Non-linear effects in electrolytes at large applied voltage

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Abstract

The steady state of ions diffusion in polymer electrolytes at arbitrary applied voltage is analyzed in the framework of the Nernst-Planck-Poisson equation (NPP). The exact solution of the set of equations is found without the assumption of low ions concentration. The solution is independent of the kinetic properties of the system. At constant voltage there is a master curve for concentration in terms of the initial concentration. Enhancing the voltage causes an increase of the ion concentration gradient and consequently the applicability of the NPP is violated for high voltages. The analytical finding is estimated by using experimental data from recent measurements (P. Kohn et al Phys. Rev. Left. 99, 086104 (2007)). As the result we find an upper bound for the validity of the NPP. Above this voltage higher order gradient terms become relevant.

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I. INTRODUCTION

Polymer electrolytes characterized as amorphous structure are widely used for solid state ionics devices such as lithium ion batteries [1], fuel cells, electrochemical displays etc. The material is a composite one consisting of dissociated ions which are dissolved in a polymer or glassy matrix. Very recently the motions of proteins in densely grafted layers of polyelectrolyte brushed has been studied [2] or the dynamics of polyelectrolyte transport through a protein channel as a function of applied voltage [3]. The understanding of the ionic transport mechanism in polymer materials is of basic interest and has attracted attentions over several decades, for a recent review on the history, the applications of ionic transport and structure as well as dynamics see [4]. A number of different theoretical methods has been proposed for polyelectrolyte systems [5, 6, 7]. The activities concerning the theoretical approach for the ionic transport behavior had been reviewed in [8].

Our analysis is based on the Nernst-Planck equations supplemented by the static Poisson equation. These set of equations, abbreviated as NPP, are derived for a low charge carrier density. The diffuse charge dynamics is characterized by a linear gradient term for the ionic concentration. In addition to the diffusive charge dynamics the transport process is driven by an external field $\vec{E}$. For low voltages the linearized NPP can be solved by Laplace transforms [8], whereas for high voltages numerical solutions had been obtained in [8]. As estimated in [8] the validity of the linear approximation should be guaranteed up to 70 mV. A detailed analysis of the non-linear regime is still lacking. Otherwise, the mobility of ions has been determined recently by transient current measurements at high voltages up to the order of 300 V [9]. The problem arisen is whether the NPP with a linear concentration gradient are also valid for such high fields. Intuitively one expects that high voltages should give rise to higher order concentration gradients of the mobile ions. Otherwise, very low voltages cause only low gradients even in systems with a high concentration of ions. Thus, the limitation of the NPP is related to both high concentration of charge carriers as well high applied voltages. However our analysis offers that a high initial concentration should be irrelevant. Whereas all previous papers are mainly devoted to a numerical solution of the NPP or some modifications of those equations such as by including steric effects [10], the present paper is directly addressed to the NPP, in order to check the ability of the equations at high voltages. Despite the model is used widely it seems to be difficult to
estimate the condition under which the NPP are valid. So far, the NPP has not been solved exactly but instead of that the solution had been discussed in a linear regime where the long time behavior was found. Here we present the exact steady state solution of the full NPP. Especially we demonstrate that the solution within the linear regime may be spread up to 70 mV approximately. Otherwise the experimental measurement of the mobility is fulfilled in between 70 and 300 V [9]. Obviously the NPP is not appropriate to clarify the observations made in [9]. Apparently, a high voltages requires higher order diffusive terms.

II. THE MODEL AND THE SOLUTION

Let us consider a solution of charged particles embedded in polymer electrolyte at temperature above the glass-transition temperature of the polymer. We study completely dissociated electrolyte placed in between infinite flat electrodes at coordinates \( x = -L \) and \( x = L \). Therefore the system offers a simple one-dimensional geometry. Concentrations of the charged ions are described by continuum fields \( C_\pm(x, t) \). The charged ions are subjected to an electric field \( \vec{E} = -\nabla \phi \). The scalar potential \( \phi \) obeys the Poisson equation

\[
- \varepsilon \frac{\partial^2 \phi}{\partial x^2} = z e (C_+ - C_-) ,
\]

where \( \varepsilon \) is the dielectric permeability, \( e \) is the elementary charge and \( z e \) is the charge of the ion. Because the charge is conserved the time derivative of \( C_\pm \) is given by the spatial derivative of the corresponding ionic fluxes denoted by \( F_\pm \). Generally this flux is composed of two terms, namely the diffusive part originated by a small concentration gradient and the electric field term. This field is assumed to couple linearly to the concentration field. The set of evolution equations reads

\[
\frac{\partial C_+}{\partial t} = -\frac{\partial}{\partial x} (F_+) = -\frac{\partial}{\partial x} \left( -D \frac{\partial C_+}{\partial x} - \mu z e C_+ \frac{\partial \phi}{\partial x} \right) ,
\]

\[
\frac{\partial C_-}{\partial t} = -\frac{\partial}{\partial x} (F_-) = -\frac{\partial}{\partial x} \left( -D \frac{\partial C_-}{\partial x} + \mu z e C_- \frac{\partial \phi}{\partial x} \right) .
\]

Here \( D \) is the diffusivity and \( \mu \) denotes the mobility, for simplicity we have assumed \( D_+ = D_- = D \). Further it is supposed that the Einstein relation \( D = \mu kT \) is fulfilled. Likewise it is supposed that the Faraday currents can be neglected. The boundary conditions imposed are the disappearance of fluxes \( F_\pm = 0 \) at \( x = \pm L \). This set of equations combined with Eq. (1) are called Nernst-Planck-Poisson equations (NPP). Essentially is that Fick’s law of diffusion
is fulfilled, i.e., the ionic flux is proportional to the first derivative of concentration. At high voltage, the gradient of concentration becomes more pronounced and the consecutive equations should be changed due to higher order gradient terms. To estimate the validity of the NPP for high voltages let us consider the steady state. This state is characterized by constant ionic fluxes where the constant is zero due to the boundary conditions. For that case we found an exact solution demonstrated further. The difference of the charge carriers due Eqs. (2) can be expressed by the potential of the electric field according to Eq. (1). It results

\[ \frac{D\varepsilon}{z\varepsilon} \frac{\partial^3 \phi(x)}{\partial x^3} - \mu z e \frac{\partial \phi(x)}{\partial x} C(x) = 0 \quad \text{with} \quad C(x) = C_+(x) + C_-(x). \]  

(3)

Using Eqs. (2) and (1) the sum of the concentration satisfies

\[ -D C(x) + \frac{\mu e}{2} \left( \frac{\partial \phi(x)}{\partial x} \right)^2 = r, \]  

(4)

where \( r \) is an integration constant. Both Eqs. (3) and (4) can be combined to a single equation for the electric potential

\[ \frac{D\varepsilon}{z\varepsilon} \frac{\partial^3 \phi}{\partial x^3} - \frac{\mu z e}{D} \frac{\partial \phi}{\partial x} \left[ \frac{\mu e}{2} \left( \frac{\partial \phi}{\partial x} \right)^2 - r \right] = 0. \]  

(5)

Then the solution of the last equation can be applied to find the charge concentration via

\[ \frac{\partial \ln C_\pm(x)}{\partial x} = \mp \frac{\mu ze}{D} \frac{\partial \phi(x)}{\partial x}. \]  

(6)

Actually the solution of Eq. (5) is given in terms of Jacobian elliptic functions [12]. To that aim let us substitute \( y(x) = \phi'(x) \) in Eq. (5). After some formal steps we end up with an expression for the electric field \( E(x) \)

\[ E(x) = -\frac{d\phi(x)}{dx} = -\frac{2D}{\mu ze} \cdot q \cdot \beta \cdot \text{sn}(\beta x - x_0, q). \]  

(7)

Using Eq. (6) and the properties of the Jacobian functions [12] we get the stationary concentration profiles of the charge carriers

\[ C_\pm(x) = -\frac{D\varepsilon}{\mu z^2 e^2} \cdot q \cdot \beta^2 \cdot \left[ \text{dn}(\beta x - x_0, q) \pm q \cdot \text{cn}(\beta x - x_0, q) \right]^2. \]  

(8)

The quantities \( \text{sn}, \text{cn} \) and \( \text{dn} \) are the Jacobian elliptical functions, which are characterized by two parameters denoted as \( \beta \) and \( q \). Due to the symmetry property \( E(x) = E(-x) \) the integration constant \( x_0 \) should be equal to quarter of the period of Jacobian sinus \( x_0 = K(q), \)
where \( K(q) \) is the complete elliptic integral of the first kind \[12\]. The parameters \( \beta \) and \( q \) are determined by the following conditions:

\[
\int_{-L}^{L} C_{\pm}(x) \cdot dx = 2L \eta \\
E(\pm L) = -\frac{V}{2L}.
\] (9)

The first condition determines the total concentration \( \eta \) which is given initially. Thus, \( \eta \) is the initial particle concentration before the voltage were applied. The second condition fixes the applied voltage \( V \). After performing the integrating of the first equation in Eq. (9) and reorganization of the the second one we have

\[
E(\beta L, q) - q^2 sn(\beta L, q)cd(\beta L, q) = -\frac{\beta L}{2} (1 - q^2) = -\frac{L \eta}{2\beta q} \mu z^2 e^2 \\
cd(\beta L, q) = -\frac{V \mu z e}{L \beta q D}.
\] (10)

Here \( E(\beta L, q) \) stands for the incomplete elliptic integral of the second kind and we have introduced

\[
\text{cd}(\beta x, q) \equiv \frac{cn(\beta x, q)}{dn(\beta x, q)}.
\]

Eqs. (7), (8) together with Eqs. (10) provide the complete solution of the stationary problem of the NPP. However the conditions in Eqs.(10) for the parameters \( \beta \) and \( q \) are too complicated to get analytical results. To proceed one can use the fact that in the first equation the first term is slowly changing almost linear function, whereas the second term can be roughly approximated by just \( q \). This approximation leads to an parameter area which enables us to get reasonable values for the parameters.

III. RESULTS

All calculations were performed for a real system described in \[9\]. The experiments had been carried in thin films with \( L = 5 \cdot 10^{-5} \text{ m} \). The initial concentration \( \eta \) is varied from \( 1 \cdot 10^{21} \) to \( 1.3 \cdot 10^{24} \text{ m}^{-3} \), whereas the applied voltage \( V \) was changed from \( 1 \cdot 10^{-3} \) to \( 2.6 \cdot 10^{-1} \text{ V} \). In case the parameter \( q \) of the Jacobian elliptic function is restricted to the internal \( 0 \leq q \leq 1 \), the functions are real. Inserting the experimental data obtained in \[9\] in our solution we find \( q \gg 1 \) and \( \beta \ll 1 \). In particular it results \( q \simeq 10^9 \) and \( \beta \simeq 10^{-5} \). For such values of the parameters \( q \) and \( \beta \) the Jacobian functions become complex functions. However it appeared
that $\Im E << \Re E$ and $\Im C_\pm << \Re C_\pm$. We estimate that the imaginary part is about 7 or 8 orders of magnitude smaller than the real part. Despite of the complexity of the Jacobian functions, the solution found in the paper has a physical sense.

A. Results for constant voltage

Calculations at constant voltage $V$, defined in Eq. (9), offer that the parameter $q$ changes proportional to the initial concentration $\eta$, whereas the other parameter $\beta$ behaves proportional to $\eta^{-1}$, i.e. we can set $\beta = \tilde{\beta} / \eta$ and $q = \tilde{q} \eta$, where the tilde means a value at some definite concentration. Notice that for different applied voltage $V$ the parameters $\tilde{q}$ and $\tilde{\beta}$ are also different. As one can see from Eq. (9), the integral $\int_{-L}^{L} \frac{C(x)}{\eta} \cdot dx$ is independent on the fixed initial concentration $\eta$ indicating the existence of a master curve for $\frac{C(x)}{\eta}$. Our calculation confirms the presumption. In Fig. 1 the spatial charge distribution is shown according to Eq. (8). The different curves depicted in Fig. 1 correspond to different values for $\eta$. In Fig. 2 one observes that all these data for the concentration in terms of $\eta$ lay on a single master curve. Further discussions concerning scaling properties of the curves one can in [11]. The profile of the electric field is independent of the concentration which is demonstrated in Fig. 3, with other words the efficiency of screening is independent of $\eta$. This observation would suggest the applicability of NPP is guaranteed also for a high charge carrier concentration. According to Eq. (6) a constant electric field suggest an increasing of the concentration gradient proportional to the concentration itself. Therefore high gradients could lead to an inconsistency of NPP. Another feature mentioned is the so called charge inversion, i.e. interfacial charges attract counterions in excess of their own nominal charge. This effect were found both in theoretical [13] and experimental [14, 15] works; for an overview and discussion see [16]. But, as one can see from Fig. 2 in the framework of steady state solution of NPP this effect is absent.

B. Results for constant concentration

For different voltages but constant concentration there exists no master curve as it is shown in Fig. 4. For increasing applied voltage $V$ we find oscillations of the electric field $E(x)$. From here we conclude that the NPP equations are not longer adequate in describing the
physical situation in mind. Such oscillations appear when the period of the Jacobian sinus is sufficiently small. Analytically the criterion for the absence of oscillations is the condition $\beta L \leq K(q)$. In case of $\beta L = K(q)$ the half period of the Jacobian sinus fits exactly the capacitor between $-L \leq x \leq L$. To be more specific we have checked that for an arbitrary but fixed initial concentration $\eta$ the inequality $\beta L < K(q)$ is only satisfied in case the applied voltages fulfills $V \leq 0.22$ V. Because for $V \geq 0.23$ V the inequality is violated we conclude that there exist a kind of critical applied voltage in between $0.22 \leq V \leq 0.23$ V. If any the dependence of that result on the initial concentration is weak. But such a weak dependence should exist due to Eq. (9), which signalized that the concentration gradient is proportional to both the applied voltage $V$ and the initial concentration $\eta$.

The steady state solution of NPP equations is universal and nearly independent on specific system properties. Thus the kinetic properties should depend on the diffusion coefficient $D$. But in the expression for the steady state according to Eq. (8) there appears only the ratio $D/\mu$. If Einstein relation is fulfilled the solution is independent on the kinetic properties of the system but depends only on the temperature. In other words, different systems with the same $ze$ tend to the same steady state solution, which is however reached on different ways.

If the voltage $V$ is sufficiently high to alter the transport properties of polymers (mechanisms for a change are discussed in [17]) but not high enough to alter its dielectric permeability, the steady state will be unchanged.

IV. CONCLUSION

By getting the steady state we found a limit of the applicability of the Poisson-Nernst-Planck equations for both high voltages and high concentrations. Using the experimental data from [9] we could estimate that above $V = 0.22$ V the NPP yield unphysical results characterized by the appearance of unphysical oscillation of the solutions. Notice that the validity of the linear approximation is restricted to an applied voltage $V \leq 0.07$ V [8]. The limit of the applicability of NPP due to a high concentration of ions is not very sharp. Unlike a behavior at high voltage, in this case NPP do not contain explicit restrictions itself. Existents of the master curve for normalized concentration is an indication for that fact. The inclusion of higher order gradient terms leads a more complicated model. Otherwise the assumption that the flux is proportional to a linear gradi-
ent term is a very promising assumption which should be valid for the majority of situations.

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FIG. 1: Concentration profile $C_+(x)$ in the capacitor. Different curves correspond to different initial concentrations $\eta$. The applied voltage $V$ is assumed to be $5 \cdot 10^{-2}$ V.
FIG. 2: Concentration profile $\frac{C_+(x)}{\eta}$ in terms of the initial concentration $\eta$ in the capacitor. The applied voltage is $V = 5 \cdot 10^{-2}$ V.
FIG. 3: Electric field profile $E(x)$ within the capacitor. The profile is independent on the initial concentration $\eta$. The voltage is assumed to be $5 \cdot 10^{-2}$V.
FIG. 4: Concentration profile $C_+(x)$ versus coordinate in the capacitor. Different curves correspond to different applied voltages $V$. The initial concentration $\eta$ is $5 \cdot 10^{23}$. 