum_{i=0}^{n} a_i \, cn^i(\xi, k) \text{ and } f^{(n)}(\xi) = \sum_{i=0}^{n} \frac{\partial^n}{\partial \xi^n}\left(a_i \, cn^i(\xi, k)\right)$$ (c)

holds where $cn(\xi, k)$ means the cosine amplitude and k is the modulus. The parameter n in Equation (c) is found by balancing the highest derivative with the nonlinear terms in the reduced nODE Equation (b). 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 suitable transformations as shown later. The substitution of Equation (c) into the relevant nODE Equation (b) will yield a system of nonlinear algebraic equations with respect to the unknowns $a_0, a_1, \dots, k, \lambda$ and δ.

2.   CALCULATION OF SOLUTIONS

We convert the Eq. (3) by $u(x,t) = f(\xi)$, $\xi = \delta x - \lambda t$ to derive the nODE of the third-order

$$\delta^2 \lambda \frac{d^3 f}{d\xi^3} - \delta^2 \frac{d^2 f}{d\xi^2} + \alpha^2 \delta\lambda \frac{d^2 f}{d\xi^2} + \beta^2 \lambda \frac{d f}{d\xi} \exp[-\eta f] = 0, f = f(\xi), -\infty < \xi < \infty$$ (4)

> **Note:** The similarity transformation is called the travelling wave reduction describing any wave propagation and λ means the velocity. One of the new aspects here is the introduction of the quantity δ to generalize the method.

> We seek for solutions for which $f = F(\xi)$, $F \in R^3$ and $D \subset R^2$ is an open set excluding

$$D := \left\{(f,\xi) \in \tilde{D} : f(\xi) = 0, \partial_t \neq 0\right\}.$$

Suitable solutions are $f \in I$, I an interval so that $I \subseteq D$ and $f : I \to R^2$. Since the l.h.s of Equation (4) is a continuous function we ensure at least existence locally and due to the lemmas from Peano and Picard-Lindelöf we assume uniqueness (also at least locally) in a given domain.

The question now is: Can we integrate the nODE Equation (4) directly so that we can rewrite the nODE (4) in a complete differential form? Indeed, one has

$$\frac{d}{d\xi}\left\{ \delta^2\lambda\eta\frac{d^2 f}{d\xi^2} - \delta^2\eta\frac{df}{d\xi} + \alpha^2\delta\lambda\eta\frac{df}{d\xi} \right\} + \frac{d}{d\xi}\left\{ \beta^2\lambda e^{-\eta f} \right\} = 0. \tag{5}$$

Integrating once with c_1 as an arbitrary constant of integration gives a second-order nODE

$$\delta^2\lambda\eta\frac{d^2 f}{d\xi^2} - \delta^2\eta\frac{df}{d\xi} + \alpha^2\delta\lambda\eta\frac{df}{d\xi} + \beta^2\lambda e^{-\eta f} = c_1. \tag{6}$$

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

$$\delta^2\lambda w\frac{d^2 w}{d\xi^2} - \delta^2\lambda\left(\frac{dw}{d\xi}\right)^2 + \alpha^2\delta\lambda\, w\frac{dw}{d\xi} - \delta^2 w\frac{dw}{d\xi} - c_1 w^2 + \beta^2\lambda\, w = 0, \ w = w(\xi) \tag{7}$$

To apply the algorithm performed in Section 1(d) above it is necessary to know the quantity n in the series Equation (c). It can be shown that two values exist: $n_1 = -1$ and $n_2 = -2$.

This is not possible since this quantity must be $n \in Z^+$. Introducing a new variable $p(\xi)$ by the transformations $w_1(\xi) = p(\xi)^{-1}$ and $w_2(\xi) = p(\xi)^{-2}$ will give two second-order nODEs (balancing now leads to $n_1 = 1$ and $n_2 = 2$) for the function $p(\xi)$:

$$2\delta^2\lambda\, p\frac{d^2 p}{d\xi^2} - 2\delta^2\lambda\left(\frac{dp}{d\xi}\right)^2 + 2\alpha^2\delta\lambda\, p\frac{dp}{d\xi} - 2\delta^2 p\frac{dp}{d\xi} - \beta^2\lambda\, p^4 + c_1 p^2 = 0, \text{ for } n_1 = 1 \tag{7a}$$

$$\delta^2\lambda\, p\frac{d^2 p}{d\xi^2} - \delta^2\lambda\left(\frac{dp}{d\xi}\right)^2 + \alpha^2\delta\lambda\, p\frac{dp}{d\xi} - \delta^2 p\frac{dp}{d\xi} - \beta^2\lambda\, p^3 + c_1 p^2 = 0, \text{ for } n_2 = 2 \tag{7b}$$

Thus, from the Equation (c) the following solutions for the functions $p(\xi)$ are possible:

$$p_1(\xi) = a_0 + a_1 cn(\xi, k), \text{ for } n = 1 \tag{8a}$$

$$p_2(\xi) = a_0 + a_1 cn(\xi, k) + a_2 cn^2(\xi, k), \text{ for } n = 2 \tag{8b}$$

Putting together the Equations (c), (8a), (8b) into the nODEs (7a), (7b) two systems of nonlinear algebraic equations appear. For control purposes we only stress the first and the last equation.

1st case, $n = 1$:

$$2a_0^2\beta^2\lambda - c_1 + 2a_1^2\beta^2\lambda + \delta^2\lambda = 0,$$
$$a_1^2 + 2k\delta^2 = 0. \tag{9}$$

2nd case, $n = 2$:

$$2a_0c_1 + 2a_2c_1 - 3a_0^3\beta^2\lambda - a_0^2\beta^2\lambda - 6a_0a_2\beta^2\lambda - 3a_2^2\beta^2\lambda - 3a_2\delta^2\lambda = 0,$$
$$a_0^2c_1 + a_1^2c_1 + 2a_0a_2c_1 + a_2^2c_1 - a_0^3\beta^2\lambda - 3a_0a_1^2\beta^2\lambda - 3a_0^2a_2\beta^2\lambda - 3a_1^2a_2\beta^2\lambda - \tag{9a}$$
$$- 3a_0a_2^2\beta^2\lambda - a_2^3\beta^2\lambda - a_1^2\delta^2\lambda - 2a_0a_2\delta^2\lambda - 2a_2^2\delta^2\lambda = 0.$$

Solving these systems the following solutions are possible (the trivial solution is always a solution but meaningless for our purposes; the constants α and β are predetermined quantities and should not work as unknowns):

1st case:

(i) $a_0 = 0$, $c_1 = \delta^2\lambda(3 - 2\sqrt{3})$, $k = \frac{1}{2}(\sqrt{3} - 1) \approx 0{,}366$, $\delta \neq 0$, $\lambda \neq 0$, a_1 arbitrary, (10)

(ii) $a_0 = \pm\frac{1}{2}\sqrt{\frac{23}{6}}a_1$, $c_1 = -\frac{45\delta^2\lambda}{2}$, $k = 3$, $\delta \neq 0$, $\lambda \neq 0$, a_1 arbitrary, (10a)

(iii) $a_0 = 0$, $c_1 = \delta^2\lambda(3 + 2\sqrt{3})$, $k = -\frac{1}{2}(1 + \sqrt{3}) \approx -1{,}366$, $\delta \neq 0$, $\lambda \neq 0$, a_1 arbitrary (10b)

2nd case:

(i) $a_0 = 3a_2$, $a_1 = 0$, $c_1 = -\frac{7\delta^2\lambda}{2}$, $k = \frac{1}{2}$, $\delta \neq 0$, $\lambda \neq 0$. (10c)

An interesting role plays the constant c_1: It relates the parameters δ and λ in the similarity variable ξ if one sets $c_1 = 1$ and thus we exclude $c_1 = 0$ in the Equation (6). By using the Equations (8a) to (10c) one derives the following expressions for the functions $f(\xi)$ and therefore for the functions $u(x,t)$:

$$f_1(\xi) = \frac{1}{\eta}\ln\left[\frac{1}{a_1cn(\xi,k)}\right] = -\frac{1}{\eta}\ln[a_1cn(\xi,k)], \quad k = \frac{1}{2}(\sqrt{3} - 1),$$

$$\xi = \delta x - \frac{\lambda t}{\delta^2(3 - 2\sqrt{3})}, \tag{11}$$

$$f_2(\xi) = -\frac{1}{\eta}\ln\left[a_1\left(\sqrt{\frac{23}{24}} + dn\left(3\sqrt{3}\xi,\frac{1}{3}\right)\right)\right], \quad \xi = \delta x + \frac{2\lambda t}{45\delta^2}, \quad a_1 \text{ arbitrary}, \quad a_1 \neq 0,$$

$$\tag{11a}$$

$$f_3(\xi) = -\frac{1}{\eta} \ln\left[a_1 dn\left(\sqrt{\frac{1}{2}\left(\sqrt{3}-1\right)}\,\xi, \frac{2}{3} \right) \right], \quad \xi = \delta\,x - \frac{\lambda\,t}{\delta^2\left(3+2\sqrt{3}\right)}, \quad a_1 \text{ arbitrary,}$$

$$a_1 \neq 0, \tag{11b}$$

and for the 2nd case

$$f_4(\xi) = -\frac{1}{\eta} \ln\left[a_2\left(3 + cn^2\left(\xi, \frac{1}{2}\right) \right) \right], \quad \xi = \delta\,x - \frac{2\lambda\,t}{7\delta^2}, \quad a_2 \text{ arbitrary, } a_2 \neq 0. \tag{11c}$$

Note: To derive this solutions the basic properties of the elliptic functions (and the logarithm) was used, especially the relation for the modulus $k^2 + k'^2 = 1$, the Jacobi's real transformation for negative modulus and the transformation for imaginary arguments, e.g. [39]. Thus, for example, one has the relation $cn(u,-k) := cd(v,\mu)$ for the cosine amplitude. Elliptic functions with the special modulus $k = 1/2$, e.g. in case of the function $f_4(\xi)$ are sometimes called lemniscate functions. For the following discussions it is only necessary to consider the functions in the form $f_i(\xi)$, $i = 1,...,4$. For the constant η we have $\eta^{-1} = 0{,}0253 J C^{-1}$ and this is material independent. We assume the following domains of definition: $-1 \leq \big(sn(u), cn(u)\big) \leq 1$, $k' \leq dn(u) \leq 1$ and $-\infty \leq tn(u) \leq \infty$.

3.   SOME SPECIAL PROPERTIES

In all cases a travelling character is observed, but for all functions the argument of the logarithm may not be the unity, since in this case the solutions take infinity or become a singularity, apart from that the expressions have singularities if the denominators take zero. All functions are continuously and differentiable at least two-fold in the domain $0 < \xi < 1$, the first, the second and all higher derivatives exist and have the same behaviors as above. Some special values are summarized in the following table.

Now we are interested in further quantities. We assume an electrical field $\vec{E}_i$ and this field will be generated by a given charge distribution. Such an electric field can then be derived from the potential by application of the gradient operator $\vec{E}_i = -\nabla f_i(\xi)$ to give the following expressions and without loss of generality one can also set $a_1 = a_2 = 1$; the modulus are given by the Equations (11) to (11c):

$$\vec{E}_1(\xi) = -\frac{1}{\eta} sn(\xi, k)\, dc(\xi, k), \quad \xi \neq 1{,}7546, \tag{12}$$

$$\vec{E}_2(\xi) = -\frac{1}{\eta}\frac{\sqrt{3}\,cn\left(3\sqrt{3}\,\xi,\frac{1}{3}\right)sn\left(3\sqrt{3}\,\xi,\frac{1}{3}\right)}{\sqrt{\frac{23}{24}+dn\left(3\sqrt{3}\,\xi,\frac{1}{3}\right)}}, \tag{12a}$$

$$\vec{E}_3(\xi) = -\frac{\sqrt{2\left(\sqrt{3}-1\right)}}{3\eta}cn\left(a\xi,\frac{2}{3}\right)sd\left(a\xi,\frac{2}{3}\right), \quad a = \sqrt{\frac{1}{2}\left(\sqrt{3}-1\right)}, \tag{12b}$$

$$\vec{E}_4(\xi) = -\frac{1}{\eta}\frac{2\,cn(\xi,k)\,dn(\xi,k)\,sn(\xi,k)}{3+cn^2(\xi,k)}. \tag{12c}$$

$f_i(\xi)$	$\partial_\xi f_i(\xi)\vert_0$	$\partial_\xi f_i(\xi)\vert_1$	$\partial_{\xi\xi} f_i(\xi)\vert_0$	$\partial_{\xi\xi} f_i(\xi)\vert_1$	$\lim\limits_{\xi\to 0} f_i(\xi)$	$\lim\limits_{\xi\to 1} f_i(\xi)$
$f_1(\xi)$	0	1,2182	1	1,9993	0	0,5423
$f_2(\xi)$	0	0,0005	0	-0,0041	-0,6826	-0,5853
$f_3(\xi)$	0	0,2073	0,2440	0,1394	0	0,1126
$f_4(\xi)$	0	0,2348	0,5	-0,1301	-1,3863	-1,2105

Table 1. Some selected properties of the functions Equation (11) to Equation (11c), here $a_1 = a_2 = 1$ is considered, $i = 1,...,4$.

Note: We stress that the first expression is not defined at those points where the denominator vanishes, e.g. at the points as $cn(\xi,k) = 0$. This is equivalent with the task to look for solutions of the equation $cn(\xi,k) = 0$. The first real zero is given explicitly and the same is true for the remaining denominators.

Now we show that the fields have a conservative character since by considering Cartesian coordinates, e.g. $\xi = (\xi_x,\xi_y,\xi_z)$ the relation $rot\,\vec{E}_i(\xi) = 0$ holds (the field is irrotational or equivalently, the existence of the potential is secured since the curl of the field vanishes).

To show that the fields are really solenoidal one introduces Cartesian coordinates in the Equations (12) to (12c) so that $\vec{E}_i(\xi) = (E_x,E_y,E_z)$. Here also $a_1 = a_2 = 1$ is assumed and we suppress the factor η^{-1} and dropping all

arguments. The calculation is performed only for the first component $\vec{E}_1(\xi)$, the remaining are similar. With a unit vector $\vec{e}_i$ one has:

$$rot\vec{E}_1 = \vec{\nabla} \times \vec{E}_1 = \begin{vmatrix} \vec{e}_x & \vec{e}_y & \vec{e}_z \\ \partial_x & \partial_y & \partial_z \\ E_x & E_y & E_z \end{vmatrix} = \vec{e}_x \begin{vmatrix} \partial_y & \partial_z \\ E_y & E_z \end{vmatrix} - \vec{e}_y \begin{vmatrix} \partial_x & \partial_z \\ E_x & E_z \end{vmatrix} + \vec{e}_z \begin{vmatrix} \partial_x & \partial_y \\ E_x & E_y \end{vmatrix}. \quad (13)$$

Now it follows that

$$rot\,\vec{E}_{1,x} = \left| \partial_y\left(\frac{sn(z,k)\,dn(z,k)}{cn(z,k)} \right) - \partial_z\left(\frac{sn(y,k)\,dn(y,k)}{cn(y,k)} \right) \right| + ... = 0,\ x \neq 0,\ y \neq 0,$$

$$z \neq 0 \qquad (13a)$$

All the individual terms disappear and therefore the rotation is zero and thus the field is solenoidal.

To derive the charge density one has to apply the divergence operator upon the electric field (ξ acts as a local coordinate once again) so that $\rho_i(\xi) = 1/(4\pi)\vec{\nabla} \cdot \vec{E}_i(\xi)$. This yields complicate expressions with elliptic functions; one can assume these as a kind of superposition. One has:

$$\rho_1(\xi) = \frac{1}{4\pi\eta}\left\{ dn^2(\xi,k) - k^2 sn^2(\xi,k) + dn^2(\xi,k)\,tn^2(\xi,k) \right\}, \qquad (14)$$

$$\rho_2(\xi) = \frac{\left\{ 27\,dn(\xi,k)\,sn^2(\xi,k)\left(\sqrt{138}+12\,dn(\xi,k)\right) + cn^2(\xi,k)\times \right.}{\pi\eta\left(\sqrt{138}+12\,dn(\xi,k)\right)}$$

$$\frac{\times dn(\xi,k)\left(\sqrt{138}+12\,dn(\xi,k)\right) + 4\,sn^2(\xi,k)\right\}}{\pi\eta\left(\sqrt{138}+12\,dn(\xi,k)\right)}, \qquad (14a)$$

$$\rho_3(\xi) = \frac{1}{12}\left(\sqrt{3}-1\right)\left(-\frac{1}{\pi\eta}\,sn^2(a\xi,k) + \frac{1}{3\,\pi\eta}\,cd^2(a\xi,k) \right)\times$$

$$\times\left(\frac{1}{12\,\pi\eta} + \frac{1}{8}\,sd^2(a\xi,k) \right),\ a = \sqrt{\frac{1}{2}\left(\sqrt{3}-1\right)}, \qquad (14b)$$

$$\rho_4(\xi) = \frac{1}{4\,\pi\eta\left(3+cn^2(\xi,k)\right)^2}\times\left(- 6\,dn^2(\xi,k)\,sn^2(\xi,k) + cn^4(\xi,k)\times\right.$$

$$\times\left(2\,dn^2(\xi,k) - sn^2(\xi,k)\right) + cn^2(\xi,k)\right)\left(-3\,sn^2(\xi,k) + 2\,dn^2(\xi,k)\left(3+sn^2(\xi,k)\right)\right).$$

$$(14c)$$

Let a be a specific distance e.g. from the electrode surface to the centre of the (hydrated) ion in the OHL. The total charge $q_{i,tot}$ contained in the OHL is obtained by integrating the charge densities $\rho_i(\xi)$ from the electrode surface with the reference point taken at infinity. Therefore one has to integrate once the expressions for the charge densities given in the Equations (14) to (14c). For the first density $\rho_1(\xi)$ one has:

$$q_{1,tot} = \int_a^\infty \rho_1(\xi)d\xi = \frac{1}{4\pi\eta}\left\{\int_a^\infty dn^2(\xi,k)d\xi - k^2\int_a^\infty sn^2(\xi,k)d\xi + \int_a^\infty dn^2(\xi,k)tn^2(\xi,k)d\xi\right\}.$$

(15)

The first and the second integration can be done exactly but the third term causes troubles and can be handled only numerically. This is a standard procedure for any numerical integration processes and will not be performed here. An alternative way is, since all the elliptic functions are continuous functions to consider known series representations by changing integration and sums. Otherwise the Weierstrass expansions [40], [41] of the involved elliptic functions can be made. This reflects, among other things, the immense difficulties in dealing such problems (convergence of the considered integrals is assumed). To reach the goal faster we suggest another possibility: Determining the first and the second integrals exactly and signing the last term by

$$\int_a^\infty dn^2(\xi,k)tn^2(\xi,k)\,d\xi \equiv \int_a^\infty R(\xi,k)d\zeta\;.$$

Then, integrating once, one has, in principle

$$q_{1,tot} = \frac{1}{4\pi\eta}\left\{ ak - \frac{k\,E(am(a,k),k)}{dn(a,k)\sqrt{1-k\,sn^2(a,k)}} - \frac{dn(a,k)E(am(a,k),k)}{\sqrt{1-k\,sn^2(a,k)}} + \right.$$

$$\left. + \frac{k^2 sn^2(a,k)E(am(a,k),k)}{dn(a,k)\sqrt{1-k\,sn^2(a,k)}} + \int_a^\infty R(\xi,k)d\xi + C\right\},$$

(15a)

in which $E(.,.)$ is the elliptic integral of the second kind and $am(.,.)$ is the Jacobian amplitude. Taking the limit of each term, that is $a \rightarrow 0$ the terms approaches to zero except the third. This guarantees charge conservation so that charge cannot disappears anywhere. Here it is amplified how fast mathematical problems can grow up making problems unsolvable (at least analytically). In Equation (15a) the special case $k = 1$ yields:

$$q_{1,tot} = \frac{a + 2\coth(a)\,E(-gd(a),1)}{4\pi\eta} + \int_a^\infty \tanh^2(\xi)\,d\xi\,, \tag{15b}$$

in which the argument of the elliptic integral of the second order the Guderman function (or hyperbolic amplitude) occurs defined by $\frac{\pi}{2} - 2\arctan(e^a) =: -gd(a)$. In principle one also can consider the case $k = 0$ which gives a linear connection explicitly

$$q_{1,tot} = -\frac{a}{4\pi\eta} + \int_a^\infty \tan^2(\xi)\,d\xi\,. \tag{15c}$$

However one should bear in mind that the first, the second and the fourth term vanishes leading to the fact that essential contributions to the charge density could be lost. In fact, the expressions (15b) and (15c) represent the classical result known from electrostatics. For comparative purposes we show a graphical representation of these functions in Figure 6 (remember that $E(\varphi,0) = \varphi$ and $E(\varphi,1) = \sin\varphi$).

> **Note:** It is possible to handle the expression $R(\xi,k)$ such that one assumes also special values for the modulus, e.g. $k = 0,1$. Then the elliptic functions degenerate to the usual circular and hyperbolic functions, resp., leading to integrals of the general form
>
> $$R(u,0) = \int_a^\infty \tan^2(u)\,du \ \text{ and } \ R(u,1) = \int_a^\infty \tanh^2(u)\,du\,.$$
>
> However one has to specify appropriate conditions to handle the divergence of these integrals. Otherwise an anti derivative of $R(\xi,k)$ exists in general and one has the expression
>
> $$\int R(\xi,k)\,d\xi = \int dn^2(\xi,k)\,tn^2(\xi,k)\,d\xi = \xi - 2E(\xi) + dn(\xi,k)\,tn(\xi,k) + C\,.$$
>
> If necessary one can make use of the formula for the double argument, in detail
>
> $$dn^2(\xi,k)\,tn^2(\xi,k) = \big((1 - cn(2\xi)/((1 + cn(2\xi))\big)^2\,.$$
>
> For the Gudermann function one has $gd(x) = 2\arctan(e^x) - \pi/2$. To prove this one has to show that both sides of the last relation vanishes as $x = 0$. Left side: $gd(0) = \arctan(\sinh(0)) = \arctan(0) = 0$, right side: $2\arctan(e^0) - \pi/2 = 1 - \pi/2 = 2\frac{\pi}{4} - \frac{\pi}{2} = 0$.

As a last remark we stress the possibility to express the cosine amplitude by theta- and sigma-functions; to give an example the solution Equation (11) reads, once again with $a_1 = 1$ as

$$f_1(\xi) = \frac{1}{\eta}\ln\left[\frac{1}{cn(\xi,k)}\right] \equiv \frac{1}{\eta}\ln\left[\frac{\sigma_3(\xi,k)}{\sigma_1(\xi,k)}\right] \equiv -\frac{1}{2\eta}\ln\left[\frac{\vartheta_2(v)}{\vartheta_4(v)}\frac{k'}{k}\right]. \tag{16}$$

Note: We want to show up here different ways to express solutions, the user can then apply a preferred representation. It is also possible to express these solutions in terms of the Weierstrassian $\wp$-function. Thus one has, in principle, the relation

$$\wp(u; g_2, g_3) = e_3 + (e_1 - e_3) ns^2(u\sqrt{e_1 - e_3}, k)$$

where u means a general argument of the ns-function, g_2, g_3 are the invariants of the $\wp$-function and e_1 and e_3 are the roots of the equation $4t^3 - g_2 t - g_3 = 0$ which are all different. To complete, the modulus of the ns-function is expressed by $k^2 = (e_2 - e_3)/(e_1 - e_3)$ for known values of the e_i. The involved functions are meromorphic and double-periodic, the σ_i are odd and entire functions; the ϑ_i are even and entire. To clarify the relationship we present the connection between σ_1 and ϑ_1, one has in detail $\sigma_1(u) = C_1 \exp\left[(\gamma u^2)/(2\omega)\right]\vartheta_1\left(\frac{1}{2} - v\right)$, [39], [46]. Also one has to take care the regularity of the arguments of the logarithm.

4. A NUMERICAL STATEMENT – PRACTICAL FUNCTION SERIES REPRESENTATIONS

For fast numerical calculations it is convenient to have series representations, therefore we calculate some ascending power series formulas for the solution functions Equation (11) to Equation (11c). The functions, derived from the transformation of the log-function are valid up to the given order valid at $\xi > 0$:

$$f_1(\xi) = \frac{1}{2\eta}\xi^2 - \frac{(-2+\sqrt{3})}{12\eta}\xi^4 + \frac{(5+2\sqrt{3})}{90\,\eta}\xi^6 + \frac{(23+12\sqrt{3})}{1260\,\eta}\xi^8 + \dots + O[\xi]^{10}, \tag{17}$$

$$f_2(\xi) = \frac{1}{\eta}\ln\left[\frac{12}{12+\sqrt{138}}\right] + \frac{54}{\eta(12+\sqrt{138})}\xi^2 + \frac{81(120+13\sqrt{138})}{2\eta\left(12+\sqrt{138}\right)^2}\xi^4 + \dots + O[\xi]^6, \tag{17a}$$

$$f_3(\xi) = \frac{1}{3\eta\sqrt{2}}\xi^2 - \frac{1}{27\eta}\xi^4 + \frac{7}{1215\sqrt{2}\,\eta}\xi^6 + ... + O[\xi]^8 \tag{17b}$$

$$f_4(\xi) = -\frac{\ln 4}{\eta} + \frac{1}{4\eta}\xi^2 - \frac{3}{32\eta}\xi^4 + \frac{23}{960\eta}\xi^6 - ... + O[\xi]^8. \tag{17c}$$

Note: Consider the first function series $f_1(\xi)$, where the necessary condition $\lim_{\xi\to 0} f_i(\xi) = 0$ holds. The terms thus form a sequence of zeros and also for the function $f_3(\xi)$. Since the function $f_1(\xi)$ is continuous (at least in the considered domain), the sum function is also a continuous function. In principle one has series of the general form $f_i(\xi) = a\xi^2 + b\xi^4 + c\xi^6 + ... = \Sigma d\xi^n$. Although the terms form a null sequence, such series are divergent. For practical calculations, only the first terms (row fractionation after the quadratic term) are important. The series $f_2(\xi)$ and $f_4(\xi)$ are divergent anyway since they do not form a null sequence. If one needs series for great arguments, asymptotic formulas are necessary. But here one has to be careful because the limit $\xi\to\infty$ does not exist. By using asymptotic series the divergence does not play any role.

Similar formulas can also be derived for the electric fields and charge densities (the convergence should be checked by appropriate methods). Another useful series representation in terms of circular functions (in the sense of a Fourier series) is given by the following formula; we only present the first function $f_1(\xi)$, Equation (11), similar expressions could be obtained for the remaining:

$$f_1(\xi) = -\frac{1}{\eta}\left\{ \ln\left[\cos\left(\frac{\pi\xi}{2K}\right)\right] - 4\sum_{n=1}^{\infty}\frac{1}{n}\frac{q^n}{1+(-1)^n q^n}\sin^2\left(\frac{\pi n\xi}{2K}\right)\right\} \tag{18}$$

where $q = \exp[-\pi K'/K]$ and K, K' are the complete elliptic integrals $K = K(k)$. Here the expansion is valid in every strip of the form $\left|\mathrm{Im}\,\pi\xi/(2K)\right| < 1/2\pi\,\ln\tau$ with τ as a parameter with positive imaginary part [39,40].

From the Table 1, it is seen that the limiting values $\lim_{\xi\to 0} f_i(\xi)$ vanish for the functions $f_1(\xi)$ and $f_3(\xi)$, the functions $f_2(\xi)$ and $f_4(\xi)$ remain finite and real. Otherwise taking $\lim_{\xi\to\infty} f_i(\xi)$ it is seen that these limits do not exist. From this standpoint one can say that these functions are not stable in the sense of the stability of solutions which require that the function(s) must vanish as $\xi\to\infty$ (thus the limits must exist). This might cause troubles in quantum-mechanical considerations in which the potential functions must "behave well" but such types of functions are known and can be used by suitable assumptions (no square

integrability). Also for a fast overview one can solve the Equations (7a) and (7b) in terms of a power series representation; here we give formulas valid up to order two with arbitrary coefficients $a_i \neq 0$ and $\lambda = \delta = c_1 = 1$. Due to the similar structure of these nODEs the series hardly differ; and one gets, for the eq.(7a)

$$p_1(\xi) = a_0 + a_1 \xi + \frac{1}{4}\left(a_0^3 \beta^2 - a_0 - 2(\alpha^2 - 1)a_1 + \frac{2a_1^2}{a_0} \right)\xi^2 + O[\xi]^3, \qquad (19)$$

and similar for the Equation (7b)

$$p_2(\xi) = a_0 + a_1 \xi + \frac{1}{2}\left(a_0^2 \beta^2 - a_0 - (\alpha^2 - 1)a_1 + \frac{a_1^2}{a_0} \right)\xi^2 + O[\xi]^3. \qquad (19a)$$

5. SUMMARY – BENEFITS AND DISADVANTAGES – OPEN PROBLEMS

I.   Transient electrodynamical (and electrochemical) problems are notoriously difficult to solve (in the general case one needs Green's tensors and/or vector potentials) and uniqueness is not always given (solutions depending upon roots are involved so that branch cuts must be taken into account).

II.   In this study we showed that a nPDE, the Equation (1) which has the meaning of a modified Poisson-Boltzmann Equation can be solved analytically by application of pure algebraic steps. The highly nonlinear equation was introduced by the author recently [33] to describe time depending electrochemical processes and/or charge transfer upon electrodes.

III. We applied an algebraic approach containing elliptic functions explicitly. It is remarkable that classes of solutions derived by this special method differ completely from solutions of the DHT in their behaviour. It is a special hallmark of algebraic methods that one cannot predict appropriate solutions in the sense of the solubility of the nonlinear algebraic system of polynomial equations. Several other approaches are used but none of them leads to useful results.

IV.   The success and/or failure strongly depends upon the solubility of the nonlinear algebraic system. Due to the experience of the author such systems are often over determined and the number of equations n_e is greater than the number of unknowns n_u. The ideal case is therefore $n_e = n_u$ and by

skillful considerations in combination with the physical reality the outer form of the nonlinear algebraic system can be controlled. Thus we expand the original similarity variable $\xi = x - \lambda t$ to $\xi = \delta x - \lambda t$. The purpose of the similarity variable is twofold: It reduces a given nPDE to a nODE – this always works, and, if one seeks for, due to the physical situation, a traveling wave solution. One cannot, in general predict the solution manifold; that means that by use of the traveling wave reduction one has no guarantee to generate a traveling motion. In each case one has at least to check whether the solution represents a traveling wave motion or not.

V.   A further important fact is given by the integration constant c_1 in the Equations (7a) and (7b), respectively. Only in the context of soliton theory one can set $c_i = 0$ (in view of a localized wave). Generally it is not allowed to set it zero as happen in several papers. Otherwise an interesting feature can be observed here: The constant c_1 relates the parameters δ and λ.

VI.   The difference of the method used here to other algebraic methods is enormous. Most algebraic methods are based upon the fact that the unknown solution function satisfies a nODE of the first order [42], [43], [44], and [45] to mention some examples. Thus the name of the (algebraic) method comes from the used nODE, e.g. the hyperbolic tangent method (including the Riccati Equation as the cornerstone), the exponential transform method, the Weierstrass transform method, the Lambert function transform method and so on. Here, in our analysis the unknown solution function (the cosine amplitude function, Equation (c) and its derivatives can be used independently from any nODEs. Of course, the function and their derivatives have to satisfy general mathematical properties such like continuity, differentiability and existence in a given domain.
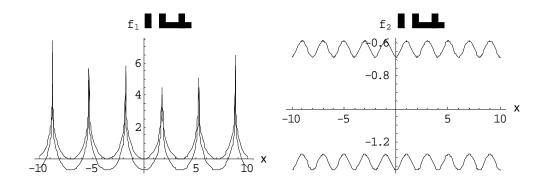
Note: For all scientists and engineers who are dealing with elliptic functions we recommend the excellent formula collection from Byrd and Friedmann, [46]. This attractive and unique treatment as well as the classical Abramowitz/Stegun [39] should be a standard equipment for all mathematical considerations.

VII.   In fact, the algorithm works efficiently and solutions of the highly nPDE, the Equation (1) and the Equation (3) respectively can be derived without
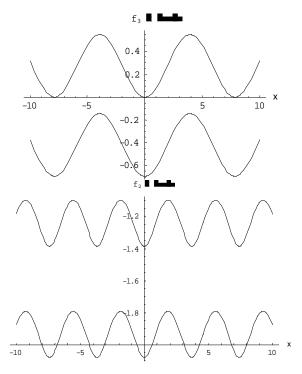
any problems. Problems may appear by further using of the solution functions, e.g. the analytic determination of the total charge, the Equation (15). Here only a numerical procedure is possible. Also the solution procedure of the nonlinear algebraic system, the Equations (9) and (9a), respectively may cause troubles. If one is interested in dealing higher order nPDEs, the degree of the system will increase rapidly and long computing time is expected. Due to the experience of the author many of such systems are satisfied only by the trivial solution and the algebraic solution process will fail.
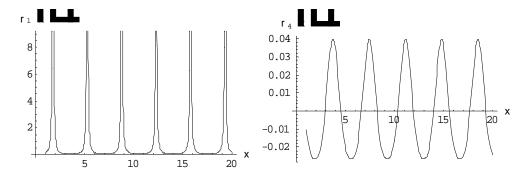
VIII.   In the present analysis the EQS approximation was used and no magnetic effect were considered. To handle this case a further extensions will be done in future. Another aspect is the fact that the particles involved have quantum-like properties and another theory is necessary. Thus a quantum mechanical approach will be considered as a next task.
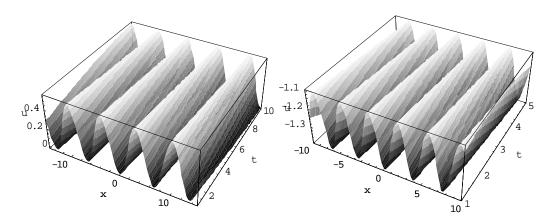

Figure 1. The solution function $f_1(\xi)$, Equation (11), left and the solution function $f_2(\xi)$, Equation (11a), right. Both functions show a travelling character. The graphs are generated by using the constant $a_1 = \pm 1$. The influence of the constant $\eta^{-1} = 0{,}0253$ (numerically) is such that it shifts the graphs upon the vertical axis and this true for all further graphics.
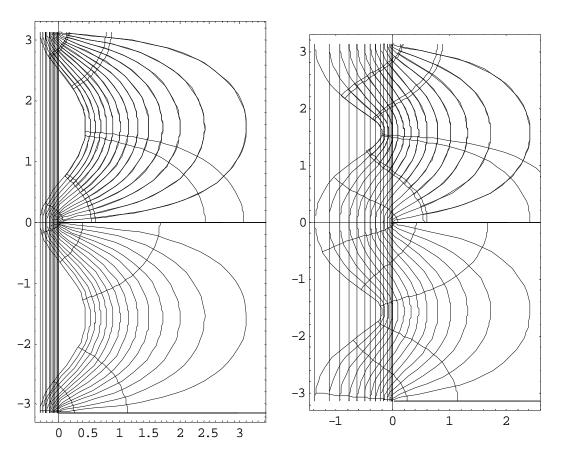
Figure 2. The solution function $f_3(\xi)$, Equation (11b), left and the solution function $f_4(\xi)$, Equation (11c), right. Also both functions show a travelling character. The functions are generated by using the constant $a_1 = \pm 1$ and $a_2 = \pm 1$.
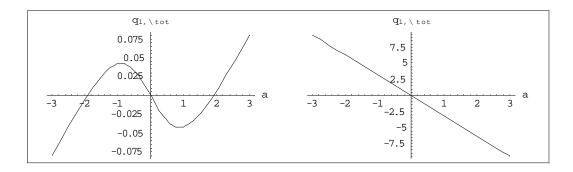
Figure 3. A planar sketch of the charge densities $\rho_1(\xi)$, left and $\rho_4(\xi)$, right. Here, also $a_1 = a_2 = 1$ was used. The functions show periodic behaviour once again. The periodic peaks left may be interpreted as a charge distribution near a charged particle (e.g. analogously in a crystal lattice).

Figure 4. A three-dimensional plot of the functions $u_4(x,t)$, left and $u_3(x,t)$ right. The functions have the modulus $k = \frac{1}{2}$ and $k = \frac{2}{3}$ respectively and the values $\delta = \lambda = 1$ were used.

Figure 5. A graphical representation of the function Equation (11) in the principal form $\approx -\ln\left[cn(\xi,k)\right]$ with the modulus $k = 0,3660$ and for $0 < \xi < \pi/4$ left and $0 < \xi < \pi/2$ right without the influence of the constant η. One can see the poles in the given domain surrounded by symmetrical 'field line distribution'.

Figure 6. A planar sketch of the charge densities, the Equations (15b) left and (15c) right without the integral contributions. If one interprets the distance "a" as the seat of a charge generating size, then, on both sides of a charge accumulation is lockable). In this model the central ion is thought to be located in the centre. The increasing (decreasing) part up to the maximum (minimum) matches domains of higher concentrated charged areas.

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