

# Unsteady analytical solutions to the Poisson–Nernst–Planck equations

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Received 22 March 2012, in final form 26 September 2012

Published 29 October 2012

Online at [stacks.iop.org/JPhysA/45/455204](http://stacks.iop.org/JPhysA/45/455204)

## Abstract

It is shown that the Poisson–Nernst–Planck equations for a single ion species can be formulated as one equation in terms of the electric field. This previously not analyzed equation shows similarities to the vector Burgers equation and is identical with it in the one dimensional case. Several unsteady exact solutions for one and multidimensional cases are presented. Besides new mathematical insights which these first known unsteady solutions give, they can serve as test cases in computer simulations to analyze numerical algorithms and to verify code.

PACS numbers: 02.30.Jr, 82.45.Gj

(Some figures may appear in colour only in the online journal)

## 1. Introduction

More than 120 years ago, Nernst [1] and Planck [2] found the proper mathematical description for a process which we call electrodiffusion, but the mathematical analysis of the Poisson–Nernst–Planck (PNP) equations is still far from complete. In full 3D space only the steady equations and the long time behaviour of unsteady solutions have been examined in terms of existence, stability and uniqueness, see e.g. [3]. For the 1D case some deeper insights into the structure of solutions were gained. Especially the steady two species system was studied qualitatively in [4] and static solutions for such a system with insulating (zero flux) boundary conditions have been derived in [5]. Further, unsteady solutions for the linearized equations were found [6]. To our knowledge, there is no publication known to give explicit unsteady solutions to the full (nonlinear) PNP system.

In this paper the analysis of the single species PNP system and the resulting unsteady solutions serve mainly two purposes: first, to contribute to the mathematical analysis by showing the connections between the PNP system and an equation similar (in 1D identical) to Burgers equation; second, to present a set of explicit unsteady solutions which can be

used in a test suite for the analysis and verification of numerical codes. The second point seems especially important if one looks at the (currently inevitable) procedure for unsteady numerical tests, where the original PNP equations need to be modified to result in a previously constructed, artificial solution, see e.g. [7].

The rest of the paper is organized as follows. In section 2 we give a short introduction to the PNP equations. In section 3 we perform the analysis of the single species system, whereas the boundary conditions are discussed in section 4. The 1D case is investigated in section 5, where also several exemplary solutions are given. The construction of 2D/3D solutions out of 1D solutions is discussed in section 6. In section 7 some comments on the spherical symmetric case can be found. Section 8 gives the conclusions.

## 2. The PNP model

Ions drifting through a static solvent can be described by the PNP system, consisting of the Nernst–Planck equation (stating the conservation of mass)

$$\frac{\partial n_i}{\partial t} + \nabla \cdot \mathbf{F}_i = 0 \quad (1)$$

with the ion flux

$$\mathbf{F}_i = -D_i (\nabla n_i + z_i n_i \nabla \phi), \quad (2)$$

and the Poisson equation

$$\nabla \cdot (\epsilon \nabla \phi) = -\frac{e^2 n^*}{\epsilon_0 k T} \sum_i z_i n_i. \quad (3)$$

$n_i$  is the relative concentration (with respect to a scaling concentration  $n^*$ ),  $z_i$  is the valence and  $D_i$  the (possibly position dependent tensorial) diffusion coefficient of the ion species  $i$ .  $\phi$  is the relative electric potential energy with respect to the thermal energy ( $\phi = eU/kT$  with  $U$  in Volts, for room temperature  $\phi = 1$  corresponds to about 25 mV).  $\epsilon$  is the relative permittivity (which again may be position dependent and tensorial) and  $T$  is the temperature of the solvent.

Equations (1) and (3) constitute a nonlinear system of  $i + 1$  partial differential equations. Equation (3) is of elliptic type, while (1) by itself represents a system of  $i$  uncoupled advection–diffusion equations with the variable advective velocity field  $\mathbf{v}_i = -D_i z_i \nabla \phi$ .

## 3. The single species system

If we only consider a single ion species (with concentration  $n$  and valence  $z$ ) and further assume the diffusion coefficient as well as the relative permittivity to be spatially independent and isotropic, we can write the system (1) and (3) as

$$\frac{\partial n}{\partial t} = D \nabla \cdot (\nabla n + zn \nabla \phi) \quad (4)$$

$$\Delta \phi = -\frac{zn}{\lambda^2} \quad (5)$$

with the characteristic length scale

$$\lambda = \sqrt{\frac{\epsilon \epsilon_0 k T}{e^2 n^*}}.$$

For a monovalent species ( $|z| = 1$ ) the right-hand side of (5) is directly connected to the Debye length  $\lambda_{\text{Deb}}^2 = \lambda^2 / \sum_i z_i^2 n_i$ , therefore we have  $\Delta \phi = -1/(z \lambda_{\text{Deb}}^2)$ .

With the scaling of length and time coordinates through the introduction of dimensionless variables  $\mathbf{x} = \mathbf{r}/\lambda$  (where  $\mathbf{r}$  is the original space variable) and  $\tau = tD/\lambda^2$  in (4) and (5) we get

$$\frac{\partial n}{\partial \tau} = \nabla \cdot (\nabla n + zn\nabla\phi) \quad (6)$$

$$\Delta\phi = -zn. \quad (7)$$

Introducing the electric field  $\mathbf{E} = -\nabla\phi$ , equation (7) reads

$$\nabla \cdot \mathbf{E} = zn. \quad (8)$$

If we use (8) to eliminate  $n$  from (6) and use the equality of mixed partials for  $\mathbf{E}$  (this equality relies on the existence and continuity of the respective mixed derivatives of  $\mathbf{E}$ , which translates with (8) to the existence and continuity of  $\partial n/\partial t$ ) we can integrate (6) once in space and arrive at

$$\frac{\partial \mathbf{E}}{\partial \tau} = \nabla \nabla \cdot \mathbf{E} - z\mathbf{E}(\nabla \cdot \mathbf{E}) + \nabla \times \mathbf{G}, \quad (9)$$

where the last term  $\nabla \times \mathbf{G}$  is a gauge field with an arbitrary and possibly time dependent vector field  $\mathbf{G}(\mathbf{x}, \tau)$  (resulting from the spatial integration). With the transformations

$$\mathbf{E}' = -z\mathbf{E} \quad \text{and} \quad \mathbf{G}' = -z\mathbf{G} \quad (10)$$

plus the fact that  $\mathbf{E}$  is a conservative field by definition (so we can use the fact that  $\nabla \nabla \cdot \mathbf{E} = \nabla \cdot \nabla \mathbf{E} = \Delta \mathbf{E}$ ), equation (9) reduces to

$$\frac{\partial \mathbf{E}'}{\partial \tau} = \Delta \mathbf{E}' + \mathbf{E}'(\nabla \cdot \mathbf{E}') + \nabla \times \mathbf{G}'. \quad (11)$$

Even for a vanishing source term  $\nabla \times \mathbf{G}'$ , this is unfortunately not the vector Burgers equation, since  $\mathbf{E}'(\nabla \cdot \mathbf{E}') \neq (\mathbf{E}' \cdot \nabla)\mathbf{E}'$ . Therefore the vectorial extension of the classical Hopf–Cole transformation is of no use here. Although no comparable general solution procedure is outlined in this work, we present several exact solutions to (11) in the following sections. There were found no further references to equations like (11) in the literature.

## 4. Boundary conditions

### 4.1. Nernst–Planck equation

On the boundary  $\partial\Omega$  of the considered domain  $\Omega$ , a condition for the ion flux (2) may be given for the Nernst–Planck equation (1) through specification of the (possibly time dependent) normal component of the ion flux  $\mathbf{F}$  over the boundaries, i.e.  $\mathbf{n} \cdot \mathbf{F} = f(\tau)$ . Translated to our new variable  $\mathbf{E}'$  the condition reads

$$\mathbf{n} \cdot (\partial \mathbf{E}' / \partial \tau - \nabla \times \mathbf{G}') = f(\tau) \quad \text{on } \partial\Omega. \quad (12)$$

We distinguish two relevant cases. The first one is a zero flux (or closed) system,  $f = 0$ . The second one is an in or outflow condition  $f \neq 0$  (corresponding to an electric current with regard to a given boundary surface). With respect to the concentration  $n$  the flux condition is indeed a Robin boundary condition (i.e. a weighed combination of Dirichlet and Neumann boundary conditions) as can be seen from (2).

### 4.2. Poisson equation

For the Poisson equation (3), a Dirichlet boundary value has to be prescribed at at least one point on  $\partial\Omega$ , since the potential is only defined up to a spatial constant. Apart from that either Dirichlet or Neumann conditions can be prescribed.

### 4.3. Conditions for analytic solutions

Normally, analytic solutions are given on an unbounded domain. If we therefore choose a boundary  $\partial\Omega$ , the solution itself defines the boundary condition type and its values on  $\partial\Omega$ . Depending on the solution, the construction of different boundary conditions is possible and will be discussed in the given examples below.

## 5. Solutions in the 1D case

In one space dimension (11) reads

$$\frac{\partial E'}{\partial \tau} = \frac{\partial^2 E'}{\partial x^2} + E' \frac{\partial E'}{\partial x} + g(\tau), \quad (13)$$

where  $g(\tau)$  is the (spatially independent) 1D remnant of the gauge field  $\nabla \times \mathbf{G}'$ . With the transformations (cf [8])

$$\eta = E' - \int_{\tau_0}^{\tau} g(\bar{\tau}) \, d\bar{\tau} =: E' - \Gamma(\tau) \quad (14)$$

$$y = x + \int_{\tau_0}^{\tau} (\tau - \bar{\tau}) g(\bar{\tau}) \, d\bar{\tau} =: x + \gamma(\tau) \quad (15)$$

we arrive at the classical (scalar) Burgers equation

$$\frac{\partial \eta}{\partial \tau} = \frac{\partial^2 \eta}{\partial y^2} + \eta \frac{\partial \eta}{\partial y}. \quad (16)$$

From the physical point of view, the transformations (14) and (15) describe the action of an external, spatially constant (but possibly time dependent) electric field  $\Gamma$  which moves the ions through space (done by the shift  $\gamma$  in the spatial coordinate).

One family of solutions to (16) can be found through the well-known Hopf–Cole transformation

$$\eta = 2 \frac{\partial}{\partial y} (\ln \psi) = \frac{2}{\psi} \frac{\partial \psi}{\partial y}, \quad (17)$$

resulting in the heat equation

$$\frac{\partial \psi}{\partial \tau} = \frac{\partial^2 \psi}{\partial y^2}. \quad (18)$$

Note that from the definition of  $E'$  in 1D ( $E' = z \partial \phi / \partial x$ ) we have

$$\phi(x, \tau) = \frac{1}{z} [2 \ln \psi(x + \gamma, \tau) + x\Gamma] + \phi_0(\tau), \quad (19)$$

with an arbitrary function  $\phi_0(\tau)$ . Finally, the concentration is given by

$$n(x, \tau) = -\frac{2}{z^2} \frac{\partial^2}{\partial x^2} [\ln \psi(x + \gamma, \tau)].$$

The flux boundary condition (12) for the Nernst–Planck equation translates with (14) to

$$\partial \eta / \partial \tau = f(\tau) \quad \text{on } \partial\Omega. \quad (20)$$

Given one of the several solutions to (18), we can now construct solutions to the Poisson–Nernst–Planck system.

### 5.1. Examples in 1D

The given examples below refer to the system (6) and (7), the solutions are therefore given as  $n(x, \tau)$  and  $\phi(x, \tau)$ .

*5.1.1. Spatially homogeneous outflow.* The simplest possible example is that of a spatially homogeneous evolution of the concentration, i.e.  $n = n(\tau)$ . Although we could derive even this result with the help of the formalism developed in the previous sections, it is easier to deduce from (8) that in this case the electric field must have the form  $E = zn$ . From the definition of  $E$  and (6) then follows the ODE  $dn/d\tau = -z^2n^2$  which has the solution

$$n(\tau) = \frac{1}{\theta + \tau},$$

with an arbitrary constant  $\theta$ . The solution describes a symmetric flow away from  $x = 0$ . The respective potential is

$$\phi(x, \tau) = -\frac{z}{2}n(\tau)x^2 + \phi_0(\tau) = -\frac{z}{2} \frac{x^2}{\theta + \tau} + \phi_0(\tau). \quad (21)$$

This example is well suited as a simple numerical test. We start at  $\tau = 0$  with a constant concentration  $n(0) = 1/\theta$  as the initial condition. Setting one boundary at  $x = 0$ , we define a closed (no flux) boundary there, since the flux is given as  $F(x, \tau) = z^2n^2(\tau)x$ . At the second boundary, say  $x = x_0$ , we then just have to set the (time dependent) outflow condition  $f(\tau) = z^2n^2(\tau)x_0$  (cf section 4)<sup>1</sup>. For the potential  $\phi$  there are two possible boundary condition settings which produce the same result (up to a free constant): we could either use the values of (21) at both boundaries for a Dirichlet condition, or we set  $\phi$  to an arbitrary value at  $x_0$  (say,  $\phi(x_0, \tau) = 0$ ) and use the Neumann zero condition at  $x = 0$  ( $\partial\phi/\partial x|_0 = 0$ ) which is an inherent property of the solution (21).

*5.1.2. Closed system.* In this more advanced examples we describe the full formalism needed to construct an analytic solution. At first, we have to choose a solution for (18), in this example it reads (cf [9] for an extensive list)

$$\psi(y, \tau) = e^{-C^2\tau} \sin(Cy + A) + B, \quad (22)$$

where  $A, B, C$  are free parameters. Then we can use (17) to find the respective solution  $\eta(y, \tau)$  to the Burgers equation (16). Choosing  $g = 0$  in (13) reduces (14) and (15) to  $E' = \eta$  and  $x = y$ . Using (10) we get the electric field

$$E(x, \tau) = -\frac{2C}{z} \frac{\cos(Cx + A)}{Be^{C^2\tau} + \sin(Cx + A)}. \quad (23)$$

With (8), the solution for the concentration then is

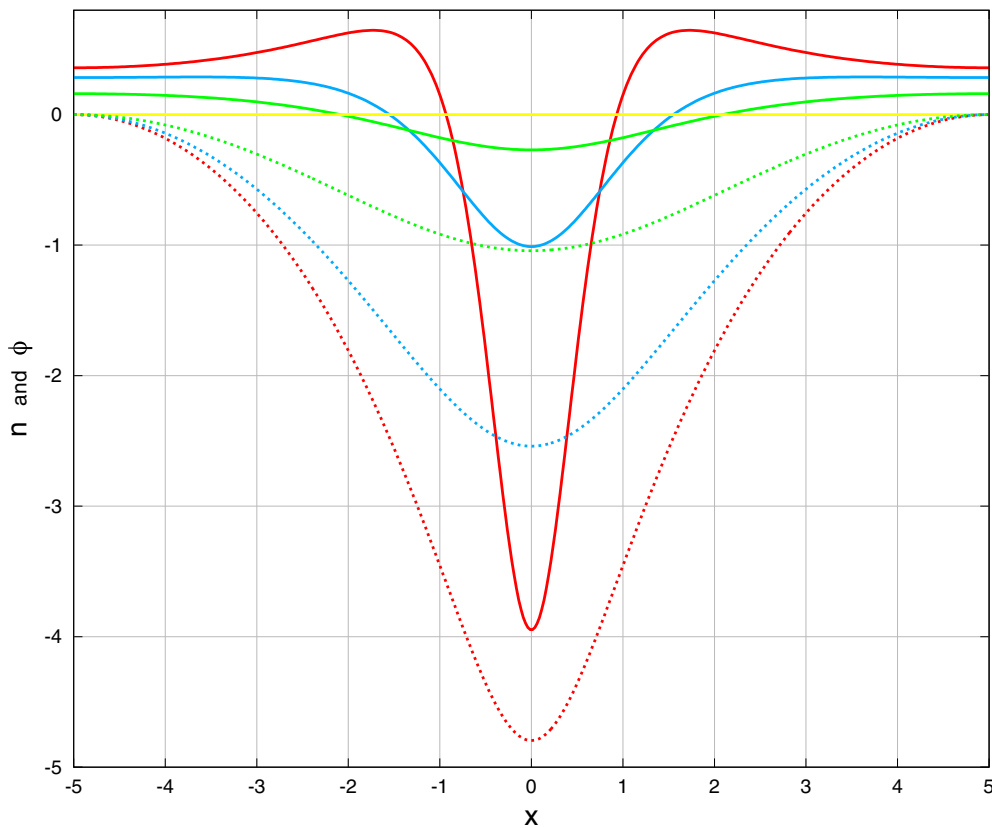
$$n(x, \tau) = \frac{2C^2}{z^2} \frac{1 + Be^{C^2\tau} \sin(Cx + A)}{[Be^{C^2\tau} + \sin(Cx + A)]^2}, \quad (24)$$

and the potential is given with (22) and (19) as

$$\phi(x, \tau) = \frac{2}{z} \ln[e^{-C^2\tau} \sin(Cx + A) + B] + \phi_0(\tau). \quad (25)$$

This solution is periodic in space with the period  $P := 2\pi/C$ . Further, it has the zero flux property (cf section 4) at  $x^0(j) = (\pi j - A + \pi/2)/C$ ,  $j \in \mathbb{Z}$ . Therefore we get a closed (insulated) system, if the boundaries are positioned at two of these zero flux points. The distance between two consecutive  $x^0$  is  $P/2$ . For  $B \leq 1$  the solution has singularities. For  $B > 1$  there always exist regions where  $n < 0$  (if a full spatial period is considered), meaning that the ions behave like oppositely charged particles in those regions. Even if this property appears strange from a physical perspective, it causes no problems if we want to use this

<sup>1</sup> From the point of view of a numerical test it is more convenient here to prescribe Neumann zero conditions for  $n$  at all boundaries.



**Figure 1.** The concentration (24) and the potential (25) for the closed system example.  $n(x, \tau)$  (solid lines) and  $\phi(x, \tau)$  (dotted lines) are shown for  $\tau = 0$  (red), 1 (blue), 3 (green) and 10 (yellow).

example as a numerical test (except numerical schemes which rely on the positivity of  $n$ , of course); there is no mathematical reason for  $n$  to be strictly positive. Since  $n$  can be negative, it is possible that the total charge  $Q$  between two arbitrary zero flux points  $x_{1,2}^0 = x^0(j_{1,2})$  is zero. It is the case here, because from (8) and (23) we find  $Q$  to be proportional to

$$z \int_{x_1^0}^{x_2^0} n(x, \tau) dx = E(x_2^0, \tau) - E(x_1^0, \tau) = 0.$$

As a numerical example, the choice  $A = -0.5\pi$ ,  $B = 1.2$ ,  $C = 0.2\pi$  covers a full period between the zero flux points  $x^0(\pm 1) = \pm 5$ . If these positions are chosen as boundaries, the example presents a closed system with vanishing total charge. The concentration and the potential are depicted in figure 1, where  $\phi_0(\tau)$  is chosen such that  $\phi(\pm 5, \tau) = 0$ .

**5.1.3. Pure advection.** We give another example, where an otherwise stationary solution is advected through space with constant velocity. If  $\psi$  is given as a simple product of space and time dependence,  $\eta(y)$  does not depend explicitly on time, cf (17), (but possibly implicitly through  $y$ ). From the linear combination of two basic solutions to (18) given by

$\psi(y, \tau) = \exp(A^2\tau \pm Ay)$  we can therefore construct a stationary solution  $\eta(y)$  to (16) with the use of (17)

$$\eta(y) = 2A \tanh(Ay). \tag{26}$$

To give an example for the usage of the gauge field  $g(\tau)$ , i.e. the inclusion of an external electric field, we choose the simple case of a delta distribution  $g(\tau) = -v\delta(\tau)$  with a constant  $v$ . From (14) and (15) (with  $\tau_0=0$ ) we get the external field<sup>2</sup>  $\Gamma = -v$ , the shift  $\gamma = -v\tau$  and therefore  $y = x - v\tau$ . The electric field then reads

$$E(x, \tau) = -\frac{1}{z}[2A \tanh(A(x - v\tau)) - v].$$

With (8), the concentration is

$$n(x, \tau) = -\frac{2A^2}{z^2}[1 - \tanh^2(A(x - v\tau))]. \tag{27}$$

The concentration profiles are advected through space with the velocity  $v$ . The potential is given with (19) as

$$\phi(x, \tau) = \frac{1}{z}[2 \ln \cosh(A(x - v\tau)) - xv] + \phi_0(\tau). \tag{28}$$

For  $x \rightarrow \pm\infty$  the potential becomes asymptotically linear with the slope  $(\pm 2A - v)/z$ . The concentration profiles are kept ‘in shape’ due to electric forces (proportional to  $\nabla\phi$ ) at the domain boundaries, in contrast to the vanishing boundary forces in the previous example (section 5.1.2) where the profiles flattened out with time. Regarding the negativity of the concentrations ( $n(x, \tau) < 0$  everywhere) we refer to the comments from the previous section 5.1.2.

In figure 2 the concentration and the potential are shown with  $A = v = 1$  in the interval  $[-3, 5]$ , where  $\phi_0(\tau)$  is chosen such that  $\phi(5, \tau) = 0$  and the other Dirichlet boundary value  $\phi(-3, \tau)$  is then computed according to (28). Boundary conditions for  $n$  may be specified directly as Dirichlet with values from (27), or as flux conditions with  $f(\tau)$  calculated from (20) and (26).

## 6. Solutions in the 2D/3D case

### 6.1. Construction from 1D solutions

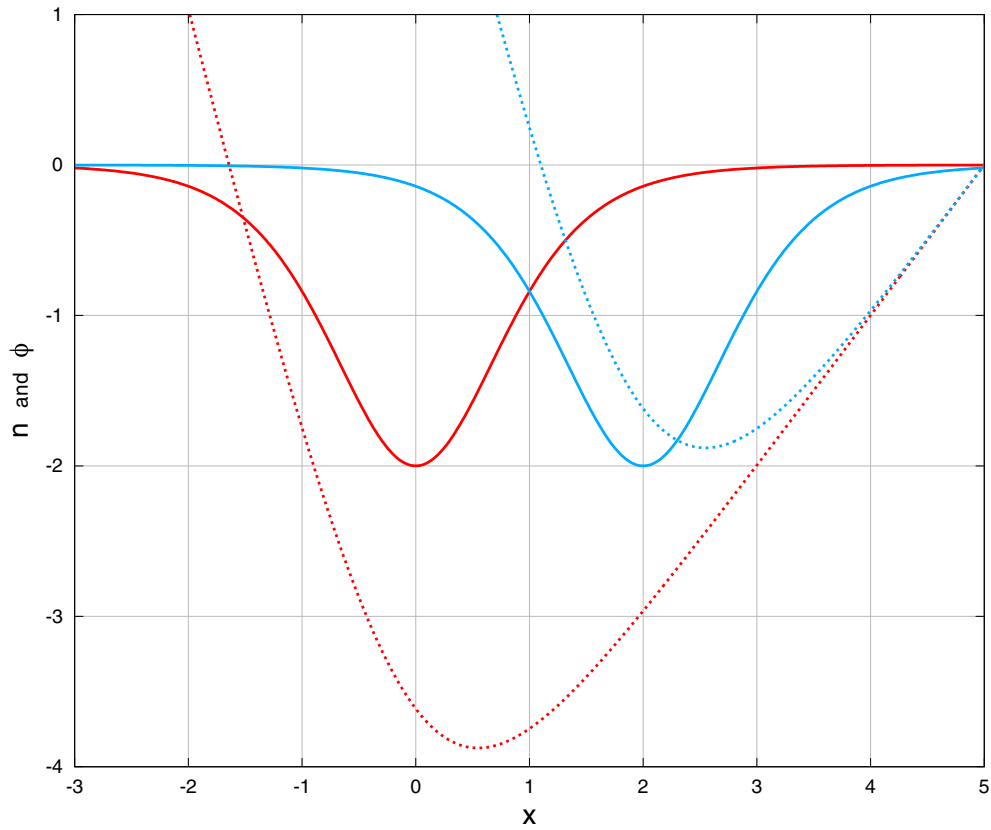
Looking back at (11), it is clear that for multidimensional problems in Cartesian coordinates the only coupling between the different dimensions (coordinate directions) comes from the divergence term  $\nabla \cdot \mathbf{E}'$ . This gives the opportunity to construct one family of solutions in 2D/3D from the 1D solutions. Assuming that the solution  $\mathbf{E}'$  is identical in each dimension and these identical components are denoted by  $\tilde{E}'$ , it follows immediately from the form of the divergence in  $N$ -dimensional Cartesian space, that (11) can be written for each component as

$$\frac{\partial \tilde{E}'}{\partial \tau} = \frac{\partial^2 \tilde{E}'}{\partial x^2} + N\tilde{E}' \frac{\partial \tilde{E}'}{\partial x} + \tilde{g}(\tau).$$

(The gauge field also needs identical components  $\tilde{g}$ , of course.) Under these special assumptions equation (11) has indeed the same structure as the vector Burgers equation. With a transformation similar to (10)

$$E' = N\tilde{E}' \quad \text{and} \quad g = N\tilde{g}$$

<sup>2</sup> This simplest example of a gauge transformation represents indeed one of the symmetry groups for the solutions to (16).



**Figure 2.** The concentration (27) and the potential (28) for the pure advection example.  $n(x, \tau)$  (solid lines) and  $\phi(x, \tau)$  (dotted lines) are shown for  $\tau = 0$  (red) and 2 (blue).

we then produce equation (13) again. Therefore, every solution in 1D (see section 5.1) can be used to construct new solutions in 2D/3D!

Assuming the  $N$ -dimensional space vector is denoted by  $\mathbf{x}$  with Cartesian components  $x_k$ , ( $k = 1, \dots, N$ ) and the 1D solution is given (e.g. like in section 5.1.2 with (22) as  $\psi(x, \tau)$ , (23) as  $E(x, \tau)$  and (24) as  $n(x, \tau)$ ). Then the electric field  $\mathbf{E}$  has the components  $E_k = E(x_k, \tau)/N$ , and the concentration is given as

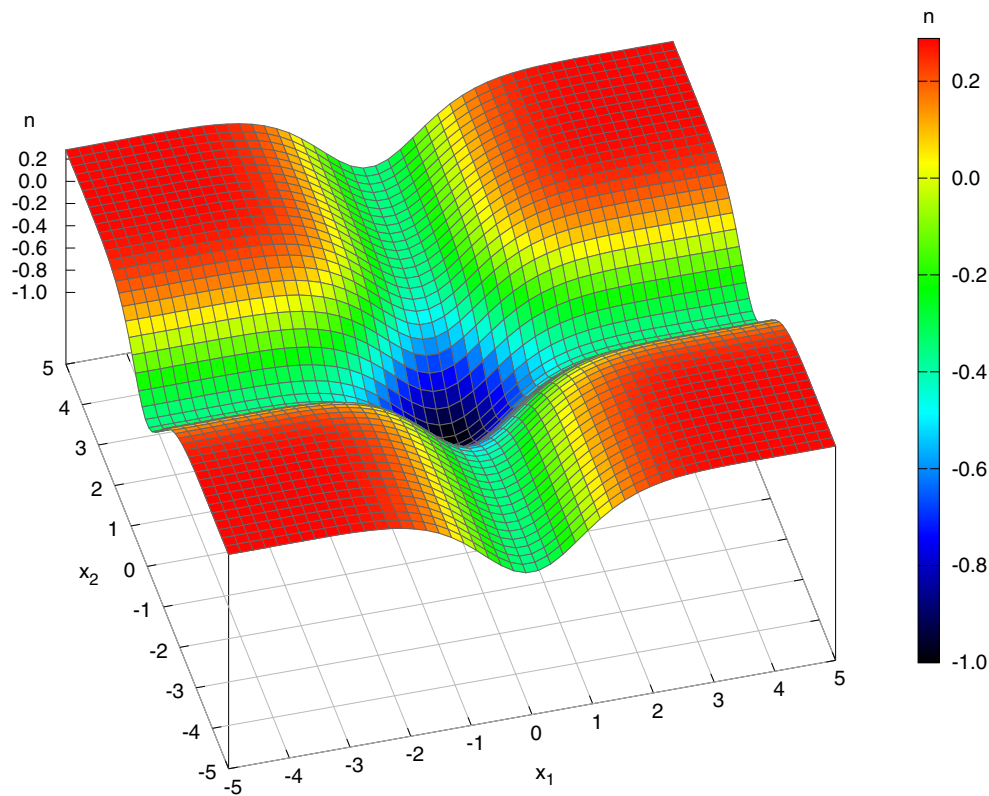
$$n(\mathbf{x}, \tau) = n(x_1, \dots, x_N, \tau) = \frac{1}{N} \sum_{k=1}^N n(x_k, \tau), \tag{29}$$

and analogous the potential reads

$$\phi(\mathbf{x}, \tau) = \phi(x_1, \dots, x_N, \tau) = \frac{1}{N} \sum_{k=1}^N \phi(x_k, \tau). \tag{30}$$

The concentration and the potential for the closed system example (cf section 5.1.2, with the same numerical values  $A, B, C$ ) are shown in 2D in figures 3 and 4.





**Figure 3.** The concentration (29) for the closed system example in 2D.  $n(\mathbf{x}, \tau) = n(x_1, x_2, \tau)$  is shown for  $\tau = 1$ .

### 6.2. Other cases equivalent to Burgers equation

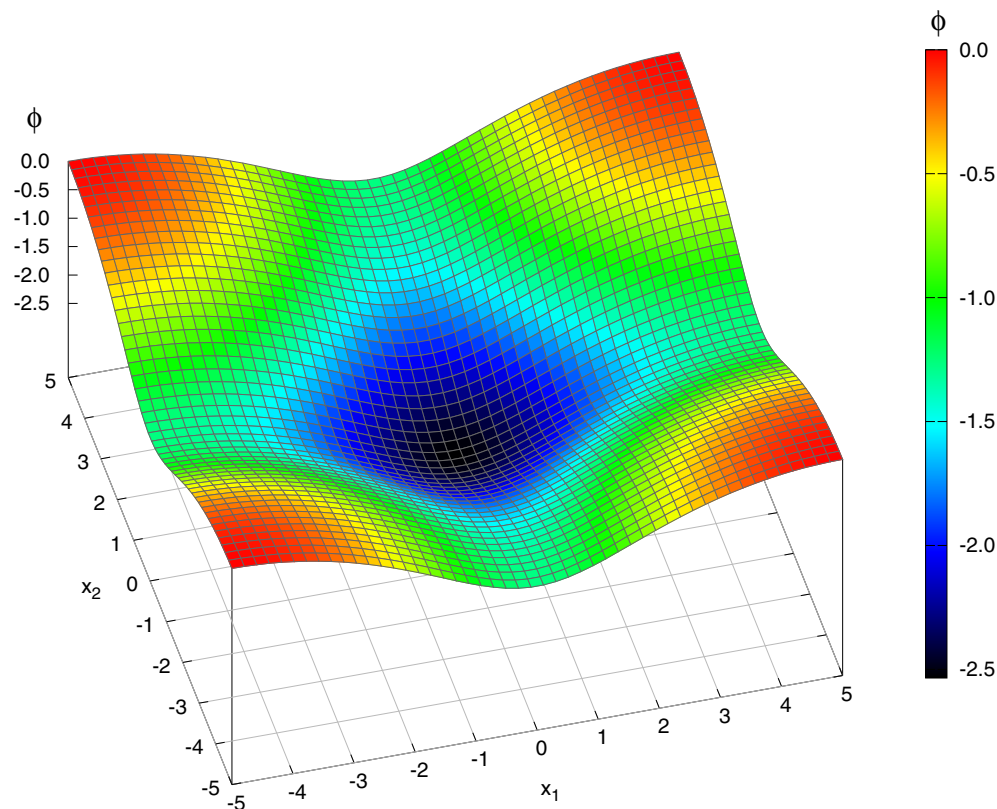
As in the case we have just examined, certain assumptions about the solutions to (11) will lead to a formal equivalence of (11) and the vector Burgers equation. Another such example occurs if the electric field  $\mathbf{E}$  has only one direction but its absolute value  $E$  may vary arbitrarily in space, i.e. (again in Cartesian coordinates)  $\mathbf{E}(\mathbf{x}) = (E(\mathbf{x}), 0, 0)$ . But this case has no physical relevance for our problem since this field is only conservative (i.e. can be written as  $\nabla\phi$ ) if it depends exclusively on  $x_1$  (the coordinate of the field direction). But this is nothing else but the 1D case again.

### 7. Spherical symmetric case

Equation (11) written in spherical coordinates, assuming spherical symmetry (i.e. the angular components are zero), is given as

$$\frac{\partial E'_r}{\partial \tau} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial E'_r}{\partial r} \right) - \frac{2E'_r}{r^2} + \frac{E'_r}{r^2} \frac{\partial}{\partial r} (r^2 E'_r) + \frac{g(\tau)}{r^2}, \quad (31)$$

where  $E'_r$  is the radial component of the electric field and  $r$  is the radius. The gauge field  $g(\tau)/r^2$  is restricted to the given radial dependency (since it has to be divergence free).



**Figure 4.** The potential (30) for the closed system example in 2D.  $\phi(\mathbf{x}, \tau) = \phi(x_1, x_2, \tau)$  is shown for  $\tau = 1$ .

A dimensional analysis shows that there exists a family of self-similar solutions to (31), i.e. the equation is invariant under the following scaling transformation:

$$E'_r(r, \tau) = \tau^{-1/2}H(s) \quad \text{and} \quad s = \tau^{-1/2}r. \tag{32}$$

This is only possible if we set  $g(\tau) = \tau^{-1/2}g_0$  with an arbitrary constant  $g_0$ . Introducing (32) into (31) we arrive at an ODE which can be further reduced by the transformation  $H(s) = [K(s) + g_0]/s^2$  resulting

$$\frac{d^2K}{ds^2} + \left( \frac{K + g_0}{s^2} - \frac{2}{s} + \frac{s}{2} \right) \frac{dK}{ds} - K = 0. \tag{33}$$

Several analytic methods to solve (33) fail and a Lie-group analysis (to find possible hidden symmetries) yielded no useful results. But the reduction to an ODE offers at least simpler and independent ways to produce numerical solutions to the problem.

### 7.1. The limit $s \gg 1$

Additionally, we consider the limit  $s \gg 1$  for (33). Recalling (32), this condition translates to  $r \gg \sqrt{\tau}$ , meaning ‘for large (and with time increasingly larger) radii’. In this limit the bracket

in (33) reduces to  $s/2$  (provided  $K$  is bounded by  $s^2$  for  $s \rightarrow \infty$ , which is valid if  $E'_r$  does not diverge for  $r \rightarrow \infty$ ) and we obtain the linear ODE

$$\frac{d^2K}{ds^2} + \frac{s}{2} \frac{dK}{ds} - K = 0. \tag{34}$$

The general solution of (34) is given by the linear combination

$$K = A \left( \sqrt{\pi} \left[ \frac{s^2}{2} + 1 \right] [1 - \operatorname{erf}(s/2)] - s e^{-s^2/4} \right) + B \left( \frac{s^2}{2} + 1 \right), \tag{35}$$

with free constants  $A$  and  $B$  and the error function  $\operatorname{erf}(x)$ . The first term  $A(\dots)$  in (35) decreases to zero exponentially for  $s \rightarrow \infty$ . Therefore, we need to consider only the second term  $B(\dots)$  in our limit. Back substitution of  $K$  to get  $H$  and  $E'_r$  together with (10) finally gives the electric field

$$E_r(r, \tau) = -\frac{1}{z} \left[ \frac{B}{2\sqrt{\tau}} + \frac{(B + g_0)\sqrt{\tau}}{r^2} \right]$$

and with (8) the concentration

$$n(r, \tau) = -\frac{1}{z^2} \frac{B}{r\sqrt{\tau}}.$$

This solution describes a rarefaction process, the concentration ( $n > 0$  if  $B < 0$ ) decreases steadily with time and the ion flux is pointing outward.

## 8. Conclusions

We have uncovered a connection between the single species Poisson–Nernst–Planck (PNP) system and a nonlinear equation for the respective electric field. This equation (11) may be considered a member of the family of nonlinear, vector-valued drift-diffusion equations. The further investigation of this equation regarding the differences compared to the vector Burgers equation (the most famous member of this family) may provide additional insight into the structure of (11) and its solutions.

A general procedure has been derived to find solutions to the problem in one dimension, because in this case the equation can be brought to the form of the classical (scalar) Burgers equation. Thus, we were able to give several time dependent solutions and realized different types of boundary conditions, including zero flux (insulating) conditions.

The especially simple form of the divergence operator in Cartesian coordinates offered the possibility to construct multidimensional solutions out of 1D solutions, where the spatial dependency is identical in each coordinate direction. It is noted that this procedure is not possible for the vector Burgers equation.

Finally, an exemplary approach to find solutions in the spherical symmetric case has been outlined, showing that there are various promising ways to search for further solutions to the problem.

Since the PNP system has been investigated by the scientific community for more than a century, we want to emphasize the novelties in this paper through a comparison with the recent literature.

The analytic solutions given here are the first discovered time dependent (non-stationary) exact solutions at all. It is explicitly stated in the introduction of [6] that there are no known exact analytical solutions to the full time dependent PNP system yet. Further, there is an extensive analysis and an in-depth historical review of the electrodiffusion problem in [10], where no indications of any known exact solutions are given. This is the case for [10] itself and all thematically relevant references therein. Other recent publications about theoretical

aspects of electrodiffusion also do not contain any information on exact solutions, see, e.g. [11–13].

A second novelty is the connection between the single species PNP system and the equation (11) for the electric field. If this connection would already be known, it might find its way into a review like [10] but it is not given there or in any of the above mentioned references. Besides journal articles, such a connection (if known) is likely to be found in respective textbooks on electrodiffusion. One of the up-to-date books on this topic is [14] which includes a detailed physical and mathematical analysis of the PNP system, but a connection to equation (11) could not be found. Other classical textbooks like [15, 16] or [17] contain no information regarding this point either.

Another novelty is the equation (11) itself. A detailed search in respective journals (e.g. ‘*Journal of Differential Equations*’ or ‘*Journal of Mathematical Physics*’) shows that the literature on vector-valued partial differential equations (PDE) is generally rare except for famous cases like e.g., the Navier–Stokes equation. A discussion of an equation like (11) was not found. A further extremely rich source of information on nonlinear PDEs is the handbook [8] which contains thousands of equations and references to relevant publications from the last centuries (fortunately including lots of the vast amount of Russian contributions to the topic). Nothing comparable to equation (11) was found in [8]. Another brilliant textbook is [18], covering up-to-date developments in the area of nonlinear PDE’s with a huge number of examples from all fields of theoretical physics. Again, no references to an equation like (11) could be found.

Therefore, since (11) has not been discussed before (although it apparently describes a physical process, namely the dynamics of the electric field for a single species electrolyte), the other properties of (11) derived in this work are new, too. This includes the construction of solutions in the multidimensional case from 1D solutions (cf section 6) as well as the findings for the spherical symmetric case in section 7.

## Acknowledgments

This work was funded through a grant from the German Ministry of Education and Research (BMBF, 01GQ1003A).

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