

A new time dependent approach for solving electrochemical interfaces Part I: theoretical considerations using lie group analysis

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Abstract In this paper we introduce a nonlinear partial differential equation (nPDE) of the third order to 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 of the meaning of the nonlinear Poisson-Boltzmann Equation (PBE) and therefore we call it the modified Poisson-Boltzmann Equation (mPBE). In the present first part of this extensive study we derive the equation from the electromagnetics from a quasistatic perspective, or more precisely the electroquasistatic approximation (EQS). Our main focus will be the analysis via the Lie group formalism and since that up to now no symmetry calculation is available we believe that it seems indispensable to apply this method yielding a deeper insight into the behaviour of the solution manifold of this new equation following electrochemical considerations. We determine the classical Lie point symmetries including algebraic properties. Similarity solutions in a most general form and suitable nonlinear transformations are obtained. In addition, a note relating to potential and generalized symmetries is drawn. Moreover we show how the equation leads to approximate symmetries and we apply the method to the first time. The second part appearing shortly after will deal with algebraic solution methods and we shall show that closed-form solutions can be calculated without any numerical methods. Finally the third part will consider appropriate electrochemical experiments proving the model under consideration.

Keywords Debye-Hückel theory · Electroquasistatic · Nonlinear partial differential equations · Lie group analysis · Non-classical symmetries · Approximate symmetries · Potential symmetries · Poisson-Boltzmann Equation

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1 Preliminaries

We summarize some known ideas and give a short overview whereby the remarks are far from being complete. We restrict ourselves as short as possible however some important notes should indicate whereby we follow a historical point of view.

1.1 A short note to the Debye-Hückel theory (DHT)

An advance in understanding of the distribution of charges around an ion in aqueous solution was achieved by Debye and Hückel [1–3]. The idea lay in the formulation of a model for the time-average distribution of ions in very dilute solutions of electrolytes. From this distribution they were able to calculate the electrostatic potential contributed by the surrounding ions to the total electrostatic potential at the reference ion and hence, the chemical potential change arising from the ion-ion interaction. Earlier, Helmholtz [4] was the first to develop a double-layer model wherein he proposed a simple charge separation at the interface.

The interface separates two layers of opposite charges, one in the electrode and the other in the solution (not restricted to aqueous solutions).

Gouy [2,5] 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 [2,6].

Ions in the double layer are not compact as described in the Helmholtz model and free ions able to move are called the diffuse layer.

Chapman [7] established the steady-state governing equation for the diffuse layer, the Poisson-Boltzmann equation. This equation is based on the combination of the electrostatic basic equation, the Poisson Equation and the Boltzmann distribution. For steady-state conditions, if we impose zero flux at the boundaries and integrate the conservation of mass equation, the concentration can be expressed in terms of bulk molarity. By substituting this into Gauss's law a nonlinear second-order partial differential equation is derived.

The model is referred to as the Gouy-Chapman model. The predicted behaviour depends upon the surface potential. This model is valid for low surface potential and diluted electrolytes.

Using the Debye-Hückel approximation which is based upon the assumption that the electric potential is very small (e.g. 20 mV), the Poisson-Boltzmann Equation can be linearized and a closed-form solution can be obtained [2].

However, for other than very low voltages and molarity, extremely high concentrations and voltage gradients are predicted near the electrode. The overestimation results from idealization of the ions as point charges.

Stern [8] improved the Gouy-Chapman model by assuming a finite ion size and by dividing the electrolyte into two layers, referred to as the Stern layer and the diffuse layer.

The Stern layer (a fixed layer) has an assumed thickness approximately equal to the radius of one hydrated ion (e.g. about 0.5 nm). The electric potential distribution in the Stern layer is assumed to decrease linearly and there is no free charge in the Stern

layer. The second layer of the electrolyte is governed by the Gouy-Chapman model. This model shows good agreement with the experiments for nonspecifically adsorbed ions on the electrode. For specifically adsorbed ions, which means ions tightly bound to the electrodes by chemical interactions, Grahame [9] revised the Stern model using three layers: the inner Helmholtz layer (IHL), the outer Helmholtz layer (OHL) and the diffuse layer. The difference between the Grahame model and the Stern model is the existence of specific adsorption [2]. The combination of the Gouy-Chapman model and the Stern layer is still considered to be a reasonable model and a transient version. The transient version will be obtained by combining the Nernst-Planck equation, conservation of mass and Gauss equations.

Herein, this transient version will be referred to as the Nernst-Planck-Poisson-modified Stern model or simply the Nernst-Planck-Poisson (NPP) model if there is no modified Stern layer.

Several well-known names arise during the past 80 decades improving given models or developing new which are suitable to get a deeper insight into this field such like Bjerrum [10], Gronwall, La Mer, Sandved [11], Onsager [12], Kirkwood [13], Falkenhagen [14], Ghosh [15], Smoluchowski [16], Parker [17], Walden [18], Planck [19], Fuoss [20], Kortüm [21] to mention some honoured scientists from historical point of view and extensive developments are not finalized up to now.

1.2 Electromagnetics from a quasistatic perspective

We give a short introduction [22–26] concentrating the subject which will be need later.

Maxwell's equations (ME) are fundamental in describing electromagnetic phenomena and valid over a wide range of spatial and temporal scales. Normally, both the electric and magnetic fields are given by the laws of Coulomb and Biot-Savart. As soon as there is any time dependence we have to use the full MEs containing all their compliance.

The quasistatic limit of the MEs is a kind of $c \rightarrow \infty$ limit (the fields propagate at once) obtained by neglecting time retardation. EQS has important applications modelling transient phenomena in approximating theories for materials with low conductivity (or low-frequency approximation).

The crucial step is the fact that the time-dependent electric field may derived from a scalar potential which is the solution of a certain nPDE of the third-order in our case.

Transient electrodynamical problems are not easy to solve in general, e.g. by occurring solutions depending on roots we have to take into account some branch points. In media with a finite conductivity a static field is not possible and the pertinent relaxations time is given by $\tau = \epsilon_0 \epsilon / \sigma$ [26], where ϵ is the relative permittivity and σ the conductivity.

For metals (e.g. copper) the relaxation time is in the range of 10^{-18} s. Otherwise, new developments on the material sector produces materials with a relative dielectric constant in the range $2 < \epsilon < 4$ and a conductivity of about 10^{-9} S/m. Then the decay rate is approximately $\tau \approx 10^{-3}$ s and this is long compared to other time constants of

the system (e.g. an electromagnetic field passes through a panel). This is exactly the field where EQS can be applied, [24,26].

In the following we are only interested in electric fields and capacities so that magnetic and/or inductive effects can be neglected.

Moreover, EQS also means that the primary fields are not coupled. They follow the time behaviour of the sources producing the secondary fields (e.g. the magnetic field). But the great difference is that these fields do not react back. So it follows that solutions of EQS problems can never be traveling electromagnetic waves [22].

2 Derivation of the model equation

We again point out that the basic assumption of the DHT is the connection between the electrostatic Poisson equation and the Boltzmann distribution. However, this needs some assumptions: (1) the forces are short-ranged, (2) we only undertake Coulomb forces (no dispersion forces), (3) the involved particles are assumed to be point-like and unpolarized, (4) the dielectric constant of the solution is assumed to be the same as the solvent, (5) electrolytes are dissociated completely.

To derive our new model equation considering time dependence we start from the MEs [25]:

$$\begin{aligned} \text{rot}\vec{E} &= -\frac{\partial\vec{B}}{\partial t}, \quad \text{rot}\vec{H} = \vec{j} + \frac{\partial\vec{D}}{\partial t} = \sigma\vec{E} + \varepsilon_0\varepsilon\frac{\partial\vec{E}}{\partial t} + \vec{j}_e, \\ \text{div}\vec{B} &= 0, \quad \text{div}\vec{D} = \text{div}(\varepsilon_0\varepsilon\vec{E}) = \rho. \end{aligned} \tag{2.1}$$

It is assumed that there is both a weak current density due to the electric field and an impressed current density \vec{j}_e . The EQS assumption now means that the sources act slowly so that the fields change slowly and the conductivity σ is rather small (\vec{B} , \vec{E} and \vec{D} have the usual meaning).

Therefore the magnetic fields (thus the solenoidal part of the electric field) are negligibly small.

So, otherwise we can set $\frac{\partial\vec{B}}{\partial t} \approx 0$ or $\frac{\partial\vec{D}}{\partial t} \approx \frac{\partial\vec{E}}{\partial t} \neq 0$ from the EQS assumption.

For that reason the electric field is derived from a scalar potential, so that we have the conclusion: $-\text{rot}\vec{E} = \frac{\partial\vec{B}}{\partial t} \approx 0 \Rightarrow \vec{E} = -\text{grad}u$. Taking the divergence of the second equation of (2.1) we derive at an equation containing the unknown potential function $u = u(x, t)$ depending upon their time derivative:

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

The next step is that we need a relation to the Boltzmann distribution since the charge density $\bar{\rho}_e$ of the r.h.s. of the (2.2) is unknown. It is obvious from the DHT that we set

$$\bar{\rho}_e = \sum_{i=1}^N z_i e_0 N_i^0 \exp\left[-\frac{z_i e_0 \Delta u}{kT}\right], \quad \Delta u = u_0 - u_L. \tag{2.3}$$

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; z_i is the charge number, e_0 the elementary charge, k the Boltzmann constant, T is the temperature and N_i^0 is the particle number in the bulk. Then we have

$$\sigma \Delta u + \varepsilon_0 \varepsilon \frac{\partial}{\partial t} \Delta u + \frac{\partial}{\partial t} \left\{ \sum_{i=1}^N z_i e_0 N_i^0 \exp \left[-\frac{z_i e_0 u}{kT} \right] \right\}. \quad (2.3a)$$

Interchanging the sum and the derivative we then have after the time differentiation

$$\sigma \Delta u + \varepsilon_0 \varepsilon \frac{\partial}{\partial t} \Delta u - \sum_{i=1}^N \left\{ z_i^2 e_0^2 N_i^0 \frac{\partial u}{\partial t} \exp \left[-\frac{z_i e_0 u}{kT} \right] \right\}. \quad (2.3b)$$

Then we divide by the conductivity and introduce the abbreviations

$$\frac{\varepsilon_0 \varepsilon}{\sigma} = \tau, \quad \frac{e_0 z_i}{kT} = \eta, \quad \frac{1}{\sigma kT} \sum_{i=1}^N \left(z_i^2 e_0^2 N_i^0 \right) = \mu^2, \quad (2.4)$$

where the quantity μ has the dimension (SI units): $\dim[\mu] = s.m^{-2}$. Comparing this with the expression obtained in the DHT we here have the dimension of a reciprocal diffusion constant.

In addition, we finally derive at the following nPDE of the third order for the unknown time-depending potential function $u = u(x, t)$:

$$\frac{\partial^2 u}{\partial x^2} + \tau \frac{\partial^3 u}{\partial x^2 \partial t} - \mu^2 \frac{\partial u}{\partial t} e^{-\eta u} = 0, \quad u = u(x, t), \quad -\infty < x < \infty. \quad (2.5)$$

At this stage 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 $u = u(x, t)$. The potential function $u = u(x, t)$ plays the same role as in the DHT, therefore one can regard (2.5) as an extended ‘modified PBE’ with time dependence involved explicitly. Further, for our purposes we assume very diluted (1,1)-electrolytes in the first instance and conductivities should be in the range of $0 \leq \sigma \leq 10^{-3} S/m$.

The derived equation is suitable to model electrochemical problems as well we believe that the equation allows a deeper insight in the hydrated ion structure which will be shown soon.

Table 1 Different values of the quantities B and μ^{-1} , (2.6) for water by assuming temperature dependence

| T/K | $B \times 10^6 / s.m^{-2}$ | $\mu^{-1} \times 10^{-6} / m^2.s^{-1}$ |
|--------|----------------------------|--|
| 271.15 | 3.75 | 0.27 |
| 273.15 | 3.47 | 0.29 |
| 275.15 | 3.02 | 0.33 |
| 277.15 | 2.44 | 0.41 |
| 281.15 | 1.17 | 0.86 |
| 283.15 | 1.85 | 0.54 |
| 299.15 | 0.75 | 1.34 |
| 307.15 | 0.51 | 1.96 |
| 323.15 | 0.24 | 4.17 |

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

$$\begin{aligned} \mu^2 &= \frac{e_0^2 N_A}{1000 \sigma k T} \frac{1}{2} \sum_i c_i z_i^2 \rightarrow \mu \frac{e_0^2 N_A}{1000 \sigma k T} I \rightarrow \mu \\ &= \left(\frac{e_0^2 N_A}{1000 \sigma k T} \right)^{1/2} \sqrt{I} \rightarrow \mu = B \sqrt{I}, \end{aligned} \tag{2.6}$$

which is more useful in practical calculations later as well as by interpreting double layer devices.

Numerical examples for water at various temperatures are given in Table 1.

Note: We can not directly compare the quantity μ with the expression obtained in the DHT since it contains the electrical conductivity. As mentioned earlier the quantity might be matched a special kind of diffusion-like quantity. This is a reasonable assumption since ions surrounded by their hydrated water molecules will diffuse through the OHL.

We further remarked that the model is valid only for much diluted electrolytes. To imagine the behaviour of the quantity μ we calculated values for potassium chloride in Table 2 for different temperatures at a constant concentration, that is $c = 0.01 \text{ molL}^{-1}$. To give a graphical impression of the functional dependence we refer to the Figs. 1 and 2. We further find it useful to calculate values for (2,1)- and (1,2)-electrolytes. Here we assume a constant room temperature, that is $T = 20^\circ\text{C}$ and sodium sulphate and calcium sulphate, respectively are chosen as standard examples.

We refer to the Tables 3 and 4. For these cases we also show some graphical representations. Further explanations are given at the end of the tables and figures, respectively (Fig. 4).

Let us now go back in studying the nPDE, (2.5). We seek for solutions for the nPDE, (2.5) for which $u = F(x, t)$, $F \in C^3(D)$, $D \subset R^2$ is an open set and further we exclude $D := \left\{ (u(x, t)) \in \tilde{D} : u \neq 0, u_x \neq 0, u_t \neq 0, \dots \right\}$ and a positive time $t > 0$.

Table 2 Calculated values for the quantities B and μ^{-1} , (2.6) as an example concerning a (1,1)-electrolyte, in this example potassium chloride is used by temperature variation; the second column gives the relating conductivity (from Kohlrausch) and a standard concentration of $c = 0, 01 \text{ mol L}^{-1}$ is assumed

| T/K | $\kappa \times 10^{-4} \Omega^{-1} m^{-1}$ | $B \times 10^6 / s.m^{-2}$ | $\mu^{-1} \times 10^{-6} / m^2.s^{-1}$ |
|--------|--|----------------------------|--|
| 273.15 | 7.76 | 3.25 | 3.08 |
| 288.15 | 11.47 | 2.60 | 3.84 |
| 289.15 | 11.73 | 2.57 | 3.89 |
| 291.15 | 12.25 | 2.48 | 4.03 |
| 292.15 | 12.51 | 2.47 | 4.04 |
| 293.15 | 12.78 | 2.44 | 4.09 |
| 295.15 | 13.32 | 2.37 | 4.19 |
| 297.15 | 13.86 | 2.33 | 4.29 |
| 298.15 | 14.13 | 2.30 | 4.34 |

Suitable classes of solutions are $u \in I$, I an interval so that $I \subseteq D$ and $u : I \rightarrow R^2$.

Now we close this section and our next interest is to present the group properties of (2.5) and moreover we show how we can derive solutions of advanced character by the Lie group formalism.

There is no doubt that an intensive scrutiny is necessary but otherwise we believe that the derivation does not lead to any confusion.

Our new time-depending model is derived analogues to the DHT leading to a modified PBE under the assumption of the EQS.

Note: For the following we suppress the item ‘classes’, so ‘classes of solutions’ are simply ‘solutions’ of the (2.5).

3 Classical symmetry analysis—algebraic group properties

We take up now the developments given in [27–30] omitting all technical details.

To use symmetry groups in any application we first deduce the symmetries of (2.5).

The result is a well-defined system of ten linear homogeneous PDEs (describing the point symmetries) for the infinitesimals $\xi_i = \xi_i(x, u)$ and $\phi_i = \phi_i(x, u)$.

These constitute the so-called determining equations for the symmetries of (2.5) derived by Fréchet’s derivative [31–35]:

$$\frac{\partial \xi_1}{\partial u} = \frac{\partial \xi_2}{\partial u} = \frac{\partial \xi_1}{\partial t} = \frac{\partial \xi_2}{\partial x} = \frac{\partial^2 \phi}{\partial u^2} = 0, \quad (3)$$

$$\mu^2 \frac{\partial \phi}{\partial t} - e^{u\eta} \left\{ \frac{\partial^2 \phi}{\partial x^2} - \tau \frac{\partial^3 \phi}{\partial^2 x \partial t} \right\} = 0, \quad (3.1)$$

$$\mu^2 \left\{ \eta \phi - 2 \frac{\partial \xi_1}{\partial x} + \frac{\partial \xi_2}{\partial t} + \tau \frac{\partial^2 \phi}{\partial t \partial u} \right\} + e^{u\eta} \frac{\partial^3 \phi}{\partial x^2 \partial t} = 0, \quad (3.2)$$

$$\mu^2 \eta \left\{ \phi - 2 \frac{\partial \xi_1}{\partial x} \right\} + \tau e^{u\eta} \frac{\partial^3 \phi}{\partial x^2 \partial u} = 0, \quad (3.3)$$

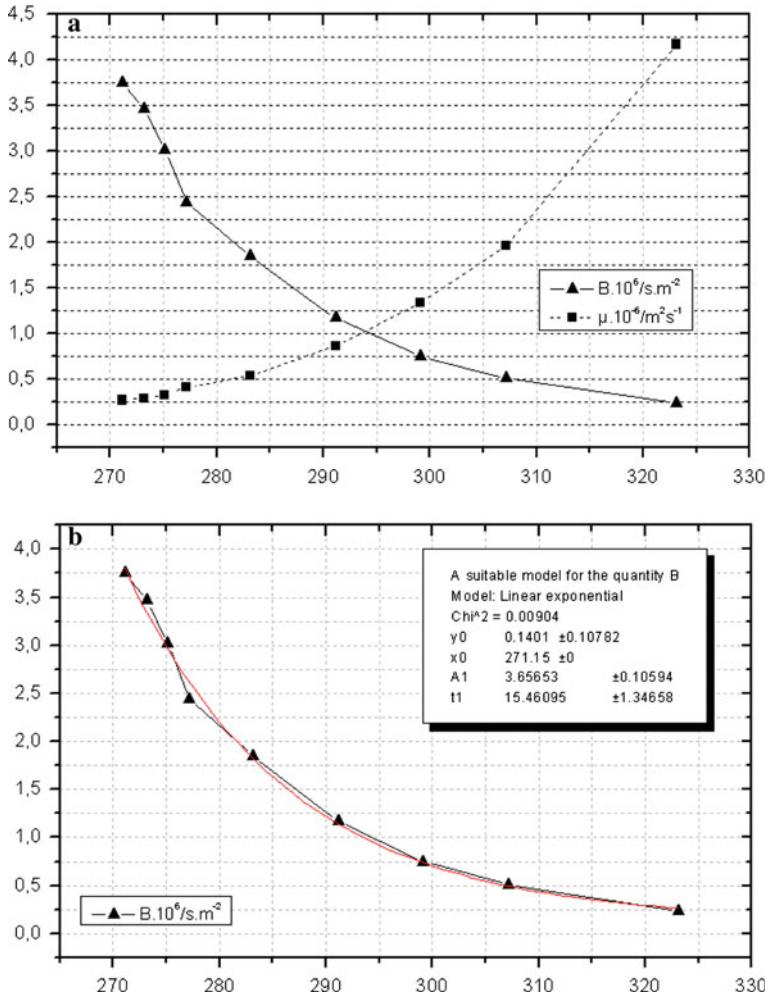


Fig. 1 **a** A graphical representation of the temperature dependence of the quantities B and μ^{-1} , (2.6) calculated from the values obtained from the Table 1. The functional run either for the quantities B and μ^{-1} show an increasing and decreasing trend which is analyzed in the figure above. **b** An example for an exponential fit for the quantity B following the values from Table 1 The quantity B is represented by the following general function $\sim y_0 + a_1 \exp\left[\frac{x-x_0}{t}\right]$. We note that the quantity t here means a parameter not being the time. Since B and μ^{-1} are reciprocal the same approximate formula for μ^{-1} can be assumed

$$2 \left\{ \tau \frac{\partial^3 \phi}{\partial x \partial t \partial u} + \frac{\partial^2 \phi}{\partial x \partial u} \right\} - \frac{\partial^2 \xi_1}{\partial x^2} = 0, \tag{3.4}$$

$$2 \frac{\partial^2 \phi}{\partial x \partial u} - \frac{\partial^2 \xi_1}{\partial x^2} = 0. \tag{3.5}$$

Solving the above given set of (3) to (3.5) we derive the infinitesimals

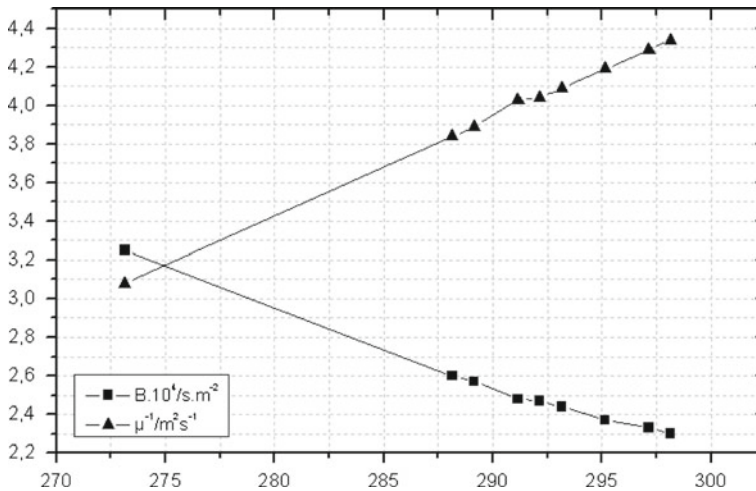


Fig. 2 The temperature dependence of the quantities B and μ^{-1} , (2.6) in case of an (1,1)-electrolyte. Here potassium chloride is under consideration following the values from Table 2. Both of the quantities show approximately a linear behaviour in the considered temperature domain

$$\xi_1 = k_2 + k_3x, \quad \xi_2 = k_1, \quad \phi = 2k_3/\eta \quad (3.6)$$

The result shows that the symmetry group of (2.5) constitutes an infinite three-dimensional point group where the group parameters are denoted by k_i , $i = 1, 2, 3$. It is of interest that the infinitesimal ϕ depends upon the parameter η . Equation (2.5) admits a three-dimensional Lie algebra L of its classical infinitesimal point symmetries relating to the following vector fields:

$$V_1 = \partial_x, \quad V_2 = \partial_t, \quad V_3 = \frac{2\partial_u}{\eta} + x\partial_x. \quad (3.7)$$

This group of three fields contains translations in time and space so that $\{t' \rightarrow t + \lambda, x' \rightarrow x + \lambda\}$ holds for $\{V_1, V_2\}$ and the associated differential operators V_3 is related to dilatation operations. These symmetry vector fields form a Lie algebra L by:

$$[V_2, V_3] = V_2, \quad [V_3, V_2] = -V_2. \quad (3.8)$$

For this three-dimensional Lie algebra the commutator table (Table 5) for the V_i is a (3×3) -table whose (i, j) th entry expresses the Lie bracket $[V_i, V_j]$ given in (3.8).

The table is skew-symmetric and the diagonal elements vanish. The coefficient $C_{i,j,k}$ is the coefficient of V_i of the (i, j) th entry of Table 1 and the related structure constants can be read from the table to give

$$C_{2,3,2} = -1, \quad C_{3,2,2} = 1. \quad (3.9)$$

Table 3 Calculated values for the quantities B and μ^{-1} , (2.6) as an example concerning an (2,1)-electrolyte, the calculation assumes calcium sulphate using different concentrations considering room temperature

| $c/val.l^{-1}$ | $\kappa \times 10^{-4} \Omega^{-1} m^{-1}$ | $B/s.m^{-2}$ | $\mu^{-1} \times 10^{-4} / m^2.s^{-1}$ |
|----------------|--|--------------|--|
| 0.0001 | 12.03 | 2610.02 | 5.42 |
| 0.0002 | 23.81 | 1855.27 | 7.62 |
| 0.0005 | 57.47 | 1194.17 | 11.84 |
| 0.001 | 109.29 | 865.96 | 16.33 |
| 0.005 | 450.45 | 426.54 | 33.16 |
| 0.01 | 806.45 | 318.78 | 44.36 |

Table 4 Calculated values for the quantities B and μ^{-1} , (2.6) as an example concerning an (1,2)-electrolyte, the calculation assumes sodium sulphate using different concentrations by considering room temperature

| $c/val.l^{-1}$ | $\kappa \times 10^{-4} \Omega^{-1} m^{-1}$ | $B/s.m^{-2}$ | $\mu^{-1} \times 10^{-4} / m^2.s^{-1}$ |
|----------------|--|--------------|--|
| 0.0001 | 11.57 | 2661.46 | 6.51 |
| 0.0002 | 22.99 | 1888.06 | 9.17 |
| 0.0005 | 56.82 | 1200.98 | 14.42 |
| 0.001 | 111.73 | 856.45 | 20.22 |
| 0.005 | 529.10 | 393.57 | 44.01 |
| 0.01 | 1015.23 | 284.12 | 60.96 |

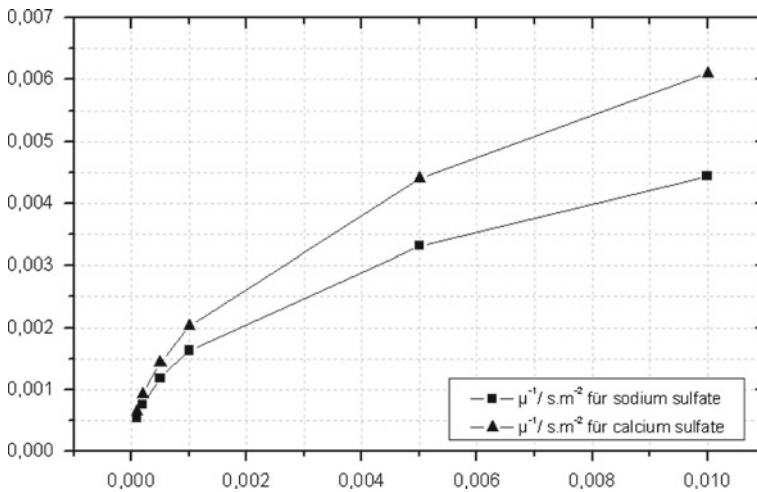


Fig. 3 The run of the quantity μ^{-1} , (2.6) for multi-valued (n,m)-electrolytes depending on the concentration and assuming room temperature, say, $T = 20^\circ C$. The increase for calcium sulphate is faster as for sodium sulphate. It might be of general interest to prove this behaviour for other electrolytes

Table 5 The commutator table of the nPDE (2.5)

| | V_1 | V_2 | V_3 |
|-------|-------|-------|--------|
| V_1 | 0 | 0 | 0 |
| V_2 | 0 | 0 | $-V_2$ |
| V_3 | 0 | V_2 | 0 |

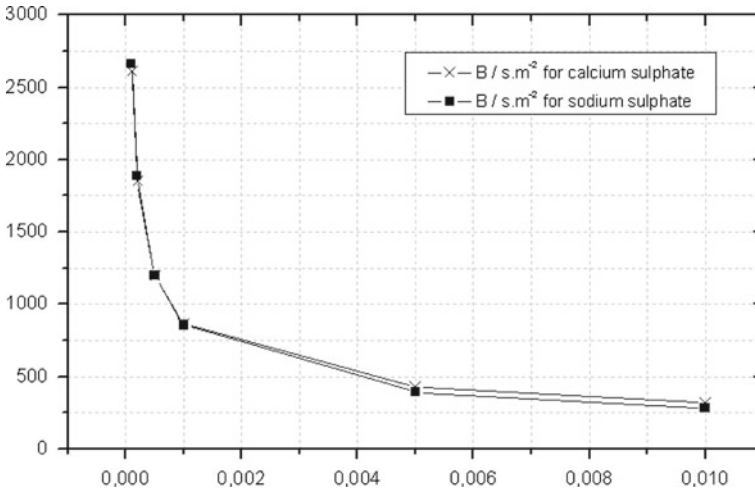


Fig. 4 The run of the quantity B (2.6) for multi-valued (n,m)-electrolytes depending on the concentration and assuming room temperature, say, $T = 20\text{ }^\circ\text{C}$. On the contrary to the qualitative run of Fig. 3 here we are confronted with the fact that for (n,m)-electrolytes the dependencies differ hardly. In the domain in which the concentration increases a linear behaviour is expected

Theorem *The Lie algebra of (2.5) is solvable.*

Proof A Lie algebra L is called solvable if $V^{(n)} = 0$ for some $n > 0$. It can be shown that L is reducible to $V^{(3)} = 0$ starting by the ideal $\{V^{(1)}, \dots, V^{(3)}\}$ since the algebra is three-dimensional. □

Other useful algebraic group properties are mentioned: Equation (2.5) has the Casimir operator by V_1 , the group order is three containing seven subgroups. These subgroups are important later to perform a similarity reduction deducing suitable solutions of (2.5).

The metric ($3 \otimes 3$ Cartanian tensor) satisfies:

$$g_{ij} = \begin{pmatrix} 0 & \cdots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \cdots & 1 \end{pmatrix} \text{ with } \det(g) = 0, \tag{3.10}$$

The condition $\det(g) = 0$ means that the given algebra is therefore degenerate and commutative.

Note: Alternatively one can write (3.10) with (3.9) $g_{im} = \sum_{i,k=1}^n c_{ik}^i c_{mi}^k$.

3.1 Similarity solutions

Let us now discuss the most important similarity solutions for special subgroups. From the total sum of seven cases four of them belong to non-solvable cases and one case covers the case below.

If we set the group parameters $k_1 = k_3 = 1$ and $k_2 = 0$, the following nODE of the third order

$$e^{\eta S} \left(\eta \left(\tau \frac{d^3 S}{d\zeta^3} + (1 + \tau) \frac{d^2 S}{d\zeta^2} + \frac{dS}{d\zeta} \right) - 2 \right) - \eta \mu^2 \frac{dS}{d\zeta} = 0, \quad S = S(\zeta), \tag{3.11}$$

results. We have $S : R \times R \rightarrow R, \zeta \in R, -\infty \leq \zeta \leq \infty, D := \{(S, \zeta) \in \tilde{D} : S(\zeta) \neq 0\}$ and also for the derivatives. The similarity variable ζ together with the relevant nonlinear transformation reads as $t - \ln x = \zeta, S = u - 2 \ln x / \eta$.

Following Peanos’ theorem the r.h.s of (3.11) is bounded on the entire real axis so we can expect that solutions exist at least (locally in this sense).

The highly nODE, (3.11) cannot be solved analytically. However we performed a closed-form series representation up to order four depending on the series coefficients a_i through

$$S(\zeta) = a_2 \zeta^2 + \frac{1 - a_2 \eta (1 + \tau)}{3 \eta \tau} \zeta^3 - \frac{1 + \tau - a_2 \eta (1 + \tau (1 + \mu^2 + \tau))}{12 \eta \tau^2} \zeta^4 + O[\zeta]^5. \tag{3.11a}$$

Here the parameter a_2 can be chosen arbitrary but $a_2 \neq 0$. Converting back by the help of the nonlinear transformations and assuming $a_2 = 1$ we finally get a solution for (2.5)

$$u(x, t) = \frac{2 \ln x}{\eta} + (t - \ln x)^2 + \frac{(1 - \eta (1 + \tau)) (t - \ln x)^3}{3 \eta \tau} - \frac{(1 + \tau - \eta (1 + \tau (1 + \mu^2 + \tau))) (t - \ln x)^4}{12 \eta \tau^2}. \tag{3.11b}$$

Note: We found a second case which is fulfilled by the nODE (3.11) for the group constants is $k_1 = k_2 = k_3 = 1$ leading to the transformations $t - \ln(1 + x) = \zeta, S = u - 2 \ln(1 + x) / \eta$. In Fig. 5 we present the solution (3.11b) graphically.

Another important case arise at the choice $k_1 = k_2 = 1, k_3 = 0$. We have $t - x = \zeta, u = S$, and the relating nODE of the third order is given by

$$e^{\eta S} \left\{ \tau \frac{d^3 S}{d\zeta^3} + \frac{d^2 S}{d\zeta^2} \right\} - \mu^2 \frac{dS}{d\zeta} = 0, \quad S = S(\zeta), \tag{3.12}$$

where $S : R \times R \rightarrow R, \zeta \in R, -\infty \leq \zeta \leq \infty, D := \{(S, \zeta) \in \tilde{D} : S \neq 0, S' \neq 0, S'' \neq 0, S''' \neq 0\}$,

Fig. 5 A three-dimensional surface plot of the potential function $u(x, t)$ (3.11b) in the sense of a logarithmic series representation up to order four. The initial state $t = 0$ represents a pure logarithmic dependence and the function tends to infinity either for the cases $x \rightarrow \infty$ and $t \rightarrow \infty$

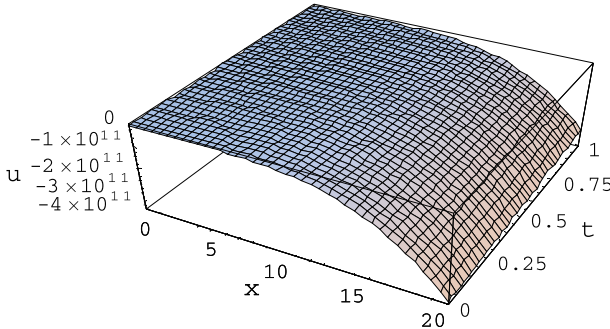
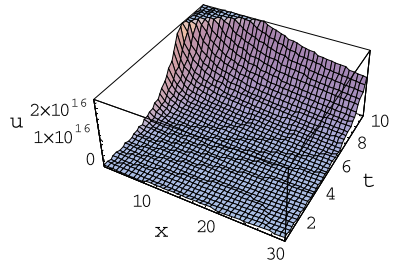


Fig. 6 A three-dimensional surface plot of the potential function $u(x, t)$ (3.12b) in the sense of a logarithmic series representation up to order four. The function shows an increase of continuity tending to infinity for large values of the dependent variables

D is a domain and \tilde{D} is a sub-domain. Also we both require locally existence of solutions and uniqueness to ensure the requirement of possible solutions in the sense of proper solutions. Equation (3.12) is not integrable analytically so we follow the analysis above to derive a closed-form power representation

$$S(\zeta) = -3\tau a_3 \zeta^2 + a_3 \zeta^3 - \frac{(1 + \mu^2 \tau) a_3}{4\tau} \zeta^4 + O[\zeta]^5. \tag{3.12a}$$

Again, by converting back a particular solution of (2.5) is written as

$$u(x, t) = -3\tau (t - x)^2 + (t - x)^3 - \frac{(1 + \mu^2 \tau) (t - x)^4}{4\tau}, \tag{3.12b}$$

where we used $a_3 = 1$ for simplicity. It is remarkable that the constant $\eta = (z_i e_0)/(kT)$ does not influence the solution which is completely determined by electrochemical quantities.

In Fig. 6 we show the graphical run of the potential function (3.12b) by assuming suitable values.

Note: By calculating the series one has to solve a nonlinear polynomial system of equations for the series coefficients. In total we get six solutions whereby four of them are of trivial form only. From the remaining two solutions we decided to present one solution. The system is only solvable if we require $a_0 = 0$.

4 The non-classical case I: potential symmetries (PS)

For more technical details we refer to [36–38], respectively. We find it helpful to point out some basic notes: Classical symmetries of a (n)PDE are point transformations (PT) which guarantee the invariance of the solution space. The invariance condition from which solutions follow is given by $D_{\Delta(\eta)}|_{\Delta=0} = 0$, D , means the Fréchet’s derivative.

When describing non-local symmetries it is convenient to introduce a new variable $v(x)$ by additional equations which are connected with the original equations in the variable $u(x)$.

The original system Δ is closely connected to a potential system Ψ so that some properties of Δ are still contained in Ψ .

This definition introduces a potential symmetry as a PT of an auxiliary system, the potential system, $\Psi_n, n \in Z^+$ [36,37]. In case of the mPBE we found the following: The mPBE admits two possible potential systems Ψ_1 and Ψ_2 . Both systems can be formulated for three dependent variables $V_i, i = 1, 2, 3$ and these variables are treated in their derivations w.r.t. the independent variables and are denoted by subscript:

Potential system Ψ_1

$$\begin{aligned}
 u + \frac{\partial V_2}{\partial t} + \tau u - xu_x - x\tau \frac{\partial^2}{\partial x \partial t} &= 0 \\
 x\mu^2 e^{-\eta u} + \frac{\partial V_2}{\partial x} &= 0
 \end{aligned}
 \tag{4.1}$$

Potential system Ψ_2

$$\begin{aligned}
 u + \frac{\partial V_3}{\partial t} + \tau \frac{\partial u}{\partial t} &= 0 \\
 \frac{\partial V_3}{\partial x} + V_1 &= 0 \\
 \mu^2 e^{-\eta u} + \frac{\partial V_1}{\partial x} &= 0
 \end{aligned}
 \tag{4.2}$$

Unlike other evolution equations having two or more potential systems, this case is much unexpected. Calculating the infinitesimals we see that no new potential symmetry occurs:

$$\begin{aligned}
 \xi_1 = k_3 x & \quad \xi_2 = k_1 \\
 \varphi_1 = \frac{2k_3}{\eta} & \quad \varphi_2 = k_2 - \frac{2k_3 t}{\eta}
 \end{aligned}
 \tag{4.3}$$

It is also of interest to compare with the classical case, (3.6). The dimension of the group remains equal and infinite and no new potential symmetry could observe. The unexpected fact however is that the second potential system contains three dependent variables. This behaviour indicates that the second potential system is a second stage potential system derived from a precursor.

5 The non-classical case II: generalized symmetries (GS)

We find it advisable to mention some basic notes. It is obvious from Lie theory that point symmetries are a subset of generalized symmetries [39,40].

The determination of the characteristics for the general case follows by a similar algorithm as in the case of point transformations (PT) in the classical case.

Classical symmetries of any (n)PDE (in general form $\Delta = 0$) are PT as mentioned which guarantee the invariance and so PT are created by infinitesimal transformations.

The determining equations for the characteristics $G S_\alpha$ are consequences of the relation

$$pr\vec{v}_{GS}\Delta|_{\Delta=0} = 0, \quad (5)$$

where $pr\vec{v}_{GS}$ denotes the prolongation of the vector field v_{GS} and GS means generalize symmetry. The main difference however is the fact that in general the characteristics depend on derivatives of an infinite order. If the order is equal to identity we arrive at the so-called contact transformations. By increasing the order of derivatives $n > 1$ we shall find higher order GS.

In case of $n = 1$ for the mPBE, (2.5) we found GS depending on the first derivative:

$$GS_1(x, t, u, u_x, u_t) = -\frac{k_2}{\eta} + (k_1 + k_2x)u_x. \quad (5.1)$$

Here the symmetry differs from the point symmetry given in (3.6). We are confronted with a two-dimensional finite group of transformations where the second part $\partial u/\partial x$ is related to dilatation operations. Obviously, (5.1) represents a contact transformation. During our computer experiments for calculating the case $n = 2$ we observed an enormously long computing time so we were not able to find a closed-form expression.

6 Approximate symmetries

In this section we follow [36,41,42], respectively and our intension is to present new results without referring too much theory. Let us introduce ε as a small parameter measuring the influence of the nonlinear term of the mPBE, (2.5) so that we can write

$$u_{xx} + \tau u_{xt} - \varepsilon(\mu^2 \eta \tau u_t e^{-\eta u}) = 0 \quad \text{with } \varepsilon \neq 0. \quad (6.1)$$

First order approximate symmetries lead to a surprising result

$$\begin{aligned} \xi_1 &= k_1 + [k_5 + (k_6 + k_7x)x]\varepsilon + \frac{x}{2}[(k_8 + k_9u)\eta + (u\eta - 2)k_3x] \\ \xi_2 &= (k_4 + k_9)\tau - (k_2 + k_9)\varepsilon\tau \\ \phi &= k_8 + k_9u + k_3ux + [(k_9 + k_7x)u + k_8]\varepsilon. \end{aligned} \quad (6.2)$$

Here we have another unexpected situation comparing with the symmetries given above.

The order increases to the dimension nine and remains finite. The generating vector fields are deduced to

$$\begin{aligned}
 V_1 &= \partial_x, V_2 = -\varepsilon\tau\partial_t, V_3 = ux\partial_u + \left[\frac{x^2}{2}(u\eta - 2) \right] \partial_x, V_4 = -\tau\partial_t, V_5 = \varepsilon\partial_x, \\
 V_6 &= ux\varepsilon\partial_u + x^2\varepsilon\partial_x, V_7 = x\varepsilon\partial_x, V_8 = (1 + \varepsilon)\partial_u + \frac{x\eta}{2}\partial_x, \\
 V_9 &= (u + u\varepsilon)\partial_u + \frac{ux\eta}{2}\partial_x + \tau(1 - \varepsilon)\partial_t,
 \end{aligned}
 \tag{6.3}$$

and the associated coefficients of these vector field herein are calculated

$$\begin{aligned}
 &\{(1, 0), (0)\}, \quad \{(0, -\varepsilon\tau), (0)\}, \quad \left\{ \left(\frac{x^2}{2}(u\eta - 2), 0 \right), (ux) \right\}, \quad \{(0, -\tau), (0)\}, \\
 &\{(\varepsilon, 0), (0)\}, \quad \{(x\varepsilon, 0), (0)\}, \quad \left\{ \left(x^2\varepsilon, 0 \right), (ux\varepsilon) \right\}, \quad \left\{ \left(\frac{x\eta}{2}, 0 \right), (1 + \varepsilon) \right\}, \\
 &\left\{ \left(\frac{ux\eta}{2}, -\tau(1 - \varepsilon) \right), (u(1 + \varepsilon)) \right\}.
 \end{aligned}
 \tag{6.4}$$

In total we have 28 possible combinations of the vector fields. Possible reductions can be calculated by combining several sub-groups, e.g. that is $V_l \otimes V_m \otimes V_n$ with $\{l, m, n\} = 1, 2, \dots, 9$.

Most of the cases belong to non-solvable cases; we have only three possibilities to generate new solutions. We summarize all possibilities including the nonlinear transformation both for the similarity variable as well as the similarity function and the related nODEs which have to be solved:

Case A: $t + x(1 + \varepsilon)\tau = \zeta, u = S$, derived by the combination $V_1 \otimes V_2 \otimes V_4$,

$$e^{\eta S}(1 + \varepsilon^2) \left(\tau^2 \left(\frac{d^2 S}{dS^2} + \tau \frac{d^3 S}{dS^3} \right) \right) - \varepsilon\mu^2 \frac{dS}{dS} = 0, \quad \varepsilon \neq 0. \tag{6.5}$$

Case B: $t + \frac{\varepsilon x\tau}{1 + \varepsilon} = \zeta, u = S$, derived by the combination $V_1 \otimes V_2 \otimes V_5$,

$$\varepsilon \left(-(1 + \varepsilon)^2 \eta \mu^2 \frac{dS}{d\zeta} + e^{\eta S} \left(\varepsilon\tau \left(\tau \frac{d^2 S}{d\zeta^2} + \frac{d^3 S}{d\zeta^3} \right) \right) \right) = 0, \quad \varepsilon \neq 0. \tag{6.6}$$

Case C:

$$t + \frac{x\tau}{1 + \varepsilon} = \zeta, u = S, \text{ derived by the combination } V_1 \otimes V_4 \otimes V_5, \tag{6.7}$$

the governing nODE is the same as above.

Let us discuss for example the highly nODE, (6.5) in lowest perturbation order, that is $\varepsilon = 1$.

For the (6.5) we have the following basic assumptions $S : R \times R \rightarrow R$, $\zeta \in R$, $-\infty \leq \zeta \leq \infty$, $D := \{(S, \zeta) \in \tilde{D} : S \neq 0, S' \neq 0, S'' \neq 0, S''' \neq 0\}$, where D is a domain and \tilde{D} is a sub-domain.

We both require locally existence of solution(s) and uniqueness to ensure the requirement of possible solutions in the sense of proper solutions.

Equation (6.5) is not integrable analytically so we follow the analysis above.

It is stressed that, depending upon the solution-manifold of the nonlinear algebraic system for the series coefficients a_i in the power series, we have two possibilities to perform the series coefficients. Therefore a closed-form representation valid up to order four is given by

$$S_1(\zeta) = a_1\zeta + \left\{ \frac{\varepsilon\mu^2 a_1}{2(1+\varepsilon^2)\tau^2} - 3\tau a_3 \right\} \zeta^2 + a_3\zeta^3 - \frac{\{(3a_1a_3 + \eta a_1^2(a_2 + 3\tau a_3)) - 2a_2(a_2 + 3\tau a_3)\}}{12\tau a_1} \zeta^4 + O[\zeta]^5. \quad (6.8)$$

$$S_2(\zeta) = -3\tau a_3\zeta^2 + a_3\zeta^3 - \frac{\{(\varepsilon\mu^2 + \tau + \varepsilon^2\tau) a_3\}}{4\{(1+\varepsilon^2)\tau^2\}} \zeta^4 + O[\zeta]^5. \quad (6.8a)$$

For later calculations power series representations are always useful, however by considering approximate symmetries we only need the series up to order two. Since the solutions depend quadratic on ε we have to expand the result up to order two in ε around $\varepsilon = 0$.

Surprisingly, both expressions have the same solution in lowest order approximation e.g., that is by converting back

$$u(x, t) = 3t\tau(t - 2x) - 3x^2\tau^3. \quad (6.8b)$$

This approximate solution is also seen in Fig. 7 as a three-dimensional surface representations where reasonable values were used.

Note: Following the EQS assumption a suitable value for τ in all calculations is $\tau \approx 10^{-7}$.

It is proven that the function tends to infinity as $x \rightarrow \infty$ and $t \rightarrow \infty$. The behaviour to approach the regular point (0, 0) means $\lim_{x \rightarrow 0, t \rightarrow 0} u(x, t) \rightarrow \{3t^2\tau, -3x^2\tau^3\}$ by calculating one after another limit.

Consider, e.g. that the solution approaches at the regular point (0, 1) by different directions.

Then it is proven, that the values differ depending from the direction, that is $-3a^3$ and $3a$, $\forall a \in R$.

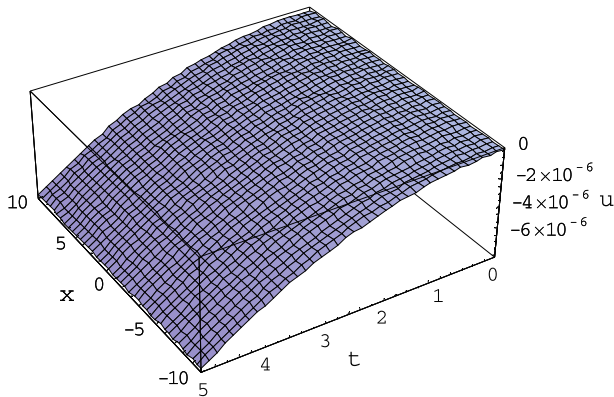


Fig. 7 A three-dimensional surface plot of the approximate solution function, (6.8b). A small bend influenced by the quadratic polynomial contribution is remarkable. For large values of the arguments the function tends to infinity for $x \rightarrow \infty$ and $t \rightarrow \infty$. By approaching the regular point $(0, 1)$ two different real values could found

7 Conclusion, outlook and further intensions

The present project consists of three parts: The first part which is given in the underlying paper deals with a new nPDE which can be interpreted as an extension of the usual DHT.

The new benefit is that we are able to admit time dependence explicitly without any assumptions of electrodynamical statements relating to time-dependent processes called time retardation.

As soon as there is any time dependence we have to use the full ME with all their complexity.

Time retardation is a fundamentally important and also a complicating feature. Even if the effect is small it will not vanishing which makes the theory unnecessarily complicated. The model under consideration is also suitable both for low frequency electrodynamics and the transition from statics to electrodynamics (the Laplacian in the DHT is from elliptic type and therefore time-independent).

Therefore the quasistatic limit in the ME is a kind of $c \rightarrow \infty$ limit obtained by neglecting time retardation.

The nPDE derived from the EQS is now recognized as a ‘modified Poisson-Boltzmann Equation’ (mPBPE) and is mathematically a nonlinear partial differential equation of the third-order.

By applying the model we have to assume the same restrictions as in the DHT cited in Sect. 2. Moreover both the time relaxation and electric conductivity is also restricted to certain electrolytes and electrode materials.

Firstly we determine the classical Lie point symmetries and a complete group characterization including algebraic properties is given. The nPDE (2.5) under consideration admits an infinite three-dimensional symmetry group of point transformations allowing a similarity reduction to deduce suitable solutions.

We deduce the similarity variable ζ and the determining equation for the similarity function $S(\zeta)$ for the classical case. These complicate nODEs are solved in an approximate way by using suitable series representations. We further study the non-classical case relating to potential symmetries. We showed that two potential systems exist but no new symmetries occur. We identify the second potential system as a second stage potential.

The nPDE further admits generalized symmetries which differ from that in the classical case.

In addition, approximate symmetries are also suitable to generate suitable solutions.

The approximate symmetry behaviour differs completely from the classical case so we are led to study only three solvable cases from practical importance.

We refer to the fact that all nODEs derived by a similarity reduction from the origin nPDE are solved by numerical standard procedures.

In the second part we shall show that the nPDE, (2.5) 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 shall not need any numerical methods although the nPDE, (2.5) under consideration is highly nonlinear in the potential.

The last part of the project will deal with suitable electrochemical experiments such like impedance spectroscopy so we shall prove the model under consideration.

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