QUARTERLY OF APPLIED MATHEMATICS
VOLUME L, NUMBER 1
MARCH 1992, PAGES 105-107

A NONSTATIONARY PROBLEM IN THE THEORY OF ELECTROLYTES

BY

A. KRZYWICKI AND T. NADZIEJA

Wrocław University, Wrocław, Poland

Abstract. The equations describing the density of ions which appear in the theory of electrolytes take the form $f_t = f_{xx} + (fu_x)_x$, $u_{xx} = -f$, in the one-dimensional case. In the paper the existence of solutions and their behaviour as time goes to infinity is discussed.

Consider an electrolyte consisting of identical ions which move under the influence of mutual interactions and which are contained in a subdomain Ω of $\mathbb{R}^3$. The temporal development of the charge density $f(t, x)$ and of the potential of electric field $u(t, x)$ is described by the following system of equations (see [1]):

$$f_t = \Delta f + \operatorname{div}(f\nabla u), \tag{1}$$

$$\Delta u = -4\pi f. \tag{2}$$

For simplicity we put all physical constants equal to one.

One usually assumes the boundary conditions

$$(\nabla f + f\nabla u)\nu|_{\partial\Omega} = 0, \tag{3}$$

where ν denotes the exterior normal of $\partial\Omega$,

$$u|_{\partial\Omega} = 0, \tag{4}$$

and the initial condition

$$f(0, x) = f_0(x). \tag{5}$$

Condition (3) implies that the total charge $\gamma = \int_\Omega f$ of ions in Ω remains unchanged for all $t \geq 0$.

The physicists claim that as time t goes to infinity, f and u go to the stationary states f_∞ and u_∞, respectively. Moreover, f_∞ has the Boltzmann form, $f_\infty = \exp(-u_\infty)$ with u_∞ satisfying the Poisson-Boltzmann equation

$$\Delta u_\infty = -\exp(-u_\infty) \tag{6}$$

and $\int_\Omega \exp(-u_\infty) = \gamma$.

Received August 21, 1990.
1991 *Mathematics Subject Classification*. Primary 35Q53.
Key words and phrases. System of parabolic-elliptic equations, existence of solutions, electrolytes.

We will prove all these facts by elementary methods in the one-dimensional case when Eqs. (1) and (2) take the form

$$f_t = f_{xx} + (f u_x)_x, \tag{7}$$

$$u_{xx} = -f. \tag{8}$$

To make our problem as simple as possible we take $\Omega = (-1, 1)$ and assume that f_0 in (5) is an even function. The invariance of Eqs. (7), (8) with respect to the transformation $x \to -x$ allows us to infer that the solutions f, u also have this property and thus we can replace $(-1, 1)$ by $(0, 1)$ with boundary conditions

$$u_x(t, 0) = 0, \qquad f_x(t, 0) = 0, \tag{9}$$

$$u(t, 1) = 0, \tag{10}$$

$$f_x(t, 1) + f(t, 1)u_x(t, 1) = 0, \tag{11}$$

and the initial condition

$$f(0, x) = f_0(x). \tag{12}$$

Note that using (8) and (9) we can replace $u_x(t, 1)$ appearing in (11) by $-\int_0^1 f(t, y)\,dy$. We assume that f_0 is smooth, positive, and satisfies the compatibility condition $f_x(0) = 0$, $f_x(1) - f_0(1)\int_0^1 f_0(s)\,ds = 0$ necessary for the regularity of f, which is assumed to be a classical solution of (7)–(12).

THEOREM. The problem (7)–(12) has a unique solution $f(t, x)$, $u(t, x)$, $u(t, x) \to u_\infty(x)$, $f(t, x) \to \exp(-u_\infty(x))$ as t goes to ∞ and u_∞ satisfies $(u_\infty)'' = -\exp(-u_\infty)$. Moreover, $\int_0^1 \exp(-u_\infty) = \int_0^1 f_0$.

Proof. Condition (11) implies that if f is a solution of our problem, then $\int_0^1 f = \sigma = \text{const}$. This fact will be used below. Put $Q(t, x) = \int_0^x f(t, s)\,ds$. It is easy to verify that Q satisfies Burgers' equation

$$Q_t = Q_{xx} - QQ_x \tag{13}$$

and the relations

$$Q(t, 0) = 0, \qquad Q(t, 1) = \sigma, \qquad Q_0(x) = Q(0, x) = \int_0^x f_0(s)\,ds. \tag{14}$$

Let us introduce a new function v given by the formula

$$v(t, x) = \exp\left(-\frac{1}{2}\int_0^x Q(t, s)\,ds - \frac{1}{2}\int_0^t Q_x(\tau, 0)\,d\tau\right),$$

which is a slight modification of a transformation due to E. Hopf. Proceeding as usual one shows that the function v is a solution of the problem

$$\begin{aligned} &v_t = v_{xx}, \\ &v_x(t, 0) = 0, \qquad v_x(t, 1) + \tfrac{\sigma}{2} v(t, 1) = 0, \\ &v(0, x) = \exp\left(-\tfrac{1}{2}\int_0^x Q_0(s)\,ds\right). \end{aligned} \tag{15}$$

We also have $Q = -2v_x/v$. Therefore Q is a solution of (13), (14) if $v > 0$. From the last relation in (15) our supposition holds true if the argument t is sufficiently small, say $t < t_0$. Suppose that $v(t_0, x_0) = 0$ for some $x_0 \in [0, 1]$. The case $x_0 \in (0, 1)$ would contradict the strong maximum principle, and the cases $x_0 = 0$ or $x_0 = 1$ would contradict Hopf's lemma [2]; therefore $v > 0$. A similar application of the maximum principle shows that $v_x \leq 0$, hence $Q \geq 0$. To show that $f = Q_x > 0$ we first note that the equation satisfied by f is of the form $f_t = af_{xx} + bf$ with a, b continuous; therefore the same arguments as before may be applied [2].

The standard Fourier method allows us to represent the solution v in the form $v(t, x) = \sum_{n=1}^{\infty} a_n \exp(-\lambda_n^2 t)\cos(\lambda_n x)$, where the λ_n are positive solutions of the equation $\lambda = \frac{\sigma}{2}\operatorname{cotan}\lambda$.

Now

$$-\frac{1}{2}Q = \frac{v}{v_x} = -\frac{\sum_{n=1}^{\infty} a_n \exp(-\lambda_n^2 t)\lambda_n \sin(\lambda_n x)}{\sum_{n=1}^{\infty} a_n \exp(-\lambda_n^2 t)\cos(\lambda_n x)},$$

hence $\lim_{t\to\infty} Q(t, x) \to 2\lambda_1 \tan\lambda_1 x$ due to $a_1 > 0$. In a similar way we find $\lim_{t\to\infty} f(t, x) = \lim_{t\to\infty} Q_x(t, x) = f_\infty(x)$, where $f_\infty(x) = 2\lambda_1^2/\cos\lambda_1 x$. It is easy to verify that the function $u_\infty(x) = -\ln f_\infty(x)$ satisfies the equation $u'' = -\exp(-u)$ with $\int_0^1 \exp(-u) = \sigma$, which finishes the proof.

References

[1] P. Debye and E. Hückel, *Zur Theorie der Electrolyte.* II, Phys. Zft. **24**, 305–325 (1923)

[2] A. Friedman, *Partial Differential Equations of Parabolic Type*, Prentice-Hall, Englewood Cliffs, N.J., 1964