ANNALES
POLONICI MATHEMATICI
LIV.2 (1991)

Poisson–Boltzmann equation in $\mathbb{R}^3$

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Abstract. The electric potential u in a solute of electrolyte satisfies the equation

$$\Delta u(x) = f(u(x)), \quad x \in \Omega \subset \mathbb{R}^3, \quad u|_{\partial\Omega} = 0.$$

One studies the existence of a solution of the problem and its properties.

I. It is known that some sorts of polymeric chains, called polyelectrolytes, when put into a container with a suitable electrolyte, dissociate into a polymeric core and mobile ions. The latter together with the ions and counterions of the solute produce an electric field whose potential u satisfies the Poisson equation $\Delta u = -4\pi\rho$. Assuming that the charge density ρ varies in accordance with the Boltzmann law $\rho = Ce^{\alpha u}$, where C is a normalization parameter and α characterizes the charge of ion, we are led to the following problem:

$$\Delta u = f(u), \qquad u : \Omega \subset \mathbb{R}^3 \to \mathbb{R}, \tag{1}$$

where

$$f(u) = \sigma\mu_0 e^{\alpha u} + N(\mu_+ e^{\beta u} - \mu_- e^{-\beta u}).$$

Here α, β, σ, N are positive parameters, σ, N denote the total charges of ions dissociated from the polyelectrolyte and ions of the solute ($-N$ being the charge of the corresponding counterions) and

$$\mu_0 = \Big(\int_\Omega e^{\alpha u}\Big)^{-1}, \qquad \mu_\pm = \Big(\int_\Omega e^{\pm\beta u}\Big)^{-1}. \tag{2}$$

Moreover, if the polyelectrolyte is removed from the container the only boundary condition will be

$$u|_{\partial\Omega} = 0. \tag{3}$$

For physical background see [5].

1985 *Mathematics Subject Classification*: Primary 35J60, 78A35.
Key words and phrases: Poisson–Boltzmann equation, existence of solution.

Using the Leray–Schauder theorem and some idea suggested by [2] we will show that the problem (1), (3) has a unique solution. Moreover, the form of the estimates obtained permits us to control the behaviour of the solutions as $N \to 0$ and as $N \to \infty$ and when Ω expands to the whole space. Though similar to the case considered in [2], [3], the problem discussed in the present paper differs in some important details.

All solutions under consideration are classical, Ω is a bounded domain in $\mathbb{R}^3$ with C^2 boundary.

II. We start with two lemmas.

LEMMA 1. *If u is a solution of* (1), (3) *then $u \le 0$ and $f(u) \ge 0$ in Ω.*

Proof. Integrating (1) over Ω we obtain $\int_\Omega f(u) = \sigma > 0$, therefore the set $\widetilde{\Omega} = \{x \in \Omega : f(u(x)) < 0\}$ cannot be equal to Ω. We shall show that $\widetilde{\Omega}$ is empty. If not, let ω be its connected component. We have $f(u) = 0$ on the boundary $\partial\omega$ and $\Delta u = f(u) < 0$ in ω, hence u restricted to ω attains its minimal value u_0 on $\partial\omega$, $f(u_0) = 0$ and $u(x) > u_0$ for $x \in \omega$. However, $f(u)$ with fixed μ_0, $\mu_\pm$ is a strictly increasing function of u, so the last inequality would give us $f(u(x)) > 0$ in ω, which contradicts the definition of $\widetilde{\Omega}$.

Some auxiliary facts will be needed. Let u, v be arbitrary functions continuous on $\overline{\Omega}$. For any positive real λ define

$$I_\lambda(u,v) = \int_\Omega (\mu_u e^{\lambda u} - \mu_v e^{\lambda v})(u - v) \tag{4}$$

where

$$\mu_u^{-1} = \int_\Omega e^{\lambda u}, \qquad \mu_v^{-1} = \int_\Omega e^{\lambda v}.$$

Then

$$I_\lambda(u,v) \ge 0\,. \tag{5}$$

A short and elegant proof is given in [2], for completeness of exposition we repeat it here. Since the function $u \to e^u$ is increasing we have for any pair of functions u, v and reals l, m

$$\int_\Omega (e^{\lambda(u+l)} - e^{\lambda(v+m)})\,((u+l) - (v+m)) \ge 0\,. \tag{6}$$

If we now choose l, m so that $\lambda l = \log \mu_u$, $\lambda m = \log \mu_v$, we may rewrite the last inequality in the form $I_\lambda(u,v) + D(u,v) \ge 0$ where

$$D(u,v) = \int_\Omega (\mu_u e^{\lambda u} - \mu_v e^{\lambda v})(l - m)$$

is obviously zero, and this completes the proof of (5). Moreover, equality holds in (5) if and only if $u - v = \text{const}$ and this will be used in the proof of the unicity of solution of (1), (3).

LEMMA 2. *Let u be a solution of the problem* (1), (3) *with μ_0, $\mu_\pm$ defined by* (2). *Then*

$$\int_\Omega |\nabla u|^2 \le 4\sigma^2 K^2 |\Omega|^{-1}, \tag{7}$$

$$|\Omega|^{-1} \le \mu_0,\ \mu_+ \le |\Omega|^{-1} \exp(2\sigma\gamma K^2 |\Omega|^{-1}), \tag{8}$$

$$|\Omega|^{-1} \exp(-2\delta\gamma K^2 |\Omega|^{-1}) \le \mu_- < |\Omega|^{-1}, \tag{9}$$

$$\frac{1}{\delta}\log\frac{N}{N+\sigma} - \frac{2\sigma\gamma K^2}{\delta|\Omega|} \le u \le 0, \tag{10}$$

where $\gamma = \max(\alpha,\beta)$, $\delta = \min(\alpha,\beta)$, K is the constant appearing in the Poincaré inequality (15) *below, and $|\Omega|$ is the volume of Ω.*

Proof. Let u be a solution of (1), (3). We define

$$H(t) = \frac{1}{2}t^2 \int_\Omega |\nabla u|^2 + \frac{\sigma}{\alpha}\log \int_\Omega e^{t\alpha u} + \frac{N}{\beta}\log\Big(\int_\Omega e^{t\beta u} \int_\Omega e^{-t\beta u}\Big)$$

for $t \in [0,1]$. Then

$$\begin{aligned} H'(t) = t \int_\Omega |\nabla u|^2 &+ \sigma \int_\Omega u e^{t\alpha u}\Big(\int_\Omega e^{t\alpha u}\Big)^{-1} \\ &+ N\Big(\int_\Omega u e^{t\beta u}\Big(\int_\Omega e^{t\beta u}\Big)^{-1} - \int_\Omega u e^{-t\beta u}\Big(\int_\Omega e^{-t\beta u}\Big)^{-1}\Big). \end{aligned}$$

We also have

$$H'(1) = \int_\Omega |\nabla u|^2 + \int_\Omega u f(u) = 0; \tag{11}$$

the last equality is obtained by multiplying (1) by u and integrating over Ω.

Consider now the difference

$$\begin{aligned} H'(1) - H'(t) = (1-t)\int_\Omega |\nabla u|^2 &+ \frac{\sigma}{1-t} I_\alpha(u, tu) \\ &+ \frac{N}{1-t} I_\beta(u, tu) + \frac{N}{1-t} I_\beta(-u, -tu). \end{aligned}$$

The right hand side of the formula results by a simple manipulation with members of $H'(t)$; I_α and I_β are defined by (4).

By the properties of I_λ, $H'(1)-H'(t)\ge 0$ for $t\in[0,1]$ and this implies, by (11), $H(1)\le H(0)$. The explicit form of the last inequality is

$$\frac{1}{2}\int_\Omega |\nabla u|^2+\frac{\sigma}{\alpha}\log\int_\Omega e^{\alpha u}+\frac{N}{\beta}\log\Big(\int_\Omega e^{\beta u}\int_\Omega e^{-\beta u}\Big) \le\left(\frac{\sigma}{\alpha}+\frac{2N}{\beta}\right)\log|\Omega|\,,$$

from which we get

$$\frac{1}{2}\int_\Omega |\nabla u|^2+\frac{\sigma}{\alpha}\log\int_\Omega e^{\alpha u}\le\frac{\sigma}{\alpha}\log|\Omega|$$

since $|\Omega|^2\le\int_\Omega e^{\beta u}\int_\Omega e^{-\beta u}$. Jensen's inequality applied to $e^{\alpha u}$ gives us

$$\frac{\alpha}{|\Omega|}\int_\Omega u\le\log\int_\Omega e^{\alpha u}+\log\frac{1}{|\Omega|}\,, \tag{12}$$

hence

$$\int_\Omega |\nabla u|^2\le-\frac{2\sigma}{|\Omega|}\int_\Omega u\,. \tag{13}$$

Using now Cauchy's inequality we have

$$\Big(\int_\Omega u\Big)^2\le|\Omega|\int_\Omega u^2\le K^2|\Omega|\int_\Omega|\nabla u|^2\,, \tag{14}$$

the last inequality resulting from the Poincaré inequality

$$\int_\Omega u^2<K^2\int_\Omega|\nabla u|^2\,. \tag{15}$$

Combining (13) with (14) we get (7), which applied to (14) gives us

$$-\int_\Omega u<2\sigma K^2\,. \tag{16}$$

Finally, from (12) and (16) we get

$$\log\int_\Omega e^{\alpha u}\ge\log|\Omega|-2\sigma\alpha K^2|\Omega|^{-1}\,,$$

from which the estimate (8) from above for μ_0 follows. The estimate from below is a simple consequence of $u\le 0$. In a similar way one finds the estimates for μ_+ and μ_-.

To prove (10) we make use of Lemma 1, which gives $f(-m)\ge 0$, where $-m=\min u<0$, or written explicitly,

$$N\mu_-e^{\beta m}\le\sigma\mu_0e^{-\alpha m}+N\mu_+e^{-\beta m}\,. \tag{17}$$

By the obvious inequality $e^{-\beta m}|\Omega|^{-1} \le \mu_-$ and the estimates of Lemma 2, this yields

$$\frac{N}{|\Omega|} \le e^{-\delta m}|\Omega|^{-1}(\sigma + N)\exp(2K^2\delta\gamma|\Omega|^{-1})$$

and consequently

$$m \le \delta^{-1}\log((\sigma+N)N^{-1}) + (\delta|\Omega|)^{-1}2K^2\sigma\gamma\,,$$

which implies (10).

III. Consider the family of problems

$$\Delta u_\lambda = \lambda f(u_\lambda), \qquad u_\lambda|_{\partial\Omega} = 0\,, \tag{18}$$

with $0 \le \lambda \le 1$. To get the estimates for u_λ similar to those of Lemma 2, it suffices to replace in f the parameter σ and N by $\lambda\sigma$ and λN respectively, which does not affect the estimates ; therefore they remain valid without any change for the whole family u_λ, $0 \le \lambda \le 1$.

The assumed C^2 regularity of $\partial\Omega$ guarantees the existence of the Green function $G(x,y)$ for the Laplace operator considered in Ω with Dirichlet zero data, satisfying the estimates

$$G(x,y) \le C|x-y|^{-1}, \qquad |\nabla_x G(x,y)| \le C|x-y|^{-2} \tag{19}$$

uniformly for x, $y \in \Omega$, $x \ne y$, with some constant C [4]. By using G we replace (18) by the equivalent integral equation

$$u_\lambda = T_\lambda u_\lambda, \qquad 0 \le \lambda \le 1\,,$$

where

$$(T_\lambda v)(x) = \lambda \int_\Omega G(x,y) f(v(y))\,dy\,.$$

The T_λ considered as operators defined on the space $C(\overline{\Omega})$ of functions continuous on $\overline{\Omega}$ with sup-norm are continuous uniformly with respect to λ, $0 \le \lambda \le 1$, and compact; this easily follows from the fact that $f(v)$ and $\nabla T_\lambda v$ are uniformly bounded on any bounded set $K \subset C(\overline{\Omega})$ by (19), which implies the equicontinuity of the family $T_\lambda v$, $v \in K$, and the possibility of applying Arzelà's theorem. This together with the a priori estimates (10) valid for the family $\{u_\lambda\}$ allows us to apply the Leray–Schauder theorem which yields the existence of solution of the problem (1), (3). The unicity may be proved exactly as in [2] by using the equality

$$\int_\Omega |\nabla w|^2 + \int_\Omega (f(u) - f(v))w = 0$$

where u, v are two solutions of (1), (3) and $w = u - v$. As is easily seen the last equality may be transformed to the form

$$\int_\Omega |\nabla w|^2 + \sigma I_\alpha(u,v) + N I_\beta(u,v) + N I_\beta(-u,-v) = 0$$

where I_α, I_β are defined by (4). From the properties of I_α, I_β formulated above it follows that $u - v = \mathrm{const}$ and because $u - v = 0$ on $\partial\Omega$ we obtain $u = v$.

Thus we have proved

THEOREM 1. *The problem* (1), (3) *has exactly one solution.*

In the case $N = 0$ the estimate (10) is useless. To get a proper estimate we may proceed as follows.

From the equation (1), which in the case under consideration has the form

$$\Delta u = \sigma\mu_0 e^{\alpha u}, \qquad u|_{\partial\Omega} = 0\,, \tag{20}$$

we deduce the relation

$$\int_\Omega |\Delta u|^2 = \sigma\mu_0 \int_\Omega e^{\alpha u}\Delta u = -\alpha\sigma\mu_0 \int_\Omega e^{\alpha u}|\nabla u|^2 + \sigma^2\mu_0$$

and therefore

$$\int_\Omega |\Delta u|^2 \le \sigma^2\mu_0 \le \sigma^2 \exp(2\sigma\alpha K^2|\Omega|^{-1})|\Omega|^{-1} \tag{21}$$

by the estimate (8) for μ_0, also valid in our case $N = 0$. Making now use of the following representation of u:

$$u(x) = \sigma\mu_0 \int_\Omega G(x,y)e^{\alpha u(y)}\,dy\,,$$

we get, applying Cauchy's inequality, (21) and (19),

$$|u| \le CD^{1/2}|\Omega|^{-1/2}\exp(\sigma\alpha K^2|\Omega|^{-1}) \tag{22}$$

with D denoting the diameter of Ω. The last inequality results by majorizing $\sup\{(\int_\Omega |x-y|^{-2}\,dy)^{1/2} : x \in \Omega\}$ in the obvious way.

Now, proceeding as before, we can prove

THEOREM 2. *There exists a unique solution of the problem* (20).

IV. Let u_N be the solution of (1), (3).

THEOREM 3. *The sequence u_N tends to u_0 uniformly on $\overline{\Omega}$ as $N \to 0$.*

P r o o f. u_N satisfies the integral equation

$$u_N(x) = \int_\Omega G(x,y) f(u_N(y))\, dy\,.$$

Hence (8), (10) and (19) yield that u_N is a family of uniformly continuous functions. Using Arzelà's theorem we can choose a uniformly convergent subsequence of $\{u_N\}$; its limit is the unique solution of (20). From this we conclude that $u_N \to u_0$.

THEOREM 4. *When $N \to \infty$, with all other parameters fixed, then the solutions $u = u_N$ of* (1), (3) *tend to zero uniformly on Ω.*

P r o o f. Let $-m = -m_N = \inf u_N$ as before. We have

$$\begin{aligned}\mu_+ e^{-\beta m} - \mu_- e^{\beta m} &= \mu_+\mu_- \int_\Omega (e^{-\beta(m+u)} - e^{\beta(m+u)}) \\ &= -2\mu_+\mu_- \int_\Omega \mathrm{sh}\beta(m+u) \le 0\end{aligned}$$

since $0 \le m + u$. Therefore the inequality $f(-m) \ge 0$ gives us

$$2\mu_+\mu_- \int_\Omega \mathrm{sh}\ \beta(m+u) \le \sigma\mu_0 N^{-1} e^{-\alpha m}\,.$$

In the sequel we consider only $N > 1$. Applying (8) and (9) we get from the last inequality

$$0 < \int_\Omega (m+u) \le CN^{-1} \tag{23}$$

with C independent of u.

Now we have

$$\int_\Omega f^4(u) = \int_\Omega f^3(u)\Delta u = -3 \int_\Omega f^2(u) f'(u) |\nabla u|^2 + f^3(0)\sigma\,.$$

Dividing the last equality by N^4 and using Lemma 2 we get

$$\int_\Omega (\mu_+ e^{\beta u} - \mu_- e^{-\beta u})^4 \le CN^{-1}\,. \tag{24}$$

The application of Hölder's inequality to

$$\nabla u(x) = \int_\Omega \nabla_x G(x,y) f(u(y))\, dy$$

gives us

$$|\nabla u(x)|^4 \le \Big(\int_\Omega |\nabla_x G(x,y)|^{4/3}\Big)^3 \int_\Omega f^4(u)\,,$$

which with the help of (24) and the estimates of G given by (19) leads to

$$|\nabla u(x)|^4 \le CN^3\,. \tag{25}$$

Here and in the sequel the same letter C will denote different constants independent of u.

Consider now the set

$$\Omega_0 = \{x \in \Omega : u(x) \ge -m/2\}$$

In Ω_0, $m + u \ge m/2$, thus the inequality (23) allows us to estimate the measure of Ω_0:

$$|\Omega_0| \le \frac{C}{mN}\,. \tag{26}$$

Let $x \in \partial\Omega_0 \setminus \partial\Omega$ and let d_x denote the distance from x to $\partial\Omega$. From (25) one gets $m/2 = |u(x)| \le Cd_x N^{3/4}$, hence

$$d_x \ge CmN^{-3/4} = \xi$$

uniformly for $x \in \partial\Omega_0 \setminus \partial\Omega$, and this implies that the boundary strip

$$S = \{x \in \Omega : \mathrm{dist}(x, \partial\Omega) \le \xi\}$$

is contained in Ω_0, consequently

$$|S| < |\Omega_0|\,. \tag{27}$$

From the assumed C^2 regularity of $\partial\Omega$ and from the fact that ξ tends to zero as $N \to \infty$, we conclude that for sufficiently large N

$$|S| > \xi|\partial\Omega|(1 - \xi \sup\{\mathcal{K}(x) : x \in \partial\Omega\}) > \frac{\xi}{2}|\partial\Omega| \tag{28}$$

where $\mathcal{K}(x)$ denotes the Gaussian curvature of $\partial\Omega$ at x and $|\partial\Omega|$ is the two-dimensional volume of $\partial\Omega$. Now from (26)–(28) we get

$$mN^{-3/4} < \frac{C}{mN}\,,$$

that is, $m < CN^{-1/8}$, which completes the proof.

Consider now the case when Ω grows to the whole $\mathbb{R}^3$. However, some restrictions on the way of this expansion will be needed. We assume that $R^{-2}|\Omega| \to \infty$ where R is the radius of the smallest ball containing Ω. As is well known, the constant K in the Poincaré inequality is less than R; therefore the last assumption implies also $K^2|\Omega|^{-1} \to 0$.

THEOREM 5. *If Ω expands to $\mathbb{R}^3$ so that the above assumption holds, then the corresponding solutions u of* (1), (3) *tend to zero uniformly on each ball.*

Proof. Consider first the case $N = \text{const}$. Then from the relation [1]

$$u = \int_{\Omega} Gf < \int_{K_R} G_R f\,,$$

where G_R is the Green function for the ball K_R of radius R containing Ω, we conclude, in view of (8) and the estimate $|G_R(x,y)| \le |x-y|^{-1}$, $x, y \in K_R$, that

$$|u(x)| \le CR^2|\Omega|^{-1}\,,$$

from which our statement follows.

If now $N \to \infty$ the desired result follows directly from the estimate (10).

V. In radially symmetric case: Ω an open ball of radius R, $\Omega = K_R$, our problem has the form

$$(r^2u')' = r^2 f(u) \tag{29}$$

where

$$f(u) = \sigma\mu_0 e^{\alpha u} + N(\mu_+ e^{\beta u} - \mu_- e^{-\beta u})\,,$$

$$\mu_0 = \Big(4\pi \int_0^R r^2 e^{\alpha u}\,dr\Big)^{-1}, \qquad \mu_\pm = \Big(4\pi \int_0^R r^2 e^{\pm\beta u}\,dr\Big)^{-1},$$

$$u'(0) = 0, \qquad u(R) = 0\,. \tag{30}$$

The existence of a solution of (29), (30) which is a radially symmetric solution of (1), (3) results from the following argument. If T is any rotation of Ω then

$$f(u(Tx)) = f(u)(Tx) = \Delta u(Tx) = (\Delta u)(Tx)\,.$$

Hence if Ω is invariant under any rotation then the solution of (1), (3), the existence and uniqueness of which has been proved, is radially symmetric. Integrating (29) over $[0,r]$ we get

$$u'(r) = r^{-2}\int_0^r s^2 f(u(s))\,ds\,. \tag{31}$$

Hence $u'(r) \ge 0$ by Lemma 1. We shall prove that $u'' \ge 0$. Suppose that $u''(\overline{r}) < 0$ for some $\overline{r} > 0$. Using (29), (31) and the monotonicity of u and f we get

$$f(u(\overline{r})) < \frac{2}{3} f(u(\overline{r}))\,,$$

a contradiction.

The positivity of u' and u'' leads to the estimates

$$0 \le u'(r) \le \sigma R^{-2}, \quad -\sigma R^{-1} \le u(r) \le 0\,.$$

Let $\Omega \subset K_R(0)$ and let u be a solution of (1), (3). We consider the following problem:

$$(r^2 v')' = r^2 f(v), \quad r \in K_R(0)\,, \qquad f(v) = \sigma\mu_0 e^{\alpha v} + N(\mu_+ e^{\beta v} - \mu_- e^{-\beta v}) \tag{32}$$

where μ_0, $\mu_\pm$ are defined by (2),

$$v'(0) = 0, \quad v(R) = 0\,. \tag{33}$$

The problem (32), (33) has exactly one solution [1]. By the positivity of f' we can easily see, applying the maximum principle, that $u \ge v$.

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Reçu par la Rédaction le 21.5.1989