ALGEBRAIC APPROACHES FOR SOLVING TIME-DEPENDENT ELECTROCHEMICAL INTERFACES

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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 an alternative algebraic method without using any approximations and numerical methods. It is shown that the equation is not integrable completely in the sense of the Painlevé-property.
Thus we show how we can integrate this highly nPDE by algebraic procedures leading to new classes of solutions importantly in electrochemical and related applications.

Key words: *Debye-Hückel Theory, Electroquasistatic, Nonlinear partial differential equation, Modified Poisson-Boltzmann Equation, Special function method, Algebraic solution techniques.*
PACS-Code: 02.30Jr; 82.45.-h; 03.50De;
AMS-Code: 35L05; 35Q53; 14H05;

1. INTRODUCTION – GENERAL REMARKS

Many problems of physical interest are described by PDEs with appropriate side conditions. These can be suitable chosen initial and/or boundary conditions.
If the equation is linear, a widely used method for solving nPDEs is known as the superposition principle if certain convergence requirements are satisfied. For nonlinear PDEs, however, the linear superposition principle cannot be applied to generate new classes of solutions.
Note: We stress the existence of a nonlinear superposition principle. This is sometimes known as the Bäcklund Transformation which means a special kind of contact transformation [1].
Later we show that the nPDE under consideration is not of Painlevé type and therefore a suitable Bäcklund system cannot be associated. Thus this fact justifies the usage of algebraic methods deriving analytical solutions if one is not interested in numerical approaches.
So, because most of the of solution methods for linear equations cannot be applied to nonlinear equations, there is no general method of finding analytical classes of solutions of nPDEs and numerical techniques are usually required for their solution.
Sometimes a transformation of variables can be found that transforms nPDEs into linear PDEs, or some other ad hoc methods (and/or assumptions) can be used to find 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. Since the time occurs in the third-order derivation explicitly we will call such types of nPDEs evolution equations (EVE) since they allow the study of time-dependent procedures in a closed form.
Any nPDE may not have the outer form $u_t = K\left[u, u_x, u_{xx}, ...\right]$ necessarily being an EV where $K\left[u, u_x, u_{xx}, ...\right]$ is a nonlinear operator in general. Equations containing e.g. $u_{xt} = K[u]$ and/or $u_{xxt} = K[u]$ are sometimes also called EVEs.
Methods of solution for nonlinear equations represent only one aspect of the theory of nPDEs. Like linear equations, questions of existence, uniqueness, and stability of solutions are of fundamental importance.

2. THE PROCEDURE UNDER CONSIDERATION

In the following note we stress the basic steps of the algorithm. Like many other 'special function' methods the benefit of the present computational algorithm, however, is the simplicity to handle difficulties appearing in dealing with nonlinear EVEs.

The crucial step is the assumption that the unknown solution functions of any nPDE under consideration are also solutions of some ordinary differential equations (ODE) which can be solved explicitly. Here in our approach we use a new formulated nODE of the first order which allows the determination of the solution manifold explicitly [2]. It is known that solutions of nonlinear EVEs can be expressed as finite series in terms of special functions, e.g. hyperbolic functions, Weierstrass and Jacobian functions [3] to [13]. Attention is given to new algebraic approaches derived by the author, e.g. [14], [15] and [16] in which the reader is shown the use and introduction of a special classes of functions, the so-called Lambert Functions.

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

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

Firstly the nPDE is converted 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 (the transformation is closely related to group theory).
Thus we have

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

The nODE (b) is integrated as long as all terms contain derivatives. Further the associated integration constants can take to be 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 $\xi \to \pm\infty$. This covers an important fact in the study of solitons.
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

$$f(\xi) = f(\omega(\xi)) = a_0 + \sum_{i=1}^{n} \cosh^{i-1}\{\omega(\xi)\}\left[a_i \sinh(\omega(\xi)) + b_i \cosh(\omega(\xi))\right] . \qquad \text{(c)}$$

Next one assumes that the function $\omega(\xi)$ satisfies a nonlinear ODE of the form

$$\frac{d\omega}{d\xi} = \omega' = 1 \pm \sinh\omega , \quad \omega : R \times R \to R \ , \ \omega \neq 0 , \ \omega' \neq 0 , \ \xi \in R , \ \omega \in R . \qquad \text{(d)}$$

The parameter n in eq.(c) is found by balancing the highest derivative with the nonlinear terms in the reduced nODE, eq.(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 some suitable transformations as shown below. Substituting (c) and (d) into the relevant nODE yields a system of nonlinear algebraic polynomial equations with respect to $a_0, a_1, \ldots., a$ and λ.
Solutions of the nODEs can be expressed explicitly by separation of variables (or direct integration) to give (an appearing integration constant is assumed to be vanish, it acts only as a shift)

$$\omega_{1,2}(\xi) = \pm 2 \arctan\left[1 \pm \sqrt{2}\tanh\left[\frac{\xi}{\sqrt{2}}\right]\right] , \quad -1 < \xi < 1 . \qquad \text{(e)}$$

The success of all algebraic methods strongly depend upon the solubility of the nonlinear polynomial system and this fact cannot be predicted in general (trivial solutions have to be rejected).
The experience shows that most of these systems are over-determined and ways to influence the solutions are restricted. However increasing the number of unknowns as shown in [17] is a suitable starting point in handling such problems.
Introducing eq.(e) into the polynomial ansatz eq.(c), solutions of the nPDE are readily obtained.
We assume some basic notes: In the first instance we look for real-valued solutions assuming that solutions exist and are unique in some domain D so that $D \subseteq R^{n+1}$ open, $D \neq 0$ and $\omega : D \to R$ continuous. Then we seek for solutions for which $\omega = F(\xi)$, where $F \in R^3$ and $D \subset R^2$ is an open set and further we exclude $D := \left\{(\omega, \xi) \in \widetilde{D} : \omega(\xi) = 0, \omega'(\xi) = 0\right\}$. Suitable solutions are $\omega \in I$, I an interval, so that $I \subseteq D$ and $\omega : I \to R^2$.
Since the r.h.s of the nODEs, eq.(d) are continuous functions we ensure at least the existence locally and due to the lemmas both from Peano and Picard-Lindelöf we assume uniqueness (also at least locally) in a considered domain.
We also note that it may necessary to expand the domain so that we admit complex-valued solutions. For the nODE, eq.(d) we require therefore:
Let $D(C)$ be a complex domain and $D(C) \subseteq$ for all holomorphic functions and further let

$\xi : C^{\infty} \times C^{\infty} \to C^{\infty}$, such that $\left\{\omega, \omega', \omega'', ..., \omega^{(n)}\right\} \neq 0$ where the prime means $d / d\xi$.

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

Note: In case of complex solutions we realize that both the real and the imaginary part assumes their usual meaning, e.g. in some complex domain the function is analytical, bounded and differentiable. To be analytical, both the real and the complex part have to satisfy the Cauchy-Riemann Equations (sometimes such functions are also called harmonic).

3. THE MODEL EQUATION

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, [18], [19] and [20].

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, [18], **(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, [19], **(iii)** a wide variety of electrokinetic phenomena that include streaming potentials, electrophoresis, electroviscous effects, e.g. [20] 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. [21], [22] and [23]. A practicable approach representing linearization describing successfully chemical quantities (e.g. the activity coefficient) was done in the past [24], [25], [26], [27].

The purpose of our recent paper [28] was to introduce time-dependence in the DHT explicitly. Therefore we used the electro quasistatic approach (EQS) for the first time [28]. 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 [29]

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

Let us formally impose 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 in electrochemical applications for the function $u = u(x,t)$. It is convenient to introduce the following abbreviations

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

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

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

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

Note: The quantity λ is seen as a pure quantity of calculation. Without any loss of generality we set $\lambda = 1$ for other considerations (especially in wave theory λ represents the velocity of a wave or a soliton).

After integration and application of the transformation $f(\xi) = \frac{1}{\eta} \ln[w(\xi)]$ we derive

$$\tau \, w \frac{d^2 w}{d\xi^2} - \tau \left(\frac{dw}{d\xi} \right)^2 - w \frac{d w}{d\xi} - \mu^2 w = 0, \ w = w(\xi) . \tag{4}$$

This nODE is the starting point to apply algebraic methods. First of all we need the parameter n 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 with C as an arbitrary constant of integration

$$2\tau p\frac{d^2p}{d\xi^2} - 2\tau\left(\frac{dp}{d\xi}\right)^2 - 2p\frac{dp}{d\xi} - \mu^2 p^4 + Cp^2 = 0, \quad p = p(\xi). \tag{5}$$

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: $p(\xi) = a_0 + a_1\omega(\xi)$ with $\omega(\xi)$ given from eq.(e).

Note: We stress that $p = 0$ is the singular point of the eq.(5).

4. THE REASON FOR ALGEBRAIC PROCEDURES – THE PAINLEVÉ PROPERTY

Today there exist three algorithms which are powerful and appropriate to solve nPDEs:

(i) The inverse scattering transform [30].

(ii) The calculation of similarity solutions by Lie's theory[31].

(iii) The calculation of solutions with the Painlevé ansatz [32] also known as the complete integrability.

If an equation has the Painlevé property (or if an equation is integrable completely) we propose to calculate the Bäcklund Transformations, Lax pairs, modified equations and Miura Transformations through the expansions of the solutions about the singular manifold. In other words one knows the complete solution manifold in the neighborhood of the singularity of any nPDE under consideration. Algebraic methods are therefore necessary if the P-property is not given.

Note: The word 'integrability' has several meanings. One notion of integrability which Painlevé analysis examines is the existence of solutions as Laurent series on open sets of the complex time variable. Integrability demands that these solutions are consistent, or match on the overlapping pieces of the sets on which they are defined. In other words this notion of integrability means the existence of meromorphic solutions.

Now let us show the following important theorem of long-ranged effects:

Theorem: The nPDE, eq.(1) does not possess the Painlevé property.

Proof: Since the nODEs, eq.(4) and eq.(5) could derived from the nPDE eq.(1) via the similarity transformation $u(x,t) = f(\xi)$, $\xi = x - \lambda t$, $\lambda \in R^{\pm}$, it is sufficient to show that the nODE eq.(5) has the Painlevé property. Also, without loss of generality we can set the constants τ and μ equal the identity in order to prove the P-property. Further we assume the solution of the nODE eq.(5) in the form $f \sim \alpha(z - z_0)^p$ where $\mathrm{Re}(p) < 0$, z_0 arbitrary, and substitute it into eq.(5).

Then α and p could determined so that different sets of terms may balance to provide the values of these coefficients. For each choice of p, the terms that balance in the eq.(5) are suitable for a possible expansion near the singularity. Here we find two possibilities: $p_1 = -1$ and $p_2 = -\frac{1}{2}$.

If any p is a fraction we have a branch point and the eq.(5) does not possess the P-property [33] ®

Note: At this stage of the analysis one cannot decide between algebraic and/or logarithmic branch points as the singularities. So, to represent the solution in case of occurrence of branch points it is necessary to introduce logarithmic terms in the solution more and more. Alternatively, psi-series can be used [32].

5. ALGEBRAIC CLASSES OF SOLUTIONS

Let us now proceed further to derive solutions of the nPDE, eq.(1). At the end of the Chapter 3 we saw that the balancing number is given by $n = 1$ and therefore a linear ansatz is suitable.

We substitute eq.(c) and eq.(d) into the nODE eq.(5) and change it into polynomial identities for the variable $\omega(\xi)$ by using the standard relations for the hyperbolic functions. Then all terms with the same power in $\cosh^k\omega\sinh^l\omega$, $k,l = 0,1,....$ are collected and set to zero their coefficients to get a nonlinear algebraic system of polynomial equations which has to be solved for the unknowns a, a_0, a_1, b_1 and C in a consistent way whereby it may happen that the solutions are only of trivial form and therefore useless for the solution manifold of eq.(5) and hence for the nPDE eq.(1), respectively.

In total we find nine nonlinear polynomial equations for four unknowns which is solved by

$$a_0 = \pm b_1\left(1+\sqrt{2}\right), \quad a_1 = \pm b_1, \quad C = 2\sqrt{2}, \tag{6}$$

$$a_0 = \pm b_1\left(1-\sqrt{2}\right), \quad a_1 = \pm b_1, \quad C = -2\sqrt{2}. \tag{6a}$$

Undoing all transformations one calculates by considering the positive sign only

$$f_1(\xi)=\frac{1}{\eta}\ln\left[\frac{1}{8b_1^2}\left(e^{\sqrt{2}\,\xi}-1\right)^2\right]=\underbrace{\frac{1}{\eta}\ln\frac{1}{8b_1^2}}_{const.}+\frac{2}{\eta}\ln\left[\left(e^{\sqrt{2}\,\xi}-1\right)\right],\ \xi=x-t,\ \xi\in R\setminus\{0\},\qquad(7)$$

with arbitrarily chosen b_1 but one has to restrict $b_1\notin R^-$. Further, the argument of the logarithm function may not assume the identity since the function vanishes.

Numerically for η^{-1} one can set $\frac{1}{43}$ and if we choose $b_1=1$ the constant becomes $-\frac{1}{43}\ln\frac{1}{8}\approx -0{,}05$. Thus we can write for the potential function

$$f_1(\xi)=-0{,}05+\frac{2}{43}\ln\left[\left(e^{\sqrt{2}\,\xi}-1\right)\right],\quad \xi\in R\setminus\left\{0,\ \ln 2/\sqrt{2}\right\}\qquad(7a)$$

Note: We refer to the fact that the function $f_1(\xi)$ becomes singular and therefore we have to exclude some values of the set of the domain of definition. These are solutions of the transcendental equation $e^{\sqrt{2}\xi}=1$. Therefore we explicitly have to exclude $D_1:=\left\{\xi\in\widetilde{D}_1:\xi=\ln 2/\sqrt{2}\right\}$ where D_1 means a suitable domain, e.g. $D_1(R^2)=\widetilde{D}_1(R^2)$.

We already stated that the success of all algebraic methods is directly connected with the solubility of the nonlinear algebraic system of polynomial equations. It is important to stress that the usage of similar nODEs, e.g. $\omega'=1\pm\cosh\omega$ and/or $\omega'=1\pm\sinh\omega\cosh\omega$ fails since the algebraic system admits only the trivial solution and is therefore useless for determining the solution manifold of eq.(5) and eq.(1) respectively.

One cannot estimate a priori whether or not a given nonlinear algebraic system of polynomial equations is soluble. In other words the basic question is a question of the existence of nontrivial solutions and this question is still under consideration. For general remarks relating to this field of interest the reader may consult [2].

6. SOME SELECTED PROPERTIES

Since the main intension is to show how one can derive solutions alternatively, it is of interest to stress some principal properties of the function eq.(7). For practical applications the function should be real-valued. It is proven that in the domain $\xi>0$ the function assumes real-valued and positive as one can see in the in the left part of the Fig.1 and this domain reveals to practical interests.

It is proven further that the following limit properties hold: $\lim_{\xi\to\pm 0} f_1(\xi)=-\infty$ and $\lim_{\xi\to\pm\infty} f_1(\xi)=\infty$.

Let us assume that the function eq.(7) represents any time-dependence, e.g. $f_1(x,t)$. In this case time-dependence is described by a logarithm function containing a fast raising function in which the argument tends to infinity. The right part of the Fig.1 shows the principal run for different time points.

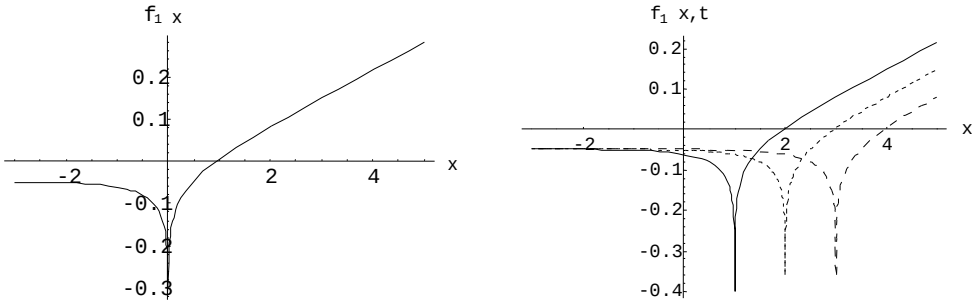

Fig.1 Left: The run of the potential function eq.(7). The discontinuity at the point $\xi=0$ is clearly seen. This kind of function is related with the initial condition $t=0$. Right: The time variation of the function for different time points: Full line: $t=1$, short dotted line: $t=2$, dotted line: $t=3$. By increasing the time the peaks move in the positive direction where one assumes $\lambda=1$.

The first and the second derivation exist and become singular at the point $\xi = 0$. Taking into account the second derivative so that

$$\frac{d^2}{d\xi^2} f_1(\xi) = \begin{cases} < 0 & .... \ \xi = 1 \\ \text{inf} & .... \ \xi = 0 \\ < 0 & .... \ \xi = -1 \end{cases} \tag{8}$$

holds (inf. means infinite) one deduces that the function is not stable. The first derivative however

$$f'(\xi) = \frac{d f_1}{d\xi} = \Phi(\xi) = \frac{2\sqrt{2}\, e^{\sqrt{2}\xi}}{43(e^{\sqrt{2}\xi} - 1)} \tag{9}$$

can be interpreted as a field which can be derived from the potential generally. This field may not have singularities in the denominator at the point $\xi = 0$. The contribution of the constant can be cancelled in the first order. For practical calculations at the regular point $\xi = 1$ one can assume a series representation up to order two in the form

$$\Phi(\xi) = \frac{2\sqrt{2}\, e^{\sqrt{2}}}{43(e^{\sqrt{2}} - 1)} - \frac{4 e^{\sqrt{2}}(\xi - 1)}{43(e^{\sqrt{2}} - 1)^2} + \frac{2\sqrt{2}\, e^{\sqrt{2}}(1 + e^{\sqrt{2}})(\xi - 1)^2}{43(e^{\sqrt{2}} - 1)^3} + O\left[\xi - 1\right]^3. \tag{10}$$

Unfortunately the algorithm (by Taylor) which was used does not provide any ready way to determine the radius of convergence of the series. One can say that by considering higher order terms the series converges relatively slow.
By applying the divergence operator on the electric field (ξ acting as the local coordinate) we get
an expression for the charge density explicitly

$$\rho(\xi) = \frac{\varepsilon_0}{\pi} \frac{e^{\sqrt{2}\,\xi}}{43(e^{\sqrt{2}\,\xi} - 1)^2} = \frac{\varepsilon_0}{172\,\pi} \operatorname{csch}^2\left[\frac{\xi}{\sqrt{2}}\right] = \frac{\varepsilon_0}{172\,\pi} W(\xi) = B\, W(\xi), \tag{11}$$

where $W(\xi)$ is used instead of the exponential term. Since the charge density may not vanish we have to exclude some values, e.g. we have $\xi \in R^{\pm} \setminus \left\{\xi = \pm\sqrt{2}\, \operatorname{csc} h(1)\right\}$.

In Fig.2 we show the principal run of the charge density by leaving off the numerical constants $B = \frac{\varepsilon_0}{172\,\pi}$. It is remarkable that the charge density in this case represents a kind of unit density.

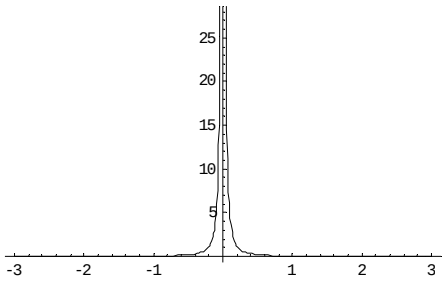

Fig.2 The charge density, eq.(11) plotted without the constants. The principal behaviour can be seen as a unit charge. The function is not analytical at the point $\xi = 0$.

In the Fig.3 the run of the connection of the function $W(\xi)$ and the charge density $\rho(\xi)$ for positive values of the argument is shown whereby a linear dependence is observed.

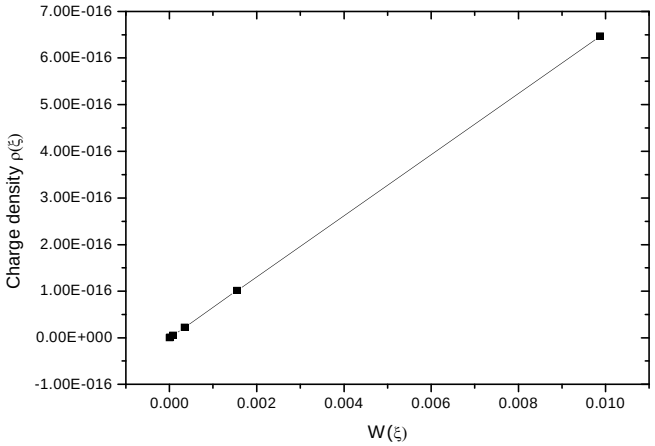

Fig.3 The behaviour of the function $\rho(\xi)$ for positive values of the argument. A linear connection between the charge density and the function $W(\xi)$ is observed.

Let d be a given specific distance similiarly as in the DHT (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. Thus, from eq.(11) we have

$$q_{tot} = -\frac{\varepsilon_0}{\pi}\int_d^\infty \rho(\xi)\, d\xi = -\frac{\varepsilon_0}{\pi}\frac{2\sqrt{2}}{43\,(e^{\sqrt{2}\,d}-1)}\ ,\quad d \neq 0\ , \tag{12}$$

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

Let us study the limit case for large distances. It is shown that $q_{tot} \to 0$ as $d \to \infty$. This is also in agreement with the boundary conditions assumed earlier and matches our expectation exactly.

The limit case for small distances, say $d \to 0$ is not defined due to the singularity at the point $d = 0$. Thus one has to exclude this point as done above.

In the following we shortly examine the statistical point of view and we shall explore a motion in which the particles can jump through a distance d_s in a time τ_D.

Consider a random walk in which each step (jump) is trough a distance d_s to the left or right. The net distance travelled after N steps is equal to the difference between the number of steps to the right N_r and to the left N_l, that is $(N_r - N_l)/d_s$. We have $n = N_r - N_l$ and the total number of jumps is $N = N_r + N_l$. The number of ways of performing a walk is expressed by the binomial coefficient so that we have

$$W = \frac{N!}{N_r!\,N_l!} = \frac{N}{(\frac{1}{2}(N+n))!\,(\frac{1}{2}(N-n))!}, \tag{f}$$

and the probability of the net distance walked being $n\,d_s$ is given by

$$P = \frac{W}{2^N} = \frac{N}{(\frac{1}{2}(N+n))!\,(\frac{1}{2}(N-n))!\,2^N}\ . \tag{g}$$

For a 'hiking' taking n steps 2^N possibilities are realized because each single step moves left or right. The result, eq.(g) differs completely from the 'classical' solution of the linear diffusion equation. If we allow the time so (as large as possible) that the particle can perform a host of jumps the factorial is approached by Stirling's formula to give

$$\ln N! = \ln N(N+\tfrac{1}{2}) - N + \ln(2\pi)^{1/2}\ . \tag{h}$$

For small net distances, say $n << N$ and using the approximation $\ln(1+z) \approx z$ we finally find after some calculations for the jump probability

$$P = \sqrt{\frac{2\tau_D}{\pi t}} \exp\left[-\frac{z^2 \tau_D}{2 t d_s^2}\right]. \qquad \text{(i)}$$

Note that the number of steps taken in a time t is given as $N = t/\tau_D$ and the net distance travelled from the origin is $\xi = n d_s$. In our model we understand by the origin the OHL so that the particles can move towards the electrode surface. This movement is supported by additional factors, e.g. external electric and/or magnetic fields and other gradients. Further note that the jumps are of discrete form. In Fig.4 we show the graphical dependence of the jump probability from the distance.

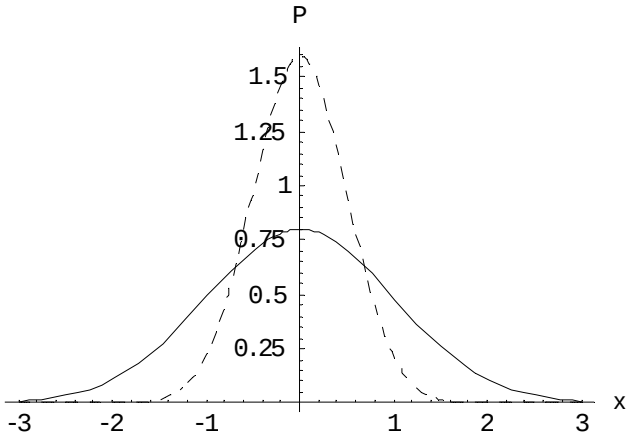

Fig.4 The dependence of the jump probability from the local coordinate. The dotted line refers to $t_1 = 0{,}25$ and the full line represents $t_2 = 1$. In the diagram, $t_2 > t_1$ and the distribution becomes flatter and flatter. Since τ_D means a system immanent quantity it can be chosen arbitrarily, here we assume $\tau_D = 1$. Further we assume a unit distance, that means we can set $d_s = 1$. At any particular time t, a bell-shaped distribution curve is obtained.

7. CONCLUSION AND OUTLOOK

In this study 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 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 an algebraic approach introduced by the author earlier recognizing the fact that classes of solutions 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. Aapart from trivial solutions of the homogeneous nonlinear algebraic system in some cases it may happen that such systems can be solved only by numerical standard procedures.

From mathematical point of view it is necessary to analyze this unusual behaviour in future papers.

Such algebraic approaches can be changed by different ways. It is possible to vary both the series, eq.(c) and the nODE, eq.(d). Tedious calculations done before has shown that if one uses the nODE $\omega' = 1 \pm \cosh\omega$ (letting equal the series ansatz in the present form) only trivial solutions are obtained. The same result is obtained by using the nODE $\omega' = 1 \pm \sinh\omega\cosh\omega$. Finally, using the negative sign in eq.(d) the algebraic polynomial system also produces trivial solutions.

It is clear that the result of trivial solutions means a restriction for the algorithm. On the other hand the number of appropriate nODEs is also restricted (questions of stability, existence and uniqueness cannot be answered for all nODEs satisfyingly).

But the benefit of algebraic methods is the easiness in handling the algorithm and otherwise the possibility to translate the approach into any computer languages independently from the given

problem. From the derived time-depending potential expressions for the relating field and the charge density could obtained. Further, for the present model an appropriate relaxation time relating to diffusion processes through the OHL is performed. This specific system time seems as a suitable starting point for experimental tests.
Moreover, an expression for the total charge contained in the OHL follows naturally. This amount of charge has a counterpart (due to charge neutrality) on the electrode surface.

9. ACKNOWLEDGMENTS

The work is supported by the Government of Styria under the contract number D-1638000041.
The author is grateful to Professor Otto Fruhwirth, Institute of Chemical Technologies of Materials, Technical University Graz, Austria, whose suggestions have improved considerably the quality of the author's intensions.

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