

# **A New Time Dependent Approach for Solving Electrochemical Interfaces Theoretical Considerations Using Algebraic Approaches**

Alfred Huber

e-mail: dr.alfredhuber@gmx.at

A-8062 Kumberg, Prottesweg 2a

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## **Abstract**

Recently we introduced a nonlinear partial differential equation (nPDE) of the third order for the first time. This new model equation allows the extension of the Debye-Hückel Theory (DHT) considering time dependence explicitly. This also leads to a new formulation in the meaning of the nonlinear Poisson-Boltzmann Equation (nPBE) and therefore we call it the modified Poisson-Boltzmann Equation (mPBE).

The purpose of the present paper is to analyze the new model equation by algebraic methods without using any approximations and numerical methods.

We show how we can integrate a highly nPDE leading to suitable classes of solutions importantly in electrochemical applications.

Generalized relations for the potential, the charge density, and the electric field are given in an analytical way for special classes of solutions involving time dependence explicitly.

Conclusions are supported by studying some test examples such like potassium chloride and other many-valued electrolytes.

## **1. Preliminaries**

To evaluate the potential distribution around a central ion and/or describing the potential of electrodes the classical Debye-Hückel Theory (DHT) is used. Here the electric double layer interaction is the central point or to be more precisely, the electrode-electrolyte interface is assumed as a basis of electrostatics. Under equilibrium conditions the time-average forces are the same in all directions and at all points in the bulk of the electrolyte (assuming to be isotropic perfectly and homogeneous) and there are no net preferentially directed electrical fields.

The fundamental equation describing electrical interfaces and/or the potential distribution around the central ion is a combination of the Poisson-Equation (from electrostatic view) and the Boltzmann law of distribution, [1–3].

However, the theory remains time-independent explicitly. Solutions of the nPBE have thus found applicability in explaining the physics of a wide variety of phenomena, some of which are: **(i)** the estimation of ionic radii in solutions, [3], **(ii)** the theory of the disjoining pressure due to the overlapping of diffuse double layers and its application to instability phenomena in thin liquid films, [4], **(iii)** a wide variety of electrokinetic phenomena that include streaming potentials, electrophoresis, electroviscous effects, e.g. [5] to mention some examples.

Another point is the fact that the PBE, due to the nonlinearity (acting as an exponential function), can only be solved by numerical standard methods, e.g. [6–8]. A practicable approach representing linearization describing chemical quantities (e.g. the activity coefficient) was done in the past, [9, 10].

We stress that the DHT approximation is based upon the assumption that the electric potential is very small (that is in the range of 20 mV). Under this circumstance the nPBE can be linearized and closed-form solutions can be obtained.

**Note:** Several modifications of the Boltzmann distribution function exists. The most favourite is considered by assuming higher terms in the series representation [12] and secondly, analogues to the eigen volume of a real gas the distribution function will be modified by using a suitable ‘number of vacancy’ instead of the ionic atmosphere [13].

It is necessary to mention that the DHT is valid only by considering some further reasonable conditions, e.g. [9, 11].

### 1.1 Some known results

At this stage let us summarize some known results. The purpose of our recent paper [11] was to introduce time-dependence in the DHT explicitly. Therefore we used the electro quasistatic approach (EQS) for the first time [14].

The crucial step is the fact that the time-dependent electric field may derived from a scalar potential which is a solution of a certain nPDE of the third order [11]:

$$\frac{\partial^2 u}{\partial x^2} + \tau \frac{\partial^3 u}{\partial x^2 \partial t} - \mu^2 \frac{\partial u}{\partial t} e^{-\eta u} = 0, \quad u = u(x, t), \quad -\infty < x < \infty. \quad (1)$$

Let us formally impose boundary conditions so that  $\lim_{x \rightarrow -\infty} u_0 = u_L$  and  $\lim_{x \rightarrow \infty} \frac{du}{dx} = 0$  holds; they are necessary conditions later for the function  $u = u(x, t)$ .

**Note:**  $u_L$  is the potential ‘deep in the bulk’ referring to as the (diffusive) Gouy-Chapman layer. We stress that we need not make use of the condition  $z_i e_0 \psi \ll kT$ , where  $\psi$  means any potential.

The potential function  $u = u(x, t)$  plays the same role as in the DHT, therefore one can regard eq.(1) as an extended ‘modified nPBE’ with time dependence involved explicitly.

Further for our purposes we assume much diluted (1,1)-electrolytes in the first instance and conductivities should be in the range of  $0 \leq \sigma \leq 10^{-3} S/m$ . It is convenient to introduce the following abbreviations

$$\frac{\varepsilon_0 \varepsilon}{\sigma} = \tau, \quad \frac{e_0 z_i}{k T} = \eta, \quad \frac{1}{\sigma k T} \sum_{i=1}^N \left( z_i^2 e_0^2 N_i^0 \right) = \mu^2, \quad (2)$$

where  $\tau$  means a characteristic system time in the range of  $\tau \approx 10^{-7} s$ . The quantity  $\mu$  has the dimension  $\dim[\mu] = s \cdot m^{-2}$  referring to a reciprocal diffusion constant if we compare with the expression obtained in the DHT.  $\mu^2$  depends upon the conductivity and temperature reciprocally.

**Note:** There is a deeper connection to eq.(1). To show this let us repeat some basics from the EQS.

Normally, both the laws of Coulomb and Biot-Sarvart [15] are suitable to introduce a static theory of electromagnetism being still time-independent.

The question is: How should these static laws generalized leading to an explicit time-dependence? 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  $\sigma$  is rather small.

For EQS we both assume  $\partial B / \partial t \approx 0$  and the vanishing of the displacement current and the electric field is derived from a scalar potential. Let us now stress the general case known as the Darwin Model [16]: Both the conductivity and a time-dependent external current  $\vec{j}_e$  are prescribed. The total current may be written as  $\vec{j} = \vec{j}_e + \sigma(-\nabla V - \partial A / \partial t)$ .

We further use the Coulomb gauge, that is  $\nabla A = 0$  and the dynamics of the potentials is determined by the continuity equation so that we can write

$$- \varepsilon_0 \frac{\partial}{\partial t} \Delta V - \nabla \left( \sigma \nabla V + \sigma \frac{\partial A}{\partial t} \right) = -\nabla \vec{j}_e. \quad (1^*)$$

This equation represents a kind of ‘Poisson Equation’ for a time-dependent impressed current and/or if we take the r.h.s. by the charge density through  $\partial \rho_e / \partial t$  similar as in the DHL.

This type of continuity equation has some similarity with the diffusion equation and therefore, naturally, diffusion-like quantities should appear.

One can further ask for the applicability of the EQS. Considering the law of Gauß, charges and fields are linked by the relation

$$\frac{\varepsilon_0 E}{L} = \rho, \quad (2^*)$$

where  $L$  means a characteristic system length (here e.g. from the electrode surface towards deep in the bulk).

Both the EQS and MQS are predicated on having sufficiently slow time variations (low frequencies) and sufficiently small dimensions so that

$$\frac{\mu_0 \varepsilon_0 L^2}{\tau^2} \ll 1 \quad \rightarrow \quad \frac{L}{c} \ll \tau, \quad (3^*)$$

where  $c = \sqrt{\mu_0 \varepsilon_0}$ .

The ratio  $L/c$  is the time required for an electromagnetic wave to propagate at the velocity  $c$  over a length  $L$  characterizing the system. Thus the EQS is valid if an electromagnetic wave can propagate a characteristic length of the system in a time that is short compared to times  $\tau$  of interest (corresponding to small frequencies).

Whether we ignore the magnetic induction and use the EQS or neglect the displacement current times of interest  $\tau$  must be long compared to the time  $\tau_{em}$  required for an electromagnetic wave to propagate at the velocity  $c$  over the largest length  $L$  of the system. Hence one can write

$$\tau_{em} = \frac{L}{c} \ll \tau. \tag{4*}$$

We stress the difference that static is just a particular case of Maxwellian Equations (ME) whereas quasistatic keeps an approximation.

In [11] we showed that the eq. (1) admits an infinite three-dimensional point group representing translations as well as dilatation operations.

We derived different similarity solutions for the potential function  $u = u(x, t)$  and in addition we showed that the eq. (1) does not admit any potential symmetry but we found generalized symmetries also closely related to dilatation operations.

Different cases for approximate symmetries could derive for the first time whereas the approximate symmetry behaviour differs completely from the classical case.

In total we showed that it is possible to derive solutions of electrochemical importance by the method of group theory (especially the so-called similarity solutions).

## 2. Algebraic solution procedures

Let us now proceed further in studying the nPDE, eq. (1) seeking for solutions for which we assume  $u = F(x, t)$ ,  $F \in C^3(D)$  and  $D \in R^2$  is an open set.

We exclude values for which  $D := \{u(x, t) \in \tilde{D} : u \neq 0, u_x \neq 0, u_t \neq 0, \dots\}$  and consider a positive time  $t > 0$ . Suitable classes of solutions are  $u \in I$ ,  $I$  an interval so that  $I \subseteq D$  and  $u : I \rightarrow R^2$ .

We state our main intension: We wish to solve the nPDE, eq.(1) analytically by use of algebraic methods. In the following note we summarize the basic facts of the hyperbolic tangent method [17] which is used below to handle the highly nPDE, eq. (1).

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

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

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  $\lambda$  is a constant to be determined. Thus we have

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

The nODE (b) is integrated as long as all terms contain derivatives. Further the associated integration constants can take to zero in view of the localized solutions one is looking for. This is a necessary (but not sufficient) condition that  $f(\xi)$  tends to zero as  $\xi \rightarrow \pm\infty$ .

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

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

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

$$\omega'(\xi) = \frac{d\omega}{d\xi} = k(1 - \omega^2(\xi)) \quad (d)$$

and  $k$  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  $a_0, a_1, \dots, k$  and  $\lambda$ . Solutions of the Riccati Equation can be expressed depending upon the constant  $k$

$$w(\xi) = -\sqrt{-k} \tanh(\sqrt{-k} \xi), \quad w(\xi) = -\sqrt{-k} \coth(\sqrt{-k} \xi), \quad \text{for } k < 0, \quad (e)$$

$$w(\xi) = \sqrt{k} \tan(\sqrt{k} \xi) - \sqrt{k} \cot(\sqrt{k} \xi). \quad \text{for } k > 0. \quad (f)$$

Remark: The case  $k = 0$  will be excluded although a solution exists [17]. It represents an useless solution for our purposes.

## 2.1 The application of special algebraic methods

### a) The hyperbolic tangent method

Firstly we convert the eq.(1) by  $u(x, t) = f(\xi)$ ,  $\xi = x - \lambda t$  to derive the nODE of the third order

$$\lambda \tau \frac{d^3 f}{d\xi^3} - \frac{d^2 f}{d\xi^2} - \lambda \mu^2 \frac{df}{d\xi} \exp[-\eta f] = 0, \quad f = f(\xi), \quad -\infty < \xi < \infty. \quad (3)$$

**Note:** The similarity transformation is called the traveling wave reduction describing any wave propagation and  $\lambda$  means the velocity. However if we assume the EQS model solutions of electromagnetic field problems can not represent traveling waves. Therefore the quantity  $\lambda$  is seen as a pure quantity of calculation. Without any loss of generality we set  $\lambda = 1$  for later considerations.

Then 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  $D := \{(f, \xi) \in \tilde{D} : f(\xi) = 0\}$ . Suitable solutions are  $v \in I$ ,  $I$  an interval so that  $I \subseteq D$  and  $v: I \rightarrow R^2$ . Since the l.h.s of eq.(3) is a continuous functions 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.

We also note that it may necessary to expand the domain so that we admit complex-valued solutions. For the nODE, eq.(3) we therefore require:

Let  $D(C)$  be a complex domain,  $D(C) \subseteq C \times C$  for all holomorphic functions and further let

$$\xi: C^\infty \times C^\infty \rightarrow C^\infty \text{ so that } \{f, f', f'', \dots, f^{(n)}\} \neq 0 \text{ where the prime means } d/d\xi.$$

Simultaneously as in the real-valued case we further require that the nODE, eq.(3) has at least one solution and the solution is unique. The solution develops completely in an interval  $I$  for which  $\{\xi, f(\xi) | \xi \in I\} \subset D(C) \forall \xi \in I$  holds and so we ensure complex-valued solutions of eq.(3).

The question is: Can we integrate the nODE so that we can write the nODE, eq.(3) in a complete differential form? Indeed, we have

$$\frac{\partial}{\partial \xi} \left\{ \tau \eta \frac{d^2 f}{d\xi^2} - \eta \frac{df}{d\xi} \right\} + \frac{\partial}{\partial \xi} \left\{ \mu^2 e^{-\eta f} \right\} = 0. \quad (4)$$

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

$$\tau \eta \frac{d^2 f}{d\xi^2} - \eta \frac{df}{d\xi} - \mu^2 e^{-\eta f} + c_1 = 0. \quad (5)$$

The meaning of the constant  $c_1$  will be clear later. The transformation  $f(\xi) = \frac{1}{\eta} \ln[w(\xi)]$  removes the exponential function yielding a further nODE of the second-order

$$\tau w \frac{d^2 w}{d\xi^2} - \tau \left( \frac{dw}{d\xi} \right)^2 - w \frac{dw}{d\xi} - \mu^2 w = 0, \quad w = w(\xi). \quad (6)$$

This nODE is the starting point to apply algebraic methods.

First of all we need the parameter of the series, eq.(c). Balancing the highest-order nonlinear term and the highest-order linear term results in  $n = -2$ . This is impossible since the number must be  $n \in Z^+$ . We employ the transformation  $w = p(\xi)^{-2}$  to derive a further second-order nODE

$$2\tau p \frac{d^2 p}{d\xi^2} - 2\tau \left( \frac{dp}{d\xi} \right)^2 - 2p \frac{dp}{d\xi} + \mu^2 p^4 = 0, \quad p = p(\xi). \quad (7)$$

Now the balancing procedure results in the suitable form  $n=1$  and the polynomial ansatz of the first order for the function  $p(\xi)$  is appropriate:  $p = a_0 + a_1 \omega$  from the series, eq.(c).

The following result is of interest: If we set  $c_1 = 0$  (meaning as a shift) the corresponding nonlinear algebraic system admits only the trivial solution; therefore a solution of eq.(7) is a pure constant resulting from the eqs.(e) and (f).

However if we admit the constant  $c_1$  acting as an unknown and the quantities  $\mu$  and  $\tau$  being as free parameters the following solutions are obtained

$$\text{Case (i) } k < 0: f_0(\xi) = \frac{1}{\eta} \ln \left[ \frac{4}{a_1^2 \left\{ \sqrt{c_1} \left( \cot \left[ \frac{\sqrt{c_1}}{2} \xi \right] - \tan \left[ \frac{\sqrt{c_1}}{2} \xi \right] \right) - 2 \right\}^2} \right], \quad (7a)$$

where the constants  $a_1$  and  $c_1$  can be chosen arbitrarily.

It is seen that such classes of functions are of singular character and hence a practical use is not of relevance. Otherwise, singular classes of solutions represent a necessary contribution to the solution-manifold of eq.(6). On the contrary, choosing the parameter  $k$  to be positive we obtain

$$\text{Case (ii) } k > 0: f_{1,2}(\xi) = \begin{cases} \frac{1}{\eta} \ln \left[ \frac{4}{a_1^2 \left( 2 + \sqrt{c_1} \tanh \left[ \frac{\sqrt{c_1}}{2} \xi \right] \right)^2} \right], \\ \frac{1}{\eta} \ln \left[ \frac{4}{a_1^2 \left( 2 + \sqrt{c_1} \coth \left[ \frac{\sqrt{c_1}}{2} \xi \right] \right)^2} \right], \end{cases} \quad (7b)$$

where the constants  $a_1$  and  $c_1$  also can be chosen arbitrarily. To prevent complex-valued solutions, however,  $c_1$  should be  $c_1 \in R^+$ . Surprisingly the first solution represents a continuously non-singular solution where we have to exclude such values from the set of definition where the argument of the logarithm takes the identity. Therefore the solution is valid for all values for which  $\xi \in R \setminus \{0, -2 \tanh^{-1}(4)\}$  and the second solution is of singular character once again.

**b) The hyperbolic sine method**

Alternatively to generate classes of solutions we apply the sinh-method [18]. This method is also a practical useful approach. In the following note a short overview is given.

**Note:** Instead of the series eq.(c) a suitable combination of hyperbolic sine- and cosine functions is introduced so that

$$f(\xi) = a_0 + \sum_{i=0}^n (a_i \cosh w + b_i \sinh w) \sinh^{i-1} w, \quad (8)$$

using an auxiliary function  $w = w(\xi)$  which is also a solution of the first-order equation

$$\frac{dw}{d\xi} = \sinh w, \quad w = w(\xi), \quad (9)$$

where solutions of eq.(9) are expressed in the following form (equally thought as a transformation):

$$\sinh w = -\operatorname{cosech} \xi \quad \text{and} \quad \cosh w = -\operatorname{coth} \xi. \quad (10)$$

From balancing we know that  $n = 1$  holds, therefore the linear ansatz  $p = a_0 + a_1 \sinh \omega + b_1 \cosh \omega$  is appropriate. Introducing into eq.(7) we derive the nonlinear algebraic system of polynomial equations consisting of nine equations for three unknowns. Surprisingly, the solution is also of trivial form by assuming  $c_1 = 0$  and therefore useless for our purposes.

**c) The application of an exponential transform method – regular analytical solutions**

This method developed by the author [19] has been applied successfully to solve the nODE, eq.(7) in a closed-form. From the knowledge below we conclude that it is necessary to require  $c_1 \neq 0$ .

**Note:** We find it useful to state out the basic steps of this method. We do not change the series eq.(c) but solutions we are looking for are solutions of the following first-order differential equation (a generalized Riccati Equation)

$$\frac{dw}{d\xi} = (Aw(\xi) - a)(Bw(\xi) - b), \quad (11)$$

whereby solutions of eq.(11) are represented in terms of exponential functions so that the constants A, B, a and b may not vanish commonly

$$w(\xi) = \frac{b \exp[Ab\xi + aB\xi] - a \exp(C_1)}{B \exp[Ab\xi + aB\xi] + A \exp(C_1)}, \quad \xi \neq \frac{1}{Ab - aB} \ln[-Ae^{C_1}/B]. \quad (12)$$

Here  $C_1$  is a further constant of integration and A, B, a and b are arbitrary constants ( $\omega(\xi)$  acts as the auxiliary function).

The benefit of this new approach is given by the fact that we have introduced several constants which can be chosen arbitrarily. This constants influence the nonalgebraic system of polynomial equations positively (it is known that most of the polynomial systems are over-determined; by increasing the number of unknowns however, the number of equations can be reduced so that the 'degree of over-determination' is also reduced).

We finally derive the nonlinear algebraic system of polynomial equations consisting of five equations for seven unknowns.

In total we get seven solutions (two of them are of trivial form) and from the remaining five solution we decided to choose the cases

$$\text{Case (i)} \quad a = 0, \quad b = -a_0B/a_1, \quad c_1 = 2aB, \quad B \neq 0. \quad (13)$$

$$\text{Case (ii)} \quad a = -a_0A/a_1, \quad c_1 = \frac{2(a_1bA + a_0AB)}{a_1}, \quad A \neq 0, \quad B \neq 0, \quad a_1b + a_0B \neq 0. \quad (13a)$$

If we use the linear ansatz  $p = a_0 + a_1\omega$  and inserting the above given parameter values we derive the following expressions for the function  $f_i(\xi)$ ,  $i = 1, 2$  in a most general form:

$$\text{Case (i)} \quad f_1(\xi) = \frac{1}{\eta} \ln \left[ 2a_0 + \frac{(a_1b - a_0B) \exp[Ab\xi]}{B \exp[Ab\xi] + A \exp \left[ -\frac{2a_0AB}{a_1} + \frac{a_0AB\xi}{a_1} \right]} \right], \quad (13b)$$

$$\text{Case (ii)} \quad f_2(\xi) = \frac{1}{\eta} \ln \left[ 2a_0 + \frac{(a_1b - a_0b) \exp[Ab\xi]}{B \exp[Ab\xi] + A \exp \left[ \frac{2(a_1bA + a_0AB)}{a_1} + \frac{a_0AB\xi}{a_1} \right]} \right], \quad (13c)$$

where the constants  $a_0, a_1, b, A$  and  $B$  can be chosen arbitrarily restricted by  $a_1 \neq 0$ .

Furthermore, two sub-cases by using different values of the parameters can be considered:

Let  $a_0 = a_1 = b = A = B = 1$ , then both of the cases (i) and (ii) reduces to a constant expression

$$f_{2,1}(\xi) = f_2(\xi) = -\frac{\ln 4}{\eta}, \quad (14)$$



where  $\eta$  follows from eq.(2). Otherwise, let  $a_0 = a_1 = A = B = 1$  and  $b = -1$ . Then we have

$$f_{2,2}(\xi) = \frac{1}{\eta} \ln \left[ \frac{1}{4} e^{-4\xi} (e^2 + e^{2\xi})^2 \right], \quad (14a)$$

$$f_{2,3}(\xi) = \frac{1}{\eta} \ln \left[ e^{-2\xi} \cosh^2 \xi \right]. \quad (14b)$$

To be a regular function we have to exclude some values where the argument may not assume the identity. We require that we exclude those values of the domain of definition for which

$\forall \xi \setminus \{1, -i(i + \pi), 1 - \ln(\pm i\sqrt{3})\}$  for the function  $f_1$  and  $\forall \xi \setminus \{0, \pm i\pi, -\cosh^{-1}(\pm i/\sqrt{3})\}$  for the function  $f_2$ , here  $i$  means  $i^2 = -1$ .

**Note:** If we admit complex-valued solutions the above given complex-valued conditions have to be considered.

We assumed that for the constant  $c_1$  the requirement  $c_1 \neq 0$  holds. By considering this fact it is possible to calculate classes of solutions both by the tanh- and sinh-method.

However, these functions are of singular character and therefore useless in practise. Otherwise the importance of such functions is found in the fact that they are included in the solution-manifold as mentioned earlier.

The application of the tanh-method results in classes of functions depending upon the parameter  $k$  :

$$\text{Case (a) } k < 0: f_{1,2}(\xi) = \begin{cases} \frac{1}{\eta} \ln \left[ \frac{\tanh^2[\mu a_0 \xi]}{a_0^2 \mu^2} \right] \\ \frac{1}{\eta} \ln \left[ \frac{\coth^2[\mu a_0 \xi]}{a_0^2 \mu^2} \right] \end{cases}, \quad a_0 \neq 0, \quad (15)$$

$$\text{Case (b) } k > 0: f_3(\xi) = \frac{1}{\eta} \ln \left[ \frac{1}{a_0^2 (1 + \mu a_0 (\tan[\mu a_0 \xi] - \cot[\mu a_0 \xi]))^2} \right], \quad (15a)$$

where  $a_0$  means an arbitrary constant.

In addition, by using the sinh-method the following function exemplifies the singular character

$$f(\xi) = \frac{1}{\eta} \ln \left[ \frac{1}{b_1^2 (1 - \coth \xi - \operatorname{cosech} \xi)^2} \right], \quad b_1 \neq 0, \quad (16)$$

where  $b_1$  also means an arbitrary constant.

**Note:** Several other algebraic approaches for solving the highly nonlinear nPDE, eq.(1) exist, especially those developed by the author, e.g. [20] and [21] but we believe it is sufficient to apply the given standard procedures. The most important fact however is the possibility to solve the eq.(1) without any numerical methods. From this standpoint one can say that the derived solutions are all of analytical character representing exact classes of solutions.

## 2.2 Analysis

Let us summarize in short: Our main task is to solve the nPDE, eq.(1) in an analytical way dispensing numerical approaches. This can be done by keeping in mind the special function methods. Although the eq.(1) is highly nonlinear, algebraic methods can therefore be applied successfully. By using several methods different solutions could be obtained and in addition it is of interest to compare these solutions.

**Note:** The crucial step is the assumption that the unknown solution function of any nPDE under consideration is also a solution of some ordinary differential equations which can be solved explicitly. However there is no guarantee that the algorithm works successfully. It might happen that solutions of the nonlinear polynomial system of equations admit only trivial solutions (some nPDE, e.g. the Sine Gordon Equation admits only  $n = 0$ ). Further general remarks to algebraic methods can be found in [21] and [22].

Let us start with the most important regular potential function from Case (ii),  $f_1(\xi)$ , eq.(7b). It is seen that the second solution  $f_2(\xi)$  of eq.(7b) represents singular character as well as the function  $f_0(\xi)$ . Firstly the function  $f_1(\xi)$  satisfies the above given boundary conditions. Surprisingly, the potential does not depend upon the parameter  $\mu$ . It is proven that  $\lim_{\xi \rightarrow 0} f_1(\xi) \approx -\frac{1}{21} \log[3/2]$  and  $\lim_{\xi \rightarrow \infty} (df_1/d\xi) = 0$ . The first expression means that the derived potential takes any value that the potential in the bulk can have. The negative sign can be directly connected with a negative charge environment. Further we detect that the potential depends upon the temperature. In Tab.1 values for a specific temperature domain are given and Fig.1 shows graphically the linear dependence where we assume the absolute value for the potential function.

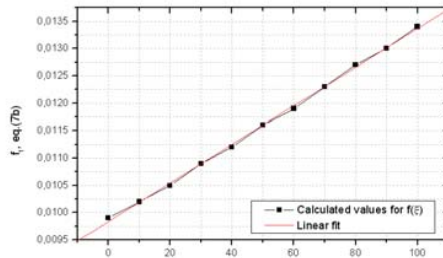


Fig.1 The temperature dependence of the potential function  $f_1(\xi)$ , eq.(7b). The potential depends linearly upon the temperature and can be described by a relation like  $f = a + b\xi$  with  $a = 0,00984$  and  $b = 3,5 \times 10^{-5}$ . The relative error is approximately  $R \approx 0,99948$  and the standard deviation is calculated to be  $\approx 4 \times 10^{-5}$ . Note that the absolute value of the potential function is assumed. Without loss of generality we chose the arbitrary constants  $a_1 = c_1 = 1$  and a single-valued electrolyte  $z_i = 1$  is assumed.

That means that by increasing the temperature the diffusive layer expands more and more into the inner part of the electrolyte.

We remark that no adsorption effects occur so that we have the OHL (**O**uter **H**elmholtz **L**ayer; referred as the Stern layer having an assumed thickness approximately equal to the radius of one hydrated ion) as a maximal distance thinkable from the electrode surface.

**Note:** It is reasonable to assume that the whole excess charge is located in the OHL because due to the finite electrical conductivity and perturbations of the electrical forces due to the Brownian movements the space charge has a maximum in the OHL. The adjacent domain is known as the diffusive layer which tends as deep in the solution as the electrical conductivity decreases.

$T / ^\circ C$	$f_1(\xi) \times (-1)$	$e_0 / kT$
0	0,0099	42,45
10	0,0102	40,94
20	0,0105	39,55
30	0,0109	38,25
40	0,0112	37,02
50	0,0116	35,88
60	0,0119	34,8
70	0,0123	33,79
80	0,0127	32,83
90	0,0130	31,93
100	0,0134	31,07

Tab.1 Calculated values for the temperature dependence of the potential function  $f_1(\xi)$ , eq.(7b). T means the temperature in  $^\circ C$ ,  $e_0$  is the elementary charge and  $k$  means the Boltzmann constant. Note that the absolute value of the potential function is assumed.

The electric field can derived from the potential by application of the gradient operator to give

$$\vec{E}(\xi) = \frac{1}{22(2 + \sinh[\xi] + 2 \cosh[\xi])} = \frac{1}{22 \left( 2 + \exp[\xi] + \exp[-\xi] + \frac{1}{2}(\exp[\xi] - \exp[-\xi]) \right)}, \quad (17)$$

where we converted the hyperbolic functions into pure exponentials.

If we assume complex-valued arguments the denominator may not assume values for which the denominator vanishes, that is  $\xi \setminus \{i\pi, -\cosh^{-1}[-5/3]\}$ .

**Note:** The electric field can be represented in form of a convergent analytical power series since all contributions in the second part of eq.(17) are convergent functions with a convergence radius of  $R = \infty$ . We explicitly have the representation

$$\vec{E}(\xi) = \left\{ 22 \left( 2 + \sum_{k=0}^{\infty} \frac{\xi^k}{k!} + \sum_{k=0}^{\infty} \frac{(-1)^k \xi^k}{k!} + \sum_{k=0}^{\infty} \frac{\xi^{2k+1}}{\Gamma[2(1+k)]} \right) \right\}^{-1}, \quad (17a)$$

where  $\Gamma(\cdot)$  means the Gamma function. It is seen that the electric field can be approached in first order by an exponential function.

Introducing the similarity variable  $\xi = x - \lambda t$ ,  $\lambda = 1$ , we compute the time-dependent electric field

$$\vec{E}(x, t) = \frac{1}{22 \{ \sinh[x-t] - 22(1 + \cosh[x-t]) \}}, \quad (17b)$$

where we resigned to write out the exponential representation.

In Fig.2 we both show the potential function  $f_1(\xi)$  representing a typical kink-like behaviour as well as the solution surface for the time-dependent electrical field. This bell-shaped continuous electric field takes a finite value as  $\xi \rightarrow 0$ , vanishes as  $\xi \rightarrow \infty$  and this is in agreement with the potential's property.

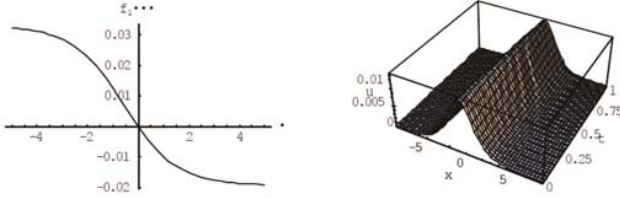


Fig.2 Left: The stable kink-solution for the potential function  $f_1(\xi)$ , eq.(7) satisfying the boundary conditions.

Right: The solution surface for the time-depended electric field, eq.(7b). This continuous function shows a marked peak representing a maximum of charge.

By applying the divergence operator upon the electric field ( $\xi$  acting as the local coordinate) we get the charge density by

$$\rho(\xi) = -\frac{\epsilon_0}{4\pi} \frac{(\cosh[\xi] + 2 \sinh[\xi])}{22(2 + 2 \cosh[\xi] + \sinh[\xi])^2} = -\frac{\epsilon_0}{4\pi} \frac{(3 \exp[2\xi] - 1) \exp[\xi]}{11(1 + 4 \exp[\xi] + 3 \exp[2\xi])^2} = -\frac{\epsilon_0}{4\pi} W(\xi), \quad (17c)$$

where  $W(\xi)$  is used instead of the hyperbolic and exponential term, respectively. Fig.3 shows the

run of the function eq.(17c). Introducing the relaxation time by  $\tau = \frac{\epsilon_0 \epsilon}{\sigma}$  one can express the charge

density time-dependent so that we have the connection

$$\rho(x-t) = -\frac{\tau \sigma}{4\pi \epsilon} W(x-t) \rightarrow \tau = \frac{\epsilon}{\sigma} \operatorname{div} \vec{E}. \quad (17d)$$

Here the charge density is directly proportional to the conductivity and the relaxation time and inversely proportional to the relative dielectric constant of the electrolyte.

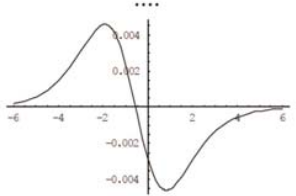


Fig.3 The behaviour of the charge density, eq.(17c) at  $t = 0$ . To specific humps on both sides of the domains could be observed (the function changes the sign). In this model the central ion is thought to be located in the centre. The increasing (decreasing) part up to the maximum (minimum) matches domains of higher concentrated charged areas. It is shown that  $\rho(\xi) \rightarrow 0$  as  $\xi \rightarrow \pm\infty$  holds. Beyond the OHL the space charge is a decreasing function.

Theoretical calculated values can be seen in the Tab.2 and Tab.2a, respectively and Fig.4 shows the behaviour of the function for some different many-valued electrolytes.

$\xi$	$C \times W(\xi)$	$C \times W(\xi)$	$C \times W(\xi)$
0	$1,14 \cdot 10^{-15}$	$7,1 \cdot 10^{-14}$	$9,1 \cdot 10^{-14}$
1	$1,81 \cdot 10^{-15}$	$1,13 \cdot 10^{-13}$	$1,14 \cdot 10^{-13}$
2	$1,16 \cdot 10^{-15}$	$7,24 \cdot 10^{-14}$	$9,25 \cdot 10^{-14}$
3	$5,29 \cdot 10^{-16}$	$3,31 \cdot 10^{-14}$	$4,24 \cdot 10^{-14}$
4	$2,11 \cdot 10^{-16}$	$1,32 \cdot 10^{-14}$	$1,69 \cdot 10^{-14}$
5	$8,02 \cdot 10^{-17}$	$5,01 \cdot 10^{-15}$	$6,42 \cdot 10^{-15}$
6	$2,89 \cdot 10^{-17}$	$1,87 \cdot 10^{-15}$	$2,39 \cdot 10^{-15}$
7	$1,10 \cdot 10^{-17}$	$6,89 \cdot 10^{-16}$	$8,82 \cdot 10^{-16}$
8	$4,01 \cdot 10^{-18}$	$2,54 \cdot 10^{-16}$	$3,25 \cdot 10^{-16}$
9	$1,5 \cdot 10^{-18}$	$9,35 \cdot 10^{-17}$	$1,2 \cdot 10^{-16}$
10	$5,5 \cdot 10^{-19}$	$3,44 \cdot 10^{-17}$	$4,4 \cdot 10^{-17}$

$\xi$	$C \times W(\xi)$	$C \times W(\xi)$	$C \times W(\xi)$
0	$-1,14 \cdot 10^{-15}$	$-7,1 \cdot 10^{-14}$	$-9,1 \cdot 10^{-14}$
-1	$9,57 \cdot 10^{-16}$	$6 \cdot 10^{-14}$	$7,68 \cdot 10^{-14}$
-2	$1,83 \cdot 10^{-15}$	$1,14 \cdot 10^{-13}$	$1,46 \cdot 10^{-13}$
-3	$1,23 \cdot 10^{-15}$	$7,71 \cdot 10^{-14}$	$9,87 \cdot 10^{-14}$
-4	$5,77 \cdot 10^{-16}$	$3,6 \cdot 10^{-14}$	$4,61 \cdot 10^{-14}$
-5	$2,32 \cdot 10^{-16}$	$1,45 \cdot 10^{-14}$	$1,88 \cdot 10^{-14}$
-6	$8,38 \cdot 10^{-17}$	$5,52 \cdot 10^{-15}$	$7,1 \cdot 10^{-15}$
-7	$3,23 \cdot 10^{-17}$	$2,06 \cdot 10^{-15}$	$2,63 \cdot 10^{-15}$
-8	$1,22 \cdot 10^{-17}$	$7,6 \cdot 10^{-16}$	$9,73 \cdot 10^{-16}$
-9	$4,48 \cdot 10^{-18}$	$2,8 \cdot 10^{-16}$	$3,59 \cdot 10^{-16}$
-10	$1,65 \cdot 10^{-18}$	$1,03 \cdot 10^{-16}$	$1,32 \cdot 10^{-16}$

Tab.2/2a Theoretical values of the function  $W(\xi)$  for different many-valued electrolytes. The first column of the right table represents potassium chloride, the second and the third column represents calcium sulphate and sodium sulphate, respectively. The constant  $C$  is assumed to be  $C_{KCl} = 4 \times 10^{-13}$ ,  $C_{CaSO_4} = 2,5 \times 10^{-11}$  and  $C_{Na_2SO_4} = 3,2 \times 10^{-11}$ .

Note that a standard concentration of  $c = 0,01 \text{ mol/l}$  at a standard temperature of  $T = 273,15 \text{ K}$  is assumed.

**Note:** Otherwise it follows from eq.(17d) that the relaxation time is directly proportional to the relative dielectric constant of the medium and inversely proportional to the conductivity and the function  $W(\xi)$ . In addition, a direct connection of the divergence of the electric field in the OHL is seen. This relation is therefore suitable for proofing in experiments later.

Let  $a$  be a specific distance (from the electrode surface to the centre of the hydrated ions in the OHL). 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.(17c)

$$q_{tot} = -\frac{\epsilon_0}{4\pi} \int_a^{\infty} \rho(\xi) d\xi = -\frac{\epsilon_0}{88\pi} \frac{1}{(2 + 2 \cosh[a] + \sinh[a])} \quad (17e)$$

and  $q_{tot}$  takes a function of the distance. The situation is analogous to that from the DHT where a central ion of charge  $+z_i e_0$  is enveloped by a cloud containing the total charge  $-z_i e_0$ .

**Note:** The total charge in eq.(17e) is considered at the time  $t=0$ , so it follows from the similarity variable  $\xi = x-t \rightarrow x = \xi$  as a local coordinate. In the DHT it was found that the electrical effect of the cloud on the central ion could be simulated by placing the entire charge of the cloud,  $-z_i e_0$  at the distance  $\kappa^{-1}$  from the central ion.

Let us study two limit cases: **(i)** for small distances, say,  $a \rightarrow 0$ , the total charge tends to a constant factor:  $q_{tot} = -\epsilon_0 / 352\pi$ ; **(ii)** for large distances it is shown that  $q_{tot} \rightarrow 0$  as  $a \rightarrow \infty$ . This is also in agreement with the boundary conditions assumed earlier and matches our expectation exactly.

Further potential solutions are given by the relations eqs.(14a) and (14b), respectively.

Due to the similarity we decided to discuss the solution eq.(14a). It is of interest to stress that the solution is a continuous function but does not satisfy the boundary conditions. Moreover, it is shown that either for the cases  $\xi \rightarrow 0$  and  $\xi \rightarrow \infty$  the function takes a real valued number and does not vanish, as it must.

Let us now discuss the solution for Case (a),  $k < 0$ , eq.(15) of the form

$$f_{p,1}(\xi) = \frac{kT}{e_0 z_i} \ln \left[ \frac{\tanh^2[\mu a_0 \xi]}{a_0^2 \mu^2} \right], \quad a_0 \neq 0, \quad (18)$$

with arbitrary chosen  $a_0$ . The limiting analysis shows that the function takes  $-\infty$  as  $\xi \rightarrow 0$  and vanishes as  $\xi \rightarrow \infty$ . Such classes of solutions are called peakon-solution representing a singular

behaviour at  $\xi = 0$ . It is further shown that  $\left. \frac{\partial}{\partial \xi} f_{p,1} \right|_{\xi=0}$  takes complex infinity.

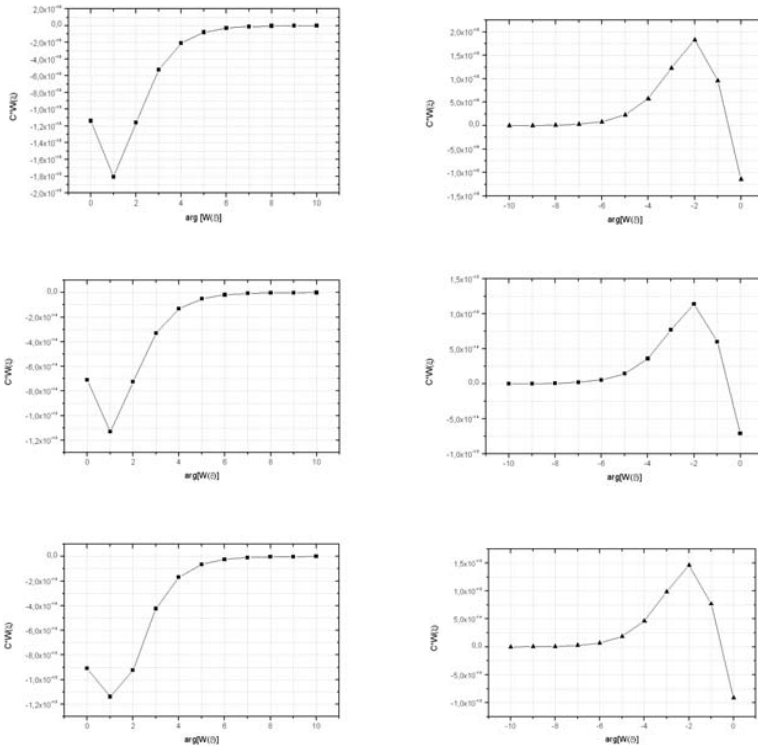


Fig.4 The behaviour of the function  $W(\xi)$ , eq.(17d) for different electrolytes. Left from top to bottom: A positive argument of  $W(\xi)$  is used and the curves show potassium chloride, calcium sulphate and sodium sulphate. Right from top to bottom: Special values for a negative argument; the electrolytes are the same. The valence might not influence the function  $W(\xi)$ . No significant differences between (1,1)-, (2,1)- and (1,2)-electrolytes could be observed. In all cases the function  $W(\xi)$  tends to a domain of saturation.

That means that both the function and the first derivative are discontinuous at the point  $\xi = 0$ .

In Fig.5 we show a planar plot where a similarity to the unit potential (and/or charge) is remarkable. The second solution  $f_{p,2}(\xi)$  containing the hyperbolic cotangent remains also singular and does not match a situation usefully for our purposes.

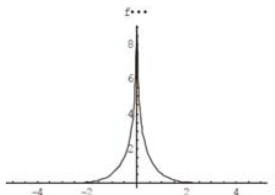


Fig.5 The peakon-solution for the potential function, eq.(18). A similarity to a unit potential is seen.

### 3. Conclusion and outlook

In this second part we showed that the nPDE, Eq. (1) in the meaning of a modified Poisson-Boltzmann Equation can be solved analytically by algebraic methods.

Such solutions also represent the unknown potential and can be seen as exact closed-form solutions since we need not any numerical methods although the nPDE, Eq. (1) under consideration is highly nonlinear in the potential.

We applied three different algebraic approaches recognizing the fact that classes of solutions differ completely in their behaviour. It is a special hallmark of algebraic methods that one can not predict appropriate solutions. From the mathematical point of view it is necessary to analyze this unusual behaviour in future papers. We further detected that solutions depend critically upon some parameters (in the case of the hyperbolic tangent method the parameter  $c_1$ ).

Moreover, regular as well as singular solutions occur and also the hyperbolic sine method generates different results. Further solutions obtained by application of a method derived by the author are given. For a specific case the potential function can be calculated as a continuous function satisfying the boundary conditions. From the potential, the electric field, the charge density and the total charge in the OHL could derive whereby the results correlate the real physical situation.

For different many-valued electrolytes the new generalized potential function  $W(\xi)$  is calculated and graphical representations are suitable to clarify the dependence.

However, similar to other models, suitable assumptions have been made e.g. the ions are spheres, we have no dispersion forces and we also neglect effects of adsorption. Further, from the EQS, additional restrictions are necessary.

In spite of these assumptions it is possible to formulate time-dependence in the present model.

In the third paper following soon we will study new results by applying the capacitor model including diffusion-like processes and effects of adsorption.

In one of our next papers we will show the structure of an electrolyte near a special central ion (praseodymium was used) by experiments and we will show the difference to (1,1)-electrolytes explicitly. We shall study the behaviour of special mixtures with organic solvents to analyze deviations from the simple case.



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