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Non-equilibrium steady states of electrolyte interfaces

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E-mail: markus.bier@thws.de**Keywords:** Poisson-Nernst-Planck theory, non-equilibrium steady state, electrolyte interface, Gouy-Chapman model**Abstract**

The non-equilibrium steady states of a semi-infinite quasi-one-dimensional univalent binary electrolyte solution, characterised by non-vanishing electric currents, are investigated by means of Poisson-Nernst-Planck (PNP) theory. Exact analytical expressions of the electric field, the charge density and the number density are derived, which depend on the electric current density as a parameter. From a non-equilibrium version of the Grahame equation, which relates the total space charge per cross-sectional area and the corresponding contribution of the electric potential drop, the current-dependent differential capacitance of the diffuse layer is derived. In the limit of vanishing electric current these results reduce to those within Gouy-Chapman theory. It is shown that improperly chosen boundary conditions lead to non-equilibrium steady state solutions of the PNP equations with negative ion number densities. A necessary and sufficient criterion on surface conductivity constitutive relations is formulated which allows one to detect such unphysical solutions.

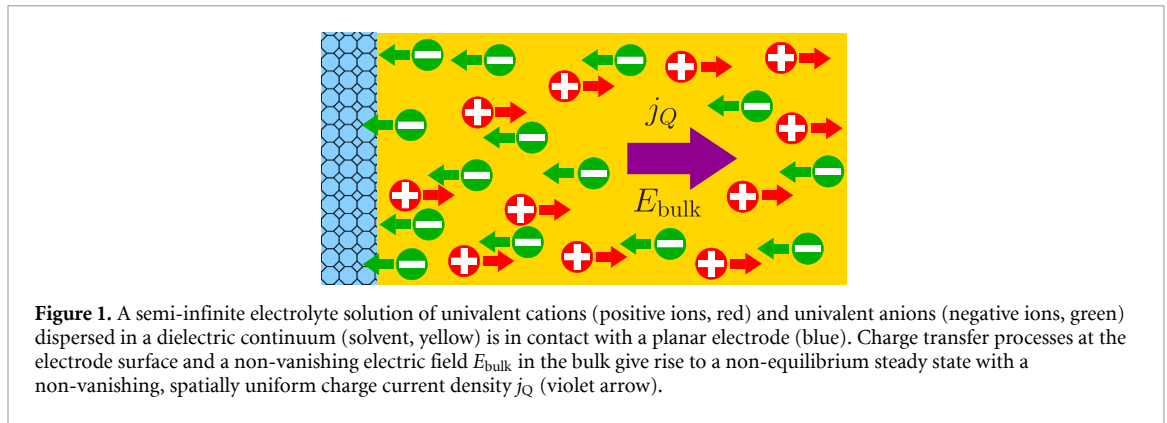
1. Introduction

The dynamics of ions in external electric fields determines the properties of numerous important natural and technological processes such as the formation of a membrane potential in biological cells via ion channels [1–7], the charging and discharging of batteries by charge transfer reactions at electrodes [8, 9], the motion of colloids exploiting electrokinetic effects of ionic solvent components [10–12] as well as the suppression of electric currents by insulation fluids in high electric fields [13–16].

For low ion densities and in the absence of hydrodynamic interactions Poisson-Nernst-Planck (PNP) theory [10, 17, 18] is an established and widely used theoretical framework in order to address these questions by considering the distributions of the electric field, the charge density the ion number densities etc. However, in studies of ion channels, high concentrated battery electrolytes and colloid migration steric effects of ions have been noted to be relevant [19–21] so that extensions of the PNP theory to include steric effects and hydrodynamic interactions are currently under investigation [22–24].

In contrast, ideal insulation fluids for high voltage applications would be void of ions and carefully prepared real insulation fluids contain only a few. Hence ionic steric effects and ion-ion correlations should be weak in that type of systems and hydrodynamic interactions might be negligible for highly viscous solvents such that PNP theory can be considered a well justified starting point [25]. However, in order to sustain the insulation property the ion concentration has to stay low for long times. Hence, understanding the mechanisms of charge generation in insulation fluids is an important topic which has been under investigation for many decades [15, 16, 26–30].

Unlike for nano-sized ion channels or colloids, the functioning of insulation fluids requires a truly macroscopic spatial extension of length scales of the order 1 cm and above. Hence a clear separation of length scales occurs: Within distances of molecular size from (typically metallic) surfaces electrochemical processes can occur, which provide the most important sources for ion generation, as electric fields are strongest there. Further away from the surfaces an extended bulk fluid with smooth distributions of the electric field and ions is present. The smoothness of these distributions allows for a description in terms of (partial) differential equations and the smallness of the ion number densities justifies the applicability of the PNP equations



(see section 2.2 below). Moreover, the macroscopic character of high-voltage insulation systems quite naturally motivates to study electric currents theoretically in terms of a simple one-dimensional model comprising a planar electrode in contact with a semi-infinite electrolyte solution, similar to the investigations of Gouy and Chapman [10, 11, 31–34] more than a century ago for conditions of thermodynamic equilibrium (see figure 1).

Surprisingly, such a simple *semi-infinite* Gouy-Chapman model for the diffuse layer out of thermodynamic equilibrium has apparently *not* yet been studied analytically, whereas analytical solutions have well been obtained for the mathematically more complicated situation of *finite* one-dimensional electrolytes, involving Jacobi elliptic functions, perturbation expansions or simplifying approximations [35–47].

It is the purpose of the present work to analytically solve the PNP equations (section 2.2) for non-equilibrium steady states of a semi-infinite quasi-one-dimensional univalent binary electrolyte solution (section 2.1). Note that it is not the aim here to justify the assumptions of PNP theory in any specific real system or to discuss the range of validity of PNP theory in general. Rather the standard PNP theory, which is widely used in the various fields of application mentioned above, is applied to analyse the semi-infinite Gouy-Chapman model. It turns out that the solutions can be represented in terms of elementary functions and the expressions are of similar complexity as the Gouy-Chapman results for thermodynamic equilibrium (section 2.3). Moreover, a generalization of the Grahame equation, which for thermodynamic equilibrium expresses the surface charge density in terms of the surface potential [10, 11, 34], to non-equilibrium steady states is derived (section 2.4). This allows to discuss the dependence of the distributions of the electric field as well as of charge and ion number density on the electric current (section 3.1). Moreover, it is shown that the profiles as well as the Grahame relation and the differential capacitance of the space charge region reduce to the well-known Gouy-Chapman results for vanishing electric current (section 3.2). A novel feature of the considered semi-infinite model, which is shown to occur only out of equilibrium, is the occurrence of solutions of the PNP equations with negative ion number densities (section 3.3). This leads to the conclusion, that particular care is required in choosing appropriate boundary conditions in order to avoid such unphysical solutions (section 4).

2. Model and formalism

2.1. Setup

Consider a semi-infinite univalent binary electrolyte solution, which is bounded by a single planar electrode (see figure 1). The solvent is described as a dielectric continuum of temperature T and dielectric constant ϵ . Cations (positive ions, valency $Z_+ = 1$, diffusion constant D_+ , number density ρ_+) and anions (negative ions, valency $Z_- = -1$, diffusion constant D_- , number density ρ_-) migrate in an electric field E , which is oriented in normal direction of the electrode. Due to the planar symmetry, the electric field $E(x)$ and the number densities $\rho_{\pm}(x)$ are functions of the distance $x \geq 0$ from the electrode, but they are independent of the lateral position. Charge transfer processes close to the electrode surface allow for an electric current to occur in the system. Several mechanisms contributing to the surface current are under investigation for many decades, e.g. electrochemical reactions, charge carrier injection, field-enhanced dissociation and electron emission [15, 16, 28]. As the present analysis is independent of the precise charge transfer process, no specific surface conductivity model is chosen in the following.

It is assumed that a sufficiently long waiting time has elapsed such that the system has attained a steady state in which the electric field E and the number densities ϱ_{\pm} are time-independent. Moreover, at large distances $x \rightarrow \infty$ from the electrode these quantities are assumed to approach the constant bulk limits $E(x) \rightarrow E_{\text{bulk}}$ and $\varrho_{\pm}(x) \rightarrow \varrho_{\text{bulk}}/2$. Consequently, for $E_{\text{bulk}} = 0$ the system is in thermodynamic equilibrium, whereas for $E_{\text{bulk}} \neq 0$ it is in a non-equilibrium steady state. In a non-equilibrium steady state a non-vanishing, spatially uniform electric current density $j_Q \neq 0$ is present, which requires concomitant charge transfer processes to occur at the electrode surface.

2.2. Governing equations

In order to quantify the steady states of the system described in the previous section 2.1 the governing equations are derived within PNP theory in the following.

Given ion number densities $\varrho_{\pm}(x)$ the *total ion number density*

$$\varrho(x) = \varrho_+(x) + \varrho_-(x), \quad (1)$$

and the *charge density*

$$q(x) = e(\varrho_+(x) - \varrho_-(x)), \quad (2)$$

with the elementary charge e are defined. At large distances $x \rightarrow \infty$ from the electrode these quantities approach the limits $\varrho(x) \rightarrow \varrho_{\text{bulk}}$ and $q(x) \rightarrow 0$.

By means of Gauss' law [48] the derivative $E'(x)$ of the electric field is related to the charge density $q(x)$:

$$\varepsilon_0 \varepsilon E'(x) = q(x), \quad (3)$$

where ε_0 is the vacuum permittivity. This shows that approaching a constant bulk electric field $E(x) \rightarrow E_{\text{bulk}}$ in the limit $x \rightarrow \infty$ implies local charge neutrality $q(x) \rightarrow 0$ in the bulk.

The Nernst-Planck equations [10, 17, 18]

$$j_{\pm}(x) = D_{\pm} (-\varrho'_{\pm}(x) \pm \beta e \varrho_{\pm}(x) E(x)), \quad (4)$$

where $1/\beta = k_B T$ with the Boltzmann constant k_B denotes the thermal energy, describe the current densities of ions due to diffusion in a density gradient and drift in the electric field. Note that no advection contribution occurs in the present quiescent solvent.

In general the time dependence of the ion number densities $\varrho_{\pm}(x, t)$ is given by the continuity equations

$$\dot{\varrho}_{\pm}(x, t) = -j'_{\pm}(x, t), \quad (5)$$

which describe conservation of the number of ions. However, a steady state is time-independent ($\dot{\varrho}_{\pm} = 0$) such that the current densities $j_{\pm}(x, t)$ are spatially uniform and time-independent:

$$0 = j'_{\pm}(x, t) \quad \Leftrightarrow \quad j_{\pm}(x, t) = \text{const} = j_{\pm}. \quad (6)$$

Equations (3), (4) and (6) form a system of ordinary differential equations for $\varrho_{\pm}(x)$ and $E(x)$, which can be solved uniquely by prescribing five integration constants. Two of these integration constants are given by the values j_{\pm} , or, equivalently, by the pair of values of the *total number current density*

$$j_N = j_+ + j_-, \quad (7)$$

and the *charge current density*

$$j_Q = e(j_+ - j_-). \quad (8)$$

The remaining three integration constants can be obtained from the bulk values $\varrho(x) \rightarrow \varrho_{\text{bulk}}$ and $q(x) \rightarrow 0$ for $x \rightarrow \infty$ as well as from the electric field strength $E(0)$ at the electrode at $x = 0$. Note that equation (15) below shows that the bulk value $E(x) \rightarrow E_{\text{bulk}}$ for $x \rightarrow \infty$ depends on the values of j_Q and ϱ_{bulk} , i.e. E_{bulk} cannot serve as an independent integration constant.

In order to simplify the later calculations the following *reduced current densities* are introduced:

$$J_N = \frac{j_+}{D_+} + \frac{j_-}{D_-} = -\varrho'(x) + \beta q(x) E(x) \quad (9)$$

$$J_Q = e \left(\frac{j_+}{D_+} - \frac{j_-}{D_-} \right) = -q'(x) + \beta e^2 \varrho(x) E(x). \quad (10)$$

As $\varrho'(x) \rightarrow 0$ (due to $\varrho(x) \rightarrow \varrho_{\text{bulk}}$), $q(x) \rightarrow 0$ and $E(x) \rightarrow E_{\text{bulk}}$ for $x \rightarrow \infty$, equation (7) implies $J_N = 0$, hence, from equation (7),

$$\frac{j_+}{D_+} = -\frac{j_-}{D_-}. \quad (11)$$

Consequently

$$j_Q = e \left(1 + \frac{D_-}{D_+} \right) j_+ = -e \left(\frac{D_+}{D_-} + 1 \right) j_-, \quad (12)$$

which allows one to express the ionic current densities j_{\pm} in terms of the charge current density j_Q . This leads to the relation

$$J_Q = \frac{e j_+}{D_+} - \frac{e j_-}{D_-} = \frac{2}{D_+ + D_-} j_Q = \frac{j_Q}{D}, \quad (13)$$

between the charge current density j_Q and the reduced charge current density J_Q with the *average diffusion constant*

$$D = \frac{D_+ + D_-}{2}. \quad (14)$$

Similarly, as $q'(x) \rightarrow 0$ (due to $q(x) \rightarrow 0$), $\varrho(x) \rightarrow \varrho_{\text{bulk}}$ and $E(x) \rightarrow E_{\text{bulk}}$ for $x \rightarrow \infty$, equation (8) leads to

$$J_Q = \beta e^2 \varrho_{\text{bulk}} E_{\text{bulk}}. \quad (15)$$

By using equation (13) one infers

$$j_Q = D \beta e^2 \varrho_{\text{bulk}} E_{\text{bulk}} = S_{\text{bulk}} E_{\text{bulk}}, \quad (16)$$

with the *bulk conductivity*

$$S_{\text{bulk}} = D \beta e^2 \varrho_{\text{bulk}}. \quad (17)$$

2.3. Analytical solution

In the following the PNP equations (3)–(5) of the considered system are solved analytically.

In a first step inserting equation (3) in equation (7) yields

$$\begin{aligned} 0 &= -\varrho'(x) + \beta \varepsilon_0 \varepsilon E'(x) E(x) \\ &= \left(-\varrho(x) + \frac{\beta \varepsilon_0 \varepsilon}{2} E(x)^2 \right)', \end{aligned} \quad (18)$$

which implies

$$-\varrho(x) + \frac{\beta \varepsilon_0 \varepsilon}{2} E(x)^2 = \text{const.} \quad (19)$$

Evaluation of the constant by taking the limit $x \rightarrow \infty$ leads to

$$\varrho(x) = \varrho_{\text{bulk}} + \frac{\beta \varepsilon_0 \varepsilon}{2} \left(E(x)^2 - E_{\text{bulk}}^2 \right). \quad (20)$$

By inserting equations (3) and (20) in equation (8) one obtains the inhomogeneous non-linear ordinary differential equation for the electric field $E(x)$

$$\varepsilon_0 \varepsilon E''(x) = \beta e^2 \left(\varrho_{\text{bulk}} - \frac{\beta \varepsilon_0 \varepsilon}{2} E_{\text{bulk}}^2 \right) E(x) + \frac{\beta^2 e^2 \varepsilon_0 \varepsilon}{2} E(x)^3 - J_Q. \quad (21)$$

This equation resembles equation (A.9) of [49] and equation (48) of [36].

Introducing the excess electric field $\Delta E(x) = E(x) - E_{\text{bulk}}$ transforms the differential equation (21) to the homogeneous differential equation

$$\Delta E''(x) = \frac{\beta e^2}{\varepsilon_0 \varepsilon} (\varrho_{\text{bulk}} + \beta \varepsilon_0 \varepsilon E_{\text{bulk}}^2) \Delta E(x) + \frac{3}{2} \beta^2 e^2 E_{\text{bulk}} \Delta E(x)^2 + \frac{1}{2} \beta^2 e^2 \Delta E(x)^3. \quad (22)$$

With the Debye length $1/\kappa$ defined by $\kappa^2 = 4\pi \ell_B \varrho_{\text{bulk}}$, where $\ell_B = \beta e^2 / (4\pi \varepsilon_0 \varepsilon)$ is the Bjerrum length [10, 11, 50, 51], one can introduce the dimensionless *electric flux* parameter

$$\eta = \frac{\beta e j_Q}{\kappa S_{\text{bulk}}} = \frac{\beta e E_{\text{bulk}}}{\kappa}, \quad (23)$$

which quantifies the deviation of a steady state from thermodynamic equilibrium ($\eta = 0$) in terms of the charge current density j_Q . The values $\eta = \pm 1$ correspond to a charge current density $j_Q = \pm S_{\text{bulk}} \kappa / (\beta e)$ generated by a bulk electric field $E_{\text{bulk}} = \pm \kappa / (\beta e)$. The notion of electric flux η allows one to rewrite equation (22) in the form

$$\Delta E''(x) = \kappa^2 (1 + \eta^2) \Delta E(x) + \frac{3}{2} \beta e \kappa \eta \Delta E(x)^2 + \frac{1}{2} \beta^2 e^2 \Delta E(x)^3. \quad (24)$$

Finally the transformation

$$y = \kappa x \sqrt{1 + \eta^2}, \quad \widehat{E}(y) = \frac{\beta e \Delta E(x)}{\kappa}, \quad (25)$$

is used to rewrite equation (24) in the form

$$\widehat{E}''(y) = \widehat{E}(y) + \frac{3\eta}{2(1+\eta^2)} \widehat{E}(y)^2 + \frac{1}{2(1+\eta^2)} \widehat{E}(y)^3. \quad (26)$$

A first integral of equation (26) is found by multiplication with $\widehat{E}'(y)$ and the integration constant is fixed by using $\widehat{E}'(y) \rightarrow 0$ and $\widehat{E}(y) \rightarrow 0$ for $y \rightarrow \infty$:

$$\widehat{E}'(y)^2 = \widehat{E}(y)^2 \left(1 + \frac{\eta}{1+\eta^2} \widehat{E}(y) + \frac{1}{4(1+\eta^2)} \widehat{E}(y)^2 \right). \quad (27)$$

It can be shown, that the expression inside the parentheses is bounded from below by $1/(1+\eta^2)$ for any value of $\widehat{E}(y)$, hence

$$|\widehat{E}'(y)| \geq |\widehat{E}(y)| / \sqrt{1+\eta^2} \quad \text{for all } y \geq 0. \quad (28)$$

Moreover, from equation (26) one infers that for $y \rightarrow \infty$ the asymptotic behavior of $\widehat{E}(y)$ is monotonic, i.e. constant or exponential, but not oscillatory. Consequently, due to the limit $\widehat{E}(y) \rightarrow 0$ for $y \rightarrow \infty$, only three cases can occur: $\widehat{E}(y)$ for $y \geq 0$ is either (i) constantly zero ($\widehat{E}(y) = 0$) or (ii) positive ($\widehat{E}(y) > 0$) and strictly monotonically decreasing ($\widehat{E}'(y) < 0$) or (iii) negative ($\widehat{E}(y) < 0$) and strictly monotonically increasing ($\widehat{E}'(y) > 0$). Otherwise if, say, $\widehat{E}(y)$ approaches the limit $\widehat{E}(y) \rightarrow 0$ for $y \rightarrow \infty$ from above, but $\widehat{E}(y)$ was not monotonically decreasing for all $y \geq 0$, there would be a local maximum at some position $y = y^*$ with $\widehat{E}'(y^*) = 0$ but $\widehat{E}(y^*) > 0$, which contradicts equation (28). A similar contradiction arises from the assumption of a non-monotonically increasing behavior when approaching the bulk limit from below.

In the above cases (ii) and (iii) $\widehat{E}'(y)$ and $\widehat{E}(y)$ have opposite sign, so that equation (27) leads to

$$\widehat{E}'(y) = -\widehat{E}(y) \sqrt{1 + \frac{\eta}{1+\eta^2} \widehat{E}(y) + \frac{1}{4(1+\eta^2)} \widehat{E}(y)^2}, \quad (29)$$

which relates the value $\widehat{E}(y)$ and the derivative $\widehat{E}'(y)$. This equation is obviously true also for case (i).

For cases (ii) and (iii) separation of variables leads to the solution [52]

$$\widehat{E}(y) = \frac{2(1+\eta^2)\widehat{E}_0}{\sinh(y) \sqrt{\widehat{E}_0^2 + (2(1+\eta^2) + \widehat{E}_0\eta)^2} + \cosh(y) (2(1+\eta^2) + \widehat{E}_0\eta) - \widehat{E}_0\eta}, \quad (30)$$

with the value $\widehat{E}(0) = \widehat{E}_0$ at the electrode surface $y = 0$ playing the role of the integration constant. The solution $\widehat{E}(y) \equiv 0$ of case (i) is obtained from equation (30) with $\widehat{E}_0 = 0$.

2.4. Grahame equation

An important result in the thermodynamic equilibrium theory of electrolyte interfaces is an expression for the surface charge density in terms of the surface potential, which is commonly referred to as *Grahame equation* [10, 11, 34]. Here an analogous expression is derived for steady state conditions.

Integration of the excess electric field $\Delta E(x)$ leads to the *excess voltage*

$$\Delta U = \int_0^{\infty} dx \Delta E(x), \quad (31)$$

which measures deviations from local charge neutrality expressed by the charge density $q(x) = \varepsilon_0 \varepsilon \Delta E'(x)$. It adds to the voltage required to sustain the bulk electric field E_{bulk} . Using equations (25) and (29) one obtains [52]

$$\begin{aligned} \beta e \Delta U &= \frac{1}{\sqrt{1+\eta^2}} \int_0^{\infty} dx \kappa \sqrt{1+\eta^2} \frac{\beta e \Delta E(x)}{\kappa} \\ &= \frac{1}{\sqrt{1+\eta^2}} \int_0^{\infty} dy \widehat{E}(y) \\ &= -\frac{1}{\sqrt{1+\eta^2}} \int_0^{\infty} dy \frac{\widehat{E}'(y)}{\sqrt{1 + \frac{\eta \widehat{E}(y)}{1+\eta^2} + \frac{\widehat{E}(y)^2}{4(1+\eta^2)}}} \\ &= 2 \left(\operatorname{arsinh} \left(\frac{1}{2} \widehat{E}(0) + \eta \right) - \operatorname{arsinh}(\eta) \right). \end{aligned} \quad (32)$$

Using equation (3) the total charge per cross-sectional area of the diffuse layer can be calculated by

$$\int_0^{\infty} dx q(x) = \varepsilon_0 \varepsilon \int_0^{\infty} dx \Delta E'(x) = -\varepsilon_0 \varepsilon \Delta E(0). \quad (33)$$

This total charge per cross-sectional area of the space charge region is balanced by an *excess surface charge density* $\Delta \sigma$ at the electrode surface, which has the same magnitude but the opposite sign: $\Delta \sigma = \varepsilon_0 \varepsilon \Delta E(0)$. It expresses the excess of the *total surface charge density*

$$\sigma = \sigma_{\text{bulk}} + \Delta \sigma, \quad (34)$$

compared to the surface charge density $\sigma_{\text{bulk}} = \varepsilon_0 \varepsilon E_{\text{bulk}}$, which generates the bulk electric field E_{bulk} . By introducing the *saturation charge density* [53]

$$\sigma_{\text{sat}} = \frac{e\kappa}{\pi \ell_B} = 4\varepsilon_0 \varepsilon \frac{\kappa}{\beta e}, \quad (35)$$

one obtains the relation

$$\widehat{E}(0) = \frac{\beta e \Delta E(0)}{\kappa} = 4 \frac{\Delta \sigma}{\sigma_{\text{sat}}}, \quad (36)$$

by means of which equation (32) can be rewritten as

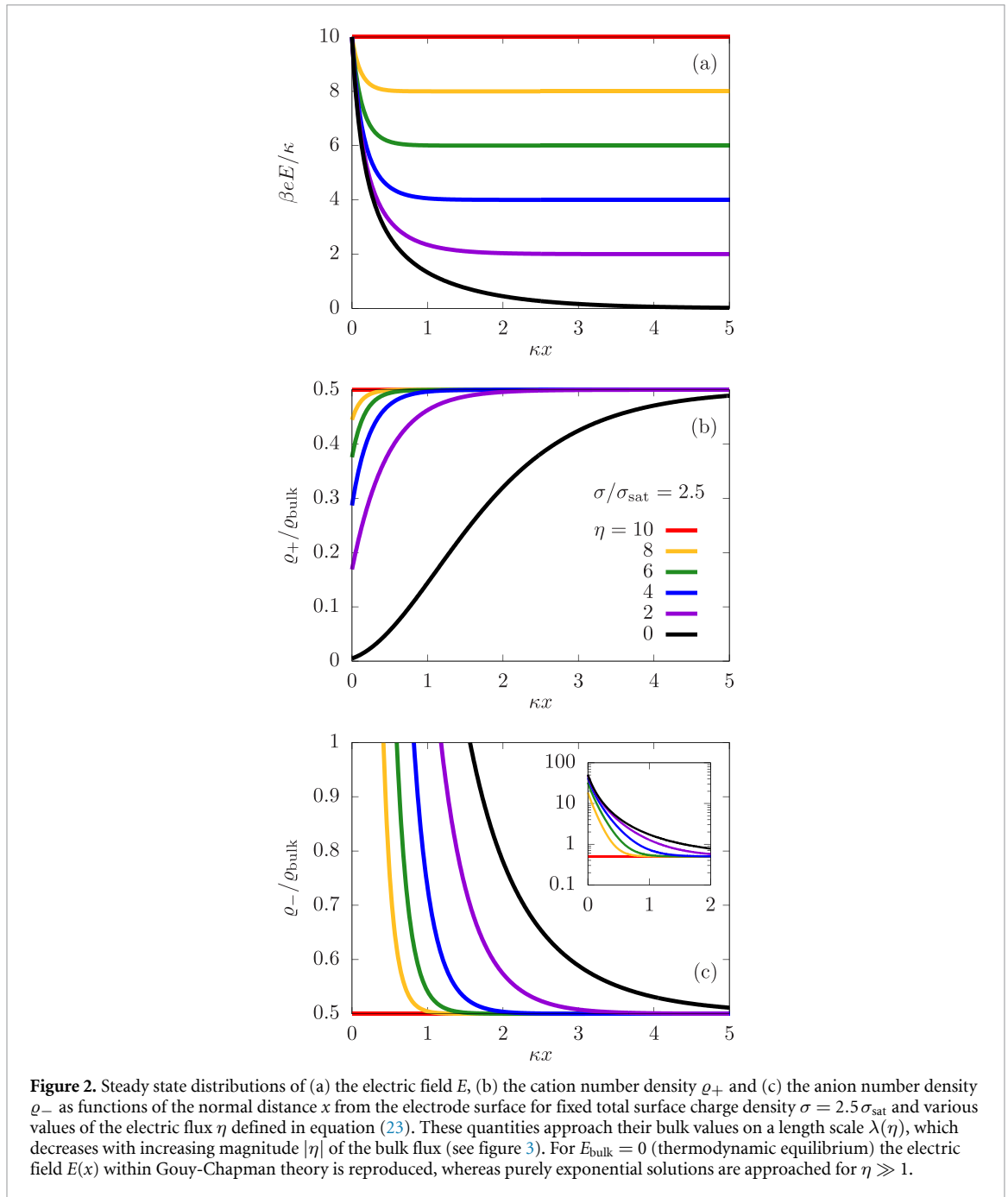
$$\beta e \Delta U = 2 \left(\operatorname{arsinh} \left(2 \frac{\Delta \sigma}{\sigma_{\text{sat}}} + \eta \right) - \operatorname{arsinh}(\eta) \right). \quad (37)$$

Solving equation (37) for the excess surface charge density $\Delta \sigma$ one obtains the *Grahame equation*

$$\Delta \sigma = \frac{\sigma_{\text{sat}}}{2} \left(\sqrt{1+\eta^2} \sinh \left(\frac{\beta e \Delta U}{2} \right) + \eta \left(\cosh \left(\frac{\beta e \Delta U}{2} \right) - 1 \right) \right). \quad (38)$$

The derivative of the excess surface charge density $\Delta \sigma$ w.r.t. the excess voltage ΔU leads to the *differential capacitance* of the diffuse layer

$$C = \frac{\partial \Delta \sigma}{\partial \Delta U} = \frac{\beta e \sigma_{\text{sat}}}{4} \left(\sqrt{1+\eta^2} \cosh \left(\frac{\beta e \Delta U}{2} \right) + \eta \sinh \left(\frac{\beta e \Delta U}{2} \right) \right). \quad (39)$$

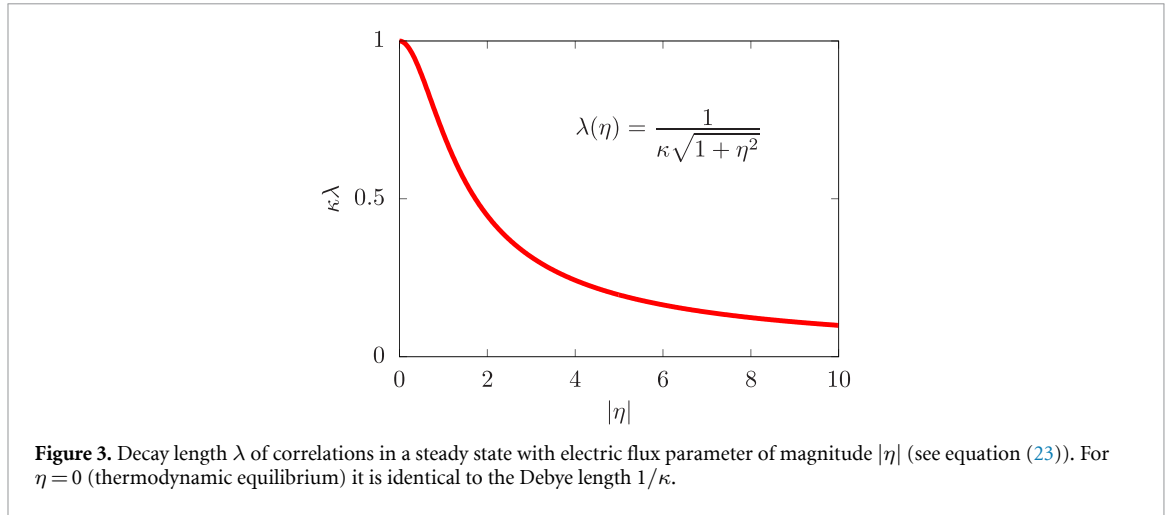


3. Results and discussion

3.1. Steady state distributions

Some typical examples of steady state distributions of the electric field $E(x)$, the cation number density $\rho_+(x) = (\rho(x) + q(x)/e)/2$ and the anion number density $\rho_-(x) = (\rho(x) - q(x)/e)/2$ are displayed in figure 2. These profiles correspond to the largely arbitrary choice of total surface charge density $\sigma = 2.5\sigma_{\text{sat}}$ and electric flux $\eta \in \{0, 2, 4, 6, 8, 10\}$.

Hypothetical pure water of $\text{pH} = 7$, i.e. with total ion number density in the bulk of $\rho_{\text{bulk}} = 2 \cdot 10^{-7} \text{ M}$, at $T = 300 \text{ K}$ has Bjerrum length $\ell_B \approx 0.7 \text{ nm}$ and Debye length $1/\kappa \approx 1 \mu\text{m}$ so that $\sigma_{\text{sat}} \approx 7 \cdot 10^{-5} \text{ C m}^{-2}$, which corresponds to an electric field $E_{\text{sat}} = \sigma_{\text{sat}}/(\varepsilon_0 \varepsilon) \approx 100 \text{ V mm}^{-1}$ at the electrode. Furthermore, assuming a bulk conductivity $S_{\text{bulk}} = 5 \cdot 10^{-6} \text{ S m}^{-1}$ (see [54]) an electric flux $\eta = 1$ corresponds to a charge current density of $j_Q \approx 0.1 \text{ A m}^{-2}$. However, these values can vary in a wide range for various materials, and the purpose of the present work is not to discuss a particular system in detail.



The electric field $E(x) = E_{\text{bulk}} + \Delta E(x)$ is obtained from the analytical solution equation (30) in conjunction with equation (25). The total number density $\varrho(x)$ is obtained from equation (20) and the charge density $q(x)$ is calculated via equation (3).

For $\eta = 0$ (thermodynamic equilibrium, $j_Q = 0$) the bulk electric field vanishes, $E_{\text{bulk}} = 0$ (see equation (23)), hence $\Delta E(x) = E(x)$, and equation (30) reduces to (see equation (25))

$$\frac{\beta e \Delta E(x)}{\kappa} = \frac{\hat{E}_0}{\sqrt{1 + \left(\frac{1}{2}\hat{E}_0\right)^2} \sinh(\kappa x) + \cosh(\kappa x)}, \quad (40)$$

which coincides with the electric field derived within Gouy-Chapman theory [10, 11, 31–34].

For $|\eta| \gg \max(1, |\hat{E}_0|)$ equation (30) simplifies to

$$\frac{\beta e \Delta E(x)}{\kappa} \simeq \hat{E}_0 \exp\left(-\frac{x}{\lambda(\eta)}\right), \quad (41)$$

with the length scale

$$\lambda(\eta) = \frac{1}{\kappa \sqrt{1 + \eta^2}}, \quad (42)$$

i.e. the excess electric field $\Delta E(x)$ becomes purely exponential. This is consistent with the fact that equation (26) reduces to the linear equation $\hat{E}''(y) = \hat{E}(y)$ for $|\eta| \rightarrow \infty$. It is remarkable that the governing equation (26) becomes simple far away from thermodynamic equilibrium.

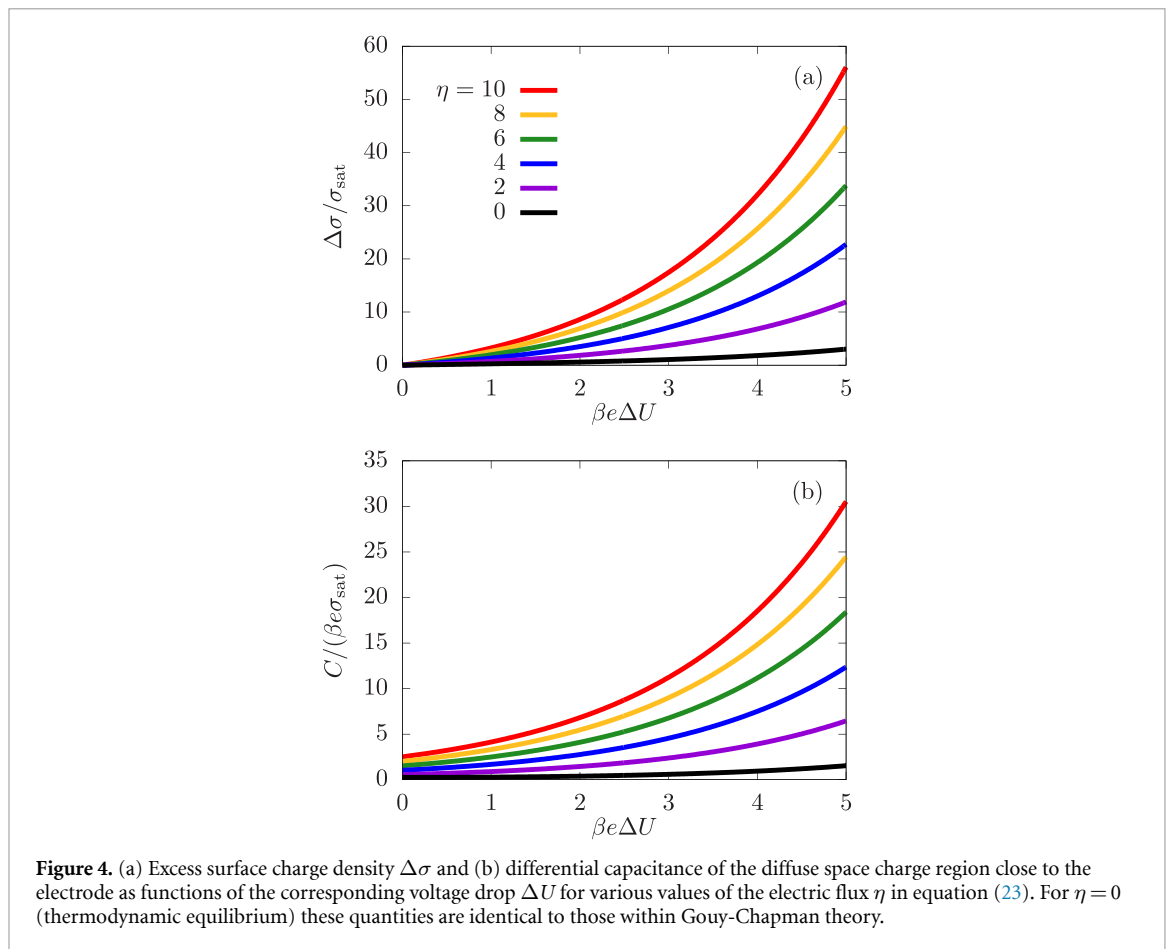
According to equation (25) the position dependence of the excess electric field $\Delta E(x)$ for arbitrary values of the electric flux η is determined by length scale $\lambda(\eta)$ in equation (42):

$$\frac{\beta e \Delta E(x)}{\kappa} = \hat{E} \left(\frac{x}{\lambda(\eta)} \right). \quad (43)$$

In particular, according to equation (30), for $x \gg \lambda(\eta)$, $\Delta E(x)$ exhibits an exponential asymptotic decay on the length scale $\lambda(\eta)$.

The dependence of length scale $\lambda(\eta)$ on the electric flux parameter η is displayed in figure 3. For $\eta = 0$ (thermodynamic equilibrium, $j_Q = 0$) this equals the Debye length $\lambda(0) = 1/\kappa$, whereas it decreases $\lambda(\eta) \simeq 1/(\kappa|\eta|)$ for $|\eta| \rightarrow \infty$. However, the detailed position dependence of $\Delta E(x)$ is irrelevant from the practical point of view if $|\eta|$ is so large that the length scale $\lambda(\eta)$ is of molecular size or below.

In summary, with increasing electric flux $|\eta| \sim |j_Q|$ the electric field changes from the Gouy-Chapman form in thermodynamic equilibrium to a purely exponential dependence far away from thermodynamic equilibrium. In parallel the corresponding relevant length scale $\lambda(\eta)$ decays from the Debye length $1/\kappa$ to zero.



3.2. Space charge

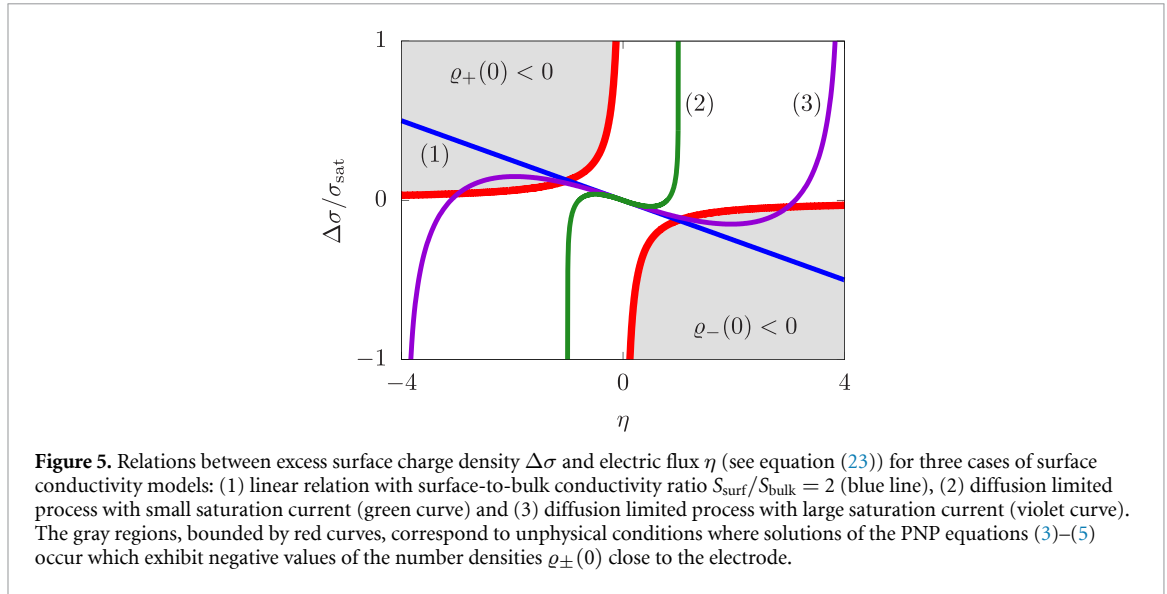
At distances $x \gg \lambda(\eta)$ the electric field and the densities become spatially uniform (see figure 2). Depending on the processes taking place at the electrode surface deviations from spatial uniformity can occur there, which are commonly referred to as the formation of *space charges*. In the theory of electrolyte solutions in thermodynamic equilibrium this space charge region is traditionally called the *diffuse layer* [10, 11, 34, 55].

In the notation of section 2.4 the amount of space charge per cross-sectional area is given by $-\Delta\sigma$, where $\Delta\sigma$ denotes the excess surface charge density, which is the charge per cross-sectional area on the electrode surface induced by the space charge. The relation of $\Delta\sigma$ to the excess voltage ΔU of the space charge region (see equation (31)) is called the Grahame equation (38), in analogy to the equation of the same name within the theory of electrolyte solutions in thermodynamic equilibrium [10, 11, 34].

Figure 4(a) displays this relation for electric flux $\eta \in \{0, 2, 4, 6, 8, 10\}$. For $\eta = 0$ (thermodynamic equilibrium, $j_Q = 0$) the traditional Grahame equation is found, whereas for a given excess voltage $\Delta U > 0$ the amount of space charge increases upon increasing the electric flux η . According to equation (38), for $\eta \rightarrow \infty$ this increase is asymptotically proportional to η . Hence the mean capacitance $\Delta\sigma/\Delta U$ increases upon increasing the electric flux, which can be attributed to the decrease of the diffuse layer thickness $\lambda(\eta)$ upon increasing $|\eta|$.

Figure 4(b) displays the differential capacitance C , i.e. the derivative of the excess surface charge $\Delta\sigma$ w.r.t. the excess voltage ΔU , given in equation (39). For $\eta = 0$ (thermodynamic equilibrium, $j_Q = 0$) the well-known Gouy-Chapman capacitance is found [10, 11], whereas C increases upon increasing the electric flux η . From equation (39) one infers an asymptotically proportional dependence of C on η for $\eta \rightarrow \infty$. This dependence on η can again be attributed to the decrease of the diffuse layer thickness $\lambda(\eta)$ upon increasing $|\eta|$.

Note that within PNP theory no packing effects due to finite molecular sizes of the ions are taken into account. This precludes the decrease of the differential capacitance C for large values of the excess voltage ΔU , which otherwise would set in once the inner Helmholtz plane is fully occupied such that additionally adsorbed ions have to be accommodated at larger distances from the electrode surface [19, 21, 56, 57].



3.3. Surface conductivity models

Physically meaningful number densities $\rho_{\pm}(x)$ have to be non-negative, i.e. $\rho_{\pm}(x) \geq 0$, everywhere. Using equations (1) and (2) to rewrite this condition as $\rho_{\pm} = (\rho_{\pm} q/e)/2 \geq 0$, leads to $e\rho \geq \mp q$, which is equivalent to $e\rho \geq |q|$. The latter inequality in turn is equivalent to the two conditions

$$e \geq 0 \quad \text{and} \quad e|\rho| \geq |q|. \quad (44)$$

Writing

$$e = \rho_{\text{bulk}} \left(1 + \eta \hat{E} + \frac{1}{2} \hat{E}^2 \right) \quad (45)$$

$$q = -e \rho_{\text{bulk}} \hat{E} \sqrt{1 + \eta^2 + \eta \hat{E} + \frac{1}{4} \hat{E}^2}, \quad (46)$$

by using equations (3), (20) and (29) one can reformulate $e|\rho| \geq |q|$, i.e. $e^2 \rho^2 \geq q^2$, as

$$1 + 2\eta \hat{E} \geq 0. \quad (47)$$

Moreover, if equation (47), i.e. $e|\rho| \geq |q|$, is fulfilled, one immediately finds from equation (45) and $\hat{E}^2 \geq 0$ that

$$e = \frac{\rho_{\text{bulk}}}{2} \left(1 + \underbrace{1 + 2\eta \hat{E} + \hat{E}^2}_{\geq 0} \right) \geq 0, \quad (48)$$

i.e. the second inequality in equation (44) implies the first. To summarize the above reasoning: The physical condition of non-negative number densities ρ_{\pm} is fulfilled if and only if equation (47) holds.

Whereas equation (47) is fulfilled for $\eta \hat{E} \geq 0$, it might be violated for $\eta \hat{E} < 0$. As \hat{E} is monotonic (see section 2.3) equation (47) is fulfilled if and only if it holds at the electrode surface, i.e. $1 + 2\eta \hat{E}(0) \geq 0$. Using equation (36) the physical requirement equation (47) of non-negative number densities ρ_{\pm} can be formulated in terms of the excess surface charge density:

$$1 + 8\eta \frac{\Delta\sigma}{\sigma_{\text{sat}}} \geq 0. \quad (49)$$

Figure 5 provides a graphical representation of equation (49) in the $\Delta\sigma$ - η -plane. For $\eta \neq 0$ (non-equilibrium steady state, $j_Q \neq 0$) condition equation (49) is equivalent to

$$\frac{\Delta\sigma}{\sigma_{\text{sat}}} \geq -\frac{1}{8\eta} \quad \text{for } \eta > 0 \text{ and} \quad (50)$$

$$\frac{\Delta\sigma}{\sigma_{\text{sat}}} \leq -\frac{1}{8\eta} \quad \text{for } \eta < 0. \quad (51)$$

If equation (50) is violated the PNP solution leads to $\varrho_-(0) < 0$, whereas if equation (51) is violated the PNP solution yields $\varrho_+(0) < 0$ (see the gray regions in figure 5). Note that the parameter range $\eta, \Delta\sigma, \Delta U \geq 0$ of the examples in sections 3.1 and 3.2 has been chosen on purpose in order to fulfill condition equation (49).

For $\eta = 0$ (thermodynamic equilibrium, $j_Q = 0$) condition equation (49) is fulfilled for all excess surface charge densities $\Delta\sigma$, i.e. negative number density solutions within PNP theory can occur for non-equilibrium steady states, but not for states in thermodynamic equilibrium.

In order to demonstrate the applicability of the previous result consider the particular case of surface processes which give rise to a strictly linear constitutive relation between charge current j_Q and total electric field $E(0)$ at the electrode surface:

$$j_Q = S_{\text{surf}}E(0). \quad (52)$$

The proportionality factor S_{surf} is called the *surface conductivity* here. Using equations (23) and (36) one can rewrite equation (52) of the linear surface conductivity model as

$$\frac{\Delta\sigma}{\sigma_{\text{sat}}} = \frac{1}{4} \left(\frac{S_{\text{bulk}}}{S_{\text{surf}}} - 1 \right) \eta. \quad (53)$$

The case of a surface-to-bulk conductivity ratio $S_{\text{surf}}/S_{\text{bulk}} = 2$ is represented by the blue line labeled with '(1)' in figure 5. The fact that this line crosses over into the gray regions, where the conditions equations (50) and (51) are violated, shows that the purely linear surface conductivity model cannot be applied under these conditions for too large electric fluxes. Obviously the same argument applies to any system with $S_{\text{surf}} > S_{\text{bulk}}$ (high surface conductivity), because then the slope of the corresponding line is negative so that intersections with the unphysical gray regions occur for sufficiently large electric flux $|\eta|$. It should be noted that in the gray regions of figure 5 no mathematical problems arise: equations (30), (45) and (46) are the solutions of the PNP equations for steady states (see section 2.2). But these steady state solutions of the PNP equations may be physically meaningless due to the occurrence of negative number densities.

In systems with $S_{\text{surf}} \leq S_{\text{bulk}}$ (low surface conductivity) the linear model equation (52) leads to a line equation (53) in figure 5 with non-negative slope, which does not intersect the gray regions, i.e. no negative number densities occur under these conditions. However, it is possible that other quantities exist, for which the PNP solutions exhibit unphysical properties. Moreover, whether the linear surface conductivity model equation (52), even if no unphysical values occur, is able to quantitatively describe real systems is an unrelated question.

In fact, the linear surface conductivity model equation (52) can be expected to be an acceptable description for sufficiently small surface fields only, because for large surface fields saturation of the charge density current j_Q sets in due to an exhaustion of ions. Such diffusion limited surface processes can be described by the constitutive relation [8, 9]

$$E(0) = -\text{sign}(j_Q) \frac{j_{Q\text{sat}}}{S_{\text{surf}}} \ln \left(1 - \frac{|j_Q|}{j_{Q\text{sat}}} \right), \quad (54)$$

where $j_{Q\text{sat}} > 0$ is the saturation charge current density and S_{surf} is the differential conductivity in the limit of infinitesimal surface electric fields. In figure 5 the case of $S_{\text{surf}}/S_{\text{bulk}} = 2$ for two different values of the saturation charge current density $j_{Q\text{sat}}$ are shown by the curves labeled '(2)' and '(3)'. The green curve '(2)' demonstrates that for sufficiently small $|j_{Q\text{sat}}|$ no negative ion number densities occur, although a highly conductive surface is present at weak surface fields. However, the violet curve '(3)' for too large $|j_{Q\text{sat}}|$ does exhibit unphysical solutions inside the gray regions. Hence, great care is required to choose appropriate surface conductivity models, which, in conjunction with the PNP equations, lead to physical solutions.

4. Conclusions

In the present work the analytical solution equation (30) of the PNP equations for steady states (see section 2.2) of a semi-infinite univalent binary electrolyte solution in contact with a planar electrode (figure 1) has been derived. It can be expected to play a similar role as the Gouy-Chapman solution [10, 11, 31–34] for thermodynamic equilibrium, to which the derived solutions reduce for the case of a vanishing charge current density (figure 2). The characteristic length scale of the electric field as well as the number and charge density profiles, which in thermodynamic equilibrium is given by the Debye length, decreases for non-equilibrium steady states upon increasing the magnitude of the charge current density (figure 3). The Grahame equation, which expresses the surface charge density at the electrode in terms of the voltage [10, 11, 34], is generalized to non-equilibrium steady states (equation (38)). The excess surface charge density at the

electrode and the differential capacitance of the space charge layer for given excess voltage are found to vary with the current charge density of non-equilibrium steady states (figure 4). Finally it is found that, in contrast to the case of thermodynamic equilibrium within Gouy-Chapman theory [10, 11, 31–34], the excess surface charge density may not take an arbitrary value for a given non-vanishing charge current density of a non-equilibrium steady state: Steady state solutions of the PNP equations exist which give rise to physically meaningless negative ion number densities (figure 5). A concise criterion is formulated which can serve to identify such unphysical solutions (equation (49)).

The most remarkable observation of the present work, i.e. the existence of steady state solutions of the PNP equations which are physically meaningless, calls for further investigation. Two approaches are conceivable:

First, as Gauss' law equation (3) and the continuity equation (5) are unexceptionable for fundamental physical reasons, one could suggest to modify the Nernst-Planck equation (4) in order to avoid unphysical solutions. The two main approximations underlying PNP theory are the neglect of ion-ion correlations (typically brought about by small ion densities) and of hydrodynamic interactions (achievable by a high viscosity of the solvent) [10, 17, 18, 25]. The development of more advanced approaches on the dynamics of electrolyte solutions to cover, e.g. steric effects, hydrodynamic interactions, field-dependent diffusivities (Wien effect) or field-enhanced dissociation are the topic of numerous investigations [15, 16, 22–25, 28]. However, whether not accounting for any of these bulk effects is responsible for the occurrence of the unphysical non-stationary steady state solutions found in section 3.3 is an open question for now.

Second, noting that the unphysical feature of negative number densities in section 3.3 does not occur in the bulk but close to the electrode surface may suggest to focus on the precise modeling of surface processes, e.g. electrochemical reactions, charge carrier injection, field-enhanced dissociation or electron emission [15, 16, 26–30]. From a macroscopic point of view, e.g. within PNP theory, surface processes are described in terms of constitutive relations, which give rise to certain boundary conditions and which, based on the findings of section 3.3, have to fulfill equation (49). The question as to which features of surface processes are sufficient and/or necessary to guarantee non-negative ion number densities close to the electrode is again an open one at the moment.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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