Transport properties of polymer electrolytes

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Chapter 1

Introduction

1.1 Motivation and aims of the Thesis

Transport processes are widely spread in everyday life and important for both fundamental science and technology. They are responsible for a transfer of matter, charge, energy etc. and therefore observable in a broad variety. In particular, a transfer of regular particles or quasi particles is an essential process considered in condensed matter physics.

Transport phenomena have attracted the attention of scientists a long time ago. Indeed, every motion can be considered as a mass transfer. If we consider a motion of a solid body as a whole, it is conventional to apply classical mechanics. The motion of a liquid substance is a good example of transport processes. Attempts to describe a torrent of water started the era of hydrodynamics. Nowadays this theory is highly developed, see (2; 3), and applied to so many industrial problems that sometimes is even considered as a branch of engineering. In solids, mass transfer is suppressed due to a very low value of a diffusion coefficient. In other words, it is difficult to move a small part of a solid body through this body without damaging it. But transport processes can be very strong in solids as well. For example a transfer of heat. One should notice its mathematical similarity to a mass transfer in fluids. Moreover, heat transfer was originally described by the caloric theory which introduces a special liquid called caloric whose flow is responsible for heat transfer. Only in the middle of the 19th century the caloric

theory was superseded by thermodynamics. Another nontrivial example of transport processes is momentum transfer in fluids, which is physically originated due to viscosity.

Despite all examples of transport processes given above have a different origin and are related to different physical properties, they are all described by similar equations and show a similar behavior. This fact can be easily understood because in all examples the transmitted substance was considered as a fluid whose flow ensures the transport. The motion of every single particle of this fluid is irrelevant; only the motion of all particles as a whole is of interest. In this case it is appropriate to apply a continuum description. Instead of considering individual particles, one introduces a spatiotemporal field $C(\vec{r}, t)$ representing the particle number concentration, that is a number of particles located in a small volume V_r around the point $\vec{r}$ at the moment t. The number of particles in this volume, N_r, should fulfill the relation $1 \ll N_r \ll N$, where N is the total number of particles in the system. Therefore, this approach is sometimes called mesoscopic. The concentration $C(\vec{r}, t)$ is the ratio $\frac{N_r}{V_r}$, i.e. in SI units $C(\vec{r}, t)$ yields the number of particles per m^3. Within the approach, the particles lose their individuality; they are non-distinguishable. Thus, the case of a constant density $C(\vec{r}, t)$ can be realized either by fixed positions of all particles or by their stochastic motion with different velocities in different directions. Both situation are macroscopically equivalent. This fact represents one of the advantages of a continuum model, namely the possibility to omit all microscopical details of motion which are difficult to describe and which are usually irrelevant. As long as particles move chaotically, there is no macroscopical mass transfer. On the other hand, the system can be subjected to an external force which creates a preferable direction of motion for particles and, as a consequence, a systematic drift appears. This flux of particles is responsible for a transport and, of course, leads to a change of the concentration $C(\vec{r}, t)$.

If initially the concentration is not uniform, a particle flux will appear even without the influence of the external force. To illustrate this, let us consider a classical example of such a system: a pollutant in the air. At the initial moment $t = 0$, at the origin of coordinates $\vec{r} = 0$ an emission of a substance is initiated. The aim is to find out how this spot will spread out in space and time, i.e. to find

the concentration $C(\vec{r}, t)$. The governing equations for this process are nowadays very well known under the name of Fick's laws of diffusion. They were formulated by a German physiologist Adolf Eugen Fick in 1855, but much earlier a similar mathematical treatment was done by a French mathematician and physicist Jean Baptiste Joseph Fourier concerning the problem of heat transfer.

Fick's first law states that the particle flux is proportional to the concentration gradient,

$$\vec{F}(\vec{r}, t) = -D\nabla C(\vec{r}, t), \qquad (1.1)$$

where the coefficient D is the diffusion coefficient measured in $\frac{m^2}{s}$. D is a specific property of the substance and, in the simplest approximation, is supposed to be independent of the concentration $C(\vec{r}, t)$. The minus sign is a consequence of the second law of thermodynamics and indicates that the flux is directed from regions with higher concentration to regions with lower concentration, that is the systems tends to a homogeneous state with higher entropy.

Fick's second law provides the equation for the concentration. It follows from Fick's first law and the mass conservation law which states that the total number of particles in the system is fixed. If there are no particle sources, it reads

$$\dot{C}(\vec{r}, t) = -\mathrm{div}\vec{F}(\vec{r}, t), \qquad (1.2)$$

where the dot denotes a time derivative. The minus sign reflects the fact that the particle concentration decreases whenever particles flow out of the volume. Inserting Fick's first law into Eq. 1.2 yields Fick's second law,

$$\dot{C}(\vec{r}, t) = D\triangle C(\vec{r}, t). \qquad (1.3)$$

This is a second-order parabolic partial differential equation which is well known as diffusion equation. All examples of transport properties shown above are described by this equation. In case of heat transfer Eq. 1.3 was derived by Fourier and describes a diffusion of quasi particles. Fourier's law states that the heat flux $\vec{q}(\vec{r}, t)$ is proportional to the negative temperature gradient,

$$\vec{q}(\vec{r}, t) = -k_T\nabla T(\vec{r}, t), \qquad (1.4)$$

where k_T is the thermal conductivity. Combined with the energy conservation law it gives the heat equation,

$$\dot{T}(\vec{r}, t) = k_T \triangle T(\vec{r}, t), \qquad (1.5)$$

This equation has the same form as the diffusion equation and is used in condensed matter physics to describe heat transport.

Eq. 1.3 can be easily generalized to the multispecies case, i.e. where particles of different kind are present. The mass conservation law is very general and valid for each species. In this case, Fick's first law reads

$$\vec{F}_i(\vec{r}, t) = -D_i \nabla C_i(\vec{r}, t), \qquad (1.6)$$

where the index i denotes the ith species. One can see that fluxes of different species are independent from each other. This is realized in so called ideal solutions, see (4). If the solution is not ideal, the flux is expressed by the chemical potential of the correspondent species, $\bar{\mu}_i(\vec{r}, t)$,

$$\vec{F}_i(\vec{r}, t) = -\frac{D_i C_i(\vec{r}, t)}{RT} \nabla \bar{\mu}_i(\vec{r}, t), \qquad (1.7)$$

where R is the gas constant and T is the temperature. Though, often the system can be considered as an ideal mixture.

Coming back to the pollutant-in-the-air problem, Fick's second law allows to solve it. Performing Fourier transformation of the diffusion equation, Eq. 1.3, from the $\vec{r}$- to the $\vec{k}$-representation we get

$$\dot{C}(\vec{k}, t) = -Dk^2 C(\vec{k}, t). \qquad (1.8)$$

The solution of the last equation is

$$C(\vec{k}, t) = \exp(-Dk^2 t). \qquad (1.9)$$

Inverting Eq. 1.9 back into $\vec{r}$-representation it results

$$C(\vec{r}, t) = \frac{1}{(4\pi Dt)^{\frac{3}{2}}} \exp\left(-\frac{r^2}{4Dt}\right). \qquad (1.10)$$

In the same manner one can find the Green's function of the diffusion equation which will be used later.

Eq. 1.10 defines the concentration as a spherically symmetric function of co-ordinates because it involves only r^2. The problem becomes more complicated when the system is subjected to an external field which breaks the rotational symmetry. In the case of the pollutant-in-the-air problem, as a reasonable experimental realization, the external field could be the gravity. This force can not be screened and to some extend can be considered as a constant drifting force. In the present work we will consider the external electric field which can be screened and therefore definitively is a function of coordinate and time. Though, the transport equations are still based on the diffusion equation.

Let us consider an initially homogeneous system containing only two species, one of which is positively charged particles and another one is negatively charged particles. At the initial moment the system is subjected to an external electric field which causes a redistribution of the ions, and consequently changes the electric field within the system because of screening. The particle flux consists of a diffusive part and a contribution originated by the external field,

$$\vec{F}_{\pm}(\vec{r}, t) = -D_{\pm} \nabla C_{\pm}(\vec{r}, t) \pm \mu_{\pm} z_{\pm} e C_{\pm}(\vec{r}, t) \vec{E}(\vec{r}, t) , \qquad (1.11)$$

where e is the elementary charge, $z_{\pm}$ are valences of the ions, and $\vec{E}(\vec{r}, t)$ is the electric field strength. The second term defines the mobility of ions, $\mu_{\pm}$, as the ratio of their terminal drift velocity to the applied force. It is supposed that the mobility is related to the diffusion coefficient via the Einstein relation, $D_{\pm} = \mu_{\pm} k_B T$, where k_B is the Boltzmann constant. Sometimes, when one deals with charged particles, the mobility is defined as a ratio of the particle terminal drift velocity to the applied electric field. In this case Einstein's relation reads $D = \frac{\mu k_B T}{ze}$.

Equations for $\vec{F}_{+}(\vec{r}, t)$ and $\vec{F}_{-}(\vec{r}, t)$ are coupled by the electric field. Due to screening, the electric field is not independent of the concentrations but related to them via the Poisson equation,

$$\nabla \cdot \vec{E}(\vec{r}, t) = \frac{e}{\epsilon} \left(z_+ C_+(\vec{r}, t) - z_- C_-(\vec{r}, t) \right) , \qquad (1.12)$$

where ϵ is the permittivity of the medium.

The problem is formulated quite generally without specifying the physical origin or particular properties of the considered system. Typically, this approach is

applied to systems of two types. The first one is electrolytes which are substances containing free mobile ions. From the definition one can see that systems of this group cover a wide range of applications spreading from ion batteries to biological systems such as diffusion through a membrane or a narrow ion channel. Another type of systems is semiconductors where a role of ions is played by electrons and holes. Despite electrolytes and semiconductors are physically different systems, they are described by the same set of equations.

To obtain the transport equations let us insert fluxes from Eqs. 1.11 into Fick's first law, Eq. 1.7. This leads to

$$\dot{C}_\pm(\vec{r},t) = D_\pm \Delta C_\pm(\vec{r},t) \mp \mu_\pm z_\pm e \nabla \cdot \left(C_\pm(\vec{r},t)\vec{E}(\vec{r},t) \right) . \qquad (1.13)$$

The transport equations, Eqs. 1.13, combined with the Poisson equation, Eq. 1.12, are called Poisson-Nernst-Planck (PNP) equations. They describe a diffusion of charged particles in an external electric field and are of interest in this work. Despite the PNP equations were formulated a long time ago, they are still widely used in their original form. In some papers, see (5), possible modifications of the PNP equations are considered in order to take into account additional restrictions which could be imposed by the experimental realization, such as for example steric effects which can be essential at very high applied voltages. Nevertheless, we will consider only the original PNP equations because they are able to describe the main experimental realizations and to predict the main features of the system behavior. In spite of their importance, the exact solution of the PNP equation is still unknown. In general, there is a lack of analytical results in this topic. This fact became a motivation for the present work. On the other hand, one should not underestimate the progress achieved so far. Therefore, before presenting the new results we will describe already known findings. As every physical problem, the diffusion of charged particles in an external electric field can be treated numerically, analytically, and mathematically in a sense that mathematical properties of equations are of interest apart of a physical context. Let us discuss all these possibilities separately.

The main progress has been probably achieved by numerical solutions because using various computational schemes one can treat a great number of different systems with different geometries and with complicated boundary conditions which

are difficult to take into account analytically. A lot of simulation procedures have been developed, (6; 7), using different boundary conditions, (8), for different geometries, (9), et cetera. Much effort and different assumptions have been made to speed up the calculations, (10). The steady state of the PNP equations has been studied as well, (11). Because the present work is focused on an analytical treatment, we only refer to the corresponding literature concerning the discussion and explanation of the simulations.

Analytical solutions are much rarer than numerical ones and, if available, are still restricted to very simple systems. First results were obtained by Gouy and Chapman, (12), and Debye and Hueckel, (13; 14), at the beginning of the twentieth century and became the classics of statistical physics. Those theories deal with the steady state solutions to systems with different geometries. The Debye-Hueckel theory treats the problem in the linear regime for a spherically symmetric system, while the Gouy-Chapman theory provides an exact solution of the full nonlinear problem for a semi-infinite plane system. Later another exact solution for the system of similar simple geometry was found in (15). The common feature of all these solutions is that they are expressed in terms of elementary functions and related to systems with a very simple geometry and trivial boundary conditions. The steady state solution of more complicated systems can be expressed only via non-elementary functions and, therefore, is seldom analyzed. In some cases one can consider a linear regime when deviations of the particle concentration from a constant is small and the PNP equations can be simplified. But even in the linear regime non-elementary functions have to be sometimes used as demonstrated in (16), where the case of three different species is considered, and the steady state solution is expressed via Bessel functions. As shown in (17), the general steady state solution of the PNP equations is only expressed via Jacobi elliptic functions. This makes the analysis of the general solution much more complicated and explains a lack of exact results. One of the goals of the present work is to close this gap. So far, the main efforts are directed to a development of new numerical procedures giving more precise results and taking less calculation costs. One should mention that the stationary PNP equations are equivalent to the Poisson-Boltzmann equation which describes many other physical systems and also should be analyzed analytically.

The dynamical problem seems to be even more complicated. Its general time-dependent solution should be related to Jacobi elliptic functions because the system is expected to tend to a steady state which is expressed via these functions. From a theoretical point of view, the electric field and the particle concentrations are of interest, although the direct measurement of these quantities is often quite difficult to perform experimentally. For biological systems these profiles could be of particular importance. In contrast, for electrolytes another quantity is of interest, namely the external current. This current is generated in the external circuit by a motion of ions in the space between the electrodes and can be extracted from experimental data. Consequently, in order to compare theoretical results with experimental data, one has to calculate the external current. This is an advantage to a theoretical analysis, because, as we will see later, it is much easier to find a reasonable approximate expression for the external current than for the particle concentrations. Recently the problem in plane geometry was considered very detailed in (18). According to the authors the behavior of the system can be generally influenced by two parameters: the applied voltage v and the initial concentration of particles η, which suggests a consideration of four limiting cases: (i) the diffusion limited case where both v and η are small, (ii) the double layer limited case where η is large and v is small, (iii) the geometry limited case where η is small and v is large, (iv) the space charge limited case where both v and η are large. Regimes where v is large are also called regimes without diffusion. In each regime the PNP equations can be simplified drastically and therefore can be solved. These results, as shown in (18), can be fit to experimental observations and reveal main features of the system behavior. However, the applicability of the regimes is not absolutely clear and can be questionable due to the unreliability of assumptions these regimes are based on. To illustrate this point one should notice that the applicability of regimes is restricted not only by values of v and η but also by the moment of time. Non of the regimes can be valid in the long time limit. Regimes without diffusion are not valid because the time derivative of the concentration is small only whenever the diffusive and the electric field parts in Eq. 1.13 nearly cancel each other, which means that the diffusive part can not be neglected. Regimes with small v are considered to describe the linear regime, because a small value of the applied voltage requires automatically

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a small deviation of the concentration from its initial value η. The solution was obtained by a formal separation of time and coordinate variables. But mathematically these equations can not be solved by this method because the spatial part of the solution coincides with the steady state solution, which in turn automatically claims that all time derivatives are zero. Thereby, all regimes suggested in (18) fail in the long-time limit. Nevertheless, this approach yields reasonable predictions which can be fit to experimental results. Some papers are devoted solely to the problem in the linear regime, which can serve as a starting point in searching an approximate solution to the full nonlinear problem. However, even in the linear regime the PNP equations have not been solved exactly. In (19) the long-time limit was considered by a separation of variables. The coordinate dependence of the concentration is different to the one presented in (18) because the spatial part of the solution was not equal to the steady state. On the other hand, this means that their long-time-limit solution does not tend to the steady state solution. A similar contradiction was found in (20). The authors did not separate variables but their solution does not tend to the steady state one as well. In spite of this logical contradiction, both solutions presented in (19) and (20) yield the correct time constant and can be fit to experimental results. All the different solutions mentioned above are not applicable in the long-time regime. They contain logical contradictions but provide more or less correct predictions which are in agreement with experiment data. This paradox will be explained in Chapter 4 together with presenting the solution free from such drawbacks.

The PNP equations are designed to describe a diffusion of charged particles in an external electric field. Such processes are realized experimentally very often and therefore should be investigated. On the other hand, there is a pure mathematical interest in the PNP equations. They represent a set of nonlinear coupled partial differential equations, which is worth to be analyzed. We will not discuss all related details. A very comprehensive and profound discussion is given in (21). Although the results obtained there can be hardly used to explain experimental data, they are important for the entire concept of the PNP approach. For example, it was shown that according to the PNP equations the particle concentrations $C_{\pm}(\vec{r}, t)$ can never be negative. Mathematical analysis of general properties of the PNP equations can be used to establish the borders of

applicability of the approach. For instance, intuitively it is obvious that it is restricted to not very high applied voltages. A high applied voltage should lead to very steep concentration gradients which are beyond Fick's law of diffusion.

In the view of the problems summarized above, the present work is aimed to overcome the lack of analytical results by providing a self-consistent treatment and noncontradictory analytical solution of the PNP equations. The dissertation is organized as follows. In the next section of this chapter the system of interest is described and the problem to solve is formulated. In Chapter 2 an overview of different models and methods is presented. The common terminology is introduced and the governing equations are derived and discussed. Although all these results were obtained earlier, they reflect the general understanding of the problem. Chapters 3 and 4 represent mainly new results. In Chapter 3 the general steady state solution of the PNP is found. In contrast to other works, the solution is analyzed directly in terms of Jacobi elliptic functions. A systematic approach is proposed to find a reasonable approximate solution in terms of elementary functions. It is shown that the approximation scheme is valid in a wide range of parameters characterizing the system. Further, the solution of the one-dimensional problem is extended into more general cases which were so far realized only by means of numerical simulations. Finally in Chapter 4 the dynamical problem is investigated in the linear regime. A response to DC and AC voltages is found. In contrast to other works, all boundary and initial conditions are fulfilled. In the long-time limit the system reaches the steady state.

1.2 Systems studied

Let us consider a binary, symmetric, completely dissociated electrolyte enclosed by two parallel planar electrodes located at $x = \pm L$ as sketched in Fig. 1.1. The word binary means that there are only two types of charged particles: positive and negative. All positive particles are identical to each other. The same is valid for negative particles. The word symmetric indicates that the initial concentrations and charges of these species are the same, $\eta_+ = \eta_- = \eta$ and $|z_+| = |z_-| = z$. The substance containing free ions is supposed to be a polymer. Such systems are called polymer electrolytes. They should not be confused with so called

polyelectrolytes. Polyelectrolytes are polymers whose repeating units have an electrolyte group. These groups can dissociate making the polymer charged. Thus, properties of polyelectrolytes are similar to those of both electrolytes and polymers. Generally speaking, if in a polymer electrolyte all ions of the same kind are fixed in space, the behavior is similar to that of a polyelectrolyte. In other words, in polymer electrolyte there is the same number of positive and negative particles which can move through an electrically neutral polymer matrix, whereas in polyelectrolyte there are only positive or only negative ions which can move through a charged media.
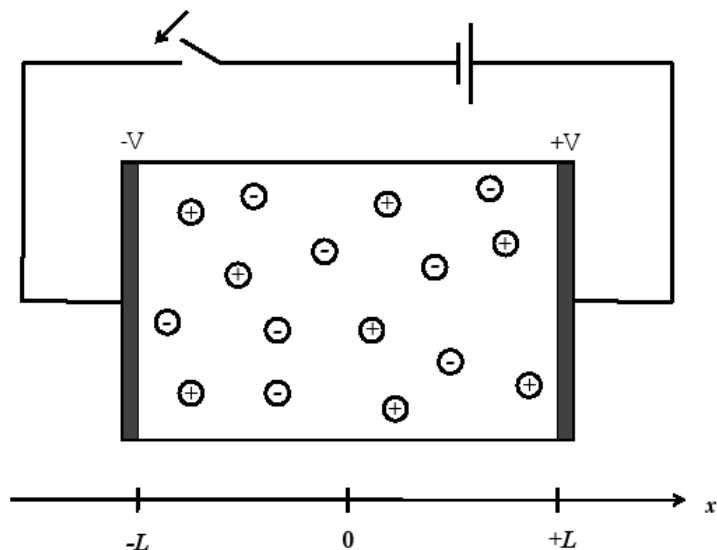
Figure 1.1: Sketch of the system

In the present work we consider mainly polymer electrolytes, thought in the linear regime the treatment of polyelectrolytes is very similar. This will be demonstrated in Chapter 4.

The system is kept on a constant temperature higher than the polymer glass transition one, which allows a particle migration. Without the influence of external forces the system is homogeneous; the particle concentrations do not depend on coordinate and are equal to η. At the initial moment a voltage is applied to the electrodes enforcing ions to move and therefore making the system in-

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homogeneous. As far as the system is not homogeneous, particle concentration gradients appear and try to return the system into the homogeneous state. The competition of these two processes defines the evolution of the system. As long as diffusive and electric parts do not give the same contribution, the evolution of the system takes place. The general theoretical task is to find the time and spatial dependencies of the particle concentrations $C_\pm(\vec{r}, t)$ and the electric field $\vec{E}(\vec{r}, t)$ between the electrodes. Because the electrodes are supposed to be flat and infinite, the system can be considered as one-dimensional, and hence a vector $\vec{r}$ can be replaced by a coordinate x.

Ions move within the polymer matrix whose properties are supposed to be time-independent. This also means, a change of the electric field and the ion concentrations has no influence on the matrix and as well there are no chemical reactions, like for example a charge absorption by the polymer. This allows the consideration of the charge migration without specifying a particular chemical structure of the matrix that of course is responsible for some physical properties of the system, such as the dielectric constant or the diffusion coefficient. It is a challenging task to predict them for a taken polymer matrix theoretically, but this lies beyond the scope of our research. In the present work all physical parameters of the system are supposed to be known. The particle diffusion constant D and the mobility μ are related to each other via the Einstein relation, $D = \mu k_B T$. Moreover, it is supposed that dynamical properties of positive and negative particles are the same, $D_+ = D_- = D$ and $\mu_+ = \mu_- = \mu$, which is suggested by experimental data, see for example (22) and citations therein. However, in some cases concerning mainly semiconductors, this assumption could be inapplicable.

The system is locked between two metal electrodes which are supposed to be ideal conductors. At their surfaces chemical reactions can take place. Since the polymer is supposed to be chemically neutral, chemical reactions involve only mobile ions. In other words, ions can appear or disappear at the surface of electrodes but not in the bulk. Such processes are called Faradaic processes because they lead to a Faradaic current. Consequently, an absence of Faradaic current means that ions are locked between the electrodes and can not pass through them. Since this work is focused on general properties, in particular on understanding of the diffusion in an external field, further it is supposed that

Faradaic processes can be neglected. For a discussion of the treatment of systems with Faradaic processes see (23; 24).

As it was stated above, the main theoretical goal is to find the spatiotemporal concentration profiles $C_{\pm}(x, t)$ and the electric field distribution $E(x, t)$. In order to compare theoretical predictions with experimental data, one should calculate the external current. When the voltage has been just applied, an excess of electrons appears at the electrodes. As the electrodes are ideal conductors, this process occurs infinitely fast and corresponds to an infinite current in the external circuit. Then particles start to move inducing additional charge on the electrodes and, consequently, causing the external current. This current can be extracted from experimental data on dielectric spectroscopy and can be used to compare experimental and theoretical results.

Chapter 2

Overview of models and methods

The system of interest was described in general in Section 1.2. The current Chapter reveals the main properties of the system and the main approaches to treat them. The conventional terminology is introduced and explained following the historical development of the subject. Models presented here are the basics of electrochemistry; their deep and complete discussion can be found in numerous books and textbooks, e.g. see (1; 17; 25; 26).

2.1 Electrical circuit model

2.1.1 General idea

At the initial moment a dc voltage is applied, which creates a nonzero charge density at the electrodes. As a response to the applied voltage, mobile charged particles begin to move within the polymer matrix, and the charge excess appears near the electrode surface. Since Faradaic processes are neglected, ions can not cross the electrodes, and the behavior of the electrode-solutions interface is analogous to that of a capacitor. A capacitor consists of two parallel electrodes and thus is the simplest electrical circuit element. This fact gave the name to the model. The basic idea of replacing the actual system by an equivalent circuit belongs to Kohlrausch (27). The first mathematical theory of Kohlrausch's "polarization capacitance" was given by Warburg (28; 29).

Let us for the beginning consider a conventional capacitor. When a potential is applied across it, a charge q^m will be accumulated at the electrode until it satisfies the equation $q^m = c\,v$, where c is the capacitance of the capacitor[1], and v is the applied voltage. If the electrode-solution interface is considered as a capacitor, one of its electrodes is the electrolyte and the charge at this electrode, q^s, is accumulated due to a redistribution of ions in the solution. The charge on another, real electrode comes from the battery. For a capacitor, at every moment $q^m = -q^s$. In this simplified case, the electrode-solution interface consists of two electrical layers. Such an interface coined the name the electrical double layer introduced by Helmholtz. He considered only a very narrow layer close to the electrode. Nowadays this layer is considered as a part of the double layer.

Despite, as it turned out, the double layer is not really double, this term is still used for such interfaces. In fact, its solution part is thought to consist of several layers, see Fig. 2.1. The first, closest to the electrode one is called the inner layer. Sometimes it is also called the compact or Helmholtz or Stern layer. The name compact layer was introduced by Stern in 1924 when he suggested decomposing the double layer into a layer in Helmholtz sense described above, which explains the second offered name, and diffuse or Gouy part which will be introduced later. Because the idea to consider the inner layer as a separate part of the double layer belongs to Stern, this layer bears sometimes his name. The inner layer contains solvent molecules which are in contact with the electrode, that is they are said to be specifically adsorbed. The average position of electrical centers of specifically adsorbed ions is called the inner Helmholtz plane (IHP) and is located at the distance x_1, see Fig. 2.1, from the electrode. The corresponding charge density provided by specifically adsorbed ions in this inner layer is denoted by σ^i. According to the definition, $\sigma^i = \frac{q^i}{S}$, where S is the area of the electrode. Solvated ions can not approach the electrode closer than to a distance x_2. Centers of those nearest ions are located on the outer Helmholtz plane (OHP). The interaction of these ions involves only long-range electrostatic forces, so the ions are said to be nonspecifically adsorbed. In contrast to specifically adsorbed ions, the interaction of nonspecifically adsorbed ions is independent of their chemical properties. The

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[1]Conventionally, the capital C is used to denote a capacitance but this letter was already reserved for the concentration.

compact layer has a strong impact on the rates of electrode processes for instance the electrode reaction kinetics. The nonspecifically adsorbed ions are distributed in a three-dimensional region at the scale of the screening length, forming the diffuse layer. This layer completes the double layer. Thus, the total excess charge density in the solution part of the double layer, σ^s, is a sum of the excess charge density in the diffuse layer, σ^d, and the charge density in the Stern layer, σ^i,

$$\sigma^s = \sigma^i + \sigma^d = -\sigma^m \, .$$

According to the definition, the boundary between the diffuse layer and the bulk electrolyte is not well defined and they can be seeing as a single, continuous region. This is definitely a drawback if this approach but already such a simple model can provide reasonable, experimentally justified predictions. Though in some cases, see for example (30), the fit of experimental data is not sufficiently precise.
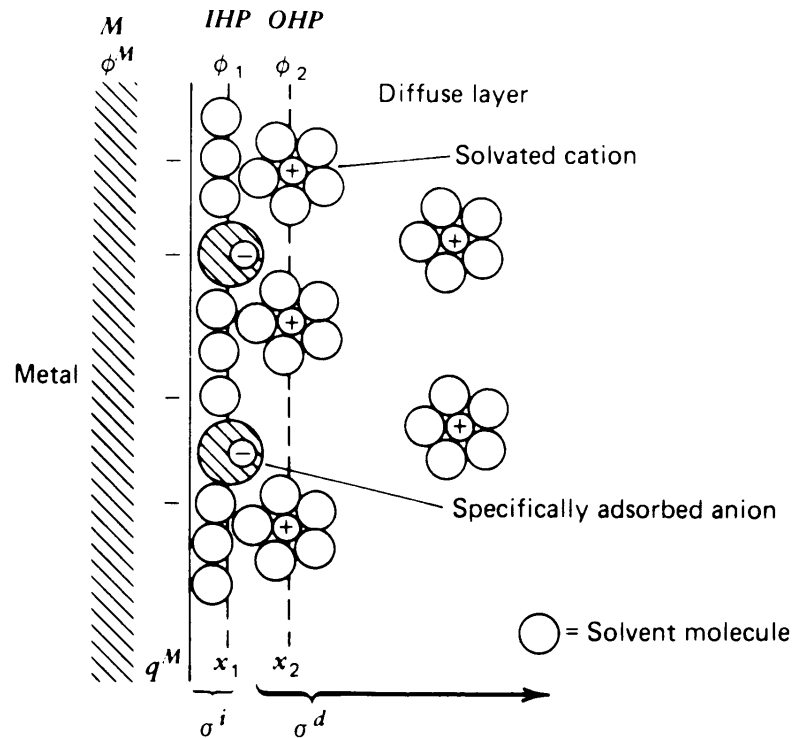

Figure 2.1: Model of the electrode-solution, double-layer region. (taken from (1))

Let us apply a step voltage to the system and calculate the external current which, according to experimental data, is nearly exponential. Since the double layer in the vicinity of each electrode was replaced with a capacitor, we have, as schematically depicted in Fig. 2.2, two identical capacitors separated by a resistor. At any time the sum of voltages across the resistor, V_R, and the capacitors, $2V_c$,
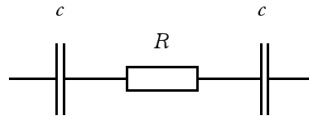
Figure 2.2: Schematic representation of the system within the electrical circuit model

must be equal to the applied voltage V,

$$V = V_R + 2V_c = JR + 2\frac{q}{c}.$$

Using the definition of the current $J = \dot{q}$, one finds

$$\frac{dq}{dt} = \frac{V}{R} - \frac{2q}{Rc}.$$

For an initially uncharged capacitor it yields

$$q = \frac{Vc}{2}\left[1 - \exp(\frac{-2t}{Rc})\right].$$

Taking a time derivative we finally get

$$J = \frac{V}{R}\exp\left(\frac{-2t}{Rc}\right).$$

The current decays exponentially with time constant $\tau = Rc/2$. For example, if $R = 1\Omega$ and $c = 20\mu F$, $\tau = 10\mu sec$, or double-layer charging is 95% complete in $30\mu sec$.

The quantity τ depends on parameters introduced in the model: R and c. To find values of these parameters, more sophisticated model of the double layer should be considered.

2.1.2 Models for a double layer structure

In the previous section we introduced the double layer and described its general properties. In this section we will discuss its structure in more detail. Since the metallic electrode is a good conductor, the electrons will concentrate at its surface, forming a very narrow layer. Helmholtz was the first one who supposed that ions in the solution intend to form a layer of countercharges close to the electrode as well. These two layers he united into a double layer and suggested to consider them as a parallel-plate capacitor (31; 32). In this case, the charge density σ and the voltage drop between the plates, v, are related via

$$\sigma = \frac{\epsilon}{d}v \,,$$

where ϵ is the permittivity of the medium [1], and d is the interplate distance. The differential capacitance is

$$c_d \equiv \frac{d\sigma}{dv_d} = \frac{\epsilon}{d} \,. \tag{2.1}$$

Eq. 2.1 reveals the drawback of the model. Unlike electrons at the electrode which is supposed to be an ideal conductor, ions in the solution do not form a layer which thickness can be neglected. For systems with lower initial concentration η, the charge excess spreads wider into the bulk than for systems with higher η. Also higher applied voltage means higher force acting on ions and dragging them closer to the electrode. So, the thickness of the layer and, consequently, c_d should depend on both applied voltage and initial concentration, but, according to Eq. 2.1, c_d is independent of them. Therefore the model should take into account the structure of the solution part of the double layer, which was not considered by Helmholtz. Gouy and Chapman independently proposed the model based on the statistical mechanical approach for it and introduced the diffuse layer.

Let us consider a solution of different types of ions which are in thermal equilibrium. Thermal equilibrium claims that particles are Boltzmann distributed,

$$C_i(x) = \eta_i \exp\left(\frac{-z_i e\phi(x)}{k_B T}\right) \,. \tag{2.2}$$

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[1] In some treatments, the permittivity of the medium is denoted as $\epsilon\epsilon_0$, where ϵ is the dielectric constant of the medium, and ϵ_0 is the permittivity of free space.

The subscript i denotes different ion species, η_i is the initial concentration of the corresponding species, e is the elementary charge, z_i is the ion valency, so $z_i e$ is the charge of the ion. The potential of electric field $\phi(x)$ is measured with respect to the bulk solution. The charge density is

$$\rho(x) = e \sum_i C_i(x) z_i \,, \tag{2.3}$$

where i runs over all ionic species. From electrostatics it is known that $\rho(x)$ is related to the potential by the Poisson equation,

$$\rho(x) = -\epsilon \frac{d^2\phi(x)}{dx^2} \,. \tag{2.4}$$

Here and further we use the static Poisson equation because the velocity of charge migration is low. A correspondent estimation will be presented at the end of the next section. Combining Eqs. 2.2 and 2.4 together and taking into account Eq. 2.3 we get the Poisson-Boltzmann equation describing the coordinate dependence of the potential,

$$\frac{d^2\phi(x)}{dx^2} = -\frac{e}{\epsilon} \sum_i \eta_i z_i \exp\left(-\frac{z_i e\phi(x)}{k_B T}\right) \,. \tag{2.5}$$

To solve this equation, we use the identity

$$\frac{d^2\phi}{dx^2} = \frac{1}{2}\frac{d}{d\phi}\left(\frac{d\phi}{dx}\right)^2 \,, \tag{2.6}$$

which turns the Poisson-Boltzmann equation into

$$d\left(\frac{d\phi(x)}{dx}\right)^2 = -\frac{2e}{\epsilon} \sum_i \eta_i z_i \exp\left(-\frac{z_i e\phi(x)}{k_B T}\right) d\phi(x) \,. \tag{2.7}$$

Integration gives

$$\left(\frac{d\phi(x)}{dx}\right)^2 = \frac{2k_B T}{\epsilon} \sum_i \eta_i \exp\left(-\frac{z_i e\phi(x)}{k_B T}\right) + \text{constant} \,. \tag{2.8}$$

The integration constant can be found from the condition that far from the electrode $\phi = 0$ and $\frac{d\phi}{dx} = 0$. Thus,

$$\left(\frac{d\phi(x)}{dx}\right)^2 = \frac{2k_B T}{\epsilon} \sum_i \eta_i \left[\exp\left(\frac{-z_i e\phi(x)}{k_B T}\right) - 1\right] \,. \tag{2.9}$$

For symmetrical electrolytes this expression can be simplified [1] to

$$\frac{d\phi(x)}{dx} = -\left(\frac{8k_BT\eta}{\epsilon}\right)^2 \sinh\left(\frac{ze\phi(x)}{2k_BT}\right) . \tag{2.10}$$

Eq. 2.10 can be integrated

$$\int_{\phi_0}^{\phi(s)} \frac{d\phi}{\sinh(ez\phi/2k_BT)} = -\left(\frac{8k_BT\eta}{\epsilon}\right)^{0.5} \int_0^s dx , \tag{2.11}$$

where s is the distance from the electrode, and ϕ_0 is the applied potential. Integration yields

$$\frac{\tanh(ze\phi(s)/4k_BT)}{\tanh(ze\phi_0/4k_BT)} = e^{-\kappa s} , \tag{2.12}$$

or

$$\phi(s) = \frac{4k_BT}{ze}\text{arctanh}\left(\tanh(ze\phi_0/4k_BT)\,e^{-\kappa s}\right) , \tag{2.13}$$

where the Debye screening length λ_D is introduced according to

$$\frac{1}{\lambda_D} \equiv \kappa = \left(\frac{2\eta z^2 e^2}{\epsilon k_BT}\right)^{0.5} . \tag{2.14}$$

Interesting to note that Debye was not the first one who derived this expression. His work dates back to 1923 and is a part of his seminar work with Hueckel, (13; 14), on charge screening in bulk electrolytes. They were dealing with the spherical screening cloud around an ion, and, due to the low potentials involved, they linearized the transport equations, allowing them to handle general electrolytes. But more than a decade earlier, considering the identical semi-infinite problem of screening near a flat, blocking electrode, Gouy obtained the exact solution of the full nonlinear equations for the equilibrium potential profile in several cases of binary electrolytes, $z_+/z_- = 1$ and 2, see (33). Though his solution is not general and appropriate only for this particular case. It is difficult to generalize it to other systems. A few years later, Chapman, (34), independently derived Gouy's solution for a univalent electrolyte, $z_+ = z_- = 1$. He also gave a simple form for the charge voltage relation of the diffuse-layer capacitor, Eq. 2.17. So that, λ_D is sometimes called the Gouy-Chapman length.

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[1]Another way to solve this equation is to use a substitution $y = \exp(-\alpha\phi)$.

Eq. 2.12 describes the potential profile in the diffuse layer. At large applied potentials the diffuse layer is relatively compact and the potential decreases rapidly with increasing distance from the electrode. At small ϕ_0 the decline of $\phi(x)$ is smoother and approaches an exponential form. As an estimation, if $(ze\phi_0/4k_BT) \lesssim 0.25$ then $\tanh(ze\phi(s)/4k_BT) \cong (ze\phi(s)/4k_BT)$ which leads to

$$\phi(s) = \phi_0 e^{-\kappa s} . \tag{2.15}$$

This relation is a good approximation for $\phi_0 \lesssim 25/z\, mV$ at room temperature. To find the charge density in the vicinity of the electrode one has to integrate the Poisson equation, Eq. 2.4. This gives

$$\sigma^m = -\sigma^s = (8k_BT\epsilon\eta)^{0.5} \sinh\left(\frac{ze\phi_0}{2k_BT}\right) , \tag{2.16}$$

and, consequently, the differential capacitance is

$$c_d = \frac{d\sigma^m}{d\phi_0} = \epsilon\kappa \cosh\left(\frac{ze\phi_0}{2k_BT}\right) . \tag{2.17}$$

This simple Gouy-Chapman theory is already able to predict general properties of the system qualitatively. However, real systems show different behavior at high applied potentials and the actual capacitance is usually lower than the predicted one. Moreover, as one can see from Eq. 2.17, the differential capacitance increases unlimited with increasing applied potential ϕ_0. This could lead to the breakdown of the theory because, as it was pointed out in the previous section, at high applied potentials the double layer becomes narrower making the theory more precise. But here we have an inverse effect. To avoid this problem, Stern suggested a generalization of the theory, (35) see also (36). In the Gouy-Chapman theory it is supposed that ions are infinitely small and can approach the electrode infinitely close. In systems with low electrolyte concentration or at low applied potentials the fraction of these ions is low and can be neglected. However, in other cases the diffuse layer becomes more compact and influence of these ions increases. Such ions are situated at the distances smaller than x_2, see Fig. 2.1, in the layer between the electrode and the outer Helmholtz plane (OHP). The Poisson-Boltzmann equation can be applied at distance $x \geqslant x_2$. Repeating the

steps described above we get the equation for the potential profile of a symmetric electrolyte,

$$\int_{\phi_2}^{\phi(s)} \frac{d\phi}{\sinh(ez\phi/2k_BT)} = -\left(\frac{8k_BT\eta}{\epsilon}\right)^{0.5}\int_{x_2}^{s} dx\,. \tag{2.18}$$

Integration gives

$$\frac{\tanh(ze\phi(s)/4k_BT)}{\tanh(ze\phi_2/4k_BT)} = e^{-\kappa(s-x_2)}\,, \tag{2.19}$$

where ϕ_2 is the potential at x_2 with respect to the bulk solution. The field strength at x_2 is given according to Eq. 2.10,

$$\left(\frac{d\phi(x)}{dx}\right)_{x=x_2} = -\left(\frac{8k_BT\eta}{\epsilon}\right)^2\sinh\left(\frac{ze\phi_2}{2k_BT}\right)\,. \tag{2.20}$$

Since ions can not approach the electrode infinitely close forming the so called compact layer, the charge density there is zero. From the Poisson equation, Eq. 2.4, it follows that the potential profile is linear. The total potential drop across the double layer is

$$\phi_0 = \phi_2 - \left(\frac{d\phi(x)}{dx}\right)_{x=x_2} x_2\,. \tag{2.21}$$

Note that all of the charge on the solution side resides in the diffuse layer, and its magnitude is related to ϕ_2. Performing the same steps as earlier we find

$$\sigma^m = -\sigma^s = -\epsilon\left(\frac{d\phi(x)}{dx}\right)_{x=x_2} = (8k_BT\epsilon\eta)^{0.5}\sinh\left(\frac{ze\phi_2}{2k_BT}\right)\,. \tag{2.22}$$

Substitution of ϕ_2 from Eq. 2.21 leads to

$$\sigma^m = (8k_BT\epsilon\eta)^{0.5}\sinh\left[\frac{ze}{2k_BT}\left(\phi_0 - \frac{\sigma^m x_2}{\epsilon}\right)\right]\,. \tag{2.23}$$

Differentiation of Eq. 2.23 reveals the expression for the differential capacitance,

$$c_d = \frac{d\sigma^m}{d\phi_0} = \frac{(2\epsilon z^2 e^2\eta/k_BT)^{0.5}\cosh(ze\phi_2/2k_BT)}{1 + (x_2/\epsilon)(2\epsilon z^2 e^2\eta/k_BT)^{0.5}\cosh(ze\phi_2/2k_BT)}\,, \tag{2.24}$$

or in a more convenient way,

$$\frac{1}{c_d} = \frac{x_2}{\epsilon} + \frac{1}{(\epsilon\kappa\cosh(ze\phi_2/2k_BT)}\,. \tag{2.25}$$

From this equation it follows that the capacitance is made up of two components that can be separated in the reciprocal, exactly as it should be for two capacitors in series.

$$\frac{1}{c_d} = \frac{1}{c_H} + \frac{1}{c_D} \, . \tag{2.26}$$

Here c_H corresponds to the capacitance of the charge held at the OHP, c_D is
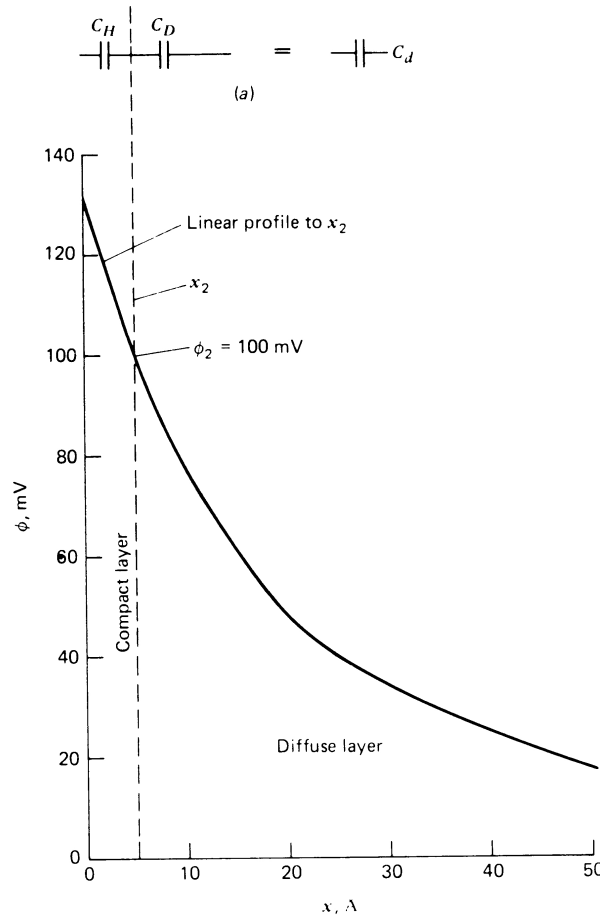
Figure 2.3: Potential profile according to the Gouy-Chapman-Stern theory and a view of the differential capacitance as a series of Helmholtz layer and diffuse layer capacitances. (taken from (1))

the capacitance of the truly diffuse charge. c_H is independent of the applied potential. The capacitance c_d shows a complex behavior. At low electrolyte concentrations it is governed by the c_D as in the Gouy-Chapman theory. At large

electrolyte concentrations or as well in dilute media but at large applied potential, c_D becomes large and gives no longer a contribution to c_d which value gets closer to c_H. To illustrate the main features and the differences of the Gouy-Chapman and Gouy-Chapman-Stern theories, let us consider Fig. 2.3.

The potential profile is calculated according to Eq. 2.19. Right next to the electrode within the Stern layer the potential decreases linearly. Without Stern's modification, it would be an exponential decay passing into a decay within the diffuse layer.

Despite the Gouy-Chapman-Stern theory presented here deals with the simplest model of the compact layer, it is able to predict a behavior of real systems in many cases. On the other hand, even the most sophisticated fits to experimental data still suffer from ambiguities. One problem is the somewhat arbitrary distinction between the diffuse layer and the bulk electrolyte, mentioned above. Furthermore, some specific features of the system have not been included into the model, such as, for example, differences in x_2 for anions and cations. There is also a pure physical restriction. Here the actual physical system was replaced by a simplified model. But, as it was shown in (37), the non-uniform change of ionic concentration can not be fully represented by homogeneous circuit elements.

2.2 Mesoscopic transport model

This approach is based on the mechanics of continua. Its advantage over the electrical circuit approach is that no assumptions of the double layer structure, even existence of the double layer itself, are necessary. Only general assumptions of the mechanics of continua are used. This allows a very general mathematical formulation of the problem and extension of results and developed methods to other systems. However, the description of the electrode-solution interface is still problematic due to interaction between ions and the material of the electrode and the fact that ions can not come infinitely close to the electrode. These effects can not be taken into account in the frame of the mechanics of continua. Therefore the conception of the Stern layer could be sometimes involved.

According to the formalism of the mechanics of continua, (3), positive and negative particles are considered as continuum fields with correspondent particles

concentration density. This makes it possible to use the standard statistical treatment. Usually it is done within Euler formulation of mechanics of fluids, (38).

To derive the main equations of this treatment, let us consider a small volume A bounded by the imaginary surface Ω. And let us for the beginning suppose that there is only one type of ions which concentration is denoted by $C(\vec{r}, t)$. The total number of particles in the volume is

$$\iiint_A C(\vec{r}, t) dA \,.$$

This is a time dependent function and changes by two processes. First of all, particles can just flow away from the volume through its surface Ω. If particles flux is denoted by $\vec{F}(\vec{r}, t)$, the number of flown particles is determined by a surface integral of the normal component of the flux,

$$\oiint_\Omega \vec{F}(\vec{r}, t) \cdot \vec{n} \, d\Omega \,,$$

where $\vec{n}$ is the outward pointing unit normal vector of the boundary. On the other hand, particles can appear or disappear due to for example recombination processes within the volume A. Corresponding change of their total number is

$$\iiint_A \sigma(\vec{r}, t) dA \,,$$

where $\sigma(\vec{r}, t)$ is a density of charge sources. Consequently, as a balance of those three terms shown above one yields

$$\iiint_A \dot{C}(\vec{r}, t) dA = - \oiint_\Omega \vec{F}(\vec{r}, t) \cdot \vec{n} \, d\Omega + \iiint_A \sigma(\vec{r}, t) dA \,. \tag{2.27}$$

Using the Gauss - Ostrogradsky theorem one can rewrite it as

$$\iiint_A \left\{ \dot{C}(\vec{r}, t) + (\nabla \cdot \vec{F}(r, t)) - \sigma(\vec{r}, t) \right\} dA = 0 \,, \tag{2.28}$$

where the operator nabla is introduced. Because the volume A is arbitrary it follows

$$\dot{C}(\vec{r}, t) = -\mathrm{div}(\vec{F}(\vec{r}, t)) + \sigma(\vec{r}, t) \,. \tag{2.29}$$

The quantities $\vec{F}(\vec{r}, t)$ and $\sigma(\vec{r}, r)$ depend on the system considered and can describe a wide range of processes. The flux $\vec{F}(\vec{r}, t)$ can be caused by the influence of any external force or convective effects. Or it can be a consequence of being in non-inertial frame when the system is, for instance, rotating. $\sigma(\vec{r}, t)$ can originate from chemical reactions or describe an external source of ions. So that, it is necessary to adopt Eq. 2.29 to the system of interest, deciding which effects are to be neglected and which are to be taken into account. We will consider a chemically stable case when there are no chemical reactions, that is there are no sources of ions, which makes $\sigma(\vec{r}, t) = 0$ and turns Eq. 2.29 into

$$\dot{C}(\vec{r}, t) = -\mathrm{div}(\vec{F}(\vec{r}, t)) \tag{2.30}$$

representing a general form of the charge conservation law for closed system.

According to the first law of diffusion, the flux is proportional to the gradient of the chemical potential,

$$\vec{F}(\vec{r}, t) = -\left(\frac{C(\vec{r}, t)D}{RT}\right)\nabla\bar{\mu}(\vec{r}, t)\,. \tag{2.31}$$

One should distinguish $\bar{\mu}$ and μ. $\bar{\mu}$ means the chemical potential whereas μ stands for the mobility. D is the diffusion coefficient, $D > 0$. The minus sign in Eq. 2.31 arises because the direction of the flux opposes the direction of increasing $\bar{\mu}$. If the system has been put out of the homogeneous state, it tends to return back. If in addition to the gradient of $\bar{\mu}$ there are some other factors that can influence the system, corresponding terms should be added to the flux. Since we are interested in the system containing mobile charged particles subjected to the external electric field, this additional term should describe the influence of the electric field. In this case the flux reads

$$\vec{F}(\vec{r}, t) = -\left(\frac{C(\vec{r}, t)D}{RT}\right)\nabla\bar{\mu}(\vec{r}, t) - ze\mu C(\vec{r}, t)\nabla\phi(\vec{r}, t)\,.$$

The second term represents the Coulomb interaction of ions. Supposing that concentration gradients are not very high, i.e. low enough to allow a use of Ficks first law, see Eq. 1.6 and its discussion, Eq. 2.31 yields

$$\vec{F}(\vec{r}, t) = -D\nabla C(\vec{r}, t) - ze\mu C(\vec{r}, t)\nabla\phi(\vec{r}, t)\,. \tag{2.32}$$

Inserting this into the mass conservation law, Eq. 2.30, we get the Nernst-Planck equation,

$$\dot{C}(\vec{r},t) = \text{div}\left(D\nabla C(\vec{r},t) + ze\mu C(\vec{r},t)\nabla\phi(\vec{r},t)\right). \tag{2.33}$$

If there are several species, this equation is valid for each of them. The concentration $C(\vec{r},t)$ should be replaced by $C_i(\vec{r},t)$, where i corresponds to various species. In this case, Eq. 2.33 reads

$$\dot{C}_i(\vec{r},t) = \text{div}\left(D_i\nabla C_i(\vec{r},t) + z_ie\mu_iC_i(\vec{r},t)\nabla\phi(\vec{r},t)\right). \tag{2.34}$$

Eq. 2.33 contains two valuables, $C(\vec{r},t)$ and $\phi(\vec{r},t)$, but this is only one equation. To close the system, the Poisson equation should be added

$$\rho(\vec{r},t) = -\epsilon\frac{d^2\phi(\vec{r},t)}{dx^2}, \tag{2.35}$$

where $\rho(\vec{r},t)$ is a charge density, $\rho(\vec{r},t) \equiv -zeC(\vec{r},t)$. Strictly speaking, one should use the time-dependent Poisson equation,

$$\rho(\vec{r},t) = -\epsilon\left(\frac{d^2\phi(\vec{r},t)}{dx^2} - \frac{d^2\phi(\vec{r},t)}{c^2dt^2}\right), \tag{2.36}$$

but a velocity of the charge movement is not very high, so the last term can be neglected. A corresponding estimation will be given at the end of this section.

Eqs. 2.33 and 2.35 represent the Poisson-Nernst-Planck equations abbreviated further as PNP.

Let us now apply this approach to the system of interest described in Chapter 1.2. For this purpose we will rewrite Eqs. 2.34 for two species in one dimensional case and formulate boundary and other conditions. As it was pointed out in Section 1.2, the system consists of a thin film placed between two electrodes which are supposed to be infinite. This provides a one-dimensional problem and the vector $\vec{r}$ can be replaced by the coordinate across the film, x.

The one-dimensional PNP equations for binary, symmetric polymer electrolyte read

$$\dot{C}_\pm(x,t) = \left(DC'_\pm(x,t) \pm \mu zeC_\pm(x,t)\phi'(x,t)\right)',$$
$$-\epsilon\phi''(x,t) = ze(C_+(x,t) - C_-(x,t)) \equiv \rho(x,t). \tag{2.37}$$

The first term on the right hand side of the first equation represents Fick's law of diffusion which limited applicability could be one of the reasons of the breakdown of the PNP. This will be discussed in Chapter 3. The second term describes the Coulomb interaction of ions. Without this term the resulting equations would describe a pure diffusion. If $\phi_\pm$ is the external potential imposed by the external circuit on the electrodes, then

$$\phi = \phi_\pm \mp \lambda_S \phi' \quad \text{at} \quad x = \pm L \,,$$

where λ_S is an effective thickness for the Stern layer. As it was described in the previous section, the compact layer is designed to account an interaction of ions with electrodes. Since its treatment was already explained, we will not consider any chemical effects. Instead of that we will concentrate on pure diffusion in the external field. So, the boundary conditions are

$$\phi_+ - \phi_- = v \,,$$

or, equivalently,

$$\int_{-L}^{L} E(x,t) = v \,.$$

At the initial moment the system is supposed to be homogeneous. This is the general formulation of the problem treated in two following chapters. In the remaining part of this chapter we will describe main features of the system behavior.

For times $t < 0$, no voltage is applied, and the initial concentration is uniform, $C_\pm(x, t \leq 0) = \eta$. For $t > 0$, a constant voltage v is applied between the electrodes, and the evolution of the concentrations and the electric field is to be found. As $t \to \infty$, the bulk electric field at the midplane, $x = 0$, decays from its initial value $v/(2L)$ to almost zero due to screening by diffuse charge which moves from one electrode to another.

If the applied potential is much smaller than the thermal voltage, $v \ll k_B T/(ze)$, PNP equations can be linearized and turned into only one equation for the charge density $\rho(x,t)$,

$$\dot{\rho}(x,t) \approx D(\rho''(x,t) - \kappa^2 \rho(x,t)) \,, \tag{2.38}$$

where $\kappa = \lambda_D^{-1}$ is the inverse Debye screening length. This equation is called the Debye-Falkenhagen equation (39). The linearization procedure and the physical meaning of linear regime will be discussed in Chapter 4.

To solve Eq. 2.38 it is convenient to use Laplace transformation defined by

$$\tilde{f}(z) = \int_0^\infty d\tau e^{-z\tau} f(\tau) \,. \tag{2.39}$$

As $\rho(x, t \leq 0) = 0$, the Laplace transform of Eq. 2.38 is

$$\tilde{\rho}''(x, z) = k^2(z)\tilde{\rho}(x, z) \,, \tag{2.40}$$

where

$$k^2(z) = \frac{z}{D} + \kappa^2 \,. \tag{2.41}$$

Due to symmetry properties of the PNP, which will be discussed in Chapter 4, $\rho(x, t)$ should be antisymmetric. The general antisymmetric solution to Eq. 2.40 is

$$\tilde{\rho}(x, z) = A(z)\sinh(kx) \,, \tag{2.42}$$

where the constant $A(z)$ is determined by the constraint $\tilde{F}_\pm(x = \pm L, z) = 0$. Taking into account the Poisson equation, Eq. 2.35, it yields for the potential

$$\tilde{\phi}(x, z) = -A(z)\frac{\cosh(kL)}{\epsilon k^2}\left(\frac{\sinh(kx)}{\cosh(kL)} + \frac{kzx}{\kappa^2 D}\right) \,, \tag{2.43}$$

where

$$A(z) = \frac{-k^2\epsilon V z^{-1}\text{sech}(kL)}{\tanh(kL) + \frac{kzL}{\kappa^2 D}} \,. \tag{2.44}$$

It is problematic to invert these equations analytically but still some conclusions can be drawn, (40). Let us focus on the Laplace transform of the charge density at the anode, $\rho(x = L, z)$. For times much longer than the Debye time $\tau_D = \lambda_D^2/D$, we consider the limit, $z \ll \kappa^2 D$, in which the Laplace transform takes the much simpler asymptotic form,

$$\tilde{\rho}(x = L, z) \sim \frac{\epsilon V \kappa^2 z^{-1}}{1 + \tau_\rho z} \,, \tag{2.45}$$

where

$$\tau_\rho = \frac{L}{\kappa D}\left[\coth(\kappa L) - (\kappa L)^{-1}\right] \,. \tag{2.46}$$

Since the Laplace transform of $1 - \exp(-\tau/\tau_0)$ is $z^{-1}/(1+z\tau_0)$, this result clearly shows that the buildup of the charge screening layer occurs exponentially with the characteristic time given by Eq. 2.46, which is of order $\tau_c = L/\kappa D$ if $\kappa L \gg 1$.

Coming back to the problem concerning the use of the static Poisson equation instead of the dynamic one the knowledge of the time constant τ_c allows us to justify this statement. To make a highly overrated estimation of the average velocity of the charge, $\bar{v}$, let us suppose that during the evolution it should cross the whole system, from one electrode to other. In this case,

$$\bar{v} \cong \frac{L}{\tau_c} = \frac{D}{\lambda_D} \, ,$$

which gives a very low velocity for all real systems and justifies the use of the static equation.

2.3 Comparison of approaches

The electrical circuit approach was one of the first approaches and brought a new terminology which is still in common use. But it can not describe dynamical properties precisely enough because when electrode-solution interface is replaced by a capacitor, it is supposed that $q^m = -q^s$. For an ideal capacitor this equation is correct, but a solution is not an ideal conductor. The changes of q^s would always lag that of q^m. In this view, the transport approach is more preferable. It is not based on any assumptions concerning the double layer structure. On the other hand, in the steady state these both approaches lead to the same result. In this section we will demonstrate that the steady state of the PNP equations, Eqs. 2.37, is equivalent to the Poisson-Boltzmann equation, Eqs. 2.5.

To proof the equivalence in the general case, let us consider a three dimensional system containing an arbitrary number of different ions. $C_i(\vec{r})$ is the concentration of the ionic species i calculated at the point $\vec{r}$. The steady state is characterized by the claim that all time derivatives are zero. In this case the PNP equations read

$$k_B T \nabla \ln C_i^{st}(\vec{r}) + e z_i \nabla \phi^{st}(\vec{r}) = 0 \, , \tag{2.47}$$

$$\epsilon \nabla^2 \phi^{st}(\vec{r}) + \sum_i e z_i C_i^{st}(\vec{r}) = 0 \, . \tag{2.48}$$

The total number of particles is obtained by integrating the concentration over the whole system,

$$N_i = \int_V C_i(\vec{r})dV \, . \tag{2.49}$$

Integration of Eq. 2.47 gives

$$C_i^{st}(\vec{r}) = A_i \exp\left(-\frac{ez_i\phi^{st}(\vec{r})}{k_B T}\right) \, , \tag{2.50}$$

where the integration constant A_i is defined by

$$A_i = \frac{N_i}{\int_V \exp\left(-\frac{ez_i\phi^{st}(\vec{r})}{k_B T}\right) dV} \, . \tag{2.51}$$

Inserting this result into Eq. 2.48 we obtain the Poisson-Boltzmann equation,

$$\epsilon \nabla^2 \phi^{st}(\vec{r}) + \sum_i ez_i A_i \exp\left(-\frac{ez_i\phi^{st}(\vec{r})}{k_B T}\right) = 0 \, . \tag{2.52}$$

Chapter 3

Steady state solution of the PNP

3.1 Derivation of the steady state

To treat the system described in Section 1.2, we use a mesoscopic transport model presented in Section 2.2. In the current chapter we consider the steady state solution, whereas the dynamical problem will be discussed in Chapter 4.

Concentrations of positive and negative ions, $C_\pm(x,t)$, and a potential of the electric field, $\phi(x,t)$, are governed by the Poisson-Nernst-Planck equations (PNP),

$$\dot{C}_\pm(x,t) = -F'_\pm(x,t) = D\left(C'_\pm(x,t) \pm \frac{ze}{k_B T}C_\pm(x,t)\phi'(x,t)\right)',$$
$$-\epsilon\phi''(x,t) = ze\left(C_+(x,t) - C_-(x,t)\right). \qquad (3.1)$$

The stationary state means that all time derivatives are set to zero. That implies the fluxes $F^{st}_\pm(x)$ are constant. Since hereafter in this chapter only steady state values are considered, the superscript st will be omitted to simplify the notation. Because particle fluxes at electrodes turn to zero, $F_\pm(x = \pm L, t) = 0$, transport equations read

$$C'_\pm(x,t) \pm \frac{ze}{k_B T}C_\pm(x,t)\phi'(x,t) = 0. \qquad (3.2)$$

The steady state is independent of the diffusion coefficient or mobility, i.e. systems with different D and μ tend to the same stationary state. Physically this means that the steady state does not depend on dynamical properties of the system. A difference of charge carrier concentrations, $C_+(x) - C_-(x)$, with a help of

the Poisson equation, can be expressed in terms of the electric field potential. Subtraction of Eqs. 3.2 from each other gives

$$k_B T \frac{\epsilon}{ze} \phi'''(x) - ze\phi'(x)C(x) = 0\,, \tag{3.3}$$

where $C(x) = C_+(x) + C_-(x)$ is the total particle concentration. Summing Eqs. 3.2 one gets an equation for $C(x)$,

$$-C(x) + \frac{\epsilon}{2k_B T}\left(\frac{\partial\phi(x)}{\partial x}\right)^2 = r\,, \tag{3.4}$$

where r is an integration constant. Both Eqs. 3.3 and 3.4 can be combined to a single equation for the potential $\phi(x)$,

$$\frac{\epsilon}{ze}\frac{\partial^3\phi}{\partial x^3} - \frac{ze}{k_B T}\frac{d\phi}{dx}\left[\frac{\epsilon}{2k_B T}\left(\frac{\partial\phi}{\partial x}\right)^2 - r\right] = 0\,. \tag{3.5}$$

The ion concentrations $C_\pm(x)$ can be found according to

$$\frac{\partial \ln C_\pm(x)}{\partial x} = \mp\frac{ze}{k_B T}\phi'(x)\,. \tag{3.6}$$

The solution of Eq. 3.5 is given in terms of Jacobi elliptic functions, see (41), which are functions of two variables. Some of their properties are summarized in Appendix A. The electric field distribution reads

$$E(x) = -\phi'(x) = -\frac{2k_B T}{ze}\,\tilde{q}\,\tilde{k}\,\mathrm{sn}(\tilde{k}x + x_0, \tilde{q})\,. \tag{3.7}$$

Here sn stands for the Jacobi elliptic sine, x_0 is an integration constant, $\tilde{q}$ and $\tilde{k}$ are parameters to be found from the boundary conditions. Using Eq. 3.6, the stationary concentration profile of the charge carriers can be written as

$$C_\pm(x) = -\frac{\epsilon k_B T}{2z^2 e^2}\,\tilde{k}^2\left[\mathrm{dn}(\tilde{k}x + x_0, \tilde{q}) \pm \tilde{q}\,\mathrm{cn}(\tilde{k}x + x_0, \tilde{q})\right]^2\,. \tag{3.8}$$

The quantities cn and dn are likewise Jacobi elliptic functions. Due to the symmetry property $E(x) = E(-x)$, the integration constant x_0 is equal to a quarter of the period of the Jacobi sine. From here one concludes, $x_0 = K(q)$, where $K(q)$ is the complete elliptic integral of the first kind. Consequently, the steady state solution for the electric field can be rewritten as

$$E(x) = -\frac{2k_B T}{ze}\,\tilde{q}\,\tilde{k}\,\mathrm{cd}(\tilde{k}x, \tilde{q})\,. \tag{3.9}$$

For the concentrations it reads

$$C_{\pm}(x) = -\lambda_D^2 \, \eta \, \tilde{k}^2 (1 - \tilde{q}^2) \frac{\left[1 \mp \tilde{q} \, \mathrm{sn}(\tilde{k}x, \tilde{q})\right]^2}{\mathrm{dn}^2(\tilde{k}x, \tilde{q})} \,. \tag{3.10}$$

Here the Debye screening length introduced in Eq. 2.14 appears,

$$\lambda_D = \sqrt{\frac{\epsilon k_B T}{2z^2 e^2 \eta}} \,.$$

The parameters of the Jacobi functions, $\tilde{k}$ and $\tilde{q}$, are defined by the following conditions:

$$\int_{-L}^{L} C_{\pm}(x) \, dx = 2L\eta \,, \quad \int_{-L}^{L} E(x) \, dx = v \,. \tag{3.11}$$

The first condition reflects the conservation of the total charge, where η is the initial charge concentration. The second condition indicates that the potential difference between the electrodes is simply the applied voltage v. Performing the integration of the first equation in Eqs. 3.11 and taking into account the second one we get

$$
\begin{aligned}
\tilde{E}(\tilde{k}L, \tilde{q}) - \tilde{q}^2 \mathrm{sn}(\tilde{k}L, \tilde{q})\mathrm{cd}(\tilde{k}L, \tilde{q}) &= \frac{L}{2\lambda_D^2 \tilde{k}} \left[1 + \lambda_D^2 \tilde{k}^2 (1 - \tilde{q}^2)\right] \,, \\
\ln\left(\frac{1 + \tilde{q} \, \mathrm{sn}(\tilde{k}L, \tilde{q})}{1 - \tilde{q} \, \mathrm{sn}(\tilde{k}L, \tilde{q})}\right) &= \frac{vze}{2k_B T} \,.
\end{aligned}
\tag{3.12}
$$

Here $\tilde{E}(\tilde{k}L, \tilde{q})$ stands for the incomplete elliptic integral of the second kind. Both equations determine the parameters $\tilde{k}$ and $\tilde{q}$ in terms of the initial concentration η and the applied voltage v. Eqs. 3.9 and 3.10 combined with Eqs. 3.12 provide the exact solution of the stationary PNP.

To find the parameters $\tilde{q}$ and $\tilde{k}$, let us first consider the special case of $v = 0$. This claims, $C_{\pm}(x) = \eta$ and $E(x) = 0$. The electric field is proportional to the product of three quantities: $\tilde{k}$, $\tilde{q}$ and $\mathrm{cd}(\tilde{k}x, \tilde{q})$, one of which must be zero in order to ensure $E(x) = 0$ for every x. The requirement $\mathrm{cd}(\tilde{k}x, \tilde{q})=0$ gives a condition for $\tilde{k}$ and $\tilde{q}$, leading to a periodic solution. $\tilde{k} = 0$ claims that the concentration is likewise equal to zero. So, the single unique non-trivial realization is given by the condition $\tilde{q} = 0$. According to Eq. 3.10 we get

$$C_{\pm}(x) = -\lambda_D^2 \, \eta \, \tilde{k}^2 = \eta \,. \tag{3.13}$$

Hence, the parameter $\tilde{k}$ reads

$$\tilde{k} = \frac{i}{\lambda_D} \, .$$

Due to the relation $\mathrm{sn}(0, \tilde{q}) = 0$, the mid-plane concentration is

$$C_\pm(x = 0) = -\lambda_D^2 \, \eta \, \tilde{k}^2 (1 - \tilde{q}^2) \, . \tag{3.14}$$

At small applied voltage this concentration is a constant and, consequently, $\tilde{k}$ is a constant, too. In this case the function $\mathrm{sn}(\tilde{k}x, \tilde{q})$ is pure imaginary which enforce the parameter $\tilde{q}$ to be likewise imaginary in order to make $\tilde{q}\mathrm{sn}(\tilde{k}x, \tilde{q})$ real. In other words, if $\tilde{k}$ and $\tilde{q}$ exhibit only an imaginary part, the solution is real, and the concentration of the particles is positive despite the minus sign in front of Eq. 3.10. Instead of solving Eqs. 3.12 directly, one can use the following procedure. The parameter $\tilde{q}$ is fixed, and then the another parameter $\tilde{k}$ is chosen in such a manner that the charge conservation is fulfilled. Finally we calculate the applied voltage which corresponds to these parameters. The results suggest to introduce new parameters k and q according to $\tilde{k} = ik$ and $\tilde{q} = iq$.

The representation in terms of Jacobi functions is not very practical because they depend very sensitive on the parameters $\tilde{k}$ and $\tilde{q}$. For the analytical treatment and the comparison with experiments it is also desirable to use merely elementary functions. Now let us find an approximate but more transparent version of the steady state solution, which is appropriate for most of the experimental realizations for which the PNP equations seem to be applicable.

Despite q is small, the quality of an expansion with respect to q remains questionable because the corresponding series converges very slow. On the other hand, it is known that the charge excess is located very close to the electrodes, which justifies a consideration of the concentration profile at the left and at the right parts of the cell separately. At the mid-plane both the left-part and right-part concentrations should coincide. The same is valid for the electric field. The electric field is a symmetric function and the concentration of positive ions in the left part of the cell is symmetric to the one of negative ions in the right part, $C_+(x) = C_-(-x)$. Let us consider for example the right half of the cell. Introducing the distance from the electrode $s = L - x$ as a new variable we find

that according to Eqs. 3.9 and 3.10 the electric field is

$$
\begin{aligned}
E(s) &= -\frac{2k_BT}{ze}\,\tilde{q}\,\tilde{k}\,\mathrm{cn}(\tilde{k}L,\tilde{q}) \times \\
&\quad \frac{\mathrm{cn}(\tilde{k}L,\tilde{q})\mathrm{cn}(\tilde{k}s,\tilde{q}) - \mathrm{sn}(\tilde{k}L,\tilde{q})\mathrm{sn}(\tilde{k}s,\tilde{q})\mathrm{dn}(\tilde{k}L,\tilde{q})\mathrm{dn}(\tilde{k}s,\tilde{q})}{\mathrm{dn}(\tilde{k}L,\tilde{q})\mathrm{dn}(\tilde{k}s,\tilde{q}) + \tilde{q}^2\mathrm{sn}(\tilde{k}L,\tilde{q})\mathrm{sn}(\tilde{k}s,\tilde{q})\mathrm{cn}(\tilde{k}L,\tilde{q})\mathrm{cn}(\tilde{k}s,\tilde{q})}\,.
\end{aligned}
$$

A similar expression can be derived for the concentration. Up to now the result is still exact. Further we will omit a prefactor $1 - \tilde{q}^2$ in the expression for the concentrations because, as it will be shown soon, $1 - \tilde{q}^2 \simeq 1$. There are functions of two different arguments: $\tilde{k}L$ and $\tilde{k}s$. Every function of the argument $\tilde{k}L$ should be expressed by a new constant

$$
\gamma \equiv q\,\mathrm{cn}(\tilde{k}L,\tilde{q}), \tag{3.15}
$$

where the following identities were used: $\mathrm{sn}^2(a,b) + \mathrm{cn}^2(a,b) = 1$ and $\mathrm{dn}^2(a,b) + b^2\mathrm{sn}^2(a,b) = 1$. For a typical system $kL \gg 1$ which makes $\mathrm{cn}(\tilde{k}L,\tilde{q}) \gg 1$. Therefore, the unity in the first identity can be neglected. $\mathrm{dn}(\tilde{k}L,\tilde{q})$ is of the order of 1. From the second identity it follows that $q \ll 1$. All functions with the argument $\tilde{k}s$ should be expanded with respect to $\tilde{q}$. Note that such an expansion is not useful for $\mathrm{cn}(\tilde{k}L,\tilde{q})$ because it gives a series of the powers of $q\cosh(kL)$, but $q\cosh(kL)$ is of the order of the unity and, consequently, the series would converge very slow. On the other hand, it is sufficiently to take into account only the first term in the expansion of $\mathrm{cn}(\tilde{k}s,\tilde{q})$ because $L \gg s$. Mathematically, the approximation is applicable as long as $q\cosh(k\tilde{s}) \ll 1$ where $\tilde{s}$ is the minimal value of s for which the concentration can be considered as a constant. Obviously, $\tilde{s}$ should not exceed L, otherwise contributions from the left and the right electrodes can not be separated. Finally we get

$$
\begin{aligned}
C_{\pm}(s) &= \lambda_D^2 k^2 \eta \left(\frac{1 + \gamma^2\sinh^2(ks) \pm \gamma(\cosh(ks) - \alpha\sinh(ks))}{\alpha + \gamma^2\sinh(ks)\cosh(ks)} \right)^2, \\
E(s) &= \frac{2k_BT}{ze}k\gamma\frac{\cosh(ks) - \alpha\sinh(ks)}{\alpha + \gamma^2\sinh(ks)\cosh(ks)}\,.
\end{aligned} \tag{3.16}
$$

These equations correspond to Eqs. 3.9 and 3.10, and parameters $\tilde{k}$ and $\tilde{q}$ were changed to more convenient for the approximate solution k and γ.

The condition for the applied voltage, see Eqs. 3.11, reads

$$2 \int_0^L E(s) \cdot ds = v \,.$$

Because $L \gg \lambda_D$, due to screening $E(L) \approx 0$ and the upper limit of the integral can be shifted to infinity. Performing the integration we get

$$
\begin{aligned}
v &= \frac{4k_B T}{ze} \gamma \int_0^\infty \frac{\cosh(f) - \alpha \sinh(f)}{\alpha + \gamma^2 \sinh(f) \cosh(f)} df \qquad (3.17) \\
&= \frac{2k_B T}{ze(2 - \gamma^2)} \left\{ (1 + \alpha)^2 \ln \left(\frac{1 + \gamma + \alpha}{1 - \gamma + \alpha} \right) + (1 - \alpha)^2 \ln \left(\frac{1 + \gamma - \alpha}{\gamma - 1 + \alpha} \right) \right\} \,.
\end{aligned}
$$

For a convenient representation we introduced the parameter α according to $\alpha^2 + \gamma^2 = 1$. Inverting Eq. 3.17 with respect to γ one gets

$$\gamma = \frac{\exp(\frac{vze}{2k_B T}) - 1}{\exp(\frac{vze}{2k_B T}) + 1} \,. \qquad (3.18)$$

Note that γ is independent of specific properties of the system and depends only on the ratio of the electric and thermal energy $\frac{vze}{k_B T}$. In a similar manner the condition of total charge conservation can be treated. According to Eqs. 3.11 it results

$$2L\eta = \int_{-L}^{L} C_+(x) dx = \lambda^2 k^2 \eta \left\{ \int_0^\infty (C_+(s) - 1) ds + \int_0^\infty (C_-(s) - 1) ds + 2L \right\} \,.$$

The first term on the right hand side represents the particle excess in the right half of the cell; the second term on the right hand side represents the particle excess in the left half of the cell. If no voltage is applied, i.e. $\gamma = 0$, the particle distribution is homogeneous and these two terms equal zero. The third term is the background, namely the concentration at the mid-plane. If $v = 0$, this concentration is equal to η. Particle excess represented by two first terms, is a deviation of the particle concentration from this background. Performing the integration one gets the expression for the parameter k,

$$k = \sqrt{\frac{1}{\lambda_D^2} + \frac{(1 - \alpha)^2}{\alpha^2 L^2}} - \frac{(1 - \alpha)}{\alpha L} \,. \qquad (3.19)$$

According to Eqs. 3.16 k defines the concentration far away from the electrode, $C_\pm(s \to \infty)$, which corresponds to the mid-plane concentration $C_\pm(x = 0)$. A

detailed discussion is presented in the next section. At $v = 0$ k is equal to the inverse Debye screening length. When v increases, k decreases and, consequently, $C_\pm(x = 0)$ decreases as well.

Eqs. 3.16 together with the conditions Eqs. 3.17 and 3.19 provide the approximate solution of the PNP equations applied to the system described in Section 1.2. The applicability of this solution depends on both the applied voltage v and the initial concentration η. The dependence on η is performed indirectly by the Debye screening length. The approximate solution is applicable as long as $q \cosh(k\tilde{s}) \ll 1$. If $\lambda_D^{-1} L \gg 1$ and the applied voltage is not high, this inequality is guaranteed. At higher v q increases and becomes of the order of 1. $\tilde{s}$ can be replaced with its maximal reasonable value: L. It turns the estimation of applicability into $kL > R$, where $\exp(-R) \ll 1$. Using Eq. 3.19 this leads to a restriction for v expressed via α,

$$\alpha > \frac{2R}{\lambda_D^{-2} L^2 - R^2 + 2R} . \tag{3.20}$$

If $R = 5$, $\exp(-R)$ is less than one percent of unity. The inequality $\lambda_D^{-1} L > R$ means that contributions from the electrodes can be considered separately. The estimation Eqs. 3.20 replaces this constraint with $kL > R$ giving an additional restriction for the applied voltage. With increasing v k decreases and finally can become rather small making $kL < R$. Therefore, at very high applied voltages the approximate solution is not applicable.

3.2 Properties of the solution

In the previous section we found the exact and approximate solutions of the stationary PNP equations. The approximate solution is applicable for a wide range of values of the applied voltage v and initial concentration η. Both solutions are determined by two parameters only: the Debye screening length, λ_D, and the size of the system, L. The dependence on the initial concentration can be scaled off by measuring all concentrations in terms of it, $C_\pm(x) \to \frac{C_\pm(x)}{\eta}$. This follows immediately from Eq. 3.19 and is in agreement with the first equation of Eqs. 3.11. In a similar manner the dependence on the temperature and the

valence of the ion can be eliminated. For this purpose, the applied voltage should be measured in terms of the dimensionless thermal voltage, $v \to v\frac{ze}{k_B T}$, see Eq. 3.9 and Eqs. 3.11. The influence of the applied voltage is expressed by the parameter γ or, equivalently, α. According to Eq. 3.18, γ increases from 0 to 1 when the applied voltage goes from 0 to infinity. α changes from 1 to 0, respectively. The dielectric constant is also present in the PNP equations but does not appear in the solution explicitly. It has an implicit influence via the Debye screening length.

At small applied voltage the charge profile is exponential as predicted by the linear theory. According to Eq. 3.19, the increase of applied voltage causes an increase of the screening length k^{-1}. But also the spatial dependence of the concentration changes, see Eqs. 3.16, which does not allow the charge excess to spread into the bulk. The effective screening length decreases, whereas the concentration gradient increases. The decrease of the screening length is more pronounced at high applied voltage, since at small applied voltage, namely in linear regime, the screening length does not change at all and is equal to the Debye screening length. The enhancement of the concentration gradient is noticeable already at lower v. This situation is illustrated in Fig. 3.1, where the nonlinear solution is compared with the one of the linear theory predicting an exponential decay. The nonlinear solution provides a much steeper gradient. Intuitively this result can be easily understood by considering the PNP equations, Eqs. 3.2,

$$\left| \frac{\partial C_\pm(x)}{\partial x} \right| \sim E(x)C_\pm(x) \xrightarrow{v \to 0} E(x)\eta \,. \tag{3.21}$$

In the linear regime the concentration on the right hand side can be replaced by the initial one. In the nonlinear regime the concentration is generally significant higher than η, and therefore the concentration gradient increases compared to the linear regime.

Beyond the linear regime the whole nonlinear steady state of PNP equations is equivalent to the Poisson-Boltzmann equation, as it was shown in Section 2.3, which solution was found by Gouy and is presented in Section 2.1, see Eq. 2.12. At small and middle applied voltages both solutions coincide perfectly. Gouy derived his solution for a half-space. To apply it to a finite system one has to find the solutions for the left and the right electrodes separately. At the mid-plane
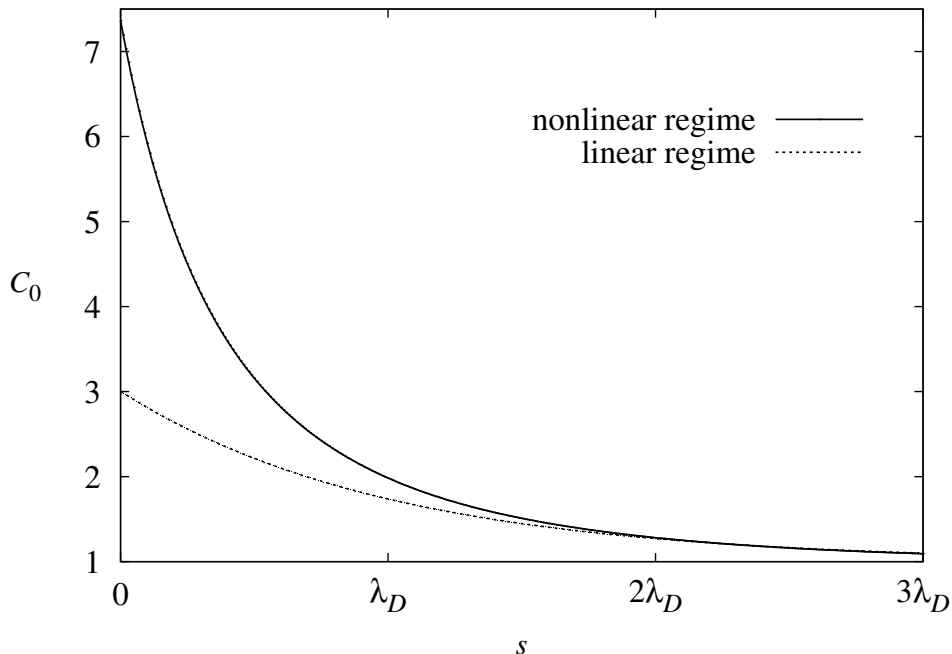
Figure 3.1: Normalized concentration $C_0 = C_+(s)/\eta$ in the vicinity of the electrode in the linear regime and according to the nonlinear theory. $L = 5 \cdot 10^{-5}$ m, $\lambda = 10^{-7}$ m and $v = 0.15V$. s is a distance from the electrode.

both solutions should coincide. This procedure is based on the same assumptions that were made to derive the approximate solution. At higher voltages there is a difference between our approximate solution and the Gouy-Chapman solution, shown qualitatively in Fig. 3.2. According to Eq. 2.2, $C_\pm(s) \xrightarrow{s\to\infty} \eta$[1], whereas, according to Eqs. 3.16, $C_\pm(s) \xrightarrow{s\to\infty} \eta\lambda_D^2 k^2$ meaning that the concentration changes in the middle of the cell, far away from the electrode. This change is a consequence of the charge conservation law and becomes noticeable when the particle concentration becomes small in the vicinity of another electrode. Because Eq. 2.12 was derived for a semi-infinite case, the concentrations far away from the electrode remains constant. On the other hand, it is obvious that in finite systems at high applied voltage the mid-plane concentration should decrease and finally lead to a complete separation of charged particles. So, Gouy-Chapman theory can not describe this effect whereas in our theory the mid-plane concentration decreases

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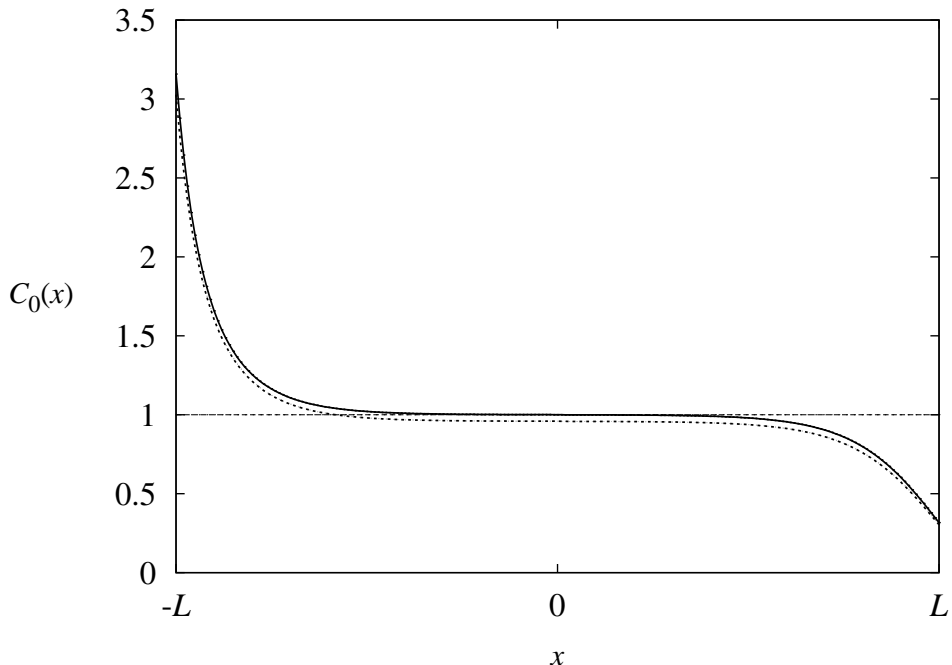[1]In Chapter 2 a distance form the electrode was denoted by x.

Figure 3.2: Coordinate dependence of the normalized concentration, $C_0(x) = C_+(x)/\eta$, depicted qualitatively. The Gouy-Chapman solution (dotted line) and our approximate solution (solid line).

automatically. The solution presented in the previous section is more general than Eq. 2.12. The large the system is, the better the Gouy-Chapman theory should work and the higher voltage has to be applied to create a noticeable difference between the solutions. This voltage can be easily estimated. Let us assume that the change of the mid-plane concentration is noticeable if $C_\pm(x = 0) = \varsigma\eta$, where for instance $\varsigma = 0.98$. $C_\pm(x = 0)$ is defined by the parameter k. The related value of the parameter α and, consequently, the applied voltage follow from Eq. 3.19,

$$\alpha = \frac{2\sqrt{\varsigma}}{2\sqrt{\varsigma} + (1 + \varsigma)L\kappa} \, .$$

The higher κL is, the smaller α corresponds the fixed ς. This result shows that for many experimental systems the conventional Eq. 2.12 can be used instead of Eq. 3.16. At lower voltage the size of the system is irrelevant and the profiles depend on the Debye screening length only. The Gouy-Chapman solution is very similar to our approximate solution because they both are derived under the

assumption that influences of the left and right electrodes can be separated. Altogether we are dealing with three different solutions: the Gouy-Chapman solution and our exact and approximate solutions. The mid-plane concentration according to our solutions decreases with increasing applied voltage, whereas according to the Gouy-Chapman solution it remains constant. On the other hand, by introducing a prefactor into the Gouy-Chapman solution one can match its mid-plane concentration with the one predicted by our solutions. In this case, as long as the approximate solution is applicable, all three solutions give the same results. At very high applied voltage all solutions show different behavior. Though, the Gouy-Chapman and our approximate solutions predict the same particle concentrations calculated at the electrodes, $C_\pm(x = \pm L)$. Notice that the prefactor incorporated into the Couy-Chapman solution is not a part of their theory and was introduced to fit the mid-plane concentration. Also this prefactor ensures the fulfillment of the charge conservation law. It can be easily seen by comparison of the Gouy-Chapman solution with our solutions satisfying the charge conservation law automatically. In general, the Poisson-Boltzmann equation is a second order differential equation which solution can have only two arbitrary constants. In the Gouy-Chapman solution these constants are already fixed, see its derivation in Chapter 2, and there is no freedom or flexibility for matching the solution to any boundary conditions or experimental constraints. As it was mentioned in the introduction, the general solution can be expressed only via Jacobi elliptic functions. A great advantage of our solution is that it can be easily and naturally extended and applied to other cases and geometries. And even in the same flat geometry but not in the case of symmetric electrolyte, i.e. $\eta_+ \neq \eta_-$, the application of the Gouy-Chapman approach is problematic in a sense that the final expressions for the potential and the concentrations can not be found explicitly, but only with help of, for example, perturbation theory. Using our solution, the final expressions can be found as easy as in the case of symmetric electrolyte. This will be shown in Section 3.3.1.

As one can see from Eqs. 3.12 or Eq. 3.18, the dependence of the electric field or the potential on the applied voltage becomes weaker for higher voltages. Independently of the initial concentration, such a weak dependence is realized when

approximately 99% of the total charge have been transmitted. In this case a complete separation of the charged particles should be achieved, and consequently the charge concentration changes slow. This effect can not be described by Eq. 2.12 because $C(x = 0) \neq \eta$. For higher voltages a further charge separation takes place because of a decrease of the mid-plane concentration. Due to the charge conservation law the charge profile has to change also near the electrodes. When charge separation is achieved, the mid-plane concentration becomes almost zero and does not have much influence on the one in the vicinity of the electrode. The value of the applied voltage, necessary for a complete ion separation, depends on the initial concentration. The higher the initial concentration is, the higher voltage should be applied. For low concentrations as $10^{18}m^{-3}$, this voltage is about $1.5V$, which is in agreement with the assumption made and experimentally verified in (42). For higher initial concentration another restriction of the PNP should appear. The effective screening length decreases when the initial concentration increases. If the effective screening length is of the order of the ion size, this continuum theory should fail. For a rough estimation let us suppose that the PNP equations are valid as long as the screening length is higher than the atomic length $10^{-10}m$. The initial concentration $\eta = 10^{24}m^{-3}$ is related to the applied voltage $v = 0.7V$ which is far from the value where complete charge separation is attained. For $\kappa = 10^7 m^{-1}$ and $L = 5 \cdot 10^{-5} m^{-1}$ we get $v = 1.1V$. From here we conclude that PNP equations are inapplicable to explain experiments at very high voltages and high concentrations as observed in (22). In that regime the PNP should be either modified or supplemented by a completely different approach. It is obvious that at a very short atomic scale mean-field like models based on classical laws are inappropriate. It is interesting to note that for high-concentrated systems this short distance limit is achieved approximately at the same applied voltage as the close-package limit is achieved. The corresponding concentration is of the order $10^{28}m^{-3}$. For such a high concentration Fick's law is not be valid. It should be modified in such a manner to make the concentration gradients lower. Consequently, the effective screening length increases, so that a classical theory could be reliable.

3.3 Generalizations of the solution

In previous sections exact and approximate solutions of the stationary PNP equations were found in 1-D case for two types of ions. Consequently, there are at least two possible generalizations: a multidimensional case, especially 3-D, and the presence of more than two species. We are interested in the general solution which can be applied to a wide range of systems. Obviously, it will contain unknown constants which should be found for every particular experimental realization. In some cases this procedure can be tricky and difficult to perform analytically. Our aim is to provide analytical expressions for the electric fiend and particle concentrations. So far, many systems can be described only numerically and the main progress is related to a development of various computational schemes, see (10; 11) and citations there. Our results are directed to fill the lack of analytical results. Having the analytical expression one can find the unknown constants numerically if it is not possible to do analytically, employing much less of computational efforts. Building up an approximate solution is possible as well.

3.3.1 Multispecies case

Let us consider a one-dimensional flat system with i species which have the same charge $z_i e$ which can be though positive or negative, $|z_i| \equiv z$. The electrolyte is not necessary symmetric, that is $\eta_i \neq \eta_k$. The steady state of corresponding PNP equations reads

$$C_i'(x) - \frac{z_i e}{k_B T} C_i(x) E(x) = 0 \,,$$
$$\epsilon E'(x) = e \sum_i C_i(x) z_i \,. \tag{3.22}$$

To solve them the similar procedure is used. Summing the transport equations over i gives

$$C'(x) - \frac{e}{k_B T} E(x) \sum_i C_i(x) z_i = 0 \,, \tag{3.23}$$

where $C(x) = \sum_i C_i(x)$. This equation is equivalent to Eq. 3.4. Multiplying the transport equations with z_i and then summing over i we get

$$\epsilon E''(x) + \frac{z^2 e^2}{k_B T} C(x) E(x) = 0 \,, \tag{3.24}$$

which is equivalent to Eq. 3.3. The electric field obeys the same equation, Eq. 3.5, and the concentrations can be found from

$$\frac{\partial \ln C_i(x)}{\partial x} = \frac{z_i e}{k_B T} E(x) \,, \tag{3.25}$$

which is equivalent to Eq. 3.6. Consequently, the solution of Eqs. 3.22 reads

$$E(x) = -\frac{2 k_B T}{z e} \tilde{q}\, \tilde{k}\, \mathrm{sn}(\tilde{k} x + x_0, \tilde{q}) \,, \tag{3.26}$$

$$C_i(x) = -A_i \tilde{k}^2 \left[\mathrm{dn}(\tilde{k} x + x_0, \tilde{q}) + \frac{z_i}{z} \tilde{q}\, \mathrm{cn}(\tilde{k} x + x_0, \tilde{q}) \right]^2 . \tag{3.27}$$

The Poisson equation gives restrictions for A_i,

$$\sum_i A_i z_i = 0 \,, \tag{3.28}$$

and

$$\sum_i A_i = \frac{\epsilon k_B T}{z^2 e^2} \,. \tag{3.29}$$

If N is a number of present species, then there are $N+3$ constants: A_i, $\tilde{k}$, $\tilde{q}$, x_0. There are also $N+3$ conditions: Eqs. 3.28 and 3.29 from Poisson's equation, the boundary condition for the potential,

$$\int_{-L}^{L} E(x) dx = v \,, \tag{3.30}$$

and i conservation laws,

$$\int_{-L}^{L} C_i(x) dx = 2\eta_i L \,. \tag{3.31}$$

If all initial concentrations are equal, $\eta_i = \eta$, constants A_i can be evaluated,

$$A_i = \frac{\epsilon k_B T}{2 N_\pm z^2 e^2} \,, \tag{3.32}$$

where $N_\pm$ is a total number of species having the same charge, positive or negative, as the considered one.

Eqs. 3.26 and 3.27 show that the generalization on the multispecies case leads to a redefinition of the constants but does not change an analytical dependence. This result is valid in general multidimensional case. Therefore, the generalization on the n-D case will be done in a simple flat geometry, for the sake of transparency of the explanation.

3.3.2 n-dimensional Boltzmann equation

As it was proven in Section 2.3, the stationary PNP equations are equivalent to the Poisson-Boltzmann equation. In titles of some of the papers cited above, only the Boltzmann equation is mentioned. Therefore we decided to do the same with the title of this section. We will consider the general n-D case, though in the literature the main attention is given to systems with 2-D geometry, namely to conical pores. For a typical example see (6).

The generalization procedure is simple and dictated by the natural reasons. In 1-D problem all quantities can only be scalars. In n-D case the concentration remains a scalar, but the electric field should become a vector. A coordinate x is replaced by a vector $\vec{r}$. Arguments of all Jacobi functions representing the solution, i.e. $kx + x_0$ and q, should be scalars. That means q and x_0 are scalars and k is a vector. $\vec{k} \cdot \vec{r}$ is a scalar product. According to this, the generalization reads

$$\vec{E}(\vec{r}) = -\frac{2k_BT}{ze}\, q\,\vec{k}\,\mathrm{sn}(\vec{k} \cdot \vec{r} + x_0, q)\,, \tag{3.33}$$

$$C_{\pm}(\vec{r}) = \lambda_D^2 \eta\,\vec{k}^2 \left[\mathrm{dn}(\vec{k} \cdot \vec{r} + x_0, q) \pm q\,\mathrm{cn}(\vec{k} \cdot \vec{r} + x_0, q)\right]^2\,. \tag{3.34}$$

The concentrations $C_{\pm}(\vec{r})$ are scalars, and the electric field becomes a vector $\vec{E}(\vec{r})$ automatically. Eqs. 3.33 and 3.34 show that the generalization on the multidimensional case leads to a replacement of the scalar k by a vector $\vec{k}$ but does not change an analytical dependence.

Chapter 4

Solution of the PNP in the linear regime

4.1 Treatment of the conventional problem

4.1.1 General properties of the linear regime

Whereas the previous chapter is devoted to the steady state solution of the Poisson-Nernst-Planck equations, the present one is focused on the dynamical problem. The global aim is the analysis of the full nonlinear equations, but to start with, the linearized version of the PNP is considered. Even in the linear regime there exists no analytical dynamical solution which does not have any internal logical contradictions as it was discussed in the introduction. An analytical solution in the linear regime can be used as a starting point to treat the nonlinear problem. It also offers some insight into the general understanding of the spatiotemporal behavior and common properties of charge migration. For many systems the linear regime approximation gives reasonable predictions. Especially it concerns biological systems where a high voltage is not applicable. In polymer electrolytes low voltage experiments allow to avoid totally or at least to minimize chemical reactions at the electrode surface, which are difficult to take into account.

As long as we consider the linear regime, the meaning of this term should be clarified. There are two different interpretation of the linear regime which should

not be confused one with another. On the one hand, the PNP equations are based on Fick's law of diffusion which is valid only in the linear regime, i.e. in the approximation of a linear gradient of the concentration. On the other hand, the PNP equations are nonlinear and, as any nonlinear equation, can be linearized and considered also in so called linear regime. These both interpretations of linear regime have different borders of applicability and describe different physical situations.

To be more specific let us consider the linearization procedure. Conventionally, the concentration is divided into two parts: a constant, namely the initial concentration, and a deviation from this constant, i.e. $C_\pm(x, t) = \eta + \delta_\pm(x, t)$. The linear regime is characterized by the assumption $\delta_\pm(x, t) \ll \eta$ which should be valid for each coordinate x at every time t. Inserting this into the PNP equations, Eqs. 2.37, we get

$$\dot{\delta}_\pm(x, t) = D \left(\delta'_\pm(x, t) \pm \frac{ze}{kT} \left[\eta + \delta_\pm(x, t) \right] \phi'(x, t) \right)',$$
$$-\epsilon \phi''(x, t) = ze \left(\delta_+(x, t) - \delta_-(x, t) \right). \tag{4.1}$$

Neglecting $\delta_\pm(x, t)$ with respect to η one gives

$$\dot{\delta}(x, t) = D \left(\delta''(x, t) \pm \frac{ze}{kT} \eta \phi''(x, t) \right),$$
$$-\epsilon \phi''(x, t) = ze \left(\delta_+(x, t) - \delta_-(x, t) \right). \tag{4.2}$$

This set of equations represents the PNP equations in the linear regime. The equations are similar to those of the nonlinear problem, however in the second term on the right-hand side of transport equations the concentration $C_\pm(x, t)$ is replaced by the initial concentration η. This approximation allows a decoupling of the transport equations from each other by introducing the charge density $\rho(x, t)$,

$$\rho(x, t) \equiv ze \left(C_+(x, t) - C_-(x, t) \right). \tag{4.3}$$

Equivalently it can be written as

$$\rho(x, t) = ze \left(\delta_+(x, t) - \delta_-(x, t) \right). \tag{4.4}$$

Subtracting the transport equations in Eqs. 4.2 from each other we get

$$\dot{\rho}(x, t) = D \left(\rho''(x, t) - \kappa^2 \rho(x, t) \right), \tag{4.5}$$

where the inverse Debye screening length κ, see Eq. 2.14, appears automatically. The last equation is called Debye-Falkenhagen equation and was derived in (39). In comparison with the full PNP equations the linearized version offers a drastic simplification: instead of a set of three coupled equations the problem is reduced to a single equation. Simultaneously it also reveals one of the most difficult points of the PNP approach. On the first sight, the linearized problem should be solvable. Indeed, the Debye-Falkenhagen equation is found in many different fields of physics and several solutions are known, for example

$$\rho(x,t) = \frac{1}{\sqrt{Dt}} \exp\left(-\frac{x^2}{4Dt} - \kappa^2 t\right) ,$$

or

$$\rho(x,t) = \frac{x}{(Dt)^{\frac{3}{2}}} \exp\left(-\frac{x^2}{4Dt} - \kappa^2 t\right) .$$

However, all these solutions do not satisfy the boundary conditions and symmetry properties imposed on the model. As it was pointed out in Section 2.2, the standard treatment using Laplace transformation runs into the same problem. In order to find an appropriate solution of the Debye-Falkenhagen equation compatible with the specific boundary conditions, let us first consider general properties of Eq. 4.5.

The subtraction of the full nonlinear transport equations from each other leads to

$$\dot\rho(x,t) = D\left(\rho''(x,t) - \frac{z^2 e^2}{\epsilon k_B T}(C_+(x,t) + C_-(x,t))\rho(x,t)\right) . \tag{4.6}$$

A comparison of this equation with the linearized version, Eq. 4.5, shows that the total concentration of particles is conserved in the linear regime,

$$C_+(x,t) + C_-(x,t) = 2\eta . \tag{4.7}$$

Using the definition of the charge density, Eq. 4.3, one can express the concentrations $C_\pm(x,t)$ via $\rho(x,t)$,

$$C_\pm(x,t) = \eta \pm \frac{\rho(x,t)}{2ze} . \tag{4.8}$$

Let us now consider the symmetry of the concentration fields. A parity transformation of the PNP equations, Eqs. 4.2, reveals the identity $C_+(-x,t) =$

$C_-(x,t)$. This symmetry has a deep physical background and follows from the symmetric behavior of positive and negative particles in an electric field because a change of x to $-x$ leads to a change of the sign $\pm$ to $\mp$ in the transport equations. Thus, a parity transformation is equivalent to a change of the particle charge from positive to negative and vice versa. Consequently, the charge density becomes antisymmetric,

$$\rho(x,t) = ze(C_+(x,t) - C_-(x,t)) = ze(C_+(x,t) - C_+(-x,t)),$$
$$\rho(-x,t) = ze(C_+(-x,t) - C_-(-x,t)) = ze(C_+(-x,t) - C_+(x,t)). \qquad (4.9)$$

These symmetry properties are valid in the full nonlinear model. The linear regime imposes one additional symmetry on the particle concentrations. According to Eqs. 4.8, deviations of the particle concentrations from a constant are antisymmetric, $C_\pm(x,t) - \eta = C_\pm(-x,t) + \eta$. This condition claims that the concentration at the midplane is constant, $C_\pm(x = 0, t) = \eta$. To illustrate qualitatively the difference between linear and nonlinear regimes let us consider Fig. 4.1. The charge concentration $C_+(x,t)$ is shown at an arbitrary but fixed moment of time. The dashed curve representing the behavior within the linear regime is symmetric and at the point $x = 0$ the concentration coincides with the initial concentration η. The bold curve representing the nonlinear regime is not symmetric and the midplane concentration is smaller than η. In the first case the charge conservation law is fulfilled automatically. In the second case the midplane shift plays a roll and is related to the asymmetry of the curve due to the particle conservation law. It would be misleading to argue that the linear regime approximation is applicable when the midplane shift is zero or small. Strictly speaking, as it will be shown later, the shift is never zero, and hence it is difficult to define what exactly the word small means. To make the situation clear let us fix the midplane shift and consider the concentration curve which can be divided into three segments: an initial slope, then a constant part, and finally again a slope. Only the first segment has a particle excess with respect to the initial concentration. The particle concentration on two other segments is smaller than η. This deficiency in particles is compensated by the particle excess on the first part of the curve. If the size of the system changes, for example increases, the size of the second part increases as well and makes the corresponding charge deficiency

larger. Obviously, such a situation can not be observed in the linear regime. Due to the charge conservation law the missing particles should appear in the vicinity of the electrode, namely on the first segment of the curve, and, consequently, increase the asymmetry of the charge profile. Therefore, the nonlinearity depends not only on the midplane shift but also on the size of the system. This fact offers a better criterion for the applicability of the linear regime. As long as a symmetric profile fulfills the conservation law, the linear regime approximation is valid. In other words, the linear regime approximation is violated when the charge profile loses the symmetry.
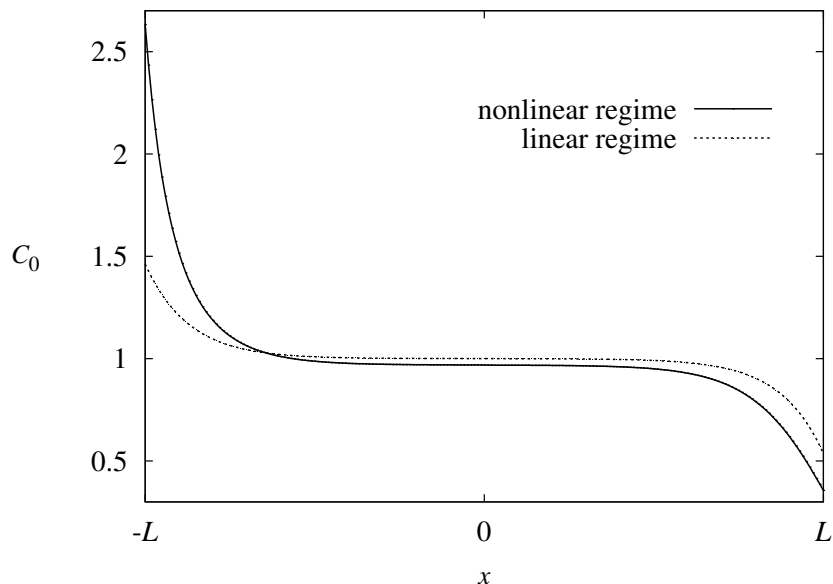

Figure 4.1: The difference between linear and nonlinear regimes, depicted qualitatively for the normalized concentration, $C_0(x, t) = C_+(x, t)/\eta$, at the fixed time.

Now we are able to formulate the criterion of the validity of the linear approximation in more mathematical terms. Simultaneously, we will demonstrate that the conservation law of the total particle concentration, $C_+(x, t) + C_-(x, t) =$ constant, can be never fulfilled at every particular point in the frame of the PNP equations, and consequently a shift of the midplane concentration is never

equal to zero. The charge conservation law is valid only for the whole system, $\int_{-L}^{L}(C_+(x,t) + C_-(x,t))dx = \text{constant}$.

The linear approximation becomes inapplicable due to increasing deviations of particle concentrations from η. Consequently, this is sufficient to consider the maximal possible deviation which is realized in the steady state, see Eqs. 3.2,

$$\frac{\partial C_+^{st}}{\partial x} + \frac{ze}{kT}\frac{\partial \phi}{\partial x}C_+^{st} = 0\,,$$
$$\frac{\partial C_-^{st}}{\partial x} - \frac{ze}{kT}\frac{\partial \phi}{\partial x}C_-^{st} = 0\,. \tag{4.10}$$

These equation can be written as

$$\frac{\partial \ln(C_+^{st})}{\partial x} = -\frac{ze}{kT}\frac{\partial \phi}{\partial x}\,,$$
$$\frac{\partial \ln(C_-^{st})}{\partial x} = +\frac{ze}{kT}\frac{\partial \phi}{\partial x}\,. \tag{4.11}$$

Summing up these equations and integrating them one gets

$$C_+^{st}(x)\,C_-^{st}(x) = \text{constant}\,.$$

This is an exact result which is valid in the nonlinear regime. Let us write the concentrations as $C_\pm(x,t) = \eta \pm \tilde{\delta}_\pm(x,t)$, where $\tilde{\delta}_\pm(x)$ are deviations from the constant. A similar representation of $C_\pm(x,t)$ was introduces in the discussion of the linearization procedure. Now the sign $\pm$ is used to guarantee that both $\tilde{\delta}_\pm(x)$ have the same sign at every point, i.e. $\frac{\tilde{\delta}_+(x)}{\tilde{\delta}_-(x)} \geq 0$. Hence, the concentration in the steady state obeys

$$C_+^{st}(x)\,C_-^{st}(x) = \eta^2 + \eta\left[\tilde{\delta}_+^{st}(x) - \tilde{\delta}_-^{st}(x)\right] - \tilde{\delta}_+^{st}(x)\,\tilde{\delta}_-^{st}(x)\,. \tag{4.12}$$

Because $C_+^{st}(x)\,C_-^{st}(x) = 2\eta$, it follows

$$\eta\left[\tilde{\delta}_+^{st}(x) - \tilde{\delta}_-^{st}(x)\right] - \tilde{\delta}_+^{st}(x)\,\tilde{\delta}_-^{st}(x) = 0\,. \tag{4.13}$$

In the linear regime according to Eq. 4.7

$$2\eta = C_+^{st}(x) + C_-^{st}(x) = 2\eta + \left[\tilde{\delta}_+^{st}(x) - \tilde{\delta}_-^{st}(x)\right]\,, \tag{4.14}$$

and, consequently,

$$\tilde{\delta}_+^{st}(x) - \tilde{\delta}_-^{st}(x) = 0\,. \tag{4.15}$$

The comparison of this result with Eq. 4.13 shows that either one can neglect the quadratic correction $\tilde{\delta}_+(x)\,\tilde{\delta}_-(x)$, which is the conventional criterion of the linear regime, or the equality $C_+(x,t) + C_-(x,t) = 2\eta$ is not valid.

In this context one should mention the restrictions imposed by the applicability of Fick's law. The PNP equations, likewise the diffusion equation, are based on the assumption of small concentration gradients, i.e. the particle flux is expanded with respect to ∇C and only the linear gradient term is kept. This assumption leads to the well established diffusion equation. On the other hand, smaller gradients mean smaller deviations from the homogenous state which is similar to the linear regime of the PNP. But the linear regimes of the PNP equations and the use of Fick's law are different problems. Usually the validity of Fick's law is assumed for the full nonlinear problem. As it was discussed at the end of Chapter 3, at very high applied voltages Fick's law have to break down, but this happens already beyond the linear regime.

Before proceeding with the solution of the linearized PNP equations one final remark should be made. In the introduction it was mentioned that in the linear regime the treatment of polymer electrolytes is very similar to that of polyelectrolytes. To demonstrate this analogy let us adopt the PNP equations for polyelectrolites. According to a description given in Section 1.2, one species, say $C_+(x,t)$, remains mobile. Another species is fixed in space, i.e. the relation $C_-(x,t) = \eta$ is valid at each time. The linearized PNP equations, Eqs. 4.2, turn into a set of two equations: the transport equation for $C_+(x,t)$ and the Poisson equation,

$$\dot{C}_+(x,t) = D\left(C'_+(x,t) + \frac{ze}{k_BT}\eta\phi'(x,t)\right)',$$
$$-\epsilon\phi''(x,t) = ze\left(C_+(x,t) - \eta\right). \tag{4.16}$$

Combining both equations together and introducing the charge density, $\rho(x,t) = ze\left(C_+(x,t) - \eta\right)$, we find

$$\dot{C}_+(x,t) = D\left(C''_+(x,t) - \frac{ze}{\epsilon k_BT}\eta\rho(x,t)\right). \tag{4.17}$$

Expressing $C_+(x,t)$ via $\rho(x,t)$ we get the Debye-Falkenhagen equation,

$$\dot{\rho}(x,t) = D\left(\rho''(x,t) - \frac{z^2e^2}{k_BT}\eta\rho(x,t)\right), \tag{4.18}$$

with the new, redefined screening length λ_D^p,

$$\lambda_D^p = \sqrt{2}\lambda_D \,. \tag{4.19}$$

Eq. 4.19 shows that screening lengths for polymer electrolytes and polyelectrolytes are proportional to each other. This redefinition of the screening length is the only one difference between the treatments of polymer electrolytes and polyelectrolytes in the linear regime.

4.1.2 Derivation of the solution

Having discussed the main properties of the linear regime let us return to the solution of the linearized PNP equations. The charge density $\rho(x,t)$ is of interest. The particle concentrations and electric field can be found from Eqs. 4.8 and the Poisson equation, respectively.

The charge density is governed by the Debye-Falkenhagen equation, Eq. 4.5. This equation should be supplemented with boundary conditions which are imposed naturally by the experimental realization,

$$\phi(x = -L, t) - \phi(x = L, t) = v(t) \,. \tag{4.20}$$

This condition reflects that the potential difference between electrodes is always equal to the applied voltage. This poses a problem because the basic equation is formulated for $\rho(x,t)$, while but boundary conditions are formulated for another function, namely for $\phi(x,t)$. To relate one function to another one can reformulate the boundary conditions in a form of a constraint,

$$\int_{-L}^{L} E(x,t) = v(t) \,. \tag{4.21}$$

In this section only the case of a constant applied voltage will be considered, i.e. $v(t) = v$. The integration of the Poisson equation gives

$$\epsilon E(x,t) = \int \rho(x,t) + f(t) \,, \tag{4.22}$$

where $f(t)$ is an arbitrary function of time. In this case the boundary conditions can be fulfilled for every $\rho(x,t)$ by an appropriate choice of the function $f(t)$.

Naturally, the charge density $\rho(x, t)$ should still satisfy the symmetry properties of the problem discussed in the previous section. Therefore, first we find the solution to the problem with arbitrary boundary conditions but with appropriate symmetry properties and then we choose the function $f(t)$ in such a manner that the boundary conditions are fulfilled.

There are a number of conventional methods to treat such a problem. Since the Debye-Falkenhagen equation is linear, the use of Laplace transformation is suggested. However, as pointed out in Section 2.2, it would be difficult to perform the inverse transformation. So, let us follow another way and make a start from the steady state solution, Eq. 3.9,

$$E^{st}(x) = -\frac{2k_B T}{ze} \, \tilde{q} \, \tilde{k} \, \mathrm{cd}(\tilde{k}x, \tilde{q}) \,. \tag{4.23}$$

In the linear regime the solution can be simplified to

$$E^{st}(x) = \frac{2k_B T}{ze} \, q \, k \, \cosh(kx) \,. \tag{4.24}$$

The boundary conditions, Eq. 4.21, yield

$$q = \frac{vze}{4k_B T} \frac{1}{\sinh(kL)} \,. \tag{4.25}$$

Here q is a dimensionless parameter proportional to the dimensionless thermal voltage $\frac{vze}{k_B T}$. From the Poisson equation it follows

$$\rho^{st}(x) = \frac{2\epsilon k_B T}{ze} \, q \, k^2 \, \sinh(kx) \,. \tag{4.26}$$

This expression can be derived in a different way without referring to the results of Chapter 3. The steady state of Eq. 4.5 reads $\rho^{st''}(x) = \kappa^2 \rho^{st}(x)$. Its general antisymmetric solution is $\rho^{st}(x) = A \sinh(\kappa x)$, where A is an integration constant. The first way of derivation, namely by using Eq. 4.26, stresses the consistency of approaches and reveals a value of A. The second way shows that in the linear regime $k = \kappa$. In Chapter 3 this equality was proved for zero applied voltage.

The steady state solution in the linear regime presented by Eq. 4.26 has two constants: k and q, which should fulfill two conditions, namely the charge conservation law and the fact that the potential difference between the electrodes

equals the applied voltage, Eq. 4.20. In the linear regime $k = \kappa$, where κ is a property of the system and can not be changed, i.e. k is fixed. According to the exact steady state solution the parameter k defines the midplane concentration. Since k is constant, the midplane concentration is constant as well, and, consequently, the midplane shift, discussed in the previous section, is zero. This also guarantees automatically the fulfillment of the charge conservation law. The parameter q represents the influence of the applied voltage. To relate the steady state solution to the dynamical problem we suggest a replacement of q by $q\,h(x,t)$, where $h(x,t)$ is an unknown function of coordinate x and time t and fulfills the constraints

$$h(x, t = 0) = 0 \quad \text{and} \quad h(x, t \to \infty) = 1\,. \tag{4.27}$$

The first constraint follows immediately from the initial condition where the voltage is not applied yet and $\rho(x, t = 0) = 0$. The second one ensures that all parameters reach their steady state values at $t \to \infty$.

The charge density $\rho(x,t)$ changes into

$$\rho(x,t) = \frac{2\epsilon kT}{ze}\, q\,\kappa^2 h(x,t)\, \sinh(\kappa x)\,. \tag{4.28}$$

Inserting this result into Eq. 4.5 we find an equation for the unknown function $h(x,t)$,

$$\sinh(\kappa x)\frac{\partial h(x,t)}{\partial t} = D\left(\sinh(\kappa x)\frac{\partial^2 h(x,t)}{\partial x^2} + 2\kappa \cosh(\kappa x)\frac{\partial h(x,t)}{\partial x}\right)\,. \tag{4.29}$$

The last equation can be simplified by introducing a new function $p(x,t)$ according to

$$h(x,t) \equiv 1 - \exp(-\gamma t)p(x,t)\,. \tag{4.30}$$

Eqs. 4.27 define the constraints for the function $p(x,t)$: $1 = p(x,0) \geq p(x,t) \geq p(x,\infty)$. In terms of $p(x,t)$ Eq. 4.29 reads

$$\frac{\partial}{\partial t}\left(p(x,t)\,\sinh(\kappa x)\right) = D\frac{\partial^2}{\partial x^2}\left(p(x,t)\,\sinh(\kappa x)\right)\,, \tag{4.31}$$

which defines $\gamma = D\kappa^2$. The last equation is nothing else but the conventional diffusion equation for $g(x,t) = \sinh(\kappa x)p(x,t)$,

$$\dot{g}(x,t) = D\,g''(x,t)\,, \tag{4.32}$$

with the initial condition $g(x, t = 0) = \sinh(\kappa x)$. To solve this equation one can use Green's function approach. Because the boundary conditions are arbitrary, one can use a conventional Green's function for the diffusion equation,

$$G(x, \xi, t) = \frac{1}{2\sqrt{\pi Dt}} \exp\left[-\frac{(x-\xi)^2}{4Dt}\right]. \tag{4.33}$$

The solution of Eq. 4.32 reads

$$g(x, t) = \int_{-L}^{L} g(\xi, 0) G(x, \xi, t) d\xi = \int_{-L}^{L} \frac{\sinh(\kappa\xi)}{2\sqrt{\pi Dt}} \exp\left[-\frac{(x-\xi)^2}{4Dt}\right] d\xi. \tag{4.34}$$

Performing the integration and coming back to the charge density we find

$$\begin{aligned}
\rho(x, t) &= \tfrac{2\epsilon k_B T}{ze} q\, \kappa^2 \left(\sinh(\kappa x) - \tfrac{1}{4}e^{\kappa x} \left\{\operatorname{erf}(\tfrac{-x+L-2\kappa Dt}{2\sqrt{Dt}}) + \operatorname{erf}(\tfrac{x+L+2\kappa Dt}{2\sqrt{Dt}})\right\}\right. \\
&\quad \left. + \tfrac{1}{4}e^{-\kappa x}\left\{\operatorname{erf}(\tfrac{-x+L+2\kappa Dt}{2\sqrt{Dt}}) + \operatorname{erf}(\tfrac{x+L-2\kappa Dt}{2\sqrt{Dt}})\right\}\right),
\end{aligned} \tag{4.35}$$

where $\operatorname{erf}(x)$ is the error function. According to Eqs. 4.8 the particle concentrations are

$$\begin{aligned}
\frac{C_\pm(x, t)}{\eta} &= 1 \pm 2q \left(\sinh(\kappa x) - \tfrac{1}{4}e^{\kappa x}\left\{\operatorname{erf}(\tfrac{-x+L-2\kappa Dt}{2\sqrt{Dt}}) + \operatorname{erf}(\tfrac{x+L+2\kappa Dt}{2\sqrt{Dt}})\right\}\right. \\
&\quad \left. + \tfrac{1}{4}e^{-\kappa x}\left\{\operatorname{erf}(\tfrac{-x+L+2\kappa Dt}{2\sqrt{Dt}}) + \operatorname{erf}(\tfrac{x+L-2\kappa Dt}{2\sqrt{Dt}})\right\}\right).
\end{aligned} \tag{4.36}$$

The expression tends to its steady state value

$$C_\pm(x, t) = \eta(1 \pm 2q \sinh(\kappa x)),$$

which coincide with the linearized version of the steady state obtained in Chapter 3, see Eq. 3.10. Integration of the Poisson equation reveals the electric field. Because $\rho(x, t)$ includes only the exponent and the error function, the integration is easy to perform analytically. It results

$$\begin{aligned}
E(x, t) &= \tfrac{v}{2}\tfrac{\kappa}{\sinh(\kappa L)} \left[\cosh(\kappa x) - \tfrac{1}{4}e^{\kappa x}\left\{\operatorname{erf}(\tfrac{-x+L-2\kappa Dt}{2\sqrt{Dt}}) + \operatorname{erf}(\tfrac{x+L+2\kappa Dt}{2\sqrt{Dt}})\right\}\right. \\
&\quad - \tfrac{1}{4}e^{-\kappa x}\left\{\operatorname{erf}(\tfrac{-x+L+2\kappa Dt}{2\sqrt{Dt}}) + \operatorname{erf}(\tfrac{x+L-2\kappa Dt}{2\sqrt{Dt}})\right\} \\
&\quad \left. - \tfrac{e^{-\kappa^2 Dt}}{2}\cosh(\kappa L)\left(\operatorname{erf}(\tfrac{x-L}{2\sqrt{Dt}}) - \operatorname{erf}(\tfrac{x+L}{2\sqrt{Dt}})\right) + f(t)\right].
\end{aligned} \tag{4.37}$$

Here the arbitrary function $f(t)$ is added in order to satisfy the constraint Eq. 4.21. The corresponding integration is very similar to the previous one.

$$\int_{-L}^{L} E(x,t)dx = \frac{\rho(x,t)}{\epsilon\kappa^2}\bigg|_{-L}^{L} + v\frac{\cosh(\kappa L)}{\sinh(\kappa L)}\frac{\sqrt{Dt}}{\sqrt{\pi}}e^{-\kappa^2 Dt}e^{-\frac{L^2}{Dt}} + 2Lf(t)\,. \quad (4.38)$$

The function $f(t)$ depends on $\rho(x = L, t)$. This shows that despite the charge density were found without taking into account the boundary conditions and using the conventional Green's function, in the finale result they are related.

The second term on the right hand site of Eq. 4.38 is very small due to the facter $\sqrt{Dt}\exp(-\frac{L^2}{Dt})$ and can be omitted. The first term reveals the expression for $f(t)$. To avoid lengthy formulas, the expression is presented under the assumption $\exp(-\kappa L) \ll 1$. This leads to

$$f(t) = -\frac{v}{8L}\text{erf}(\kappa\sqrt{Dt})\,. \quad (4.39)$$

Eqs. 4.36 - 4.39 represent the complete solution of the linearized PNP equations.

Similar to Chapter 3 one can find an approximate but more transparent solution which is valid for not too thin systems, $L\kappa > 5$, which is often realized experimentally. This constraint means that particles situated close to one of the electrodes feel no influence from the other electrode. Because both the charge concentrations and the electric field are expressed via the charge density, it is necessary to find an approximate solution only for $\rho(x,t)$. Let us consider Eq. 4.35. The second term on the right hand side gives the main contribution in the vicinity of the right electrode located at $x = L$ due to the exponential prefactor, whereas the third term contributes mainly close to the left electrode located at $x = -L$. Let us consider the second term in more details,

$$\frac{1}{4}e^{\kappa x}\left\{\text{erf}(\frac{-x + L - 2\kappa Dt}{2\sqrt{Dt}}) + \text{erf}(\frac{x + L + 2\kappa Dt}{2\sqrt{Dt}})\right\}\,. \quad (4.40)$$

Due to the properties of the error function, the expression in brackets changes in the interval $[-2, +2]$. If $x \approx L$, the second term in Eq. 4.40 is nearly unity at every time. At the initial moment the argument of the error function is infinite,

then it decreases and then it goes again to infinity. Setting its time derivative to zero one can find its minimal value, A_M,

$$A_M = \sqrt{\kappa L}\,, \tag{4.41}$$

which is achieved at the time $t = \frac{L}{\kappa D}$. $\mathrm{erf}(A_M)$ is close to unity if $\kappa L > 5$, $\mathrm{erf}(\sqrt{5}) \cong 0.9984$. Therefore the second term in Eq. 4.40 can be replaced with unity at each time. Applying the same procedure to the other terms of Eq. 4.35 one can simplify it to

$$\rho(x,t) = \frac{\epsilon k_B T}{2ze}\, q\, \kappa^2 \left(e^{\kappa x} \left\{ 1 - \mathrm{erf}\left(\frac{-x+L-2\kappa Dt}{2\sqrt{Dt}} \right) \right\} \right.$$
$$\left. - e^{-\kappa x} \left\{ 1 - \mathrm{erf}\left(\frac{x+L-2\kappa Dt}{2\sqrt{Dt}} \right) \right\} \right). \tag{4.42}$$

The error function is not an elementary function, and it would be desirable to simplify Eq. 4.42 further. However, an expansion in a series is not appropriate because the argument of the error function depends not only on coordinate but also on time and satisfies

$$-\infty < \frac{L \mp (x + 2\kappa Dt)}{\sqrt{4Dt}} < +\infty\,.$$

Consequently, it is impossible to choose an appropriate expansion. At every arbitrary but fixed spatial point at different times the argument of the error function is different. It could be small or large as well. And at some moments it can be moderate, which makes the expansion problematic.

4.1.3 Behavior of the solution

In the previous section the electric field and the particle concentrations were obtained in the frame of the linearized PNP equations. Temporal and spatial parts of the solution can not be separated from each other. A dependence on the applied voltage is represented by the parameter q defined in Eq. 4.25. This parameter appears in all expressions only as a prefactor. Because the Debye-Falkenhagen equation is linear, it can be divided by q, which would erase the dependence on the applied voltage. This means that $\rho(x,t)$ and $E(x,t)$ can be

scaled. To do so, the electric field should be represented in terms of its initial value, $E \to \frac{E(x,t)}{E_0}$, where $E_0 = \frac{v}{2L}$. According to Eq. 4.36 the initial concentration appears explicitly also as a prefactor, which suggests to measure a concentration in terms of η, $C_{\pm}(x,t) \to \frac{C_{\pm}(x,t)}{\eta}$. In these reduced units the concentrations and the electric field are independent of both the applied voltage v and the initial concentration η. The initial concentration appears implicitly via the Debye screening length λ_D which governs the evolution of the system. In Chapter 3 we found that the steady state is characterized by two parameters only: L and λ_D. In the dynamical case there are the same parameters supplemented by another one which is responsible for dynamical properties. Obviously, the diffusion coefficient must have an influence on the dynamics but its influence can also be scaled off. The diffusivity D occurs only in a combination with the time as a product Dt. Changing the diffusion coefficient from D_1 to D_2 means stretching of the time scale by $\frac{D_2}{D_1}$.

To illustrate the spatiotemporal dependence of the solution let us consider the system with $\kappa L > 5$. This eliminate the dependence on L if the coordinate is defined as a distance from the nearest electrode. The similar procedure was used in Chapter 3 concerning the applicability of the approximate solution. The charge profile $C_+(x,t)$ is shown in Fig. 4.2. Directly after applying the voltage, the concentration jumps up in a very narrow layer close to the electrode. Next, the curve swells and the particle excess spreads into the bulk forming the diffuse layer. At a finite time the coordinate dependence is not exponential and tends to the exponential decay when time goes to infinity.

One can introduce a characteristic time τ as the time which is necessarily to bring the system into the steady state. Due to its physical origin τ can be called the charging time. To estimate τ let us consider the second term in Eq. 4.35. A similar treatment of another term gives the same result. Because

$$\lim_{t \to \infty} e^{\kappa x} \left\{ \mathrm{erf}(\frac{-x + L - 2\kappa Dt}{2\sqrt{Dt}}) + \mathrm{erf}(\frac{x + L + 2\kappa Dt}{2\sqrt{Dt}}) \right\} = 0 \,,$$

and $\mathrm{erf}(3) \approx 1$, one finds for $x = -L$,

$$\tau = \left(\frac{3}{\kappa}\right)^2 \frac{1}{D} = \frac{9\lambda_D^2}{D} \,. \tag{4.43}$$
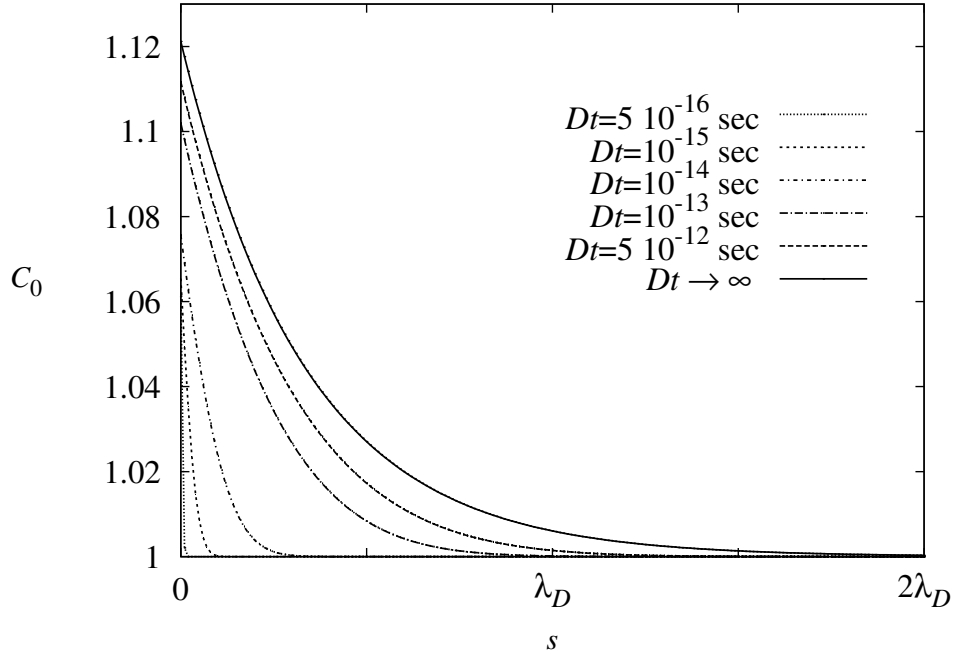
Figure 4.2: Normalized concentration $C_0 = C_+(s,t)/\eta$ near the electrode. $\kappa = 1 \cdot 10^7$ m. s is the distance from the electrode.

The prefactor 3^2 can be slightly varied because it represents the accuracy of the estimation. The quantity τ is the time scale for a diffusion across the Debye screening length λ_D.

Obviously, τ should depend on the parameters of the system. Relying on the dimension analysis, one can introduce three time scales: $\frac{L^2}{D}$, $\frac{L\lambda_D}{D}$, and $\frac{\lambda_D^2}{D}$. The first and the third time scales consist of only one size-parameter. The second time scale contains both size-parameters which makes it more reliable. In Section 2.2 exactly this time scale was obtained, see Eq. 2.46. Experimental results together with numerical simulations, see for example (40), predict the same time scale as well. Meanwhile, the solution presented above suggests the third time scale. This fact poses a big problem of the applicability of the solution and also of the whole PNP approach, which will be resolved in the next section.

4.2 Reformulation of the PNP

4.2.1 General idea

Despite the mathematical treatment is correct, the solution to the PNP equations presented above provides the charging time different form the experimental predictions. On the other hand, the PNP are based on very general assumptions and it is highly unlikely that they are not able to describe experimental results correctly. A possible explanation is that there is some additional constraint or condition which was overlooked. The system is locked between two electrodes. Because Faradaic processes are neglected, particles can not move through the electrodes, which offers the missing constraint. The particle fluxes should tend to zero at the electrodes, $F_\pm(x = \pm L, t) = 0$. This makes the problem much more complicated not only due to an additional condition to take into account but also because the problem involves a number of different functions. The fundamental equation is formulated for the charge density $\rho(x, t)$,

$$\dot\rho(x, t) = D\left(\rho''(x, t) - \kappa^2 \rho(x, t)\right).\tag{4.44}$$

The boundary conditions are formulated for another function, namely for the potential $\phi(x, t)$,

$$\phi(x = -L, t) - \phi(x = L, t) = v(t).\tag{4.45}$$

The additional constraint is imposed on the third function: the particle fluxes $F_\pm(x, t)$, and can not be fulfilled by the solution presented in the previous section,

$$F_\pm(x = \pm L, t) = 0.\tag{4.46}$$

So we have to deal with three different functions, which complicates the problem drastically. Both $F_\pm(x, t)$ and $\phi(x, t)$ are related to $\rho(x, t)$ in a nontrivial manner involving integration which would give an integro-differential equation as a constraint. Obviously, it is very desirable to avoid this. The possible way is to incorporate the constraint for the flux, Eq. 4.46, into the initial problem. In other words, we are going to reformulate the governing equation in such a manner that Eq. 4.46 is satisfied automatically. For this purpose one has to reformulate Eq. 4.44.

Let us consider the flux $F_\pm(x,t)$,

$$F_\pm(x,t) = -DC'_\pm(x,t) \mp \mu ze\eta\phi'(x,t)\,. \tag{4.47}$$

Using Eq. 4.3 one can express $C_\pm(x,t)$ via $\rho(x,t)$,

$$F_\pm(x,t) = D\left(\mp\frac{1}{2ze}\rho'(x,t) \pm \frac{ze}{k_BT}\eta E(x,t)\right)\,. \tag{4.48}$$

According to the Poisson equation $E(x,t)$ and $\rho(x,t)$ are related, see Eq. 4.22. Introducing for simplicity of notation a new function $y(x,t)$, $y(x,t) = \int \rho(x,t)dx$, Eq. 4.22 reads

$$\epsilon E(x,t) = y(x,t) + f(t)\,. \tag{4.49}$$

According to the definition the function $y(x,t)$ is symmetric, $y(x,t) = y(-x,t)$, and satisfies the Debye-Falkenhagen equation,

$$\dot{y}(x,t) = D(y''(x,t) - \kappa^2 y(x,t))\,. \tag{4.50}$$

Inserting $y(x,t)$ from Eq. 4.49 into Eq. 4.48 we get

$$F_\pm(x,t) = \mp\frac{D}{2ze}y''(x,t) \pm \frac{Dze}{\epsilon k_BT}\eta\left[y(x,t) + f(t)\right]\,, \tag{4.51}$$

or using Eq. 4.50 it results

$$F_\pm(x,t) = \mp\frac{D}{2ze}\left(\dot{y}(x,t) - \kappa^2 f(t)\right)\,. \tag{4.52}$$

In the previous section the function $f(t)$ was considered as an arbitrary one, see the discussion after Eq. 4.22. Now this function is fixed by the claim $F_\pm(x = \pm L, t) = 0$, which leads to

$$f(t) = \frac{\dot{y}(x = \pm L, t)}{\kappa^2}\,. \tag{4.53}$$

Hence the problem reads

$$\dot{y}(x,t) = D(y''(x,t) - \kappa^2 y(x,t))\,, \tag{4.54}$$

where the charge density and the electric field can be found according to

$$\rho(x,t) = y'(x,t)\,, \tag{4.55}$$

$$\epsilon E(x, t) = y(x, t) + \kappa^{-2}\dot{y}(x = \pm L, t). \qquad (4.56)$$

From the last equation the boundary conditions are

$$\int_{-L}^{L} y(x, t)dx + 2L\kappa^{-2}\dot{y}(x = \pm L, t) = \frac{v(t)}{\epsilon}. \qquad (4.57)$$

Now the constraint Eq. 4.46 is fulfilled automatically. Eq. 4.57 is still quite complicated, and the problem can not be considered as much simplified. Therefore, let us reformulate the problem in terms of the electric field. Inserting $y(x, t)$ from Eq. 4.56 into Eq. 4.50 we get

$$\epsilon\dot{E}(x, t) - \kappa^{-2}\ddot{y}(x = \pm L, t) = D(\epsilon E''(x, t) - \epsilon\kappa^2 E(x, t) + \dot{y}(x = \pm L, t)). \qquad (4.58)$$

Hereafter, for the sake of simplicity of notation the time will be redefined, $t \rightarrow \frac{t}{D}$. Consequently, the time derivative changes its dimension, and the inverse redefinition of the time in the final results, where the time derivatives were already evaluated, could be not obvious. Therefore, in the finale results the diffusion coefficient will be shown explicitly.

According to Eq. 4.56 Eq. 4.58 turns into

$$\dot{E}(x, t) = E''(x, t) - \kappa^2 E(x, t) + \dot{E}(x = \pm L, t), \qquad (4.59)$$

which is the governing equation of the reformulated problem. For $x = \pm L$ it yields

$$E''(x = \pm L, t) = \kappa^2 E(x = \pm L, t). \qquad (4.60)$$

Because $E(x, t)$ is a symmetric function, one can consider the electric field only at one point, for instance $x = -L$. Eq. 4.60 is valid at every time and can be solved by a separation of variables, which leads to

$$E(x = -L, t) = \tilde{E}(t) \exp(-\kappa(x + L)). \qquad (4.61)$$

The notation used in the last two equations might be confusing because $E(x = \pm L, t)$ is not actually a function of coordinate. It should be understood in a sense that the function is considered in a very small vicinity of the point $x = \pm L$, which extension, as it will be shown later, is not important. The choice of $\exp(-\kappa(x+L))$ instead of hyperbolic sine or cosine will be likewise justified later.

Eq. 4.61 explains the success of many approximate solutions mentioned in the introduction in predicting the external current. In every approximation it was supposed that variables can be somehow separated[1]. In the next section we will see that the current is defined by $\dot{E}(x = \pm L, t)$, that is by the electric field calculated in the point where variables can be truly separated and assumptions made in the cited papers are justified. However, variables can be separated only at $x = \pm L$. As it was also mentioned in the introduction, the PNP equations can not be solved by a separation of variables. Indeed, if $\rho(x, t) = T(t)X(x)$, from the PNP it follows that

$$X(x) \cdot \dot{T}(t) = T(t) \cdot \left(X''(x) - \kappa^2 X(x) \right), \tag{4.62}$$

so either $X(x)$ is the steady state solution and $T(t) \equiv 0$ or at $t \to \infty$ $X(x)$ does not tend to the steady state.

So far we have found the additional constraint and have reformulated the problem in order to incorporate this constraint into the governing equation. It has resulted into Eq. 4.59. Now we are going to apply this approach to two cases: the application of DC- and AC voltages. It will be supposed that $\kappa L > 3$ which is usually the case and was already discussed above. The inequality is dictated by the assumption $\exp(-2\kappa L) \ll 1$ or $2\exp(\kappa L) \approx \sinh(\kappa L) \approx \cosh(\kappa L)$. If $\kappa L \simeq 1$, the approach presented here is still valid and most of the calculations could be performed but they would by more bulky and lengthy and therefore are not shown.

4.2.2 Response to a DC voltage

At the initial moment a step voltage is applied, $v(t) = v \cdot \Theta(t)$, where $\Theta(t)$ is the Heaviside function. The basic equation, Eq. 4.59, should be supplemented with following conditions:

$$\int_{-L}^{L} E(x, t)dx = v, \tag{4.63}$$

$$E(x, t = 0) = \frac{v}{2L}, \tag{4.64}$$

---

[1]In (20) it was not supposed throughout the paper but only to find the external current.

$$E(x, t = \infty) = \frac{v}{2}\kappa\frac{\cosh(\kappa x)}{\sinh(\kappa L)}. \tag{4.65}$$

Eq. 4.63 coincides with Eq. 4.21 and was already discussed. Eq. 4.64 follows from Eq. 4.63 and the fact that at the initial moment the charge distribution is homogeneous and the electric field is constant. Eq. 4.65 represents the steady state solution, see Eq. 4.24 and Eq. 4.25.

Let us integrate Eq. 4.59 from $-L$ to L. Using Eq. 4.63 one gets

$$0 = \int_{-L}^{L} E''(x, t)dx - \kappa^2 v + 2L\dot{E}(x = -L, t), \tag{4.66}$$

or

$$-E'(x = -L, t) + L\dot{E}(x = -L, t) = \frac{\kappa^2 v}{2}. \tag{4.67}$$

Inserting here Eq. 4.61 it yields

$$\kappa\exp(-\kappa(x+L))\tilde{E}(x = -L, t) + L\exp(-\kappa(x+L))\dot{\tilde{E}}(x = -L, t) = \frac{\kappa^2 v}{2}, \tag{4.68}$$

where exponents should be replaced with unity because the equation is valid only at $x = -L$. This is a first-order differential equation which solution is well known,

$$E(x = -L, t) = \frac{v}{2}\left(\kappa - A\exp(-\alpha t)\right), \tag{4.69}$$

where $\alpha = \frac{\kappa}{L}$. The integration constant A can be found from the initial condition, Eq. 4.64,

$$A = \kappa - L^{-1}. \tag{4.70}$$

If in Eq. 4.61 we use not one exponent but a linear combination of those as it should be done to find the general solution, i.e. $\tilde{E}(t)\exp(-\kappa(x + L)) + \tilde{E}_1(t)\exp(\kappa(x + L))$, after more expensive calculations we would anyway end up with Eq. 4.69. In the discussion after Eq. 4.61 it was stated that the function $E(x = -L, t)$ should be considered in a small vicinity of the point $x = -L$, which size is not important. This statement is justified by the fact that the final result, Eq. 4.69, is formulated exclusively at the point $x = -L$ and does not depend on coordinate.

In a view of Eq. 4.69, the governing equation, Eq. 4.59, can be rewritten as

$$\dot{E}(x, t) = E''(x, t) - \kappa^2 E(x, t) + \frac{v}{2}\alpha A\exp(-\alpha t). \tag{4.71}$$

Eq. 4.69 represents the condition Eq. 4.63. This clearly demonstrates one of advantages of our treatment, namely that the quite complicated constraint given by an integro-differential equation, Eq. 4.57, is reduced to a simple exponential boundary condition, Eq. 4.69.

Before presenting the solution of the PNP equations, i.e. the expressions for $C_\pm(x,t)$ and $E(x,t)$, let us consider the derived equations in greater details because they already offer some important results.

In Section 2.2, using Laplace transformation it was found that the buildup of the charge screening layer occurs exponentially, see the discussion after Eq. 2.46. This result is perfectly in agreement with Eq. 4.69.

As it was discussed earlier, one of the experimentally relevant quantities is the external current. According to Ramo's theorem

$$J(t) = \epsilon \dot{E}(x = \pm L, t) \,. \tag{4.72}$$

For a derivation and discussion of Ramo's theorem see Appendix B. Using Eq. 4.69 one can find the external current,

$$J(t) = \epsilon \alpha (\kappa - L^{-1}) \exp(-\alpha t) \,. \tag{4.73}$$

$J(t = 0)$ coincides with the value found in (18). $J(t)$ decays with the correct character time $\tau = \frac{L}{D\kappa}$. In other words, the reformulation of the governing equation, performed in this section, has solved the problem posed at the end of Section 4.1, concerning a disagreement of analytical results with experimental data and numerical simulations.

Let us come back to the solution of the reformulated PNP equations, namely to Eq. 4.59 and conditions Eqs. 4.64, 4.65 and 4.69. A new functions $w(x,t)$ is introduced according to

$$w(x,t) = \frac{\exp(-\alpha t)}{\kappa L} + \frac{\cosh(\kappa x)}{\cosh(\kappa L)} - \frac{2}{\kappa v} E(x,t) \,, \tag{4.74}$$

and the problem is reformulated in terms of $w(x,t)$. It results

$$\dot{w}(x,t) = w''(x,t) - \kappa^2 w(x,t) \,, \tag{4.75}$$

$$w(x, t = 0) = \frac{\cosh(\kappa x)}{\cosh(\kappa L)} \,, \tag{4.76}$$

$$w(x, t = \infty) = 0\,, \tag{4.77}$$

$$w(x = \pm L, t) = \exp(-\alpha t)\,. \tag{4.78}$$

Performing Laplace transformation we get

$$zw(x, z) - \frac{\cosh(\kappa x)}{\cosh(\kappa L)} = w''(x, z) - \kappa^2 w(x, z)\,, \tag{4.79}$$

$$w(x = \pm L, z) = \frac{1}{z + \alpha}\,. \tag{4.80}$$

The general symmetric solution to this set of equations reads

$$w(x, z) = \frac{\cosh(\kappa x)}{z \cosh(\kappa L)} - \frac{\alpha}{z(z + \alpha)} \frac{\cosh(\sqrt{\kappa^2 + z}\,x)}{\cosh(\sqrt{\kappa^2 + z}\,L)}\,. \tag{4.81}$$

To invert this result one has to take the following integral

$$w(x, t) = \frac{1}{2\pi i} \int_{a-i\infty}^{a+i\infty} \exp(zt) w(x, z) dz\,, \tag{4.82}$$

where the real number a is sufficiently large so that all poles of $w(x, z)$ lie on the left-hand side from the line along which the integral is taken. The integral will be evaluated in the frame of theory of functions of a complex variable. Following the conventional procedure we extend z onto the whole complex plane and choose the contour of integration in a way to enclose all poles as shown in Fig. 4.3. The integral over the whole contour is a sum of the integral over the arc ∂C, which as usual tends to zero, and the integral along the vertical line, which we are interested in. According to the Cauchy residue theorem the integral over the whole contour γ is proportional to the sum of all residues lying within the contour,

$$\oint_\gamma f(z) dz = 2\pi i \sum_{n=k}^{\infty} f(z, a_k)\,, \tag{4.83}$$

where $f(z, a_k)$ denotes a residue of $f(z)$ calculated at the point $z = a_k$. To find the poles of $w(x, z)$ one has to find zeros of the denominator of the right-hand side of Eq. 4.81. Two poles are obvious: $z = 0$ and $z = -\alpha$. Other zeros are determined by the equation

$$\cosh(\sqrt{\kappa^2 + z}\,L) = 0\,. \tag{4.84}$$

Hence,

$$\sqrt{\kappa^2 + z}L = i\left(\frac{\pi}{2} + \pi n\right), \tag{4.85}$$

where n is the integer running from $-\infty$ to ∞. Solving this equation for z we get

$$z_n = -\frac{1}{L^2}\left(\frac{\pi}{2} + \pi n\right)^2 - \kappa^2 + i0, \tag{4.86}$$

The poles are located on the negative part of the real axis as depicted in Fig. 4.3, but now n should run from 0 to ∞, otherwise some poles would be counted twice.
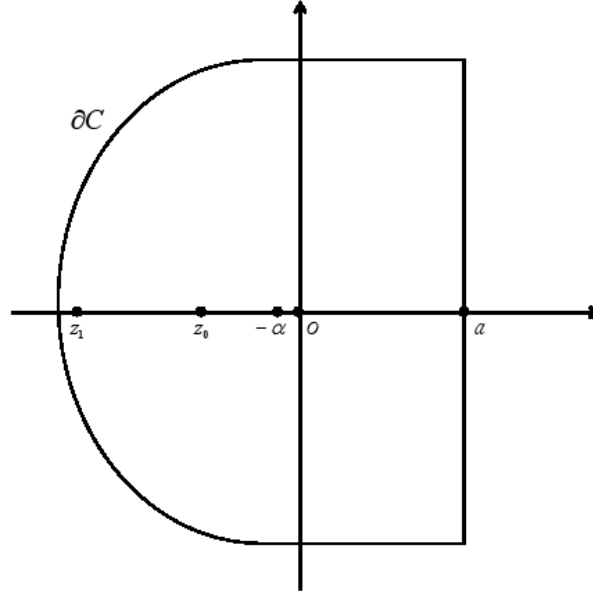

Figure 4.3: Contour of integration

The function $w(x, z)$ consists of two terms, see Eq. 4.81. Integration of the first one gives

$$\frac{1}{2\pi i}\int_{a-i\infty}^{a+i\infty}\exp(zt)\frac{\cosh(\kappa x)}{z\cosh(\kappa L)}dz = \frac{\cosh(\kappa x)}{\cosh(\kappa L)}\Theta(t). \tag{4.87}$$

Further the Heaviside step function will be omitted because we consider only $t > 0$. Integration of the second term reveals

$$\frac{\cosh(\kappa x)}{\cosh(\kappa L)} - e^{-\alpha Dt}\frac{\cosh(\sqrt{\kappa^2 - \alpha}x)}{\cosh(\sqrt{\kappa^2 - \alpha}L)} + \frac{\pi\alpha}{L^2}e^{-\kappa^2 Dt}S(x, t), \tag{4.88}$$

where

$$S(x,t) = \sum_{n=0}^{\infty}(-1)^n \exp\left(-\frac{\pi^2}{4L^2}(1+2n)^2 Dt\right)\cos\left(\frac{\pi}{2L}(1+2n)x\right)\frac{1+2n}{z_n(z_n+\alpha)}.$$
(4.89)

So, we have inverted the Laplace transform of $w(x,t)$. Coming back to the electric field we find

$$E(x,t) = \frac{v}{2}\kappa\left\{\frac{\cosh(\kappa x)}{\cosh(\kappa L)} - e^{-\alpha Dt}\left(\frac{\cosh(\sqrt{\kappa^2-\alpha}x)}{\cosh(\sqrt{\kappa^2-\alpha}L)} - \frac{1}{\kappa L}\right) + \frac{\pi\alpha}{L^2}e^{-\kappa^2 t}S(x,t)\right\}.$$
(4.90)

Using Eq. 4.8 and the Poisson equation we finally get

$$\frac{C_{\pm}(x,t)}{\eta} = 1 \pm \frac{v}{2}\frac{ze}{k_B T}\left(\frac{\sinh(\kappa x)}{\cosh(\kappa L)} - e^{-\alpha Dt}\frac{\sinh(\sqrt{\kappa^2-\alpha}x)}{\cosh(\sqrt{\kappa^2-\alpha}L)}\sqrt{1-\frac{1}{\kappa L}}\right.$$
$$\left. + \frac{\pi\alpha}{\kappa L^2}e^{-\kappa^2 Dt}S'(x,t)\right).$$
(4.91)

Eqs. 4.90 and 4.91 present the solution of the PNP equations in the linear regime when a DC voltage is applied.

The sum $S(x,t)$ plays a role only on the short-time scale. It is a decreasing function of time multiplied by $e^{-\kappa^2 t}$, i.e. its contribution will disappear rapidly with a character time $\tau = \kappa^{-2}D^{-1}$. If the evolution on the short-time scale is of interest, $S(x,t)$ can be easily summed up numerically because it converges fast.

The symmetry properties described in Section 4.1.3 are still valid, so we do not repeat them again. At the initial moment the charge concentrations and the electric field are expressed by the nontrivial function $S(x,t)$ which decays rapidly. When $S(x,t)$ becomes negligible, the concentration and the electric field profiles are almost exponential. The higher κL is, the closer they are to an exponent.

4.2.3 Response to an AC voltage

In this section we will consider a response to an AC applied voltage, i.e. $v(t) = v\cos(\omega t)$. The case of a DC applied voltage discussed in the previous section can be looked on as a limiting case of an AC voltage with $\omega \to 0$. Any other, nonharmonic signal can be expanded into Fourie series and represented as a sum of

harmonic signals. Because the governing equation, Eq. 4.59, is linear, a response to nonharmonic signal is a sum of its Fourie harmonics.

The case of an AC applied voltage has been considered by many authors. In my personal opinion, the best analytical investigation so far was performed more than fifty years ago by Macdonald in (43). Though, since that time many other papers have been published. For the state of the art see (8) and citations therein. The analytical solution of the PNP equations has not been found yet.

To solve the problem the governing equation, Eq. 4.59, should be supplemented with a constraint given by the boundary condition,

$$\int_{-L}^{L} E(x,t)dx = v\cos(\omega t)\,, \tag{4.92}$$

and the initial condition

$$E(x,t=0) = \frac{v}{2L}\,. \tag{4.93}$$

Following the line proposed in Section 4.2.2, the electric field in the vicinity of the left electrode satisfies

$$E(x=-L,t) = \tilde{E}(t)\exp(-\kappa(x+L))\,. \tag{4.94}$$

Integrating Eq. 4.59 from $-L$ to L and taking into account Eq. 4.92 one finds

$$-v\omega\sin(\omega t) = \int_{-L}^{L} E''(x,t)dx - \kappa^2 v\cos(\omega t) + 2L\dot{E}(x=-L,t)\,, \tag{4.95}$$

or

$$-v\omega\sin(\omega t) = -2E'(x=-L,t) - \kappa^2 v\cos(\omega t) + 2L\dot{E}(x=-L,t)\,. \tag{4.96}$$

Using Eq. 4.94 we get

$$L\dot{\tilde{E}}(t) + \kappa\tilde{E}(t) = \frac{v}{2}\left(-\omega\sin(\omega t) + \kappa^2\cos(\omega t)\right)\,. \tag{4.97}$$

The solution of this linear differential equation of the first order is well known,

$$E(x=-L,t) = \exp(-\alpha t)\left(A + \frac{v}{2L}\int e^{\alpha t}(-\omega\sin(\omega t) + \kappa^2\cos(\omega t))dt\right)\,, \tag{4.98}$$

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where A in an integration constant and $\alpha = \frac{\kappa}{L}$. Finally, we get

$$E(x = -L, t) = \frac{v}{2L(\alpha^2 + \omega^2)} \left\{ \omega \sin(\omega t)(\kappa^2 - \alpha) + \cos(\omega t)(\alpha\kappa^2 + \omega^2) \right\} + Ae^{-\alpha t},$$
(4.99)

where the constant A should be found from the initial condition, Eq. 4.93. The case $\omega = 0$ means that the applied voltage is constant, and the problem is equivalent to the one considered earlier. Indeed, in this case Eq. 4.99 turns into Eq. 4.69. We have already discussed the short-time behavior and usually an AC voltage is applied over a long period of time, therefore we will consider the long-time behavior, or so called stationary regime. It is not a steady state in a direct sense because the steady state supposes that all time derivatives are zero. In the long-time regime all initial conditions are irrelevant. According to Eq. 4.99 this regime begins after the time $\tau = \frac{L}{\kappa D}$ when $A \exp(-\alpha t) \to 0$. The short-time behavior can be still considered within the approach, and the equations can be solved. However, we will omit the detailed calculations because they are bulky and similar to those presented in the previous section. Furthermore, we are going to demonstrate another approach for solving the PNP equations, which is not applicable for the short-time regime.

From Eq. 4.99, using Ramo's theorem one can find the external current. In the stationary regime it reads

$$J(t) = J_0 \cos(\omega t + \varphi_0),$$
(4.100)

where

$$J_0 = \frac{v\epsilon\omega D}{2(\kappa^2 D^2 + \omega^2 L^2)} \sqrt{\kappa^6 D^2 + \frac{\omega^4 L^2}{D^2} + \omega^2 \kappa^2 (\kappa^2 L^2 + 1)},$$
(4.101)

and

$$\tan(\varphi_0) = \frac{\kappa^3 D^2 + \omega^2 L}{D\omega\kappa(\kappa L - 1)}.$$
(4.102)

Note that at $\omega \to \infty$ $J_0 \to \infty$ as well. This is a direct consequence of the fact that the PNP equations neglect the inertia of particles, which poses an additional restriction of the applicability. This can be seen from the expression for the flux, Eq. 4.47. The flux and, consequently, the drift velocity are proportional to the

applied force. In contrast, according to Newton's second law the acceleration should be proportional to the applied force.

Let us formulate the equations to solve.

$$\dot{E}(x,t) = E''(x,t) - \kappa^2 E(x,t) + \dot{E}(x = \pm L, t), \tag{4.103}$$

with the boundary condition

$$E(x = \pm L, t) = \frac{v}{2L(\alpha^2 + \omega^2)} \left\{ \omega \sin(\omega t)(\kappa^2 - \alpha) + \cos(\omega t)(\alpha\kappa^2 + \omega^2) \right\}. \tag{4.104}$$

Similar to the previous section this boundary condition is represented by the integral constraint, Eq. 4.92. Introducing a new function $p(x,t)$ according to

$$E(x,t) = p(x,t) + \frac{v\omega}{2L(\alpha^2 + \omega^2)} \left[\omega \cos(\omega t) - \alpha \sin(\omega t) \right], \tag{4.105}$$

it gives

$$\dot{p}(x,t) = p''(x,t) - \kappa^2 p(x,t),$$
$$p(x = \pm L, t) = \frac{v\kappa^2}{2L(\alpha^2 + \omega^2)} \left\{ \omega \sin(\omega t) + \alpha \cos(\omega t) \right\}. \tag{4.106}$$

Because the initial condition is not relevant, one can choose $p(x, t = 0) = 0$. Performing Laplace transformation we get

$$zp(x,z) = p''(x,z) - \kappa^2 p(x,z),$$
$$p(x = \pm L, z) = \frac{v\kappa^2}{2L(\alpha^2 + \omega^2)} \left\{ \frac{\alpha z + \omega^2}{z^2 + \omega^2} \right\}. \tag{4.107}$$

The general solution of this equation is

$$p(x,z) = \frac{v\kappa^2}{2L(\alpha^2 + \omega^2)} \frac{\alpha z + \omega^2}{z^2 + \omega^2} \frac{\cosh(\sqrt{\kappa^2 + z}x)}{\cosh(\sqrt{\kappa^2 + z}L)}. \tag{4.108}$$

Basing on the results presented in Section 4.2.2 one can easily invert this expression. We would end up with a sum similar to Eq. 4.89, which decays fast. But we will follow another way and will find the solution under the assumption $\kappa L > 5$. This assumption means that one can separately consider the influences of the left

and the right electrodes. Consequently, the system can be divided into two parts, any if which represents the influence of the corresponding electrode,

$$p(x, z) = p^l(x, z) + p^r(x, z).$$ (4.109)

Accordingly, Eq. 4.108 splits into two parts as well. The left one is

$$p^l(x, z) = \frac{v\kappa^2}{2L(\alpha^2 + \omega^2)} \frac{\alpha z + \omega^2}{z^2 + \omega^2} \exp(-\sqrt{z + \kappa^2}(x + L)),$$ (4.110)

and the right one is similar to the left one but x is be replaced with $-x$,

$$p^r(x, z) = \frac{v\kappa^2}{2L(\alpha^2 + \omega^2)} \frac{\alpha z + \omega^2}{z^2 + \omega^2} \exp(\sqrt{z + \kappa^2}(x - L)).$$ (4.111)

So we will solve Eq. 4.110 and then add a symmetric part, Eq. 4.111.

Inversion of Eq. 4.110 is simple. There are only two poles at $z = \pm i\omega$ which give

$$
\begin{aligned}
p^l(x, t) &= \tfrac{v\kappa^2}{4Li(\alpha^2 + \omega^2)} \left([\omega + i\alpha] \exp(i\omega t - \sqrt{\kappa^2 + i\omega}(x + L)) \right. \\
&\quad \left. - [\omega - i\alpha] \exp(-i\omega t - \sqrt{\kappa^2 - i\omega}(x + L)) \right).
\end{aligned}
$$ (4.112)

Adding here a symmetric expression for $p^r(x, t)$ and coming back to the electric field we get

$$
\begin{aligned}
E(x, t) &= \tfrac{v}{2L(\alpha^2 + \omega^2)} \left(\omega^2 \cos(\omega t) - \alpha\omega \sin(\omega t) \right. \\
&\quad -i\tfrac{\kappa^2}{2} e^{i\omega t}(\omega + i\alpha) \left[\exp(-\sqrt{\kappa^2 + i\omega}(x + L)) + \exp(\sqrt{\kappa^2 + i\omega}(x - L)) \right] \\
&\quad \left. +i\tfrac{\kappa^2}{2} e^{-i\omega t}(\omega - i\alpha) \left[\exp(-\sqrt{\kappa^2 - i\omega}(x + L)) + \exp(\sqrt{\kappa^2 - i\omega}(x - L)) \right] \right),
\end{aligned}
$$ (4.113)

or

$$
\begin{aligned}
E(x, t) &= \tfrac{v}{2L(\alpha^2 + \omega^2)} \left(\omega^2 \cos(\omega t) - \alpha\omega \sin(\omega t) \right. \\
&\quad + \kappa^2 e^{-\gamma(x+L)} \left\{ \alpha \cos(\delta(x + L) - \omega t) - \omega \sin(\delta(x + L) - \omega t) \right\} \\
&\quad \left. + \kappa^2 e^{\gamma(x-L)} \left\{ \alpha \cos(\delta(x - L) + \omega t) + \omega \sin(\delta(x - L) + \omega t) \right\} \right),
\end{aligned}
$$ (4.114)

where

$$\gamma = \sqrt{\frac{\sqrt{\kappa^4 + \omega^2} + \kappa^2}{2}}, \quad \delta = \sqrt{\frac{\sqrt{\kappa^4 + \omega^2} - \kappa^2}{2}}.$$ (4.115)

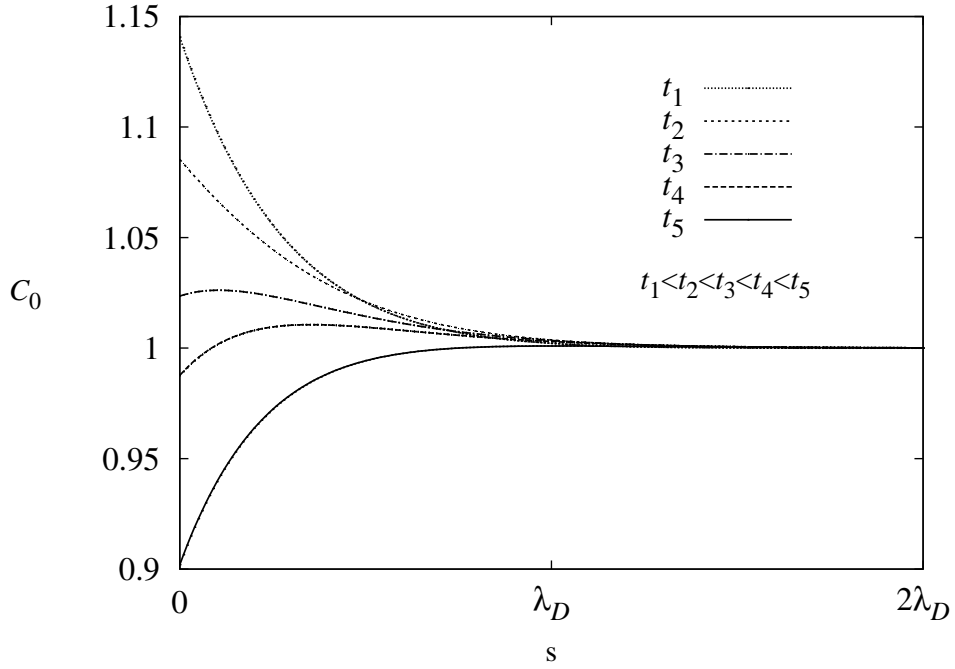Redefining the time and inserting the diffusion coefficient D explicitly we end up with

$$E(x,t) = \frac{vD}{2(\kappa^2 D^2 + \omega^2 L^2)} \left(\frac{\omega^2 L}{D} \cos(\omega t) - \kappa\omega\sin(\omega t) \right.$$
$$+ \kappa^2 e^{-\gamma(x+L)} \left\{ D\kappa\cos(\delta(x+L) - \omega t) - \omega L \sin(\delta(x+L) - \omega t) \right\}$$
$$\left. + \kappa^2 e^{\gamma(x-L)} \left\{ D\kappa\cos(\delta(x-L) + \omega t) + \omega L \sin(\delta(x-L) + \omega t) \right\} \right) , (4.116)$$

where

$$\gamma = \sqrt{\frac{\sqrt{D^2\kappa^4 + \omega^2} + D\kappa^2}{2D}}, \quad \delta = \sqrt{\frac{\sqrt{D^2\kappa^4 + \omega^2} - D\kappa^2}{2D}} . \qquad (4.117)$$

Figure 4.4: Normalized concentration $C_0 = C_+(s,t)/\eta$ calculated at different moments. s is the distance from the electrode.

Consequently, the particle concentrations are

$$\frac{C_\pm(x,t)}{\eta} = 1 \mp v\frac{ze}{k_B T} \frac{D\delta}{2(\kappa^2 D^2 + \omega^2 L^2)} \times$$
$$\left(e^{-\gamma(x+L)} \left\{ D\kappa\sin(\delta(x+L) - \omega t) + \omega L \cos(\delta(x+L) - \omega t) \right\} \right.$$
$$\left. + e^{\gamma(x-L)} \left\{ D\kappa\sin(\delta(x-L) + \omega t) - \omega L \cos(\delta(x-L) + \omega t) \right\} \right) . \quad (4.118)$$

Eqs. 4.116, 4.118 and 4.117 present the solution of the linearized PNP equations in the stationary regime when AC voltage is applied.

At low frequency of the applied voltage the particles move slowly and $C_\pm(x, t)$ are monotonous functions. At higher frequency the change of the concentration in the bulk lags that at the electrode and $C_\pm(x, t)$ are not monotonous as one can see in Fig. 4.4. With increasing ω the magnitude of oscillations likewise the deep of penetration of the perturbation into the bulk decreases. If $\omega \rightarrow \infty$, $C_\pm(x, t) \rightarrow \eta$.

Chapter 5

Conclusion and future perspectives

The Poisson-Nernst-Planck equations describe a diffusion of charged particles in the applied electric field. Due to a very general formulation of the problem they can be employed to treat a wide range of experimental situations realized in systems of different physical nature. The PNP equations were formulated more than one century ago, but, despite the long history, their general solution is still unknown and a lot of papers deal with this problem. The present Thesis is devoted to the analysis of the PNP equations. The study can be roughly divided into two parts: the treatment of the steady state of the full nonlinear problem and the treatment of the dynamical problem in the linear regime.

In the stationary regime the PNP equations are equivalent to the Poisson-Boltzmann equation. Therefore, all conclusions are applicable to this equation as well. The exact nonlinear solution for a binary symmetric system was expressed in terms of Jacobi elliptic functions. In contrast to other studies, we analyzed the solution in its general, not simplified form. For the case of a finite plane system the approximate solution was shown. If the size of the system is large, its behavior is similar to that of an infinite plane system for which the PNP equations were solved by Gouy and Chapman. By introducing a prefactor into the Gouy-Chapman solution one can extend it onto a finite system. Such an extension is adequate as long as the midplane concentration does not tend to zero. At very high applied voltages the PNP equations should be inapplicable due to a violation of Ficks law. Basing on the exact steady state solution an upper estimation of

the applied voltage was found giving a limitation of the applicability of the PNP approach. As the next step, the general solution of the stationary PNP equations was found for the multispecies and multidimensional cases.

The dynamical problem was considered in the linear regime for two main general cases: an DC- and AC applied voltage. In both cases for the first time, it was found the analytical solution valid at every time and for every coordinate as well for every initial concentration but under a single assumption that $\lambda_D \ll L$. Already at $5\lambda_D < L$ gives quite precise results. In contrast to other investigations, we did not split the system into different regions where different, specific for each particular region assumptions are valid. Our solution describes the system as a whole. No preliminary assumptions of the double layer structure were done as well.

The response to a DC applied voltage is described on the short-time scale by a complicated function that decays rapidly with a character time $\tau = \lambda_D^2 D^{-1}$. For $t > \tau$, the spatial dependence of the particle concentrations and the electric field is nearly exponential. The steady state is archived as well exponentially on the time scale $\lambda_D L D^{-1}$. These exponential time and coordinate dependencies explain the correct prediction of the charging time made in frames of other approaches. In contrast to these solutions, our solution does not contain logical contradictions and satisfies all boundary and initial conditions.

The response to an AC voltage was considered in the stationary regime as the more relevant experimental realization. Though the present approach is valid on every time scale and can be applied for a description of the short-time behavior as well. The corresponding procedure was described. Analytical expressions for the particle concentrations and the electric field were found. At a high frequency of the applied voltage a change of the concentration in the bulk lags that at the electrode. The external current was also calculated. Basing on the frequency dependence of the external current the border of applicability of the PNP approach at very high frequencies of the applied voltage was pointed out. When inertia of the particles become relevant, the PNP equations should be modified.

AC experiments at low applied voltages are used to find the mobility of ions in electrolytes. For this purpose the dielectric spectroscopy is usually employed. The analytical expression for the external current offers an alternative approach.

Due to the presence of the electrolytic cell in the electrical circuit, the electric current changes its magnitude and phase which can be measured. From these data the mobility and the Debye screening length can be extracted. A development of this new, alternative approach is a plan for the nearest future.

Other future perspectives concern the further theoretical study of the Poisson-Nernst-Planck equations. In the present Thesis the new approach for solving the PNP equations in the linear regime has been developed. This approach can be applied to the full nonlinear problem whose analytical solution is of a great interest. In the linear regime there are some open questions as well. The PNP equations describe not only electrolytes but also semiconductors. The assumption $D_+ = D_-$ is usually valid in electrolytes but can be inapplicable in semiconductors. Hence, the case $D_+ \neq D_-$ should be considered. Another possible generalization of the results obtained in the Thesis is also dictated by an experimental realization. One of the new ideas used in our approach is that the condition of disappearance of the particle fluxes at the electrodes is incorporated into the governing equation and, therefore, is fulfilled automatically. This condition means that Faradaic processes are neglected. Though, for some systems such an assumption is inapplicable. Therefore, the assumption $F_\pm(x = \pm L, t) = 0$ should be replaced by $F_\pm(x = \pm L, t) = a$, where a is a function of time defined by the kinetics of chemical processes at the electrodes.

Appendix A

Jacobi elliptic functions

The Jacobi elliptic functions were introduced by Carl Gustav Jacob Jacobi at 1827 as the inverse of the elliptic integrals. Approximately at the same time Niels Henrik Abel independently studied properties of these functions. Earlier in 1799 Carl Friedrich Gauss gave some attention to one of them, namely to the Jacobi elliptic sine. The Jacobi functions are the particular case of the elliptic functions. From theoretical point of view it is easier and more conventional to consider them as a ratio of so called theta functions. Moreover, some properties of the Jacobi functions is tremendously difficult to prove without knowledge of the theory of theta functions. For more details see (44). Because our aim is to give a general impression of the Jacobi functions avoiding mathematical difficulties, we will defined them another way. Let us consider the integral

$$t = \int_0^u \frac{dy}{\sqrt{1 - y^2}} = \arcsin(u) \,. \tag{A.1}$$

This integral implicitly defines a function $u(t)$,

$$u(t) = \sin(t) \,. \tag{A.2}$$

Strictly speaking, the integral A.1 is defined in the range $\pi/2 < t < \pi/2$ corresponding to the positive sign of $\sqrt{1 - y^2}$. Inversion of the integral, that is a step from Eq. A.1 to Eq. A.2, extends $u(t)$ onto the total number axis, making the function continuous and differentiable at each point. Consider now the

generalization of the integral A.1,

$$t = \int_0^u \frac{dy}{\sqrt{(1 - y^2)(1 - q^2 y^2)}}.$$

<div align="right">(A.3)</div>

Inversion of this integral gives

$$u = \mathrm{sn}(t, q).$$

<div align="right">(A.4)</div>

The function $\mathrm{sn}(t, q)$ is called Jacobi elliptic sine. The parameter q is called elliptic modulus or just modulus. In the literature some times one can find another notation: $\mathrm{sn}(t, m)$. m is also called modulus, $m \equiv q^2$. Sometimes instead of q the letter k is used. Although, this parameter can be omitted in the notation at all, $\mathrm{sn}(t)$. In addition to the Jacobi sine the following functions are introduced: Jacobi elliptic cosine $u = \mathrm{cn}(t, q)$ as the inverse of the integral

$$t = \int_0^u \frac{dy}{\sqrt{(1 - y^2)(q'^2 + q^2 y^2)}},$$

<div align="right">(A.5)</div>

and delta amplitude $u = \mathrm{dn}(t, q)$ as the inverse of

$$t = \int_0^u \frac{dy}{\sqrt{(1 - y^2)(y^2 - q'^2)}},$$

<div align="right">(A.6)</div>

where the so called complementary modulus $q' = \sqrt{1 - q^2}$ is introduced. In addition to those functions, Jacobi introduced the notation $\mathrm{am}(t)$ as the inverse of

$$t = \int_0^{\mathrm{am}(t)} \frac{d\alpha}{\sqrt{1 - q^2 \sin^2(\alpha)}}.$$

<div align="right">(A.7)</div>

The function $\mathrm{am}(t)$, sometimes also denoted as $\varphi(t)$, is called the amplitude. Using $\mathrm{am}(t)$ one can relate Jacobi elliptic functions to trigonometric ones,

$$\mathrm{sn}(t) = \sin(\mathrm{am}(t)), \quad \mathrm{cn}(t) = \cos(\mathrm{am}(t)), \quad \mathrm{dn}(t) = \Delta(\mathrm{am}(t)),$$

where

$$\Delta u = \sqrt{1 - q^2 \sin^2(u)},$$

which explains the name of $\mathrm{dn}(t)$ as a function Δ of the amplitude $\mathrm{am}(t)$.

$\mathrm{sn}(t)$, $\mathrm{cn}(t)$ and $\mathrm{dn}(t)$ have a letter n at the end of their names. To write a ratio of any pair of Jacobi functions the following rule is used: the n is omitted

and the name for the new function is formed from the letters left. To denote the inverse function the letters should swap their places. For instance,

$$\frac{\mathrm{cn}(t)}{\mathrm{dn}(t)} \equiv \mathrm{cd}(t)\,,$$

$$\frac{1}{\mathrm{sn}(t)} \equiv \mathrm{ns}(t)\,.$$

This notation was introduced by James Glaisher in (45).

For all $q < 1$ the Jacobi elliptic functions are real and periodic. $\mathrm{sn}(t, q)$ and $\mathrm{cn}(t, q)$ have a period $4K$, $\mathrm{dn}(t, q)$ has a period $2K$, where

$$K \equiv K(q) = \int_0^1 \frac{dy}{\sqrt{(1-y^2)(1-q^2 y^2)}} = \int_0^{\pi/2} \frac{d\alpha}{\sqrt{1 - q^2 \sin^2(\alpha)}}$$

is the complete elliptic integral of the first kind [1]. If integration is taking not up to 1 but up to an arbitrary number, this integral is called incomplete,

$$F(t, q) = \int_0^t \frac{dy}{\sqrt{(1-y^2)(1-q^2 y^2)}}\,.$$

There is also the incomplete integral of the second kind $E(t, q)$,

$$E(t, q) = \int_0^t \sqrt{1 - q^2 \sin^2(\alpha)}\,d\alpha\,,$$

and the corresponding complete integral $E(q)$, $E(q) \equiv E(\pi/2, q)$.

It is easy to find asymptotic periods of the elliptic integrals. At $q \to 0$ $K \to \pi/2$. At $q \to 1$ $K \to \infty$. Consequently, the asymptotic behavior of the Jacobi functions is: at $q \to 0$ the Jacobi functions are expressed via trigonometric functions; at $q \to 1$ the Jacobi functions are expressed via hyperbolic functions,

$$\mathrm{sn}(t, 0) = \sin(t)\,, \qquad \mathrm{sn}(t, 1) = \mathrm{th}(t)\,, \tag{A.8}$$

$$\mathrm{cn}(t, 0) = \cos(t)\,, \qquad \mathrm{cn}(t, 1) = \mathrm{sech}(t)\,, \tag{A.9}$$

$$\mathrm{dn}(t, 0) = 1\,, \qquad \mathrm{dn}(t, 0) = \mathrm{sech}(t)\,. \tag{A.10}$$

---

[1] As every elliptic function the Jacobi functions have two periods: real and complex. Each of them is expressed via $K(q)$. For example, $\mathrm{sn}(t + 4K(q) + 2iK(q'), q) = \mathrm{sn}(t, q)$.

Likewise trigonometric and hyperbolic functions, the Jacobi elliptic functions obey similar identities:

$$\text{sn}^2(t,q) + \text{cn}^2(t,q) = 1 \,, \tag{A.11}$$

$$\text{dn}^2(t,q) + q^2\text{sn}^2(t,q) = 1 \,. \tag{A.12}$$

For $0 < q < 1$, Jacobi functions change smoothly from one asymptotic case to another. To visualize this let us consider Fig. A.1. When $q = 0$, the function
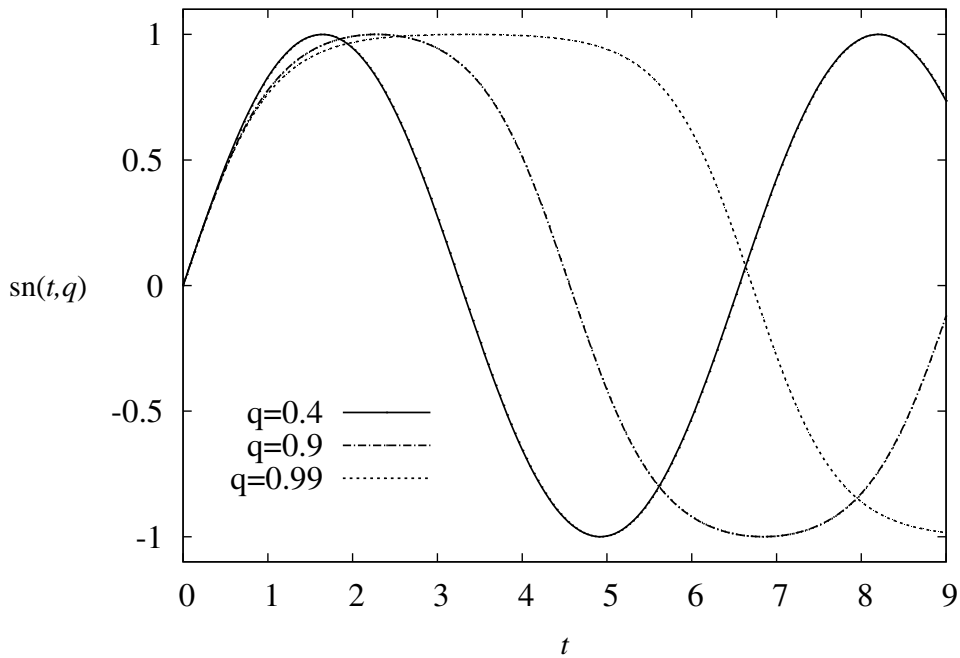

Figure A.1: Dependence of $\text{sn}(t,q)$ on t shown at different q.

is a trigonometric sine. With increasing q the period increases as well tending to infinity at $q \to 1$. In this case, $\text{sn}(t,q)$ approaches a hyperbolic tangent.

Appendix B

Ramo's theorem

Ramo's theorem, or the Shockley-Ramo theorem, was derived by Shockley (46) and Ramo (47) in the context of vacuum tube technique at the late thirties. For a modern interpretation and general discussion see (48).

The Shockley-Ramo theorem is a consequence of Green's reciprocal theorem which follows immediate from Green's second identity. Green's reciprocity is a static analogous of Lorentz's reciprocity. Because velocities of charged particles are low and magnetic properties are neglected, only the electrostatic case will be discussed.

Let $\phi_1(\vec{r})$ denote the electric potential resulting from a total charge density $\rho_1(\vec{r})$, and $\phi_2(\vec{r})$ denotes the electric potential resulting from a total charge density $\rho_2(\vec{r})$. If the charges are localized within the volume V, Green's reciprocal theorem states

$$\int_V \rho_1(\vec{r})\phi_2(\vec{r})dV = \int_V \rho_2(\vec{r})\phi_1(\vec{r})dV . \tag{B.1}$$

Consider a number of perfect conductors shown in Fig. B.1. ϕ_i^* is the potential of the ith electrode which is supplied by an infinitely narrow wire. Within the volume the charge is distributed with the charge density $\rho(\vec{r})$. The potential at every arbitrary point of the volume beyond the conductors consist of two contributions,

$$\phi(\vec{r}) = \sum_i \phi_i(\vec{r}) + \phi_\rho(\vec{r}) , \tag{B.2}$$

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where $\phi_i(\vec{r})$ is the potential which would be created by the conductor i in absence of other conductors and charges in the medium, $\rho(\vec{r}) = 0$, and $\phi_\rho(\vec{r})$ is the potential which would be created by the charge density $\rho(\vec{r})$ in the absence of all conductors. According to Eq. B.1 the charge generated on the electrode i is

$$Q_i = \sum_k C_{ik}(\phi_k^* - \phi_i^*) - \int_V \rho(\vec{r})\frac{\phi_i(\vec{r})}{\phi_i^*}dV \,, \tag{B.3}$$

where $C_{ik} = Q_k/\phi_i^*$, and Q_k is the charge on the electrode k if all other electrodes and the medium are absent. In our system the first term in Eq. B.2 is irrelevant
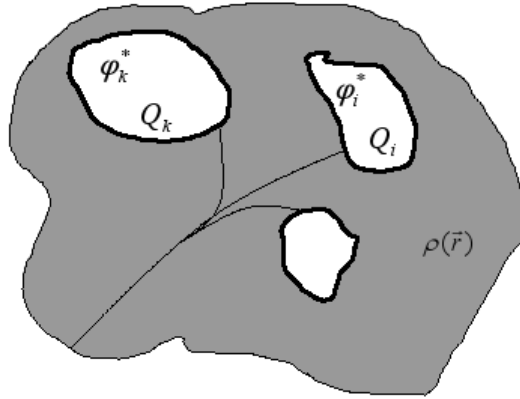
Figure B.1: System with four electrodes

because this charge on the electrodes is fixed by the applied voltage. Its contribution to the external current is the Dirac impulse which will be omitted. For a symmetric system of two parallel flat electrodes we get

$$Q = \frac{1}{2L} \int_{-L}^{L} \rho(x)x\,dx \,. \tag{B.4}$$

If the charge density depends on time, the external current is a time derivative of the charge generated on the electrodes,

$$J(t) \equiv \dot{Q}(t) = \frac{1}{2L} \int_{-L}^{L} \dot{\rho}(x,t)x\,dx \,. \tag{B.5}$$

Despite it is conventionally called the external current, strictly speaking it is a current density, that is a current that would be measured if the electrodes had a

unit area. Consequently, its dimension is $ampere \cdot meter^{-2}$. Taking $\rho(x,t)$ from the Poisson equation and integrating by parts Eq. B.5 one yields

$$J(t) = \epsilon \dot{E}(x = \pm L, t) - \frac{\epsilon}{2L}\dot{v}(t) \, . \qquad (B.6)$$

If the applied voltage is constant, $v(t) = v$, then

$$J(t) = \epsilon \dot{E}(x = \pm L, t) \, . \qquad (B.7)$$

Using the definition of the flux and the PNP equations, Eq. B.7 can be written as

$$J(t) = \frac{ze}{2L} \int_{-L}^{L} (F_+(x,t) - F_-(x,t))dx \, , \qquad (B.8)$$

that is the flux of the charge inside the cell is related to that outside the cell. The charge redistribution inside the cell is performed by the movement of ions, whereas the charge flux outside the cell is made by electrons. At the initial moment the ion concentrations and the electric field are constant, $C_\pm(x, t = 0) = \eta$, $E(x, t = 0) = \frac{v}{2L}$, which makes the integration of Eq. B.8 trivial,

$$J(t = 0) = \frac{vz^2 e^2 \mu \eta}{L} = \frac{v}{2L} D\epsilon\kappa^2 \, . \qquad (B.9)$$

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Eidesstattliche Erklärung

Hiermit erkläre ich, dass meine Dissertation selbständig verfasst wurde und nur die angegebenen Hilfsmittel und Quellen benutzt wurden. Die Dissertation wurde an keiner anderen Universität oder Hochschule eingereicht.

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List of Publications

- A. Ananev, V. Bogdanov, A. Cereyon, B. Champagnon, A. Golovnev L. Maksimov, S. Nemilov, S. Smerdin and V. Solovyev. Low scattering phosphate glasses // Abstracts of 8th International Otto Schott Colloquium. July 23-27 2006.

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