QUARTERLY OF APPLIED MATHEMATICS
VOLUME LVII, NUMBER 4
DECEMBER 1999, PAGES 637-659

ELECTRODIFFUSIONAL FREE BOUNDARY PROBLEM, IN A BIPOLAR MEMBRANE (SEMICONDUCTOR DIODE), AT A REVERSE BIAS FOR CONSTANT CURRENT

By

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Abstract. A singular perturbation problem, modeling one-dimensional time-dependent electrodiffusion of ions (holes and electrons) in a bipolar membrane (semi-conductor diode) at a reverse bias is analyzed for galvanostatic (fixed electric current) conditions. It is shown that, as the perturbation parameter tends to zero, the solution of the perturbed problem tends to the solution of a limiting problem which is, depending on the input data, either a conventional bipolar electrodiffusion problem or a particular electrodiffusional time-dependent free boundary problem. In both cases, the properties of the limiting solution are analyzed, along with those of the respective boundary and transition layer solutions.

0. Introduction. In our recent paper [1] we analyzed the electrodiffusional free boundary problem that arose asymptotically in the singularly perturbed model of electrodialysis for a vanishing perturbation parameter. This model concerned the passage of a specified direct electric current through a layer of univalent electrolyte adjacent to the wall (cathode, cation exchange membrane) selectively permeable to positive ions (cations) only. The simplest version of the governing equations was

$$t > 0\colon p_t^\varepsilon = (p_x^\varepsilon + p^\varepsilon \phi_x^\varepsilon)_x \quad \forall x \in (0,1), \tag{0.1}$$

$$t > 0\colon n_t^\varepsilon = (n_x^\varepsilon - n^\varepsilon \phi_x^\varepsilon)_x \quad \forall x \in (0,1), \tag{0.2}$$

$$t > 0\colon \varepsilon\phi_{xx}^\varepsilon = n^\varepsilon - p^\varepsilon \quad \forall x \in (0,1). \tag{0.3}$$

Here $p^\varepsilon(x,t)$, $n^\varepsilon(x,t)$, $\phi^\varepsilon(x,t)$ are, respectively, the cation and anion (negative ions) concentrations and the electric potential. Equations (0.1) and (0.2) are the Nernst-Planck

Received November 4, 1997.
1991 *Mathematics Subject Classification.* Primary 35M10, 35G30, 35J25.

equations for electrodiffusion of the cations and anions, respectively. These equations merely express conservation of each ionic species, with the expressions in parentheses standing for the respective ionic flux (with a minus sign). The first term in these expressions stands for the ordinary diffusional flux component, whereas the second stands for the migration in the electric field. Equation (0.3) is the Poisson equation, with $p^\varepsilon - n^\varepsilon$ being the space charge density. The small parameter ε in (0.3), the squared dimensionless Debye length, lies in the range $10^{-12} < \varepsilon < 10^{-4}$ for realistic macroscopic systems. The source and implications of smallness of ε may be verbalized as follows (for a detailed discussion of these issues the reader is referred to Ref. [2]). One gram-equivalent of ionic species carries a very large electric charge. This is why any appreciable deviation from the local concentration balance of the ionic species on a macroscopic scale should require a presence of immense electric fields acting on the same scale. Absence of such fields at and near the equilibrium implies that for quasi-equilibrium conditions any appreciable space charge (comparable to the local ionic concentration) must be confined to boundary layers (double electric layers in physico-chemical terminology) of the order of thickness $\sqrt{\varepsilon}$. This is not necessarily the case for strongly nonequilibrium conditions, considered in [1] and in the present paper.

Combining Eqs. (0.1)–(0.3) yields the continuity equation for the electric current density whose integration implies

$$\varepsilon\phi^\varepsilon_{xt} + p^\varepsilon_x - n^\varepsilon_x + (p^\varepsilon + n^\varepsilon)\phi^\varepsilon_x = -I(t). \tag{0.4}$$

Here $I(t)$ is the electric current density. The first term on the left-hand side of (0.4) stands for the displacement current, whereas the second and the third correspond to the diffusion and conduction current components, respectively. For galvanostatic (fixed current) conditions, considered in Ref. [1],

$$I(t) = I = \text{const} \tag{0.5}$$

where I is specified by the boundary conditions.

The main result of Ref. [1] consisted in proving that for $\varepsilon \to 0$, $I > I^{\text{lim}} = 4$, the solution of the perturbed problem (0.1)–(0.5) with the respective boundary-initial conditions tends to that of the following free boundary problem:

$$c_t = c_{xx}, \quad \forall x \in (0, R(t)),\ R(t) \in (0,1), \tag{0.6}$$

$$c \equiv 0, \quad \forall x \in (R(t), 1), \tag{0.7}$$

$$c(R(t), t) = 0, \tag{0.8}$$

$$c_x(R(t), t) = -\frac{I}{2}. \tag{0.9}$$

Here

$$c(x,t) \stackrel{\text{def}}{=} \lim_{\varepsilon\to 0} p^\varepsilon(x,t) = \lim_{\varepsilon\to 0} n^\varepsilon(x,t). \tag{0.10}$$

In addition to this result, the limiting problem for $I < I^{\text{lim}}$ has been analyzed, along with the asymptotics for the boundary layers solutions (for both $I < I^{\text{lim}}$ and $I > I^{\text{lim}}$) and that for the "empty" zone $R(t) < x < 1$, developing for $I > I^{\text{lim}}$.

The outlined treatment thus addressed one of the few basic functional elements of membrane transport—passage of ions from the electrolyte solution into a charge-selective object (ion-exchange membrane, metal electrode). Another prototypical situation concerns the transfer of ions between different objects of this type, in particular with alternating charge selectivity. This is namely the case in a bipolar membrane—a sandwich formed by an anion exchange membrane (A) adjacent to a cation exchange membrane (B)—the object of our study in this paper. Bipolar membranes are used, in particular, for acid-base generation. Acid-base generation occurs as a result of water electrolysis under the action of strong nonequilibrium electric fields that develop around the A-B junction upon the passage of a specified direct electric current from A to B (see Refs. [3]–[5]). This electric field and the pertaining development of the space charge fronts, irrespectively of the related electrolysis, is the issue that we are concerned with here. The entire setup we are about to study is mathematically identical to that for a reversely biased semiconductor diode operated at a constant current. The simplest relevant time-dependent model problem treated here reads

$$t > 0\colon p_t^\varepsilon = (p_x^\varepsilon + p^\varepsilon \phi_x^\varepsilon)_x \quad \forall x \in (-1, 1), \tag{0.11}$$

$$t > 0\colon n_t^\varepsilon = \alpha(n_x^\varepsilon - n^\varepsilon \phi_x^\varepsilon)_x \quad \forall x \in (-1, 1), \tag{0.12}$$

$$t > 0\colon \varepsilon\phi_{xx}^\varepsilon = N(x) + n^\varepsilon - p^\varepsilon, \quad N(x) = \begin{cases} N, & 0 < x < 1 \\ -N, & -1 < x < 0 \end{cases} \quad \forall x \in (-1, 1), \tag{0.13}$$

$$x = -1\colon p^\varepsilon + N = n^\varepsilon = n_0, \tag{0.14}$$

$$x = 1\colon p^\varepsilon = n^\varepsilon + N = p_0, \tag{0.15}$$

$$\phi^\varepsilon(-1, t) = 0, \tag{0.16}$$

$$x = 1\colon p_x^\varepsilon - \alpha n_x^\varepsilon + (p^\varepsilon + \alpha n^\varepsilon)\phi_x^\varepsilon + \varepsilon\phi_{xt}^\varepsilon = -I, \tag{0.17}$$

$$t = 0\colon p^\varepsilon(x, 0) = p_0^\varepsilon(x) > 0, \quad n^\varepsilon = n_0^\varepsilon(x) > 0. \tag{0.18}$$

Here $p^\varepsilon(x,t), n^\varepsilon(x,t)$ are the cation (hole) and anion (electron) concentrations, respectively (in parentheses we include the respective semiconductor terms); $\phi^\varepsilon(x,t)$ is the electric potential; ε is the squared dimensionless Debye length; $N(x)$ is the fixed charge density of the bipolar membrane (doping function); I in (0.17) is the specified current density in the system; p_0, n_0 in (0.14), (0.15) are the fixed concentrations of the respective species at the outer edges of the bipolar membrane, determined by the external solution concentrations, assumed symmetric for simplicity along with the fixed charge in the membrane and equal ionic mobilities. Equations (0.11)–(0.13) are again the standard Nernst-Planck equations describing electrodiffusion of ions and the related electric field. The boundary condition (0.16) normalizes the electric potential by fixing it at one point ($x = -1$) at an arbitrary (zero) value.

The nonvanishing fixed charge density, changing sign, is the main feature distinguishing the present setup from electrodialysis (see Ref. [1]), where the electric current flows from a region with a zero fixed charge into an ideally permselective membrane. This structural difference between the two setups yields some considerable differences of both physical and mathematical nature in the response to the passage of a direct electric current. Below we schematically outline some of these differences to be analyzed in the bulk of this paper.

In Fig. 1 (a)–(c) we present a sketch of the steady-state ionic concentration profiles in a bipolar membrane, for a small ε, at three consecutive values of the current I. For $I = 0$ (a), the essentially constant concentrations in the quasi-electroneutral regions $-1 < x < O(\varepsilon^{1/2}), O(\varepsilon^{1/2}) < x < 1$ are connected through a transition "double electric" ("space charge") layer of thickness $O(\varepsilon^{1/2})$. For $0 < I < I^{\text{lim}} = 2p_0(\frac{p_0}{N} - 1)$, ionic concentration gradients are formed in the electroneutral layers, although the very division of the space into electroneutral bulk and a transition layer remains valid. So far the general picture is qualitatively identical to that in electrodialysis. For $I = I^{\text{lim}}$ (b), the interface concentrations of the minority carriers (anions on the left and cations on the right of the interface) approach zero whereas that of the majority carriers approach the respective finite fixed charge concentration. This is different from the respective situation in electrodialysis where both ionic concentrations nearly vanish at the interface. Thereafter, for $I > I^{\text{lim}}$ (c), a macroscopic space charge zone, essentially void of ions, appears around the interface. The size of this zone increases with growth of I above I^{lim}. At the outer edges of this space charge zone the majority ions concentration varies abruptly from a low value to almost N within a transition layer of width $O(\varepsilon^{\frac{1}{2}})$. This discontinuity of the majority carrier concentration at the boundary of the space charge zone is another difference between the bipolar membrane and electrodialysis setups. Still another difference between electrodialysis and bipolar setups lies in the distribution of the electric fields, unreflected in the above sketches. In electrodialysis the electric field increases without bound as $\varepsilon \to 0$ for $I \geq I^{\text{lim}}$ already at the outer edge of the electroneutral layer ($x = R(t) - 0$), whereas in the bipolar case it does so only inside the space charge zone.

In an evolutionary problem, with the space charge zone initially absent, it is expected to appear at some moment and thereafter evolve in time. In the limit $\varepsilon \to 0$, with the shrinking width of the transition layers, free boundaries corresponding to the edges of the space charge zone are expected to appear. The subject of the present paper is the analysis of asymptotic occurrence of the respective free boundary problem when $\varepsilon \to 0$, including the structure of the space charge zone and the transition layers. In particular, it is proven for the simplest "symmetric" formulation (0.11)–(0.18) that for $I > I^{\text{lim}}$ and $\varepsilon \to 0$ the solution tends to that of the following free boundary problem:

$$c_t = \left(c_x - \frac{NI}{c}\right)_x \quad \text{and } c(x,t) > N \quad \forall x > R(t), \qquad c(x,t) \equiv 0 \quad \forall x < R(t), \tag{0.19}$$

$$c(R(t) + 0, t) = N, \tag{0.20}$$

$$N\dot{R}(t) = I - c_x(R(t) + 0, t). \tag{0.21}$$

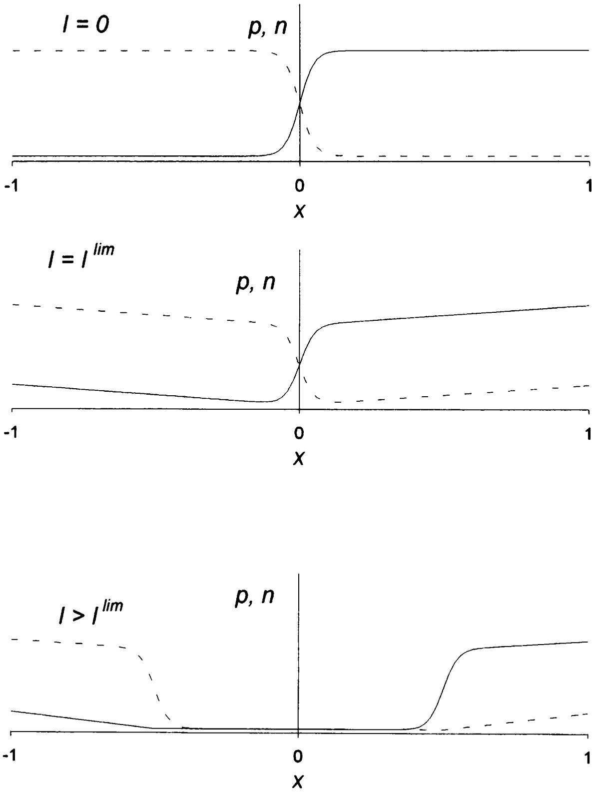

FIG. 1. Sketch of charge carriers concentrations (positive—continuous line, negative—dashed line) for different values of current.

Here $R(t)$ is the position of the free boundary ("positive" edge of the space charge zone, extending, due to symmetry, upon the segment $-R(t) < x < R(t)$) and

$$c \stackrel{\text{def}}{=} \lim_{\varepsilon \to 0}(p^\varepsilon + n^\varepsilon). \tag{0.22}$$

Asymptotic occurrence of the free boundary problems for the space charge around the p-n transition in a semiconductor diode at a reverse bias has been studied on several occasions [6]–[9], for potentiostatic (fixed voltage) steady-state conditions. Brezzi with coauthors ([6], [7]) were first to pinpoint this problem and study it for a one-dimensional steady-state setup. This work was followed by that of Caffarelli and Friedman ([8]) who analyzed a related simplified steady-state model problem in R^N. Schmeiser in [9] studied the full steady-state problem in R^2 with realistic boundary conditions by formal asymptotic methods. The distinctive feature of the potentiostatic mode of operation as opposed to the galvanostatic (fixed current) one, studied here, is that in the former the position of the free boundary does not evolve in time and depends solely on the magnitude of the applied voltage (of order $O(\varepsilon^{-1})$).

This paper is organized as follows. In Sec. 1 we obtain estimates on the solution of the problem (0.11)–(0.18), uniform in ε, and employ these estimates to prove the convergence of the solution of this problem when $\varepsilon \to 0$ to that of the respective limiting problem, whose fine structure is analyzed in Sec. 2. This includes the proof of smoothness of the free boundary, uniformly in time; convergence of the solution of the time-dependent problem to that of the steady-state one; and monotonicity of the free boundary for a positive initial flux. In the final Sec. 3 we analyze the solution of the perturbed problem in the transition layer and in the space charge zone. In particular, we find the characteristics of the solution that remain continuous and smooth upon the limiting transition $\varepsilon \to 0$, along with the leading-order corrections to the limiting solutions in the space charge zone, and transition and boundary layer solutions.

1. Uniform estimates on the solution and the limiting transition $\varepsilon \to 0$. In this section we obtain estimates, uniform in ε, on the solution of the model problem (0.11)–(0.18) and study the asymptotic solution in the limit $\varepsilon \to 0$.

First of all, let us define flux functions J_p^ε, J_n^ε as follows:

$$J_p^\varepsilon \stackrel{\text{def}}{=} p_x^\varepsilon - p^\varepsilon \phi_x^\varepsilon + \frac{I}{2}, \qquad J_n^\varepsilon \stackrel{\text{def}}{=} \alpha(n_x^\varepsilon - n^\varepsilon \phi_x^\varepsilon) - \frac{I}{2}. \tag{1.1a,b}$$

Next, let us first formulate the following two existence and uniqueness theorems. The proofs of these theorems are rather technical and may be obtained by a straightforward modification of the respective proofs of Theorems 1 and 2 of Ref. [1].

THEOREM 1 (Existence). Let $n_0^\varepsilon, p_0^\varepsilon$ and $J_n^\varepsilon(x,0)$, $J_p^\varepsilon(x,0)$ belong to the spaces

$$C^{1+\gamma}[-1,1] \cap C^{2+\gamma}[-1,0] \cap C^{2+\gamma}[0,1], \quad C^{2+\gamma}[-1,1], \quad 0<\gamma<1,$$

respectively, such that the following consistence conditions hold:

$$p_0^\varepsilon(-1) + N = n_0^\varepsilon(-1) = n_1, \quad p_0^\varepsilon(1) = n_0^\varepsilon(1) + N = p_1, \quad J_{nx}^\varepsilon(\pm 1, 0) = J_{px}^\varepsilon(\pm 1, 0) = 0,$$

$$n_{0x}^\varepsilon|_{x=\pm 1} \neq 0, \qquad p_{0x}^\varepsilon|_{x=\pm 1} \neq 0,$$

$$\frac{p_{0xx}^\varepsilon - p_0^\varepsilon(n_0^\varepsilon + N(x) - p_0^\varepsilon)}{p_{0x}^\varepsilon}\Big|_{x=-1} = -\frac{n_{0xx}^\varepsilon + n_0^\varepsilon(n_0^\varepsilon + N(x) - p_0^\varepsilon)}{n_{0x}^\varepsilon}\Big|_{x=-1},$$
$$\frac{p_{0xx}^\varepsilon - p_0^\varepsilon(n_0^\varepsilon + N(x) - p_0^\varepsilon)}{p_{0x}^\varepsilon}\Big|_{x=1} = -\frac{n_{0xx}^\varepsilon + n_0^\varepsilon(n_0^\varepsilon + N(x) - p_0^\varepsilon)}{n_{0x}^\varepsilon}\Big|_{x=1}.$$

Then, there exists a solution of the model problem (0.11)–(0.18) $n^\varepsilon, p^\varepsilon, \phi^\varepsilon$ with $p^\varepsilon, n^\varepsilon$, and ϕ^ε belonging to the functional space $C^{1+\gamma}([-1,1]*[0,T])$ and J_n^ε, J_p^ε to the functional space $C^{2+\gamma,1+\gamma/2}([-1,1]*[0,T])$ for every $T>0$.

THEOREM 2 (Uniqueness). The solution of the problem (0.11)–(0.18) is unique in the spaces mentioned in Theorem 1.

Furthermore, let us establish uniform a priori estimates on the solutions $p^\varepsilon, n^\varepsilon, \phi^\varepsilon$.

LEMMA 1. Let the conditions of Theorem 1 hold together with the following additional ones:

(i) functions $p_0^\varepsilon(x), n_0^\varepsilon(x)$ are bounded uniformly in ε;

(ii) functions $J_n^\varepsilon(x,0)$, $J_p^\varepsilon(x,0)$ are bounded uniformly in ε.

Then the functions $p^\varepsilon(x,t), n^\varepsilon(x,t), J_n^\varepsilon(x,t), J_p^\varepsilon(x,t)$ are bounded uniformly in ε $\forall x \in [-1,1], t>0$.

Proof of Lemma 1. First, let us establish a uniform maximum principle for the solutions $p^\varepsilon, n^\varepsilon$. In order to do this we rewrite the equations (0.11), (0.12) in the following form:

$$p_t^\varepsilon = p_{xx}^\varepsilon + \phi_x^\varepsilon p_x^\varepsilon + p^\varepsilon \frac{N(x) + n^\varepsilon - p^\varepsilon}{\varepsilon}, \tag{1.2}$$

$$n_t^\varepsilon = \alpha n_{xx}^\varepsilon - \alpha\phi_x^\varepsilon n_x^\varepsilon - \alpha n^\varepsilon \frac{N(x) + n^\varepsilon - p^\varepsilon}{\varepsilon}. \tag{1.3}$$

Taking into account the boundary conditions (0.14), (0.15) and using the maximum principle for Eqs. (1.2), (1.3), one can prove that

$$0 < p^\varepsilon, n^\varepsilon \quad \forall (x,t) \in [0,1] * [0,T]. \tag{1.4}$$

Therefore, in order to show that the solutions are bounded uniformly in ε we must find the upper estimates on the functions $n^\varepsilon, p^\varepsilon$. The main difficulty here is the existence of the boundary layer at the point $x = 0$ (because of discontinuity of $N(x)$) causing inability to expect boundedness of the derivatives $p_x^\varepsilon, n_x^\varepsilon$ or even their belonging to the L^2 space globally in $(-1,1) * (0,T)$. On the other hand, we can prove that the flux functions $J_p^\varepsilon, J_n^\varepsilon$ are bounded in the whole of the domain $[-1,1] * [0,T]$ uniformly in ε. In order to do this, let us write down the boundary value problem for functions $J_n^\varepsilon, J_p^\varepsilon$ as

$$J_{pt}^\varepsilon = J_{pxx}^\varepsilon + \phi_x^\varepsilon J_{px}^\varepsilon + p^\varepsilon \frac{(J_n^\varepsilon - J_p^\varepsilon)}{\varepsilon}, \tag{1.5}$$

$$J_{nt}^\varepsilon = \alpha(J_{nxx}^\varepsilon - \phi_x^\varepsilon J_{nx}^\varepsilon + n^\varepsilon \frac{(J_p^\varepsilon - J_n^\varepsilon)}{\varepsilon}, \tag{1.6}$$

$$J_{px}^\varepsilon = J_{nx}^\varepsilon = 0 \quad \text{for } x = \pm 1. \tag{1.7}$$

Let us prove the following maximum principle for problem (1.5)–(1.7):

$$\max_{[-1,1]*[0,T]} (|J_n^\varepsilon|, |J_p^\varepsilon|) \le \max_{[-1,1]} (|J_n^\varepsilon(x,0)|, |J_p^\varepsilon(x,0)|). \tag{1.8}$$

The proof is standard for parabolic-type equations. Let us define the auxiliary functions Q and P by the equalities

$$Q = J_n^\varepsilon e^{-\gamma t}, \qquad P = J_p^\varepsilon e^{-\gamma t}, \qquad \gamma > 0. \tag{1.9a,b}$$

The boundary value problem for Q and P reads

$$P_t + \gamma P = P_{xx} + \phi_x^\varepsilon P_x + p^\varepsilon \frac{(Q - P)}{\varepsilon}, \tag{1.10}$$

$$Q_t + \gamma Q = \alpha \left(Q_{xx} - \phi_x^\varepsilon Q_x + n^\varepsilon \frac{(P - Q)}{\varepsilon} \right), \tag{1.11}$$

$$P_x = Q_x = 0 \quad \text{for } x = \pm 1. \tag{1.12}$$

Let us assume that a positive interior maximum of the function P exists at the point (x_0, t_0): $P(x_0, t_0) = \max_{[-1,]*[0,T]} P > 0$. Since the function p^ε is positive, using Eq. (1.10) we obtain that

$$\max P = P(x_0, t_0) < Q(x_0, t_0) \le \max Q. \tag{1.13a}$$

Assuming the existence of the positive interior maximum of the function Q at the point (x_1, t_1) using Eq. (1.11) and positivity of n^ε we obtain

$$\max Q = Q(x_1, t_1) < P(x_1, t_1) \le \max P. \tag{1.13b}$$

Due to the boundary conditions (1.12), inequalities (1.13a,b) are also valid for possible maxima at $x = \pm 1$. Since these inequalities yield a contradiction, we conclude that

$$\max_{[-1,1]*[0,T]} (P, Q) \le \max_{[-1,1]} (J_n^\varepsilon(x,0), J_p^\varepsilon(x,0), 0). \tag{1.14a}$$

Taking the limit $\gamma \to 0$ in (1.14a) we obtain

$$\max_{[-1,1]*[0,T]} (J_n^\varepsilon, J_p^\varepsilon) \le \max_{[-1,1]} (J_n^\varepsilon(x,0), J_p^\varepsilon(x,0), 0). \tag{1.14b}$$

The same consideration with negative γ yields the minimum principle and completes the proof of estimate (1.8).

Let us define the function $\operatorname{sign}_\delta \phi_x^\varepsilon$ by

$$\operatorname{sign}_\delta \phi_x^\varepsilon \stackrel{\text{def}}{=} \frac{\phi_x^\varepsilon}{\sqrt{\phi_x^{\varepsilon 2} + \delta}}. \tag{1.15}$$

Since

$$\int_{-1}^{1} (J_p^\varepsilon - J_n^\varepsilon) \operatorname{sign}_\delta \phi_x^\varepsilon \, dx = \int_{-1}^{1} \left((p^\varepsilon - n^\varepsilon)_x + (p^\varepsilon + n^\varepsilon)\phi_x^\varepsilon + \frac{I}{2}\left(1 + \frac{1}{\alpha}\right)\right) \operatorname{sign}_\delta \phi_x^\varepsilon \, dx, \tag{1.16}$$

integration by parts, making use of Eq. (0.13) and the boundedness of the left-hand side of equality (1.16) yield

$$\int_{-1}^{1} \left(\frac{\delta \varepsilon \phi_{xx}^{\varepsilon 2}}{(\phi_x^{\varepsilon 2} + \delta)^{3/2}} + (p^\varepsilon + n^\varepsilon)\phi_x^\varepsilon \operatorname{sign}_\delta \phi_x^\varepsilon \right) dx < C_1 \tag{1.17}$$

for all $t > 0$.

Taking the limit as $\delta \to 0$ we obtain

$$\int_{-1}^{1} (p^\varepsilon + n^\varepsilon)|\phi_x^\varepsilon| dx\, dt < C_1, \quad \forall t > 0. \tag{1.18}$$

Taking into account the definitions (1.1a,b) and the estimate (1.8), the latter estimate yields

$$\int_{-1}^{1} (|p_x^\varepsilon| + |n_x^\varepsilon|)\, dx < C_2, \quad \forall t > 0. \tag{1.19}$$

Since the functions $p^\varepsilon(x,t), n^\varepsilon(x,t)$ are constant independent of ε at $x = \pm 1$, estimate (1.19) yields

$$0 < p^\varepsilon, n^\varepsilon < C_3, \quad \forall x \in [-1,1],\ t > 0,\ \varepsilon > 0. \tag{1.20}$$

This completes the proof of Lemma 1.

In the remainder of this section we use the following standard scheme to prove the convergence of the perturbed solution to the limiting one as the perturbation parameter ε tends to 0.

(i) The estimates obtained in Lemma 1 allow us to choose a converging subsequence of the solutions of the problem (0.11)–(0.18).

(ii) We shall study the fine structure of the limit of the aforementioned subsequence and find the formulation of the limiting problem.

(iii) We shall prove that the limiting problem possesses a unique solution, and this uniqueness theorem will yield the convergence of the whole sequence of the perturbed solutions as the perturbation parameter ε tends to 0.

In what follows we restrict ourselves to consideration of the symmetric formulation of (0.11)–(0.18). Thus, in addition to the symmetry of the fixed charge distribution (0.13), we assume symmetry of the boundary and initial conditions:

$$n_1 = p_1, \qquad p_0^\varepsilon(x) = n_0^\varepsilon(-x) \quad \forall x \in (-1,1),\ \forall \varepsilon > 0,\ \alpha = 1. \tag{1.21a–c}$$

These assumptions yield symmetry of solutions to the problem (0.11)–(0.18):

$$n^\varepsilon(x,t) = p^\varepsilon(-x,t), \quad \phi_x^\varepsilon(-x,t) = \phi_x^\varepsilon(x,t), \quad J_n^\varepsilon(x,t) = -J_p^\varepsilon(-x,t) \quad \forall x \in [-1,1], t > 0. \tag{1.22a–c}$$

Let us formulate the main result of this section.

THEOREM 3. Let the conditions of Theorem 1 and Lemma 1 hold together with conditions (1.21) and the following additional ones:

$$p_0^\varepsilon(x) - n_0^\varepsilon(x) \to N, \quad p_0^\varepsilon(x) + n_0^\varepsilon(x) \to c_0(x) \quad \text{in } L^2(0,1).$$

Then the sequence of solutions $(p^\varepsilon, n^\varepsilon, \phi^\varepsilon)$ has the following limit as $\varepsilon \to 0$:

$$p^\varepsilon + n^\varepsilon \to c(x,t), \quad p^\varepsilon - n^\varepsilon \to \begin{cases} N, & x \geq R(t), \\ 0, & 0 < x < R(t) \end{cases} \quad \text{in } L^2(0,1) * (0,T)\ \forall T > 0,$$

$$\phi_x^\varepsilon(x,t) \to \begin{cases} -\infty, & 0 < x < R(t), \\ \phi_x(x,t), & x \geq R(t) \end{cases} \quad \text{in } L^2(R(t),1) * (0,T)\ \forall T > 0.$$

The functions $c(x,t), R(x,t)$ are the solutions of the following limiting free boundary problem: Find a Lipschitz continuous function $R(t)$ and a function $c(x,t)$ continuous outside of the region $(0,\infty) * (0, R(t))$ such that

$$c_t = c_{xx} - \left(\frac{NI}{c}\right)_x \quad \text{and } c(x,t) > N \quad \forall x \notin (0, R(t)),\ t > 0, \tag{1.22a,b}$$

$$c(R(t)+0,t) = N, \quad \forall t > 0 \text{ such that } R(t) \neq 0, \tag{1.23a,b}$$

$$\dot{R}(t) = I - c_x(R(t)+0,t) \quad \forall t > 0 \text{ such that } R(t) \neq 0, \tag{1.24}$$

$$c_x(0,t) = \frac{NI}{c},\ c(0,t) > N \quad \forall t > 0 \text{ such that } R(t) = 0, \tag{1.25a,b}$$

$$c(1,t) = c_1 \stackrel{\text{def}}{=} 2p_1 - N > N, \quad \forall t > 0, \qquad c(x,0) = c_0(x) \quad \forall x \in (0,1) \tag{1.26a,b}$$

and $\phi(x,t)$ can be found a posteriori by the equality

$$\phi_x = -\frac{I}{c} \quad \forall x \in (R(t), 1]. \tag{1.27}$$

Proof of Theorem 3. Due to the equality

$$(p^\varepsilon n^\varepsilon)_x = n^\varepsilon J_p^\varepsilon + \frac{p^\varepsilon J_n^\varepsilon}{\alpha} - \frac{I}{2}\left(p^\varepsilon - \frac{n^\varepsilon}{\alpha}\right), \tag{1.28}$$

estimate (1.8) yields that the spatial derivative $(p^\varepsilon n^\varepsilon)_x$ is bounded in $[-1,1] * [0,T]$ uniformly in ε:

$$(p^\varepsilon n^\varepsilon)_x < C_4. \tag{1.29}$$

Let us define now the scaled potential $\tilde{\phi}^\varepsilon$ as follows:

$$\tilde{\phi}^\varepsilon = \varepsilon \phi^\varepsilon. \tag{1.30}$$

The Poisson equation (0.13) and estimate (1.20) yield

$$\tilde{\phi}^\varepsilon_{xx} = N(x) + n^\varepsilon - p^\varepsilon, \tag{1.31a}$$

$$\int_{-1}^{1} (p^\varepsilon + n^\varepsilon)|\tilde{\phi}^\varepsilon_x| < C_1\varepsilon. \tag{1.31b}$$

Taking into account estimates (1.20), (1.29) we obtain

$$\tilde{\phi}^\varepsilon_x \in C^{0,1}[-1,1] \quad \forall t > 0 \text{ uniformly in } \varepsilon > 0. \tag{1.32}$$

Using estimates (1.8), (1.19), (1.20), (1.32) we can choose the sequence ε_m such that $\varepsilon_m \to 0$ as $m \to \infty$ and

$$p^{\varepsilon_m} \to p, \; n^{\varepsilon_m} \to n \text{ strongly in } L^p(-1,1) * (0,T) \quad \forall p > 0, \tag{1.33a,b}$$

$$J_p^{\varepsilon_m} \to J_p, \; J_n^{\varepsilon_m} \to J_n \text{ weakly in } L^p(-1,1) * (0,T) \quad \forall p > 0, \; T > 0, \tag{1.33c,d}$$

$$\tilde{\phi}^{\varepsilon_m} \to \tilde{\phi} \text{ in } C^{1+q}[-1,1] \quad \forall q \in (0,1), \; t > 0 \tag{1.34}$$

as $m \to \infty$. The aforementioned estimates also yield the boundedness of the limit functions p, n, J_n, J_p and Lipschitz continuity in x of the function $\tilde{\phi}_x$.

Taking the limit $m \to \infty$ in statements (1.31) we obtain

$$\tilde{\phi}_{xx} = N(x) + n - p \text{ in the } L^p \text{ sense}, \tag{1.35a}$$

$$\int_{-1}^{1} (p+n)|\tilde{\phi}_x|\, dx = 0. \tag{1.35b}$$

These equalities yield that on the set $A(t) = \{x \in [-1,1] \colon \tilde{\phi}_x \neq 0\}$ the function $p(x,t) + n(x,t)$ vanishes almost everywhere and

$$\tilde{\phi}_{xx} = N(x) \text{ almost everywhere on } A(t) \quad \forall t > 0. \tag{1.36}$$

Let us study now the fine structure of the set $A(t)$. Since the product pn is not equal to zero at $x = \pm 1$ and is Lipschitz continuous in x, Eq. (1.35b) yields $\tilde{\phi}_x(\pm 1, t) = 0 \; \forall t > 0$. Making use of (1.36) we obtain that the function $\tilde{\phi}_x$, Lipschitz continuous in x, decreases in x for $x < 0$ and increases in x for $x > 0$. Therefore, the set $A(t)$ is connected and a nonnegative function $R(t)$ exists such that

$$A(t) = (-R(t), R(t)) \subset (-1,1). \tag{1.37}$$

Using estimate (1.35b) we obtain that

$$p(x,t) = n(x,t) = 0 \quad \forall x \in (-R(t), R(t)),\ t > 0. \tag{1.38a}$$

Outside the set $A(t), \tilde{\phi}_x(x,t) = 0$ and, taking into account Eq. (1.31b), we find

$$p(x,t) - n(x,t) = N(x) \quad \forall x \notin (-R(t), R(t)),\ t > 0. \tag{1.38b}$$

Using statement (1.38b), we can improve the above estimates on the functions $p^\varepsilon, n^\varepsilon, \phi^\varepsilon$ outside the set $A(t)$. In order to do this, we may use the convergences (1.33a,b) and find that the Lebesgue measure of the set

$$M_m(t) = \{1 > x > R(t)\colon |p^{\varepsilon_m}(x,t) - n^{\varepsilon_m}(x,t) - N| > \eta > 0\}$$

tends to zero as $m \to \infty\ \forall t > 0, \eta > 0$

$$\lim_{m\to\infty} |M_m(t)| = 0. \tag{1.39}$$

Let us consider two arbitrary points x_1, x_2 such that $x_1 < x_2$ and $x_1, x_2 \notin M_m(t)$. Employing once more the procedure used earlier for estimates (1.18), (1.19), we obtain

$$\int_{x_1}^{x_2} (|p_x^{\varepsilon_m}| + |n_x^{\varepsilon_m}| + (p^{\varepsilon_m} + n^{\varepsilon_m})|\phi_x^{\varepsilon_m}|)\, dx < C_4(\eta + |x_2 - x_1|) \tag{1.40}$$

and, consequently,

$$|p^{\varepsilon_m}(x_1,t) - p^{\varepsilon_m}(x,t)| + |p^{\varepsilon_m}(x_2,t) - p^{\varepsilon_m}(x,t)| < C_5(\eta + |x_2 - x_1|), \quad \forall x \in (x_1, x_2). \tag{1.41}$$

This estimate yields that

$$p^{\varepsilon_m}(x,t) > \frac{N}{2}, \quad \forall x \in (x_1, x_2) \tag{1.42}$$

if $|x_2 - x_1| < (\frac{N}{2} - \eta(C_5 + 1))/C_4$.

Making use of the convergence (1.39), we conclude that there exists a sequence $\delta_m > 0$ such that $\delta_m \to 0$ as $m \to \infty$ and

$$p^{\varepsilon_m}(x,t) > \frac{N}{2} \quad \forall x \in (R(t) + \delta_m, 1],\ t > 0. \tag{1.43a}$$

A similar estimate may also be obtained for n^{ε_m} in the respective symmetric part of the interval $[-1, 1]$, yielding

$$n^{\varepsilon_m}(x,t) > \frac{N}{2} \quad \forall x \in [-1, -R(t) - \delta_m),\ t > 0. \tag{1.43b}$$

Combining these estimates with estimate (1.18) we obtain

$$\int_{-1}^{-R(t)-\delta_m} |\phi_x^{\varepsilon_m}|\, dx + \int_{R(t)+\delta_m}^{1} |\phi_x^{\varepsilon_m}|\, dx < C_6, \quad \forall t > 0. \tag{1.44}$$

Let us now multiply $J_p^{\varepsilon_m} + J_n^{\varepsilon_m}/\alpha$ by the test function $\phi_x^{\varepsilon_m}\psi$, where $\psi(x) \in C^\infty[-1,1]$, $\psi(x) = 0\ \forall x \in [-R(t) - \delta, R(t) + \delta]$ for some $\delta > 0$, $\psi(x) = 1\ \forall x \notin (-R(t) - 2\delta, R(t) + 2\delta)$. Then, integrating the resulting function over the interval $(-1, 1)$ and using estimates (1.14), (1.44), we find

$$\phi_x^{\varepsilon_m} \in L^2(-1, -R(t) - \delta) \cup (R(t) + \delta, 1) \quad \forall \delta > 0,\ t > 0 \tag{1.45a}$$

uniformly in m. Using the boundedness of the functions $J_p^\varepsilon, J_n^\varepsilon$ we obtain

$$p_x^{\varepsilon_m}, n_x^{\varepsilon_m} \in L^2(-1, -R(t) - \delta) \cup (R(t) + \delta, 1) \quad \forall \delta > 0,\ t > 0. \tag{1.45b}$$

The two latter statements allow us to find the limiting functions J_p, J_n outside the interval $(-R(t), R(t))$:

$$J_p = p_x + p\phi_x + \frac{I}{2}, \quad J_N = \alpha(n_x - n\phi_x) - \frac{I}{2}, \quad \forall x \in [-1, -R(t)) \cup (-R(t), 1]. \tag{1.46a,b}$$

Since the functions J_p, J_n are bounded and $p_x - n_x$ vanishes outside the interval $(-R(t), R(t))$, we find, taking the difference $J_p - J_n/\alpha$, that

$$|\phi_x| < C_7, \quad \forall x \in [-1, -R(t)) \cup (-R(t), 1] \tag{1.47a}$$

and, consequently,

$$|p_x|, |n_x| < C_8, \quad \forall x \in [-1, -R(t)) \cup (-R(t), 1]. \tag{1.47b}$$

The last estimates imply smoothness of the limiting concentrations and potential outside of the interval $(-R(t), R(t))$.

Let us consider next the interior of the region $A(t) = (-R(t), R(t))$. Defining the functions $\Phi(x,t), \Psi(x,t)$ as

$$\Phi(x,t) = \int_0^x p(x,t)\,dx, \qquad \Psi(x,t) = \int_0^x n(x,t)\,dx, \tag{1.48a,b}$$

we find that

$$\Phi_t = J^p(x,t) - J^p(0,t), \qquad \Psi_t = J^n(x,t) - J^n(0,t). \tag{1.49a,b}$$

Since the functions $\Phi(x,t), \Psi(x,t)$ are Lipschitz continuous in x and t and vanish for $x \in [-R(t), R(t)]$ we obtain, using equalities (1.49),

$$J^p(x,t) = J^p(0,t), \quad J^n(x,t) = J^n(0,t) \quad \forall x \in (-R(t), R(t)). \tag{1.50a,b}$$

Therefore, the flux functions are constant in x in the interior of region $A(t)$.

We can also find ϕ_x as a function of $c = p + n$ and c_x outside this region. In order to do that, let us define the functions $\widetilde{\Phi}(x,t), \widetilde{\Psi}(x,t)$ as

$$\widetilde{\Phi}(x,t) = \int_x^1 p(x,t)\,dx, \qquad \widetilde{\Psi}(x,t) = \int_x^1 (n(x,t) + N(x))\,dx. \tag{1.51a,b}$$

Since

$$\widetilde{\Phi}_t = J^p(1,t) - J^p(x,t), \qquad \widetilde{\Psi}_t = J^n(1,t) - J^n(1,t), \tag{1.52a,b}$$

and

$$\widetilde{\Phi} - \widetilde{\Psi} = 0, \quad \forall x \in (R(t), 1)$$

then

$$J^p(x,t) - J^n(x,t) = J^p(1,t) - J^n(1,t) = \lim_{\varepsilon \to 0} \varepsilon \phi_{xt}^\varepsilon(1,t) = 0 \quad \forall x \in (R(t), 1). \tag{1.53}$$

Using equalities (1.46), we obtain

$$\phi_x = -\frac{2I + (1-\alpha)c_x}{(1+\alpha)c + (1-\alpha)N} \quad \forall x \in (R(t), 1]. \tag{1.54a}$$

The same calculations for $x \in [-1, -R(t))$ yield

$$\phi_x = -\frac{2I + (1-\alpha)c_x}{(1+\alpha)c - (1-\alpha)N} \quad \forall x \in [-1, R(t)). \tag{1.54b}$$

Let us now find the respective limiting initial-boundary value problem. By considering the total ionic concentration $c^\varepsilon(x,t) = p^\varepsilon(x,t) + n^\varepsilon(x,t)$, we observe that it satisfies the following equation:

$$c_t^\varepsilon = (J_p^\varepsilon + J_n^\varepsilon)_x. \tag{1.55}$$

Let us multiply this equation by a smooth test function $\psi(x,t)$ such that $\psi(x,T) = 0$, $\psi(\pm 1, t) = 0$ and integrate over the region $(-1,1) * (0,T)$. Then

$$\int_0^T \int_{-1}^1 c^\varepsilon \psi_t \, dx \, dt = \int_0^T \int_{-1}^1 (J_p^\varepsilon + J_n^\varepsilon)\psi_x \, dx \, dt + \int_{-1}^1 c^\varepsilon(x,0)\psi(x,0)\, dx. \tag{1.56}$$

Taking the limit $m \to \infty$ in Eq. (1.56), we obtain

$$\begin{aligned} \int_0^T \int_{-1}^1 c\psi_t \, dx\, dt &= \int_0^T \int_{-1}^1 (J_p + J_n)\psi_x \, dx\, dt + \int_{-1}^1 c(x,0)\psi(x,0)\, dx \\ &= \int_0^T \Bigg((J_p(0,t) + J_n(0,t))(\psi(R(t),t) - \psi(-R(t),t)) \\ &\quad + \int_{(-1,-R(t))\cup(R(t),1)} \Bigg(\frac{1+\alpha}{2} c_x \\ &\qquad - \frac{(1-\alpha)c + (1+\alpha)N(x)}{2} \frac{2I + (1-\alpha)c_x}{(1+\alpha)c + (1-\alpha)N(x)} \Bigg) \psi_x \, dx \Bigg) dt \\ &\qquad + \int_{-1}^1 c(x,0)\psi(x,0)\, dx. \end{aligned} \tag{1.57}$$

Using estimates (1.47), we find

$$c(-1,t) = 2n_1 - N; \qquad c(1,t) = 2p_1 - N; \qquad c(\pm(R(t)+0),t) = N; \tag{1.58a–d}$$

$$c(x,t) = 0 \quad \forall x \in (-R(t), R(t)) \quad \text{if } R(t) > 0. \tag{1.58e}$$

Equations (1.57), (1.58) are the weak formulations of the respective limiting free boundary problem. In order to obtain a strong formulation we must prove the smoothness of the free boundary $x = \pm R(t)$. Next, applying integration by parts in (1.58), we will find the conditions on the free boundary.

Considering (1.57), we observe that the following equation holds in a weak sense:

$$c_t = (J_p + J_n)_x \quad \forall x \in (-1,1),\ t > 0. \tag{1.59}$$

Let us consider two moments of time t_1, t_2 assuming $R(t_1) = R_1$, $R(t_2) = R_2$, $R_2 > R_1$. Thus, $c(x,t_i) = 0$ for $x \in (-R_i, R_i)$, $c(x,t_i) \geq N$ for $|x| > R_i$, $i = 1,2$. Integrating Eq. (1.59) over the rectangle $(-R_2, R_2) * (t_1, t_2)$, we obtain

$$\int_{(-R_2,-R_1)\cap(R_1,R_2)} c(x,t_1)\, dx \leq \max_{(x,t)} |J_p(x,t) + J_n(x,t)| |t_2 - t_1|. \tag{1.60}$$

Since $c(x,t_1) \geq N$ in the interval $(-R_2, R_1)$, inequality (1.60) yields

$$|R(t_2) - R(t_1)| \leq C_9|t_2 - t_1| \quad \forall t_1, t_2 > 0, \tag{1.61a}$$

and the free boundaries $x = \pm R(t)$ are Lipschitz continuous. Therefore, for almost all $t > 0$, there exists a derivative $\dot{R}(t)$ and

$$\dot{R}(t) \in L^\infty(0,\infty). \tag{1.61b}$$

Using statements (1.61) we can obtain the following strong formulation of the limiting problem instead of the integral one: Find a Lipschitz continuous function $R(t)$ and a function $c(x,t)$ continuous outside the region $(0,\infty) * (-R(t), R(t))$ such that

$$c_t = \frac{1+\alpha}{2} c_{xx} = \left(\frac{((1-\alpha)c + (1+\alpha)N(x))(2I + (1-\alpha)c_x)}{2((1+\alpha)c + (1-\alpha)N(x))} \right)_x \tag{1.62a,b}$$
$$\text{and } c(x,t) > N \quad \forall x \notin (-R(t), R(t)),\ t > 0,$$

$$c(R(t)+0,t) = c(-R(t)-0,t) = N \quad \forall t > 0 \text{ such that } R(t) \neq 0, \tag{1.63a,b}$$

$$\dot{R}(t) = I - \frac{c_x(R(t)+0,t) - c_x(-R(t)-0,t)}{2} \quad \forall t > 0 \text{ such that } R(t) \neq 0, \tag{1.64}$$

$$c(-1,t) = 2n_1 - N > N, \quad c(1,t) = 2p_1 - N > N \ \forall t > 0, \tag{1.65a,b}$$

$$c(x,0) = c_0(x) \quad \forall x \in (-1,1). \tag{1.65c}$$

In the general nonsymmetric case we did not succeed in proving the uniqueness of the limiting problem. For this reason, in the rest of the proof let us employ the requirement of symmetry (1.21). This assumption yields the respective symmetry of the solutions of problem (0.11)–(0.18) and of the solution of the limiting problem (1.62)–(1.65). Problem (1.22)–(1.26) is the reformulation of the limiting problem (1.62)–(1.65) for the symmetric case.

We shall prove the uniqueness of the solution of the free boundary problem (1.62)–(1.65) using the so-called enthalpy method developed by Kamin ([10]) and Oleinik ([11]). At first, let us reformulate the problem (1.22)–(1.26) in the form of a singular parabolic equation, holding uniformly in the region $(0,1) * (0.\infty)$. Defining the function θ as

$$\theta \stackrel{\text{def}}{=} \theta(c) \stackrel{\text{def}}{=} \begin{cases} 0 & \text{for } c \leq N, \\ c - N & \text{for } c > N, \end{cases} \tag{1.66}$$

we find that the free boundary problem (1.22)–(1.26) is equivalent to the following one in a weak formulation: Find a function $c(x,t)$ such that $\theta(c)$ is Lipschitz continuous in x in $(0,1) * (0,T)$ $\forall T > 0$, $\theta(1,t) = c_1 - N > 0$ and

$$\int_0^T \int_0^1 c\psi_t \, dx\, dt = \int_0^T \int_0^1 \left(\theta_x - \frac{NI}{\theta + N} + I \frac{\theta + N - c}{N} \right) \psi_x \, dx\, dt + \int_0^1 c(x,0)\psi(x,0)\, dx \tag{1.67}$$

for all smooth functions $\psi(x,t)$ such that $\psi(x,T) = \psi(1,t) = 0$.

Equation (1.67) is the so-called enthalpy formulation of the free boundary problem (1.22)–(1.26). Here θ is the analog of the temperature and c is the analog of enthalpy in the Stefan problem.

Let us assume that there exist two solutions $c^1(x,t)$ and $c^2(x,t)$ of problem (1.67) satisfying the same initial and boundary data. Denoting $\tilde{c} = c^1 - c^2$, and taking the difference of the integral identities satisfied by c^1, c^2, we obtain the equality

$$\int_0^T \int_0^1 \tilde{c}(\psi_t + \mu\psi_{xx} + \frac{I}{N}(\mu - 1)\psi_x - \mu\frac{NI}{(\theta_1 + N)(\theta_2 + N)}\psi_x)\, dx\, dt = 0. \tag{1.68}$$

In (1.68)

$$\mu = \frac{\theta_1 - \theta_2}{c_1 - c_2} = \frac{\theta(c_1) - \theta(c_2)}{c_1 - c_2} \tag{1.69}$$

with $0 < \mu < 1$. The function $\psi(x,t)$ vanishes at $x = 0$, $t = T$ and $\psi_x(x,t)$ vanishes at $x = 0$.

Let us consider a sequence of the initial-boundary value problems:

$$\psi_t^n + (\mu^n + \delta)\psi_{xx}^n + \frac{I}{N}(\mu^n - 1)\psi_x^n - \mu\frac{NI}{(\theta_1 + N)(\theta_2 + N)}\psi_x^n = F(x,t), \tag{1.70}$$

$$\psi^n(x,T) = 0, \quad \forall x \in (0,1), \qquad \psi^n(1,t) = 0, \qquad \psi_x^n(0,t) = 0, \quad \forall t \in (0,T) \quad \text{(1.71a–c)}$$

with smooth nonnegative bounded functions $\mu^n(x,t)$, strongly convergent to $\mu(x,t)$ in $L^2(0,1) * (0,T)$ and smooth function $F(x,T)$.

Using the maximum principle, we obtain

$$|\psi^n(x,t)| \le T \max_{x,t} |F(x,t| \quad \forall x \in (0,1),\ t \in (0,T). \tag{1.72}$$

Since the functions c^1, c^2 do not vanish at the boundary $x = 1$, the equality $\mu = 1$ should hold in some neighborhood of this boundary. Using the local estimates, we can prove that in this neighborhood the solutions ψ^n are uniformly smooth. Therefore,

$$\max_t |\psi_x^n(1,t)| < C_9 \quad \forall n. \tag{1.73}$$

To derive the latter estimate independent of the index n, let us multiply Eq. (1.70) by ψ_{xx}^n and then integrate over $(0,1)$ (for any $t = \text{const.} > 0$). It follows from a simple computation that

$$\int_0^1 (\mu^n + \delta)\psi_{xx}^{n2} dx - \frac{d}{dt}\int_0^1 \psi_x^{n2}\, dx < \frac{2I}{N}C_9 + C_{10}\int_0^1 \psi_x^{n2}\, dx + \int_0^1 F_x^2(x,t)\, dx \tag{1.74}$$

which, by the Gronwall inequality, implies that

$$\max_{t\in(0,T)} \int_0^1 \psi_x^{n2} dx + \int_0^T \int_0^1 (\mu^n + \delta)\psi_{xx}^{n2}\, dx\, dt \le C_{11}. \tag{1.75}$$

The last estimate together with Eq. (1.70) yields

$$\int_0^T \int_0^1 (\psi_t^{n2} + \psi_x^{n2})\, dx\, dt + \int_0^T \int_0^1 (\mu^n + \delta)\psi_{xx}^{n2}\, dx\, dt \le C_{12}. \tag{1.76}$$

From (1.76), via a standard diagonalization, we can select a subsequence strongly convergent in $L^2(0,1)*(0,T)$ and weakly in $W_2^{2,1}$ to a function $\psi^\delta(x,t)\in W_2^{2,1}(0,1)*(0,T)$ such that

$$\int_0^T\int_0^1(\psi_t^{\delta 2}+\psi_x^{\delta 2})\,dx\,dt+\int_0^T\int_0^1\delta\psi_{xx}^{\delta 2}\,dx\,dt\le C_{12}. \tag{1.77}$$

We substitute the resulting function into identity (1.68) to obtain

$$\int_0^T\int_0^1\tilde{c}F\,dx\,dt=\int_0^T\int_0^1\tilde{c}\delta\psi_{xx}^{\delta}\,dx\,dt. \tag{1.78}$$

It follows from (1.77) that

$$\int_0^T\int_0^1\tilde{c}\delta\psi_{xx}^{\delta}\,dx\,dt\to 0 \text{ as } \delta\to 0. \tag{1.79}$$

Thus we obtain

$$\int_0^T\int_0^1\tilde{c}F\,dx\,dt=0 \tag{1.80}$$

with an arbitrary smooth function $F(x,t)$. Therefore, function $\tilde{c}$ coincides with zero, and we proved the uniqueness of the solution of the limiting problem. This completes the proof of Theorem 3.

2. The fine structure of the solution of the limiting problem. In this section we study the properties of the solution of the limit problem (1.22)–(1.26).

The uniform in ε estimates obtained in the previous section yield the following result:

LEMMA 2. The free boundary $R(t)$ is Lipschitz continuous in time and $\theta(c)$ is Lipschitz continuous in x for all $t>0$, $x\in(0,1)$ uniformly in time.

REMARK. Using the local parabolic estimates, we can prove C^∞-smoothness of the limiting concentration c and the free boundary $R(t)$ for all $x\ge R(t)$ and for all moments of time $t>0$, except for those t_0 for which $\lim_{t\to t_0-0}c(0,t)=N$.

Lemma 2 immediately yields the following result:

LEMMA 3. The solution $(c(x,t)),R(t))$ tends to the respective steady-state solution $(c_\infty(x),R_\infty)$ as $t\to\infty$ in the following sense:

$$\lim_{t\to\infty}R(t)=R_\infty,\qquad \lim_{t\to\infty}\theta(c(x,t))=\theta(c_\infty(x)) \text{ in the Hölder norm,}$$

$$c_\infty\frac{dc_\infty}{dx}=NI \text{ and } c_\infty>N \text{ for } x>R_\infty>0, \tag{2.2a,b}$$

$$\text{if } R_\infty>0,\ c_\infty(R_0)=N, \tag{2.3}$$

$$c_\infty(1)=c_1. \tag{2.4}$$

We can also prove the following monotonicity result for the free boundary $R(t)$.

LEMMA 4. Let the following assumption hold:

$$c_{0x}(x,0) - \frac{NI}{c_0(x,0)} \geq 0 \quad \forall x \in (0,1). \tag{2.5}$$

Then

$$\theta_x - \frac{NI}{\theta + N} + I\frac{\theta + N - c}{N} \geq 0 \quad \forall x \in (0,1),\ \forall t > 0, \tag{2.6}$$

and

$$\dot{R}(t) \geq 0 \quad \forall t > 0. \tag{2.7}$$

Proof of Lemma 4. To prove Lemma 4, let us consider once more the weak ("enthalpy") formulation of the free boundary problem (1.67):

$$c_t = (\theta(c)_x - \frac{NI}{\theta(c) + N} + \frac{I}{N}(\theta(c) + N - c))_x, \tag{2.8}$$

$$(\theta(c)_x - \frac{NI}{\theta(c) + N} + \frac{I}{N}(\theta(c) + N - c))|_{x=0} = 0, \tag{2.9}$$

$$\theta(1,t) = c_1 - N > 0, \qquad c(x,0) = c_0(x). \tag{2.10a,b}$$

Equation (2.6) holds in a weak sense.

We regularize the singular initial-boundary value problem, defining a sequence of monotonic smooth functions $\theta^n(c)$ such that

$$1 > (\theta^n)' > \frac{1}{n} > 0, \theta^n \in C^2, \theta^n \to \theta \text{ in the Hölder norm.} \tag{2.11a–c}$$

Let us define c^n as a solution of the regularized problem:

$$c_t^n = (\theta^n(c^n)_x - \frac{NI}{\theta^n(c^n) + N} + \frac{I}{N}(\theta^n(c^n) + N - c^n))_x, \tag{2.12}$$

$$(\theta^n(c^n)_x - \frac{NI}{\theta^n(c^n) + N} + \frac{I}{N}(\theta^n(c^n) + N - c^n))|_{x=0} = 0, \tag{2.13}$$

$$\theta^n(1,t) = c_1 - N > 0, \qquad c^n(x,0) = c^0(x). \tag{2.14a,b}$$

Considering the function v,

$$v \stackrel{\text{def}}{=} \theta^n(c^n)_x - \frac{NI}{\theta^n(c^n) + N} + \frac{I}{N}(\theta^n(c^n) + N - c^n), \tag{2.15}$$

we find that it is a solution of the following initial-boundary value problem:

$$v_t = (\theta^n)'v_{xx} + (\theta^n)''c_x^n v_x + \frac{NI}{(\theta^n + N)^2}(\theta^n)'v_x + \frac{I}{N}((\theta^n)' - 1)v_x, \tag{2.16a}$$

$$v|_{x=0} = 0, \quad v_x|_{x=1} = 0, \quad v|_{t=0} \leq 0. \tag{2.16b–d}$$

Applying the maximum principle to problem (2.16) we obtain

$$v(x,t) = (\theta^n(c^n))_x - \frac{NI}{\theta^n(c^n) + N} + \frac{I}{N}(\theta^n(c^n) + N - c^n) \leq 0 \quad \forall x \in (0,1),\ t > 0. \tag{2.17}$$

In order to derive an estimate independent of the index n, let us multiply Eq. (2.12) by θ^n_t and integrate over $(0,1)*(0,T)$. It follows by a simple computation that

$$\int_0^T\int_0^1 ((\theta^n(c^n))^2_t + (\theta^n(c^n))^2_x)\,dx\,dt < C_{13}. \tag{2.18}$$

Using estimate (2.11a) together with (2.18) we obtain

$$c^n \to c \text{ in } L^2(0,1)*(0,T), \quad \theta^n(c^n) \to \theta(c) \text{ in } W_2^{1,1}(0,1)*(0,T) \text{ as } n\to\infty. \tag{2.19}$$

Combining (2.19) with (2.17) completes the proof of Lemma 4.

3. Characteristics continuous and smooth over Region C and the boundary layers. Boundary layers solutions. In the previous section we have proved the local continuity and smoothness, uniform in ε, of the solutions (outside the boundary layers at $x = 0, R(t)$). In this section we shall find those characteristics of the system that preserve their uniform-in-ε boundedness and smoothness throughout the boundary layers and the "empty" Region C ($c = 0$) (i.e., those combinations of the original dependent variables) despite the singularities that appear in the original variables in these regions upon the transition $\varepsilon \to 0$. These characteristics will be subsequently employed to analyze the asymptotic behavior of the solution in the boundary layers.

LEMMA 5. The functions n^ε and p^ε are of the order $O(\varepsilon)$ locally in Region C. The function ϕ^ε is of the order $O(\frac{1}{\varepsilon})$ in Region C.

$$\lim_{\varepsilon\to 0}\varepsilon\phi^\varepsilon_x = \begin{cases} N(x-R(t)) & \text{if } x\in[0,R(t)]; \\ 0 & \text{if } x > R(t)\end{cases} \text{ in Hölder norm,} \tag{3.1a}$$

$$\lim_{\varepsilon\to 0}\frac{p^\varepsilon}{\varepsilon} = \lim_{\varepsilon\to 0}\frac{n^\varepsilon}{\varepsilon} = \frac{N\dot{R}-I}{2N(x-R(t))} \text{ in a weak sense locally in } [0,R(t)). \tag{3.1b}$$

Proof of Lemma 5. Let us define the following functions:

$$\tilde{p}^\varepsilon = \frac{p^\varepsilon}{\varepsilon}, \qquad \tilde{n}^\varepsilon = \frac{n^\varepsilon}{\varepsilon}, \qquad \tilde{\phi}^\varepsilon = \varepsilon\phi^\varepsilon. \tag{3.2a–c}$$

Using the properties (1.32)–(1.36), we find

$$\tilde{\phi}^\varepsilon_x \to \tilde{\phi}_x = \begin{cases} N(x-R(t)), & \text{for } 0 < x \le R(t), \\ 0 & \text{for } R(t) < x < 1,\end{cases} \text{ in Hölder norm.} \tag{3.3}$$

Furthermore, we find using (1.50a,b) that in a weak sense in the interval $(0,R(t))$

$$\lim_{\varepsilon\to 0} J^\varepsilon_p = \lim_{\varepsilon\to 0} p^\varepsilon\phi_x + \frac{I}{2} = \lim_{\varepsilon\to 0}\tilde{p}^\varepsilon\tilde{\phi}_x + \frac{I}{2} = J_p(0,t), \tag{3.4a}$$

$$\lim_{\varepsilon\to 0} J^\varepsilon_n = \lim_{\varepsilon\to 0} n^\varepsilon\phi^\varepsilon_x - \frac{I}{2} = \lim_{\varepsilon\to 0}\tilde{n}^\varepsilon\tilde{\phi}^\varepsilon_x - \frac{I}{2} = J_n(0,t). \tag{3.4b}$$

Moreover, the limiting function $\tilde{\phi}_x$ is separated away from zero in the interval $(0, R(t)-\delta)$, $\delta > 0$ by the inequality $\tilde{\phi}_x > N\delta$ (see (3.3)). This implies, taking into account the Hölder convergence in (3.3), that weak limits of $\tilde{p}^\varepsilon$ and $\tilde{n}^\varepsilon$ exist in this interval:

$$\tilde{p} \overset{\text{def}}{=} \lim_{\varepsilon\to 0}\tilde{p}^\varepsilon, \qquad \tilde{n} \overset{\text{def}}{=} \lim_{\varepsilon\to 0}\tilde{n}^\varepsilon, \tag{3.5a,b}$$

and

$$\tilde{p} = \frac{J_p(0,t) - \frac{I}{2}}{\tilde{\phi}_x}, \qquad \tilde{n} = \frac{-J_n(0,t) - \frac{I}{2}}{\tilde{\phi}_x}. \tag{3.6a,b}$$

Making use of the symmetry of the problem, we find that

$$J_p(0,t) + J_n(0,t) = 0 \Rightarrow \tilde{p} = \tilde{n} \quad \forall x \in (0, R(t)). \tag{3.7a,b}$$

Furthermore, passing to the limit $\varepsilon \to 0$ in the difference $p^\varepsilon - n^\varepsilon$, we obtain

$$\lim_{\varepsilon\to 0}(p^\varepsilon - n^\varepsilon) \overset{\text{def}}{=} C(x,t) = \begin{cases} N, & x \in (R(t), 1], \\ 0, & x \in [0, R(t)), \end{cases} \tag{3.8}$$

and the following equation holds in a weak sense:

$$C_t = (J_p - J_n)_x. \tag{3.9}$$

Taking into account the existence of the sharp free boundary $x = R(t)$, separating the "empty" and "normal" zones, we find that

$$N\dot{R} = [J_p - J_n]_{x=R(t)+0}^{x=R(t)-0} = 2J_p(0,t). \tag{3.10}$$

Therefore,

$$\tilde{p} = \tilde{n} = \frac{N\dot{R} - I}{2N(x - R(t))}. \tag{3.11}$$

This completes the proof of Lemma 5.

We turn now to the study of the behavior of the solution inside the boundary layers. We shall begin with considering the boundary layer at $x = 0$ nonadjacent to Region C. Let us assume that $c(0, t_0) > N$. Then the following result holds.

LEMMA 6. The solutions $n^\varepsilon, p^\varepsilon, \phi^\varepsilon$ converge, as $\varepsilon \to 0$, in the Hölder norm with respect to the boundary layer variable $\tilde{x}$,

$$\tilde{x} = \frac{x}{\sqrt{\varepsilon}}, \tag{3.12}$$

to the limiting solutions n^0, p^0, ϕ^p:

$$p^0 = \frac{\sqrt{c_0^2 - N^2}}{2} e^{-\phi^0}, \qquad n^0 = \frac{\sqrt{c_0^2 - N^2}}{2} e^{\phi^0}, \tag{3.13a,b}$$

$$\phi^0_{\tilde{x}} = -\sqrt{N\left(\phi^0 - \ln\sqrt{\frac{c_0 - N}{c_0 + N}}\right) + \frac{\sqrt{c_0^2 - N^2}}{2}(e^{\phi^0} + e^{-\phi^0}) - c_0^2}, \quad \phi^0(0) = 0. \tag{3.14}$$

Here $c_0 = c(0, t_0)$.

Proof of Lemma 6. As mentioned previously (see (1.29)),

$$p^\varepsilon n^\varepsilon \to \frac{c^2 - N^2}{4} \text{ as } \varepsilon \to 0 \text{ in } C^\alpha[0,1] \text{ for } t = t_0 \text{ and } \alpha \in [0,1). \tag{3.15}$$

Transformation to the boundary layer variable $\tilde{x}$ yields

$$p^\varepsilon_{\tilde{x}} + p^\varepsilon \phi^\varepsilon_{\tilde{x}} = \varepsilon\left(J_p^\varepsilon - \frac{I}{2}\right), \qquad n^\varepsilon_{\tilde{x}} - n^\varepsilon \phi^\varepsilon_{\tilde{x}} = \varepsilon\left(J_n^\varepsilon + \frac{I}{2}\right), \tag{3.16a,b}$$

$$\phi^{\varepsilon}_{\tilde{x}\tilde{x}} = N + n^{\varepsilon} - p^{\varepsilon}, \tag{3.17}$$

and, using the uniform-in-ε boundedness of the right-hand sides of the identities (3.16), (3.17), we obtain that the functions $p^{\varepsilon}(\tilde{x}, t_0), n^{\varepsilon}(\tilde{x}, t_0), \phi^{\varepsilon}_{\tilde{x}\tilde{x}}(\tilde{x}, t_0)$ are Lipschitz continuous uniformly in ε. Using the condition of symmetry, we observe that

$$p^{\varepsilon}(0, t_0) = n^{\varepsilon}(0, t_0) \tag{3.18}$$

and, taking the limit $\varepsilon \to 0$, we obtain the existence of the following limits:

$$\lim_{\varepsilon\to 0} p^{\varepsilon} = p^0(\tilde{x}), \quad \lim_{\varepsilon\to 0} n^{\varepsilon} = n^0(\tilde{x}), \quad \lim_{\varepsilon\to 0} \phi^{\varepsilon} = \phi^0(\tilde{x}), \quad p^0 n^0 = \frac{c(0, t_0)^2 - N^2}{4} \tag{3.19a–d}$$

which are solutions of the following boundary-value problem $\forall \tilde{x} \in (0, \infty)$:

$$p^0_{\tilde{x}} + p^0 \phi^0_{\tilde{x}} = 0 \quad \forall \tilde{x} \in (0, \infty), \tag{3.20a}$$

$$n^0_{\tilde{x}} - n^0 \phi^0_{\tilde{x}} = 0 \quad \forall \tilde{x} \in (0, \infty), \tag{3.20b}$$

$$\phi^0_{\tilde{x}\tilde{x}} = n^0 - p^0 \quad \forall \tilde{x} \in (0, \infty), \tag{3.20c}$$

$$p^0(0) = n^0(0). \tag{3.20d}$$

In order to compute the formulation of the problem (3.20), we have to find two additional boundary conditions. One is provided by use of the normalization condition for the potential, namely,

$$\phi^0(0) = 0. \tag{3.20e}$$

Furthermore, by rewriting estimate (1.18) in terms of the boundary layer variables, we obtain

$$\int_0^{\infty} (p^0 + n^0)|\phi^0_{\tilde{x}}|\, d\tilde{x} < C_1. \tag{3.21}$$

This implies, taking into account equality (3.17d) and the Lipschitz continuity of $\phi^0_{\tilde{x}\tilde{x}}$, the following boundary condition at infinity:

$$\lim_{\tilde{x}\to\infty} (p^0(\tilde{x}) - n^0(\tilde{x})) = N. \tag{3.20f}$$

Finally, solution of the problem (3.20a–f) yields expressions (3.13a,b), (3.14). Q.E.D.

Let us assume next the case $0 < R(t) < 1$ and consider the transition layer at $x = R(t)$ in which function p^{ε} varies from 0 to N. The main features of the respective transition layer solution are summarized by the following lemma.

LEMMA 7. Whenever Region C exists, for ε tending to 0, the functions $n^{\varepsilon}, p^{\varepsilon}$ converge in the Hölder norm with respect to the suitably defined transition layer variable $\hat{x}$ (see (3.36)) respectively to 0 and p^1, defined as

$$p^1 = \frac{N}{2} e^{-\phi^1}. \tag{3.22a}$$

Here ϕ^1 is defined by the relation

$$\hat{x} = -\frac{1}{\sqrt{N}} \int_0^{\phi^1} \frac{ds}{\sqrt{2s + e^{-s} - 2 + 2\ln 2}}. \tag{3.22b}$$

Proof of Lemma 7. We begin with proving that the thickness of the transition layer at the free boundary $x = R(t)$ is of the order of $\sqrt{\varepsilon}$. Let us define the function $R^\varepsilon_\delta(t)$ as:

$$R^\varepsilon_\delta(t) = \begin{cases} 0 & \text{if } p^\varepsilon(0,t) \geq \delta, \\ \max\{x_0 > 0, p^\varepsilon(x,t) < \delta \in (0,N), \forall x < x_0\}. \end{cases} \tag{3.23}$$

By this definition

$$p^\varepsilon \leq \delta \quad \forall x \in (0, R^\varepsilon_\delta(t)]. \tag{3.24}$$

Let us define the set Y as

$$Y = \{(x,t)\colon R^\varepsilon_\delta(t) \leq x \leq 1\}. \tag{3.25}$$

Set Y is connected by this definition and

$$p^\varepsilon(x,t) \geq \delta \quad \forall x \in \partial Y. \tag{3.26}$$

It follows from Eqs. (0.11), (0.13) that the following inequalities hold at the inner minimum point of p^ε in Y:

$$p^\varepsilon \geq n^\varepsilon + N > N \tag{3.27}$$

and

$$p^\varepsilon \geq \delta \quad \text{in } Y. \tag{3.28}$$

Thus, we have shown that

$$p^\varepsilon < \delta \quad \forall x \in [0, R^\varepsilon_\delta(t)), \tag{3.29a}$$

$$p^\varepsilon \geq \delta \quad \forall x \in [R^\varepsilon_\delta(t), 1]. \tag{3.29b}$$

Let us define the interval M^ε_δ as follows:

$$M^\varepsilon_\delta(t) = \{x\colon x \in (R^\varepsilon_\delta(t), R^\varepsilon_{N-\delta}(t))\}. \tag{3.30}$$

Estimates (3.29a,b) yield

$$p^\varepsilon(x,t) \in [\delta, N-\delta) \quad \forall x \in M^\varepsilon_\delta(t). \tag{3.31}$$

Let us estimate the measure of the set $M^\varepsilon_\delta(t)$. Inequality (1.18) and expression (3.31) yield

$$\int_{M^\varepsilon_\delta(t)} |\phi_x| \, dx < \frac{C_1}{\delta}. \tag{3.32}$$

Since

$$\frac{N-\delta}{\varepsilon} > \phi^\varepsilon_{xx} > \frac{\delta}{\varepsilon} \quad \forall x \in M^\varepsilon_\delta(t), \tag{3.33}$$

then

$$\int_{M^\varepsilon_\delta(t)} |\phi_x| \, dx > \frac{\delta}{\varepsilon} |M^\varepsilon_\delta(t)|^2. \tag{3.34}$$

The latter estimate, together with (3.32), yields

$$|M^\varepsilon_\delta(t)| < \frac{C_1\sqrt{\varepsilon}}{\delta^2}. \tag{3.35}$$

Let us define the transition layer variable $\hat{x}$ as

$$\hat{x} \stackrel{\text{def}}{=} \frac{x - R^{\varepsilon}_{N/2}}{\sqrt{\varepsilon}}. \tag{3.36}$$

Rewriting estimates (1.18) and (3.33) in terms of $\hat{x}$ and using (3.29) yields

$$\int_{R^{\varepsilon}_{\delta}(t)}^{\frac{1}{\sqrt{\varepsilon}}} |\phi_{\hat{x}}| d\hat{x} < \frac{C_1}{\delta}, \tag{3.37a}$$

$$N - \delta > \phi^{\varepsilon}_{\hat{x}\hat{x}} > \delta \quad \forall x \in M^{\varepsilon}_{\delta}(t), \tag{3.37b}$$

and, consequently,

$$|\phi_{\hat{x}}| < \frac{C_1}{\delta} + (N - \delta)\frac{|M^{\varepsilon}_{\delta}(t)|}{\sqrt{\varepsilon}} \quad \text{in } M^{\varepsilon}_{\delta}(t). \tag{3.38}$$

Furthermore, using estimate (1.8) for the flux function J^{ε}_{p} yields

$$|p_{\hat{x}}| < \frac{C_1}{\delta} + (N - \delta)\frac{|M^{\varepsilon}_{\delta}(t)|}{\sqrt{\varepsilon}} \quad \text{in } M^{\varepsilon}_{\delta}(t). \tag{3.39}$$

Since p varies from δ to $N - \delta$ and M^{ε}_{δ} and the sequence M^{ε}_{δ} decreases in δ, we conclude that

$$|M^{\varepsilon}_{\delta}| > C_{14}\sqrt{\varepsilon}. \tag{3.40}$$

Thus, we have proved that the thickness of the transition layer at the free boundary $x = R(t)$ is of the order of $\sqrt{\varepsilon}$.

The uniform-in-ε smoothness of functions $p^{\varepsilon}(\hat{x}, t), n^{\varepsilon}(\hat{x}, t), \phi^{\varepsilon}(\hat{x}, t)$ implies that

$$|p^{\varepsilon}_{\hat{x}}|, |n^{\varepsilon}_{\hat{x}}|, |\phi^{\varepsilon}_{\hat{x}}| < C_{15}, \tag{3.41}$$

which yields for $\varepsilon \to 0$ the existence of the following limits:

$$\lim_{\varepsilon \to 0} p^{\varepsilon} = p^1(\hat{x}, t), \qquad \lim_{\varepsilon \to 0} n^{\varepsilon} = n^1(\hat{x}, t), \qquad \lim_{\varepsilon \to 0} \phi^{\varepsilon} = \phi^1(\hat{x}, t). \tag{3.42a–c}$$

The respective limiting functions are the solutions of the following boundary-value problem:

$$p^1_{\tilde{x}} + p^1\phi^1_{\tilde{x}} = 0 \quad \forall \tilde{x} \in (-\infty, \infty), \tag{3.43a}$$

$$n^1_{\tilde{x}} - n^1\phi^1_{\tilde{x}} = 0 \quad \forall \tilde{x} \in (-\infty, \infty), \tag{3.43b}$$

$$\phi^1_{\tilde{x}\tilde{x}} = N + n^1 - p^1 \quad \forall \tilde{x} \in (-\infty, \infty), \tag{3.43c}$$

$$p^1(0) = \frac{N}{2}. \tag{3.43d}$$

To complete the formulation of the problem (3.43), we have to supplement it with boundary conditions. One of them follows from the uniform smoothness of the functions $p^{\varepsilon}n^{\varepsilon}$. Indeed, since $p^{\varepsilon}(R(t), t)n^{\varepsilon}(R(t), t) \to 0$ as $\varepsilon \to 0$ we have

$$n^1(0) = 0, \tag{3.43e}$$

which yields, upon solving (3.43b),

$$n^1 \equiv 0 \quad \forall \hat{x} \in (-\infty, \infty). \tag{3.44}$$

With (3.44) system (3.43) simplifies to

$$p^1_{\tilde{x}} + p^1\phi^1_{\tilde{x}} = 0 \quad \forall \tilde{x} \in (-\infty, \infty), \tag{3.45a}$$

$$\phi^1_{\tilde{x}\tilde{x}} = N - p^1 \quad \forall \tilde{x} \in (-\infty, \infty), \tag{3.45b}$$

$$p^1(0,t) = \frac{N}{2}. \tag{3.45c}$$

Decreasing the sets $M^\varepsilon_\delta(t)$ in δ together with estimates (3.35), (3.40) yields

$$p^1(-\infty, t) = 0, \qquad p^1(\infty, t) = N. \tag{3.45d,e}$$

Finally, the last missing boundary condition is that of the normalization of potential,

$$\phi^1(0,t) = 0. \tag{3.45f}$$

Solving the boundary value problem (3.45) yields expressions (3.22a,b) which concludes the proof of Lemma 7.

4. Concluding remarks. The results of this paper, concerning the limit problems (Theorem 3), are formulated so as to cover both the regular limit of locally electroneutral electrodiffusion and that of formation of the free boundary. Qualitatively, the respective results may be phrased as follows: for currents below the limiting value, the free boundary either does not appear at all, or, having appeared due to exotic initial conditions, disappears in a finite time. In contrast to this, for currents above the limiting one, the free boundary appears in finite time and persists indefinitely. Finally, let us point out that the uniqueness of the solution to the limiting free boundary problem has been obtained here for the symmetric case only. The respective uniqueness question for the general nonsymmetric setup remains open.

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