Approximation of weak solution for the problem of a pH-gradient creation in isoelectrofocusing

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The mathematical model describing the stationary natural pH-gradient arising under the action of an electric field in an aqueous solution of ampholytes is constructed and investigated. The model is a part of a more general model of the isoelectrofocusing process. Investigation is based on the approximation of a weak solution by the piecewise continuous non-smooth functions. The method can be used for solving classes of problems for ordinary differential equations with a small parameter at the highest derivatives and the turning points.

1. Introduction

This paper is devoted to the mathematical modelling of the isoelectrofocusing (IEF) and the studying of the natural pH-gradient creation in aqueous solution of an amphoteric substance. We expect to investigate the onset of a piecewise constant pH-gradients at large values of voltage or electric current density, so-called anomalous regimes.

IEF is a method of fractionation of multicomponent mixtures (proteins, peptides and amino acids) into individual components with the help of an electric field in a medium with non-uniform pH distribution. The heart of the IEF method is the amphoteric properties of substances. In other words, amino acid, proteins and peptides have both acid and the base properties. At pH = pI, where pI is so-called isoelectric point, the electrophoretic mobility of substance equals zero. pI is the individual characteristic of amphoteric substance.

In particular, almost all amino acids have various isoelectric points. This allows us to identify them on pI values. In the presence of a pH-gradient in...
electrophoretic chamber, components of the mixture move under the action of the external electric field until their electrophoretic mobility is equal to zero. As a result of their movement in the electrophoretic chamber, stationary distribution component occurs in accordance with individual pI values.

The IEF method, along with the chromatography, the isotachophoresis and the zone electrophoresis, is one of the most demanded methods of mixture fractionation in biology, chemistry and medicine. It is enough to tell that this method was widely used for the Human Genome Project. Resolution of the IEF method, which is the possibility of identification of the large quantity of the mixture component, depends on completeness of the information about pH-gradient.

There are various ways to create pH-gradient in solution: creation of the artificial gradients with the help of the special, so-called, buffer solution; creation of the immobilized gradients with the help of the organization of rigid chemical structures; creation of the natural gradients arising in solution as a result of a mixture components self-organization (for more details, see [1–6]).

The natural pH-gradients are the most attractive from the point of view of simplicity of application. These gradients were discovered by [7–10], first theoretically and then experimentally. For a long time, it was assumed that the natural pH-gradients, more precisely a spatial distribution of pH, are linear or, at least, are close to linear. The distribution of substances in solution is close to a Gaussian distribution. However, in 2000–2006 (see [11–18]) with the help of numerical simulation of the non-stationary problem, it was revealed that the natural pH-gradients at large intensity of the external electric field in the stationary mode have a step function profile and the distribution of concentration close to rectangular profiles. These results were partially confirmed by experiments. The theoretical explanation of the observed phenomenon was presented in [19], where the rough asymptotic formulae describing step function pH were obtained. Further, more exact relations were given, in particular, in [20].

From the mathematical point of view, the modelling of the stationary natural pH-gradients problem is reduced to the solution of the ordinary differential equations (ODEs) for distribution of concentration, under some algebraic constraint and integral conditions. At large intensity of an electric field (or large density of an electric current), the system of the equations is stiff: ODEs have the small parameter at the highest derivatives and have the turning points. Numerical integration of this problem also becomes complicated, because solutions for separate concentrations are focused in some regions of the integration interval and exponentially decrease outside these regions.

In this paper, the approximate method based on approximation of the weak solution by piecewise continuous functions is developed. The various approximations of the solution are presented and the error estimates are given. This method can be used for the solution of classes of problem with a small parameter at the highest derivatives and a large number of turning points.

The paper is organized as follows. In §2, the general equations of electrophoresis are described. In §3, the basic stationary equations governing the IEF process and pH-gradient are described. In §4, the weak formulation of the original problem is given. In §§5 and 6, the piecewise-smooth approximation of weak solutions, the choice of the approximating functions, the algorithm for the approximation of weak solutions and examples of approximation are presented. In §7, the other method of selecting the approximating functions is given. In §8, the weak solutions approximation at moderate parameters are demonstrated. Appendix A contains the method of the integral asymptotic evaluation.

2. General equations

The general non-stationary equations (in dimensionless variables) describing the process of natural pH-gradient creation in multicomponent chemically active media have the following form
(see [1,2,19,21,22]):

\[ \partial_t a_k + \text{div } i_k = 0, \quad i_k = -\varepsilon \mu_k \nabla a_k + \mu_k c_k(\psi) a_k E, \quad k = 1, \ldots, n, \]  

(2.1)

\[ \sum_{k=1}^{n} c_k(\psi) a_k = 0 \]  

(2.2)

and

\[ j = \sum_{k=1}^{n} (-\varepsilon \mu_k \nabla c_k(\psi) a_k) + \mu_k a_k(\psi) a_k E, \quad \text{div } j = 0, \]  

(2.3)

where \( a_k, i_k \) are the analytical concentration and the flux density of the components, \( E \) is the intensity of the external electric field, \( j \) is the density of the electric current, \( \psi \) is the acidity function of the mixture, \( \mu_k c_k(\psi), \mu_k \delta_k > 0, \varepsilon \mu_k \) are the electrophoretic mobility, partial conductivity, characteristic mobility and diffusion coefficient of the components.

The \( \psi \)-function used in chemistry is connected with concentration of hydrogen ions and acidity function \( \psi \) by relations

\[ \text{pH} = -\log[H^+], \quad [H^+] = K_w e^{\psi}, \quad \text{pH} = -\log K_w - \psi \log e, \]

where \([H^+]\) is the concentration of hydrogen ions \((\text{mol l}^{-1})\), \( K_w = 10^{-7} \text{mol}^{-1} \) is the autodissociation constant of water (ion product for water is \( K_w^2 = 10^{-14} \text{mol}^2 \text{l}^{-2} \)).

Equations (2.1) are the usual diffusion equations with transport under action of an electric field. The algebraic equation (2.2) is the electroneutrality condition. Equation (2.3) is the general Ohm’s law. To close the equations system (2.1)-(2.3), we define the dependence of electrophoretic mobility and partial conductivity on \( \psi \), i.e. functions \( c_k = c_k(\psi), \sigma_k = \sigma_k(\psi) \).

The dissociation reactions for the amphoteric substances mixture have the following form [1,2,19,22]

\[ \text{H}^+ \text{R} \rightleftharpoons R_0^+ + \text{H}^+, \quad \text{R}_0^+ \rightleftharpoons A_i + \text{H}^+. \]

Here, \( R_0^+ \) is zwitterion (‘neutral’ ion), \( A_i \) and \( B_i \) are the dissociation constants for acid (\( R_i^- \)) and base (\( \text{H}^+ \text{R} \)) groups, \( \text{H}^+ \) is the hydrogen ion. For example, for amino acid \( \text{NH}_3^+ \text{RCOO}^- \), where \( \text{NH}_3^+ \) is the amino group, \( \text{R} \) is amino acid residue, \( \text{COO}^- \) is the carboxyl group, we have \( \text{H}^+ \text{R} \rightleftharpoons \text{NH}_3^+ \text{RCOO}^{-} \), \( \text{R}_0^+ \rightleftharpoons \text{NH}_2^+ \text{RCOO}^{-} \).

The specified reactions proceed almost instantly and balance conditions of this reactions allow determination of the dependence of the electrophoretic mobility and the partial conductivity on the acidity function \( \psi \) [1,21]

\[ c_i(\psi) = \frac{\sinh(\psi - \psi_i)}{\cosh(\psi - \psi_i) + \delta_i}, \quad \sigma_i(\psi) = \frac{\cosh(\psi - \psi_i)}{\cosh(\psi - \psi_i) + \delta_i}, \]  

(2.4)

where \( \delta_i > 0 \) is the dimensionless parameter, \( \psi_i \) is the isoelectric point (electricphoretic mobility \( \mu_i c_i \) is equal to zero at \( \psi = \psi_i \), i.e. \( \mu_i c_i(\psi_i) = 0 \)).

Note the important role of the electroneutrality condition for the description of transport process in chemically active media. The algebraic equation (2.2) defines the function \( \psi \). This equation is the instant regulator of the process. Permutations of the component concentrations \( a_k \) lead to change of acidity function \( \psi \). In turn, the kinetic coefficients of \( c_k(\psi), \sigma_k(\psi) \) have influence on transport of the component \( a_k \).

Finally, we specify connection between dimensional and dimensionless variables

\[ \tilde{x} = x L_s, \quad \tilde{t} = \frac{L_s t}{E_s \mu_s}, \quad \tilde{a}_k = a_k C_s, \quad \tilde{E} = EE_s, \quad \tilde{j} = jF_s C_s E_s \mu_s, \quad \varepsilon = \frac{R_s T_s}{F_s E_s L_s}. \]  

(2.5)

Here, \( L_s, t_s, E_s, C_s \) are the characteristic length, time, intensity of the electric field and analytical concentration; \( \mu_s \) is the characteristic mobility; \( F_s \approx 96485.34 \text{C} \cdot \text{mol}^{-1} \) is the Faraday’s number, \( R_s \approx 8.314462 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \) is the universal gas constant, \( T_s \) is the absolute temperature of the
mixture. In practice of IEF, the voltage $E_\ast L_\ast$ changes usually from 1 to 10 kV, and temperature is $T_\ast \approx 293$ K. In this case, parameter $\varepsilon$ changes from $2.5 \cdot 10^{-5}$ to $2.5 \cdot 10^{-6}$.

3. Stationary problem

We formulate the problem of determining the stationary natural pH-gradient in the one-dimensional case. The one-dimensional case is the most popular, because usually the long cylindrical electrophoretic chamber (e.g. capillars) is used for IEF. In other cases, for IEF, the flat thin plates are used for which the characteristic size in the direction of an electric field action is much larger than other plate sizes [3,4]. Information about stationary pH-gradient is most important for interpretation of experimental results. Of course, to obtain the stationary solution of the equations (2.1)–(2.4), the numerical integration of the non-stationary problem can be used (see [11,12]). Such a method is good because it allows the dynamics of the process to be traced. However, for large number of mixture components, the numerical integration of the non-stationary problem requires a long time. It is obvious that instead of using the numerical integration of the non-stationary problem it is more efficient to solve the stationary problem directly.

We require the impermeability condition on the boundary of the electrophoretic chamber:

$$i_k|_{x=0,L} = 0, \quad k = 1, \ldots, n.$$  \hfill (3.1)

In the one-dimensional case, the solution of the electric current continuity equation (2.3) is $j = j(t)$. For a stationary problem, it is natural to consider

$$j(t) = j_0,$$  \hfill (3.2)

where $j_0$ is the constant electric current density. Strictly speaking, in dimensionless variables, the length of the electrophoretic chamber is $L = 1$ and the electric current density is $j_0 = 1$. However, for interpretation of results it is more convenient to use $L$ and $j_0$.

The problem (2.1)–(2.3) for determining functions $a_k(x), \ k = 1, \ldots, n, \ \psi(x)$ transforms to the following form

$$\frac{1}{\lambda} \frac{d a_k}{d x} = \frac{a_k \theta_k(\psi) \sum_{i=1}^{n} a_i \theta_i'(\psi)}{\sigma \sum_{i=1}^{n} a_i (\theta_i^2(\psi) + \theta_i'(\psi))}, \quad k = 1, \ldots, n, \quad 0 \leq x \leq L,$$  \hfill (3.3)

$$\sum_{k=1}^{n} a_k \theta_k(\psi) = 0,$$  \hfill (3.4)

$$\int_{0}^{L} a_k(x) \, dx = M_k,$$  \hfill (3.5)

$$\sigma = \sum_{i=1}^{n} \mu_i a_i \theta_i'(\psi), \quad \theta_i(\psi) = \frac{\varphi_i'(\psi)}{\varphi_i(\psi)}, \quad \varphi_i(\psi) = \cosh(\psi - \psi_i) + \delta_i$$  \hfill (3.6)

and

$$\lambda = \frac{j_0}{\varepsilon},$$  \hfill (3.7)

where $M_k$ is the quantity of $a_k$ on the interval $[0, L]$, $\lambda$ is the parameter.

Note that dimensionless parameter $\lambda$ plays a central role in our investigation. This parameter is proportional to the voltage $E_\ast L_\ast$, see equations (2.5).

The additional conditions (3.5) are consequences of the mass conservation law. We add these conditions, because conditions (3.1) are not enough to solve the stationary problem.

The detailed description of transformation from the equations (2.1)–(2.3) to the equations (3.3)–(3.6) is contained in [19,20]. Here, we mention only that for such transformation it is enough to present the equation (2.3) in the form $j = \sigma (E - \varepsilon \psi')$ and then exclude $(E - \varepsilon \psi')$ from the equations.
The system (3.3)–(3.6) has an integral which one can obtain by the summation of all
equations (3.3) and taking into account (3.4)
\[ \sum_{i=1}^{n} a_i = a_0 \equiv L^{-1} \sum_{i=1}^{n} M_i, \quad (3.8) \]
where the constant \( a_0 \) is defined using (3.5).

We note that \( \psi(x) \) is a monotone decreasing function. This property is easy to validate
by differentiating the electroneutrality equation (3.4) under the assumption of a sufficient
smoothness:
\[ \frac{d\psi}{dx} = -\frac{\lambda}{\sigma} \sum_{i=1}^{n} a_i (\theta_i^2(\psi) + \theta_i'(\psi)) < 0. \quad (3.9) \]
The negativity of the derivative follows from the relations (3.6). In fact, the functions \( a_k(x) \) are not
equal to zero simultaneously and \( \theta_i^2(\psi) + \theta_i'(\psi) > 0 \).

As has been already mentioned, the solution of (3.3)–(3.8) for large values of the parameter \( \lambda \)
difficulties owing to the presence of a small parameter \( 1/\lambda \) at the highest derivatives and
the turning points at \( \psi = \psi_i \). Preliminary numerical analysis shows that for large values of \( \lambda \) the
concentrations are localized in some segments of the interval \([0, L]\) (each in its own segment) and
are exponentially small outside these segments. It means that when used for numerical
integration, for example, the shooting method [23] is complicated. In fact, the initial conditions at
one of the ends of the segment are of the order \( O(\exp^{-\lambda}) \) and for their determination a very detailed
initial approximation is required (see [19,20,22,24–26]). However, for example, in [19], it is shown
that the asymptotic solutions tend to some generalized functions: the profile of the concentrations \( a_k(x) \) has almost rectangular shape. Such behaviour of the solutions, as will be shown below,
allows us to construct a continuous piecewise-smooth approximation of solutions, refusing from
the function smoothness and going to the weak formulation of the problem.

The main goal of this paper is the construction of the piecewise continuous approximation of a
weak solution of the problem (3.3)–(3.8) for given parameters \( \mu_k, \delta_k, M_k, k = 1, \ldots, n \), which have
order \( O(1) \), and the large parameter \( \lambda \gg 1 \).

4. The weak formulation of the stationary problem

As usual, we call the weak solution of the problem (3.3)–(3.8) the functions \( a_k(x), k = 1, \ldots, n, \psi(x) \)
satisfying the equations
\[ I_k \equiv \int_0^L \left( a_k \frac{dV_k}{dx} + \frac{\lambda a_k \theta_k(\psi) \sum_{i=1}^{n} a_i \theta_i'(\psi)}{\sigma \sum_{i=1}^{n} a_i (\theta_i^2(\psi) + \theta_i'(\psi))} V_k \right) \, dx = 0, \quad V_k(0) = 0, \quad V_k(L) = 0, \quad (4.1) \]

\[ \sum_{k=1}^{n} a_k \theta_k(\psi) = 0, \quad (4.2) \]

\[ \int_0^L a_k(x) \, dx = M_k, \quad (4.3) \]

and
\[ \sum_{i=1}^{n} a_i = a_0 \equiv L^{-1} \sum_{i=1}^{n} M_i, \quad \sigma = \sum_{i=1}^{n} \mu_i \theta_i'(\psi), \quad \theta_i(\psi) = \frac{\psi_i'(\psi)}{\varphi_i(\psi)}, \quad \varphi_i(\psi) = \cosh(\psi - \psi_i) + \delta_i. \quad (4.4) \]

Here, \( V_k(x) \) are arbitrary sufficiently smooth functions satisfying the natural boundary conditions.

Note that the relations (3.4) and (3.5), i.e. the electroneutrality condition and conditions of
the mass conservation, remain the same. The relation (4.4), i.e. the integral (3.8) of the system
(3.3), is not the implementation of the system (4.1). For the weak formulation of the problem the
relation (4.4), in principle, can be discarded. The most reasonable, of course, is to assume that the condition (4.4) holds, thus preserving some additional properties of the original problem (3.3)–(3.8). Naturally, in the case when the functions $a_k(x), k = 1, \ldots, n$, $\psi(x)$ are sufficiently smooth, the weak solution of (4.1)–(4.4) will be the strong solution of the original problem (3.3)–(3.8).

5. Piecewise-smooth approximation of weak solutions

We define the partition of interval $[0, L]$ by the set of points (figure 1)

$$0 = x_1 < y_1 < x_2 < y_2 < \cdots < y_{k-1} < x_k < y_k < x_{k+1} < \cdots < y_{n-1} < x_n < y_n = L.$$ 

The method of selection of the points $x_k, y_k$ is specified in §6.

We choose the functions $a_k$ satisfying the following properties

$$\text{supp } a_k = [x_k - h_k, y_k + h_{k+1}], \quad k = 1, \ldots, n;$$

$$\text{supp } a_{k-1} \cap \text{supp } a_k = [x_k - h_k, x_k]$$

and

$$h_1 = 0, \quad h_k = x_k - y_{k-1}, \quad k = 2, \ldots, n, \quad h_{n+1} = 0.$$ (5.1)

Note that the assumption about finite support of functions $a_k$, of course, is heuristic. However, we operate in the usual way, trying to construct an approximation suitable for numerical methods, for example, the finite-elements method. Below, we prove that this approximation is possible, and we give appropriate estimations of solutions.

To solve problem (4.1)–(4.4), we use approximation (figure 1)

$$a_k(x) = \begin{cases} 0, & x \leq x_k - h_k = y_{k-1}, \\ \tilde{a}_k(x), & x_k - h_k = y_{k-1} \leq x \leq x_k, \\ a_0, & x_k \leq x \leq y_k, \\ \tilde{\tilde{a}}_k(x), & y_k \leq x \leq x_{k+1} = y_k + h_{k+1}, \\ 0, & y_k + h_{k+1} = x_{k+1} \leq x \end{cases}$$

and

$$\psi(x) = \begin{cases} \psi^{(k)}(x), & x_k - h_k = y_{k-1} \leq x \leq x_k, \\ \psi_k, & x_k \leq x \leq y_k, \\ \psi^{(k+1)}(x), & y_k \leq x \leq x_{k+1} = y_k + h_{k+1}. \end{cases}$$ (5.2) (5.3)

Here, $\tilde{a}_k(x)$, $\tilde{\tilde{a}}_k(x)$, $\psi^{(k)}(x)$, $\psi^{(k+1)}(x)$ are sufficiently smooth functions (in appropriate intervals) satisfying the continuity conditions

$$\tilde{a}_k(x_k - h_k) = 0, \quad \tilde{\tilde{a}}_k(x_k) = a_0, \quad \tilde{\tilde{a}}_k(y_k) = a_0, \quad \tilde{\tilde{a}}_k(y_k + h_{k+1}) = 0$$ (5.4)

and

$$\psi^{(k)}(x_k - h_k) = \psi_{k-1}, \quad \psi^{(k)}(x_k) = \psi_k$$

and

$$\psi^{(k+1)}(y_k) = \psi_k, \quad \psi^{(k+1)}(y_k + h_{k+1}) = \psi_{k+1}.$$ (5.5)

(a) The reduction of the integrals $I_k$

We introduce the notation for integrand functions

$$G_k(a; \psi) \equiv a_k \frac{dV_k}{dx} + \frac{\lambda a_k a_k(\psi) \sum_{i=1}^{n} a_i a_i(\psi)}{\sigma(a; \psi) \sum_{i=1}^{n} a_i a_i(\psi)} V_k, \quad \sigma(a; \psi) \equiv \sum_{i=1}^{n} \mu_i a_i a_i(\psi)$$ (5.6)

and

$$F_k(a; \psi) \equiv -\frac{d\mu_k}{dx} + \frac{\lambda a_k a_k(\psi) \sum_{i=1}^{n} a_i a_i(\psi)}{\sigma(a; \psi) \sum_{i=1}^{n} a_i a_i(\psi)} = a = (a_1, a_2, \ldots, a_n).$$ (5.7)
The choice of \( a_k(x), \psi(x) \) in the form (5.2) and (5.3) allows to write integrals (4.1) in the form

\[
I_k = \int_{x_k-h_k}^{x_k} G_k(a; \psi^{(k)}) \, dx + \int_{x_k}^{y_k} \frac{dV_k}{dx} + \int_{y_k}^{y_k+h_k} G_k(a; \psi^{(k+1)}) \, dx.
\]

Here, we take into account the relations \( \theta_k(\psi_k) = 0 \).

The smoothness of the functions \( \bar{a}_k, \bar{a}_{k-1}, \psi_k, \psi_k^{(k+1)} \) allows use of integration by parts. Taking into account (5.4), we obtain

\[
I_k = \int_{x_k-h_k}^{x_k} F_k(a; \psi^{(k)}) V_k \, dx + \int_{y_k}^{y_k+h_k} F_k(a; \psi^{(k+1)}) V_k \, dx. \tag{5.8}
\]

(b) The choice of the approximating functions

The functions \( a_k(x), k = 1, \ldots, n, \psi(x) \) defined by the relations (5.2) and (5.3) will be the solution of the problem (4.1)–(4.4) if \( I_k \to 0 \) at \( \lambda \to \infty \). Using the special selection of functions \( \psi^{(k)}(x), \bar{a}_k(x), \tilde{a}_k(x) \), we show that \( I_k \to 0 \) at \( \lambda \to \infty \).

We focus only on the first integral of (5.8), i.e. the integral over the interval \([x_k-h_k, x_k]\). For the second integral, all of the arguments remain valid.

It is convenient to change variables

\[ x = x_k - h_k + th_k, \quad 0 \leq t \leq 1, \quad dx = h_k \, dt. \tag{5.9} \]

Then, the first integral (5.8) has the form

\[
I_k^0 = \int_0^1 F_k(t) V_k(x_k - h_k + th_k) h_k \, dt, \tag{5.10}
\]

where (see (5.7))

\[
F_k(t) = F_k(a(t); \psi^{(k)}(t)) = \frac{\lambda a_k \theta_k(\psi^{(k)})}{\alpha(a(t); \psi^{(k)})} \sum_{i=k-1}^{k-1} a_i \theta_i'(\psi^{(k)}) + \theta_i(\psi^{(k)}) \right). \tag{5.11}
\]

We omitted the ‘overline’ symbols, i.e. \( \tilde{a}_k = a_k, \tilde{a}_{k-1} = a_{k-1} \). For functions \( a_m(x_k - h + th), m = k-1, k, \psi^{(k)}(x_k - h + th) \) after substitution (5.9), we use previous notation

\[ a_m(t) = a_m(x_k - h_k + th_k), \psi^{(k)}(t) = \psi^{(k)}(x_k - h_k + th_k). \]

Note conditions (5.1) means that only the functions \( a_{k-1} \) and \( a_k \) are not equal to zero on the interval \([x_k - h_k, x_k]\). We use this fact writing the formula (5.11).
Again, taking into account conditions (5.1), we obtain (4.2) and (4.4) on the interval \([x_k - h_k, x_k]\) as

\[ a_{k-1} + a_k = a_0, \quad \theta_{k-1} a_{k-1} + \theta_k a_k = 0. \quad (5.12) \]

This linear system allows us to easily determine the dependence of the \(a_{k-1}, a_k\) on \(\psi^{(k)}\)

\[ a_{k-1}(t) = \frac{a_0 \theta_k(\psi^{(k)}(t))}{\theta_k(\psi^{(k)}(t)) - \theta_{k-1}(\psi^{(k)}(t))}, \quad a_k(t) = -\frac{a_0 \theta_{k-1}(\psi^{(k)}(t))}{\theta_k(\psi^{(k)}(t)) - \theta_{k-1}(\psi^{(k)}(t))}. \quad (5.13) \]

Substitution of (5.13) into (5.11) and substitution of \(F_k(t)\) into (5.10) shows that the integral \(I^0_k\) is a nonlinear functional \(I^0_k = I^0_k[\psi^{(k)}]\). It means that to obtain the required result: \(I^0_k[\psi^{(k)}] \to 0\) as \(\lambda \to \infty\), it is enough to choose only function \(\psi^{(k)}(t)\).

The function \(\psi^{(k)}(t)\) must be a monotonically decreasing function satisfying the conditions (5.5)

\[ \psi^{(k)}(t)|_{t=0} = \psi_{k-1}, \quad \psi^{(k)}(t)|_{t=1} = \psi_k, \quad \psi'(t) < 0. \quad (5.14) \]

The requirement that \(\psi^{(k)}(t)\) is monotonically decreasing is dictated by the monotonicity condition of the respective function for the original problem (see (3.9)).

Note that conditions (5.14) automatically imply the conditions (5.4)

\[ a_{k-1}(t)|_{t=0} = a_0, \quad a_{k-1}(t)|_{t=1} = 0, \quad a_k(t)|_{t=0} = 0, \quad a_k(t)|_{t=1} = a_0. \quad (5.15) \]

The natural constraints on the choice of the function \(\psi^{(k)}(t)\) are imposed by the condition of the existence of integral \(I^0_k\) and the integrals (4.3).

Unfortunately, we cannot choose a function \(\psi^{(k)}(t)\), so that the condition \(F_k(t) = 0\) will be valid. Analysis shows that the requirement of \(F_k(t) = 0\) is equivalent to the equation (3.9). In this case, the integrals (4.3) have singularities.

(c) Evaluation of integrals \(I^0_k\)

We show that the appropriate choice of \(\psi^{(k)}(t)\) allows us to obtain the estimate \(h_k = O(\lambda^{-1})\) and \(I^0_k = O(\lambda^{-1})\) at \(\lambda \to \infty\).

Using infinite differentiability of functions \(V_k\) and the Taylor series expansion in a neighbourhood of some point \(t = t_0\) (or for old variables \(\bar{x} = x_k - h_k + t_0 h_k\)) for the integral (5.10), we have

\[ I^0_k = h_k V_k(\bar{x}) \int_0^1 F_k(t) \, dt + h_k^2 \frac{dV_k(\bar{x})}{dx} \int_0^1 \int_0^1 F_k(t - t_0) \, dt \, dt + \cdots. \quad (5.16) \]

The rough estimate of the function \(F_k(t)\) is \(F_k(t) = O(\lambda)\). It means that the first term in (5.16) has the order \(O(h_k \lambda)\) and is not small when \(\lambda \to 0\) even if \(h_k = O(\lambda^{-1})\).

To delete the first term in (5.16), we require

\[ \int_0^1 F_k(t) \, dt = 0. \quad (5.17) \]

Then

\[ I^0_k = h_k^2 \frac{dV_k(\bar{x})}{dx} \int_0^1 \int_0^1 F_k(t - t_0) \, dt \, dt + \cdots \quad (5.18) \]

Using the requirements (5.17) and (5.11), we obtain

\[ \frac{1}{h_k} \int_0^1 \frac{da_k(t)}{dt} \, dt = \lambda \int_0^1 \Phi_k(t) \, dt, \quad (5.19) \]

where

\[ \Phi_k(t) = \frac{a_k(t) \theta_k(\psi^{(k)}(t)) \sum_{i=k-1}^k a_i(t) \theta'_i(\psi^{(k)}(t))}{\sigma(a(t); \psi^{(k)}(t)) \sum_{i=k-1}^k a_i(t) \theta'_i(\psi^{(k)}(t)) + \theta'_i(\psi^{(k)}(t))}. \quad (5.20) \]
Finally, taking into account (5.15), we rewrite (5.19) as
\[
h_k = \frac{a_0}{\lambda \int_0^1 \Phi_k(t) \, dt}.
\] (5.21)

Thus, the special choice of the monotonically decreasing function \( \psi^{(k)}(x) \) satisfying (5.14) implies the relations
\[
\int_0^1 \Phi_k(t) \, dt = O(1), \quad h_k \int_0^1 a_k(t) \, dt = O(1) \quad \text{and} \quad h_k = O(\lambda^{-1}), \quad I_k^0 = O(\lambda^{-1}).
\]

The last estimates mean that the approximation (5.2) and (5.3) is a weak solution of (4.1)–(4.4) at \( \lambda \to \infty \).

6. The algorithm for the approximation of weak solutions

Here, we present a simple algorithm for constructing an approximation (5.2) and (5.3). We assume that the parameters \( \psi_k, \delta_k, \mu_k, M_k, k = 1, \ldots, n, L \) are given, \( a_0 \) is defined by (3.8), and the parameter \( \lambda \) is large enough.

1. On each unknown interval \([x_k - h_k, x_k] \), \( k = 2, \ldots, n \), we choose some monotonically decreasing function \( \psi^{(k)}(t) \) satisfying the conditions (5.14). According to the formulae (5.13), we define the function \( a_{k-1}(t), a_k(t), k = 2, \ldots, n \) on each interval \([x_k - h_k, x_k] \). Using equations (5.20) and (5.21), we calculate the lengths of segments \( h_k, k = 2, \ldots, n \).

2. On each interval \([x_k - h_k, x_k] \), we calculate the \( m_{k-1}^{(k)}, m_k^{(k)} \):
\[
m_{k-1}^{(k)} = h_k \int_0^1 a_{k-1}(t) \, dt, \quad m_k^{(k)} = h_k \int_0^1 a_k(t) \, dt, \quad k = 2, \ldots, n. \] (6.1)

3. Taking into account the conditions (4.3), we determine
\[
y_{k-1} = x_{k-1} + a_0^{-1}(m_{k-1} - m_{k-1}^{(k)} - m_k^{(k)}), \quad x_k = y_{k-1} + h_k, \quad k = 2, \ldots, n,
\]
\[
m_1^{(1)} = 0, \quad x_1 = 0, \quad y_n = L.
\]

Note the violation of inequalities
\[
m_{k-1} - m_{k-1}^{(k)} - m_k^{(k)} > 0, \quad k = 2, \ldots, n
\]
means that the parameter \( \lambda \) is not chosen large enough.

(a) Examples of approximation

We restrict the consideration by the case when
\[
\mu_k = \mu, \quad \delta_k = \delta, \quad k = 1, \ldots, n. \] (6.2)

It is easy to obtain
\[
\int_0^1 \Phi_k(t) \, dt = -\frac{1}{\mu} \int_0^1 \varphi'_{k-1} \varphi'_k | \psi = \psi^{(k)}(t) \rangle \, dt
\]
or
\[
\int_0^1 \Phi_k(t) \, dt = -\frac{1}{\mu} \int_{\psi_1}^{\psi_k} \varphi'_{k-1}(\psi) \varphi'_k(\psi) - \varphi'_{k-1}(\psi) \varphi''_k(\psi) \, d\psi \psi^{(k)}(t) / dt | \psi = t(\psi^{(k)}) \rangle \, d\psi, \] (6.3)

where \( t = t(\psi) \) is the inverse function of the function \( \psi = \psi^{(k)}(t) \). The inverse function exists, because \( \psi^{(k)}(t) \) is monotonic function.
(i) The linear function

The simplest choice of \( \psi^{(k)}(t) \) though perhaps, not the best, is the linear function

\[
\psi^{(k)}(t) = (1 - t)\psi_{k-1} + t\psi_k = \psi_{k-1} - t\Delta\psi_k, \quad \Delta\psi_k = \psi_{k-1} - \psi_k > 0. \tag{6.4}
\]

In this case, the integral in (6.3) is calculated easily. Using (5.21), we obtain

\[
h_k = \frac{2a_0\mu \Delta\psi_k \sinh\Delta\psi_k}{\lambda(\Delta\psi_k \cosh\Delta\psi_k - \sinh\Delta\psi_k)}. \tag{6.5}
\]

Using (6.2) for integrals in (6.1), we obtain

\[
m^{(k)}_{k-1} = m^{(k)}_k = \frac{1}{2}h_ka_0, \quad k = 2, \ldots, n. \tag{6.6}
\]

Note that the formula (6.6) will be valid always, if \( \psi^{(k)}(t) \) is odd with respect to \( t = 1/2 \).

The disadvantage of the choice \( \psi^{(k)}(t) \) as the linear function, in particular, is the presence of large magnitude discontinuities of the derivative at the points \( x_k, y_k \). In the case of (6.4), the gap derivative, for example, at the point \( x = x_k \) is

\[
\psi'(x_k + 0) - \psi'(x_k - 0) = h_k^{-1}\Delta\psi_k = O(\lambda), \quad \Delta\psi_k = O(1). \tag{6.7}
\]

(ii) The nonlinear function

Other choice of \( \psi^{(k)}(t) \) is a nonlinear function, for example,

\[
\psi^{(k)}(t) = \frac{\psi_k + \psi_{k-1}}{2} + \frac{\psi_k - \psi_{k-1}}{2} \tanh \beta_k(2t - 1), \quad \psi^{(k)}(0) = \psi_{k-1}, \quad \psi^{(k)}(1) = \psi_k, \tag{6.8}
\]

where \( \beta_k > 0 \) are some parameters.

In this case, the gap derivative is (compare with (6.7))

\[
\psi'(x_k + 0) - \psi'(x_k - 0) = \frac{2\beta_k \Delta\psi_k}{h_k \sinh 2\beta_k} < \frac{\Delta\psi_k}{h_k}, \quad \Delta\psi_k = \psi_{k-1} - \psi_k > 0. \tag{6.9}
\]

The value of \( h_k \) is determined by the formula (5.21)

\[
h_k = \frac{a_0}{\lambda} \int_0^1 \Phi_k(t) \, dt,
\]

where

\[
\int_0^1 \Phi_k(t) \, dt = \frac{\tanh \beta_k}{\mu\beta_k \Delta\psi_k \sinh \Delta\psi_k} \int_{\psi_{k-1}}^{\psi_k} \frac{\sinh(\psi - \psi_k) \sinh(\psi - \psi_{k-1}) \, d\psi}{1 - [(2\psi - \psi_{k-1} - \psi_k)/\Delta\psi_k]^2 \tanh^2 \beta_k}.
\]

Values of \( m^{(k)}_{k-1} \) and \( m^{(k)}_k \) are again determined by the formula (6.6).

(b) The generalized solution

Note that the result of the approximation only weakly depends on the type of function \( \psi^{(k)} \). In other words, \( h_k \to 0 \) at \( \lambda \to \infty \) for almost all monotonic decreasing functions \( \psi^{(k)} \) which satisfy (5.5). Calculating the limit as \( \lambda \) tends to infinity we get \( h_k = 0 \), and the formulae

\[
a_k(x) = \begin{cases} 0, & x \leq x_k, \\ a_0, & x_k \leq x \leq y_k, \\ \psi(x) = \psi_k, & x_k \leq x \leq y_k, \quad k = 1, \ldots, n \end{cases} \tag{6.10}
\]

give the generalized solution of the original problem.

Although, almost all approximations constructed in accordance with the algorithm give (6.10), the results for moderate values of \( \lambda \) can be used to construct approximate weak solutions.
7. Another way to select the approximating function

Here, we describe an approximation that is different from (5.2) and (5.3). For the sake of simplicity, we restrict the consideration to the case when the parameters satisfy (6.2).

We define the partition of interval \([0, L]\) by the set of points (figure 2)

\[
0 = X_1 < X_2 < \cdots < X_{k-1} < X_k < X_{k+1} < \cdots < X_n < X_n = L.
\]

To construct the solution of problem (4.1)–(4.4), we use the approximation (figure 2):

\[
a_k(x) = \begin{cases} 
0, & x \leq X_{k-1}, \\
\tilde{a}_k(x), & X_{k-1} \leq x \leq X_k, \\
\tilde{a}_k(x), & X_k \leq x \leq X_{k+1}, \\
0, & X_{k+1} < x 
\end{cases}, \quad k = 1, \ldots, n, \tag{7.1}
\]

and

\[
\psi(x) = \psi^{(k)}(x), \quad X_{k-1} \leq x \leq X_k, \quad k = 2, \ldots, n. \tag{7.2}
\]

Here, as before, \(\tilde{a}_k(x), \tilde{a}_k(x), \psi^{(k)}(x), \psi^{(k+1)}(x)\) are functions which are smooth at appropriate intervals and satisfy to continuity conditions (compare with (5.4), (5.5)):

\[
\tilde{a}_k(X_{k-1}) = 0, \quad \tilde{a}_k(X_k) = a_0, \quad \tilde{a}_k(X_k) = a_0, \quad \tilde{a}_k(X_{k+1}) = 0 \tag{7.3}
\]

and

\[
\psi^{(k)}(X_{k-1}) = \psi_{k-1}, \quad \psi^{(k)}(X_k) = \psi_k, \quad \psi^{(k+1)}(X_k) = \psi_{k+1}, \quad \psi^{(k+1)}(X_{k+1}) = \psi_{k+1}. \tag{7.4}
\]

Further, we repeat almost verbatim the reasoning of §5a–c. We consider the integrals on the interval \([X_{k-1}, X_k]\) (symbols ‘overline’ are omitted)

\[
Q_k = \int_{X_{k-1}}^{X_k} F_k(a; \psi^{(k)}) V_k \, dx, \tag{7.5}
\]

where \(F_k(a; \psi^{(k)})\) is defined by (5.7) and has the form (see (5.11))

\[
F_k(a; \psi^{(k)}) = -\frac{d a_k}{dx} + \frac{\lambda a_k \theta_k(\psi^{(k)})}{\sigma(a; \psi^{(k)})} \sum_{i=k-1}^{k} a_i \theta_i'(\psi^{(k)}) + \frac{\lambda \sum_{i=k-1}^{k} a_i \theta_i^2(\psi^{(k)})}{\sigma(a; \psi^{(k)})} + \sum_{i=k-1}^{k} a_i \theta_i' \theta_i(\psi^{(k)}) - \theta_k(\psi^{(k)}) \tag{7.6}
\]

As before, the concentration \(a_k\) on the interval \([X_{k-1}, X_k]\) is determined by the relations (5.13)

\[
a_k(t) = \frac{a_0 \theta_k(\psi^{(k)})}{\theta_k(\psi^{(k)}) - \theta_{k-1}(\psi^{(k)})}, \quad a_k(t) = \frac{a_0 \theta_{k-1}(\psi^{(k)})}{\theta_k(\psi^{(k)}) - \theta_{k-1}(\psi^{(k)})}. \tag{7.7}
\]

We assume that \(\psi^{(k)}(x)\) is defined by the differential equation

\[
\frac{d \psi^{(k)}}{dx} = -\frac{\lambda \sum_{i=k-1}^{k} a_i \theta_i^2(\psi^{(k)})}{\sigma(a; \psi^{(k)})} + \frac{\lambda \sum_{i=k-1}^{k} a_i \theta_i' \theta_i(\psi^{(k)})}{\sigma(a; \psi^{(k)})} - \omega_k^2 < 0, \tag{7.8}
\]

where \(\omega_k^2 > 0\) is some parameter.

For small \(\omega_k^2\), the equation (7.8) is a perturbation of the equation (3.9) for the original problem (3.3)–(3.8). Choice of \(\omega_k^2 = 0\), unfortunately, is impossible. It is easy to validate that if the approximation of (7.1) and (7.7) is chosen then integrals in (4.3) contain singularity, as

\[
\sum_{i=k-1}^{k} a_i \theta_i^2(\psi^{(k)}) = 0 \quad \text{at } \psi^{(k)} = \psi_{k-1} \quad \text{or } \psi^{(k)} = \psi_k. \tag{7.9}
\]

We add the condition (7.4) to the equation (7.8). One of these conditions is required for the Cauchy problem, and the other one determines the difference \((X_k - X_{k-1})\).

Taking into account that functions \(a_{k-1}\) and \(a_k\) depend only on the \(\psi^{(k)}\) we change the derivative \(d a_k/dx\) by \(d a_k/d\psi^{(k)} \cdot d \psi^{(k)}/dx\) in the formula (7.6). Differentiating the system (5.12)

\[
\frac{d a_k}{dx} = -\frac{\lambda \sum_{i=k-1}^{k} a_i \theta_i(\psi^{(k)})}{\sigma(a; \psi^{(k)})} + \frac{\lambda \sum_{i=k-1}^{k} a_i \theta_i' \theta_i(\psi^{(k)})}{\sigma(a; \psi^{(k)})} - \omega_k^2 < 0, \tag{7.8}
\]
with respect to $\psi$ and taking into account (7.7), we obtain the derivative $d\psi_k/dx$ from (7.8) after simple transformations, we have

$$F_k(a; \psi^{(k)}) = -\frac{\omega^2}{2} \sum_{i=k-1}^{k} a_i \theta'_i(\psi^{(k)})$$ (7.10)

(a) The choice of the parameter $\omega^2_k$

It is possible to choose the parameter $\omega^2_k \rightarrow 0$ at $\lambda \rightarrow \infty$. Then, the estimation $F_k(a; \psi^{(k)}) = O(\omega^2_k)$ means that the approximation (7.1)–(7.4), (7.7) and the solution $\psi^{(k)}$ of the differential equation (7.8) are the weak solution of (4.1)–(4.4).

We restrict the consideration by the case

$$\psi_{k-1} - \psi_k = \Delta \psi, \quad k = 2, \ldots, n, \quad M_1 = M_n = \frac{1}{2}M$$
and

$$M_k = M, \quad k = 2, \ldots, n - 1, \quad \mu_k = \mu, \quad \delta_k = \delta, \quad k = 1, \ldots, n.$$ (7.11)

We introduce the notation for the right side of the differential equation (7.8)

$$R_k(\psi^{(k)}) = \frac{\sum_{i=k-1}^{k} a_i \theta_i(\psi^{(k)})}{\sigma(a; \psi^{(k)}) \sum_{i=k-1}^{k} a_i (\theta_i(\psi^{(k)}) + \theta_i'(\psi^{(k)}))}.$$ (7.12)

Then, the length of the interval $[X_{k-1}, X_k]$ has the form

$$H_k = X_k - X_{k-1} = \int_{X_{k-1}}^{X_k} dx = \int_{\psi_{k-1}}^{\psi_k} \frac{d\psi}{\psi'(x)} = -\int_{\psi_{k-1}}^{\psi_k} \frac{d\psi}{\lambda R_k(\psi) + \omega^2_k}.$$ (7.13)

It is easy to validate that in the case (7.11) all the parameters $\omega^2_k = \omega^2$ and the distribution of the concentrations of $a_k(x)$, $\psi^{(k)}(x)$ and $R_k(\psi^{(k)})$ are symmetric functions with respect to the midpoint of a segment $[X_{k-1} - X_k]$. The values $X_k$ are defined by relations

$$X_2 - X_1 = \frac{1}{2}H, \quad X_k - X_{k-1} = H, \quad k = 3, \ldots, n - 1, \quad X_n - X_{n-1} = \frac{1}{2}H,$$ (7.14)

where

$$H = \int_{\psi_k}^{\psi_{k-1}} \frac{d\psi}{\lambda R_k(\psi) + \omega^2}.$$ (7.15)

Using the symmetric properties of function $R_k(\psi)$, one can obtain the asymptotic relation as $\omega^2/\lambda \rightarrow 0$ (see detail in appendix A):

$$\frac{1}{2} \lambda H = -\frac{1}{R_k'(\psi_k)} \ln \frac{\omega^2}{R_k(\psi_k)} + \ln W \frac{\omega^2}{R_k'(\psi_k)} + O(\omega^2 \ln \omega^2), \quad \psi_k = \frac{1}{2}(\psi_{k-1} + \psi_k), \quad \omega^2 = \frac{\omega^2}{\lambda},$$

where $W$ is a constant that does not depend on $\lambda$ and $\omega^2_0$. 
Then, we have
\[ \frac{\omega^2}{\lambda} = \lambda W R_k(\psi*) \exp(-\frac{\lambda}{2} H R_k'(\psi_k)) \to 0, \quad |Q_k| = O(\omega^2), \quad \lambda \to \infty. \] (7.15)

This estimate means that the approximation (7.1)–(7.4), (7.7) and (7.8) is a weak solution of the problem.

Note the derivative \( d\psi/dx \) is continuous at the points \( X_k \) when the parameters satisfy (7.11). In the general case, the gap derivatives, obviously, would be equal \( \omega_k^2 - \omega_{k-1}^2 \).

For practical accurate calculations, we should solve equation (7.13) relative to \( \omega^2 \) at given value \( H_k \), which for the case (7.11) is defined by the conditions (see (4.3))

\[ \int_{X_{k-1}}^{X_k} a_k \, dx = \frac{1}{2} a_0 H_k = \frac{1}{2} M_k. \] (7.16)

8. Weak solutions approximation at moderate value of the parameter \( \lambda \)

Despite the fact that the main result for the weak solution of the problem is obtained for \( \lambda \to \infty \), it can be efficiently used at moderate values of the parameter \( \lambda \). In appendix A, the comparison of the numerical solution of the equation (7.13) and asymptotic formula (7.15) is presented.

To illustrate the method of the weak solution construction, we choose the following parameters

\[ \psi_1 = 5, \quad \Delta \psi = 1, \quad n = 11, \quad \mu = 1, \quad \delta = 3, \quad M = 0.1, \quad L = 1, \quad \lambda = 200 \]

and

\[ \mu_k = \mu, \quad \delta_k = \delta, \quad k = 1, \ldots, 11; \quad M_k = M, \quad k = 2, \ldots, 10, \quad M_1 = M_{11} = \frac{1}{2} M. \] (8.1)

Using (7.11), (7.14) and (3.8), we have

\[ H_1 = \cdots = H_{10} = H = 0.1, \quad a_0 = 1. \] (8.2)

At \( \lambda = 200 \), we obtain (see appendix A)

\[ W = 5.968, \quad R_k'(\psi_k) = 1.035, \quad R_k(\psi_k) = 0.227. \]

Using formula (7.15) (or (A 10)), we have

\[ \omega^2 \approx 0.00868. \]

We solve the equation (7.8) with initial condition \( \psi^{(k)}(X_{k-1}) = \psi_{k-1} \) on the interval \([X_{k-1}, X_k]\) and simultaneously determine the concentration \( a_k \) with the help of formulae (7.7).
In figure 3, the results of numerical integration are shown. Note that in the case (8.1) and (8.2) it is enough to solve the initial value problem on any one interval and then to continue solution on subsequent intervals ‘periodically’.

In figure 4, the differences between numerical and weak solutions are demonstrated. Starting from parameters \( \lambda = 30 \), we have a good agreement between the weak solution and the numerical solution of original problem (3.3)–(3.6).

9. Conclusion

The described technique of the weak solutions construction for the original problem is quite specific. Its success is primarily due to the fact that the presence of a small parameter at the highest derivatives and turning points dictates special structure of solution. For large values of the parameter \( \lambda \), the functions \( a_k \) are almost completely concentrated on certain intervals. Moreover, these functions exponentially decrease outside of their own intervals (see (5.1) and §§5 and 7). It allows splitting of a system of \( n \) equations into separate subsystems containing only two equations. However, this involves the additional difficulties. The problem of determination of the acidity function becomes singular. The removing of this singularity is possible by the introduction of some perturbation of the problem (see (7.8) and §7).

One of the most interesting results is the fact that at \( \lambda = \infty \) a generalized solution of the original problem is obtained (see (6.10)). At moderate values of the parameter \( \lambda \), approximation of a weak solution is actually the asymptotic of the original problem solution. Confirmation of this fact is a good coincidence of the weak solution of the problem and the numerical solution of the problem. In more detail, the process of separation is described in [22,26] which give the solution of the non-stationary problem and contain the general IEF theory (see also [24,25]). In particular, figure 5 illustrates the solution of the initial-boundary value problem (2.1)–(2.3). For the calculations, we used the parameters from equations (8.1). These results show that the solution of the non-stationary problem tends (as \( t \to \infty \)) to the solution of the stationary problem considered in §8.

Unfortunately, to give the correct mathematical definition of the term ‘high current density’ is difficult. This is because for various multicomponent mixtures the values of the corresponding high current density depends on the number of components, the composition and concentrations, etc. We can only say that because the parameter values \( \lambda \approx 30 \) our theory is well supported by numerical experiments for real multicomponent mixtures. For example, for a 10 component mixture of amino acids with mobilities \( \mu_k \approx 2 \cdot 10^{-8} \text{ m}^2/(\text{V} \cdot \text{s}) \), \( M_k \approx 0.01 \text{ mol} \), sectional area
Figure 5. The solution of non-stationary problem (2.1)–(2.3) at $\lambda = 200$. The distribution of the concentration as $t = 1, t = 5$, and $t = 40$, see (8.1).

$S_a \approx 10^{-5}$ m$^2$ and length $L_a \approx 0.1$ m$^2$, the value $\lambda \approx 30$ corresponds to voltage $E_sL_a \approx 250$ V and electric current $I_s \approx 7.5$ µA (for detail, see [25]). In [22,24–26], we present the results of calculations for real mixtures. In particular, these results have a good agreement with the results of papers [11–15].

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Appendix A. Asymptotic evaluation of integral (7.13)

Using the symmetric properties of function $R_k(\psi)$, we can obtain

$$
\frac{1}{2} \lambda H_k = \int_{\psi_*}^{\psi_{k-1}} \frac{d\psi}{R_k(\psi) + \omega_0^2}, \quad \omega_0^2 = \frac{\omega^2}{\lambda}, \quad \psi_* = \frac{1}{2} (\psi_k + \psi_{k-1}).
$$

(A 1)

We recall that

$$
R_k(\psi_{k-1}) = 0, \quad R'_k(\psi_{k-1}) < 0, \quad R'_k(\psi_*) = 0, \quad R_k(\psi_*) > 0.
$$

(A 2)

We change variables

$$
R_k(\psi) = \tau, \quad R_k(\psi_*) = \tau_0 > 0, \quad \mathcal{F}(\tau) = \frac{1}{R'_k(\psi)}.
$$

(A 3)

Then, we can rewrite (A 1) in the form of

$$
\frac{1}{2} \lambda H_k = \int_{R_k(\psi_*)=\tau_0}^{R_k(\psi_{k-1})=0} \frac{d\tau}{R'_k(\psi)(\tau + \omega_0^2)} = \int_{\tau_0}^{0} \mathcal{F}(\tau) d\tau.
$$

(A 4)

Note that the integrand has the integrable singularity in the vicinity of point $\tau = \tau_0$. Actually, using (A 3) and the Taylor expansion, we have

$$
R_k(\psi) = \tau = R_k(\psi_*) + \frac{1}{2} R''_k(\psi_*)(\tau - \tau_0)^2 + \cdots = \tau_0 + \frac{1}{2} R''_k(\psi_*)(\psi - \psi_*)^2 + \cdots,
$$

$$
(\psi - \psi_*) \approx \left( \frac{2(\tau - \tau_0)}{R''_k(\psi_*)} \right)^{1/2}, \quad \tau < \tau_0, \quad R''_k(\psi_*) < 0,
$$

$$
R'_k(\psi) = R''_k(\psi_*) (\psi - \psi_*) + \cdots \approx R''_k(\psi_*) \left( \frac{2(\tau - \tau_0)}{R''_k(\psi_*)} \right)^{1/2}
$$

and

$$
\mathcal{F}(\tau) = O((\tau_0 - \tau)^{-1/2}), \quad \tau \to \tau_0.
$$

(A 5)
Further, we present (A 4) in the form (we construct the asymptotic following [27])

$$\frac{1}{2} \lambda H_k = \mathcal{F}(0) \ln \left( \frac{\omega_0^2}{\tau_0 + \omega_0^2} \right) + \int_{\tau_0}^{0} \frac{\mathcal{F}(\tau) - \mathcal{F}(0)}{\tau + \omega_0^2} \, d\tau. \quad (A 6)$$

We keep only principal terms and write

$$\frac{1}{2} \lambda H_k = \mathcal{F}(0) \ln \left( \frac{\omega_0^2}{\tau_0 + \omega_0^2} \right) + \int_{\tau_0}^{0} \frac{\mathcal{F}(\tau) - \mathcal{F}(0)}{\tau + \omega_0^2} \, d\tau + O(\omega_0^2 \ln \omega_0^2) \quad \text{as} \quad \omega_0^2 \to 0. \quad (A 7)$$

Taking into account that \( R'_k(\psi) = -R'_k(\psi-1) > 0 \), we obtain

$$\frac{1}{2} \lambda H_k = -\frac{1}{R'_k(\psi)} \ln \left( \frac{\omega_0^2}{R_k(\psi_0)} \right) + \ln W R_k(\psi) + O(\omega_0^2 \ln \omega_0^2), \quad (A 8)$$

where

$$W = \exp \left\{ R'_k(\psi) \int_{\tau_0}^{0} \frac{\mathcal{F}(\tau) - \mathcal{F}(0)}{\tau} \, d\tau \right\}. \quad (A 9)$$

Finally, we have

$$\omega_0^2 = \lambda W R_k(\psi_0) \exp(-\frac{1}{2} \lambda H_k R'_k(\psi)) \to 0, \quad \lambda \to \infty. \quad (A 10)$$

Integral in formula (A 9) has not singularity and can be calculated by numerical methods.

The results of calculation are presented on figure 6 for the following parameters:

$$\psi_{k-1} - \psi_k = \Delta \psi, \quad \mu_k = \mu, \quad \delta_k = \delta.$$
In Table 1, the numerical solution $\omega^2$ of the equation (7.13) and asymptotic values $\omega_a^2$ calculated by formula (A 10) is presented for the following parameters

$$\psi_k - 1 = \Delta \psi = 1, \quad \mu_k = \mu = 1, \quad \delta_k = \delta = 15, \quad a_0 = 1, \quad H_k = 0.25.$$ 

References


27. Fedoryuk MV. 1987 *Asymptotics, integrals and series*. Moscow, Russia: Nauka.