CONVERGENCE OF AN IMPLICIT EULER GALERKIN SCHEME FOR POISSON–MAXWELL–STEFAN SYSTEMS

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Abstract. A fully discrete Galerkin scheme for a thermodynamically consistent transient Maxwell–Stefan system for the mass particle densities, coupled to the Poisson equation for the electric potential, is investigated. The system models the diffusive dynamics of an isothermal ionized fluid mixture with vanishing barycentric velocity. The equations are studied in a bounded domain, and different molar masses are allowed. The Galerkin scheme preserves the total mass, the nonnegativity of the particle densities, their boundedness, and satisfies the second law of thermodynamics in the sense that the discrete entropy production is nonnegative. The existence of solutions to the Galerkin scheme and the convergence of a subsequence to a solution to the continuous system is proved. Compared to previous works, the novelty consists in the treatment of the drift terms involving the electric field. Numerical experiments show the sensitive dependence of the particle densities and the equilibration rate on the molar masses.

1. Introduction

The Maxwell–Stefan equations describe the dynamics of a fluid mixture in the diffusive regime. They have numerous applications, for instance, in sedimentation, dialysis, electrolysis, and ion exchange. While Maxwell–Stefan models have been investigated since several decades from a modeling and simulation viewpoint in the engineering literature (e.g. [13]), the mathematical and numerical analysis started more recently [1, 16]. The global existence of weak solutions under natural conditions was proved in [6, 21] for neutral mixtures. In case of ion transport, the electric charges and the self-consistent electric potential need to be taken into account. To our knowledge, no mathematical results are available in the literature for such Poisson–Maxwell–Stefan models. In this paper, we prove the existence of a weak solution to a structure-preserving fully discrete Galerkin scheme and its convergence to the continuous problem. This provides, for the first time, a global existence result for Poisson–Maxwell–Stefan systems.

1.1. **Model equations.** We consider an ionized fluid mixture consisting of n components with the partial mass density ρ_i, partial flux J_i, and molar mass M_i of the ith species. The

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evolution of the particle densities ρ_i is governed by the partial mass balance equations

$$\partial_t\rho_i + \operatorname{div} J_i = r_i(x), \quad i = 1,\ldots,N, \tag{1}$$

where r_i are the production rates satisfying $\sum_{i=1}^n r_i(x) = 0$ and $\sum_{i=1}^n J_i = 0$. The molar concentrations are defined by $c_i = \rho_i/M_i$ and $x_i = c_i/c$ are the molar fractions, where $c_{\rm tot} = \sum_{i=1}^n c_i$ denotes the total concentration and we have set $x = (x_1,\ldots,x_n)$. The partial fluxes J_i and the gradients of the molar fractions x_i are related by the (scaled) Maxwell–Stefan equations

$$-\sum_{j=1}^N k_{ij}(\rho_j J_i - \rho_i J_j) = D_i := \nabla x_i + (z_i x_i - (\rho\cdot x)\rho_i)\nabla\Phi, \quad i = 1,\ldots,n. \tag{2}$$

where $k_{ij} = k_{ji}$ are the rescaled (reciprocal) Maxwell–Stefan diffusivities, D_i is the driving force, z_i the electric charge of the ith component, and Φ the electric potential. We refer to Section 2 for details on the modeling. These equations are coupled to the (scaled) Poisson equation

$$-\lambda\Delta\Phi = \sum_{i=1}^n z_i c_i + f(y), \tag{3}$$

where λ is the scaled permittivity and $f(y)$ is a fixed background charge. The equations are solved in a bounded domain $\Omega \subset \mathbb{R}^d$ ($d \geq 1$) and supplemented by the boundary conditions

$$J_i\cdot\nu = 0 \quad \text{on } \partial\Omega,\ i = 1,\ldots,n, \tag{4}$$

$$\Phi = \Phi_D \quad \text{on } \Gamma_{\rm D}, \quad \nabla\Phi\cdot\nu = 0 \quad \text{on } \Gamma_{\rm N}, \tag{5}$$

where $\Gamma_{\rm D}$ models the electric contacts, $\Gamma_N = \partial\Omega\backslash\Gamma_{\rm D}$ is the union of insulating boundary segments, and ν denotes the exterior unit normal vector to $\partial\Omega$. This means that the mixture cannot leave the container Ω and an electric field is applied at the contacts $\Gamma_{\rm N}$. The initial conditions are given by

$$\rho_i(\cdot,0) = \rho_i^0 \quad \text{in } \Omega, \quad i = 1,\ldots,n. \tag{6}$$

We assume that the total mass is constant initially, $\sum_{i=1}^n \rho_i^0 = 1$, which implies from (1) that the total mass is constant for all times, $\sum_{i=1}^n \rho_i(t) = 1$, expressing total mass conservation.

Observe that (2) defines a linear system in the diffusion fluxes. Since $\sum_{i=1}^n D_i = 0$, the kernel of that system is nontrivial, and we need to invert the relation between the fluxes J_i and the driving forces D_i on the orthogonal component of the kernel. It was shown in [21, Section 2] that we can write (2) as $D' = -A_0 J'$, where $D' = (D_1,\ldots,D_{n-1})$, $J' = (J_1,\ldots,J_{n-1})$, and $A_0 \in \mathbb{R}^{(n-1)\times(n-1)}$ is invertible; see Section 3.1 for details. The nth components are recovered from $D_n = -\sum_{i=1}^{n-1} D_i$ and $J_n = -\sum_{i=1}^{n-1} J_i$. Thus, (1) can be written compactly as the cross-diffusion system [1, 21]

$$\partial_t\rho' - \operatorname{div}(A_0^{-1}D') = r'(x),$$

where $\rho' = (\rho_1, \ldots, \rho_{n-1})$. However, A_0^{-1} is not positive definite. To obtain a positive definite diffusion matrix, we need to transform the system. With the so-called entropy variables

$$w_i = \frac{\log x_i}{M_i} - \frac{\log x_n}{M_n} + \left(\frac{z_i}{M_i} - \frac{z_n}{M_n}\right)\Phi, \quad i = 1, \ldots, n-1, \tag{7}$$

we may formulate (1) as

$$\partial_t \rho' - \operatorname{div}(B\nabla w) = r'(x), \tag{8}$$

where $B = (B_{ij}) \in \mathbb{R}^{(n-1)\times(n-1)}$ is symmetric and positive definite; see Section 3.1 for details. Here, ρ' and x are interpreted as (invertible) functions of w and Φ. This transformation is well known in nonequilibrium thermodynamics, where w_i is called the electrochemical potential and B is the mobility or Onsager matrix.

The transformation to entropy variables has two important advantages. First, introducing the entropy

$$H(\rho) = \int_\Omega h(\rho)dy, \quad h(\rho) = c_{\mathrm{tot}} \sum_{i=1}^n x_i \log x_i + \frac{\lambda}{2}|\nabla(\Phi - \Phi_D)|^2, \tag{9}$$

a formal computation shows that

$$\frac{dH}{dt} + \int_\Omega \nabla w : B\nabla w dy = \int_\Omega \sum_{i=1}^n r_i(x) \frac{\partial h}{\partial \rho_i} dy, \tag{10}$$

if Φ_D is constant, where $A : B$ denotes the Frobenius matrix product between matrices A and B. (A discrete analog is shown in Theorem 1 below.) Thus, if the right-hand side is nonpositive, the entropy $t \mapsto H(\rho(t))$ is a Lyapunov functional and we may obtain suitable estimates for w_i. The entropy production (the diffusion term) is nonnegative, which expresses the second law of thermodynamics. This technique has been used in [6, 21] but without electric force terms. The derivation of gradient estimates is more delicate in the presence of the electric potential; see Lemma 8. Second, the densities $\rho_i = \rho_i(w)$ are automatically positive and bounded and it holds that $\sum_{i=1}^n \rho_i(w) = 1$; see Corollary 7. This property is inherent of the transformation and it holds without the use of a maximum principle and independent of the functional setting.

The aim of this paper is to extend the global existence result of [6, 21] to Maxwell–Stefan systems with electric forces and to suggest a fully discrete Galerkin scheme that preserves the structure of the system, namely the nonnegativity of the particle densities, the L^∞ bound $\sum_{i=1}^n \rho_i = 1$, and a discrete analog of the entropy production inequality (10).

1.2. **State of the art.** Before presenting our main results, we briefly review the state of the art of Maxwell–Stefan models. They were already derived in the 19th century by Maxwell using kinetic gas theory [25] and Stefan using continuum mechanics [32]. A more mathematical derivation from the Boltzmann equation can be found in [4, 15], including a non-isothermal setting [19]. An advantage of the Maxwell–Stefan approach is that the definition of the driving forces can be adapted to the present physical situation, leading to very general and thermodynamically consistent models [2].

When electrolytes are considered, we need to take into account the electric force. Usually, this is done in the context of Nernst–Planck models [27, 29], where the diffusion flux J_i only depends on the density gradient of the ith component, thus without any cross-diffusion effects. Duncan and Toor [12] showed that cross-diffusion terms need to be taken into account in a ternary gas. Dreyer et al. [11] outline some deficiencies of Nernst–Planck models and propose thermodynamically consistent Maxwell–Stefan type models. A numerical comparison between Nernst–Planck and Maxwell–Stefan models can be found in [30].

The first global-in-time existence result to the Maxwell–Stefan equations (1)-(2) without Poisson equation was proved by Giovangigli and Massot [16] for initial data around the constant equilibrium state. The local-in-time existence of classical solutions was shown by Bothe [1]. The entropy structure of the Maxwell–Stefan system was revealed in [21], and a general global existence theorem could be shown. Further global existence results can be found in [18, 24]. The Maxwell–Stefan system was coupled to the heat equation [20] and to the incompressible Navier–Stokes equations [6]. In [15, Theorem 9.7.4] and [18, Theorem 4.3], the large-time asymptotics for initial data close to equilibrium was analyzed. The convergence to equilibrium for any initial data was investigated in [6, 21] without production terms and in [7] with production terms for reversible reactions. Salvarani and Soares proved a relaxation limit of the Maxwell–Stefan system to a system of linear heat equations [31].

Surprisingly, there are not many papers concerned with numerical schemes which preserve the properties of the solution like conservation of total mass, nonnegativity, and entropy production. Many approximation schemes can be found in the engineering literature, for instance finite-difference [22, 23] or finite-element [5] discretizations. In the mathematical literature, finite-volume [28] and mixed finite-element [26] schemes as well as explicit finite-difference schemes with fast solvers [14] were proposed. The existence of discrete solutions was shown in [26], but only for ternary systems and under restrictions on the diffusion coefficients. The schemes of [3, 28] conserve the total mass, while those of [3, 8] also preserve the L^∞ bounds. The result of [8] is based on maximum principle arguments. Note that we are able to show the L^∞ bounds without the use of a maximum principle, as a result of the formulation in terms of entropy variables, and that we do not impose any restrictions on the diffusivities (except positivity).

All the cited results are concerned with the Maxwell–Stefan equations for neutral fluids, i.e. without electric effects. In this paper, we analyze for the first time Poisson–Maxwell–Stefan systems and show a discrete entropy production inequality. The cross-diffusion terms cause some mathematical difficulties which are not present in Nernst–Planck models.

1.3. **Main results.** Let $(\theta^{(k)})$ be an orthonormal basis of $H^1_D(\Omega)$ and $(v^{(k)})$ be an orthonormal basis of $H^1(\Omega;\mathbb{R}^{n-1})$ such that $v^{(k)} \in L^\infty(\Omega;\mathbb{R}^{n-1})$. We introduce the Galerkin spaces

$$P_N = \operatorname{span}\{u^{(1)},\ldots,u^{(N)}\}, \quad V_N = \operatorname{span}\{v^{(1)},\ldots,v^{(N)}\}.$$

Furthermore, let $T > 0$ and $N \in \mathbb{N}$ and set $\tau = T/N > 0$. We impose the following assumptions:

(A1) Domain: $\Omega \subset \mathbb{R}^d$ is a bounded domain with Lipschitz boundary $\partial\Omega = \Gamma_{\rm D} \cup \Gamma_{\rm N}$, where $\Gamma_{\rm D} \cap \Gamma_{\rm N} = \emptyset$, $\Gamma_{\rm N}$ is open in $\partial\Omega$, and $\mathrm{meas}(\Gamma_{\rm D}) > 0$.

(A2) Given functions: The initial datum $\rho^0 = (\rho_1^0, \ldots, \rho_n^0)$ is nonnegative and measurable satisfying $\int_\Omega \sum_{i=1}^n \rho_i \log \rho_i dy < \infty$, $\rho_n^0 = 1 - \sum_{i=1}^{n-1} \rho_i^0 \geq 0$. The boundary data $\Phi_D \in H^1(\Omega) \cap L^\infty(\Omega)$ solves $-\lambda\Delta\Phi_D = f$ in Ω and $\nabla\Phi_D \cdot \nu = 0$ on $\Gamma_{\rm N}$. Furthermore, let $f \in L^\infty(\Omega)$.

(A3) Diffusion matrix: For any given $\rho \in [0,\infty)^n$, the transpose of the matrix $A = (A_{ij}) \in \mathbb{R}^{n\times n}$, defined by

$$A_{ij} = \begin{cases} \sum_{\ell=1,\,\ell\neq i}^n k_{i\ell}\rho_\ell & \text{for } i = j, \\ -k_{ij}\rho_i & \text{for } i \neq j, \end{cases} \tag{11}$$

has the kernel $\ker(A^\top) = \mathrm{span}\{\mathbf{1}\}$, where $\mathbf{1} = (1, \ldots, 1) \in \mathbb{R}^n$.

(A4) Production rates: The functions $r_i \in C^0([0,1]^n;\mathbb{R})$ satisfy $\sum_{i=1}^n r_i(x) \log x_i/M_i \leq 0$ for all $x \in (0,1]^n$, $i = 1, \ldots, n$.

Assumptions (A1) and (A2) are rather natural. The condition $\rho_i \log \rho_i \in L^1(\Omega)$ is needed to apply the entropy method. By definition of A, it holds that $\ker(A^\top) \subset \mathrm{span}\{\mathbf{1}\}$. If $k_{ij} > 0$ (and $\rho_j > 0$), a computation shows that $\mathrm{span}\{\mathbf{1}\} = \ker(A^\top)$. For the general case $k_{ij} \geq 0$, this property cannot be guaranteed and needs to be assumed. This explains Assumption (A3). Assumption (A4) is needed to derive the entropy production inequality (10). It is satisfied for reversible reactions; see [7, Lemma 6].

We consider the implicit Euler Galerkin scheme

$$\begin{aligned} &\frac{1}{\tau}\int_\Omega \big(\rho'(u^k + w_D, \Phi^k) - \rho'(u^{k-1} + w_D, \Phi^{k-1})\big) \cdot \phi dy + \varepsilon \int_\Omega u^k \cdot \phi dy \\ &\quad + \int_\Omega \nabla\phi : B(u^k + w_D, \Phi^k)\nabla(u^k + w_D) dy = \int_\Omega r'(x(u^k + w_D, \Phi^k)) \cdot \phi dy, \end{aligned} \tag{12}$$

$$\lambda \int_\Omega \nabla\Phi^k \cdot \nabla\theta dy = \int_\Omega \bigg(\sum_{i=1}^n z_i c_i(u^k + w_D, \Phi^k) + f(y)\bigg) dy \tag{13}$$

for $\phi \in V_N$, $\theta \in P_N$, $\varepsilon > 0$, and we have defined

$$w_D = (w_{D,1}, \ldots, w_{D,n-1}), \quad w_{D,i} = \bigg(\frac{z_i}{M_i} - \frac{z_n}{M_n}\bigg)\Phi_D. \tag{14}$$

The discrete entropy variables are given by $w^k = u^k + w_D$, and we used the notation $c_i(w^k, \Phi^k) = \rho_i(w^k, \Phi^k)/M_i$, $x_i(w^k, \Phi^k) = c_i(w^k, \Phi^k)/c_{\rm tot}^k$ for $i = 1, \ldots, n$, and $c_{\rm tot}^k = \sum_{i=1}^n \rho_i(w^k, \Phi^k)/M_i$.

At time $k = 0$, we assume that $\rho_i^0 \geq \eta > 0$ in Ω. This allows us to define w^0 via definition (7). The condition can be removed by performing the limit $\eta \to 0$ in the proof; see [6] for details. Furthermore, let $\Phi^0 \in H^1(\Omega) \cap L^\infty(\Omega)$ be the unique solution to

$$-\lambda\Delta\Phi^0 = \sum_{i=1}^n z_i \frac{\rho_i^0}{M_i} + f(y) \text{ in } \Omega, \quad \nabla\Phi^0 \cdot \nu = 0 \text{ on } \Gamma_{\rm N}, \quad \Phi^0 = \Phi_D \text{ on } \Gamma_{\rm D}.$$

This defines (w^0, Φ^0).

Theorem 1 (Existence for the Galerkin scheme)**.** *Let Assumptions (A1)-(A4) hold. Then there exists a weak solution* $(w^k,\Phi^k)\in V_N\times P_N$ *to* (12)-(13) *with* $w^k=u^k+w_D$*, satisfying*

- *preservation of* L^∞ *bounds:* $0<\rho_i^k<1$ *for* $i=1,\ldots,n$*;*
- *conservation of total mass:* $\sum_{i=1}^n\rho_i^k=1$ *in* Ω*;*
- *discrete entropy production inequality:*

$$\begin{aligned}&H(\rho^k)+\tau\int_\Omega\nabla(w^k-w_D):B(w^k,\Phi^k)\nabla w^k dy+\varepsilon\tau\int_\Omega|w^k-w_D|^2dy\\ &\quad\le\tau\int_\Omega\sum_{i=1}^n\frac{z_i}{M_i}r_i(x^k)(\Phi^k-\Phi_D)dy+H(\rho^{k-1}),\end{aligned}\tag{15}$$

where $\rho^k=\rho(w^k,\Phi^k)$*.*

Theorem 1 is proved by using a fixed-point argument in the entropy variables. Using w^k-w_D as a test function in the fully discrete version of (8), we show in Section 4 that

$$H(\rho^k)+\tau K\int_\Omega\sum_{i=1}^n|\nabla(x_i^k)^{1/2}|^2dy+\varepsilon\tau\int_\Omega|w^k-w_D|^2dy\le\tau K+H(\rho^{k-1}),$$

where $K>0$ only depends on the given data. This is an estimated version of (10). The term involving ε is needed to conclude a uniform L^2 estimate for w^k, which is sufficient to apply the Leray-Schauder fixed-point theorem in the finite-dimensional Galerkin space. The ε-independent gradient estimate for x_i^k cannot be used since it does not give an estimate for w_i^k (see (7)). It is possible to analyze system (12)-(13) for $\varepsilon=0$ – see Step 2 of the proof of Theorem 3 –, but we lose the information about w^k and obtain a solution in terms of ρ^k. The term involving ε is technical and not essential for the numerical simulations (or the structure preservation). However, we are not able to prove an existence result in terms of the entropy variable without such a regularization.

Remark 2 (Conservation of partial mass)**.** When $r_i=0$, we have from (1) conservation of the partial mass $\|\rho_i\|_{L^1(\Omega)}$. This conservation property does not hold exactly on the discrete level because of the ε-regularization. It holds that for any $\delta>0$, there exists $\varepsilon_0>0$ such that for any $0<\varepsilon<\varepsilon_0$ (ε is the value in (12)),

$$\begin{aligned}\big|\|\rho_i^k\|_{L^1(\Omega)}-\|\rho_i^0\|_{L^1(\Omega)}\big|&\le\delta\|\rho_i^0\|_{L^1(\Omega)},\quad i=1,\ldots,n-1,\\ \big|\|\rho_n^k\|_{L^1(\Omega)}-\|\rho_n^0\|_{L^1(\Omega)}\big|&\le\delta\sum_{i=1}^{n-1}\|\rho_i^0\|_{L^1(\Omega)}.\end{aligned}$$

The proof is the same as in [21, Theorem 4.1]. As $\delta>0$ can be chosen arbitrarily small, this shows that the numerical scheme preverses the partial mass approximately. □

Theorem 3 (Convergence of the Galerkin solution)**.** *Let Assumptions (A1)-(A4) hold. Let* (ρ^k,Φ^k) *be a solution to* (12)-(13) *and set*

$$\rho_i^\tau(y,t)=\rho_i^k(y),\quad x_i^\tau(y,t)=x_i^k(y),\quad c_i^\tau(y,t)=c_i^k(y),\quad\Phi^\tau(y,t)=\Phi^k(y)$$

for $y \in \Omega$, $t \in ((k-1)\tau, k\tau]$, $i = 1, \ldots, n$ and introduce the shift operator $(\sigma_\tau \rho_i^\tau)(y,t) = \rho_i^{k-1}(y)$ for $y \in \Omega$ and $t \in ((k-1)\tau, k\tau]$. Then there exist subsequences (not relabeled) such that, as $\varepsilon \to 0$, $N \to \infty$, and $\tau \to 0$,

$$\begin{aligned} \rho_i^\tau \to \rho_i \quad & \textit{strongly in } L^p(0,T;L^p(\Omega)) \textit{ for any } p < \infty, \\ x_i^\tau \rightharpoonup x_i, \quad \Phi^\tau \rightharpoonup \Phi \quad & \textit{weakly in } L^2(0,T;H^1(\Omega)), \\ \tau^{-1}(\rho_i^\tau - \sigma_\tau(\rho_i^\tau)) \rightharpoonup \partial_t \rho \quad & \textit{weakly in } L^2(0,T;H^1(\Omega)'),\ i = 1, \ldots, n, \end{aligned}$$

and the limit (ρ, Φ) satisfies for all $\phi \in L^2(0,T;H^1(\Omega;\mathbb{R}^{n-1}))$ and $\theta \in H_D^1(\Omega)$,

$$\int_0^T \langle \partial_t \rho', \phi \rangle dt + \int_0^T \int_\Omega \nabla \phi : A_0^{-1}(\rho) D' dy dt = \int_0^T \int_\Omega r'(x) \cdot \phi dy dt, \tag{16}$$

$$\lambda \int_\Omega \nabla \Phi \cdot \nabla \theta dy = \int_\Omega \bigg(\sum_{i=1}^n z_i \frac{\rho_i}{M_i} + f(y) \bigg) \theta dy, \tag{17}$$

where $D_i = \nabla x_i + (z_i x_i - (z \cdot x)\rho_i)\nabla \Phi$, $\rho_i = c_{\rm tot} M_i x_i$, and $c_{\rm tot} = \sum_{i=1}^n \rho_i / M_i$. Moreover, $\rho_n = 1 - \sum_{i=1}^{n-1} \rho_i$.

In Theorem 3, $\langle \cdot, \cdot \rangle$ denotes the duality bracket between $H^1(\Omega;\mathbb{R}^{n-1})'$ and $H^1(\Omega;\mathbb{R}^{n-1})$. The difficult part of the proof is the estimate of the diffusion term because of the contribution of the electric field. We show in Lemma 8 that

$$\int_\Omega \nabla w^k : B \nabla w^k dy \geq K \int_\Omega \sum_{i=1}^n M_i^{1/2} \frac{|D_i^k|^2}{x_i^k} dy \geq K_1 \int_\Omega \sum_{i=1}^n |\nabla (x_i^k)^{1/2}|^2 dy - K_2$$

holds for some constants K, K_1, $K_2 > 0$, which are independent of ε, N, and τ. Then the uniform L^∞ bound for x_i^k gives a uniform $H^1(\Omega)$ bound for x_i^k and consequently for ρ_i^k. Weak compactness allows us to pass to the limits $\varepsilon \to 0$ and $N \to \infty$, and the limit $\tau \to 0$ is performed by means of the Aubin-Lions lemma.

The paper is organized as follows. In Section 2, we detail the thermodynamic modeling of system (1)-(3). Some auxiliary results on the formulation of the fluxes J_i and the inversion of the map $\rho \mapsto w$ are presented in Section 3. Sections 4 and 5 are devoted to the proof of the main theorems. Finally, some numerical experiments are shown in Section 6.

2. Modeling

We consider an isothermal electrolytic mixture of n fluid components in the bounded domain $\Omega \subset \mathbb{R}^d$ ($d \geq 1$) with boundary $\partial\Omega$. We assume that the mixture is not moving, so the barycentric velocity vanishes. The thermodynamic state of the mixture is described by the partial mass densities $\rho_1, \ldots, \rho_n$ and the electric field E. We suppose the quasi-static approximation $E = -\nabla \Phi$, where Φ is the electric potential. The evolution of the mass densities $\rho_i = M_i c_i$ with the molar masses M_i and molar concentrations (or number densities) c_i is governed by the partial mass balances [10, (4)]

$$\partial_t \rho_i + \operatorname{div} J_i = r_i(x) \quad \text{in } \Omega,\ t > 0,\ i = 1, \ldots, n,$$

where $x = (x_1, \ldots, x_n)$ is the vector of molar fractions $x_i = \rho_i/(c_{\rm tot}M_i)$, $c_{\rm tot} = \sum_{i=1}^n c_i$ is the total concentration, J_i the diffusion flux, and $r_i(x)$ the mass production rate of the ith species. We assume that the total flux and the total production vanishes,

$$\sum_{i=1}^n J_i = 0, \quad \sum_{i=1}^n r_i(x) = 0,$$

which are necessary constraints to achieve total mass conservation, $\partial_t \sum_{i=1}^n \rho_i = 0$. We suppose that the total initial mass is constant in space, $\sum_{i=1}^n \rho_i^0 = \rho_{\rm tot} > 0$, which implies that the total mass is constant in space and time, $\sum_{i=1}^n \rho_i(t) = \rho_{\rm tot}$ for $t > 0$.

The electric potential Φ is given by the Poisson equation [11, (3) and (25)]

$$-\varepsilon_0(1+\chi)\Delta\Phi = F\sum_{i=1}^n z_i c_i + f(y) \quad \text{in } \Omega,$$

where ε_0 is the dielectric constant, χ the dielectric susceptibility, F the Faraday constant, z_i the charge number of the ith species, and $f(y)$ with $y \in \Omega$ models the charge of fixed background ions.

The basic assumption of the Maxwell–Stefan theory is that the difference in speed and molar fractions leads to a diffusion flux. They are implicitly given by the driving forces d_i according to [2, (200)]

$$-\sum_{j=1}^n \frac{x_j(J_i/M_i) - x_i(J_j/M_j)}{c_{\rm tot}D_{ij}} = d_i, \quad i = 1, \ldots, n,$$

where the numbers $D_{ij} = D_{ji}$ are the Maxwell–Stefan diffusivities. Inserting the definition $x_i = \rho_i/(c_{\rm tot}M_i)$, we find that

$$-\sum_{j=1}^n \frac{\rho_j J_i - \rho_i J_j}{c_{\rm tot}^2 M_i M_j D_{ij}} = d_i. \tag{18}$$

In the present situation, the driving force is given by two components, the variation of the chemical potential μ_i and the contribution of the body forces b_i [2, (211)]:

$$d_i = \frac{c_i M_i}{RT}\nabla\mu_i - \frac{\rho_i}{RT}(b_i - b_{\rm tot}), \quad i = 1, \ldots, n,$$

where R is the gas constant and T the (constant) temperature. Since (D_{ij}) is symmetric, summing (18) from $i = 1, \ldots, n$ leads to $\sum_{i=1}^n d_i = 0$. Furthermore, $\sum_{i=1}^n \nabla\mu_i$ vanishes too; see below. This shows that $b_{\rm tot} = \rho_{\rm tot}^{-1}\sum_{i=1}^n \rho_i b_i$. We assume that the only force is due to the electric field (i.e., we neglect effects of gravity), $b_i = -(z_i/M_i)F\nabla\Phi$ [30, (3)].

It remains to determine the chemical potential. We define it by $\mu_i = \partial h_{\rm mix}/\partial\rho_i$, where $h_{\rm mix}(\rho) = c_{\rm tot}RT(\sum_{i=1}^n x_i \log x_i + 1)$ is the mixing free energy density [10, (23)]. Then

$$\mu_i = \frac{1}{c_{\rm tot}M_i}\frac{\partial h_{\rm mix}}{\partial x_i} = \frac{RT}{M_i}(\log x_i + 1),$$

and the driving force becomes

$$\begin{aligned} d_i &= c_i \nabla \log x_i + \frac{\rho_i F}{RTM_i}\left(z_i - \frac{1}{\rho_{\rm tot}}\sum_{j=1}^n \frac{z_j\rho_j}{M_j}\right)\nabla\Phi \\ &= c_{\rm tot}\left(\nabla x_i + \frac{F}{RT}\left(z_i x_i - (z\cdot x)\frac{\rho_i}{\rho_{\rm tot}}\right)\nabla\Phi\right), \end{aligned} \tag{19}$$

where $z = (z_1, \ldots, z_n)$ and $x = (x_1, \ldots, x_n)$. The Gibbs-Duhem equation

$$\sum_{i=1}^n \rho_i \frac{\partial h_{\rm mix}}{\partial \rho_i} - h_{\rm mix}(\rho) = RT\sum_{i=1}^n \rho_i \frac{\log x_i + 1}{M_i} - c_{\rm tot} RT\left(\sum_{i=1}^n x_i \log x_i + 1\right) = 0$$

shows that the pressure vanishes, which is consistent with our choice of the driving force (see [2, (211)]). The driving force in [30, (7)] contains a non-vanishing pressure that is related to our expression for the total body force. The resulting driving force (19), however, is the same.

We summarize the model equations:

$$\partial_t \rho_i + \operatorname{div} J_i = r_i(x), \quad i = 1, \ldots, n, \tag{20}$$

$$-\varepsilon_0(1+\chi)\Delta\Phi = F\sum_{i=1}^n z_i c_i + f(y), \tag{21}$$

$$-\sum_{j=1}^n \frac{\rho_j J_i - \rho_i J_j}{c_{\rm tot}^3 M_i M_j D_{ij}} = \frac{d_i}{c_{\rm tot}} = \nabla x_i + \frac{F}{RT}\left(z_i x_i - (z\cdot x)\frac{\rho_i}{\rho_{\rm tot}}\right)\nabla\Phi, \tag{22}$$

and the relations

$$c_i = \frac{\rho_i}{M_i}, \quad x_i = \frac{\rho_i}{c_{\rm tot} M_i}, \quad c_{\rm tot} = \sum_{i=1}^n c_i.$$

Equations (1)-(3) are obtained from (20)-(22) after setting $\lambda = \varepsilon_0(1+\chi)/F$, $k_{ij} = 1/(c_{\rm tot}^3 M_i M_j D_{ij})$, and $D_i = d_i/c_{\rm tot}$ and after nondimensionalization. In particular, we scale the particle densities by $\rho_{\rm tot}$ (then the scaled quantities satisfy $\sum_{i=1}^n \rho_i = 1$) and the electric potential by $F/(RT)$.

3. Auxiliary results

We collect some auxiliary results needed for the existence analysis. The starting point is the relation (2) below. Observe that the coefficients k_{ij} depend on ρ_i via $c_{\rm tot} = \sum_{i=1}^n \rho_i/M_i$. This dependency does not complicates the analysis since the results in Section 3 hold pointwise for any given ρ_i and $c_{\rm tot}$ is uniformly bounded from above and below by

$$\frac{1}{\max_{i=1,\ldots,n} M_i} \le c_{\rm tot} = \sum_{i=1}^n \frac{\rho_i}{M_i} \le \frac{1}{\min_{i=1,\ldots,n} M_i}.$$

3.1. **Expressions for the diffusion fluxes.** We review three different expressions for the diffusion fluxes following [6, 21] and extend the formulas to electro-chemical potentials. We reformulate (2):

$$D_i = -\sum_{j\neq i} k_{ij}(\rho_j J_i - \rho_i J_j) = \sum_{j\neq i} k_{ij}\rho_i\rho_j\left(\frac{J_i}{\rho_i} - \frac{J_j}{\rho_j}\right). \tag{23}$$

The symmetry of (k_{ij}) implies that $\sum_{i=1}^n D_i = 0$. Compactly, we may write $D = -AJ$, where $D = (D_1, \ldots, D_n)^\top$, $J = (J_1, \ldots, J_n)^\top$, and $A = (A_{ij})$ with

$$A_{ij} = \begin{cases} \sum_{\ell=1,\,\ell\neq i}^n k_{i\ell}\rho_\ell & \text{for } i = j, \\ -k_{ij}\rho_i & \text{for } i \neq j. \end{cases} \tag{24}$$

By Assumption (A3), it holds that $\mathrm{im}(A) = \ker(A^\top)^\perp = \mathrm{span}\{\mathbf{1}\}^\perp$, where $\mathbf{1} = (1, \ldots, 1)^\top \in \mathbb{R}^n$. We conclude from [21, Lemma 2.2] that all eigenvalues of $\widetilde{A} := A|_{\mathrm{im}(A)}$ are positive uniformly in $\rho \in [0, 1]^n$ and that $\widetilde{A}$ is invertible. Since $\sum_{i=1}^n J_i = 0$, each row of $J = (J_1, \ldots, J_n)$ is an element of $\mathrm{im}(A)$, so the linear system $D = -\widetilde{A}J$ can be inverted, yielding $J = -\widetilde{A}^{-1}D$.

We obtain another formulation by inverting the system in the first $n-1$ variables. Setting $D' = (D_1, \ldots, D_{n-1})$ and $J' = (J_1, \ldots, J_{n-1})$, we can write $D' = -A_0J'$, where the matrix $A_0 = (A^0_{ij}) \in \mathbb{R}^{(n-1)\times(n-1)}$ is defined by

$$A^0_{ij} = \begin{cases} \sum_{\ell=1,\,\ell\neq i}^{n-1}(k_{i\ell} - k_{in})\rho_\ell + k_{in} & \text{if } i = j, \\ -(k_{ij} - k_{in})\rho_i & \text{if } i \neq j. \end{cases}$$

It is shown in [6, Lemma 4] that A_0 is invertible and A_0^{-1} is bounded uniformly in $\rho \in [0, 1]^n$. Thus, $J' = -A_0^{-1}D'$.

Finally, we invert the relations (23). Using $J_n = -\sum_{i=1}^{n-1} J_i$, these relations (or the equivalent form $D_i = -\sum_{j=1}^n A_{ij}J_j$) can be written as

$$\frac{D_i}{\rho_i} - \frac{D_n}{\rho_n} = -\sum_{j=1}^{n-1} C_{ij}J_j, \tag{25}$$

where

$$C_{ij} = \frac{A_{ij}}{\rho_i} - \frac{A_{in}}{\rho_i} - \frac{A_{nj}}{\rho_n} + \frac{A_{nn}}{\rho_n} = -\frac{Y_{ij}}{\rho_i\rho_j} + \frac{Y_{in}}{\rho_i\rho_n} + \frac{Y_{nj}}{\rho_n\rho_j} - \frac{Y_{nn}}{\rho_n^2},$$

$$Y_{ij} = \begin{cases} \sum_{\ell=1,\,\ell\neq i}^n k_{i\ell}\rho_i\rho_\ell & \text{for } i = j, \\ -k_{ij}\rho_i\rho_j & \text{for } i \neq j. \end{cases}$$

The matrix $-Y = (-Y_{ij}) \in \mathbb{R}^{n\times n}$ is symmetric (since (k_{ij}) is symmetric), quasi-positive, irreducible, and it has the strictly positive eigenvector $\mathbf{1}$ with eigenvalue zero. Hence, by the Perron-Frobenius theorem, the spectral bound of $(-Y_{ij})$ is a simple eigenvalue (with value zero) and the spectrum of (Y_{ij}) consists of numbers with positive real part and zero. Thus, Y is positive semidefinite.

We claim that the matrix $C = (C_{ij}) \in \mathbb{R}^{(n-1)\times(n-1)}$ is positive definite on $\operatorname{span}\{\mathbf{1}\}^\perp$. Indeed, let $y \in \operatorname{span}\{\rho\}^\perp$. Then $y\cdot\rho = 0$. Since $\mathbf{1}\cdot\rho = 1$, we have $y \notin \operatorname{span}\{\mathbf{1}\} = \ker(Y)$ and consequently, $\operatorname{span}\{\rho\}^\perp \subset \ker(Y)^c$. This means that $-Y$ is negative definite on $\operatorname{span}\{\rho\}^\perp$. A computation shows that for any vector $w = (w_1,\ldots,w_{n-1}) \in \mathbb{R}^{n-1}$, it holds that

$$\sum_{i,j=1}^{n-1} C_{ij}w_iw_j = -\sum_{i,j=1}^{n} \frac{Y_{ij}}{\rho_i\rho_j}\widetilde{w}_i\widetilde{w}_j$$

where $\widetilde{w}_i = w_i$ for $i = 1,\ldots,n-1$ and $\widetilde{w}_n = -\sum_{i=1}^{n-1} w_i$. Then $\widetilde{w} = (\widetilde{w}_1,\ldots,\widetilde{w}_n) \in \operatorname{span}\{\mathbf{1}\}^\perp$. Since $-Y$ is negative definite on $\operatorname{span}\{\rho\}^\perp$, we infer that $(-Y_{ij}/(\rho_i\rho_j))$ is negative definite on $\operatorname{span}\{\mathbf{1}\}^\perp$. Therefore, C is positive definite on $\operatorname{span}\{\mathbf{1}\}^\perp$. Its inverse $B := c_{\mathrm{tot}}C^{-1}$ with $B = (B_{ij})$ exists, only depends on the mass density vector ρ, and is positive definite uniformly for all $\rho \in [0,1]^n$ satisfying $\sum_{i=1}^n \rho_i = 1$ [6, Lemma 10]. We deduce from (25) and (2) that

$$\begin{aligned} J_i &= -\sum_{j=1}^{n-1} B_{ij}\left(\frac{D_j}{\rho_j} - \frac{D_n}{\rho_n}\right) \\ &= -\sum_{j=1}^{n-1} B_{ij}\left(\frac{\nabla\log x_j}{M_j} - \frac{\nabla\log x_n}{M_n} + \left(\frac{z_j}{M_j} - \frac{z_n}{M_n}\right)\nabla\Phi\right) \\ &= -\sum_{j=1}^{n-1} B_{ij}\nabla w_j \qquad (26) \end{aligned}$$

for $i = 1,\ldots,n-1$ and $J_n = -\sum_{i=1}^{n-1} J_i$, recalling definition (7) of w_i. We summarize:

Lemma 4 (Formulations of J_i)**.** *Equations* (23) *can be written equivalently as*

$$J = -\widetilde{A}^{-1}D, \quad J' = -A_0^{-1}D', \quad J' = -B\nabla w.$$

The last expression for J_i shows that the partial mass balances (1) can be formulated as

$$\partial_t\rho' - \operatorname{div}(B\nabla w) = r'(\rho),$$

where $\rho = \rho(w)$ and $B = B(\rho(w))$. By Definition (7), w is a function of ρ (and Φ). The inverse relation $\rho(w)$ is discussed in the following subsection.

3.2. **Inversion of $\rho \mapsto w$.** Definition (7) defines, for given $\Phi \in \mathbb{R}$, a mapping $x \mapsto w$. We claim that this mapping can be inverted. If the molar masses are all the same, $M := M_i$, this can be done explicitly:

$$\rho_i(w) = \frac{\exp(Mw_i - (z_i - z_n)\Phi)}{1 + \sum_{j=1}^{n-1}\exp(Mw_j - (z_j - z_n)\Phi)}, \quad i = 1,\ldots,n-1, \qquad (27)$$

and $\rho_n = 1 - \sum_{i=1}^{n-1}\rho_i$. Unfortunately, when the molar masses are different, we cannot derive an explicit formula. Instead we adapt first Lemma 6 in [6].

Lemma 5 (Inversion of w and x)**.** *Let $\Phi \in \mathbb{R}$ and define the function*

$$W_\Phi : \left\{ x = (x_1, \ldots, x_n) \in (0,1)^n : \sum_{i=1}^n x_i = 1 \right\} \to \mathbb{R}^{n-1}$$

by $W_\Phi(x) = (w_1(x), \ldots, w_{n-1}(x))$, where

$$w_i(x) = \frac{\log x_i}{M_i} - \frac{\log x_n}{M_n} + \left(\frac{z_i}{M_i} - \frac{z_n}{M_n} \right) \Phi, \quad i = 1, \ldots, n-1.$$

Then W_Φ is invertible and we can define $x'(w,\Phi) := W_\Phi^{-1}(w)$ and $x_n(w,\Phi) := 1 - \sum_{i=1}^{n-1} x_i$, where $x'(w,\Phi) = (x_1, \ldots, x_{n-1})$.

Proof. The proof is similar to that one of [6, Lemma 6]. Let $w = (w_1, \ldots, w_{n-1}) \in \mathbb{R}^{n-1}$ and $\Phi \in \mathbb{R}$ be given. Define the function $f : [0,1] \to [0,\infty)$ by

$$f(s) = \sum_{i=1}^{n-1} (1-s)^{M_i/M_n} \exp\left[M_i w_i - M_i \left(\frac{z_i}{M_i} - \frac{z_n}{M_n} \right) \Phi \right], \quad s \in [0,1].$$

Then f is continuous, strictly decreasing, and $0 = f(1) < f(s) < f(0)$ for $s \in (0,1)$. Hence, there exists a unique fixed point $s_0 \in (0,1)$ such that $f(s_0) = s_0$. We define

$$x_i = (1-s_0)^{M_i/M_n} \exp\left[M_i w_i - M_i \left(\frac{z_i}{M_i} - \frac{z_n}{M_n} \right) \Phi \right] > 0, \quad i = 1, \ldots, n-1. \tag{28}$$

By definition, we have $\sum_{i=1}^{n-1} x_i = f(s_0) = s_0 < 1$. We set $x_n = 1 - s_0 > 0$ such that $\sum_{i=1}^n x_i = 1$. Moreover, (28) can be written equivalently as

$$\frac{\log x_i}{M_i} + \frac{\log(1-s_0)}{M_n} + \left(\frac{z_i}{M_i} - \frac{z_n}{M_n} \right) \Phi = w_i,$$

and since $1 - s_0 = x_n$, this shows that $W_\Phi^{-1}(w) = x'$ is the inverse mapping. $\square$

Given $\rho \in [0,1]^n$, we know that $x_i = \rho_i/(c_{\text{tot}} M_i)$ for $i = 1, \ldots, n$ and $\sum_{i=1}^n x_i = 1$. This relation can be inverted too. We recall [6, Lemma 7]:

Lemma 6 (Inversion of ρ and x)**.** *Let $x' \in (0,1)^{n-1}$ and $x_n = 1 - \sum_{i=1}^{n-1} x_i > 0$ be given and define for $i = 1, \ldots, n$,*

$$\rho_i(x') = \rho_i := c_{\text{tot}} M_i x_i, \quad \text{where } c_{\text{tot}} = \left(\sum_{j=1}^n M_j x_j \right)^{-1}.$$

Then $\rho = (\rho_1, \ldots, \rho_n)$ is the unique vector satisfying $\rho_n = 1 - \sum_{i=1}^{n-1} \rho_i > 0$, $x_i = \rho_i/(c_{\text{tot}} M_i)$ for $i = 1, \ldots, n$, and $c_{\text{tot}} = \sum_{i=1}^n \rho_i/M_i$.

Combining Lemmas 5 and 6, we conclude as in [6] that the mapping $\rho \mapsto w$ can be inverted. In fact, we just have to define $\rho' = \rho'(x'(w,\Phi))$.

Corollary 7 (Inversion of ρ and w)**.** *Let $w=(w_1,\ldots,w_{n-1})\in\mathbb{R}^{n-1}$ and $\Phi\in\mathbb{R}$ be given. Then there exists a unique vector $\rho=(\rho_1,\ldots,\rho_n)\in(0,1)^n$ satisfying $\sum_{i=1}^n\rho_i=1$ such that (7) holds for $\rho_n=1-\sum_{i=1}^{n-1}\rho_i$ and $x_i=\rho_i/(c_{\rm tot}M_i)$ with $c_{\rm tot}=\sum_{i=1}^n\rho_i/M_i$. The mapping $\rho':\mathbb{R}^{n-1}\to(0,1)^{n-1}$, $\rho'(w,\Phi)=(\rho_1,\ldots,\rho_{n-1})$, is bounded.*

4. Proof of Theorem 1

Step 1: existence of solutions. The idea is to apply the Leray-Schauder fixed-point theorem. We need to define the fixed-point operator. For this, let $\chi\in L^\infty(\Omega;\mathbb{R}^{n-1})$ and $\sigma\in[0,1]$. There exists a unique solution $\Phi^k-\Phi_D\in P_N$ to the linear finite-dimensional problem

$$\lambda\int_\Omega\nabla\Phi^k\cdot\nabla\theta dy=\int_\Omega\bigg(\sum_{i=1}^n z_ic_i(\chi+w_D,\Phi^k)+f(y)\bigg)\theta dy$$

for all $\theta\in P_N$. In particular, $\Phi^k\in L^\infty(\Omega)$. Next, we wish to solve the linear finite-dimensional problem

$$a(u,\phi)=\sigma F(\phi)\quad\text{for all }\phi\in V_N,\tag{29}$$

where

$$\begin{aligned}a(u,\phi)&=\int_\Omega\nabla\phi:B(\chi+w_D,\Phi^k)\nabla u dy+\varepsilon\int_\Omega u\cdot\phi dy,\\ F(\phi)&=-\frac{1}{\tau}\int_\Omega\big(\rho'(\chi+w_D,\Phi^k)-\rho'(u^{k-1}+w_D,\Phi^{k-1})\big)dy\\ &\quad+\int_\Omega r'(x(\chi+w_D,\Phi^k))\cdot\phi dy-\int_\Omega\nabla\phi:B(\chi+w_D,\Phi^k)\nabla w_D dy\end{aligned}$$

for u, $\phi\in V_N$. Since $\chi+w_D\in L^\infty(\Omega;\mathbb{R}^{n-1})$ and $\Phi^k\in L^\infty(\Omega)$, Corollary 7 shows that $\rho(\chi+w_D,\Phi^k)$ is bounded. We know from Section 3.1 that the matrix $B=B(\chi+w_D,\Phi^k)$ is positive definite and its elements are bounded. We deduce that the forms a and F are continuous on V_N. Exploiting the equivalence of the norms in the finite-dimensional space V_N, we find that

$$a(u,u)\ge\varepsilon\|u\|^2_{L^2(\Omega)}\ge\varepsilon K_N\|u\|^2_{H^1(\Omega)}$$

for some constant $K_N>0$, which implies that a is coercive on V_N. By the Lax–Milgram lemma, there exists a unique solution $u\in V_N\subset L^\infty(\Omega;\mathbb{R}^{n-1})$ to (29) satisfying

$$\varepsilon KN\|u\|^2_{L^\infty(\Omega)}\le a(u,u)=\sigma F(u)\le K_F\|u\|_{H^1(\Omega)},\tag{30}$$

and the constants K_N and K_F are independent of τ and σ. This defines the fixed-point operator $S:L^\infty(\Omega;\mathbb{R}^{n-1})\times[0,1]\to L^\infty(\Omega;\mathbb{R}^{n-1})$, $S(\chi,\sigma)=u$. Standard arguments show that S is continuous. Since V_N is finite-dimensional, S is also compact. Furthermore, $S(\chi,0)=0$. Estimate (30) provides a uniform bound for all fixed points of $S(\cdot,\sigma)$. Thus, by the Leray-Schauder fixed-point theorem, there exists $u^k\in V_N$ such that $S(u^k,1)=u^k$, and $w^k:=u^k+w_D$, Φ^k solve (12)-(13).

Step 2: proof of the discrete entropy production inequality (15). We use the test function $\tau(w^k - w_D) \in V_N$ in (12) and set $\rho^k := \rho'(w^k, \Phi^k)$:

$$\int_\Omega (\rho^k - \rho^{k-1}) \cdot (w^k - w_D) dy + \tau \int_\Omega \nabla(w^k - w_D) : B(w^k, \Phi^k) \nabla w^k dy$$
$$+ \varepsilon\tau \int_\Omega |w^k - w_D|^2 dy \le \tau \int_\Omega r'(x^k) \cdot (w^k - w_D) dy.$$

We claim that the first term on the left-hand side is the difference of the entropies at time steps k and $k-1$. To show this, we split the entropy density into two parts, $h(\rho^k) = h_1(\rho^k) + h_2(\rho^k)$, where

$$h_1(\rho^k) = c_{\rm tot}^k \sum_{i=1}^n x_i^k \log x_i^k, \quad h_2(\Phi^k) = \frac{\lambda}{2} |\nabla(\Phi^k - \Phi_D)|^2,$$

where we recall that $x_i^k = \rho_i^k / (c_{\rm tot}^k M_i)$ and $c_{\rm tot}^k = \sum_{i=1}^n \rho_i^k / M_i$. By the convexity of h_1, we have

$$h_1(\rho^k) - h_1(\rho^{k-1}) \le \frac{\partial h_1}{\partial \rho'}(\rho^k) \cdot (\rho^k - \rho^{k-1}) = \sum_{i=1}^n (\rho_i^k - \rho_i^{k-1}) \frac{\log x_i^k}{M_i}.$$

Therefore, using $\rho_n^k - \rho_n^{k-1} = -\sum_{i=1}^{n-1} (\rho_i^k - \rho_i^{k-1})$,

$$\int_\Omega \big(h_1(\rho^k) - h_1(\rho^{k-1})\big) dx \le \int_\Omega \bigg(\sum_{i=1}^{n-1} (\rho_i^k - \rho_i^{k-1}) \frac{\log x_i^k}{M_i} + (\rho_n^k - \rho_n^{k-1}) \frac{\log x_n^k}{M_n} \bigg) dy$$
$$= \int_\Omega \sum_{i=1}^{n-1} (\rho_i^k - \rho_i^{k-1}) \bigg(\frac{\log x_i^k}{M_i} - \frac{\log x_n^k}{M_n} \bigg) dy. \tag{31}$$

For the estimate of h_2, we first observe that

$$\sum_{i=1}^{n-1} (\rho_i^k - \rho_i^{k-1}) \bigg(\frac{z_i}{M_i} - \frac{z_n}{M_n} \bigg) = \sum_{i=1}^{n-1} (\rho_i^k - \rho_i^{k-1}) \frac{z_i}{M_i} + (\rho_n^k - \rho_n^{k-1}) \frac{z_n}{M_n}$$
$$= \sum_{n=1}^{n} (\rho_i^k - \rho_i^{k-1}) \frac{z_i}{M_i}.$$

We infer from the Poisson equation (13) and Young's inequality that

$$\int_\Omega \sum_{i=1}^{n-1} (\rho_i^k - \rho_i^{k-1}) \bigg(\frac{z_i}{M_i} - \frac{z_n}{M_n} \bigg) (\Phi^k - \Phi_D) dy$$
$$= \int_\Omega \sum_{i=1}^{n} (\rho_i^k - \rho_i^{k-1}) \frac{z_i}{M_i} (\Phi^k - \Phi_D) dy = \int_\Omega \sum_{i=1}^{n} z_i (c_i^k - c_i^{k-1}) (\Phi^k - \Phi_D) dy$$
$$= \lambda \int_\Omega \nabla\big((\Phi^k - \Phi_D) - (\Phi^{k-1} - \Phi_D) \big) (\Phi^k - \Phi_D) dy$$

$$\geq \frac{\lambda}{2}\int_\Omega |\nabla(\Phi^k - \Phi_D)|^2 dy - \frac{\lambda}{2}\int_\Omega |\nabla(\Phi^{k-1} - \Phi_D)|^2 dy$$

$$= \int_\Omega \big(h_2(\Phi^k) - h_2(\Phi^{k-1})\big) dy. \tag{32}$$

Taking into account the property $r_n(\rho^k) = -\sum_{i=1}^{n-1} r_i(\rho^k)$, definition (7) of w_i^k, and Assumption (A4), we compute

$$\begin{aligned}\int_\Omega r'(x^k)\cdot(w^k - w_D)dy &= \int_\Omega \sum_{i=1}^{n-1} r_i(x^k)\bigg(\frac{\log x_i^k}{M_i} - \frac{\log x_n^k}{M_n}\bigg)dy \\ &\quad + \int_\Omega \sum_{i=1}^{n-1} r_i(x^k)\bigg(\frac{z_i}{M_i} - \frac{z_n}{M_n}\bigg)(\Phi^k - \Phi_D)dy \\ &= \int_\Omega \sum_{i=1}^{n} r_i(x^k)\frac{\log x_i^k}{M_i}dy + \int_\Omega \sum_{i=1}^{n} r_i(x^k)\frac{z_i}{M_i}(\Phi^k - \Phi_D)dy \\ &\leq \int_\Omega \sum_{i=1}^{n} r_i(x^k)\frac{z_i}{M_i}(\Phi^k - \Phi_D)dy, \end{aligned} \tag{33}$$

Combining (31)-(33) gives the conclusion.

5. Proof of Theorem 3

Let (w^k, Φ^k) be a weak solution to scheme (12)-(13) and define $\rho^k = \rho(w^k, \Phi^k)$.

Step 1: uniform estimates. We derive estimates for ρ^k and Φ^k independent of ε, τ, and N. The starting point is the discrete entropy production inequality (15), and the main task is to estimate the diffusion part.

Lemma 8 (Estimate of the diffusion part)**.** *There exist constants $K_1 > 0$ and $K_2 > 0$, both independent of ε, τ, and N, such that*

$$\int_\Omega \nabla(w^k - w_D) : B\nabla w^k dy \geq K_1 \sum_{i=1}^n \|\nabla(x_i^k)^{1/2}\|_{L^2(\Omega)}^2 - K_2.$$

Proof. We drop the superindex k in the proof to simplify the notation. Recall that $\widetilde{A} = A|_{\mathrm{im}(A)}$, where $\mathrm{im}(A) = \mathrm{span}\{\mathbf{1}\}^\perp$. We introduce as in the proof of Lemma 12 in [6] the symmetrization $\widetilde{A}_S = P^{-1/2}\widetilde{A}P^{1/2}$, where $P^{1/2} = M^{1/2}X^{1/2}$ and $M^{1/2} := \mathrm{diag}(M_1^{1/2}, \ldots, M_n^{1/2})$, $X^{1/2} := \mathrm{diag}(x_1^{1/2}, \ldots, x_n^{1/2})$. Then $\widetilde{A}_S^{-1} = P^{-1/2}\widetilde{A}^{-1}P^{1/2}$ is a self-adjoint endomorphism whose smallest eigenvalue is bounded from below by some positive constant which depends only on (k_{ij}).

Since $0 = \sum_{i=1}^n J_i = \sum_{i=1}^n (B\nabla w)_i$, we can express the last component in terms of the other components, $(B\nabla w)_n = -\sum_{i=1}^{n-1}(B\nabla w)_i$. Then

$$\nabla w : B\nabla w = \sum_{i=1}^{n-1}\bigg\{\frac{\nabla \log x_i}{M_i} - \frac{\nabla \log x_n}{M_n} + \bigg(\frac{z_i}{M_i} - \frac{z_n}{M_n}\bigg)\nabla\Phi\bigg\}\cdot(B\nabla w)_i$$

$$
\begin{aligned}
&= \sum_{i=1}^{n-1} \frac{1}{M_i}\nabla(\log x_i + z_i\Phi)\cdot(B\nabla w)_i - \frac{1}{M_n}\nabla(\log x_n + z_n\Phi)\sum_{i=1}^{n-1}(B\nabla w)_i \\
&= \sum_{i=1}^{n} \frac{1}{M_i}\nabla(\log x_i + z_i\Phi)\cdot(B\nabla w)_i.
\end{aligned}
$$

To simplify the notation, we set $\Psi_i = \nabla(\log x_i + z_i\Phi)/M_i$, and $\Psi = (\Psi_1,\ldots,\Psi_n)$. By Lemma 4, $B\nabla w = \widetilde{A}^{-1}D = P^{1/2}\widetilde{A}_S^{-1}P^{-1/2}D$. Hence,

$$
\begin{aligned}
\nabla w : B\nabla w &= \Psi : B\nabla w = \Psi : M^{1/2}X^{1/2}\widetilde{A}_S^{-1}X^{-1/2}M^{-1/2}D \\
&= \sum_{i,j=1}^{n} \Psi_i M_i^{1/2}x_i^{1/2}(\widetilde{A}_S^{-1})_{ij}x_j^{-1/2}M_j^{-1/2}D_i \\
&= \sum_{i,j=1}^{n} \big(2\nabla x_i^{1/2} + z_i x_i^{1/2}\nabla\Phi\big)M_i^{-1/2}(\widetilde{A}_S^{-1})_{ij}M_j^{-1/2} \\
&\qquad \times \big(2\nabla x_j^{1/2} + (z_j x_j^{1/2} - (x\cdot z)\rho_j x_j^{-1/2})\nabla\Phi\big). \qquad (34)
\end{aligned}
$$

In view of $\sum_{i=1}^n (B\nabla w)_i = 0$, it follows that

$$
\begin{aligned}
&\sum_{i,j=1}^{n} \big(M_i^{-1/2}x_i^{-1/2}(z\cdot x)\rho_i\nabla\Phi\big)(\widetilde{A}_S)^{-1}_{ij}M_j^{-1/2}\big(2\nabla x_j^{1/2} + (z_j x_j^{1/2} - (x\cdot z)\rho_j x_j^{-1/2})\nabla\Phi\big) \\
&\quad = \sum_{i,j=1}^{n} \big(c(z\cdot x)\nabla\Phi\big)\widetilde{A}^{-1}_{ij}\big(\nabla x_j + (z_j x_j - (x\cdot z)\rho_j\nabla\Phi\big) \\
&\quad = \big(c(z\cdot x)\nabla\Phi\big)\cdot\sum_{i=1}^{n}(B\nabla w)_i = 0.
\end{aligned}
$$

Adding this expression to (34), we find that

$$
\begin{aligned}
\nabla w : B\nabla w = \sum_{i,j=1}^{n} & M_i^{-1/2}\big(2\nabla x_i^{1/2} + (z_i x_i^{1/2} - (z\cdot x)\rho_i x_i^{-1/2}\nabla\Phi\big)(\widetilde{A}_S)^{-1}_{ij}M_j^{-1/2} \\
& \times \big(2\nabla x_j^{1/2} + (z_j x_j^{1/2} - (z\cdot x)\rho_j x_j^{-1/2}\nabla\Phi\big).
\end{aligned}
$$

The matrix $\widetilde{A}_S^{-1}$ is positive definite on $\operatorname{im}(\widetilde{A}_S) = \operatorname{span}\{\rho^{1/2}\}$. As the vector $(2\nabla x_i^{1/2} + (z_i x_i^{1/2} - (x\cdot z)\rho_i x_i^{-1/2}\nabla\Phi)_{i=1}^n$ lies in $\operatorname{span}\{\rho^{1/2}\}$, we obtain

$$
\begin{aligned}
\nabla w : B\nabla w &\ge K_B\sum_{i=1}^{n} M_i^{-1}\big|2\nabla x_i^{1/2} + (z_i x_i^{1/2} - (x\cdot z)\rho_i x_i^{-1/2}\nabla\Phi\big|^2 \\
&\ge K_1\sum_{i=1}^{n}|\nabla x_i^{1/2}|^2 - K_2\sum_{i=1}^{n}\big|(z_i x_i^{1/2} - (x\cdot z)\rho_i x_i^{-1/2}\nabla\Phi\big|^2,
\end{aligned}
$$

where $K_1 > 0$ and $K_2 > 0$ depend on $M_1, \ldots, M_n$. Since x_i and $\rho_i x_i^{-1/2} = \rho_i^{1/2}/(c_{\rm tot} M_i)$ are bounded, the previous inequality becomes

$$\nabla w : B\nabla w \geq K_1 \sum_{i=1}^{n} |\nabla x_i^{1/2}|^2 - K_3 |\nabla\Phi|^2, \tag{35}$$

where K_3 depends on K_2 and z_i.

In the following, let $K > 0$ be a generic constant independent of ε, n, and τ. We estimate the expression involving the boundary term

$$\begin{aligned} \nabla w_D : B\nabla w &= \nabla w_D : A_0^{-1} D' \\ &= \sum_{i,j=1}^{n-1} (A_0^{-1})_{ij} \left(\frac{z_i}{M_i} - \frac{z_n}{M_n}\right) \nabla\Phi_D \cdot \big(\nabla x_i + (z_i x_i - (z\cdot x)\rho_i)\nabla\Phi\big) \\ &\leq \frac{K}{\delta} + \delta \sum_{i=1}^{n-1} \big|\nabla x_i + (z_i x_i - (z\cdot x)\rho_i)\nabla\Phi\big|^2, \end{aligned}$$

where $K > 0$ depends on $\nabla\Phi_D$, z_i, M_i, and A_0^{-1}. Since $0 \leq x_i \leq 1$, we have $|\nabla x_i|^2 = 4x_i |\nabla x_i^{1/2}|^2 \leq 4|\nabla x_i^{1/2}|^2$ and therefore,

$$\nabla w_D : B\nabla w \leq \frac{K}{\delta} + 4\delta |\nabla x_i^{1/2}|^2 + \delta K |\nabla\Phi|^2. \tag{36}$$

We infer from (35) and (36) that

$$\int_\Omega \nabla(w - w_D) : B\nabla w dy \geq (K_1 - 4\delta) \sum_{i=1}^{n} \|\nabla x_i^{1/2}\|_{L^2(\Omega)}^2 - K_3 \|\nabla\Phi\|_{L^2(\Omega)}^2 - \frac{K}{\delta}.$$

By the boundedness of c_i, the elliptic estimate for the Poisson equation gives

$$\|\Phi\|_{H^1(\Omega)} \leq K(1 + \|c_i\|_{L^2(\Omega)}) \leq K. \tag{37}$$

This proves the lemma. $\square$

Combining the discrete entropy inequality (15) and the estimate of Lemma 8 and summation over k leads to the following result.

Corollary 9. *There exist constants $K_1 > 0$ and $K_2 > 0$, both independent of ε, n, and τ, such that*

$$H(\rho^k) + \tau K_1 \sum_{j=1}^{k} \sum_{i=1}^{n} \|\nabla(x_i^k)^{1/2}\|_{L^2(\Omega)}^2 + \varepsilon\tau \sum_{j=1}^{k} \|w^j - w_D\|_{L^2(\Omega)}^2 \leq \tau k K_2 + H(\rho^0). \tag{38}$$

Step 2: limit $\varepsilon \to 0$. For a fixed time step k, let $(w^\varepsilon, \Phi^\varepsilon)$ be a solution to (12)-(13) with $\rho^\varepsilon = \rho(w^\varepsilon, \Phi^\varepsilon)$ and $x_i^\varepsilon = \rho_i^\varepsilon/(c_{\rm tot}^\varepsilon M_i)$. Estimates (37) and (38) yield the following uniform bounds:

$$\|\rho_i^\varepsilon\|_{L^\infty(\Omega)} + \|x_i^\varepsilon\|_{L^\infty(\Omega)} \leq 1, \quad i = 1, \ldots, n, \tag{39}$$

$$\|x_i^\varepsilon\|_{H^1(\Omega)} + \|\Phi^\varepsilon\|_{H^1(\Omega)} + \varepsilon^{1/2} \|w_i^\varepsilon\|_{L^2(\Omega)} \leq K, \tag{40}$$

where $K > 0$ is independent of ε and N. The bound for x_i^ε in $H^1(\Omega)$ is a consequence of the bound for $(x_i^\varepsilon)^{1/2}$ in $H^1(\Omega)$ from (38) and the uniform L^∞ bound for x_i^ε from (39). It follows that $c_{\rm tot}^\varepsilon = \sum_{i=1}^n \rho_i^\varepsilon/M_i$ is uniformly bounded in $L^\infty(\Omega)$. Moreover, because of $\sum_{i=1}^n \rho_i^\varepsilon = 1$, $c_{\rm tot}^\varepsilon \ge (\max_i M_i)^{-1} > 0$ is uniformly positive. This shows that $\rho_i^\varepsilon = c_{\rm tot}^\varepsilon M_i x_i^\varepsilon$ is uniformly bounded in $H^1(\Omega)$. Oberserving that the embedding $H^1(\Omega) \hookrightarrow L^2(\Omega)$ is compact, there exist subsequences, which are not relabeled, such that as $\varepsilon \to 0$,

$$
\begin{aligned}
x_i^\varepsilon \to x_i, \quad \rho_i^\varepsilon \to \rho_i, \quad \Phi^\varepsilon &\to \Phi \quad \text{strongly in } L^2(\Omega), \\
x_i^\varepsilon \rightharpoonup x_i, \quad \rho_i^\varepsilon \rightharpoonup \rho_i, \quad \Phi^\varepsilon &\rightharpoonup \Phi \quad \text{weakly in } H^1(\Omega), \\
\varepsilon w_i^\varepsilon &\to 0 \quad \text{strongly in } L^2(\Omega).
\end{aligned}
$$

In view of the L^∞ bounds for (x_i^ε) and (ρ_i^ε), the strong convergences for these (sub-)sequences hold in $L^p(\Omega)$ for any $p < \infty$. Consequently, $c_{\rm tot}^\varepsilon \to c_{\rm tot} := \sum_{i=1}^n \rho_i/M_i$ strongly in $L^2(\Omega)$, and we can identify $\rho_i = c_{\rm tot} M_i x_i$ for $i = 1, \ldots, n$. Furthermore,

$$
c_i^\varepsilon = \rho_i^\varepsilon/M_i \to c_i := \rho_i/M_i \quad \text{strongly in } L^2(\Omega),\ i = 1, \ldots, n.
$$

Recalling definition (2) of D_i, we have

$$
D_i^\varepsilon = \nabla x_i^\varepsilon + (z_i x_i^\varepsilon - (z \cdot x^\varepsilon)\rho_i^\varepsilon)\nabla\Phi^\varepsilon \rightharpoonup D_i := \nabla x_i + (z_i x_i - (z \cdot x)\rho_i)\nabla\Phi \tag{41}
$$

weakly in $L^q(\Omega)$ for any $q < 2$ and $i = 1, \ldots, n$. Since (D_i^ε) is bounded in $L^2(\Omega)$, there exists a subsequence which converges to some function $\widetilde{D}_i$ weakly in $L^2(\Omega)$. By the uniqueness of the weak limits, we can identify $\widetilde{D}_i = D_i$. This shows that the convergence (41) holds in $L^2(\Omega)$. We deduce from the strong convergence of (x_i^ε), the boundedness of (x_i^ε) in $L^\infty(\Omega)$, and the continuity of r_i that $r_i(x^\varepsilon) \to r_i(x)$ strongly in $L^2(\Omega)$.

We know from Lemma 4 that $B(w^\varepsilon)\nabla w^\varepsilon = A_0^{-1}(\rho^\varepsilon)(D^\varepsilon)'$. As $A_0^{-1}(\rho)$ is uniformly bounded for $\rho \in [0,1]^n$ and (ρ^ε) converges strongly to ρ, we infer that $A_0^{-1}(\rho^\varepsilon) \to A_0^{-1}(\rho)$ strongly in $L^2(\Omega)$; the convergence holds even in every $L^p(\Omega)$ for $p < \infty$. Then, because of (41),

$$
A_0^{-1}(\rho^\varepsilon)(D^\varepsilon)' \rightharpoonup A_0^{-1}(\rho)D' \quad \text{weakly in } L^q(\Omega) \text{ for all } q < 2. \tag{42}
$$

In fact, since $A_0^{-1}(\rho^\varepsilon)(D^\varepsilon)')$ is bounded in $L^2(\Omega)$ and thus (up to a subsequence) weakly converging in $L^2(\Omega)$, the convergence holds in $L^2(\Omega)$.

These convergences are sufficient to perform the limit $\varepsilon \to 0$ in (12)-(13). We conclude that $(\rho^k, \Phi^k) := (\rho, \Phi)$ solves

$$
\frac{1}{\tau}\int_\Omega \big((\rho^k)' - (\rho^{k-1})'\big) \cdot \phi dy + \int_\Omega \nabla\phi : A_0^{-1}(\rho^k)\nabla\rho^k dy = \int_\Omega r'(x^k) \cdot \phi dy, \tag{43}
$$

$$
\lambda \int_\Omega \nabla\Phi^k \cdot \nabla\theta dy = \int_\Omega \bigg(\sum_{i=1}^n z_i c_i^k + f(y)\bigg)\theta dy \tag{44}
$$

for all $\phi \in V_N$, $\theta \in P_N$.

Step 3: limit $N \to \infty$. Let (ρ^N, Φ^N) be a solution to (43)-(44). Estimates (39)-(40) are independent of N. Thus, we can exactly argue as in step 2 and obtain limit functions (x, ρ, Φ) and $c_i = c_{\rm tot} M_i x_i$ for $i = 1, \ldots, n$ as $N \to \infty$. These functions satisfy (43)-(44)

for all $\phi \in V_N$ and $\theta \in P_N$ and for all $N \in \mathbb{N}$. The union of all V_N is dense in $H^1(\Omega;\mathbb{R}^{n-1})$ and the union of all P_N is dense in $H^1_D(\Omega)$. Thus, by a density argument, system (43)-(44) holds for all test functions $\phi \in H^1(\Omega;\mathbb{R}^{n-1})$ and $\theta \in H^1_D(\Omega)$.

Step 4: limit $\tau \to 0$. Let (ρ^k, Φ^k) be a solution to (43)-(44) with test functions $\phi \in H^1(\Omega;\mathbb{R}^{n-1})$ and $\theta \in H^1_D(\Omega)$. Then $\rho_i^k = c_{\rm tot}^k M_i x_i^k$ and $c_i^k = \rho_i^k/M_i$ for $i = 1, \ldots, n$. We set

$$\rho_i^\tau(y,t) = \rho_i^k(y), \quad x_i^\tau(y,t) = x_i^k(y), \quad c_i^\tau(y,t) = c_i^k(y), \quad \Phi^\tau(y,t) = \Phi^k(y)$$

for $y \in \Omega$, $t \in ((k-1)\tau, k\tau]$, $i = 1, \ldots, n$ and introduce the shift operator $(\sigma_\tau \rho^\tau)(y,t) = \rho^\tau(y)$ for $y \in \Omega$ and $t \in ((k-1)\tau, k\tau]$. Finally, we set $D_i^\tau = \nabla x_i^\tau + (z_i x_i^\tau - (z \cdot x^\tau)\rho_i^\tau)\nabla\Phi^\tau$ and $T = m\tau$ for some fixed $m \in \mathbb{N}$. Then we can write system (43)-(44) as

$$\begin{aligned} &\frac{1}{\tau}\int_0^T \int_\Omega \big((\rho^\tau)' - \sigma_\tau(\rho^\tau)'\big) \cdot \phi dydt + \int_0^T \int_\Omega \nabla\phi : A_0^{-1}(\rho^\tau)(D^\tau)' dydt \\ &\quad = \int_0^t \int_\Omega r'(x^\tau) \cdot \phi dydt, \end{aligned} \tag{45}$$

$$\lambda \int_\Omega \nabla\Phi^\tau \cdot \nabla\theta dy = \int_\Omega \bigg(\sum_{i=1}^n z_i c_i^\tau + f(y)\bigg)\theta dy \tag{46}$$

for all piecewise constant functions $\phi : (0,T) \to H^1(\Omega; R^{n-1})$ and $\theta : (0,T) \to H^1_D(\Omega)$. The entropy inequality (38), formulated in terms of (ρ^τ, Φ^τ), provides us with further uniform bounds since the right-hand side of (38) does not depend on τ:

$$\|\rho_i^\tau\|_{L^\infty(\Omega_T)} + \|x_i^\tau\|_{L^\infty(\Omega_T)} \le K, \tag{47}$$

$$\|\rho_i^\tau\|_{L^2(0,T;H^1(\Omega))} + \|x_i^\tau\|_{L^2(0,T;H^1(\Omega))} + \|\Phi^\tau\|_{L^2(0,T;H^1(\Omega))} \le K, \tag{48}$$

where we have set $\Omega_T = \Omega \times (0,T)$. As a consequence, (D_i^τ) is bounded in $L^2(0,T;H^1(\Omega))$.

It remains to derive a uniform estimate for the discrete time derivative of ρ^τ. Taking into account the uniform bound for $A_0^{-1}(\rho^\tau)$, it follows that

$$\begin{aligned} \frac{1}{\tau}\bigg|\int_0^t \int_\Omega \big((\rho^\tau)' - \sigma_\tau(\rho^\tau)'\big) \cdot \phi dydt\bigg| &\le \int_0^T \|\nabla\phi\|_{L^2(\Omega)} \|A_0^{-1}(\rho^\tau)\|_{L^\infty(\Omega)} \|(D^\tau)'\|_{L^2(\Omega)} dt \\ &\quad + \int_0^T \|r'(x^\tau)\|_{L^2(\Omega)} \|\phi\|_{L^2(\Omega)} dt \le C\|\phi\|_{L^2(0,T;H^1(\Omega))}. \end{aligned}$$

As the piecewise constant functions $\phi : (0,T) \to H^1(\Omega;\mathbb{R}^{n-1})$ are dense in $L^2(0,T; H^1(\Omega;\mathbb{R}^{n-1}))$, this estimate also holds for all $\phi \in L^2(0,T;H^1(\Omega;\mathbb{R}^{n-1}))$, and we conclude that

$$\tau^{-1}\big\|(\rho^\tau)' - \sigma_\tau(\rho^\tau)'\big\|_{L^2(0,T;H^1(\Omega)')} \le K, \quad i = 1, \ldots, n-1.$$

This estimate also holds for $i = n$ since $\rho_n^\tau = 1 - \sum_{i=1}^{n-1} \rho_i^\tau$.

By the Aubin-Lions lemma in the version of [9], there exists a subsequence of (ρ^τ) which is not relabeled such that, as $\tau \to 0$,

$$\rho_i^\tau \to \rho_i \quad \text{strongly in } L^2(\Omega_T), \ i = 1, \ldots, n.$$

In view of the L^∞ bound (47) for ρ^τ, this convergence also holds in $L^p(\Omega_T)$ for any $p < \infty$. Furthermore, by (48), we have up to subsequences,

$$x_i^\tau \rightharpoonup x_i, \quad \Phi^\tau \rightharpoonup \Phi \quad \text{weakly in } L^2(0,T;H^1(\Omega)),$$
$$\tau^{-1}(\rho_i^\tau - \sigma_\tau(\rho_i^\tau)) \rightharpoonup \partial_t\rho_i \quad \text{weakly in } L^2(0,T;H^1(\Omega)').$$

In particular, $D_i^\tau \rightharpoonup D_i$ weakly in $L^2(\Omega_T)$, and we can identify $D_i = \nabla x_i + (z_i x_i - (z\cdot x)\rho_i)\nabla\Phi$. The strong convergence of (ρ^τ) and the weak convergence of (D_i^τ) imply that

$$A_0^{-1}(\rho^\tau)(D^\tau)' \rightharpoonup A_0^{-1}(\rho)D' \quad \text{weakly in } L^q(\Omega_T),\ q<2.$$

Again, since $(A_0^{-1}(\rho^\tau)(D^\tau)')$ is bounded in $L^2(\Omega_T)$, this convergence holds in $L^2(\Omega_T)$. Furthermore, $r'(x^\tau) \to r'(x)$ strongly in $L^2(\Omega_T)$. Therefore, we can pass to the limit $\tau \to 0$ in (45)-(46) yielding (16)-(17).

Finally, the assumption $\rho_i^0 \geq \eta > 0$ can be relaxed to $\rho_i^0 \geq 0$ by passing to the limit $\eta \to 0$. This is carried out in [6, Section 3.2] and we refer to this reference for details.

6. Numerical experiments

In this section, some numerical experiments based on scheme (12)-(13) in one space dimension are presented.

6.1. **Discretization and iteration procedure.** Let $\Omega = (0,1)$ be divided into $n_p \in \mathbb{N}$ uniform subintervals of length $h = 1/n_p$. We use uniform time steps with time step size $\tau > 0$ and linear finite elements. We impose Dirichlet boundary condition for the electric potential Φ. Given the variables (w,Φ), the molar fractions x_i are computed from the fixed-point problem (see the proof of Lemma 5)

$$f(s) = \sum_{i=1}^{n-1}(1-s)^{M_i/M_n}\exp\left[M_iw_i - M_i\left(\frac{z_i}{M_i} - \frac{z_n}{M_n}\right)\Phi_0\right], \quad s\in[0,1], \tag{49}$$

with unique solution $s_0 \in (0,1)$. The molar fractions are recovered froms (28),

$$x_i = (1-s_0)^{M_i/M_n}\exp\left[M_iw_i - M_i\left(\frac{z_i}{M_i} - \frac{z_n}{M_n}\right)\Phi\right], \quad i=1,\ldots,n-1,$$

and $x_n = 1 - s_0$. Then we set (see Lemma 6) $c_{\rm tot} = \sum_{i=1}^n (M_ix_i)^{-1}$ and $\rho_i = c_{\rm tot}M_ix_i$ for $i = 1,\ldots,n$.

Instead of solving the nonlinear discrete system (12)-(13) by a full Newton method, we employ a linearized semi-implicit approach, i.e., we linearize $\rho(w,\Phi)$ and use the previous time step in the diffusion matrix $B(w)$. More precisely, let $\overline{w} \in V_N$ and $\overline{\Phi} \in P_N$ be given. We linearize $\rho(w,\Phi)$ by

$$\rho(\overline{w},\overline{\Phi}) + \nabla_{(w,\Phi)}\rho'(\overline{w},\overline{\Phi})\cdot(w-\overline{w},\Phi-\overline{\Phi}).$$

This leads to the problem in the variable $\zeta = (w-\overline{w},\Phi-\overline{\Phi})$:

$$L(\zeta,\phi) = F(\phi), \quad K(\zeta_n,\theta) = G(\theta) \quad \text{for all } \phi\in V_N,\ \theta\in P_N, \tag{50}$$

where

$$
\begin{aligned}
L(\zeta,\phi) &= \int_\Omega \nabla_{(w,\Phi)}\rho'(\overline{w},\overline{\Phi})\cdot(\zeta,\phi)dy + \tau\int_\Omega \partial_x\phi\cdot B(\overline{w},\overline{\Phi})\partial_x\zeta dy + \varepsilon\tau\int_\Omega(\zeta - w_D)\cdot\phi dy,\\
F(\phi) &= -\int_\Omega\big(\rho'(\overline{w},\overline{\Phi}) - \rho'(w^{k-1},\Phi^{k-1})\big)\cdot\phi dy - \tau\int_\Omega\partial_x\phi\cdot B(\overline{w},\overline{\Phi})\partial_x\overline{w}dy,\\
K(\zeta_n,\theta) &= \lambda\int_\Omega\partial_x\zeta_n\partial_x\phi dy - \int_\Omega\sum_{i=1}^n\frac{z_i}{M_i}\nabla_{(w,\Phi)}\rho_i(\overline{w},\overline{\Phi})\cdot\zeta\theta dy,\\
G(\theta) &= -\lambda\int_\Omega\partial_x\overline{\Phi}\partial_x\theta dy + \int_\Omega\bigg(\sum_{i=1}^n z_i\frac{\rho_i(\overline{w},\overline{\Phi})}{M_i} + f(y)\bigg)\theta dy.
\end{aligned}
$$

The iteration with starting point $(w_h^{(0)},\Phi_h^{(0)}) := (w^{k-1},\Phi^{k-1})$ is then defined by $(w_h^{(m+1)},\Phi_h^{(m+1)}) := (\overline{w},\overline{\Phi}) + \zeta$ for $m\ge 0$. The iteration stops when $\|\zeta\|_{\ell^\infty} < \varepsilon_{\rm tol}$ for some tolerance $\varepsilon_{\rm tol} > 0$ or if $m \ge m_{\max}$ for a maximal number of iterations. We summarize the scheme in Algorithm 1.

Algorithm 1 (Pseudo-code for the finite-element scheme in entropy variables.)

procedure MAXWELL-STEFAN SYSTEM IN ENTROPY VARIABLES
  Set $(\overline{w}_h^{(0)},\overline{\Phi}_h^{(0)}) = (w^{k-1},\Phi^{k-1})$, $\rho_h^{(0)} = \rho'(\overline{w}_h^0,\overline{\Phi}_h^0)$, $x_h^{(0)} = \rho_h^{(0)}/(M_ic_h^{(0)})$, $c_h^{(0)} = \sum_{i=1}^n(\rho_h^{(0)})_i/M_i$, $m = 0$, $\varepsilon > 0$, and $m_{\max}$.
  while $err > \varepsilon$ **do**
    Solve linear system (50) with solution ζ.
    Set $(\overline{w}_h^{(m+1)},\overline{\Phi}_h^{(m+1)}) := (\overline{w}_h^m,\overline{\Phi}_h^m) + \zeta$.
    Solve the fixed-point problem (49) with solution s_0.
    Compute $x_h^{(m+1)}$ and $\rho_h^{(m+1)}$.
    Set err $:= \|(\overline{w}_h^{(m+1)},\overline{\Phi}_h^{(m+1)}) - (\overline{w}_h^{(m)},\overline{\Phi}_h^{(m)})\|_{\ell^\infty}$.
    $(m+1) \leftarrow (m)$.
    if $m > m_{\max}$ or err $< \varepsilon$ **then**
      Break
    end if
  end while
end procedure

The linear system (50) and the fixed-point problem (49) are solved using MATLAB. We choose the numerical parameters $h = 10^{-2}$, $\tau = 10^{-3}$, $\varepsilon_{\rm tol} = 10^{-10}$, and $\varepsilon = 2^{-52} \approx 2.2204\cdot 10^{-16}$ (the scheme works also for $\varepsilon = 0$).

We have compared our results with the solutions from a finite-element scheme derived from the original system in the variables ρ_i and a Picard iteration procedure for the nonlinear discrete system. It turned out that the results are basically the same, i.e. $\|\rho_i - \rho_i(w,\Phi)\|_{L^\infty(\Omega)} \le 10^{-10}$.

6.2. **Numerical examples.** In all numerical examples, we neglect reaction terms and choose the diffusivities according to [3, 13]: $D_{12} = 0.833$, $D_{13} = 0.680$, and $D_{23} = 0.168$ for $n = 3$. The charges are given by $z_1 = z_2 = 1$ and $z_3 = 0$ and the initial data is defined as in [3]:

$$\rho_1^0(y) = \begin{cases} 0.7 & \text{for } y < 0.25, \\ -2(0.7-\eta)y - 2(0.25\eta - (0.7\cdot 0.75)) & \text{for } 0.25 \le y < 0.75, \\ \eta & \text{for } 0.75 \le y \le 1 \end{cases}$$

for $\eta = 10^{-5}$, $\rho_2^0(y) = 0.2$, and $\rho_3^0(y) = (1-\rho_1^0-\rho_2^0)(y)$ for $y \in \Omega = (0,1)$.

For the first example, the boundary conditions for the electric potential are supposed to be in equilibrium, i.e. $\Phi(y) = 0$ for $y \in \{0,1\}$. The dynamics of the particle densities and the electric potential are shown in Figure 1. The solution at time $t = 17$ is essentially stationary and, in fact, in equilibrium. Because of the choice of the parameters, the stationary solution is symmetric around $x = \frac{1}{2}$.

The situation changes drastically when the molar masses are different (example 2). Figure 2 shows the stationary solutions with the same parameters as in the previous example except $M_1 = 6$. Here, the discrete relative entropy is defined by

$$H^*(\rho_h^k) = \int_0^1 \bigg(c_{\mathrm{tot},h}^k \sum_{i=1}^n (x_h^k)_i \log \frac{(x_h^k)_i}{(x_h^\infty)_i} + \frac{\lambda}{2} |\nabla(\Phi_h^k - \Phi_h^\infty)|^2 \bigg) dy,$$

where (ρ_h^k, Φ_h^k) is the finite-element solution at time $k\tau$ and $(x_h^\infty, \Phi_h^\infty)$ is the stationary solution. The integral and gradients are computed by the trapezoidal and gradient routines of MATLAB. The semi-logarithmic plot of the relative entropy shows that the entropy converges to zero exponentially fast.

For example 3, we choose the same initial conditions and parameters as before, but we take non-equilibrium boundary data $\Phi(0) = 10$, $\Phi(1) = 0$. The solutions at time $t = 8$ for various molar masses M_1 are displayed in Figure 3. Since ρ_1 and ρ_2 have both positive charge and the potential on the left boundary is positive, both species avoid the left boundary and move to the right.

In example 4, we interchange the roles of M_1 and M_2, i.e., we choose $M_1 = 1$ and $M_2 \in \{2, 4, 6\}$. We observe in Figure 4 that the first species is more concentrated at the right boundary while in the previous example, this holds true for the second species.

The previous examples show that the convergence rate to equilibrium strongly depends on the ratio of the molar masses. It turns out that this effect is triggered by the drift term, and without electric field, the convergence rates are similar for different molar masses. This behavior can be observed in Figure 5 (example 5), where we have taken the same parameters as in the previous example but neglect the electric field. In this situation, the steady state is constant in space and explicitly computable; indeed, we have $\rho_i^\infty = \mathrm{mean}(\Omega)^{-1}\|\rho_i^0\|_{L^1(\Omega)}$. Note that the steady state in the previous examples is not constant.

Finally, we compute the numerical convergence rate when the grid size tends to zero for the situation of example 3 (non-equilibrium boundary conditions for the potential). We choose the time $t = 0.01$ and the time step size $\tau = 10^{-4}$. The solutions are computed on

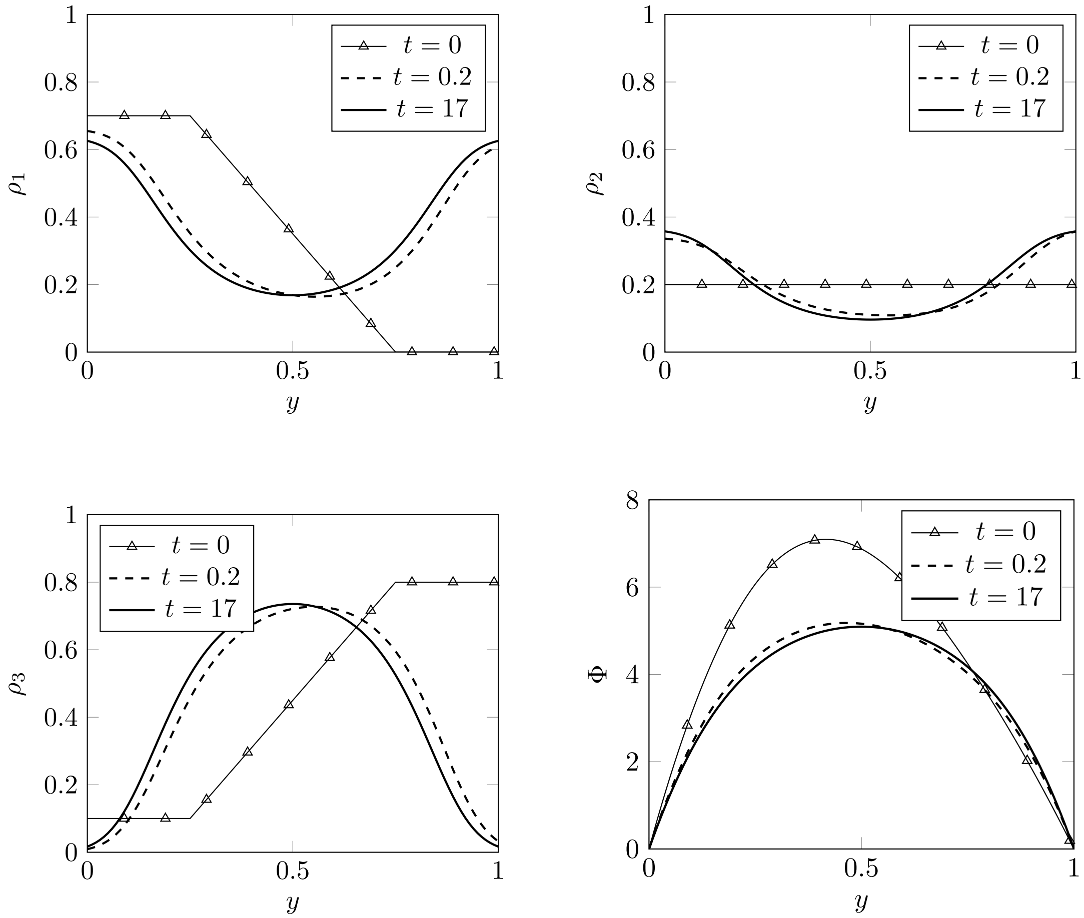

FIGURE 1. Example 1: Particle densities ρ_i and electric potential for molar masses $M_1 = M_2 = M_3 = 1$ versus position at various times. The boundary conditions for the electric potential are in equilibrium.

nested meshes with grid sizes $h \in \{0.01, 0.005, 0.0025, 0.0006, 0.0001\}$ and compared to the reference solution, computed on a very fine mesh with 25601 elements ($h \approx 4 \cdot 10^{-5}$). As expected, we observe a second-order convergence in space; see Figure 6.

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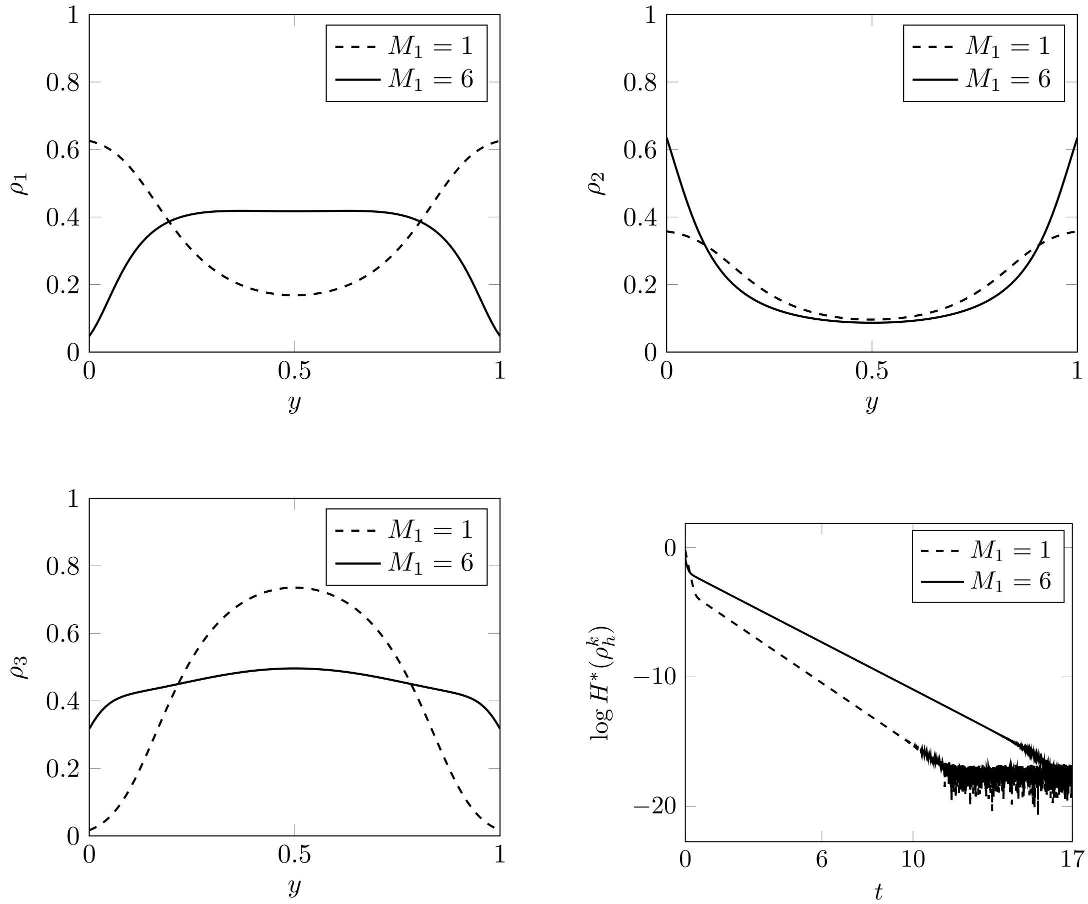

FIGURE 2. Example 2: Particle densities ρ_i at time $t = 4$ versus position and relative entropy (bottom right) for molar masses $M_1 = 6$ and $M_2 = M_3 = 1$. The boundary conditions for the electric potential are in equilibrium.

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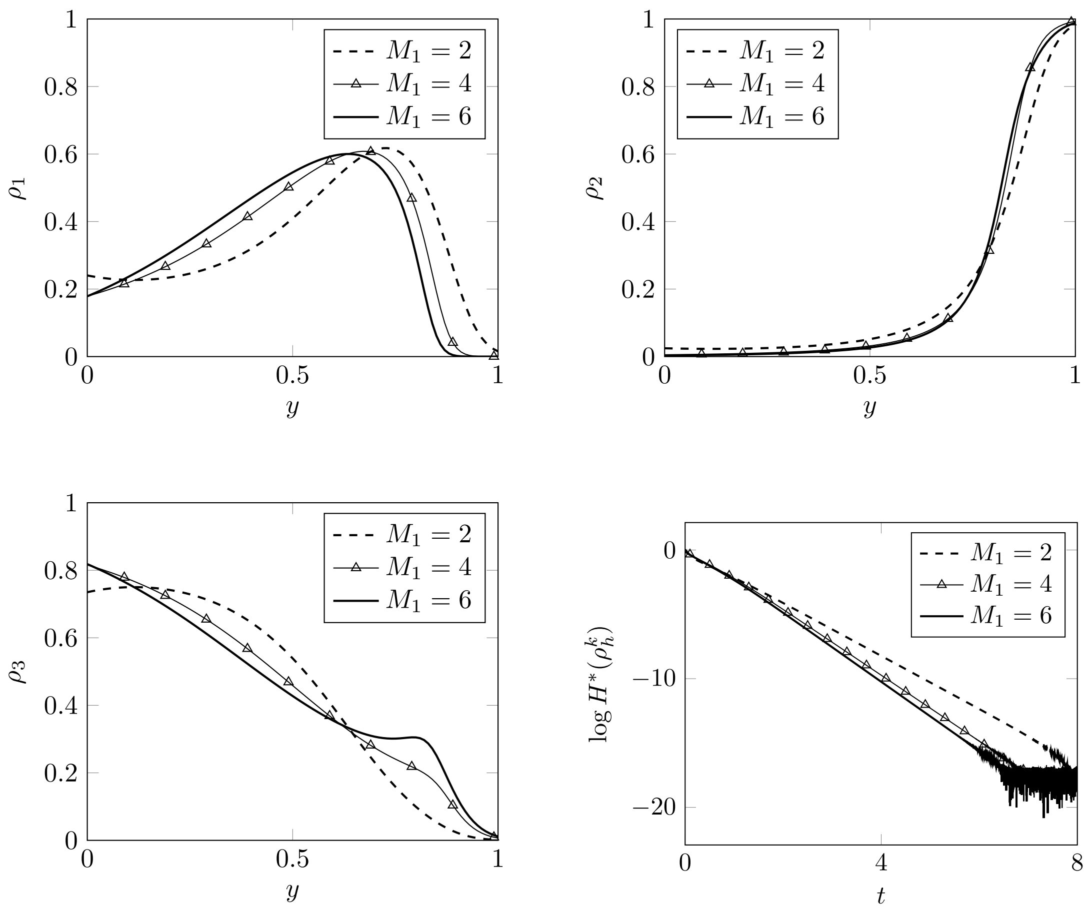

FIGURE 3. Example 3: Particle densities ρ_i at time $t = 8$ versus position and relative entropy (bottom right) for various molar masses M_1. The boundary conditions for the electric potential are not in equilibrium.

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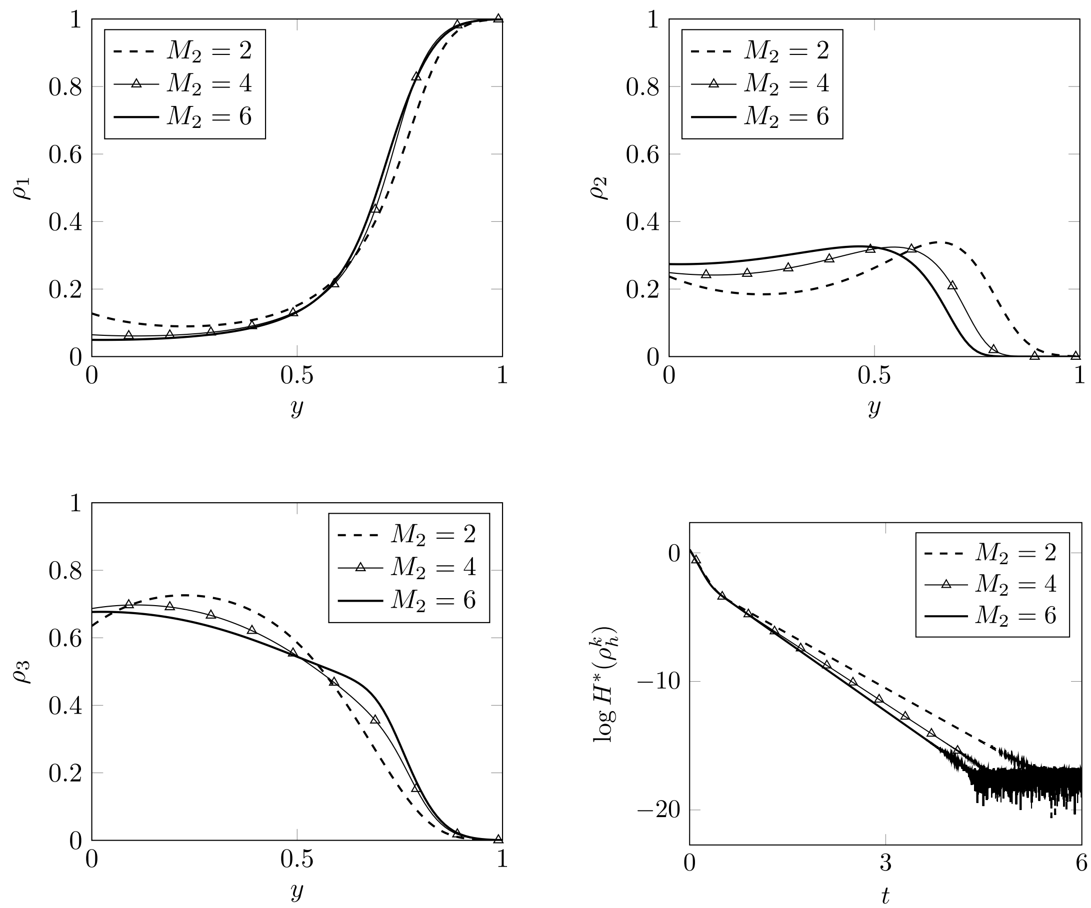

FIGURE 4. Example 4: Particle densities ρ_i at time $t = 8$ versus position and relative entropy (bottom right) for various molar masses M_2. The boundary conditions for the electric potential are not in equilibrium.

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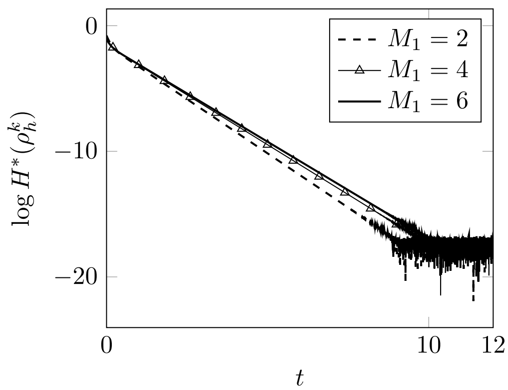

FIGURE 5. Example 5: Semi-logarithmic plot of the relative entropy $H^*(\rho_h^k)$ versus time, without electric potential and for different molar masses.

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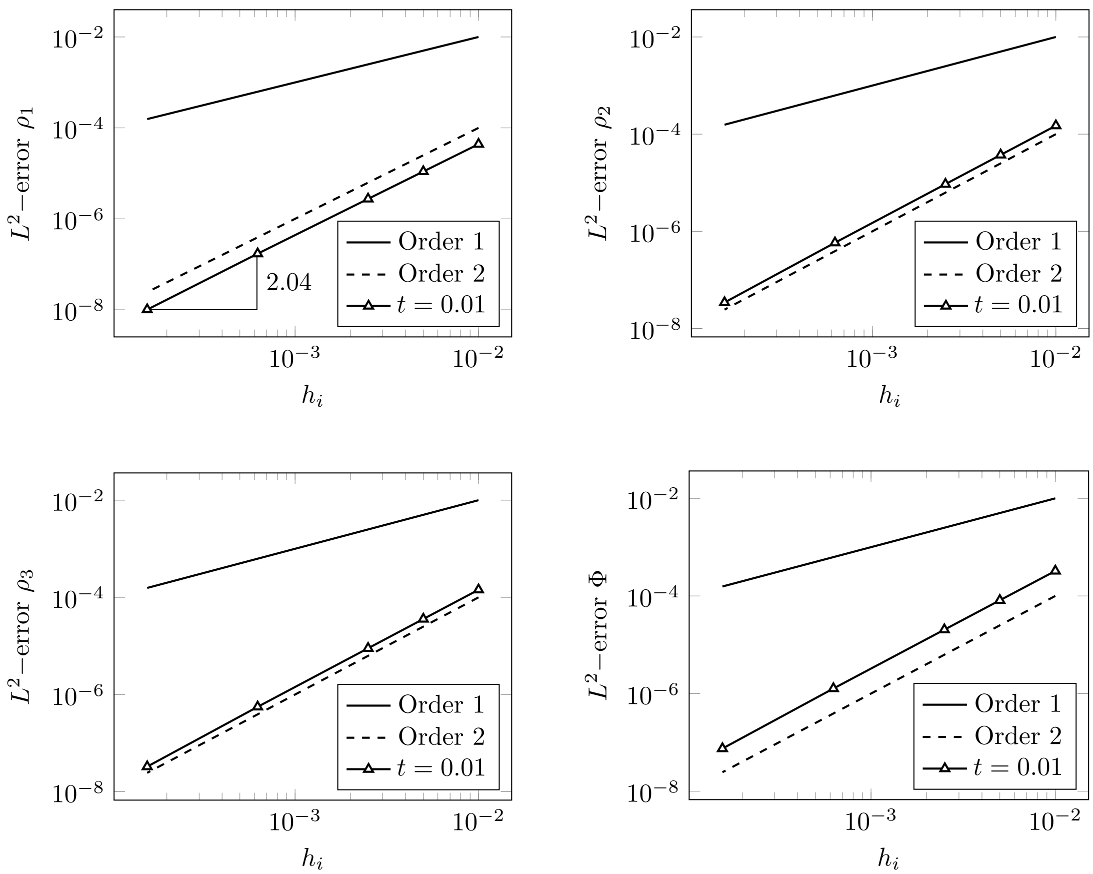

FIGURE 6. Discrete L^2-error relative to the reference solution for the densities and the potential (bottom right) at time $t = 0.01$.