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On existence and uniqueness of the equilibrium state for an improved Nernst-Planck-Poisson system

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This work deals with a model for a mixture of charged constituents introduced in [W. Dreyer et al. Overcoming the shortcomings of the Nernst-Planck model. Phys. Chem. Chem. Phys., 15:7075-7086, 2013]. The aim of this paper is to give a first existence and uniqueness result for the equilibrium situation. A main difference to earlier works is a momentum balance involving the gradient of pressure and the Lorenz force which persists in the stationary situation and gives rise to the dependence of the chemical potentials on the particle densities of every species.

1 A model for a mixture of charged constituents

The following model was introduced in [9] by W. Dreyer et al. The reader may consult this work for a detailed account on the modeling.

Let Ω be the domain occupied by the mixture. The following system of equations describes the evolution of the mixture:

$$\partial_t \rho + \nabla \cdot (\rho \boldsymbol{v}) = 0, \tag{1a}$$

$$\partial_t (m_i n_i) + \nabla \cdot (m_i n_i \boldsymbol{v} + \boldsymbol{J}_i) = 0, \quad i \in \{1, \ldots, N-1\}, \tag{1b}$$

$$\partial_t (\rho \boldsymbol{v}) + \nabla \cdot (\rho \boldsymbol{v} \otimes \boldsymbol{v}) + \nabla p = -n^F \nabla \varphi, \tag{1c}$$

$$-\varepsilon_0 \Delta \varphi = n^F. \tag{1d}$$

There are $N-1$ diffusion fluxes given by constitutive equations:

$$\boldsymbol{J}_i = -\sum_{i=1}^{N-1} M_{ij} \left(\nabla \left(\frac{\mu_j - \mu_N}{T} \right) + \frac{1}{T} \left(\frac{z_j}{m_j} - \frac{z_N}{m_N} \right) \nabla \varphi \right), \; i \in \{1, \ldots, N-1\}. \tag{2}$$

The continuity equation (1a) assures the preservation of the total mass. The $N-1$ equations (1b) are mass balance equations for $N-1$ species. Equation (1c) is the momentum balance from which the barycentric velocity $\boldsymbol{v}$ is calculated. Finally, (1d) is the Poisson equation, which determines the electrostatic potential φ.

Here,
$n_i, \; i \in \{1, \ldots, N\}$ represent the particle number densities for each constituent,
$\boldsymbol{v}$ represents the barycentric velocity,
φ represents the electrostatic potential,
$n = \sum_{i=1}^{N} n_i$ is the total particle number density of the mixture,
$\rho = \sum_{i=1}^{N} m_i n_i$ is the mass density of the mixture,
ε_0 is the dielectric permittivity,

m_i represents the mass of a particle of species $i \in \{1, \dots, N\}$,
z_i is the electric charge of one particle of the species $i \in \{1, \dots, N\}$,
$n^F = \sum_{i=1}^N z_i n_i$ represents the total electric charge density,
T denotes the absolute temperature,
p is the elastic pressure,
μ_i is the chemical potential of the species $i \in \{1, \dots, N\}$,
M_{ij} is a positive definite kinetic matrix.

The corresponding constitutive equations for p and the μ_i are given via a free energy density $\rho\psi$, which depends on the partial mass densities $\rho_i = m_i n_i$:

$$\mu_i = \frac{\partial \rho\psi}{\partial \rho_i},\ i \in \{1, \dots, N\}; \quad p = -\rho\psi + \sum_{i=1}^N \rho_i \mu_i. \tag{3}$$

We will consider the specific free energy density

$$\rho\psi = \sum_{i=1}^N \rho_i \psi_i^{\mathrm{R}} + (K - p^{\mathrm{R}})(1 - \frac{n}{n^{\mathrm{R}}}) + K \frac{n}{n^{\mathrm{R}}} \ln(\frac{n}{n^{\mathrm{R}}}) + nkT \sum_{i=1}^N \frac{n_i}{n} \ln\left(\frac{n_i}{n}\right), \tag{4}$$

which describes a so called ideal mixture. This leads to specific chemical potentials

$$\mu_i = g_i^R + \frac{K}{m_i n^R} \ln\left(\frac{n}{n^R}\right) + \frac{kT}{m_i} \ln\left(\frac{n_i}{n}\right)$$

with $g_i^R = \psi_i^R + p^R/(m_i n^R)$, and to the equation for the pressure

$$p = p^R + K\left(\frac{n}{n^R} - 1\right). \tag{5}$$

Here,
k is the Boltzmann constant,
K is the bulk modulus,
n^R, p^R and g_i^R, ψ_i^R for $i \in \{1, \dots, N\}$ are constant reference values.

As equations of the above type describe electrolytes, there are a lot of important applications. Due to this, many (recent) publications on the analysis of similar systems can be found. We can only mention a few. In [5] a Navier-Stockes-Nernst-Planck-Poisson (NSNPP) system is derived from the Maxwell-Stefan equations and by the assumption of a dilute mixture a more classical Nernst-Planck part is achieved. The authors prove local well-posedness, global well-posedness in two dimensions and asymptotic decay to the equilibrium state for the evolution system. Another treatment of the NSNPP-system can be found in [20]. In some papers the Poisson equation is replaced by an electroneutrality condition, see e.g. [2]. The Nernst-Planck-Poisson (NPP) system without an momentum balance received much attention as well, in particular as a model for semiconductors. See e.g. [11, 12, 14, 16–19] as well as [6, 7]. These papers include well-posedness results for two space dimensions and results for three space dimensions in the case of Fermi-Dirac statistics. The recent work [4] establishes an existence result for the NPP system with Boltzmann statistics in three space dimensions. The paper [19] is of particular importance for the present work, as it deals with the stationary case of NPP. In [10] a numerical analysis and numerical experiments for the discussed model are presented. Finally, in [8] the discussed model was modified to take solvation effects into account.

The analysis of the evolution system is ongoing work and will be dealt with in future publications. In the present paper we consider the simple case of thermodynamic equilibrium, that is, the corresponding stationary system with no fluxes over the boundary. The paper is organized as follows: In the next chapter we derive the equations which describe equilibrium states of the evolution system introduced above. Then we state the main result of this work. In chapter 3 we prove the existence part of the main theorem by means of an application of Schauder's Fixed Point Theorem to prove a corresponding result for an approximate problem and suitable a-priori estimates. In the fourth chapter the uniqueness part of the main result is proved with the help of the free energy functional for the system.

2 The thermodynamic equilibrium

The aim of this work is to analyse the equations, which describe equilibrium states in the presented model. Equilibria are characterised by vanishing barycentric velocity of the mixture and vanishing diffusion fluxes:

$$\boldsymbol{v} = 0 \quad \text{and} \quad \boldsymbol{J}_i = 0.$$

To determine the unknown fields φ and n_i for $i = 1, \dots, N$ in Ω, we use the Poisson equation, the stationary momentum balance, and $N-1$ equations, which guarantee vanishing diffusion fluxes.

$$\begin{aligned} -\varepsilon_0 \Delta\varphi &= n^F, \\ \nabla p &= -n^F \nabla\varphi, \\ \nabla\left(\mu_i - \mu_N + \left(\frac{z_i}{m_i} - \frac{z_N}{m_N}\right)\varphi\right) &= 0, \ \text{for } i = 1, \dots, N-1. \end{aligned} \tag{6}$$

We remind of the definition of the pressure (5) and the relation $n = \sum_{i=1}^N n_i$. The Poisson equation has to be supplemented by boundary conditions. We assume that the boundary $\partial\Omega$ is the union of two disjoint parts Γ_D and Γ_N and that

$$\varphi = \varphi^\Gamma \text{ on } \Gamma_D, \quad \nabla\varphi \cdot \nu = 0 \text{ on } \Gamma_N. \tag{7}$$

Here ν denotes the outer unit normal at a point of Γ_N. The additional side conditions of prescribed masses

$$\int_\Omega \rho_i \, dx = \tilde{M}_i, \quad i = 1, \dots, N, \tag{8}$$

complete the system.

Our next step is to transform the system (6) into a system consisting of the Poisson equation and N state equations. We use the definition of the chemical potentials $(3)_1$ and the Gibbs-Duhem equation $(3)_2$ to obtain the relation

$$\nabla p = \sum_{i=1}^N \rho_i \nabla\mu_i = \sum_{i=1}^N \rho_i \nabla(\mu_i - \mu_N) + \rho\nabla\mu_N. \tag{9}$$

Next we substitute the momentum balance $(6)_2$ for ∇p. Moreover we insert the $N-1$ equations from $(6)_3$ on the left hand side of (9). This yields

$$\nabla \left(\mu_N + \frac{z_N}{m_N} \varphi \right) = 0.$$

We conclude that solutions of the the system (6),(7) also solve the system

$$\begin{aligned} -\varepsilon_0 \Delta \varphi &= n^F \text{ in } \Omega, \\ \varphi &= \varphi^\Gamma \text{ on } \Gamma_D, \\ \nabla \varphi \cdot \nu &= 0 \text{ on } \Gamma_N, \\ \mu_i + \frac{z_i}{m_i} \varphi &= \kappa_i \text{ in } \Omega, \quad i = 1, \ldots, N, \end{aligned} \tag{10}$$

where $\kappa = (\kappa_1, \ldots, \kappa_N) \in \mathbb{R}^N$ is chosen in such a way, that (8) is satisfied. In fact the two systems are equivalent, as we see easily by using the Gibbs-Duhem equation $(3)_2$ again.

By substituting the explicit chemical potentials $(3)_1$ for an ideal mixture into $(10)_4$, we get the following state equations

$$g_i^R + \frac{K}{m_i n^R} \ln \left(\frac{n}{n^R} \right) + \frac{kT}{m_i} \ln \left(\frac{n_i}{n} \right) + \frac{z_i}{m_i} \varphi = \kappa_i \text{ in } \Omega, \quad i = 1, \ldots, N,$$

or, equivalently,

$$m_i g_i^R - \frac{K}{n^R} \ln \left(n^R \right) + \frac{K - n^R kT}{n^R} \ln (n) + kT \ln (n_i) + z_i \varphi = m_i \kappa_i \text{ in } \Omega, \quad i = 1, \ldots, N.$$

We introduce some abbreviations to improve the readability for the analysis of the system (10). We redenote for simplicity $M_i = \tilde{M}_i / m_i$ and

$$\lambda_i = \frac{1}{kT} \left(m_i \left(\kappa_i - g_i^R \right) + \frac{K}{n^R} \ln(n^R) \right)$$

for $i = 1, \ldots, N$. We also introduce $\tilde{z}_i := z_i / kT$ and $\beta = kT n^R / K > 0$. The state equations using the new notation are

$$\left(\frac{1}{\beta} - 1 \right) \ln(n) + \ln(n_i) + \tilde{z}_i \varphi = \lambda_i \text{ in } \Omega, \quad i = 1, \ldots, N. \tag{11}$$

Solving these equations for n_i yields

$$n_i(\lambda, \varphi) = \exp \left(\lambda_i - \tilde{z}_i \varphi \right) \left(\sum_{j=1}^N \exp \left(\lambda_j - \tilde{z}_j \varphi \right) \right)^{\beta - 1} \quad i = 1, \ldots, N.$$

For $\varphi \in L^\infty(\Omega)$, $\lambda \in \mathbb{R}^N$, we define

$$G_i(\lambda; \varphi) := \int_\Omega n_i(\lambda, \varphi(x)) \, dx \quad i = 1, \ldots, N.$$

Now we state the precise problem and our main result. Let $V := \{ u \in W^{1,2}(\Omega) : u|_{\Gamma_D} = 0 \}$. With respect to the data of the problem we assume that

(A1) $\Omega \subset \mathbb{R}^n$, is a bounded Lipschitzian domain with dimension $n \leq 3$, $\partial\Omega = \Gamma_D \cup \Gamma_N$, $\Gamma_D \cap \Gamma_N = \varnothing$, Γ_D is of positive surface measure;

(A2) $\varphi^\Gamma \in W^{1,2}(\Omega) \cap L^\infty(\Omega)$ with $\int_\Omega \nabla\varphi^\Gamma \nabla h = 0$ for all $h \in V$, (V as defined below);

(A3) $\varepsilon_0 > 0$, $1 > \beta > 0$, $M = (M_1, \ldots, M_N) \in \mathbb{R}^N_+$, $z_i/kT = \tilde{z}_i \in \mathbb{R}$ are constants for $i = 1, \ldots, N$.

In (A2) we assume that the boundary datum φ^Γ can be extended to a $W^{1,2}(\Omega)$ function which solves the Laplace equation (compare [13]). We are looking for a function φ and numbers $\lambda = (\lambda_1, \ldots, \lambda_N) \in \mathbb{R}^N$, such that

$$\varphi - \varphi^\Gamma \in V \cap L^\infty(\Omega), \tag{12a}$$

$$\varepsilon_0 \int_\Omega \nabla\varphi \nabla h \, dx = \int_\Omega \sum_j z_j n_j(\lambda, \varphi) h \, dx, \quad \text{for all } h \in V, \tag{12b}$$

$$G(\lambda; \varphi) = M. \tag{12c}$$

Theorem 2.1. *If the assumptions (A1)-(A3) are satisfied, then there exists an unique solution to problem* (12)*. Moreover, there is a constant C only depending on the data of the problem, such that $||\varphi||_{L^\infty(\Omega)} \leq C$ and $|\lambda| \leq C$.*

Our aim is to prove the existence part by introducing a truncated version of problem (12). This approximate system is solved using Schauder's Fixed Point Theorem. To this end we need some preliminary results on the solvability of $G(\lambda; \varphi) = M$ and some a-priori estimates.

3 Existence

In the following assume that (A1)-(A3) are fulfilled. We start with a statement about the solution operator to the problem $G(\lambda; \varphi) = M$.

Lemma 3.1. *Let $\varphi \in L^\infty(\Omega)$ and $M \in \mathbb{R}^N_+$. Then there is a unique $\lambda = \lambda(\varphi, M) \in \mathbb{R}^N$ such that $G(\lambda; \varphi) = M$. Moreover, for all $C > 0$ and $M \in \mathbb{R}^N_+$ there is a continuous function f such that*

$$\sup_{||\varphi||_{L^\infty(\Omega)} \leq C} |\lambda(\varphi, M)| < f(C, \max_{i=1,\ldots,N} M_i, \min_{i=1,\ldots,N} M_i). \tag{13}$$

Proof. We prove two preliminaries. First, we abbreviate $S(x) := \sum_{j=1}^N \exp(\lambda_j - \tilde{z}_j \varphi(x))$, and we compute for $i, k \in 1, \ldots, N$

$$\frac{\partial G_i}{\partial \lambda_k}(\lambda; \varphi) = \int_\Omega \frac{e^{(\lambda_i - \tilde{z}_i \varphi)}}{S^{1-\beta}} \left(\delta_{k,i} - (1-\beta) \frac{e^{(\lambda_k - \tilde{z}_k \varphi)}}{S} \right) dx.$$

It follows for $k = 1, \ldots, N$ that

$$\sum_{i=1}^N \frac{\partial G_i}{\partial \lambda_k} = \beta \int_\Omega S^{\beta-1} e^{(\lambda_k - \tilde{z}_k \varphi)} > 0.$$

Owing to $\beta < 1$ the non-diagonal entries of the matrix $\frac{\partial G_i}{\partial \lambda_k}(\lambda;\varphi)$ are all negative. $\frac{\partial G_i}{\partial \lambda_k}(\lambda;\varphi)$ is thus strictly diagonal dominant, positive definite and regular for all $\lambda \in \mathbb{R}^N$. Hence, the solution to $G(\lambda;\varphi) = M$ is unique if it exists.

Second, we prove that there is a continuous function f such that

$$\sup\{|\lambda(\varphi, M)| : ||\varphi||_{L^\infty(\Omega)} \leq C,\ G(\lambda;\varphi) = M\} < f(C, \max_{i=1,\dots,N} M_i, \min_{i=1,\dots,N} M_i). \tag{14}$$

In particular, all solutions to $G(\lambda;\varphi) = M$ are in a bounded set of $\mathbb{R}^N$. For given λ, consider numbers $i_0, i_1 \in 1, \dots, N$ such that

$$\max_{i=1,\dots,N} \lambda_i = \lambda_{i_0}, \quad \min_{i=1,\dots,N} \lambda_i = \lambda_{i_1}.$$

It holds

$$\begin{aligned} n_{i_0}(\lambda, \varphi(x)) &= \exp(\lambda_{i_0} - \tilde{z}_{i_0}\varphi(x)) \left(\sum_{j=1}^N \exp(\lambda_j - \tilde{z}_j \varphi(x)) \right)^{\beta - 1} \\ &= e^{\beta\lambda_{i_0}} \exp(-\tilde{z}_{i_0}\varphi(x)) \left(\sum_{j=1}^N \exp(\lambda_j - \lambda_{i_0} - \tilde{z}_j \varphi(x)) \right)^{\beta - 1}. \end{aligned}$$

Owing to the choice of i_0, $\lambda_j - \lambda_{i_0} \leq 0$ for $j \neq i_0$, and it follows that

$$\sum_{j=1}^N \exp(\lambda_j - \lambda_{i_0} - \tilde{z}_j\varphi(x)) \leq \sum_{j=1}^N \exp(|\tilde{z}_j|C).$$

Thus

$$n_{i_0}(\lambda, \varphi(x)) \geq e^{\beta\lambda_{i_0}} \frac{\exp(-|\tilde{z}_{i_0}|C)}{\left(\sum_{j=1}^N \exp(|\tilde{z}_j|C)\right)^{1-\beta}} =: e^{\beta\lambda_{i_0}} h_0(C).$$

Thus, since $G_{i_0}(\lambda;\varphi) = N_{i_0}$, it follows that

$$e^{\beta\lambda_{i_0}} \leq \frac{M_{i_0}}{h_0(C)|\Omega|} \ \Rightarrow\ \beta\lambda_{i_0} \leq \ln\left(\frac{M_{i_0}}{h_0(C)|\Omega|}\right). \tag{15}$$

Consider now

$$n_{i_1}(\lambda, \varphi(x)) = \exp(\lambda_{i_1} - \tilde{z}_{i_1}\varphi(x)) \left(\sum_{j=1}^N \exp(\lambda_j - \tilde{z}_j \varphi(x)) \right)^{\beta - 1}.$$

Analogously to above we find

$$n_{i_1}(\lambda, \varphi(x)) \leq e^{\beta\lambda_{i_1}} \frac{\exp(|\tilde{z}_{i_1}|C)}{\left(\sum_{j=1}^N \exp(-|\tilde{z}_j|C)\right)^{1-\beta}} =: e^{\beta\lambda_{i_1}} h_1(C)$$

and thus

$$M_{i_1} = G_{i_1}(\lambda;\varphi) \leq e^{\beta\lambda_{i_1}} h_1(C)|\Omega| \; \Rightarrow \beta\lambda_{i_1} \geq \ln\left(\frac{M_{i_1}}{h_1(C)|\Omega|}\right). \tag{16}$$

The estimates (15) and (16) together imply (14).

We next prove the existence by means of the implicit function theorem (see e.g. [21]). For $\tau \in [0,1]$, and $\lambda \in \mathbb{R}^N$, we define a function $H : \mathbb{R}^N \times [0,1] \to \mathbb{R}^N$ via

$$H(\lambda,\tau) := G(\lambda;\varphi) - \tau M - (1-\tau)G(0;\varphi).$$

Owing to (14) all solutions to $H(\lambda,\tau) = 0$ are in a bounded set of $\mathbb{R}^N \times [0,1]$. Moreover, $(0,0)$ is a solution to the problem $H(\lambda,\tau) = 0$, and the derivative $H_\lambda = G_\lambda$ is regular. The implicit function theorem yields the existence of a neighbourhood $[0,\varepsilon]$ and of a C^1 function $\lambda : [0,\varepsilon] \to \mathbb{R}^N$ with $\lambda(0) = 0$, such that $H(\lambda(\tau),\tau) = 0$ for $\tau \in [0,\varepsilon]$.

To finish the proof we define τ^* as the supremum over all $\tau \in [0,1]$, such that the problem $H(\lambda,\tau) = 0$ possesses a solution. Now assume $\tau^* < 1$. We choose a sequence $\tau_k \to \tau^*$ from below and by our assumption we have $\lambda(\tau_k) \in \mathbb{R}^N$ such that $H(\lambda(\tau_k),\tau_k) = 0$. Since all solutions to the equation are in a bounded set of $\mathbb{R}^N$, $\lambda(\tau_k) \to \lambda^*$ for a subsequence, and thus $H(\lambda^*,\tau^*) = 0$. But owing to the regularity of the derivative $H_\lambda(\lambda^*,\tau*)$ and the implicit function theorem, we can continue the solution in an intervall $[0,\tau^*+\varepsilon]$, showing that τ^* was not the supremum. □

In the next Lemma, we establish an abstract bound for the positive part of the solutions to the equation $G(\lambda;\varphi) = M$.

Lemma 3.2. *Let $M \in \mathbb{R}^N_+$. For $\varphi \in L^\infty(\Omega)$, denote $\lambda(\varphi, M) \in \mathbb{R}^N$ the unique solution to $G(\lambda;\varphi) = M$. Then, for all $C > 0$*

$$\sup_{\substack{\varphi \in L^\infty(\Omega) \\ ||\varphi||_{W^{1,1}(\Omega)} \leq C}} \max_{i=1,\dots,N} |\lambda_i(\varphi, M)| < \infty.$$

Proof. We show that the λ_i are bounded from above. To get the full assertion of the Lemma the boundedness from below can be proved analogously. We argue assuming that the claim is not true. Then, we can construct a sequence of functions $\{\varphi_m\} \in L^\infty(\Omega) \cap W^{1,1}(\Omega)$ such that $||\varphi_m||_{W^{1,1}(\Omega)} \leq C$, and such that the solutions λ^m to $G(\lambda^m;\varphi_m) = M$ satisfy $\max_{i=1,\dots,N} \lambda_i^m \to +\infty$. Since $\{1,\dots,N\}$ is a discrete set, there is also a subsequence of $m \to \infty$ (still denoted by m) and an $i_0 \in \{1,\dots,N\}$ such that $\max_{i=1,\dots,N} \lambda_i^m = \lambda_{i_0}^m$ for all m. For this sequence holds

$$\begin{aligned} n_{i_0}(\lambda^m, \varphi_m(x)) &= \exp\left(\lambda_{i_0}^m - \tilde{z}_{i_0}\varphi_m(x)\right) \left(\sum_{j=1}^N \exp\left(\lambda_j^m - \tilde{z}_j\varphi_m(x)\right)\right)^{\beta-1} \\ &= e^{\beta\lambda_{i_0}^m} \exp\left(-\tilde{z}_{i_0}\varphi_m(x)\right) \left(\sum_{j=1}^N \exp\left(\lambda_j^m - \lambda_{i_0}^m - \tilde{z}_j\varphi_m(x)\right)\right)^{\beta-1}. \end{aligned}$$

Observe that $\lambda_j^m - \lambda_{i_0}^m \leq 0$ for all $j \neq i_0$. Thus,

$$\sum_{j=1}^N \exp\left(\lambda_j^m - \lambda_{i_0}^m - \tilde{z}_j\varphi_m(x)\right) \leq \sum_{j=1}^N \exp\left(-\tilde{z}_j\varphi_m(x)\right).$$

We now exploit that $\{\varphi_m\}$ is bounded in $W^{1,1}(\Omega)$. Due to the Rellich theorem (see e.g. [13]), $\{\varphi_m\}$ is compact in $L^1(\Omega)$, and therefore, the subsequence can be chosen so that $\varphi_m(x) \to \varphi(x)$ almost everywhere in Ω. The limes $\varphi \in L^1(\Omega)$ is almost everywhere finite. Using Fatou's Lemma, $\beta < 1$ and the calculations above, we show

$$\begin{aligned} M_{i_0} &= \liminf_{m\to\infty} G_{i_0}(\lambda^m;\varphi_m) = \liminf_{m\to\infty} \int_\Omega n_{i_0}(\lambda^m,\varphi_m(x)) \geq \int_\Omega \liminf_{m\to\infty} n_{i_0}(\lambda^m,\varphi_m(x)) \\ &\geq \int_\Omega \liminf_{m\to\infty} e^{\beta\lambda_{i_0}^m} \liminf_{m\to\infty} e^{-\tilde{z}_{i_0}\varphi_m(x)} \left(\sum_{j=1}^N e^{-\tilde{z}_j\varphi_m(x)}\right)^{\beta-1}. \end{aligned}$$

Since the first factor under the integral converges to ∞, the second factor has to converge to 0. This implies that $|\varphi_m| \to \infty$ almost everywhere in Ω, which contradicts $\varphi_m \to \varphi$ in $L^1(\Omega)$. $\square$

These two Lemmas will help to establish an existence result for a truncated system. For $m \in \mathbb{N}$ and $\varphi \in L^1(\Omega)$, define a truncation operator at level m via

$$[\varphi]^{(m)}(x) := \begin{cases} m & \text{for } \varphi(x) > m \\ \varphi(x) & \text{for } -m \leq \varphi(x) \leq m \\ -m & \text{for } \varphi(x) < m. \end{cases}$$

For each $m \in \mathbb{N}$, we prove the solvability of the problem

$$\begin{aligned} &-\varepsilon_0\Delta\varphi = \sum_{j=1}^N z_j n_j(\lambda,[\varphi]^{(m)}) \text{ in } \Omega, \\ &\varphi = \varphi^\Gamma \text{ on } \Gamma_D, \quad \nabla\varphi\cdot\nu = 0 \text{ on } \Gamma_N, \\ &G(\lambda;[\varphi]^{(m)}) = M. \end{aligned} \tag{17}$$

The solvability of (17) follows from a fixed point procedure. Consider given $\hat{n}_1,\ldots,\hat{n}_N \in L^2(\Omega)$ such that $n_i \geq 0$ and $\int_\Omega \hat{n}_i = M_i$ for $i = 1,\ldots,N$. It is possible (compare e.g. [13]) to find a unique weak solution to the problem

$$-\varepsilon_0\Delta\varphi = \sum_{j=1}^N z_j\hat{n}_j \text{ in } \Omega, \quad \varphi = \varphi^\Gamma \text{ on } \Gamma_D, \quad \nabla\varphi\cdot\nu = 0 \text{ on } \Gamma_N. \tag{18}$$

We obtain that $\varphi \in W^{1,2}(\Omega)$. Using Lemma 3.1, there is a unique $\lambda \in \mathbb{R}^N$ such that

$$G(\lambda;[\varphi]^{(m)}) = M.$$

We define an image element $T(\hat{n}) \in [L^2(\Omega)]^N$ via

$$T(\hat{n})_i := n_i(\lambda,[\varphi]^{(m)}) = \exp\left(\lambda_i - \tilde{z}_i[\varphi]^{(m)}\right)\left(\sum_{j=1}^N \exp\left(\lambda_j - \tilde{z}_j[\varphi]^{(m)}\right)\right)^{\beta-1}.$$

The mapping T from $[L^2(\Omega)]^N$ into itself is well defined. Moreover, T maps the following closed convex set $\mathcal{M}$ into itself

$$\mathcal{M} := \left\{ n \in [L^2(\Omega)]^N : n \geq 0, \int_\Omega n = M \right\}.$$

We next show that T is compact. Suppose that $\{\hat{n}_k\}$ is a bounded sequence in $\mathcal{M} \subset [L^2(\Omega)]^N$. Then, the corresponding solutions φ_k to (18) are bounded in $W^{1,2}(\Omega)$, and there is a subsequence of $\{\varphi_k\}$ converging to a φ almost everywhere in Ω. Owing to the Lemma 3.1, the solutions λ^k to $G(\lambda^k; [\varphi]^{(m)}) = M$ are in a bounded set of $\mathbb{R}^N$. This is due to the truncation that ensures that $[\varphi_k]^{(m)}$ is in a bounded set of $L^\infty(\Omega)$. Thus, $\lambda_k \to \lambda$ for a subsequence. Hence, $|n_i^k| \leq C$ and $n_i^k \to n_i$ almost everywhere in Ω as $k \to \infty$, where

$$n_i = \exp\left(\lambda_i - \tilde{z}_i[\varphi]^{(m)}\right) \left(\sum_{j=1}^N \exp\left(\lambda_j - \tilde{z}_j[\varphi]^{(m)}\right) \right)^{\beta - 1}, \; i = 1, \ldots, N.$$

This ensures the convergence $T(\hat{n}_k)_i \to n_i$ in $L^2(\Omega)$ for $i = 1, \ldots, N$ and thus the compactness of T as a mapping from $[L^2(\Omega)]^N$ into itself. The continuity of T is proved analogously. Hence, T possesses due to the Schauder theorem (see e.g. [21]) a fixed point in $\mathcal{M}$, that solves (17).

It remains to carry over the passage to the limit for $m \to +\infty$ in (17). This relies on two last estimates.

Lemma 3.3. *If $\varphi \in W^{1,2}(\Omega)$ is a weak solution to the problem* (18)*, then for all $1 \leq p < d/(d-1)$ ($d =$ space dimension)*

$$\begin{aligned} ||\nabla\varphi||_{L^p(\Omega)} &\leq c(||\varphi^\Gamma||_{W^{1,2}(\Omega)}, ||\sum_{j=1}^N z_j \hat{n}_j||_{L^1(\Omega)}) \\ &= c(||\varphi^\Gamma||_{W^{1,2}(\Omega)}, M_1, \ldots, M_N). \end{aligned}$$

Proof. Theory of elliptic equations with right-hand side in L^1 (see e.g. [3]). □

Lemma 3.3 ensures that the solution $\varphi = \varphi_m$ to (17) is such that $\sup_{m \in \mathbb{N}} ||\varphi_m||_{W^{1,1}(\Omega)} \leq C$. In particular, it follows from Lemma 3.2 for the solutions to $G(\lambda^m; [\varphi_m]^{(m)}) = M$ that $\sup_{m \in \mathbb{N}} \sup_{i=1,\ldots,N} |\lambda_i^m| \leq +\infty$. With these informations, it follows at last that

Lemma 3.4. *The solution φ_m to the problem*

$$\begin{aligned} &\varphi_m - \varphi^\Gamma \in V \\ &\varepsilon_0 \int_\Omega \nabla\varphi_m \cdot \nabla h = \int_\Omega \sum_{j=1}^N z_j n_j(\lambda^m; [\varphi_m]^{(m)}) h, \quad \forall h \in V \end{aligned} \tag{19}$$

satisfies $||\varphi_m||_{L^\infty(\Omega)} \leq C$.

Proof. We begin by defining the numbers

$$\lambda_0 := \sup_{\substack{\varphi \in L^\infty(\Omega) \\ ||\varphi||_{W^{1,1}(\Omega)} \le C}} \sup_{i=1,\dots,N} |\lambda_i(\varphi, M)|$$

and $\varphi_0 \in \mathbb{R}$ as solution of the equation

$$0 = f(\varphi_0), \text{ where } f(\varphi) = \sum_{j=1}^{N} z_j \exp(\lambda_j - \tilde{z}_j \varphi). \tag{20}$$

Note that $f'(\varphi) < 0$, i.e. f is strictly decreasing and $\lim_{\varphi \to \pm\infty} f(\varphi) = \mp\infty$. Thus, there is a unique φ_0, which is bounded from above and below by constants depending on λ_0.

Now choose in (19) a test function of the form $h_+ = (\varphi - \gamma)^+$ with $\gamma \ge \max\{\varphi_0, \sup_{\Gamma^D} \varphi^\Gamma\}$. Then $h_+ \in V$ and $\nabla\varphi\nabla h_+ = (\nabla h_+)^2$ (see e.g. [15, Lemma 7.6.]). Therefore testing (19) with h_+ and using (20) yields

$$\begin{aligned}
\varepsilon_0 \int_\Omega (\nabla h_+)^2 &= \int_\Omega \sum_{j=1}^{N} z_j n_j(\lambda, [\varphi]^{(m)}) h_+ \\
&= \int_\Omega \sum_{j=1}^{N} z_j \exp(\lambda_j - \tilde{z}_j [\varphi]^{(m)}) \left(\sum_{k=1}^{N} \exp(\lambda_k - \tilde{z}_k [\varphi]^{(m)}) \right)^{\beta-1} h_+ \\
&\le \sum_{j=1}^{N} z_j \exp(\lambda_j - \tilde{z}_j \varphi_0) \int_\Omega \left(\sum_{k=1}^{N} \exp(\lambda_k - \tilde{z}_k [\varphi]^{(m)}) \right)^{\beta-1} h_+ \\
&= 0.
\end{aligned}$$

Hence, $h_+ = 0$, i.e. $\varphi \le \max\left\{\varphi_0, ||\varphi^\Gamma||_{L^\infty(\Omega)}\right\}$. A bound from below is obtained in an analogous way. □

We thus have established that the sequence φ_m is uniformly bounded in $W^{1,2}(\Omega) \cap L^\infty(\Omega)$. For m sufficiently large, the truncation operator ceases to work, and the solution to (17) is in fact a solution of (12).

4 Uniqueness

In this section we prove the uniqueness part of Theorem 2.1. To this end we introduce a functional F, which is related to the free energy (4) of the system (1). It turns out, that the state equations (11) are the Euler-Lagrange equations for F. We proceed by showing that F is strongly convex. Thus, a solution of problem (12) is also a minimum of F and we can show that there is at most one minimum of F.

As we know that the solution of (12) is bounded from above and away from 0 by the data of the problem, we study F on the set

$$\mathcal{M}_R := \{(n_1, \dots, n_N) \in [L^2(\Omega)]^N : R^{-1} < n_i < R \text{ for } i = 1, \dots, N\}$$

for R big enough. Consider the functional $F : \mathcal{M}_R \to \mathbb{R}$ given by

$$\begin{aligned} F(n_1, \dots, n_N) = \int_\Omega & -\beta^{-1} n + \sum_{j=1}^N n_j \ln(n_j) + (\beta^{-1} - 1) n \ln(n) \\ & - \frac{\varepsilon_0}{2kT} (\nabla \varphi)^2 + \frac{1}{kT} n^F \varphi^\Gamma + \sum_{j=1}^N \lambda_j (M_j - n_j)\, dx. \end{aligned} \tag{21}$$

The side condition of prescribed masses (8) are incorporated into F by Lagrange multipliers λ_i. For the following computations φ is treated as a function of $(n_1, \dots, n_N)$ given by $\varphi = 1/\varepsilon_0 \Delta_0^{-1}(n^F) + \varphi^\Gamma$. The inverse Laplace operator $\Delta_0^{-1} : L^2(\Omega) \to V$ is defined for $f \in L^2(\Omega)$ by

$$\Delta_0^{-1}(f) := u, \text{ where } u \in V \text{ satisfies } \int_\Omega \nabla u \cdot \nabla h = \int_\Omega f h, \text{ for all } h \in V$$

(This is well defined, compare [1] and [13]). Now we write the part of the functional F involving the electro static potential φ as

$$\Phi(n_1, \dots, n_N) := \frac{\varepsilon_0}{2kT} \int_\Omega (\nabla \varphi)^2 \; dx = \frac{\varepsilon_0}{2kT} \int_\Omega \left(\nabla \left(\frac{1}{\varepsilon_0} \Delta_0^{-1} \left[n^F \right] + \varphi^\Gamma \right) \right)^2 \; dx.$$

For $u = (u_1, \dots, u_N),\ v = (v_1, \dots, v_N) \in \mathcal{M}_R$ a strait forward calculation yields

$$DF(n_1, \dots, n_N)[u] = \int_\Omega \sum_{j=1}^N \left(\ln(n_j) + (\beta^{-1} - 1) \ln(n) + \tilde{z}_j \varphi - \lambda_j \right) u_j \, dx \tag{22}$$

and

$$\begin{aligned} D^2 F(n_1, \dots, n_N)[u, v] = \int_\Omega & \sum_{j=1}^N \frac{u_j v_j}{n_j} + (\beta^{-1} - 1) \frac{1}{n} \left(\sum_{j=1}^N u_j \right) \left(\sum_{j=1}^N v_j \right) \\ & + \frac{1}{\varepsilon_0 kT} \nabla \left(\Delta_0^{-1} \left(\sum_{j=1}^N z_j u_j \right) \right) \cdot \nabla \left(\Delta_0^{-1} \left(\sum_{j=1}^N z_j v_j \right) \right) \; dx. \end{aligned} \tag{23}$$

By (22) we see that the state equations (11) are the Euler-Lagrange equations of F, as claimed.

Lemma 4.1. *Let $F : M_R \to \mathbb{R}$ be given as in* (21)*. Then it holds*

$$D^2 F(n_1, \dots, n_N)[u, u] \geq \frac{1}{R} ||u||^2_{L^2(\Omega)}$$

for all $(n_1, \dots, n_N) \in M_R$ and all $u \in M_R$.

Proof. Using $\beta < 1$ equation (23) implies

$$D^2 F(n_1, \dots, n_N)[u, u] \geq \int_\Omega \sum_{j=1}^N \frac{u_j u_j}{n_j} \geq \frac{1}{R} \int \sum_{j=1}^N u_j^2 \tag{24}$$

$\square$

Lemma 4.2. *The functional F given by* (21) *has at most one minimum in $\mathcal{M}_R$.*

Proof. From Lemma 4.1 we infer that for all $u, v \in \mathcal{M}_R$ it holds

$$
\begin{aligned}
&F(u) + F(v) - 2F\left(\frac{u+v}{2}\right) \\
&= \int_0^1 \frac{d}{ds}\left(F\left(\frac{u+v}{2} + \frac{s}{2}(u-v)\right) + F\left(\frac{u+v}{2} + \frac{s}{2}(v-u)\right)\right) ds \\
&= \int_0^1 \left(DF\left(\frac{u+v}{2} + \frac{s}{2}(u-v)\right) - DF\left(\frac{u+v}{2} + \frac{s}{2}(v-u)\right)\right)[u-v] ds \\
&= \int_0^1 \int_0^1 \frac{d}{dt}\left(DF\left(\frac{u+v}{2} + \frac{s}{2}(v-u) + ts(u-v)\right)\right)[u-v] dt\, ds \\
&= \int_0^1 s \int_0^1 D^2F\left(\frac{u+v}{2} + \frac{s}{2}(v-u) + ts(u-v)\right)[u-v, u-v] dt\, ds \\
&\geq \int_0^1 s \int_0^1 \frac{1}{R}||u-v||_{L^2}^2 dt\, ds = \frac{1}{2R}||u-v||_{L^2}^2.
\end{aligned}
$$

Now let $u, v \in \mathcal{M}_R$ be two minima of F. Then

$$
0 \geq F(u) + F(v) - 2F\left(\frac{u+v}{2}\right) \geq \frac{1}{2R}||u-v||_{L^2}^2.
$$

Thus, $u = v$ almost everywhere in Ω. □

This completes the proof of Theorem 2.1.

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