MATHEMATICAL MODELING AND ANALYSIS OF PDE-MODELS FOR SEMICONDUCTOR DEVICES

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Contents

Abstract

This thesis is concerned with the study of certain aspects of semiconductor materials both from an analytical point of view as well as from an optimization perspective. On the one hand, we focus on a system of partial differential equations (PDE) which models the dynamics of negatively charged electrons and positively charged holes inside a semiconductor. This PDE-system generalizes the Shockley–Read–Hall-model which accounts for recombination, drift and diffusion of the charged particles by means of an additional internal energy level. Our main result states that the charge densities of electrons and holes converge to their equilibrium distributions at an exponential rate. Moreover, this convergence rate is independent of the mean residence time of electrons in the additional energy level. On the other hand, we investigate a material design problem in the context of photovoltaics. Given a density of positive nuclear charges inside a photovoltaic cell, we determine the resulting electronic density by solving the Kohn–Sham equations. In short, the structure of the charge density of the electrons may change under the influence of incident light due to internal electronic excitations. We prove that there exists a certain nuclear density which maximizes the change of the electronic density under the influence of a specific light. A 1D simulation of an atomic chain reveals a pronounced charge transfer for certain nuclear densities. Within a future application, one could use this charge separation to obtain an electric current. At the end, we study a PDE-model for electrons and holes in a semiconductor including the influence of the selfconsistent potential generated by these charge carriers. As the main result, we prove exponential convergence to the equilibrium for the corresponding charge densities.

Kurzfassung

Diese Arbeit beschäftigt sich mit der Untersuchung bestimmter Aspekte von Halbleitermaterialien. Dafür kommen sowohl analytische Methoden als auch Techniken der Optimierung zur Anwendung. Einerseits betrachten wir ein System partieller Differentialgleichungen (PDG), das die dynamischen Prozesse negativ geladener Elektronen und positiv geladener Löcher modelliert. Dieses PDG-System verallgemeinert das Shockley–Read–Hall-Modell, das Rekombinationen, Drift und Diffusion der Teilchen mithilfe eines zusätzlichen internen Energieniveaus beschreibt. Unser Hauptresultat besagt, dass die Ladungsdichten der Elektronen und Löcher mit exponentieller Rate zu ihren Gleichgewichtsverteilungen konvergieren. Diese Konvergenzrate ist unabhängig von der mittleren Verweildauer der Elektronen im zusätzlichen Energieniveau. Andererseits behandeln wir ein Problem der Materialgestaltung im Bereich der Photovoltaik. Zu einer gegebenen Verteilung positiver Kernladungen in einer photovoltaischen Zelle bestimmt sich die resultierende Elektronenverteilung als Lösung der Kohn–Sham-Gleichungen. Die Struktur der Elektronenladungsdichte kann sich aufgrund elektronischer Anregungen unter dem Einfluss von Licht ändern. Wir beweisen, dass es eine bestimmte Verteilung der Kernladungen gibt, die die Änderung der Elektronenverteilung unter dem Einfluss eines bestimmen Lichts maximiert. Eine 1D-Simulation einer Atomkette zeigt einen deutlichen Ladungstransfer für bestimmte Kernverteilungen. In zukünftigen Anwendungen könnte diese Ladungstrennung zur Erzeugung elektrischen Stroms genutzt werden. Am Ende studieren wir ein PDG-Modell für Elektronen und Löcher in einem Halbleiter unter dem Einfluss des selbstkonsistenten Potentials, das von diesen Ladungsträgern erzeugt wird. Das Hauptresultat ist der Beweis exponentieller Konvergenz zum Gleichgewicht für die entsprechenden Ladungsdichten.

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My mentor Prof. Dr. Gunther Peichl, who retired at the KFU Graz in 2016, deserves additional gratitude beyond the time of my doctoral studies. He is probably the person who had the biggest influence on my mathematical understanding during the undergraduate studies. As the head of the curriculum, he gave me the possibility to gain some teaching experience as a tutor already during my master studies. Later on, I have also been able to supervise several exercise classes on Linear Algebra and Analysis.

Finally, I want to thank my parents for their constant help in any situation outside of the university.

Chapter 1

Preface

This thesis is concerned with the investigation of semiconductor materials both from an analytical point of view as well as from an optimization perspective.

On the one hand, we study a PDE-model which describes recombination, drift and diffusion processes of electrons and holes inside a semiconductor. This PDE-system is a generalization of the famous Shockley–Read–Hall-model which explains the dynamics within a semiconductor material by means of an additional internal energy level. A main result, which we were able to prove in this context, states that the densities of electrons and holes approach their equilibrium distributions at an exponential rate. Moreover, this convergence rate is independent of the average residence time of electrons in this additional energy level. This project has been supervised by Prof. Dr. Klemens Fellner at the KFU Graz.

On the other hand, this thesis also contains the results of a project which has been carried out at the TU Munich together with Prof. Dr. Gero Friesecke. Here, we consider a very general model of a photovoltaic cell. We allow the positive nuclear density to belong to a certain class of measures defined on the cell, and we determine the resulting electronic density by solving the celebrated Kohn–Sham equations. In short, the structure of the negative charge density of the electrons may change under the influence of incident light due to internal electronic excitations. The central result which we have derived guarantees that there exists a certain nuclear density which maximizes the change of the electronic density under the influence of a specific light. This charge transfer can reach values about half of the diameter of the cell as we will show for a 1D model. Within a subsequent application, one could use this charge separation to obtain an electric current.

Let us discuss an important issue of the first project. The key technique for showing that solutions of the recombination-drift-diffusion system, for short RDD-system, converge to the equilibrium is the so-called *entropy method*. This approach aims to derive a functional inequality between an entropy functional $E(n, p, n_{tr})$ and the corresponding entropy production $D(n, p, n_{tr})$. In the context which we will encounter later on, the variables n, p and n_{tr} denote the density of electrons (n and n_{tr}) and holes (p) within certain energy levels. More important, the production D is defined as the negative temporal derivative of the entropy E along solutions of the RDD-system. However, since we want to obtain a *functional inequality* independent of the solution to the RDD-system, we shall prove that there exists a constant $C_{\text{EEP}} > 0$ such that

$$E(n, p, n_{tr}) - E(n_\infty, p_\infty, n_{tr,\infty}) \leq C_{\text{EEP}}\, D(n, p, n_{tr})$$

for *all* functions n, p and n_{tr} which satisfy a certain conservation law, an L^1-bound plus some natural assumptions related to our specific model. We further demand that the constant C_{EEP} within this entropy-entropy production (EEP) inequality can be determined explicitly.

There are three important advantages when employing the entropy method. First, one can easily deduce convergence to the equilibrium both in relative entropy and in L^1 provided one has shown an EEP-inequality. This follows from an application of a Gronwall lemma (for convergence in relative entropy) and a subsequent Csiszár–Kullback–Pinsker-type inequality (for L^1-convergence). Second, we do neither linearize the dynamic equations within this approach, nor do we use expansions in power series at any place. The entropy method is, thus, a completely nonlinear technique. And third, we are able to derive explicit bounds for the rate of convergence as the constant C_{EEP} can be explicitly calculated.

In the literature, the entropy method has been successfully applied to a wide range of problems. Here, we shall mention only a couple of them. A major amount of articles is devoted to semiconductor models and related problems. The authors of [3] investigate a drift-diffusion-Poisson system on $\mathbb{R}^m$, whereas a reaction-drift-diffusion system on $\mathbb{R}^m$ is considered in [13]. Note that the former article does not deal with reaction processes, while the latter one neglects the effects from a coupling to Poisson's equation. Exponential convergence to equilibrium involving drift, diffusion, reactions and Poisson's equation is, in fact, proven via the entropy approach in [21] but only on bounded Lipschitzian domains in $\mathbb{R}^2$ using a non-constructive contradiction argument.

Another group of articles is concerned with reversible chemical reaction systems. In [9], explicit exponential convergence to the equilibrium is shown by applying the entropy method to a system with nonlinear reaction terms modeling reversible reactions of two and three species. Similarly, [10] studies reversible mass action kinetics of four species on a bounded interval of the real line. We will subsequently derive uniform-in-time L^∞-bounds on n and p by interpolating the exponential decay in L^1 with the polynomially growing H^1-norm. This strategy has already been presented in this article.

Regarding the second project, we also run a simulation for studying the electronic structure within a finite chain of atoms. This 1D model serves as a first step towards a computational investigation of charge transfer phenomena in semiconductor materials. Now, there is one essential technique which allows us to (approximately) calculate the density of the electrons in an efficient way — the Kohn–Sham equations in the context of density functional theory. From a theoretical point of view, any existing information about the density of n electrons is encoded within the wave function $\Psi : \mathbb{R}^{3n} \to \mathbb{C}$ determined by the n-body Schrödinger equation

$$\mathcal{H}\Psi = \lambda\Psi$$

including the Hamiltonian $\mathcal{H}$. However, after a discretization of $\mathbb{R}$ with, say, 100 points, this problem becomes practically unsolvable for many-electron-problems. In fact, this problem turns into $\overline{\mathcal{H}}\,\overline{\Psi} = \lambda\overline{\Psi}$ with $\overline{\Psi} \in \mathbb{C}^{10^{6n}}$. Even in 1D, a problem involving 10 electrons results in a huge vector $\Psi \in \mathbb{C}^{10^{20}}$.

A widely-used alternative to the wave-function-approach is given by the *density functional theory* (DFT). A major part of its theoretical basis is constituted by the Hohenberg–Kohn theorems [24], which state that the ground state energy is correctly predicted by minimizing a functional $E[\rho]$ which only depends on the electron density $\rho : \mathbb{R}^3 \to \mathbb{R}$. Furthermore, this minimizing ρ is the density of a wave function Ψ which minimizes the quantum-mechanical energy functional $\mathcal{E}[\Psi]$. Instead of a minimization process over functions from $\mathbb{R}^{3N}$ into $\mathbb{C}$, it suffices to consider a minimization over all possible densities mapping from $\mathbb{R}^3$ into $\mathbb{R}$.

In order to tackle the problem of interacting electrons in an efficient manner, Kohn and Sham replaced the set of interacting electrons by a set of non-interacting electrons which give rise to the same density by moving in an effective potential V_{xc}. The main task within this approach is to find an appropriate approximation for V_{xc}, in particular for the exchange and correlation effects (thus the name V_{xc}). Due to the absence of interactions between the electrons in this model, the corresponding wave function equals a Slater-determinant consisting of n orbitals φ_1 to φ_n. These orbitals are determined by the *Kohn–Sham equations*

$$H[\varphi_1, \ldots, \varphi_n]\varphi_i = \lambda_i\varphi_i$$

first derived in [25]. In contrast to the Hamiltonian $\mathcal{H}$ above, the Kohn–Sham Hamiltonian H depends itself on the orbitals φ_i via the effective potential V_{xc}. The calculation of φ_1 to φ_n, thus, has to be done in a self-consistent iterative manner. See also [2] for existence of solutions to generalized Kohn–Sham models, and [7] for a numerical treatment of a Kohn–Sham model within an optimal transport framework.

Chapter 2 is concerned with the RDD-system modeling the dynamics of electrons and holes in a semiconductor. After the presentation of the central results, we shall prove a couple of propositions which will be useful for the subsequent proofs of two abstract versions of an EEP-inequality. These results are then used to prove the announced EEP-estimate and to derive exponential convergence to the equilibrium. Chapter 3 presents the results of the charge transfer project, for which we first study the Kohn–Sham equations and the ground state configuration in detail. We then come to the general existence proof of optimal nuclear densities giving rise to a maximal charge transfer inside the semiconductor. The 1D simulation discussed afterwards shows that one can in fact "design" a material which results in a large transfer of electronic charge. Finally, Chapter 4 establishes an EEP-inequality for a recombination-drift-diffusion-Poisson system including a selfconsistent potential. We discovered some necessary techniques in [19] only a couple of weeks before finishing this thesis. As the authors in [19] investigate a similar problem, some minor adaptions of the proof are already sufficient in order to apply it in our situation.

Chapter 2

A Recombination-Drift-Diffusion System Modeling Band-Trapped States

Within the first part of this thesis, we consider the following PDE-ODE drift-diffusion-recombination system:

$$\begin{cases} \partial_t n = \nabla \cdot J_n(n) + R_n(n, n_{tr}), \\ \partial_t p = \nabla \cdot J_p(p) + R_p(p, n_{tr}), \\ \varepsilon\, \partial_t n_{tr} = R_p(p, n_{tr}) - R_n(n, n_{tr}), \end{cases} \tag{2.1}$$

with

$$J_n := \nabla n + n \nabla V_n = \mu_n \nabla \left(\frac{n}{\mu_n} \right), \qquad \mu_n := e^{-V_n},$$

$$J_p := \nabla p + p \nabla V_p = \mu_p \nabla \left(\frac{p}{\mu_p} \right), \qquad \mu_p := e^{-V_p},$$

$$R_n := \frac{1}{\tau_n} \left(n_{tr} - \frac{n}{n_0 \mu_n} (1 - n_{tr}) \right), \quad R_p := \frac{1}{\tau_p} \left(1 - n_{tr} - \frac{p}{p_0 \mu_p} n_{tr} \right),$$

where $n_0, p_0, \tau_n, \tau_p > 0$ are positive recombination parameters and $\varepsilon \in (0, \varepsilon_0]$ for arbitrary but fixed $\varepsilon_0 > 0$ is a positive relaxation parameter to be detailed in the following. The main goal is to prove exponential convergence to equilibrium for solutions of system (2.1) with *explicit* rates and constants which are *independent* of ε. This approach also allows us to study the limiting case $\varepsilon \to 0$ leading to the Shockley–Read–Hall model for semiconductor recombination.

2.1 Introduction and Main Results

The physical motivation for system (2.1) originates from the studies of Shockley, Read and Hall [28, 23] on the generation-recombination statistics for electron-hole pairs in semiconductors. The involved physical processes are sketched in Figure 2.1. The starting point for our considerations is a basic model of a semiconductor consisting of two electronic energy bands: In this model, charge carriers within the semiconductor are negatively charged electrons in the conduction band and positively charged holes (these are pseudo-particles, which describe vacancies of electrons) in the valence band. The corresponding charge densities of electrons and holes are denoted by n and p, respectively. In Figure 2.1, the in-between trap-level is a consequence of appropriately distributed foreign atoms in the crystal lattice of the semiconductor material. In general, there might be multiple intermediate energy levels due to various crystal impurities. In the sequel, we will restrict ourselves to exactly one additional trap-level. The intermediate energy states facilitate the excitation of electrons from the valence band into the conduction band since this transition can now take part in two steps, each requiring smaller amounts of energy. On the other hand, charge carriers on the trap-level are not mobil and their maximal density n_{tr} is limited.

The equations for n and p in system (2.1) include the drift-diffusion terms $\nabla \cdot J_n$ and $\nabla \cdot J_p$ as well as the recombination terms R_n and R_p. The quantities V_n and V_p within the fluxes J_n and J_p are given

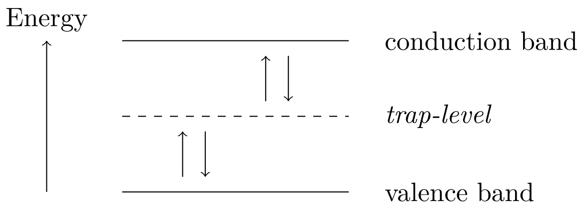

Figure 2.1: A schematic picture illustrating the allowed transitions of electrons between the various energy levels.

external time-independent potentials, which generate an additional drift for n and p. Note that more realistic drift-diffusion models would additionally consider Poisson's equation coupled to (2.1) in order to incorporate drift caused by a self-consistent electrostatic potential. However, including a self-consistent drift structure into (2.1) leads to great and still partially open difficulties in the here presented entropy method and is thus left for future works.

The reaction term R_n models transitions of electrons from the trap-level to the conduction band (proportional to n_{tr}) and vice versa (proportional to $-n(1-n_{tr})$), where the maximum capacity of the trap-level is normalized to one. Similarly, R_p encodes the generation and annihilation of holes in the valence band. But one has to be aware that the rate of hole-generation is equivalent to the rate of an electron moving from the valence band to the trap-level, which is proportional to $(1-n_{tr})$. Similar, the annihilation of a hole corresponds to an electron that jumps from the trap-level to the valence band, which yields a reaction rate proportional to $-pn_{tr}$.

The dynamical equation for n_{tr} in (2.1) is an ODE in time and pointwise in space with a right hand side depending on n and p via R_n and R_p. In the same manner as above, one can find that all gain- and loss-terms for n_{tr} are taken into account correctly via $R_p - R_n$. We stress that there is no drift-diffusion term for n_{tr}. This is due to the correlation between foreign atoms and the corresponding trap-levels which are locally bound near these crystal impurities. As a consequence, an electron in a trap-level cannot move through the semiconductor, hence, the name trapped state.

In the recombination process, $n_0, p_0 > 0$ represent reference levels for the charge concentrations n and p, while $\tau_n, \tau_p > 0$ are inverse reaction parameter. Finally, $\varepsilon > 0$ models the lifetime of the trapped states, where lifetime refers to the expected time until an electron in a trapped state moves either to the valence or the conduction band. Note that the concentration n_{tr} of these trapped states satisfies $n_{tr} \in [0,1]$ provided this holds true for their initial concentration (cf. Theorem 2.1).

A particularly interesting situation is obtained in the (formal) limit $\varepsilon \to 0$. This quasi-stationary limit allows to derive the well known Shockley–Read–Hall model for semiconductor recombination, where the concentration of trapped states is determined from the algebraic relation $0 = R_p(p, n_{tr}) - R_n(n, n_{tr})$, which results in

$$n_{tr} = \frac{\tau_n + \tau_p \frac{n}{n_0 \mu_n}}{\tau_n + \tau_p + \tau_n \frac{p}{p_0 \mu_p} + \tau_p \frac{n}{n_0 \mu_n}}.$$

Thus, the trapped state concentration n_{tr} and its evolution can (formally) be eliminated from system (2.1), while the evolution of the charge carriers n and p is then subject to the Shockley–Read–Hall recombination terms

$$R_n(n, n_{tr}) = R_p(p, n_{tr}) = \frac{1 - \frac{np}{n_0 p_0 \mu_n \mu_p}}{\tau_n\big(1 + \frac{p}{p_0 \mu_p}\big) + \tau_p\big(1 + \frac{n}{n_0 \mu_n}\big)}.$$

Note that the above quasistationary limit has been rigorously performed in [22], even for more general models. See also [26] for semiconductor models assuming a reaction term of Shockley–Read–Hall-type.

In the following, system (2.1) is considered on a bounded domain $\Omega \subset \mathbb{R}^m$ with sufficiently smooth boundary $\partial\Omega$. In addition, we suppose that the volume of Ω is normalized, i.e. $|\Omega| = 1$, which can be achieved by an appropriate scaling of the spatial variables. We impose no-flux boundary conditions for J_n and J_p,

$$\hat{n} \cdot J_n = \hat{n} \cdot J_p = 0 \quad \text{on } \partial\Omega, \tag{2.2}$$

where $\hat{n}$ denotes the outer unit normal vector on $\partial\Omega$.

The potentials V_n and V_p are assumed to satisfy

$$V_n, V_p \in W^{2,\infty}(\Omega) \qquad \text{and} \qquad \hat{n}\cdot\nabla V_n,\ \hat{n}\cdot\nabla V_p \geq 0 \quad \text{on } \partial\Omega, \tag{2.3}$$

where the last condition means that the potentials are confining. For later use, we introduce

$$V := \max(\|V_n\|_{L^\infty(\Omega)}, \|V_p\|_{L^\infty(\Omega)}).$$

Finally, we assume that the initial states fulfill

$$(n_I, p_I, n_{tr,I}) \in L^\infty_+(\Omega)^3, \qquad \|n_{tr,I}\|_{L^\infty(\Omega)} \leq 1.$$

As a consequence of the no-flux boundary conditions, system (2.1) features conservation of charge:

$$\partial_t(n - p + \varepsilon\, n_{tr}) = \nabla\cdot(J_n - J_p)$$

and, therefore,

$$\int_\Omega (n - p + \varepsilon\, n_{tr})\, dx = \int_\Omega (n_I - p_I + \varepsilon\, n_{tr,I})\, dx =: M, \tag{2.4}$$

where $M \in \mathbb{R}$ is a real and possibly negative constant and $\varepsilon \in (0, \varepsilon_0]$ for arbitrary $\varepsilon_0 > 0$.

The following Theorem 2.1 comprises the existence and regularity results which provide the framework for our subsequent considerations. In particular, we will show that there exists a global solution to (2.1), and that $n_{tr}(t,x) \in [0,1]$ for all $t \in [0,\infty)$ and a.a. $x \in \Omega$.

Theorem 2.1 (Time-dependent system). *Let n_0, p_0, τ_n, τ_p and ε be positive constants. Assume that V_n and V_p satisfy* (2.3) *and that $\Omega \subset \mathbb{R}^m$ is a bounded, sufficiently smooth domain.*

Then, for any non-negative initial datum $(n_I, p_I, n_{tr,I}) \in L^\infty(\Omega)^3$ satisfying $\|n_{tr,I}\|_{L^\infty(\Omega)} \leq 1$, there exists a unique non-negative global weak solution (n, p, n_{tr}) of system (2.1)*, where (n,p) satisfy the boundary conditions* (2.2) *in the weak sense.*

More precisely, for all $T \in (0,\infty)$ and by introducing the space

$$W_2(0,T) := \left\{ f \in L^2((0,T), H^1(\Omega)) \,|\, \partial_t f \in L^2((0,T), H^1(\Omega)^*) \right\} \hookrightarrow C([0,T], L^2(\Omega)), \tag{2.5}$$

where we recall the last embedding e.g. from [8], we find that

$$(n,p) \in \left(W_2(0,T) \cap L^\infty((0,T), L^\infty(\Omega))\right)^2, \tag{2.6}$$

and

$$n_{tr} \in C([0,T], L^\infty(\Omega)), \quad \partial_t n_{tr} \in C([0,T], L^2(\Omega)). \tag{2.7}$$

Moreover, there exist positive constants $C_n(\|n_I\|_\infty, V_n)$, $C_p(\|p_I\|_\infty, V_p)$ and $K_n(V_n)$, $K_p(V_p)$ independent of ε such that

$$\|n(t,\cdot)\|_\infty \leq C_n + K_n t, \quad \|p(t,\cdot)\|_\infty \leq C_p + K_p t, \qquad \textit{for all } t \geq 0. \tag{2.8}$$

In addition, the concentration $n_{tr}(t,x)$ is bounded away from zero and one in the sense that for all times $\tau > 0$ there exist positive constants $\eta = \eta(\varepsilon_0, \tau, \tau_n, \tau_p)$, $\theta = \theta(C_n, C_p, K_n, K_p)$ and a sufficiently small constant $\gamma(\tau, C_n, C_p, K_n, K_p) > 0$ such that

$$n_{tr}(t,x) \in \left[\min\left\{\eta t, \frac{\gamma}{1+\theta t}\right\}, \max\left\{1-\eta t, 1-\frac{\gamma}{1+\theta t}\right\}\right] \quad \textit{for all } t \geq 0 \textit{ and a.a. } x \in \Omega \tag{2.9}$$

where the linear and the inverse linear bound intersect at time τ. As a consequence of (2.9)*, there exist positive constants μ, $\Gamma > 0$ (depending on τ, η, θ, γ, V_n, V_p) such that*

$$n(t,x), p(t,x) \geq \min\left\{\mu\frac{t^2}{2}, \frac{\Gamma}{1+\theta t}\right\} \quad \textit{for all } t \geq 0 \textit{ and a.a. } x \in \Omega \tag{2.10}$$

where the quadratic and the inverse linear bound intersect at the same time τ as above.

Remark 2.2. The existence theory of Theorem 2.1 for the coupled ODE-PDE problem (2.1) combines standard methods of parabolic methods with pointwise ODE estimates. The proof is postponed to Section 2.7. It follows previous related results like [22] by assuming L^∞-initial data and by proving L^∞-bounds in order to control nonlinear terms. We remark that the main objective of this chapter is the following quantitative study of the long-time behavior of global solutions to system (2.1).

The main tool in order to quantitatively study the large-time behavior of global solutions to system (2.1), is the entropy functional

$$E(n,p,n_{tr}) = \int_\Omega \left(n\ln\frac{n}{n_0\mu_n} - (n-n_0\mu_n) + p\ln\frac{p}{p_0\mu_p} - (p-p_0\mu_p) + \varepsilon\int_{1/2}^{n_{tr}} \ln\left(\frac{s}{1-s}\right) ds \right) dx. \tag{2.11}$$

For n and p, we encounter Boltzmann-entropy contributions $a\ln a - (a-1) \geq 0$, whereas n_{tr} enters the entropy functional via a non-negative integral term. Note that the integral $\int_{1/2}^{n_{tr}} \ln\left(\frac{s}{1-s}\right) ds$ is well defined for all $n_{tr}(x) \in [0,1]$. The continuity of the entropy E along solutions of system (2.1) will be shown in Lemma 2.11.

It is straight forward to verify that the entropy functional (2.11) is indeed a Ljapunov functional: By introducing the entropy production functional

$$D := -\frac{d}{dt}E, \tag{2.12}$$

the following relation holds true along solution trajectories of system (2.1):

$$\begin{aligned} D(n,p,n_{tr}) &= -\int_\Omega \left((\nabla\cdot J_n + R_n)\ln\left(\frac{n}{n_0\mu_n}\right) + (\nabla\cdot J_p + R_p)\ln\left(\frac{p}{p_0\mu_p}\right) + \varepsilon\ln\left(\frac{n_{tr}}{1-n_{tr}}\right)\partial_t n_{tr} \right) dx \\ &= \int_\Omega \left(J_n\cdot\frac{J_n}{n} + J_p\cdot\frac{J_p}{p} - R_n\ln\left(\frac{n}{n_0\mu_n}\right) - R_p\ln\left(\frac{p}{p_0\mu_p}\right) - \ln\left(\frac{n_{tr}}{1-n_{tr}}\right)(R_p - R_n) \right) dx \\ &= \int_\Omega \left(\frac{|J_n|^2}{n} + \frac{|J_p|^2}{p} - R_n\ln\left(\frac{n(1-n_{tr})}{n_0\mu_n n_{tr}}\right) - R_p\ln\left(\frac{p n_{tr}}{p_0\mu_p(1-n_{tr})}\right) \right) dx. \end{aligned} \tag{2.13}$$

The entropy production functional involves flux terms, which are obviously non-negative, and reaction terms of the form $(a-1)\ln a \geq 0$. Thus, the entropy E and its production D are non-negative functionals, which suggests that the entropy E is monotonically decreasing in time along solutions of system (2.1). This will be proven in Lemma 2.12. Note that the last two reaction terms in (2.13) are unbounded for $n_{tr}(t,x) \to 0, 1$ or $n(t,x), p(t,x) \to 0$ and that the entropy production is therefore potentially unbounded even for smooth solutions. However, the regularity of n and p of Theorem 2.1 as well as the bounds (2.9) for n_{tr} and the lower bounds (2.10) for n and p allow to directly verify that any solution of system (2.1) satisfies the weak entropy production law

$$E(t_1) + \int_{t_0}^{t_1} D(s)\,ds = E(t_0), \qquad \text{for all } 0 < t_0 < t_1, \tag{2.14}$$

i.e. that solutions of Theorem 2.1 only allow for initial singularities of D — due to a lacking regularity of the initial data or due to initial data $n_{tr,I}(x) \in [0,1]$, $n_I(x), p_I(x) \in [0,\infty)$.

We will further prove that there exists a unique equilibrium $(n_\infty, p_\infty, n_{tr,\infty})$ of system (2.1) in a suitable (and natural) function space. This equilibrium can be seen as the unique solution of the stationary system (2.15) or, equivalently, as the unique state for which the entropy production (2.13) vanishes. But in both situations, uniqueness is only guaranteed if the equilibrium state satisfies the conservation law (2.4) for a fixed constant M. For simplicity of the presentation, we shall introduce the following notation for integrated quantities.

Notation 2.3. For any function f, we set

$$\overline{f} := \int_\Omega f(x)\,dx$$

which is consistent with the usual definition of the average of f since $|\Omega| = 1$. Using this notation, the conservation law (2.4) rewrites as

$$\overline{n} - \overline{p} + \varepsilon\,\overline{n_{tr}} = M \in \mathbb{R}.$$

Theorem 2.4 (Stationary system). *Let $M \in \mathbb{R}$, $\varepsilon \in (0, \varepsilon_0]$ for arbitrary $\varepsilon_0 > 0$ and $(n_\infty, p_\infty, n_{tr,\infty}) \in X$ where X is defined via*

$$X := \{(n, p, n_{tr}) \in H^1(\Omega)^2 \times L^\infty(\Omega) \,\big|\, \overline{n} - \overline{p} + \varepsilon\overline{n_{tr}} = M \wedge (\exists\, \gamma > 0)\, n, p \geq \gamma \ a.e. \wedge n_{tr} \in [\gamma, 1-\gamma] \ a.e.\}.$$

Then, the following statements are equivalent.

1. *$(n_\infty, p_\infty, n_{tr,\infty})$ is a solution of the stationary system*

$$\nabla \cdot J_n(n_\infty) + R_n(n_\infty, n_{tr,\infty}) = 0, \tag{2.15a}$$
$$\nabla \cdot J_p(p_\infty) + R_p(p_\infty, n_{tr,\infty}) = 0, \tag{2.15b}$$
$$R_p(p_\infty, n_{tr,\infty}) - R_n(n_\infty, n_{tr,\infty}) = 0. \tag{2.15c}$$

2. *$D(n_\infty, p_\infty, n_{tr,\infty}) = 0$.*
3. *$J_n(n_\infty) = J_p(p_\infty) = R_n(n_\infty, n_{tr,\infty}) = R_p(p_\infty, n_{tr,\infty}) = 0$ a.e. in Ω.*
4. *The state $(n_\infty, p_\infty, n_{tr,\infty})$ satisfies*

$$n_\infty = n_* e^{-V_n}, \ \ p_\infty = p_* e^{-V_p}, \ \ n_{tr,\infty} = \frac{n_*}{n_* + n_0} = \frac{p_0}{p_* + p_0} \tag{2.16}$$

where the positive constants $n_*, p_* > 0$ are uniquely determined by the condition

$$n_* p_* = n_0 p_0 \tag{2.17}$$

and the conservation law

$$n_* \overline{\mu_n} - p_* \overline{\mu_p} + \varepsilon\, n_{tr,\infty} = M. \tag{2.18}$$

(Note that the uniqueness of n_* and p_* follows from the strict monotonicity of

$$f(n_*) := n_* \overline{\mu_n} - \frac{n_0 p_0 \overline{\mu_p}}{n_*} + \varepsilon \frac{n_*}{n_* + n_0}$$

on $(0, \infty)$ and the asymptotics $f(n_*) \to -\infty$ for $n_* \to 0^+$ and $f(n_*) \to \infty$ for $n_* \to \infty$.)

Consequently, there exists a unique positive equilibrium $(n_\infty, p_\infty, n_{tr,\infty}) \in X$ given by the formulae in (2.16)*. Furthermore, this equilibrium satisfies*

$$n_{tr,\infty} = \frac{n_*}{n_0}(1 - n_{tr,\infty}), \quad 1 - n_{tr,\infty} = \frac{p_*}{p_0} n_{tr,\infty}. \tag{2.19}$$

Remark 2.5. Proposition 2.10 below will moreover prove that for all $M \in \mathbb{R}$ the solutions n_*, p_* of (2.16)–(2.18) are uniformly positive and bounded for all $\varepsilon \in (0, \varepsilon_0]$, i.e. that there exist constants $\gamma(\varepsilon_0, M, n_0, p_0, V)$ and $\Gamma(\varepsilon_0, M, n_0, p_0, V)$ such that

$$0 < \gamma(\varepsilon_0, M, n_0, p_0, V) \leq n_*, p_* \leq \Gamma(\varepsilon_0, M, n_0, p_0, V) < \infty$$

for all $\varepsilon \in (0, \varepsilon_0]$ and arbitrary $\varepsilon_0 > 0$. This also implies that any solution of $J_n(n_\infty) = J_p(p_\infty) = R_n(n_\infty, n_{tr,\infty}) = R_p(p_\infty, n_{tr,\infty}) = 0$ a.e. in Ω lies necessarily in the function space X for a suitable choice $\gamma > 0$.

The main objective of this study is to prove exponential convergence to the unique equilibrium $(n_\infty, p_\infty, n_{tr,\infty})$ for solutions of system (2.1) and to obtain explicit bounds for the rates and constants of convergence. For this reason, we aim to derive a functional inequality of the form

$$E(n, p, n_{tr}) - E(n_\infty, p_\infty, n_{tr,\infty}) \leq C\, D(n, p, n_{tr})$$

where n, p and n_{tr} are non-negative functions satisfying the conservation law (2.4), and $C > 0$ is a constant which can be determined explicitly. This approach, which establishes an upper bound for the relative entropy in terms of the entropy production, is referred to as the entropy method and has up to now been applied in numerous articles about reaction-diffusion systems (see e.g. [16, 17, 12] and the discussion in Chapter 1). Using a Gronwall-argument, this entropy-entropy production (EEP) inequality entails exponential decay of the relative entropy. Together with a Csiszár–Kullback–Pinsker-type estimate, we finally deduce exponential convergence in L^1 for solutions to the reaction-diffusion system (2.1).

The derivation of an EEP-estimate is quite an involved task in our situation. The crucial part is the proof of an abstract EEP-estimate, which is first shown for spatially homogeneous concentrations which fulfill the conservation law (2.4) and natural L^1-bounds (cf. Proposition 2.24). This result is then extended to the case of arbitrary concentrations (cf. Proposition 2.26) satisfying the same assumptions.

Theorem 2.6 formulates the EEP-inequality, which is the main ingredient for proving exponential convergence to the equilibrium. Note that the constant C_{EEP} in the subsequent estimate (2.20) is independent of ε for $\varepsilon \in (0, \varepsilon_0]$ and arbitrary $\varepsilon_0 > 0$. As a consequence, also the convergence rate of the relative entropy is independent of ε in this sense.

Theorem 2.6 (Entropy-Entropy Production Inequality). *Let ε_0, τ_n, τ_p, n_0, p_0, M_1 and V be positive constants and consider $M \in \mathbb{R}$.*

Then, there exists an explicitly computable constant $C_{\mathrm{EEP}} > 0$ such that for all $\varepsilon \in (0, \varepsilon_0]$, the equilibrium $(n_\infty, p_\infty, n_{tr,\infty}) \in X$ from Theorem 2.4 and all non-negative functions $(n, p, n_{tr}) \in L^1(\Omega)^3$ satisfying $\|n_{tr}\|_{L^\infty(\Omega)} \le 1$, the conservation law

$$\overline{n} - \overline{p} + \varepsilon \overline{n_{tr}} = M$$

and the L^1-bound

$$\overline{n}, \overline{p} \le M_1,$$

the following entropy-entropy production inequality holds true:

$$E(n, p, n_{tr}) - E(n_\infty, p_\infty, n_{tr,\infty}) \le C_{\mathrm{EEP}} D(n, p, n_{tr}). \tag{2.20}$$

Theorem 2.6 provides an upper bound for the relative entropy in terms of the entropy production. This already implies exponential convergence of the relative entropy. The subsequent proposition now yields a lower bound for the relative entropy involving the L^1-distance of the solution to the equilibrium. This will allow us to establish exponential convergence in L^1.

Proposition 2.7 (Csiszár–Kullback–Pinsker inequality). *Let ε_0, n_0, p_0, M_1 and V be positive constants and let $M \in \mathbb{R}$.*

Then, there exists an explicit constant $C_{\mathrm{CKP}} > 0$ such that for all $\varepsilon \in (0, \varepsilon_0]$, the equilibrium $(n_\infty, p_\infty, n_{tr,\infty}) \in X$ from Theorem 2.4 and all non-negative functions $(n, p, n_{tr}) \in L^1(\Omega)^3$ satisfying $\|n_{tr}\|_{L^\infty(\Omega)} \le 1$, the conservation law

$$\overline{n} - \overline{p} + \varepsilon \overline{n_{tr}} = M$$

and the L^1-bound

$$\overline{n}, \overline{p} \le M_1,$$

the following Csiszár–Kullback–Pinsker-type inequality holds true:

$$E(n, p, n_{tr}) - E(n_\infty, p_\infty, n_{tr,\infty}) \ge C_{\mathrm{CKP}} \big(\|n - n_\infty\|^2_{L^1(\Omega)} + \|p - p_\infty\|^2_{L^1(\Omega)} + \varepsilon \|n_{tr} - n_{tr,\infty}\|^2_{L^1(\Omega)} \big).$$

Finally, Theorem 2.8 establishes exponential convergence to equilibrium in relative entropy and in L^1. We stress that in both situations the convergence rate, subsequently denoted by K, is uniformly positive for all $\varepsilon \in (0, \varepsilon_0]$ and arbitrary $\varepsilon_0 > 0$. Up to our knowledge, this is the first time where the entropy method has successfully been applied *uniformly* in a fast-reaction parameter.

Moreover, the relative entropy and the L^1-distance to the equilibrium of n and p can be estimated from above independent of ε for $\varepsilon \in (0, \varepsilon_0]$. Only $\|n_{tr} - n_{tr,\infty}\|_{L^1(\Omega)}$ is multiplied with a prefactor ε.

Theorem 2.8 (Exponential convergence). *Let (n, p, n_{tr}) be a global weak solution of system* (2.1) *as given in Theorem 2.1 corresponding to the non-negative initial data $(n_I, p_I, n_{tr,I}) \in L^\infty(\Omega)^3$ satisfying $\|n_{tr,I}\|_{L^\infty(\Omega)} \le 1$.*

Then, this solution satisfies the weak entropy production law

$$E(n, p, n_{tr})(t_1) + \int_{t_0}^{t_1} D(n, p, n_{tr})(s)\, ds = E(n, p, n_{tr})(t_0)$$

for all $0 < t_0 \le t_1 < \infty$. *Moreover, the following versions of the exponential decay towards the equilibrium* $(n_\infty, p_\infty, n_{tr,\infty}) \in X$ *from Theorem 2.4 hold true for all* $t \ge 0$*:*

$$E(n,p,n_{tr})(t) - E(n_\infty, p_\infty, n_{tr,\infty}) \le (E_I - E_\infty)e^{-Kt}$$

and

$$\|n - n_\infty\|^2_{L^1(\Omega)} + \|p - p_\infty\|^2_{L^1(\Omega)} + \varepsilon\|n_{tr} - n_{tr,\infty}\|^2_{L^1(\Omega)} \le C(E_I - E_\infty)e^{-Kt} \tag{2.21}$$

where $C := C_{\mathrm{CKP}}^{-1}$ *and* $K := C_{\mathrm{EEP}}^{-1}$ *are explicitly computable constants independent of* $\varepsilon \in (0, \varepsilon_0]$ *for arbitrary* $\varepsilon_0 > 0$ *(cf. Theorem 2.6 and Proposition 2.7). Moreover,* E_I *and* E_∞ *denote the initial entropy of the system and the entropy of the equilibrium, respectively.*

Corollary 2.9 (Uniform L^∞-bounds)**.** *The* L^1*-exponential decay* (2.21) *and the linearly growing* L^∞*-bounds* (2.8) *yield uniform-in-time* L^∞*-bounds for* n *and* p *via an interpolation argument, i.e. there exists a constant* $K > 0$ *such that*

$$\|n(t,\cdot)\|_\infty, \|p(t,\cdot)\|_\infty \le K \qquad \text{for all } t \ge 0. \tag{2.22}$$

As a consequence, the uniform bounds (2.22) *allow to improve the bounds* (2.9), (2.10) *and to obtain uniform-in-time bounds in the sense that for all* $\tau > 0$*, there exist sufficiently small constants* $\eta, \gamma, \mu, \Gamma > 0$ *such that*

$$n_{tr}(t,x) \in \big[\min\{\eta t, \gamma\}, \max\{1 - \eta t, 1 - \gamma\}\big] \tag{2.23}$$

and

$$n(t,x), p(t,x) \ge \min\Big\{\mu\frac{t^2}{2}, \Gamma\Big\} \tag{2.24}$$

for all $t \ge 0$ *and a.a.* $x \in \Omega$ *where* ηt *and* γ *as well as* $\mu t^2/2$ *and* Γ *intersect at time* $\tau > 0$.

As already announced previously, the EEP-inequality stated in Theorem 2.6 for $\varepsilon > 0$ can be used to derive an EEP-inequality for $\varepsilon = 0$. The main tool in this context is the ε-independence of the constant C_{EEP} from Theorem 2.6, which allows us to perform the limit $\varepsilon \to 0$ in (2.20). The limiting system reads

$$\begin{cases} \partial_t n = \nabla \cdot J_n(n) + R(n,p), \\ \partial_t p = \nabla \cdot J_p(p) + R(n,p), \end{cases} \tag{2.25}$$

where $J_n = \nabla n + n\nabla V_n$, $J_p = \nabla p + p\nabla V_p$, and

$$R(n,p) = \frac{1 - \frac{np}{n_0 p_0 \mu_n \mu_p}}{\tau_n\big(1 + \frac{p}{p_0\mu_p}\big) + \tau_p\big(1 + \frac{n}{n_0\mu_n}\big)}$$

denotes the Shockley–Read–Hall recombination term. This representation of $R(n,p)$ results from solving $0 = R_p(p, n_{tr}) - R_n(n, n_{tr})$ for n_{tr} and evaluating the reaction terms at n_{tr}. Using this approach, exponential convergence to equilibrium for solutions of (2.25) is then a direct consequence.

Theorem 2.1' (Time-dependent system for $\varepsilon = 0$)**.** *Let* n_0, p_0, τ_n *and* τ_p *be positive constants. Assume that* V_n *and* V_p *satisfy* (2.3) *and that* $\Omega \subset \mathbb{R}^m$ *is a bounded, sufficiently smooth domain.*

Then, for any non-negative initial datum $(n_I, p_I) \in L^\infty(\Omega)^2$*, there exists a unique non-negative global weak solution* (n,p) *of system* (2.25) *satisfying the boundary conditions* (2.2) *in the weak sense.*

More precisely, for all $T \in (0,\infty)$ *we find that*

$$(n,p) \in \big(W_2(0,T) \cap L^\infty((0,T), L^\infty(\Omega))\big)^2, \tag{2.26}$$

where the space $W_2(0,T) \hookrightarrow C([0,T], L^2(\Omega))$ *is defined in* (2.5)*. Moreover, there exist positive constants* $C_n(\|n_I\|_\infty, V_n)$*,* $C_p(\|p_I\|_\infty, V_p)$ *and* $K_n(V_n)$*,* $K_p(V_p)$ *such that*

$$\|n(t,\cdot)\|_\infty \le C_n + K_n t, \quad \|p(t,\cdot)\|_\infty \le C_p + K_p t, \qquad \text{for all } t \ge 0. \tag{2.27}$$

We further deduce that for all times $\tau > 0$ *there exist positive constants* μ*,* Γ*,* $\theta > 0$ *(depending on* τ*,* C_n*,* C_p*,* K_n*,* K_p*,* V_n*,* V_p*) such that*

$$n(t,x),\ p(t,x) \ge \min\Big\{\mu t, \frac{\Gamma}{1+\theta t}\Big\} \quad \text{for all } t \ge 0 \text{ and a.a. } x \in \Omega \tag{2.28}$$

where the bounds μt *and* $\Gamma/(1 + \theta t)$ *intersect at time* τ.

For the case $\varepsilon = 0$, we introduce the entropy functional

$$E_0(n,p) := \int_\Omega \left(n \ln \frac{n}{n_0\mu_n} - (n - n_0\mu_n) + p \ln \frac{p}{p_0\mu_p} - (p - p_0\mu_p) \right) dx,$$

which is indeed an entropy (free energy) functional of the Shockley–Read–Hall model with the entropy production (free energy dissipation) functional

$$D_0(n,p) := -\frac{d}{dt}E_0(n,p) = \int_\Omega \left(\frac{|J_n|^2}{n} + \frac{|J_p|^2}{p} - R \ln\left(\frac{np}{n_0\mu_n p_0\mu_p}\right)\right) dx \geq 0. \tag{2.29}$$

Next, we define $n_{tr}^{eq} = n_{tr}^{eq}(n,p)$ such that $R_n(n, n_{tr}^{eq}) = R_p(p, n_{tr}^{eq})$, i.e.

$$n_{tr}^{eq} := \frac{\tau_n + \tau_p \frac{n}{n_0\mu_n}}{\tau_n + \tau_p + \tau_n \frac{p}{p_0\mu_p} + \tau_p \frac{n}{n_0\mu_n}}. \tag{2.30}$$

The quantity $n_{tr}^{eq}(n,p)$ denotes the pointwise equilibrium value of the trapped states in (2.1) for fixed n and p, which corresponds to $\varepsilon = 0$. Moreover, we observe that the Shockley–Read–Hall entropy production functional (2.29) can be identified as the entropy production functional $D(n,p,n_{tr}^{eq})$ along trajectories of (2.1) with $\varepsilon = 0$ in the sense that $n_{tr} \equiv n_{tr}^{eq}(n,p)$:

$$\begin{aligned} D(n,p,n_{tr}^{eq}) &= \int_\Omega \left(\frac{|J_n|^2}{n} + \frac{|J_p|^2}{p} - R_n \ln\left(\frac{n(1-n_{tr}^{eq})}{n_0\mu_n n_{tr}^{eq}}\right) - R_p \ln\left(\frac{p n_{tr}^{eq}}{p_0\mu_p(1-n_{tr}^{eq})}\right)\right) dx \\ &= \int_\Omega \left(\frac{|J_n|^2}{n} + \frac{|J_p|^2}{p} - R \ln\left(\frac{np}{n_0\mu_n p_0\mu_p}\right)\right) dx = D_0(n,p), \end{aligned}$$

where one uses $R = R_n = R_p$ at $n_{tr} = n_{tr}^{eq}$ and that the involved integrals are finite.

From the bounds in Theorem 2.1', we conclude that any solution of system (2.25) satisfies the weak entropy production law

$$E_0(n,p)(t_1) + \int_{t_0}^{t_1} D_0(n,p)(s)\, ds = E_0(n,p)(t_0)$$

for all $0 < t_0 \leq t_1 < \infty$.

Along the lines of Theorem 2.4, we deduce that in the case $\varepsilon = 0$ there exists a unique equilibrium $(n_{\infty,0}, p_{\infty,0}) \in X_0$ where

$$X_0 := \{(n,p) \in H^1(\Omega)^2 \,|\, \overline{n} - \overline{p} = M \wedge (\exists\, \gamma > 0)\, n, p \geq \gamma \text{ a.e.}\}.$$

This equilibrium reads

$$n_{\infty,0} = n_{*,0}e^{-V_n}, \quad p_{\infty,0} = p_{*,0}e^{-V_p} \tag{2.31}$$

where $n_{*,0}, p_{*,0} > 0$ are uniquely determined by

$$n_{*,0}p_{*,0} = n_0p_0$$

and

$$n_{*,0}\overline{\mu_n} - p_{*,0}\overline{\mu_p} = M.$$

We are now in a position to formulate the EEP-inequality

$$E_0(n,p) - E_0(n_{\infty,0}, p_{\infty,0}) \leq C_{EEP} D_0(n,p)$$

involving the entropy E_0 and its production D_0 by applying an appropriate limiting argument to the EEP-inequality from Theorem 2.6.

Theorem 2.6' (Entropy-Entropy Production Inequality for $\varepsilon = 0$)**.** *Let τ_n, τ_p, n_0, p_0, M_1 and V be positive constants and consider $M \in \mathbb{R}$.*

Then, recalling the equilibrium $(n_{\infty,0}, p_{\infty,0}) \in X_0$, the following EEP-inequality holds true for all non-negative functions $(n,p) \in L^1(\Omega)^2$ satisfying the conservation law $\overline{n} - \overline{p} = M$, the L^1-bound $\overline{n}, \overline{p} < M_1$ as well as the conditions $E_0(n,p)$, $D_0(n,p)$, $D(n,p,n_{tr}^{eq}) < \infty$:

$$E_0(n,p) - E_0(n_{\infty,0}, p_{\infty,0}) \leq C_{\mathrm{EEP}} D_0(n,p), \tag{2.32}$$

where $C_{\mathrm{EEP}} > 0$ is the same constant as in Theorem 2.6.

A similar limiting process gives rise to a lower bound for $E_0(n,p) - E_0(n_{\infty,0}, p_{\infty,0})$ in terms of the L^1-distance between the solution and the equilibrium.

Proposition 2.7' (Csiszár–Kullback–Pinsker inequality for $\varepsilon = 0$). *Let n_0, p_0, M_1 and V be positive constants and $M \in \mathbb{R}$ be arbitrary.*

Then, together with the equilibrium $(n_{\infty,0}, p_{\infty,0}) \in X_0$, the subsequent Csiszár–Kullback–Pinsker-type inequality holds true for all non-negative functions $(n,p) \in L^1(\Omega)^2$ satisfying the conservation law $\overline{n} - \overline{p} = M$ and the L^1-bound $\overline{n}, \overline{p} < M_1$:

$$E_0(n,p) - E_0(n_{\infty,0}, p_{\infty,0}) \geq C_{\text{CKP}} \big(\|n - n_{\infty,0}\|_{L^1(\Omega)}^2 + \|p - p_{\infty,0}\|_{L^1(\Omega)}^2 \big),$$

where $C_{\text{CKP}} > 0$ is the same constant as in Proposition 2.7.

Theorem 2.8' (Exponential convergence for $\varepsilon = 0$). *Let (n,p) be a global weak solution of system* (2.25) *as given in Theorem 2.1' corresponding to the non-negative initial data $(n_I, p_I) \in L^\infty(\Omega)^2$.*

Then, this solution satisfies the weak entropy production law

$$E_0(n,p)(t_1) + \int_{t_0}^{t_1} D_0(n,p)(s)\, ds = E_0(n,p)(t_0)$$

for all $0 < t_0 \leq t_1 < \infty$. Moreover, the following versions of the exponential decay towards the equilibrium $(n_{\infty,0}, p_{\infty,0}) \in X_0$ hold true for all $t \geq 0$:

$$E_0(n,p)(t) - E_0(n_{\infty,0}, p_{\infty,0}) \leq (E_I - E_\infty) e^{-Kt}$$

and

$$\|n - n_{\infty,0}\|_{L^1(\Omega)}^2 + \|p - p_{\infty,0}\|_{L^1(\Omega)}^2 \leq C(E_I - E_\infty) e^{-Kt} \tag{2.33}$$

where $C := C_{\text{CKP}}^{-1}$ and $K := C_{\text{EEP}}^{-1}$ are the same constants as in Theorem 2.8. Moreover, E_I and E_∞ denote the initial entropy of the system and the entropy in the equilibrium, respectively.

In the same way as in the situation of strictly positive $\varepsilon > 0$, we may derive uniform-in-time L^∞-bounds for n and p also in the case $\varepsilon = 0$. As before, these bounds further improve the lower bounds on n and p.

Corollary 2.9' (Uniform L^∞-bounds for $\varepsilon = 0$). *There exists a constant $K > 0$ such that*

$$\|n(t,\cdot)\|_\infty, \|p(t,\cdot)\|_\infty \leq K \qquad \text{for all } t \geq 0. \tag{2.34}$$

And for all $\tau > 0$ there exist sufficiently small constants $\mu, \Gamma > 0$ such that

$$n(t,x), p(t,x) \geq \min\{\mu t, \Gamma\} \tag{2.35}$$

for all $t \geq 0$ and a.a. $x \in \Omega$, where the bounds μt and Γ intersect at time $\tau > 0$.

The remainder of this chapter is organized in the following manner. Section 2.2 contains the proof of Theorem 2.4 as well as a result on the bounds of n_∞, p_∞ and $n_{tr,\infty}$. In Section 2.3, we collect a couple of technical lemmata, and within Section 2.4, we state a preliminary proposition which serves as a first result towards an EEP-inequality. An abstract version of the EEP-estimate is proven in Section 2.5 first for constant concentrations and based on that also for general ones. This strategy has also been applied in [16]. Section 2.6 is concerned with the proofs of the EEP-inequality from Theorem 2.6, the announced exponential convergence from Theorem 2.8 and the uniform L^∞-bounds from Corollary 2.9. Moreover, the proofs of Theorem 2.6' and Theorem 2.8' are also part of this section. Finally, the existence proofs of Theorem 2.1 and Theorem 2.1' are contained in Section 2.7.

2.2 Properties of the Equilibrium

Proof of Theorem 2.4. We shall prove the equivalence of the statements in the Theorem by a circular reasoning. Assume that $(n_\infty, p_\infty, n_{tr,\infty}) \in X$ is a solution of the stationary system (2.15). In this case,

$$J_n(n_\infty),\ J_p(p_\infty),\ R_n(n_\infty, n_{tr,\infty}),\ R_p(p_\infty, n_{tr,\infty}) \in L^2(\Omega).$$

We test equation (2.15a) with $\ln(n_\infty/(n_0\mu_n))$. Due to $n_\infty \in H^1(\Omega)$ and $n_\infty \geq \gamma$ a.e. in Ω, the test function $\ln(n_\infty/(n_0\mu_n))$ belongs to $H^1(\Omega)$. We find

$$0 = -\int_\Omega \left((\nabla \cdot J_n(n_\infty) + R_n(n_\infty, n_{tr,\infty})) \ln\left(\frac{n_\infty}{n_0\mu_n}\right)\right) dx$$
$$= \int_\Omega \left(\frac{|J_n(n_\infty)|^2}{n_\infty} - R_n(n_\infty, n_{tr,\infty}) \ln\left(\frac{n_\infty}{n_0\mu_n}\right)\right) dx.$$

In the same way, we test equation (2.15b) with $\ln(p_\infty/(p_0\mu_p)) \in H^1(\Omega)$. This yields

$$0 = \int_\Omega \left(\frac{|J_p(p_\infty)|^2}{p_\infty} - R_p(p_\infty, n_{tr,\infty}) \ln\left(\frac{p_\infty}{p_0\mu_p}\right)\right) dx.$$

Moreover, we multiply (2.15c) with $\ln(n_{tr,\infty}/(1-n_{tr,\infty})) \in L^2(\Omega)$, integrate over Ω and obtain

$$0 = \int_\Omega \left((R_n(n_\infty, n_{tr,\infty}) - R_p(p_\infty, n_{tr,\infty})) \ln\left(\frac{n_{tr,\infty}}{1-n_{tr,\infty}}\right)\right) dx.$$

Taking the sum of the three expressions above, we arrive at

$$D(n_\infty, p_\infty, n_{tr,\infty}) = \int_\Omega \Bigg(\frac{|J_n(n_\infty)|^2}{n_\infty} + \frac{|J_p(p_\infty)|^2}{p_\infty}$$
$$- R_n(n_\infty, n_{tr,\infty}) \ln\left(\frac{n_\infty(1-n_{tr,\infty})}{n_0\mu_n n_{tr,\infty}}\right) - R_p(p_\infty, n_{tr,\infty}) \ln\left(\frac{p_\infty n_{tr,\infty}}{p_0\mu_p(1-n_{tr,\infty})}\right)\Bigg) dx = 0.$$

A closer look at the formula above shows that

$$-R_n(n_\infty, n_{tr,\infty}) \ln\left(\frac{n_\infty(1-n_{tr,\infty})}{n_0\mu_n n_{tr,\infty}}\right) \geq 0$$

where equality holds if and only if $R_n(n_\infty, n_{tr,\infty}) = 0$. The same argument also applies to the other reaction term. Hence, the relation $D(n_\infty, p_\infty, n_{tr,\infty}) = 0$ immediately implies $J_n(n_\infty) = J_p(p_\infty) = R_n(n_\infty, n_{tr,\infty}) = R_p(p_\infty, n_{tr,\infty}) = 0$ a.e. in Ω.

Because of $J_n(n_\infty) = J_p(p_\infty) = 0$, we know that

$$n_\infty = n_* e^{-V_n}, \quad p_\infty = p_* e^{-V_p}$$

with constants $n_*, p_* > 0$. Moreover, $R_n(n_\infty, n_{tr,\infty}) = R_p(p_\infty, n_{tr,\infty}) = 0$ gives rise to

$$n_{tr,\infty} = \frac{n_*}{n_0}(1-n_{tr,\infty}), \quad 1-n_{tr,\infty} = \frac{p_*}{p_0} n_{tr,\infty}.$$

Consequently, $n_* p_* = n_0 p_0$ and

$$n_{tr,\infty} = \frac{n_*}{n_* + n_0} = \frac{p_0}{p_* + p_0} \in (0,1).$$

The constants n_* and p_* are uniquely determined by the condition

$$n_* p_* = n_0 p_0$$

and the conservation law

$$n_* \overline{\mu_n} - p_* \overline{\mu_p} + \varepsilon\, n_{tr,\infty} = M.$$

Finally, the state

$$n_\infty = n_* e^{-V_n},\ p_\infty = p_* e^{-V_p},\ n_{tr,\infty} = \frac{n_*}{n_* + n_0} = \frac{p_0}{p_* + p_0}$$

obviously satisfies $J_n(n_\infty) = J_p(p_\infty) = R_n(n_\infty, n_{tr,\infty}) = R_p(p_\infty, n_{tr,\infty}) = 0$ a.e. in Ω which proves $(n_\infty, p_\infty, n_{tr,\infty})$ to be a solution of the stationary system. □

The announced ε-independence of the convergence rate for $\varepsilon \in (0, \varepsilon_0]$ and arbitrary ε_0 mainly builds on the subsequent "ε-independent" bounds for n_*, p_* and $n_{tr,\infty}$.

Proposition 2.10 (Bounds on the equilibrium)**.** *Let $(n_\infty, p_\infty, n_{tr,\infty}) \in X$ be the unique positive equilibrium as characterized in Theorem 2.4. Then, for all $M \in \mathbb{R}$ and for all $\varepsilon \in (0, \varepsilon_0]$ and arbitrary $\varepsilon_0 > 0$, there exist various constants $\gamma \in (0, 1/2)$ and $\Gamma \in (1/2, \infty)$ depending only on ε_0, n_0, p_0, M, V such that*

$$n_*, p_* \in [\gamma, \Gamma], \quad n_{tr,\infty} \in [\gamma, 1-\gamma]$$

and

$$n_\infty(x), p_\infty(x) \in [\gamma, \Gamma]$$

for all $x \in \Omega$.

Proof. We recall the equilibrium conditions (2.16)–(2.18) from Theorem 2.4 and observe that in the equation

$$n_* \overline{\mu_n} - \frac{n_0 p_0 \overline{\mu_p}}{n_*} = M - \varepsilon n_{tr,\infty} = M - \varepsilon \frac{n_*}{n_* + n_0},$$

the left hand side is strictly monotone increasing from $-\infty$ to $+\infty$ as $n_* \in (0, \infty)$, while the right hand side is strictly monotone decreasing and bounded between $(M, M - \varepsilon_0)$ as $n_* \in (0, \infty)$. Both monotonicity and unboundedness/boundedness imply uniform positive lower and upper bounds for n_* as explicitly proven in the following: First, we derive that

$$n_* = \frac{M - \varepsilon n_{tr,\infty}}{2\overline{\mu_n}} + \sqrt{\frac{(M - \varepsilon n_{tr,\infty})^2}{4\overline{\mu_n}^2} + \frac{n_0 p_0 \overline{\mu_p}}{\overline{\mu_n}}} > 0 \tag{2.36}$$

for all $\varepsilon \in (0, \varepsilon_0]$. Note that (2.36) is not an explicit representation of n_* since $n_{tr,\infty}$ depends itself on n_*. Because of $n_{tr,\infty} \in (0, 1)$, we further observe that

$$n_* \le \frac{|M - \varepsilon n_{tr,\infty}|}{2\overline{\mu_n}} + \sqrt{\frac{(M - \varepsilon n_{tr,\infty})^2}{4\overline{\mu_n}^2}} + \sqrt{\frac{n_0 p_0 \overline{\mu_p}}{\overline{\mu_n}}} \le \frac{|M| + \varepsilon_0}{\overline{\mu_n}} + \sqrt{\frac{n_0 p_0 \overline{\mu_p}}{\overline{\mu_n}}} \le \beta < \infty,$$

where $\beta = \beta(\varepsilon_0, n_0, p_0, M, V)$. And as a result of the elementary inequality

$$\sqrt{a+b} \ge \sqrt{a} + \frac{b}{2\sqrt{a} + \sqrt{b}}$$

for $a \ge 0$ and $b > 0$, we also conclude that

$$n_* \ge \frac{M - \varepsilon n_{tr,\infty}}{2\overline{\mu_n}} + \frac{|M - \varepsilon n_{tr,\infty}|}{2\overline{\mu_n}} + \frac{\frac{n_0 p_0 \overline{\mu_p}}{\overline{\mu_n}}}{\frac{|M - \varepsilon n_{tr,\infty}|}{\overline{\mu_n}} + \sqrt{\frac{n_0 p_0 \overline{\mu_p}}{\overline{\mu_n}}}} \ge \frac{\frac{n_0 p_0 \overline{\mu_p}}{\overline{\mu_n}}}{\frac{|M| + \varepsilon_0}{\overline{\mu_n}} + \sqrt{\frac{n_0 p_0 \overline{\mu_p}}{\overline{\mu_n}}}} \ge \alpha > 0$$

where $\alpha = \alpha(\varepsilon_0, n_0, p_0, M, V)$. Similar arguments show that corresponding bounds α and β are also available for p_*. Hence,

$$n_{tr,\infty} \in \left[\frac{\alpha}{\alpha + n_0}, \frac{\beta}{\beta + n_0}\right].$$

Due to $n_\infty = n_* e^{-V_n}$, $p_\infty = p_* e^{-V_p}$ and the L^∞-bounds on V_n and V_p, the claim of the proposition follows. □

2.3 Some Technical Lemmata

The first two lemmata state that the entropy functional $E(n, p, n_{tr})(t)$ is continuous and monotonically decreasing in time $t \ge 0$ along trajectories of system (2.1).

Lemma 2.11 (Continuity of the Entropy)**.** *The entropy*

$$E(n, p, n_{tr})(t) = \int_\Omega \left(n \ln \frac{n}{n_0 \mu_n} - (n - n_0 \mu_n) + p \ln \frac{p}{p_0 \mu_p} - (p - p_0 \mu_p) + \varepsilon \int_{1/2}^{n_{tr}} \ln\left(\frac{s}{1-s}\right) ds \right) dx$$

evaluated along solutions (n, p, n_{tr}) of system (2.1) *characterized in Theorem 2.1 is continuous at any time $t \ge 0$.*

Proof. The entropy can be reformulated as

$$E(n,p,n_{tr})(t) = \int_\Omega \left(n_0\mu_n\, g\Big(\frac{n}{n_0\mu_n}\Big) + p_0\mu_p\, g\Big(\frac{p}{p_0\mu_p}\Big) + \varepsilon \int_{1/2}^{n_{tr}} \ln\left(\frac{s}{1-s}\right) ds \right) dx$$

where $g : \mathbb{R}_{\geq 0} \to \mathbb{R}_{\geq 0}$, $g(x) := x\ln x - (x-1)$ is a continuous function. From Theorem 2.1, we know that $n \in C([0,\infty), L^2(\Omega))$ and, hence, $u := n/(n_0\mu_n) \in C([0,\infty), L^2(\Omega))$ as $1/\mu_n \in L^\infty(\Omega)$.

We proceed with proving that

$$g(u) \in C([0,\infty), L^1(\Omega)).$$

To this end, we choose a sequence $(t_k)_{k\in\mathbb{N}} \subset [0,\infty)$ converging to some $t \in [0,\infty)$ and establish the convergence $g(u)(t_k) \to g(u)(t)$ in $L^1(\Omega)$ for $k \to \infty$. Due to Vitali's convergence theorem [15], $u(t_k) \to u(t)$ in $L^2(\Omega)$ implies $u(t_k) \to u(t)$ in measure and the equi-integrability of $(|u(t_k)|^2)_{k\in\mathbb{N}}$. We recall that a sequence of measurable functions $f_k : \Omega \to \mathbb{R}$ converges *in measure* to $f : \Omega \to \mathbb{R}$, iff for every $\epsilon > 0$,

$$\lim_{k\to\infty} \big|\{x \in \Omega \mid |f_k(x) - f(x)| > \epsilon\}\big| = 0.$$

And one calls a sequence $(f_k)_{k\in\mathbb{N}} \subset L^p(\Omega)$, $p \geq 1$, *equi-integrable*, iff for any $\epsilon > 0$ there exists a $\delta > 0$ such that for all $k \in \mathbb{N}$ and all Lebesgue-sets $A \subset \Omega$, the following implication holds true:

$$|A| < \delta \implies \int_A |f_k|^p\, dx < \epsilon.$$

Moreover, Vitali's convergence theorem not only provides a necessary but also a sufficient condition for strong convergence in $L^p(\Omega)$. For verifying that $g(u)(t_k) \to g(u)(t)$ in $L^1(\Omega)$, it thus suffices to show that $g(u)(t_k) \to g(u)(t)$ in measure and that $(g(u)(t_k))_{k\in\mathbb{N}}$ is equi-integrable.

The convergence $u(t_k) \to u(t)$ in measure implies that every subsequence of $(u(t_k))_{k\in\mathbb{N}}$ has a subsequence which converges to f a.e. (see e.g. [15]). Since g is continuous, this also holds true for $g(u(t_k))_{k\in\mathbb{N}}$. And as the above characterization of convergence in measure is in fact an equivalence, we deduce that $g(u)(t_k) \to g(u)(t)$ in measure.

Concerning the equi-integrability of $(g(u)(t_k))_{k\in\mathbb{N}}$, we first observe that $g(x) \leq 1+x^2$ for all $x \in [0,\infty)$. Next, let $\epsilon > 0$ and choose $\delta_0 > 0$ such that

$$|A| < \delta_0 \implies \int_A |u(t_k)|^2\, dx < \frac{\epsilon}{2}$$

for all Lebesgue-sets $A \subset \Omega$. We then set $\delta := \min\{\epsilon/2, \delta_0\}$. Furthermore, let $k \in \mathbb{N}$ and $A \subset \Omega$ be an arbitrary Lebesgue-sets which satisfies $|A| < \delta$. We now find

$$\int_A |g(u)(t_k)|\, dx \leq \int_A \big(1 + |u(t_k)|^2\big)\, dx = |A| + \int_A |u(t_k)|^2\, dx < \frac{\epsilon}{2} + \frac{\epsilon}{2} = \epsilon.$$

This proves $g(u)(t_k) \to g(u)(t)$ in $L^1(\Omega)$ and further

$$\int_\Omega \left(n_0\mu_n\, g\Big(\frac{n}{n_0\mu_n}\Big) + p_0\mu_p\, g\Big(\frac{p}{p_0\mu_p}\Big)\right) dx\bigg|_{t_k} \to \int_\Omega \left(n_0\mu_n\, g\Big(\frac{n}{n_0\mu_n}\Big) + p_0\mu_p\, g\Big(\frac{p}{p_0\mu_p}\Big)\right) dx\bigg|_t$$

by applying the same arguments to the terms involving p and keeping in mind that μ_n, $\mu_p \in L^\infty(\Omega)$.

It remains to derive the temporal convergence of the entropy contribution for n_{tr}. Theorem 2.1 states that $n_{tr} \in C([0,\infty), L^\infty(\Omega))$. For any sequence $(t_k)_{k\in\mathbb{N}} \subset [0,\infty)$ converging to some $t \in [0,\infty)$, a straightforward calculation shows that

$$\begin{aligned}
&\left| \int_\Omega \int_{1/2}^{n_{tr}} \ln\left(\frac{s}{1-s}\right) ds\, dx\bigg|_{t_k} - \int_\Omega \int_{1/2}^{n_{tr}} \ln\left(\frac{s}{1-s}\right) ds\, dx\bigg|_t \right| \\
&\quad \leq \int_\Omega \left| \int_{n_{tr}(t)}^{n_{tr}(t_k)} \ln\left(\frac{s}{1-s}\right) ds \right| dx \leq \int_\Omega \Big| n_{tr}(t_k) - n_{tr}(t) \Big|^{\frac{1}{2}} \left(\int_{n_{tr}(t)}^{n_{tr}(t_k)} \ln\left(\frac{s}{1-s}\right)^2 ds \right)^{\frac{1}{2}} dx \\
&\quad \leq \int_\Omega \big\| n_{tr}(t_k) - n_{tr}(t) \big\|_{L^\infty(\Omega)}^{\frac{1}{2}} \left(\int_0^1 \ln\left(\frac{s}{1-s}\right)^2 ds \right)^{\frac{1}{2}} dx = \frac{\pi}{\sqrt{3}} \big\| n_{tr}(t_k) - n_{tr}(t) \big\|_{L^\infty(\Omega)}^{\frac{1}{2}} \to 0
\end{aligned}$$

for $k \to \infty$. As a consequence, the entropy $E(n,p,n_{tr})(t)$ is continuous at any $t \in [0,\infty)$. $\square$

Lemma 2.12 (Monotonicity of the Entropy)**.** *The entropy*

$$E(n,p,n_{tr})(t) = \int_\Omega \left(n \ln \frac{n}{n_0\mu_n} - (n - n_0\mu_n) + p \ln \frac{p}{p_0\mu_p} - (p - p_0\mu_p) + \varepsilon \int_{1/2}^{n_{tr}} \ln\left(\frac{s}{1-s}\right) ds \right) dx$$

is monotonically decreasing at any time $t \geq 0$ *along solutions* (n, p, n_{tr}) *of system* (2.1) *characterized in Theorem 2.1.*

Proof. For $0 < t_0 < t_1 < \infty$, the weak entropy production law

$$E(n,p,n_{tr})(t_1) + \int_{t_0}^{t_1} D(n,p,n_{tr})(s)\, ds = E(n,p,n_{tr})(t_0),$$

guarantees $E(n,p,n_{tr})(t_0) \geq E(n,p,n_{tr})(t_1)$. The continuity of $E(n,p,n_{tr})(t)$ on $[0,\infty)$ from Lemma 2.11 enables us to derive $E(n,p,n_{tr})(t_0) \geq E(n,p,n_{tr})(t_1)$ for all $0 \leq t_0 < t_1 < \infty$, where now $t_0 = 0$ is explicitly allowed. □

A particularly useful relation between the concentrations n, p and n_{tr} is the following Lemma.

Lemma 2.13. *The conservation law* $\overline{n} - \overline{p} + \varepsilon\, \overline{n_{tr}} = M$ *and the equilibrium condition* (2.19) *imply*

$$\forall\, t \geq 0: \quad (\overline{n} - \overline{n_\infty}) \ln\left(\frac{n_*}{n_0}\right) + (\overline{p} - \overline{p_\infty}) \ln\left(\frac{p_*}{p_0}\right) = \varepsilon(\overline{n_{tr}} - n_{tr,\infty}) \ln\left(\frac{1 - n_{tr,\infty}}{n_{tr,\infty}}\right). \tag{2.37}$$

Proof. With $\overline{n_\infty} - \overline{p_\infty} + \varepsilon\, n_{tr,\infty} = M$ (note that $n_{tr,\infty} = \overline{n_{tr,\infty}}$ is constant), we have $\overline{p} - \overline{p_\infty} = \overline{n} - \overline{n_\infty} + \varepsilon(\overline{n_{tr}} - n_{tr,\infty})$. We employ this relation to replace $\overline{p} - \overline{p_\infty}$ on the left hand side of (2.37) and calculate

$$(\overline{n} - \overline{n_\infty}) \ln\left(\frac{n_*}{n_0}\right) + (\overline{p} - \overline{p_\infty}) \ln\left(\frac{p_*}{p_0}\right) = (\overline{n} - \overline{n_\infty}) \ln\left(\frac{n_* p_*}{n_0 p_0}\right) + \varepsilon(\overline{n_{tr}} - n_{tr,\infty}) \ln\left(\frac{p_*}{p_0}\right).$$

Now, the first term on the right hand side vanishes due to $n_* p_* = n_0 p_0$ while we use $p_*/p_0 = (1 - n_{tr,\infty})/n_{tr,\infty}$ for the second term and obtain

$$(\overline{n} - \overline{n_\infty}) \ln\left(\frac{n_*}{n_0}\right) + (\overline{p} - \overline{p_\infty}) \ln\left(\frac{p_*}{p_0}\right) = \varepsilon(\overline{n_{tr}} - n_{tr,\infty}) \ln\left(\frac{1 - n_{tr,\infty}}{n_{tr,\infty}}\right)$$

as claimed above. □

Lemma 2.14 (Relative Entropy)**.** *The entropy relative to the equilibrium reads*

$$E(n,p,n_{tr}) - E(n_\infty,p_\infty,n_{tr,\infty}) =$$
$$\int_\Omega \left(n \ln \frac{n}{n_\infty} - (n - n_\infty) + p \ln \frac{p}{p_\infty} - (p - p_\infty) + \varepsilon \int_{n_{tr,\infty}}^{n_{tr}(x)} \left(\ln\left(\frac{s}{1-s}\right) - \ln\left(\frac{n_{tr,\infty}}{1 - n_{tr,\infty}}\right)\right) ds \right) dx.$$

Proof. By the definition of $E(n,p,n_{tr})$ in (2.11), we note that

$$E(n,p,n_{tr}) - E(n_\infty,p_\infty,n_{tr,\infty}) = \int_\Omega \left(n \ln\left(\frac{n}{n_0\mu_n}\right) - n_\infty \ln\left(\frac{n_\infty}{n_0\mu_n}\right) - (n - n_\infty) \right.$$
$$\left. + p \ln\left(\frac{p}{p_0\mu_p}\right) - p_\infty \ln\left(\frac{p_\infty}{p_0\mu_p}\right) - (p - p_\infty) + \varepsilon \int_{n_{tr,\infty}}^{n_{tr}(x)} \ln\left(\frac{s}{1-s}\right) ds \right) dx.$$

We now expand the first integrand as

$$n \ln\left(\frac{n}{n_0\mu_n}\right) = n \ln\left(\frac{n}{n_\infty}\right) + n \ln\left(\frac{n_\infty}{n_0\mu_n}\right).$$

Thus, with $n_\infty/\mu_n = n_*$, we get

$$\int_\Omega \left(n \ln\left(\frac{n}{n_0\mu_n}\right) - n_\infty \ln\left(\frac{n_\infty}{n_0\mu_n}\right) - (n - n_\infty)\right) dx$$
$$= \int_\Omega \left(n \ln\left(\frac{n}{n_\infty}\right) - (n - n_\infty)\right) dx + (\overline{n} - \overline{n_\infty}) \ln\left(\frac{n_*}{n_0}\right).$$

Together with an analogous calculation of the p-terms, we obtain

$$E(n,p,n_{tr}) - E(n_\infty, p_\infty, n_{tr,\infty}) = \int_\Omega \left(n \ln\left(\frac{n}{n_\infty}\right) - (n - n_\infty) + p \ln\left(\frac{p}{p_\infty}\right) - (p - p_\infty)\right) dx$$
$$+ (\overline{n} - \overline{n_\infty}) \ln\left(\frac{n_*}{n_0}\right) + (\overline{p} - \overline{p_\infty}) \ln\left(\frac{p_*}{p_0}\right) + \varepsilon \int_\Omega \int_{n_{tr,\infty}}^{n_{tr}(x)} \ln\left(\frac{s}{1-s}\right) ds\, dx.$$

Lemma 2.13 allows us to reformulate the second line as

$$(\overline{n} - \overline{n_\infty}) \ln\left(\frac{n_*}{n_0}\right) + (\overline{p} - \overline{p_\infty}) \ln\left(\frac{p_*}{p_0}\right) + \varepsilon \int_\Omega \int_{n_{tr,\infty}}^{n_{tr}(x)} \ln\left(\frac{s}{1-s}\right) ds\, dx$$
$$= \varepsilon(\overline{n_{tr}} - n_{tr,\infty}) \ln\left(\frac{1 - n_{tr,\infty}}{n_{tr,\infty}}\right) + \varepsilon \int_\Omega \int_{n_{tr,\infty}}^{n_{tr}(x)} \ln\left(\frac{s}{1-s}\right) ds\, dx$$
$$= \varepsilon \int_\Omega \int_{n_{tr,\infty}}^{n_{tr}(x)} \left(\ln\left(\frac{s}{1-s}\right) - \ln\left(\frac{n_{tr,\infty}}{1 - n_{tr,\infty}}\right)\right) ds\, dx,$$

which proves the claim. □

Lemma 2.15 (Classical Csiszár–Kullback–Pinsker inequality)**.** *Let $f, g : \Omega \to \mathbb{R}$ be non-negative measureable functions. Then,*

$$\int_\Omega \left(f \ln\left(\frac{f}{g}\right) - (f - g)\right) dx \geq \frac{3}{2\overline{f} + 4\overline{g}} \|f - g\|^2_{L^1(\Omega)}.$$

Proof. Following a proof by Pinsker, we start with the elementary inequality

$$3(x-1)^2 \leq (2x + 4)(x \ln x - (x - 1)).$$

This allows us to derive the following Csiszár–Kullback–Pinsker inequality:

$$\|f - g\|_{L^1(\Omega)} = \int_\Omega g \left| \frac{f}{g} - 1 \right| dx \leq \int_\Omega g \sqrt{\frac{2}{3}\frac{f}{g} + \frac{4}{3}} \sqrt{\frac{f}{g} \ln\left(\frac{f}{g}\right) - \left(\frac{f}{g} - 1\right)}\, dx$$
$$= \int_\Omega \sqrt{\frac{2}{3} f + \frac{4}{3} g} \sqrt{f \ln\left(\frac{f}{g}\right) - (f - g)}\, dx \leq \sqrt{\frac{2}{3}\overline{f} + \frac{4}{3}\overline{g}} \sqrt{\int_\Omega \left(f \ln\left(\frac{f}{g}\right) - (f - g)\right) dx}$$

where we applied Hölder's inequality in the last step. □

The subsequent Lemma provides L^1-bounds for n and p in terms of the initial entropy of the system and some further constants.

Lemma 2.16 (L^1-bounds)**.** *Due to the monotonicity of the entropy functional, any entropy producing solution of* (2.1) *satisfies*

$$\forall\, t \geq 0 : \quad \overline{n}, \overline{p} \leq \frac{5}{2} \max\{n_0 \overline{\mu_n}, p_0 \overline{\mu_p}\} + \frac{3}{4} E(n(0), p(0), n_{tr}(0)) =: M_1.$$

Proof. Employing Lemma 2.15 and Young's inequality, we find

$$\overline{n} \leq n_0 \overline{\mu_n} + \|n - n_0 \mu_n\|_{L^1(\Omega)} \leq n_0 \overline{\mu_n} + \sqrt{\frac{2}{3}\overline{n} + \frac{4}{3} n_0 \overline{\mu_n}} \sqrt{\int_\Omega \left(n \ln\left(\frac{n}{n_0 \mu_n}\right) - (n - n_0 \mu_n)\right) dx}$$
$$\leq n_0 \overline{\mu_n} + \frac{1}{3}\overline{n} + \frac{2}{3} n_0 \overline{\mu_n} + \frac{1}{2} \int_\Omega \left(n \ln\left(\frac{n}{n_0 \mu_n}\right) - (n - n_0 \mu_n)\right) dx.$$

Solving this inequality for $\overline{n}$ yields

$$\overline{n} \leq \frac{5}{2} n_0 \overline{\mu_n} + \frac{3}{4} \int_\Omega \left(n \ln \left(\frac{n}{n_0 \mu_n} \right) - (n - n_0 \mu_n) \right) dx.$$

Therefore, we arrive at

$$\overline{n} \leq \frac{5}{2} n_0 \overline{\mu_n} + \frac{3}{4} E(n, p, n_{tr}) \leq \frac{5}{2} \max\{n_0 \overline{\mu_n}, p_0 \overline{\mu_p}\} + \frac{3}{4} E(n(0), p(0), n_{tr}(0))$$

where we used the monotonicity of the entropy functional in the last step. In the same way, we may bound $\overline{p}$ from above. □

At certain points, we will have to estimate the difference between terms like $\overline{n/n_\infty}$ and $\overline{n}/\overline{n_\infty}$. Using Lemma 2.17 below, we can bound this difference by the J_n-flux-term and, hence, by the entropy production.

Lemma 2.17. *Let $f \in L^1(\Omega)$ and $g \in L^\infty(\Omega)$ such that $f \geq 0$, $g \geq \gamma > 0$ a.e. on Ω and f/g is weakly differentiable. Then, there exists an explicit constant $C(\|f\|_{L^1(\Omega)}, \|g\|_{L^\infty(\Omega)}, \gamma) > 0$ such that*

$$\left(\frac{\overline{f}}{\overline{g}} - \overline{\left(\frac{f}{g} \right)} \right)^2 \leq C \int_\Omega \left| \nabla \sqrt{\frac{f}{g}} \right|^2 dx.$$

Proof. Define

$$\delta := \frac{f}{g} - \overline{\left(\frac{f}{g} \right)}.$$

One obtains

$$f = g \left(\overline{\left(\frac{f}{g} \right)} + \delta \right)$$

and

$$\frac{\overline{f}}{\overline{g}} = \int_\Omega \frac{f}{\overline{g}} \, dx = \int_\Omega \frac{g}{\overline{g}} \left(\overline{\left(\frac{f}{g} \right)} + \delta \right) dx = \overline{\left(\frac{f}{g} \right)} + \int_\Omega \frac{g}{\overline{g}} \, \delta \, dx.$$

Therefore,

$$\left| \frac{\overline{f}}{\overline{g}} - \overline{\left(\frac{f}{g} \right)} \right| \leq \frac{\|g\|_{L^\infty(\Omega)}}{\overline{g}} \|\delta\|_{L^1(\Omega)} \leq C_P \frac{\|g\|_{L^\infty(\Omega)}}{\overline{g}} \left\| \nabla \left(\frac{f}{g} \right) \right\|_{L^1(\Omega)}$$

by applying Poincaré's inequality to δ with $\overline{\delta} = 0$ and some constant $C_P(\Omega) > 0$. As $g \geq \gamma > 0$ is uniformly positive on Ω and $\overline{g} \geq \gamma$, we arrive at

$$\left| \frac{\overline{f}}{\overline{g}} - \overline{\left(\frac{f}{g} \right)} \right| \leq C_P \frac{\|g\|_{L^\infty(\Omega)}}{\gamma^2} \left\| g \, \nabla \left(\frac{f}{g} \right) \right\|_{L^1(\Omega)}.$$

Finally, we deduce

$$\left(\frac{\overline{f}}{\overline{g}} - \overline{\left(\frac{f}{g} \right)} \right)^2 \leq \left(C_P \frac{\|g\|_{L^\infty(\Omega)}}{\gamma^2} \right)^2 \left\| \sqrt{fg} \sqrt{\frac{g}{f}} \nabla \left(\frac{f}{g} \right) \right\|_{L^1(\Omega)}^2 \leq 4 \overline{fg} \left(C_P \frac{\|g\|_{L^\infty(\Omega)}}{\gamma^2} \right)^2 \int_\Omega \left| \nabla \sqrt{\frac{f}{g}} \right|^2 dx$$

employing Hölder's inequality in the second step. □

2.4 Two Preliminary Propositions

Notation 2.18. For arbitrary functions f, we define the normalized quantity

$$\widetilde{f} := \frac{f}{\overline{f}}.$$

The following Logarithmic Sobolev inequality on bounded domains was proven in [11] by following an argument of Stroock [29].

Lemma 2.19 (Logarithmic Sobolev inequality on bounded domains). *Let Ω be a bounded domain in $\mathbb{R}^m$ such that the Poincaré (-Wirtinger) and Sobolev inequalities*

$$\|\phi - \textstyle\int_\Omega \phi\,dx\|_{L^2(\Omega)}^2 \le P(\Omega)\,\|\nabla\phi\|_{L^2(\Omega)}^2\,, \tag{2.38}$$

$$\|\phi\|_{L^q(\Omega)}^2 \le C_1(\Omega)\,\|\nabla\phi\|_{L^2(\Omega)}^2 + C_2(\Omega)\,\|\phi\|_{L^2(\Omega)}^2\,, \qquad \tfrac{1}{q} = \tfrac{1}{2} - \tfrac{1}{m}\,, \tag{2.39}$$

hold. Then, the logarithmic Sobolev inequality

$$\int_\Omega \phi^2 \ln\left(\frac{\phi^2}{\|\phi\|_2^2}\right) dx \le L(\Omega,m)\,\|\nabla\phi\|_{L^2(\Omega)}^2 \tag{2.40}$$

holds (for some constant $L(\Omega,m) > 0$).

We now apply the Log-Sobolev inequality to bound an appropriate part of the entropy functional by the flux parts of the entropy production. The normalized variables on the left hand side of the subsequent inequality naturally arise when reformulating the flux terms on the right hand side in such a way that we can apply the Log-Sobolev inequality on Ω.

Proposition 2.20. *There exists a constant $C(V) > 0$ such that*

$$\int_\Omega \left(n\ln\left(\frac{\widetilde{n}}{\widetilde{\mu_n}}\right) + p\ln\left(\frac{\widetilde{p}}{\widetilde{\mu_p}}\right)\right) dx \le C\int_\Omega \left(\frac{|J_n|^2}{n} + \frac{|J_p|^2}{p}\right) dx.$$

Proof. From the definition of J_n one obtains

$$\int_\Omega \frac{|J_n|^2}{n}\,dx = \int_\Omega \frac{\mu_n}{n}\left|\nabla\left(\frac{n}{\mu_n}\right)\right|^2 \mu_n\,dx = 4\,\overline{n}\int_\Omega \frac{\mu_n}{\overline{n}}\left|\nabla\sqrt{\frac{n}{\mu_n}}\right|^2 dx = 4\,\overline{n}\int_\Omega \frac{\mu_n}{\overline{\mu_n}}\left|\nabla\sqrt{\frac{\widetilde{n}}{\widetilde{\mu_n}}}\right|^2 dx.$$

We set

$$\phi(x) := \sqrt{\frac{\widetilde{n}}{\widetilde{\mu_n}}}, \quad \alpha := \int_\Omega \phi(x)^2\,dx$$

and define the rescaled variable $y := \alpha^{-\frac{1}{m}}x$ where m denotes the space dimension. Note that $\|\phi\|_{L^2(dx)}$ is in general different from one, whereas $\|\phi\|_{L^2(dy)} = 1$. We now estimate with $\|V_n\|_{L^\infty(\Omega)} \le V$ and the logarithmic Sobolev inequality (2.40)

$$\begin{aligned}\int_\Omega |\nabla_x\phi|^2\,dx = \int_\Omega |\alpha^{-\frac{1}{m}}\nabla_y\phi|^2\,\alpha\,dy &= \alpha^{1-\frac{2}{m}}\int_\Omega |\nabla_y\phi|^2\,dy \\ &\ge \alpha^{1-\frac{2}{m}}\frac{1}{L}\int_\Omega \frac{\widetilde{n}}{\widetilde{\mu_n}}\ln\left(\frac{\widetilde{n}}{\widetilde{\mu_n}}\right) dy = \alpha^{-\frac{2}{m}}\frac{1}{L}\frac{\overline{\mu_n}}{\overline{n}}\int_\Omega \frac{n}{\mu_n}\ln\left(\frac{\widetilde{n}}{\widetilde{\mu_n}}\right) dx.\end{aligned}$$

The corresponding estimate involving J_n reads

$$\int_\Omega \frac{|J_n|^2}{n}\,dx \ge 4\,\frac{\overline{n}}{\overline{\mu_n}}e^{-V}\int_\Omega |\nabla_x\phi|^2\,dx \ge \frac{4}{L}\alpha^{-\frac{2}{m}}e^{-2V}\int_\Omega n\ln\left(\frac{\widetilde{n}}{\widetilde{\mu_n}}\right) dx.$$

Using $\|V_n\|_{L^\infty(\Omega)} \le V$, we can bound α from above independent of the specific choice for n via $\alpha \le e^{2V}$. The same arguments apply to the terms involving p. ∎

The following Proposition contains the first step towards an entropy-entropy production inequality. The relative entropy can be controlled by the flux parts of the entropy production and three additional terms, which mainly consist of square-roots of averaged quantities. The proof that the entropy production also serves as an upper bound for these terms will be the subject of the next section.

Proposition 2.21. *There exists an explicit constant $C(\gamma,\Gamma,M_1)>0$ such that for $(n_\infty,p_\infty,n_{tr,\infty})\in X$ from Theorem 2.4 and all non-negative functions $(n,p,n_{tr})\in L^1(\Omega)^3$ satisfying $n_{tr}\le 1$, the conservation law*

$$\overline{n}-\overline{p}+\varepsilon\overline{n_{tr}}=M$$

and the L^1-bound

$$\overline{n},\overline{p}\le M_1,$$

the following estimate holds true:

$$E(n,p,n_{tr})-E(n_\infty,p_\infty,n_{tr,\infty})\le C\Bigg(\int_\Omega\left(\frac{|J_n|^2}{n}+\frac{|J_p|^2}{p}\right)dx + \left(\sqrt{\overline{\left(\frac{n}{\mu_n}\right)}}-\sqrt{n_*}\right)^2+\left(\sqrt{\overline{\left(\frac{p}{\mu_p}\right)}}-\sqrt{p_*}\right)^2+\varepsilon\int_\Omega\left(\sqrt{n_{tr}}-\sqrt{n_{tr,\infty}}\right)^2dx\Bigg). \tag{2.41}$$

(Note that the right hand side of (2.41) vanishes at the equilibrium $(n_\infty,p_\infty,n_{tr,\infty})$.)

Proof. According to Lemma 2.14, we have

$$E(n,p,n_{tr})-E(n_\infty,p_\infty,n_{tr,\infty})= \int_\Omega\left(n\ln\frac{n}{n_\infty}-(n-n_\infty)+p\ln\frac{p}{p_\infty}-(p-p_\infty)+\varepsilon\int_{n_{tr,\infty}}^{n_{tr}}\left(\ln\left(\frac{s}{1-s}\right)-\ln\left(\frac{n_{tr,\infty}}{1-n_{tr,\infty}}\right)\right)ds\right)dx.$$

Recall that $n=\widetilde{n}\,\overline{n}$, $n_\infty=\widetilde{n_\infty}\,\overline{n_\infty}$ and $\widetilde{n_\infty}=\widetilde{\mu_n}$. Using these relations, we rewrite the first two integrands as

$$n\ln\left(\frac{n}{n_\infty}\right)-(n-n_\infty)=n\ln\left(\frac{\widetilde{n}}{\widetilde{\mu_n}}\right)+n\ln\left(\frac{\overline{n}}{\overline{n_\infty}}\right)-(n-n_\infty)$$

and analogously for the p-terms. This results in

$$E(n,p,n_{tr})-E(n_\infty,p_\infty,n_{tr,\infty})=\int_\Omega\left(n\ln\left(\frac{\widetilde{n}}{\widetilde{\mu_n}}\right)+p\ln\left(\frac{\widetilde{p}}{\widetilde{\mu_p}}\right)\right)dx + \overline{n_\infty}\left(\frac{\overline{n}}{\overline{n_\infty}}\ln\left(\frac{\overline{n}}{\overline{n_\infty}}\right)-\left(\frac{\overline{n}}{\overline{n_\infty}}-1\right)\right)+\overline{p_\infty}\left(\frac{\overline{p}}{\overline{p_\infty}}\ln\left(\frac{\overline{p}}{\overline{p_\infty}}\right)-\left(\frac{\overline{p}}{\overline{p_\infty}}-1\right)\right) + \varepsilon\int_\Omega\int_{n_{tr,\infty}}^{n_{tr}}\left(\ln\left(\frac{s}{1-s}\right)-\ln\left(\frac{n_{tr,\infty}}{1-n_{tr,\infty}}\right)\right)ds\,dx. \tag{2.42}$$

The terms in the first line of (2.42) can be estimated using the Log-Sobolev inequality of Proposition 2.20. Moreover, the elementary inequality $x\ln x-(x-1)\le(x-1)^2$ for $x>0$ gives rise to

$$\overline{n_\infty}\left(\frac{\overline{n}}{\overline{n_\infty}}\ln\left(\frac{\overline{n}}{\overline{n_\infty}}\right)-\left(\frac{\overline{n}}{\overline{n_\infty}}-1\right)\right)\le\overline{n_\infty}\left(\frac{\overline{n}}{\overline{n_\infty}}-1\right)^2\le 2\overline{n_\infty}\left[\left(\overline{\left(\frac{n}{n_\infty}\right)}-1\right)^2+\left(\frac{\overline{n}}{\overline{n_\infty}}-\overline{\left(\frac{n}{n_\infty}\right)}\right)^2\right]$$

and an analogous estimate for the corresponding expressions involving p. The second term on the right hand side of the previous line can be bounded from above by applying Lemma 2.17, which guarantees a constant $C(\gamma,\Gamma,M_1)>0$ such that

$$\left(\frac{\overline{n}}{\overline{n_\infty}}-\overline{\left(\frac{n}{n_\infty}\right)}\right)^2\le C\int_\Omega\left|\nabla\sqrt{\frac{n}{n_\infty}}\right|^2dx\le\frac{C}{4\inf_\Omega n_\infty}\int_\Omega\frac{1}{n}\left|n_\infty\nabla\left(\frac{n}{n_\infty}\right)\right|^2dx\le c_1\int_\Omega\frac{|J_n|^2}{n}dx$$

for some constant $c_1(\gamma,\Gamma,M_1)>0$. Besides,

$$\left(\overline{\left(\frac{n}{n_\infty}\right)}-1\right)^2=\frac{1}{n_*^2}\left(\overline{\left(\frac{n}{\mu_n}\right)}-n_*\right)^2=\frac{1}{n_*^2}\left(\sqrt{\overline{\left(\frac{n}{\mu_n}\right)}}+\sqrt{n_*}\right)^2\left(\sqrt{\overline{\left(\frac{n}{\mu_n}\right)}}-\sqrt{n_*}\right)^2 =\frac{1}{n_*}\left(\sqrt{\overline{\left(\frac{n}{n_\infty}\right)}}+1\right)^2\left(\sqrt{\overline{\left(\frac{n}{\mu_n}\right)}}-\sqrt{n_*}\right)^2\le C(\gamma,M_1)\left(\sqrt{\overline{\left(\frac{n}{\mu_n}\right)}}-\sqrt{n_*}\right)^2.$$

See Proposition 2.10 and Lemma 2.16 for the bounds on n_*, n_∞ and $\overline{n}$. We have thus verified that

$$\overline{n_\infty}\left(\frac{\overline{n}}{\overline{n_\infty}}\ln\left(\frac{\overline{n}}{\overline{n_\infty}}\right)-\left(\frac{\overline{n}}{\overline{n_\infty}}-1\right)\right)\le c_2\left(\int_\Omega\frac{|J_n|^2}{n}\,dx+\left(\sqrt{\overline{\left(\frac{n}{\mu_n}\right)}}-\sqrt{n_*}\right)^2\right)$$

for some $c_2(\gamma,\Gamma,M_1)>0$. A similar estimate holds true for the corresponding part of (2.42) involving p.

Considering the last line in (2.42), we further know that for all $x\in\Omega$ there exists some mean value

$$\theta(x)\in(\min\{n_{tr}(x),n_{tr,\infty}\},\max\{n_{tr}(x),n_{tr,\infty}\})$$

such that

$$\int_{n_{tr,\infty}}^{n_{tr}(x)}\ln\left(\frac{s}{1-s}\right)ds=\ln\left(\frac{\theta(x)}{1-\theta(x)}\right)(n_{tr}(x)-n_{tr,\infty}). \tag{2.43}$$

Consequently,

$$\varepsilon\int_\Omega\int_{n_{tr,\infty}}^{n_{tr}(x)}\ln\left(\frac{s}{1-s}\right)ds\,dx=\varepsilon\int_\Omega\ln\left(\frac{\theta(x)}{1-\theta(x)}\right)(n_{tr}(x)-n_{tr,\infty})\,dx.$$

In fact, we will prove that there even exists some constant $\xi\in(0,1/2)$ such that

$$\theta(x)\in(\xi,1-\xi)$$

for all $x\in\Omega$. Thus, the function $\theta(x)$ is uniformly bounded away from 0 and 1 on Ω. To see this, we first note that $n_{tr,\infty}\in[\gamma,1-\gamma]$ using the constant $\gamma\in(0,1/2)$ from Proposition 2.10. In addition,

$$\left|\int_{n_{tr,\infty}}^{n_{tr}(x)}\ln\left(\frac{s}{1-s}\right)ds\right|\le\int_0^1\left|\ln\left(\frac{s}{1-s}\right)\right|ds=2\ln(2)$$

for all $x\in\Omega$. Together with (2.43), this estimate implies

$$\left|\ln\left(\frac{\theta(x)}{1-\theta(x)}\right)\right||n_{tr}(x)-n_{tr,\infty}|\le 2\ln(2).$$

We now choose an arbitrary $x\in\Omega$ and distinguish two cases. If $|n_{tr}(x)-n_{tr,\infty}|\ge\gamma/2$, then

$$\left|\ln\left(\frac{\theta(x)}{1-\theta(x)}\right)\right|\le\frac{2\ln(2)}{|n_{tr}(x)-n_{tr,\infty}|}\le\frac{4\ln(2)}{\gamma}.$$

As a consequence of $\ln(s/(1-s))\to\infty$ for $s\to1^-$ and $\ln(s/(1-s))\to-\infty$ for $s\to0^+$, there exists some constant $\xi\in(0,\gamma)$ depending only on γ such that $\theta(x)\in(\xi,1-\xi)$. If $|n_{tr}(x)-n_{tr,\infty}|<\gamma/2$, then $n_{tr,\infty}\in[\gamma,1-\gamma]$ implies $n_{tr}(x)\in(\gamma/2,1-\gamma/2)$ and, hence, $\theta(x)\in(\gamma/2,1-\gamma/2)$. In both cases, the constant ξ depends only on γ.

As a result of the calculations above, we may rewrite the last line in (2.42) as

$$\begin{aligned}\varepsilon\int_\Omega\int_{n_{tr,\infty}}^{n_{tr}(x)}&\left(\ln\left(\frac{s}{1-s}\right)-\ln\left(\frac{n_{tr,\infty}}{1-n_{tr,\infty}}\right)\right)ds\,dx\\&=\varepsilon\int_\Omega\left(\ln\left(\frac{\theta(x)}{1-\theta(x)}\right)-\ln\left(\frac{n_{tr,\infty}}{1-n_{tr,\infty}}\right)\right)(n_{tr}(x)-n_{tr,\infty})\,dx.\end{aligned}$$

Applying the mean-value theorem to the expression in brackets and observing that

$$\frac{d}{ds}\ln\left(\frac{s}{1-s}\right)=\frac{1}{s(1-s)},$$

we find

$$\begin{aligned}\varepsilon\int_\Omega&\left(\ln\left(\frac{\theta(x)}{1-\theta(x)}\right)-\ln\left(\frac{n_{tr,\infty}}{1-n_{tr,\infty}}\right)\right)(n_{tr}(x)-n_{tr,\infty})\,dx\\&=\varepsilon\int_\Omega\frac{1}{\sigma(x)(1-\sigma(x))}(\theta(x)-n_{tr,\infty})(n_{tr}(x)-n_{tr,\infty})\,dx\end{aligned}$$

with some $\sigma(x) \in (\min\{\theta(x), n_{tr,\infty}\}, \max\{\theta(x), n_{tr,\infty}\})$. Since both $\theta(x), n_{tr,\infty} \in (\xi, 1-\xi)$ for all $x \in \Omega$, we also know that $\sigma(x) \in (\xi, 1-\xi)$ for all $x \in \Omega$. Thus, $(\sigma(x)(1-\sigma(x)))^{-1}$ is bounded uniformly in Ω in terms of $\xi = \xi(\gamma)$. Consequently,

$$\begin{aligned}
\varepsilon \int_\Omega \int_{n_{tr,\infty}}^{n_{tr}(x)} \left(\ln\left(\frac{s}{1-s}\right) - \ln\left(\frac{n_{tr,\infty}}{1-n_{tr,\infty}}\right)\right) ds\, dx \\
&\le \varepsilon c_3 \int_\Omega |\theta(x) - n_{tr,\infty}||n_{tr}(x) - n_{tr,\infty}|\, dx \le \varepsilon c_3 \int_\Omega (n_{tr} - n_{tr,\infty})^2\, dx \\
&= \varepsilon c_3 \int_\Omega (\sqrt{n_{tr}} + \sqrt{n_{tr,\infty}})^2 (\sqrt{n_{tr}} - \sqrt{n_{tr,\infty}})^2\, dx \le 4\varepsilon c_3 \int_\Omega \left(\sqrt{n_{tr}} - \sqrt{n_{tr,\infty}}\right)^2 dx
\end{aligned}$$

with a constant $c_3(\gamma) > 0$ after applying the estimate $|\theta(x) - n_{tr,\infty}| \le |n_{tr}(x) - n_{tr,\infty}|$ for all $x \in \Omega$. Finally, we arrive at

$$\begin{aligned}
E(n, p, n_{tr}) - E(n_\infty, p_\infty, n_{tr,\infty}) \le C \Bigg(&\int_\Omega \left(\frac{|J_n|^2}{n} + \frac{|J_p|^2}{p}\right) dx \\
&+ \left(\sqrt{\overline{\left(\frac{n}{\mu_n}\right)}} - \sqrt{n_*}\right)^2 + \left(\sqrt{\overline{\left(\frac{p}{\mu_p}\right)}} - \sqrt{p_*}\right)^2 + \varepsilon \int_\Omega \left(\sqrt{n_{tr}} - \sqrt{n_{tr,\infty}}\right)^2 dx \Bigg)
\end{aligned}$$

with a constant $C(\gamma, \Gamma, M_1) > 0$. □

2.5 Abstract Versions of the EEP-Inequality

Notation 2.22. We set

$$n'_{tr} := 1 - n_{tr}, \quad n'_{tr,\infty} := 1 - n_{tr,\infty}$$

and define the positive constants

$$\nu_\infty := \sqrt{\frac{n_*}{n_0}} = \sqrt{\frac{n_\infty}{n_0 \mu_n}}, \quad \pi_\infty := \sqrt{\frac{p_*}{p_0}} = \sqrt{\frac{p_\infty}{p_0 \mu_p}}, \quad \nu_{tr,\infty} := \sqrt{n_{tr,\infty}}, \quad \nu'_{tr,\infty} := \sqrt{n'_{tr,\infty}}.$$

The motivation for introducing the additional variable n'_{tr} is the possibility to symmetrize expressions like $(n(1-n_{tr}) - n_{tr})^2 + (pn_{tr} - (1-n_{tr}))^2$ as $(nn'_{tr} - n_{tr})^2 + (pn_{tr} - n'_{tr})^2$. Similar terms will appear frequently within the subsequent calculations.

Remark 2.23. As already in the existence proof, we may consider n'_{tr} as a fourth independent variable within our model. In this case, the reaction-diffusion system features the following two independent conservation laws:

$$\overline{n} - \overline{p} + \varepsilon\, \overline{n_{tr}} = n_0\, \overline{\mu_n \left(\frac{n}{n_0 \mu_n}\right)} - p_0\, \overline{\mu_p \left(\frac{p}{p_0 \mu_p}\right)} + \varepsilon\, \overline{n_{tr}} = M \in \mathbb{R}, \qquad n_{tr}(x) + n'_{tr}(x) = 1 \text{ for all } x \in \Omega.$$

The special formulation of the first conservation law will become clear when looking at the following two Propositions. There, we derive relations for general variables a, b, c and d, which correspond to $\sqrt{n/(n_0\mu_n)}$, $\sqrt{p/(p_0\mu_p)}$, $\sqrt{n_{tr}}$ and $\sqrt{n'_{tr}}$, respectively.

In addition, we have the following L^1-bound (cf. Lemma 2.16):

$$\overline{n}, \overline{p} \le M_1.$$

The following Proposition 2.24 establishes an upper bound for the terms in the second line of (2.41) in the case of *constant* concentrations a, b, c and d. This result is then generalized in Proposition 2.26 to *non-constant* states a, b, c, d.

Proposition 2.24 (Homogeneous Concentrations)**.** *Let $a, b, c, d \ge 0$ be constants such that their squares satisfy the conservation laws*

$$n_0 \overline{\mu_n} a^2 - p_0 \overline{\mu_p} b^2 + \varepsilon\, c^2 = M = n_0 \overline{\mu_n} \nu_\infty^2 - p_0 \overline{\mu_p} \pi_\infty^2 + \varepsilon\, \nu_{tr,\infty}^2, \qquad c^2 + d^2 = 1 = \nu_{tr,\infty}^2 + \nu'^2_{tr,\infty}$$

for any $\varepsilon \in (0, \varepsilon_0]$ *and arbitrary* $\varepsilon_0 > 0$. *Moreover, assume*

$$a^2, b^2 \leq C(n_0, p_0, M_1, V).$$

Then, there exists an explicitly computable constant $C(\varepsilon_0, n_0, p_0, M, M_1, V) > 0$ *such that*

$$(a - \nu_\infty)^2 + (b - \pi_\infty)^2 + (c - \nu_{tr,\infty})^2 \leq C\left((ad - c)^2 + (bc - d)^2\right) \tag{2.44}$$

for all $\varepsilon \in (0, \varepsilon_0]$.

Proof. We first introduce the following change of variables: Due to the non-negativity of the concentrations a, b, c, d, we may define constants $\mu_1, \mu_2, \mu_3, \mu_4 \in [-1, \infty)$ such that

$$a = \nu_\infty(1 + \mu_1), \qquad b = \pi_\infty(1 + \mu_2), \qquad c = \nu_{tr,\infty}(1 + \mu_3), \qquad d = \nu'_{tr,\infty}(1 + \mu_4),$$

where ν_∞, π_∞, $\nu_{tr,\infty}$ and $\nu'_{tr,\infty}$ are uniformly positive and bounded for all $\varepsilon \in (0, \varepsilon_0]$ in terms of $\varepsilon_0, n_0, p_0, M$ and V by Proposition 2.10. Thus, the boundedness of a, b, c, d implies the existence of a constant $K(\varepsilon_0, n_0, p_0, M, M_1, V) > 0$, such that $\mu_i \in [-1, K]$ for all $1 \leq i \leq 4$. The left hand side of (2.44) expressed in terms of the μ_i rewrites as

$$(a - \nu_\infty)^2 + (b - \pi_\infty)^2 + (c - \nu_{tr,\infty})^2 = \nu_\infty^2 \mu_1^2 + \pi_\infty^2 \mu_2^2 + \nu_{tr,\infty}^2 \mu_3^2.$$

Employing the equilibrium conditions (2.19), we also find

$$ad - c = \nu_\infty \nu'_{tr,\infty}(1 + \mu_1)(1 + \mu_4) - \nu_{tr,\infty}(1 + \mu_3) = \nu_{tr,\infty}\left[(1 + \mu_1)(1 + \mu_4) - (1 + \mu_3)\right]$$

and

$$bc - d = \pi_\infty \nu_{tr,\infty}(1 + \mu_2)(1 + \mu_3) - \nu'_{tr,\infty}(1 + \mu_4) = \nu'_{tr,\infty}\left[(1 + \mu_2)(1 + \mu_3) - (1 + \mu_4)\right].$$

Moreover, the two conservation laws from the hypotheses rewrite as

$$n_0 \overline{\mu_n} \nu_\infty^2 \mu_1(2 + \mu_1) - p_0 \overline{\mu_p} \pi_\infty^2 \mu_2(2 + \mu_2) + \varepsilon\, \nu_{tr,\infty}^2 \mu_3(2 + \mu_3) = 0, \tag{2.45}$$

$$\nu_{tr,\infty}^2 \mu_3(2 + \mu_3) + \nu'^2_{tr,\infty} \mu_4(2 + \mu_4) = 0. \tag{2.46}$$

The relations (2.45)–(2.46) allow to express $\varepsilon\mu_3$ and $\varepsilon\mu_4$ in terms of μ_1 and μ_2, although not explicitly:

$$\varepsilon\mu_3 = -\frac{n_0 \overline{\mu_n} \nu_\infty^2}{\nu_{tr,\infty}^2} \frac{2 + \mu_1}{2 + \mu_3}\, \mu_1 + \frac{p_0 \overline{\mu_p} \pi_\infty^2}{\nu_{tr,\infty}^2} \frac{2 + \mu_2}{2 + \mu_3}\, \mu_2 =: -f_{1,3}(\mu_1, \mu_3)\mu_1 + f_{2,3}(\mu_2, \mu_3)\mu_2, \tag{2.47}$$

$$\varepsilon\mu_4 = -\frac{\nu_{tr,\infty}^2}{\nu'^2_{tr,\infty}} \frac{2 + \mu_3}{2 + \mu_4}\, \varepsilon\mu_3 =: -f_{3,4}(\mu_3, \mu_4)\, \varepsilon\mu_3 =: f_{1,4}(\mu_1, \mu_3, \mu_4)\mu_1 - f_{2,4}(\mu_2, \mu_3, \mu_4)\mu_2, \tag{2.48}$$

where the last definition follows from inserting the previous expression (2.47) for $\varepsilon\mu_3$ while the factor $2 + \mu_3$ is bounded in $[1, K + 2]$ since $\mu_i \in [-1, K]$ for all $1 \leq i \leq 4$. Therefore, all the terms $f_{i,j}$ are uniformly positive as well as bounded from above:

$$0 < \underline{C_{1,3}} \leq f_{1,3} \leq \overline{C_{1,3}} < \infty, \quad 0 < \underline{C_{2,3}} \leq f_{2,3} \leq \overline{C_{2,3}} < \infty,$$
$$0 < \underline{C_{3,4}} \leq f_{3,4} \leq \overline{C_{3,4}} < \infty, \quad 0 < \underline{C_{1,4}} \leq f_{1,4} \leq \overline{C_{1,4}} < \infty, \quad 0 < \underline{C_{2,4}} \leq f_{2,4} \leq \overline{C_{2,4}} < \infty.$$

All constants $\underline{C_{i,j}}$ and $\overline{C_{i,j}}$ only depend on ε_0, n_0, p_0, M, M_1 and V, and there exist corresponding bounds $\underline{C} > 0$ and $\overline{C} > 0$ such that for all i, j

$$\underline{C} \leq \underline{C_{i,j}}, \overline{C_{i,j}} \leq \overline{C}.$$

In order to prove (2.44), we show that under the constraints of the conservation laws (2.45)–(2.46) or, equivalently, under the relations (2.47)–(2.48), there exists a constant $C(\varepsilon_0, n_0, p_0, M, \underline{C}, \overline{C}) > 0$ for all $\varepsilon \in (0, \varepsilon_0]$ such that

$$\frac{(a - \nu_\infty)^2 + (b - \pi_\infty)^2 + (c - \nu_{tr,\infty})^2}{(ad - c)^2 + (bc - d)^2} \leq C,$$

which is equivalent to

$$\frac{\nu_\infty^2\mu_1^2+\pi_\infty^2\mu_2^2+\nu_{tr,\infty}^2\mu_3^2}{\nu_{tr,\infty}^2\left[(1+\mu_1)(1+\mu_4)-(1+\mu_3)\right]^2+\nu_{tr,\infty}'^2\left[(1+\mu_2)(1+\mu_3)-(1+\mu_4)\right]^2}\le C. \tag{2.49}$$

Recall that $\nu_\infty^2\le\Gamma/n_0$, $\pi_\infty^2\le\Gamma/p_0$ and $\nu_{tr,\infty}^2,\nu_{tr,\infty}'^2\in[\gamma,1-\gamma]$ with $\gamma\in(0,1/2)$ and $\Gamma\in(1/2,\infty)$ depending on ε_0, n_0, p_0 and M for all $\varepsilon\in(0,\varepsilon_0]$ (cf. Proposition 2.10). Since numerator and denominator of (2.49) are sums of quadratic terms, it is sufficient to bound the denominator from below in terms of its numerator omitting the prefactors ν_∞^2, π_∞^2, $\nu_{tr,\infty}^2$ and $\nu_{tr,\infty}'^2$, i.e. to prove that

$$(*):=\left[(1+\mu_1)(1+\mu_4)-(1+\mu_3)\right]^2+\left[(1+\mu_2)(1+\mu_3)-(1+\mu_4)\right]^2\ge C\left(\mu_1^2+\mu_2^2+\mu_3^2\right). \tag{2.50}$$

More precisely, we will prove that there exists a constant $c(\varepsilon_0,\underline{C},\overline{C})>0$ for all $\varepsilon\in(0,\varepsilon_0]$ such that

$$(*)=(\mu_1+\mu_4+\mu_1\mu_4-\mu_3)^2+(\mu_2+\mu_3+\mu_2\mu_3-\mu_4)^2\ge c\,(\mu_1^2+\mu_2^2)$$

and that

$$(*)=(\mu_1+\mu_4+\mu_1\mu_4-\mu_3)^2+(\mu_2+\mu_3+\mu_2\mu_3-\mu_4)^2\ge\mu_3^2.$$

For this reason, we distinguish four cases and we shall frequently use estimates like

$$\mu_i+\mu_i\mu_j=\mu_i(1+\mu_j)\ge0\quad\text{iff}\quad\mu_i\ge0\quad\text{for all}\quad1\le j\le4,$$

since $\mu_j\ge-1$ for all $1\le j\le4$. We mention already here that all subsequent constants c_1, c_2 are strictly positive and depend only on ε_0, $\underline{C}$ and $\overline{C}$ uniformly for $\varepsilon\in(0,\varepsilon_0]$.

Case 1: $\mu_1\ge0\wedge\mu_2\ge0$**:** If $\mu_3\ge0$, then (2.46) implies $\mu_4\le0$ and $\mu_2+\mu_3+\mu_2\mu_3-\mu_4\ge\mu_2$. Moreover, $\mu_3\ge0$ yields

$$f_{2,3}\mu_2\ge f_{1,3}\mu_1\;\Rightarrow\;\overline{C_{2,3}}\mu_2\ge\underline{C_{1,3}}\mu_1\;\Rightarrow\;\mu_2\ge\underline{C_{1,3}}/\overline{C_{2,3}}\,\mu_1$$

and

$$\mu_2+\mu_3+\mu_2\mu_3-\mu_4\ge\mu_2\ge\mu_2/2+\underline{C_{1,3}}/(2\,\overline{C_{2,3}})\mu_1\ge c_1(\mu_1+\mu_2).$$

Hence, $(*)\ge(\mu_2+\mu_3+\mu_2\mu_3-\mu_4)^2\ge c_2(\mu_1^2+\mu_2^2)$. Besides, $(*)\ge(\mu_2+\mu_3+\mu_2\mu_3-\mu_4)^2\ge\mu_3^2$. If $\mu_3<0$, (2.46) yields $\mu_4>0$ and $\mu_1+\mu_4+\mu_1\mu_4-\mu_3\ge\mu_1$. Since $\mu_3<0$, (2.47) implies

$$f_{1,3}\mu_1\ge f_{2,3}\mu_2\;\Rightarrow\;\overline{C_{1,3}}\mu_1\ge\underline{C_{2,3}}\mu_2\;\Rightarrow\;\mu_1\ge\underline{C_{2,3}}/\overline{C_{1,3}}\,\mu_2$$

and

$$\mu_1+\mu_4+\mu_1\mu_4-\mu_3\ge\mu_1\ge\mu_1/2+\underline{C_{2,3}}/(2\,\overline{C_{1,3}})\mu_2\ge c_1(\mu_1+\mu_2).$$

As above, $(*)\ge c_2(\mu_1^2+\mu_2^2)$. The signs $\mu_3\le0\le\mu_1,\mu_4$ yield $(*)\ge(\mu_1+\mu_4+\mu_1\mu_4-\mu_3)^2\ge\mu_3^2$.

Case 2: $\mu_1\ge0\wedge\mu_2<0$**:** (2.47) and (2.48) imply $\mu_3\le0$ and $\mu_4\ge0$, and we deduce for all $\varepsilon\in(0,\varepsilon_0]$

$$\begin{aligned}\mu_1+\mu_4+\mu_1\mu_4-\mu_3\ge\mu_4-\mu_3&=\varepsilon^{-1}(f_{1,3}+f_{1,4})\mu_1-\varepsilon^{-1}(f_{2,3}+f_{2,4})\mu_2\\&\ge\varepsilon_0^{-1}(\underline{C_{1,3}}+\underline{C_{1,4}})|\mu_1|+\varepsilon_0^{-1}(\underline{C_{2,3}}+\underline{C_{2,4}})|\mu_2|\ge c_1(|\mu_1|+|\mu_2|)\end{aligned}$$

and, thus, $(*)\ge(\mu_1+\mu_4+\mu_1\mu_4-\mu_3)^2\ge c_2(\mu_1^2+\mu_2^2)$. Since $\mu_2,\mu_3\le0\le\mu_4$, we have

$$(*)\ge(\mu_4-\mu_3-\mu_2(1+\mu_3))^2\ge\mu_3^2.$$

Case 3: $\mu_1<0\wedge\mu_2\ge0$**:** Here, $\mu_3\ge0$ due to (2.47) and, thus, $\mu_4\le0$ by (2.48), which yields for all $\varepsilon\in(0,\varepsilon_0]$

$$\begin{aligned}\mu_2+\mu_3+\mu_2\mu_3-\mu_4\ge\mu_3-\mu_4&=\varepsilon^{-1}(f_{2,3}+f_{2,4})\mu_2-\varepsilon^{-1}(f_{1,3}+f_{1,4})\mu_1\\&\ge\varepsilon_0^{-1}(\underline{C_{1,3}}+\underline{C_{1,4}})|\mu_1|+\varepsilon_0^{-1}(\underline{C_{2,3}}+\underline{C_{2,4}})|\mu_2|\ge c_1(|\mu_1|+|\mu_2|)\end{aligned}$$

and $(*)\ge(\mu_2+\mu_3+\mu_2\mu_3-\mu_4)^2\ge c_2(\mu_1^2+\mu_2^2)$. And as $\mu_1,\mu_4\le0\le\mu_3$, one has

$$(*)\ge(\mu_3-\mu_4-\mu_1(1+\mu_4))^2\ge\mu_3^2.$$

Case 4: $\mu_1 < 0 \wedge \mu_2 < 0$**:** Supposing that $\mu_3 \geq 0$ and thus $\mu_4 \leq 0$ by (2.48), we observe

$$|\mu_1 + \mu_4 + \mu_1\mu_4 - \mu_3| = \mu_3 - \mu_1 - \mu_4(1 + \mu_1) \geq -\mu_1.$$

Furthermore, $\mu_3 \geq 0$ enables us to estimate

$$f_{1,3}\mu_1 \leq f_{2,3}\mu_2 \ \Rightarrow\ \overline{C_{1,3}}\mu_1 \leq \underline{C_{2,3}}\mu_2 \ \Rightarrow\ -\mu_1 \geq -\underline{C_{2,3}}/\overline{C_{1,3}}\,\mu_2.$$

and

$$|\mu_1 + \mu_4 + \mu_1\mu_4 - \mu_3| \geq -\mu_1 \geq -\mu_1/2 - \underline{C_{2,3}}/(2\,\overline{C_{1,3}})\mu_2 \geq c_1(|\mu_1| + |\mu_2|).$$

Hence, $(*) \geq (\mu_1 + \mu_4 + \mu_1\mu_4 - \mu_3)^2 \geq c_2(\mu_1^2 + \mu_2^2)$. The second estimate in terms of μ_3^2 follows with $\mu_1, \mu_4 \leq 0 \leq \mu_3$ from

$$(*) \geq \big(\mu_3 - \mu_4 - \mu_1(1 + \mu_4)\big)^2 \geq \mu_3^2.$$

In the opposite case that $\mu_3 < 0$ and thus $\mu_4 \geq 0$ due to (2.48), we estimate

$$|\mu_2 + \mu_3 + \mu_2\mu_3 - \mu_4| = \mu_4 - \mu_2 - \mu_3(1 + \mu_2) \geq -\mu_2$$

and

$$f_{2,3}\mu_2 \leq f_{1,3}\mu_1 \ \Rightarrow\ \overline{C_{2,3}}\mu_2 \leq \underline{C_{1,3}}\mu_1 \ \Rightarrow\ -\mu_2 \geq -\underline{C_{1,3}}/\overline{C_{2,3}}\,\mu_1.$$

We, thus, arrive at

$$|\mu_2 + \mu_3 + \mu_2\mu_3 - \mu_4| \geq -\mu_2 \geq -\mu_2/2 - \underline{C_{1,3}}/(2\,\overline{C_{2,3}})\mu_1 \geq c_1(|\mu_1| + |\mu_2|)$$

and $(*) \geq (\mu_2 + \mu_3 + \mu_2\mu_3 - \mu_4)^2 \geq c_2(\mu_1^2 + \mu_2^2)$. The corresponding inequality for μ_3 reads

$$(*) \geq \big(\mu_4 - \mu_3 - \mu_2(1 + \mu_3)\big)^2 \geq \mu_3^2,$$

which follows from $\mu_2, \mu_3 \leq 0 \leq \mu_4$.

The proof of the Proposition is now complete. □

Notation 2.25. From now on, $\|\cdot\|$ without further specification shall always denote the L^2-norm in Ω.

Within the subsequent Proposition 2.26, the expressions $(ad - c)^2$ and $(bc - d)^2$ on the right hand side of (2.44) will be generalized to $\|ad-c\|^2$ and $\|bc-d\|^2$ in Equation (2.51). We will later show in the proof of Theorem 2.6 that $\|ad - c\|^2$ (and also $\|bc - d\|^2$) can be estimated from above via the reaction terms within the entropy production (2.13) when using the special choices $\sqrt{n/(n_0\mu_n)}$, $\sqrt{p/(p_0\mu_p)}$, $\sqrt{n_{tr}}$ and $\sqrt{n'_{tr}}$ for a, b, c and d.

Proposition 2.26 (Inhomogeneous Concentrations)**.** *Let $a, b, c, d : \Omega \to \mathbb{R}$ be measurable, non-negative functions such that their squares satisfy the conservation laws*

$$n_0\overline{\mu_n a^2} - p_0\overline{\mu_p b^2} + \varepsilon\,\overline{c^2} = M = n_0\overline{\mu_n}\nu_\infty^2 - p_0\overline{\mu_p}\pi_\infty^2 + \varepsilon\,\nu_{tr,\infty}^2, \qquad \overline{c^2} + \overline{d^2} = 1 = \nu_{tr,\infty}^2 + \nu_{tr,\infty}'^2$$

for any $\varepsilon \in (0, \varepsilon_0]$ and arbitrary $\varepsilon_0 > 0$. In addition, we assume

$$\overline{a^2},\, \overline{b^2} \leq C(n_0, p_0, M_1, V).$$

Then, there exists an explicitly computable constant $C(\varepsilon_0, n_0, p_0, M, M_1, V) > 0$ such that

$$\begin{aligned}&\Big(\sqrt{\overline{a^2}} - \nu_\infty\Big)^2 + \Big(\sqrt{\overline{b^2}} - \pi_\infty\Big)^2 + \|c - \nu_{tr,\infty}\|^2 \\ &\leq C\Big(\|ad - c\|^2 + \|bc - d\|^2 + \|\nabla a\|^2 + \|\nabla b\|^2 + \|a - \overline{a}\|^2 + \|b - \overline{b}\|^2 + \|c - \overline{c}\|^2 + \|d - \overline{d}\|^2\Big). \quad (2.51)\end{aligned}$$

for all $\varepsilon \in (0, \varepsilon_0]$.

Proof. We divide the proof into two steps. In the first part, we shall derive lower bounds for the reaction terms $\|ad - c\|^2 + \|bc - d\|^2$ involving $(\overline{a}\,\overline{d} - \overline{c})^2 + (\overline{b}\,\overline{c} - \overline{d})^2$. This will allow us to apply Proposition 2.24 in the second step.

Step 1: We show

$$\|ad-c\|^2 \geq \frac{1}{2}\left(\overline{a}\,\overline{d}-\overline{c}\right)^2 - c_1\left(\|a-\overline{a}\|^2+\|b-\overline{b}\|^2+\|c-\overline{c}\|^2+\|d-\overline{d}\|^2\right)$$

and

$$\|bc-d\|^2 \geq \frac{1}{2}\left(\overline{b}\,\overline{c}-\overline{d}\right)^2 - c_1\left(\|a-\overline{a}\|^2+\|b-\overline{b}\|^2+\|c-\overline{c}\|^2+\|d-\overline{d}\|^2\right)$$

with some explicitly computable constant $c_1 > 0$. For this reason, we define

$$\delta_1 := a-\overline{a}, \quad \delta_2 := b-\overline{b}, \quad \delta_3 := c-\overline{c}, \quad \delta_4 := d-\overline{d}$$

and note that $\overline{\delta_1}=\overline{\delta_2}=\overline{\delta_3}=\overline{\delta_4}=0$. Moreover,

$$|\overline{a}\,\overline{d}-\overline{c}|,\ |\overline{b}\,\overline{c}-\overline{d}| \leq C(n_0,p_0,M_1,V)$$

due to Young's inequality, $\overline{a^2}$, $\overline{b^2} \leq C(n_0,p_0,M_1,V)$ and $\overline{c^2}$, $\overline{d^2} \leq 1$.

We now define

$$S := \left\{x\in\Omega \,\middle|\, |\delta_1|\leq 1 \wedge |\delta_2|\leq 1 \wedge |\delta_3|\leq 1 \wedge |\delta_4|\leq 1\right\}$$

and split the squares of the $L^2(\Omega)$-norm as

$$\|ad-c\|^2 = \int_S (ad-c)^2\,dx + \int_{\Omega\setminus S}(ad-c)^2\,dx \tag{2.52}$$

and

$$\|bc-d\|^2 = \int_S (bc-d)^2\,dx + \int_{\Omega\setminus S}(bc-d)^2\,dx,$$

respectively. In order to estimate the first integral in (2.52) from below, we write

$$ad = (\overline{a}+\delta_1)(\overline{d}+\delta_4) = \overline{a}\overline{d}+\overline{a}\delta_4+\overline{d}\delta_1+\delta_1\delta_4, \quad c=\overline{c}+\delta_3.$$

This yields

$$\int_S (ad-c)^2\,dx = \int_S(\overline{a}\overline{d}-\overline{c})^2\,dx + 2\int_S(\overline{a}\overline{d}-\overline{c})(\overline{a}\delta_4+\overline{d}\delta_1+\delta_1\delta_4-\delta_3)\,dx + \int_S(\overline{a}\delta_4+\overline{d}\delta_1+\delta_1\delta_4-\delta_3)^2\,dx$$
$$\geq \frac{1}{2}\int_S(\overline{a}\overline{d}-\overline{c})^2\,dx - \int_S(\overline{a}\delta_4+\overline{d}\delta_1+\delta_1\delta_4-\delta_3)^2\,dx \geq \frac{1}{2}\int_S(\overline{a}\overline{d}-\overline{c})^2\,dx - C(n_0,p_0,M_1,V)\left(\overline{\delta_1^2}+\overline{\delta_3^2}+\overline{\delta_4^2}\right)$$

where we used Young's inequality $2xy \geq -x^2/2-2y^2$ for $x,y\in\mathbb{R}$ in the second step and the boundedness of δ_i, $1\leq i\leq 4$, in the last step. Similarly, we deduce

$$\int_S (bc-d)^2\,dx \geq \frac{1}{2}\int_S(\overline{b}\overline{c}-\overline{d})^2\,dx - C(n_0,p_0,M_1,V)\left(\overline{\delta_2^2}+\overline{\delta_3^2}+\overline{\delta_4^2}\right).$$

The second integral in (2.52) is mainly estimated by deriving an upper bound for the measure of $\Omega\setminus S$. For all $i\in\{1,\ldots,4\}$ we have

$$\left|\left\{\delta_i^2>1\right\}\right| = \int_{\left\{\delta_i^2>1\right\}} 1\,dx \leq \int_\Omega \delta_i^2\,dx = \overline{\delta_i^2}$$

and, hence,

$$|\Omega\setminus S| \leq \sum_{i=1}^4 \left|\left\{\delta_i^2>1\right\}\right| \leq \overline{\delta_1^2}+\overline{\delta_2^2}+\overline{\delta_3^2}+\overline{\delta_4^2}.$$

As a consequence of $|\overline{a}\,\overline{d}-\overline{c}| \leq C(n_0,p_0,M_1,V)$, we obtain

$$\int_{\Omega\setminus S}(\overline{a}\,\overline{d}-\overline{c})^2\,dx \leq C(n_0,p_0,M_1,V)\,|\{\Omega\setminus S\}| \leq C(n_0,p_0,M_1,V)\left(\overline{\delta_1^2}+\overline{\delta_2^2}+\overline{\delta_3^2}+\overline{\delta_4^2}\right).$$

This implies

$$\int_{\Omega\setminus S}(ad-c)^2\,dx \geq 0 \geq \frac{1}{2}\int_{\Omega\setminus S}(\overline{a}\,\overline{d}-\overline{c})^2\,dx - C(n_0,p_0,M_1,V)\left(\overline{\delta_1^2}+\overline{\delta_2^2}+\overline{\delta_3^2}+\overline{\delta_4^2}\right)$$

and, analogously,

$$\int_{\Omega\setminus S}(bc-d)^2\,dx \geq 0 \geq \frac{1}{2}\int_{\Omega\setminus S}(\overline{b}\,\overline{c}-\overline{d})^2\,dx - C(n_0,p_0,M_1,V)\left(\overline{\delta_1^2}+\overline{\delta_2^2}+\overline{\delta_3^2}+\overline{\delta_4^2}\right).$$

Taking the sum of both contributions to (2.52), we finally arrive at

$$\|ad-c\|^2 \geq \frac{1}{2}\left(\overline{a}\,\overline{d}-\overline{c}\right)^2 - c_1(n_0,p_0,M_1,V)\left(\overline{\delta_1^2}+\overline{\delta_2^2}+\overline{\delta_3^2}+\overline{\delta_4^2}\right) \tag{2.53}$$

and

$$\|bc-d\|^2 \geq \frac{1}{2}\left(\overline{b}\,\overline{c}-\overline{d}\right)^2 - c_1(n_0,p_0,M_1,V)\left(\overline{\delta_1^2}+\overline{\delta_2^2}+\overline{\delta_3^2}+\overline{\delta_4^2}\right). \tag{2.54}$$

Step 2: We introduce constants $\mu_i \geq -1$, $1 \leq i \leq 4$, such that

$$\overline{a^2} = \nu_\infty^2(1+\mu_1)^2, \quad \overline{b^2} = \pi_\infty^2(1+\mu_2)^2, \quad \overline{c^2} = \nu_{tr,\infty}^2(1+\mu_3)^2, \quad \overline{d^2} = \nu_{tr,\infty}'^2(1+\mu_4)^2.$$

We recall that Proposition 2.10 guarantees the uniform positivity and boundedness of ν_∞, π_∞, $\nu_{tr,\infty}$ and $\nu'_{tr,\infty}$ for all $\varepsilon \in (0,\varepsilon_0]$ in terms of $\varepsilon_0, n_0, p_0, M$ and V. Therefore, the bounds $\overline{a^2}$, $\overline{b^2} \leq C(n_0,p_0,M_1,V)$ and $\overline{c^2}$, $\overline{d^2} \leq 1$ give rise to a constant $K(\varepsilon_0,n_0,p_0,M,M_1,V) > 0$ such that $\mu_i \in [-1,K]$ for all $1 \leq i \leq 4$ uniformly for $\varepsilon \in (0,\varepsilon_0]$.

We now want to derive a formula for $\overline{a}$ in terms of δ_1 and μ_1. Since $\overline{a^2} - \overline{a}^2 = \|a-\overline{a}\|^2 = \|\delta_1\|^2 = \overline{\delta_1^2}$, one finds

$$\overline{a} = \sqrt{\overline{a^2}} - \frac{\overline{\delta_1^2}}{\sqrt{\overline{a^2}}+\overline{a}} = \nu_\infty(1+\mu_1) - \frac{\overline{\delta_1^2}}{\sqrt{\overline{a^2}}+\overline{a}} \tag{2.55}$$

and analogous expressions for $\overline{b}$, $\overline{c}$ and $\overline{d}$:

$$\overline{b} = \pi_\infty(1+\mu_2) - \frac{\overline{\delta_2^2}}{\sqrt{\overline{b^2}}+\overline{b}}, \qquad \overline{c} = \nu_{tr,\infty}(1+\mu_3) - \frac{\overline{\delta_3^2}}{\sqrt{\overline{c^2}}+\overline{c}}, \qquad \overline{d} = \nu'_{tr,\infty}(1+\mu_4) - \frac{\overline{\delta_4^2}}{\sqrt{\overline{d^2}}+\overline{d}}.$$

Furthermore,

$$\left(\sqrt{\overline{a^2}}-\nu_\infty\right)^2 = \nu_\infty^2\mu_1^2, \qquad \left(\sqrt{\overline{b^2}}-\pi_\infty\right)^2 = \pi_\infty^2\mu_2^2$$

and, similarly,

$$\begin{aligned}\|c-\nu_{tr,\infty}\|^2 &= \overline{c^2} - 2\overline{c}\nu_{tr,\infty} + \nu_{tr,\infty}^2 \\ &= \nu_{tr,\infty}^2(1+\mu_3)^2 - 2\nu_{tr,\infty}^2(1+\mu_3) + \frac{2\nu_{tr,\infty}\overline{\delta_3^2}}{\sqrt{\overline{c^2}}+\overline{c}} + \nu_{tr,\infty}^2 = \nu_{tr,\infty}^2\mu_3^2 + \frac{2\nu_{tr,\infty}}{\sqrt{\overline{c^2}}+\overline{c}}\,\overline{\delta_3^2}.\end{aligned}$$

One observes that the expansions above in terms of $\overline{\delta_i^2}$ are singular if, e.g., $\overline{a^2}$ is zero. We therefore distinguish the following two cases.

Case 1: $\overline{a^2} \geq \kappa^2 \wedge \overline{b^2} \geq \kappa^2 \wedge \overline{c^2} \geq \kappa^2 \wedge \overline{d^2} \geq \kappa^2$**:** The constant $\kappa > 0$ will be chosen according to the calculations in the other Case 2. Here, we have

$$\frac{1}{\sqrt{\overline{a^2}}+\overline{a}}, \quad \frac{1}{\sqrt{\overline{b^2}}+\overline{b}}, \quad \frac{1}{\sqrt{\overline{c^2}}+\overline{c}}, \quad \frac{1}{\sqrt{\overline{d^2}}+\overline{d}} \quad \leq \frac{1}{\kappa}$$

and

$$\frac{\nu'_{tr,\infty}}{\sqrt{\overline{a^2}}+\overline{a}}, \quad \frac{\nu_{tr,\infty}}{\sqrt{\overline{b^2}}+\overline{b}}, \quad \frac{\pi_\infty}{\sqrt{\overline{c^2}}+\overline{c}}, \quad \frac{\nu_\infty}{\sqrt{\overline{d^2}}+\overline{d}} \quad \leq C(\kappa,\varepsilon_0,n_0,p_0,M,V)$$

for all $\varepsilon \in (0,\varepsilon_0]$ due to the bounds on ν_∞ and π_∞ from Proposition 2.10. Equation (2.55) further implies

$$
\begin{aligned}
(\overline{a}\overline{d}-\overline{c})^2 = \Bigg(&\nu_\infty \nu'_{tr,\infty}(1+\mu_1)(1+\mu_4) - \frac{\nu_\infty(1+\mu_1)}{\sqrt{\overline{d^2}}+\overline{d}}\,\overline{\delta_4^2} - \frac{\nu'_{tr,\infty}(1+\mu_4)}{\sqrt{\overline{a^2}}+\overline{a}}\,\overline{\delta_1^2} \\
&+ \frac{1}{(\sqrt{\overline{a^2}}+\overline{a})(\sqrt{\overline{d^2}}+\overline{d})}\,\overline{\delta_1^2}\,\overline{\delta_4^2} - \nu_{tr,\infty}(1+\mu_3) + \frac{\overline{\delta_3^2}}{\sqrt{\overline{c^2}}+\overline{c}}\Bigg)^2 \\
&\geq \nu_{tr,\infty}^2\big((1+\mu_1)(1+\mu_4)-(1+\mu_3)\big)^2 - c_2(\kappa,\varepsilon_0,n_0,p_0,M,M_1,V)\big(\overline{\delta_1^2}+\overline{\delta_3^2}+\overline{\delta_4^2}\big)
\end{aligned}
$$

with some explicit constant c_2 thanks to $\nu_\infty\nu'_{tr,\infty} = \nu_{tr,\infty}$ (compare Equation (2.19)) and $|\mu_i|, \overline{\delta_i^2} \leq c_1(\varepsilon_0, n_0, p_0, M, M_1, V)$. In a similar fashion using $\pi_\infty \nu_{tr,\infty} = \nu'_{tr,\infty}$, one obtains

$$
\begin{aligned}
(\overline{b}\overline{c}-\overline{d})^2 = \Bigg(&\pi_\infty \nu_{tr,\infty}(1+\mu_2)(1+\mu_3) - \frac{\pi_\infty(1+\mu_2)}{\sqrt{\overline{c^2}}+\overline{c}}\,\overline{\delta_3^2} - \frac{\nu_{tr,\infty}(1+\mu_3)}{\sqrt{\overline{b^2}}+\overline{b}}\,\overline{\delta_2^2} \\
&+ \frac{1}{(\sqrt{\overline{b^2}}+\overline{b})(\sqrt{\overline{c^2}}+\overline{c})}\,\overline{\delta_2^2}\,\overline{\delta_3^2} - \nu'_{tr,\infty}(1+\mu_4) + \frac{\overline{\delta_4^2}}{\sqrt{\overline{d^2}}+\overline{d}}\Bigg)^2 \\
&\geq \nu'^2_{tr,\infty}\big((1+\mu_2)(1+\mu_3)-(1+\mu_4)\big)^2 - c_2(\kappa,\varepsilon_0,n_0,p_0,M,M_1,V)\big(\overline{\delta_2^2}+\overline{\delta_3^2}+\overline{\delta_4^2}\big).
\end{aligned}
$$

In order to finish the proof, it is — according to Step 1 — sufficient to show that

$$
\begin{aligned}
\nu_\infty^2\mu_1^2 + \pi_\infty^2\mu_2^2 + \nu_{tr,\infty}^2\mu_3^2 + \frac{2\nu_{tr,\infty}}{\sqrt{\overline{c^2}}+\overline{c}}\,\overline{\delta_3^2} \leq C_1 \Bigg(&\|\nabla a\|^2 + \|\nabla b\|^2 \\
+ \frac{1}{2}\big(\overline{a}\,\overline{d}-\overline{c}\big)^2 + \frac{1}{2}\big(\overline{b}\,\overline{c}-\overline{d}\big)^2 - 2\,c_1(n_0,p_0,M_1,V)&\left(\overline{\delta_1^2}+\overline{\delta_2^2}+\overline{\delta_3^2}+\overline{\delta_4^2}\right)\Bigg) + C_2\left(\overline{\delta_1^2}+\overline{\delta_2^2}+\overline{\delta_3^2}+\overline{\delta_4^2}\right)
\end{aligned}
$$

for appropriate constants $C_1, C_2 > 0$. But due to Step 2 it is sufficient to show that for suitable constants $C_1, C_2 > 0$,

$$
\begin{aligned}
\nu_\infty^2\mu_1^2 + \pi_\infty^2\mu_2^2 + \nu_{tr,\infty}^2\mu_3^2 + \frac{2\nu_{tr,\infty}}{\sqrt{\overline{c^2}}+\overline{c}}\,\overline{\delta_3^2} \leq C_1 \Bigg(&\|\nabla a\|^2 + \|\nabla b\|^2 \\
+ \frac{\nu_{tr,\infty}^2}{2}\big((1+\mu_1)(1+\mu_4)-(1+\mu_3)\big)^2 &+ \frac{\nu'^2_{tr,\infty}}{2}\big((1+\mu_2)(1+\mu_3)-(1+\mu_4)\big)^2 \\
- c_3(\kappa,\varepsilon_0,n_0,p_0,M,M_1,V)&\left(\overline{\delta_1^2}+\overline{\delta_2^2}+\overline{\delta_3^2}+\overline{\delta_4^2}\right)\Bigg) + C_2\left(\overline{\delta_1^2}+\overline{\delta_2^2}+\overline{\delta_3^2}+\overline{\delta_4^2}\right).
\end{aligned}
$$

Collecting all $\overline{\delta_i^2}$-terms on the right hand side, one only has to prove that

$$
\begin{aligned}
\nu_\infty^2\mu_1^2 + \pi_\infty^2\mu_2^2 + \nu_{tr,\infty}^2\mu_3^2 \leq C_1\Bigg(&\|\nabla a\|^2 + \|\nabla b\|^2 \\
&+ \nu_{tr,\infty}^2\big((1+\mu_1)(1+\mu_4)-(1+\mu_3)\big)^2 + \nu'^2_{tr,\infty}\big((1+\mu_2)(1+\mu_3)-(1+\mu_4)\big)^2\Bigg) \\
&+ \Big(C_2 - C(C_1,\kappa,\varepsilon_0,n_0,p_0,M,M_1,V)\Big)\left(\overline{\delta_1^2}+\overline{\delta_2^2}+\overline{\delta_3^2}+\overline{\delta_4^2}\right)
\end{aligned}
$$

or, equivalently,

$$
\begin{aligned}
&\left(\sqrt{\overline{a^2}}-\nu_\infty\right)^2 + \left(\sqrt{\overline{b^2}}-\pi_\infty\right)^2 + \left(\sqrt{\overline{c^2}}-\nu_{tr,\infty}\right)^2 \\
&\quad\leq C_1\left(\left(\sqrt{\overline{a^2}}\sqrt{\overline{d^2}}-\sqrt{\overline{c^2}}\right)^2 + \left(\sqrt{\overline{b^2}}\sqrt{\overline{c^2}}-\sqrt{\overline{d^2}}\right)^2 + \|\nabla a\|^2 + \|\nabla b\|^2\right) \\
&\qquad + \Big(C_2 - C(C_1,\kappa,\varepsilon_0,n_0,p_0,M,M_1,V)\Big)\left(\overline{\delta_1^2}+\overline{\delta_2^2}+\overline{\delta_3^2}+\overline{\delta_4^2}\right). \qquad (2.56)
\end{aligned}
$$

In order to verify (2.56), we start with the estimate

$$
\left(\sqrt{\overline{a^2}}-\nu_\infty\right)^2 \leq 2\left[\left(\sqrt{\frac{\overline{\mu_n a^2}}{\overline{\mu_n}}}-\nu_\infty\right)^2 + \left(\sqrt{\frac{\overline{\mu_n a^2}}{\overline{\mu_n}}}-\sqrt{\overline{a^2}}\right)^2\right]
$$

and a corresponding one involving b. The last term on the right hand side satisfies

$$\left(\sqrt{\frac{\overline{\mu_n a^2}}{\overline{\mu_n}}} - \sqrt{\overline{a^2}}\right)^2 = \frac{\left(\frac{\overline{\mu_n a^2}}{\overline{\mu_n}} - \overline{a^2}\right)^2}{\left(\sqrt{\frac{\overline{\mu_n a^2}}{\overline{\mu_n}}} + \sqrt{\overline{a^2}}\right)^2} \leq \frac{1}{\kappa^2}\left(\frac{\overline{\mu_n a^2}}{\overline{\mu_n}} - \overline{a^2}\right)^2 \leq c\int_\Omega \left|\nabla\sqrt{a^2}\right|^2 dx = c\,\|\nabla a\|^2$$

due to Lemma 2.17 with a constant $c(\kappa, n_0, p_0, M_1, V) > 0$. Similarly,

$$\left(\sqrt{\overline{b^2}} - \pi_\infty\right)^2 \leq c(\kappa, n_0, p_0, M_1, V)\left[\left(\sqrt{\frac{\overline{\mu_p b^2}}{\overline{\mu_p}}} - \pi_\infty\right)^2 + \|\nabla b\|^2\right].$$

Proposition 2.24 (with a^2, b^2, c^2 and d^2 therein replaced by $\overline{\mu_n a^2}/\overline{\mu_n}$, $\overline{\mu_p b^2}/\overline{\mu_p}$, $\overline{c^2}$ and $\overline{d^2}$) tells us that there exists an explicitly computable constant $C(\varepsilon_0, n_0, p_0, M, M_1, V) > 0$ such that

$$\left(\sqrt{\frac{\overline{\mu_n a^2}}{\overline{\mu_n}}} - \nu_\infty\right)^2 + \left(\sqrt{\frac{\overline{\mu_p b^2}}{\overline{\mu_p}}} - \pi_\infty\right)^2 + \left(\sqrt{\overline{c^2}} - \nu_{tr,\infty}\right)^2$$
$$\leq C\left(\left(\sqrt{\frac{\overline{\mu_n a^2}}{\overline{\mu_n}}}\sqrt{\overline{d^2}} - \sqrt{\overline{c^2}}\right)^2 + \left(\sqrt{\frac{\overline{\mu_p b^2}}{\overline{\mu_p}}}\sqrt{\overline{c^2}} - \sqrt{\overline{d^2}}\right)^2\right) \tag{2.57}$$

for all $\varepsilon \in (0, \varepsilon_0]$. Using an analog expansion as before, we further deduce with $\overline{d^2} \leq 1$,

$$\left(\sqrt{\frac{\overline{\mu_n a^2}}{\overline{\mu_n}}}\sqrt{\overline{d^2}} - \sqrt{\overline{c^2}}\right)^2 = \left(\sqrt{\overline{a^2}}\sqrt{\overline{d^2}} - \sqrt{\overline{c^2}} + \left(\sqrt{\frac{\overline{\mu_n a^2}}{\overline{\mu_n}}} - \sqrt{\overline{a^2}}\right)\sqrt{\overline{d^2}}\right)^2$$
$$\leq c(\kappa, n_0, p_0, M_1, V)\left(\left(\sqrt{\overline{a^2}}\sqrt{\overline{d^2}} - \sqrt{\overline{c^2}}\right)^2 + \|\nabla a\|^2\right).$$

As a corresponding estimate holds true also for the other expression on the right hand side of (2.57), we have shown that there exists a constant $C_1(\kappa, \varepsilon_0, n_0, p_0, M, M_1, V) > 0$ independent of ε for $\varepsilon \in (0, \varepsilon_0]$ such that

$$\left(\sqrt{\overline{a^2}} - \nu_\infty\right)^2 + \left(\sqrt{\overline{b^2}} - \pi_\infty\right)^2 + \left(\sqrt{\overline{c^2}} - \nu_{tr,\infty}\right)^2$$
$$\leq C_1\left(\left(\sqrt{\overline{a^2}}\sqrt{\overline{d^2}} - \sqrt{\overline{c^2}}\right)^2 + \left(\sqrt{\overline{b^2}}\sqrt{\overline{c^2}} - \sqrt{\overline{d^2}}\right)^2 + \|\nabla a\|^2 + \|\nabla b\|^2\right).$$

Choosing $C_2 > 0$ now sufficiently large, Equation (2.56) holds true.

Case 2: $\overline{a^2} < \kappa^2 \vee \overline{b^2} < \kappa^2 \vee \overline{c^2} < \kappa^2 \vee \overline{d^2} < \kappa^2$: In this case, we will not need Proposition 2.24 and we shall directly prove Equation (2.51) employing only the result of Step 1. In fact, for κ chosen sufficiently small, the states considered in Case 2 are necessarily bounded away from the equilibrium and the following arguments show that consequentially the right hand side of (2.51) is also bounded away from zero, which allows to close the estimate (2.51). As a result of the hypotheses $\overline{a^2}$, $\overline{b^2} \leq C(n_0, p_0, M_1, V)$ and $\overline{c^2}$, $\overline{d^2} \leq 1$, we use Young's inequality to estimate $\overline{a}, \overline{b}, \overline{c}, \overline{d} \leq c(n_0, p_0, M_1, V)$ and

$$\left(\sqrt{\overline{a^2}} - \nu_\infty\right)^2 + \left(\sqrt{\overline{b^2}} - \pi_\infty\right)^2 + \|c - \nu_{tr,\infty}\|^2 \leq C(\varepsilon_0, n_0, p_0, M, M_1, V)$$

with $C > 0$ uniformly for $\varepsilon \in (0, \varepsilon_0]$. We stress that the subsequent cases are not necessarily exclusive.

Case 2.1: $\overline{c^2} < \kappa^2$: First, $\overline{c} = \sqrt{\overline{c}^2} \leq \sqrt{\overline{c^2}} < \kappa$. This yields

$$\overline{d^2} = 1 - \overline{c^2} > 1 - \kappa^2 \Rightarrow \overline{d}^2 = \overline{d^2} - \overline{\delta_4^2} > 1 - \overline{\delta_4^2} - \kappa^2 \Rightarrow$$
$$\left(\overline{b}\,\overline{c} - \overline{d}\right)^2 \geq \overline{d}^2 - 2\overline{b}\,\overline{c}\,\overline{d} > 1 - \overline{\delta_4^2} - \kappa^2 - 2\overline{b}\,\overline{d}\,\kappa \geq 1 - \overline{\delta_4^2} - \kappa^2 - C(n_0, p_0, M_1, V)\,\kappa.$$

For $\kappa > 0$ sufficiently small, we then have $0 < 1 - C(n_0, p_0, M_1, V)\kappa - \kappa^2 \le (\overline{b}\,\overline{c} - \overline{d})^2 + \overline{\delta_4^2}$ and, hence,

$$\left(\sqrt{\overline{a^2}} - \nu_\infty\right)^2 + \left(\sqrt{\overline{b^2}} - \pi_\infty\right)^2 + \|c - \nu_{tr,\infty}\|^2 \le C(\varepsilon_0, n_0, p_0, M, M_1, V) \le$$
$$K(\overline{b}\,\overline{c} - \overline{d})^2 + K\overline{\delta_4^2} \le 2K\|bc - d\|^2 + (2Kc_1(n_0, p_0, M_1, V) + K)\left(\overline{\delta_1^2} + \overline{\delta_2^2} + \overline{\delta_3^2} + \overline{\delta_4^2}\right)$$

by (2.54) with some $K(\kappa, \varepsilon_0, n_0, p_0, M, M_1, V) > 0$. Let us call the parameter κ from above κ_c.

Case 2.2: $\overline{d^2} < \kappa^2$**:** Now $\overline{d} = \sqrt{\overline{d}^2} \le \sqrt{\overline{d^2}} < \kappa$ and

$$\overline{c^2} = 1 - \overline{d^2} > 1 - \kappa^2 \Rightarrow \overline{c}^2 = \overline{c^2} - \overline{\delta_3^2} > 1 - \overline{\delta_3^2} - \kappa^2 \Rightarrow$$
$$\left(\overline{a}\,\overline{d} - \overline{c}\right)^2 \ge \overline{c}^2 - 2\overline{a}\,\overline{c}\,\overline{d} > 1 - \overline{\delta_3^2} - \kappa^2 - 2\overline{a}\,\overline{c}\,\kappa \ge 1 - \overline{\delta_3^2} - \kappa^2 - C(n_0, p_0, M_1, V)\,\kappa.$$

Again $\kappa > 0$ sufficiently small gives rise to $0 < 1 - C(n_0, p_0, M_1, V)\kappa - \kappa^2 \le (\overline{a}\,\overline{d} - \overline{c})^2 + \overline{\delta_3^2}$ and

$$\left(\sqrt{\overline{a^2}} - \nu_\infty\right)^2 + \left(\sqrt{\overline{b^2}} - \pi_\infty\right)^2 + \|c - \nu_{tr,\infty}\|^2 \le C(\varepsilon_0, n_0, p_0, M, M_1, V) \le$$
$$K(\overline{a}\,\overline{d} - \overline{c})^2 + K\overline{\delta_3^2} \le 2K\|ad - c\|^2 + (2Kc_1(n_0, p_0, M_1, V) + K)\left(\overline{\delta_1^2} + \overline{\delta_2^2} + \overline{\delta_3^2} + \overline{\delta_4^2}\right)$$

for some constant $K(\kappa, \varepsilon_0, n_0, p_0, M, M_1, V) > 0$ using (2.53). This $\kappa > 0$ shall be denoted by κ_d.

Case 2.3: $\overline{a^2} < \kappa^2$**:** We first notice that $\overline{a} < \kappa$ and $2\,\overline{c}\,\overline{d} \le \overline{c}^2 + \overline{d}^2 \le \overline{c^2} + \overline{d^2} = 1$. Now, we choose $\kappa_a := \kappa > 0$ sufficiently small such that $2\kappa < \kappa_c^2$. Then, if $\overline{c^2} < 2\kappa$, we have $\overline{c^2} < \kappa_c^2$, and the estimate

$$\left(\sqrt{\overline{a^2}} - \nu_\infty\right)^2 + \left(\sqrt{\overline{b^2}} - \pi_\infty\right)^2 + \|c - \nu_{tr,\infty}\|^2 \le 2K\|bc - d\|^2 + (2Kc_1(n_0, p_0, M_1, V) + K)\left(\overline{\delta_1^2} + \overline{\delta_2^2} + \overline{\delta_3^2} + \overline{\delta_4^2}\right)$$

with $K(\kappa, \varepsilon_0, n_0, p_0, M, M_1, V) > 0$ immediately follows from Case 2.1. And if $\overline{c^2} \ge 2\kappa$, then

$$\overline{c}^2 = \overline{c^2} - \overline{\delta_3^2} \ge 2\kappa - \overline{\delta_3^2} \Rightarrow \left(\overline{a}\,\overline{d} - \overline{c}\right)^2 \ge \overline{c}^2 - 2\,\overline{a}\,\overline{c}\,\overline{d} \ge 2\kappa - \overline{\delta_3^2} - \kappa = \kappa - \overline{\delta_3^2}.$$

Consequently, $0 < \kappa \le (\overline{a}\,\overline{d} - \overline{c})^2 + \overline{\delta_3^2}$ and

$$\left(\sqrt{\overline{a^2}} - \nu_\infty\right)^2 + \left(\sqrt{\overline{b^2}} - \pi_\infty\right)^2 + \|c - \nu_{tr,\infty}\|^2 \le C(\varepsilon_0, n_0, p_0, M, M_1, V) \le$$
$$K(\overline{a}\,\overline{d} - \overline{c})^2 + K\overline{\delta_3^2} \le 2K\|ad - c\|^2 + (2Kc_1(n_0, p_0, M_1, V) + K)\left(\overline{\delta_1^2} + \overline{\delta_2^2} + \overline{\delta_3^2} + \overline{\delta_4^2}\right)$$

due to (2.53) with a constant $K(\kappa, \varepsilon_0, n_0, p_0, M, M_1, V) > 0$.

Case 2.4: $\overline{b^2} < \kappa^2$**:** Again $\overline{b} < \kappa$ and $2\,\overline{c}\,\overline{d} \le \overline{c}^2 + \overline{d}^2 \le \overline{c^2} + \overline{d^2} = 1$. Here, we choose $\kappa_b := \kappa > 0$ sufficiently small such that $2\kappa < \kappa_d^2$. If $\overline{d^2} < 2\kappa$, we have $\overline{d^2} < \kappa_d^2$, and due to Case 2.2 there exists some $K(\kappa, \varepsilon_0, n_0, p_0, M, M_1, V) > 0$ such that

$$\left(\sqrt{\overline{a^2}} - \nu_\infty\right)^2 + \left(\sqrt{\overline{b^2}} - \pi_\infty\right)^2 + \|c - \nu_{tr,\infty}\|^2 \le 2K\|ad - c\|^2 + (2Kc_1(n_0, p_0, M_1, V) + K)\left(\overline{\delta_1^2} + \overline{\delta_2^2} + \overline{\delta_3^2} + \overline{\delta_4^2}\right).$$

If $\overline{d^2} \ge 2\kappa$, then

$$\overline{d}^2 = \overline{d^2} - \overline{\delta_4^2} \ge 2\kappa - \overline{\delta_4^2} \Rightarrow \left(\overline{b}\,\overline{c} - \overline{d}\right)^2 \ge \overline{d}^2 - 2\,\overline{b}\,\overline{c}\,\overline{d} \ge 2\kappa - \overline{\delta_4^2} - \kappa = \kappa - \overline{\delta_4^2}.$$

This implies $0 < \kappa \le (\overline{b}\,\overline{c} - \overline{d})^2 + \overline{\delta_4^2}$ and

$$\left(\sqrt{\overline{a^2}} - \nu_\infty\right)^2 + \left(\sqrt{\overline{b^2}} - \pi_\infty\right)^2 + \|c - \nu_{tr,\infty}\|^2 \le C(\varepsilon_0, n_0, p_0, M, M_1, V) \le$$
$$K(\overline{b}\,\overline{c} - \overline{d})^2 + K\overline{\delta_4^2} \le 2K\|bc - d\|^2 + (2Kc_1(n_0, p_0, M_1, V) + K)\left(\overline{\delta_1^2} + \overline{\delta_2^2} + \overline{\delta_3^2} + \overline{\delta_4^2}\right)$$

with $K(\kappa, \varepsilon_0, n_0, p_0, M, M_1, V) > 0$ employing (2.54).

All arguments within Step 2 remain valid, if we finally set $\kappa := \min(\kappa_a, \kappa_b, \kappa_c, \kappa_d)$. We also observe that the constants $K > 0$ above are independent of $\varepsilon \in (0, \varepsilon_0]$. And since κ only depends on n_0, p_0, M_1 and V, we may skip the explicit dependence of C_2 on κ at the end of Case 1. This finishes the proof. □

We already pointed out that $\|ad - c\|^2$ and $\|bc - d\|^2$ can be controlled by the reaction terms of the entropy production, if we replace a, b, c, d by $\sqrt{n/(n_0\mu_n)}$, $\sqrt{p/(p_0\mu_p)}$, $\sqrt{n_{tr}}$ and $\sqrt{n'_{tr}}$ (see the proof of Theorem 2.6 in Section 2.6 for details). In this proof, also $\|\nabla a\|^2$, $\|\nabla b\|^2$, $\|a - \overline{a}\|^2$ and $\|b - \overline{b}\|^2$ may be bounded by the entropy production. However, $\|c - \overline{c}\|^2$ and $\|d - \overline{d}\|^2$ may not be estimated with the help of Poincaré's inequality since this would yield terms involving ∇n_{tr}, which do not appear in the entropy production.

Instead, we are able to derive the following estimates for $\|c - \overline{c}\|^2$ and $\|d - \overline{d}\|^2$, which describe an indirect diffusion transfer from c to b and from d to a, respectively: Even if c and d are lacking an explicit diffusion term in the dynamical equations, they do experience indirect diffusive effects thanks to the reversible reaction dynamics and the diffusivity of a and b. This is the interpretation of the following functional inequalities.

Proposition 2.27 (Indirect Diffusion Transfer)**.** *Let $a, b, c, d : \Omega \to \mathbb{R}$ be non-negative functions such that*

$$c^2 + d^2 = 1$$

holds true a.e. in Ω. Then,

$$\|c - \overline{c}\|^2 \le 4\big(\|bc - d\|^2 + \|b - \overline{b}\|^2\big) \qquad \textit{and} \qquad \|d - \overline{d}\|^2 \le 4\big(\|ad - c\|^2 + \|a - \overline{a}\|^2\big).$$

Proof. We only verify the second inequality; the first one can be checked along the same lines. First, we notice that

$$\|\overline{a}d - c\| = \|ad - c + (\overline{a} - a)d\| \le \|ad - c\| + \|a - \overline{a}\| \tag{2.58}$$

because of the bound $0 \le d \le 1$. Besides, we deduce

$$\|\overline{a}^2 d^2 - c^2\| = \|(\overline{a}d + c)(\overline{a}d - c)\| \le (1 + \overline{a})\|\overline{a}d - c\|$$

employing $0 \le c, d \le 1$. For the subsequent estimates, we need two auxiliary inequalities: For every function $f : \Omega \to \mathbb{R}$ and all $\lambda \in \mathbb{R}$, we have

$$\begin{aligned} \|f - \overline{f}\|^2 = \int_\Omega (f - \lambda + \lambda - \overline{f})^2 dx &= \int_\Omega \Big((f - \lambda)^2 - 2(f - \lambda)(\overline{f} - \lambda) + (\overline{f} - \lambda)^2\Big) dx \\ &= \int_\Omega (f - \lambda)^2 dx - (\overline{f} - \lambda)^2 \le \|f - \lambda\|^2. \end{aligned} \tag{2.59}$$

And for all $x \ge 0$, one has

$$\frac{1 + x}{\sqrt{1 + x^2}} = \frac{\sqrt{1 + 2x + x^2}}{\sqrt{1 + x^2}} \le \frac{\sqrt{2(1 + x^2)}}{\sqrt{1 + x^2}} = \sqrt{2}.$$

Since $c^2 + d^2 = 1$, we obtain

$$\begin{aligned} \|\overline{a}^2 d^2 - c^2\| = \|\overline{a}^2 d^2 + d^2 - 1\| = \|(1 + \overline{a}^2)d^2 - 1\| &= \big\|\big(\sqrt{1 + \overline{a}^2}\, d + 1\big)\big(\sqrt{1 + \overline{a}^2}\, d - 1\big)\big\| \\ &\ge \big\|\sqrt{1 + \overline{a}^2}\, d - 1\big\| = \sqrt{1 + \overline{a}^2}\left\| d - \frac{1}{\sqrt{1 + \overline{a}^2}}\right\| \ge \sqrt{1 + \overline{a}^2}\|d - \overline{d}\| \end{aligned}$$

where we applied (2.59) in the last step. Consequently,

$$\|d - \overline{d}\| \le \frac{1}{\sqrt{1 + \overline{a}^2}}\|\overline{a}^2 d^2 - c^2\| \le \frac{1 + \overline{a}}{\sqrt{1 + \overline{a}^2}}\|\overline{a}d - c\| \le \sqrt{2}\,\|\overline{a}d - c\|$$

and

$$\|d - \overline{d}\|^2 \le 2\|\overline{a}d - c\|^2 \le 4(\|ad - c\|^2 + \|a - \overline{a}\|^2)$$

using (2.58). □

2.6 EEP-Inequality and Convergence to the Equilibrium

We are now prepared to prove Theorem 2.6.

Proof of Theorem 2.6. Let $(n, p, n_{tr}) \in L^1(\Omega)^3$ be non-negative functions satisfying $n_{tr} \leq 1$, the conservation law $\overline{n} - \overline{p} + \varepsilon\overline{n_{tr}} = M$ and the L^1-bound $\overline{n}, \overline{p} \leq M_1$. Keeping in mind that $\nu_\infty = \sqrt{n_*/n_0}$ and $\pi_\infty = \sqrt{p_*/p_0}$ (cf. Notation 2.22), Proposition 2.21 guarantees that there exists a positive constant $C_1(\gamma, \Gamma, M_1) > 0$ such that

$$E(n,p,n_{tr}) - E(n_\infty, p_\infty, n_{tr,\infty}) \leq C_1 \Bigg(\int_\Omega \left(\frac{|J_n|^2}{n} + \frac{|J_p|^2}{p} \right) dx + n_0 \bigg(\sqrt{\frac{n}{n_0\mu_n}} - \nu_\infty \bigg)^2 + p_0 \bigg(\sqrt{\frac{p}{p_0\mu_p}} - \pi_\infty \bigg)^2 + \varepsilon \int_\Omega \left(\sqrt{n_{tr}} - \sqrt{n_{tr,\infty}}\right)^2 dx \Bigg). \quad (2.60)$$

Next, we have to bound the second line of (2.60) in terms of the entropy production. To this end, we apply Proposition 2.26 with the choices $a := \sqrt{n/(n_0\mu_n)}$, $b := \sqrt{p/(p_0\mu_p)}$, $c := \sqrt{n_{tr}}$ and $d := \sqrt{n'_{tr}}$ (as always $n'_{tr} = 1 - n_{tr}$). The hypotheses of this Proposition are fulfilled as a consequence of the conservation law $\overline{n} - \overline{p} + \varepsilon\overline{n_{tr}} = M$ and the L^1-bound $\overline{n}, \overline{p} \leq M_1$. As a result, we obtain

$$\begin{aligned} &\bigg(\sqrt{\overline{\frac{n}{n_0\mu_n}}} - \nu_\infty \bigg)^2 + \bigg(\sqrt{\overline{\frac{p}{p_0\mu_p}}} - \pi_\infty \bigg)^2 + \|\sqrt{n_{tr}} - \sqrt{n_{tr,\infty}}\|^2 \\ &\quad \leq C_2 \Bigg(\bigg\| \sqrt{\frac{nn'_{tr}}{n_0\mu_n}} - \sqrt{n_{tr}} \bigg\|^2 + \bigg\| \sqrt{\frac{pn_{tr}}{p_0\mu_p}} - \sqrt{n'_{tr}} \bigg\|^2 + \bigg\| \nabla\sqrt{\frac{n}{n_0\mu_n}} \bigg\|^2 + \bigg\| \nabla\sqrt{\frac{p}{p_0\mu_p}} \bigg\|^2 \\ &\qquad + \bigg\| \sqrt{\frac{n}{n_0\mu_n}} - \overline{\sqrt{\frac{n}{n_0\mu_n}}} \bigg\|^2 + \bigg\| \sqrt{\frac{p}{p_0\mu_p}} - \overline{\sqrt{\frac{p}{p_0\mu_p}}} \bigg\|^2 + \|\sqrt{n_{tr}} - \overline{\sqrt{n_{tr}}}\|^2 + \|\sqrt{n'_{tr}} - \overline{\sqrt{n'_{tr}}}\|^2 \Bigg) \end{aligned}$$

for all $\varepsilon \in (0, \varepsilon_0]$ with a constant $C_2(\varepsilon_0, n_0, p_0, M, M_1, V) > 0$. Thanks to Poincaré's inequality, we are able to bound the last two terms in the second line and the first two terms in the third line from above:

$$\bigg\| \sqrt{\frac{n}{n_0\mu_n}} - \overline{\sqrt{\frac{n}{n_0\mu_n}}} \bigg\|^2 \leq C_P \bigg\| \nabla\sqrt{\frac{n}{n_0\mu_n}} \bigg\|^2 = C_P \int_\Omega \left| \frac{1}{2}\sqrt{\frac{\mu_n}{n_0 n}} \nabla\Big(\frac{n}{\mu_n}\Big) \right|^2 dx \leq \frac{C_P}{4n_0 \inf_\Omega \mu_n} \int_\Omega \frac{|J_n|^2}{n}\, dx$$

and

$$\bigg\| \sqrt{\frac{p}{p_0\mu_p}} - \overline{\sqrt{\frac{p}{p_0\mu_p}}} \bigg\|^2 \leq C_P \bigg\| \nabla\sqrt{\frac{p}{p_0\mu_p}} \bigg\|^2 \leq \frac{C_P}{4p_0 \inf_\Omega \mu_p} \int_\Omega \frac{|J_p|^2}{p}\, dx.$$

Moreover, the elementary inequality $(\sqrt{x} - 1)^2 \leq (x-1)\ln(x)$ for $x > 0$ gives rise to

$$\begin{aligned} \bigg\| \sqrt{\frac{nn'_{tr}}{n_0\mu_n}} - \sqrt{n_{tr}} \bigg\|^2 &= \int_\Omega n_{tr} \bigg(\sqrt{\frac{nn'_{tr}}{n_0\mu_n n_{tr}}} - 1 \bigg)^2 dx \leq \int_\Omega n_{tr} \left(\frac{nn'_{tr}}{n_0\mu_n n_{tr}} - 1 \right) \ln\left(\frac{nn'_{tr}}{n_0\mu_n n_{tr}} \right) dx \\ &= \int_\Omega \left(\frac{n(1-n_{tr})}{n_0\mu_n} - n_{tr} \right) \ln\left(\frac{n(1-n_{tr})}{n_0\mu_n n_{tr}} \right) dx = -\tau_n \int_\Omega R_n \ln\left(\frac{n(1-n_{tr})}{n_0\mu_n n_{tr}} \right) dx \end{aligned}$$

and similarly

$$\bigg\| \sqrt{\frac{pn_{tr}}{p_0\mu_p}} - \sqrt{n'_{tr}} \bigg\|^2 \leq -\tau_p \int_\Omega R_p \ln\left(\frac{pn_{tr}}{p_0\mu_p(1-n_{tr})} \right) dx.$$

Proposition 2.27 further implies that

$$\begin{aligned} &\|\sqrt{n_{tr}} - \overline{\sqrt{n_{tr}}}\|^2 + \|\sqrt{n'_{tr}} - \overline{\sqrt{n'_{tr}}}\|^2 \leq \\ &\quad 4 \Bigg(\bigg\| \sqrt{\frac{n}{n_0\mu_n}} - \overline{\sqrt{\frac{n}{n_0\mu_n}}} \bigg\|^2 + \bigg\| \sqrt{\frac{p}{p_0\mu_p}} - \overline{\sqrt{\frac{p}{p_0\mu_p}}} \bigg\|^2 + \bigg\| \sqrt{\frac{nn'_{tr}}{n_0\mu_n}} - \sqrt{n_{tr}} \bigg\|^2 + \bigg\| \sqrt{\frac{pn_{tr}}{p_0\mu_p}} - \sqrt{n'_{tr}} \bigg\|^2 \Bigg). \end{aligned}$$

Combining the above estimates, we arrive at

$$\left(\sqrt{\frac{n}{n_0\mu_n}} - \nu_\infty\right)^2 + \left(\sqrt{\frac{p}{p_0\mu_p}} - \pi_\infty\right)^2 + \|\sqrt{n_{tr}} - \sqrt{n_{tr,\infty}}\|^2 \\ \leq C_3 \int_\Omega \left(\frac{|J_n|^2}{n} + \frac{|J_p|^2}{p} - R_n \ln\left(\frac{n(1-n_{tr})}{n_0\mu_n n_{tr}}\right) - R_p \ln\left(\frac{p n_{tr}}{p_0\mu_p(1-n_{tr})}\right)\right)$$

with a constant $C_3(\varepsilon_0, \tau_n, \tau_p, n_0, p_0, M, M_1, V) > 0$ uniformly for $\varepsilon \in (0, \varepsilon_0]$. With respect to (2.60), we now find

$$n_0 \left(\sqrt{\frac{n}{n_0\mu_n}} - \nu_\infty\right)^2 + p_0 \left(\sqrt{\frac{p}{p_0\mu_p}} - \pi_\infty\right)^2 + \varepsilon \int_\Omega \left(\sqrt{n_{tr}} - \sqrt{n_{tr,\infty}}\right)^2 dx \\ \leq \max\{n_0, p_0, \varepsilon_0\} \left(\left(\sqrt{\frac{n}{n_0\mu_n}} - \nu_\infty\right)^2 + \left(\sqrt{\frac{p}{p_0\mu_p}} - \pi_\infty\right)^2 + \|\sqrt{n_{tr}} - \sqrt{n_{tr,\infty}}\|^2\right) \\ \leq C_3 \max\{n_0, p_0, \varepsilon_0\} \int_\Omega \left(\frac{|J_n|^2}{n} + \frac{|J_p|^2}{p} - R_n \ln\left(\frac{n(1-n_{tr})}{n_0\mu_n n_{tr}}\right) - R_p \ln\left(\frac{p n_{tr}}{p_0\mu_p(1-n_{tr})}\right)\right).$$

And since the constant C_1 in (2.60) only depends on ε_0, n_0, p_0, M, M_1 and V (via the constants γ and Γ), we have finally proven that

$$E(n, p, n_{tr}) - E(n_\infty, p_\infty, n_{tr,\infty}) \\ \leq C_4 \int_\Omega \left(\frac{|J_n|^2}{n} + \frac{|J_p|^2}{p} - R_n \ln\left(\frac{n(1-n_{tr})}{n_0\mu_n n_{tr}}\right) - R_p \ln\left(\frac{p n_{tr}}{p_0\mu_p(1-n_{tr})}\right)\right) dx$$

for a constant $C_4(\varepsilon_0, \tau_n, \tau_p, n_0, p_0, M, M_1, V) > 0$ independent of $\varepsilon \in (0, \varepsilon_0]$. □

Proof of Proposition 2.7. Due to Lemma 2.14, we know that the relative entropy reads

$$E(n, p, n_{tr}) - E(n_\infty, p_\infty, n_{tr,\infty}) = \\ \int_\Omega \left(n \ln \frac{n}{n_\infty} - (n - n_\infty) + p \ln \frac{p}{p_\infty} - (p - p_\infty) + \varepsilon \int_{n_{tr,\infty}}^{n_{tr}} \left(\ln\left(\frac{s}{1-s}\right) - \ln\left(\frac{n_{tr,\infty}}{1-n_{tr,\infty}}\right)\right) ds\right) dx.$$

Similar to Proposition 2.21, we employ the mean-value theorem and observe that

$$\frac{d}{ds} \ln\left(\frac{s}{1-s}\right) = \frac{1}{s(1-s)} \geq 4$$

for all $s \in (0, 1)$. Thus, there exists some $\sigma(s)$ between $n_{tr,\infty}$ and s such that

$$\varepsilon \int_\Omega \int_{n_{tr,\infty}}^{n_{tr}} \left(\ln\left(\frac{s}{1-s}\right) - \ln\left(\frac{n_{tr,\infty}}{1-n_{tr,\infty}}\right)\right) ds\, dx = \varepsilon \int_\Omega \int_{n_{tr,\infty}}^{n_{tr}} \frac{1}{\sigma(s)(1-\sigma(s))}(s - n_{tr,\infty})\, ds\, dx \\ \geq 4\varepsilon \int_\Omega \int_{n_{tr,\infty}}^{n_{tr}} (s - n_{tr,\infty})\, ds\, dx = 2\varepsilon \int_\Omega (n_{tr} - n_{tr,\infty})^2\, dx \geq 2\varepsilon \|n_{tr} - n_{tr,\infty}\|^2_{L^1(\Omega)}$$

where the last inequality holds true since $|\Omega| = 1$. Moreover, we utilize the Csiszár–Kullback–Pinsker-inequality from Lemma 2.15 to estimate

$$\int_\Omega \left(n \ln\left(\frac{n}{n_\infty}\right) - (n - n_\infty)\right) dx \geq \frac{3}{2\overline{n} + 4\overline{n_\infty}} \|n - n_\infty\|^2_{L^1(\Omega)} \geq c\|n - n_\infty\|^2_{L^1(\Omega)}$$

where $c(\varepsilon_0, n_0, p_0, M, M_1, V) > 0$ is a positive constant independent of $\varepsilon \in (0, \varepsilon_0]$. As a corresponding estimate holds true also for p, we have verified that

$$E(n, p, n_{tr}) - E(n_\infty, p_\infty, n_{tr,\infty}) \geq C\left(\|n - n_\infty\|^2_{L^1(\Omega)} + \|p - p_\infty\|^2_{L^1(\Omega)} + \varepsilon\|n_{tr} - n_{tr,\infty}\|^2_{L^1(\Omega)}\right)$$

for some $C(\varepsilon_0, n_0, p_0, M, M_1, V) > 0$ uniformly for $\varepsilon \in (0, \varepsilon_0]$. □

Now, we are able to prove exponential convergence in relative entropy and in L^1.

Proof of Theorem 2.8. We first prove exponential convergence of the relative entropy

$$\psi(t) := E(n,p,n_{tr})(t) - E(n_\infty,p_\infty,n_{tr,\infty})$$

using a Gronwall argument as stated in [32]. To this end, we choose $0 < t_0 \le t_1 \le t < T$ and rewrite the entropy production law as

$$\psi(t_1) - \psi(t) = \int_{t_1}^t D(n,p,n_{tr})(s)\,ds \ge K \int_{t_1}^t \psi(s)\,ds \tag{2.61}$$

where we applied Theorem 2.6 with $K := C_{\mathrm{EEP}}^{-1}$ in the second step. Furthermore, we set

$$\Psi(t_1) := \int_{t_1}^t \psi(s)\,ds = -\int_t^{t_1} \psi(s)\,ds$$

and obtain from (2.61) the estimate $K\Psi(t_1) \le \psi(t_1) - \psi(t)$ which yields

$$\frac{d}{dt_1}\Big(\Psi(t_1)e^{Kt_1}\Big) = -\psi(t_1)e^{Kt_1} + K\Psi(t_1)e^{Kt_1} \le -\psi(t)e^{Kt_1}.$$

Integrating this inequality from $t_1 = t_0$ to $t_1 = t$ and observing that $\Psi(t) = 0$ gives rise to

$$-\Psi(t_0)e^{Kt_0} \le -\frac{\psi(t)}{K}\big(e^{Kt} - e^{Kt_0}\big).$$

As a consequence of (2.61) with $t_1 = t_0$, one has $-\Psi(t_0) \ge (\psi(t) - \psi(t_0))/K$ and, hence,

$$-\psi(t_0)e^{Kt_0} \le -\psi(t)e^{Kt}.$$

But this is equivalent to

$$E(n,p,n_{tr})(t) - E(n_\infty,p_\infty,n_{tr,\infty}) \le (E(n,p,n_{tr})(t_0) - E_\infty)e^{-K(t-t_0)}. \tag{2.62}$$

In order to arrive at

$$E(n,p,n_{tr})(t) - E(n_\infty,p_\infty,n_{tr,\infty}) \le (E_I - E_\infty)e^{-Kt},$$

for all $t \ge 0$, we observe that this relation holds true for $t = 0$. For $t > 0$, we have proven above that (2.62) is true for all $t_0 \in (0,t)$. We may, therefore, take the limit $t_0 \to 0$ in (2.62). This results in the announced exponential decay due to the continuity of the entropy $E(n,p,n_{tr})(t_0)$ from Lemma 2.11. Finally, exponential convergence in L^1 follows from Proposition 2.7. □

Proof of Corollary 2.9. We first observe that the linearly growing L^∞-bounds together with parabolic regularity for system (2.1) (see (2.81) and (2.84)) and assumption (2.3) entail polynomially growing H^1-bounds for n and p. In detail, we employ $w = e^{V_n}n$ and rewrite (2.84) as

$$\partial_t w - \Delta w = f_1 + f_2 w + f_3 \nabla w$$

where $f_i \in L^\infty([0,\infty), L^\infty(\Omega))$ for $i \in \{1,2,3\}$ and $\hat{n}\cdot\nabla w = 0$ on $\partial\Omega$. Testing this equation with $-\Delta w$ yields

$$\frac{1}{2}\frac{d}{dt}\int_\Omega |\nabla w|^2\,dx + \int_\Omega |\Delta w|^2\,dx \le \frac{1}{2}\int_\Omega \big(f_1 + f_2 w + f_3\nabla w\big)^2 dx + \frac{1}{2}\int_\Omega |\Delta w|^2\,dx$$

and further

$$\frac{d}{dt}\int_\Omega |\nabla w|^2\,dx + \int_\Omega |\Delta w|^2\,dx \le 3\int_\Omega \big(f_1^2 + f_2^2 w^2 + f_3^2|\nabla w|^2\big)dx.$$

Together with $C > 0$ satisfying $|f_i(t,x)^2| \le C$ for all $i \in \{1,2,3\}$, $t \ge 0$ and a.a. $x \in \Omega$, we derive

$$\frac{d}{dt}\int_\Omega |\nabla w|^2\,dx + \int_\Omega |\Delta w|^2\,dx \le 3C\Big(1 + \int_\Omega w^2\,dx\Big) + \Gamma\int_\Omega |w|^2\,dx + \int_\Omega |\Delta w|^2\,dx,$$

where the last two terms result from an integration by parts and Young's inequality with $\Gamma > 0$. Hence,

$$\frac{d}{dt}\int_\Omega |\nabla w|^2\,dx \le (3C+\Gamma)\Big(1+\gamma^2(C_n+K_n t)^2\Big) \le A + B\,t^2$$

by estimating $w \le \gamma n$ with some $\gamma > 0$ and via bounding the L^2-norm of n with the linearly growing L^∞-bounds from (2.8). For any fixed $t_0 > 0$ and all $t \ge t_0$, we now have

$$\|\nabla w(t)\|^2_{L^2(\Omega)} \le \|\nabla w(t_0)\|^2_{L^2(\Omega)} + A(t-t_0) + \frac{B}{3}(t^3 - t_0^3),$$

which proves the desired polynomial growth of $\|\nabla w\|_{L^2(\Omega)}$ and $\|\nabla n\|_{L^2(\Omega)}$.

Next, we use (see e.g. [30]) the Gagliardo–Nirenberg–Moser interpolation inequality

$$\|n\|_{L^\infty} \le G(\Omega)\|\nabla n\|^{\frac12}_{L^2}\|n\|^{\frac12}_{L^2}\,. \tag{2.63}$$

Then, interpolating with the exponentially decaying L^1-norm of $n - n_\infty$, we obtain

$$\|n(t,\cdot)\|_\infty \le \|n_\infty\|_\infty + \|n-n_\infty\|_\infty \le \|n_\infty\|_\infty + G\|\nabla(n-n_\infty)\|^{\frac12}_{L^2}\|n-n_\infty\|^{\frac14}_{\infty}\|n-n_\infty\|^{\frac14}_{L^1} \le K$$

due to the exponential convergence to equilibrium (2.21). The estimate for p follows in the same way.

The improved bound $n_{tr} \ge \gamma$ results from the same reasoning as in the proof of Theorem 2.1. Instead of (2.87), we now have

$$\varepsilon\partial_t n_{tr} \ge 1 - \widetilde{r}\, n_{tr}$$

with some $\widetilde{r} > 0$, which yields the time-independent lower bound $\gamma > 0$ as announced. And the corresponding lower bound $n, p \ge \Gamma$ can now be derived from (2.88) and the subsequent arguments when applying the lower bound $n_{tr} \ge \gamma$. □

Proof of Theorem 2.6'. Our goal is to derive an estimate of the form

$$E_0(n,p) - E_0(n_{\infty,0}, p_{\infty,0}) \le C_{EEP} D_0(n,p)$$

by applying the EEP-inequality from Theorem 2.6 directly to the functions n, p and n_{tr}^{eq}, where $n_{tr}^{eq} = n_{tr}^{eq}(n,p)$ is defined in (2.30). However, since we assume that n and p satisfy

$$\overline{n} - \overline{p} = M,$$

the triple (n, p, n_{tr}^{eq}) does not satisfy the conservation law with right hand side M but

$$\overline{n} - \overline{p} + \varepsilon\overline{n_{tr}^{eq}} = M + \varepsilon\overline{n_{tr}^{eq}}.$$

In order to resolve this issue, we shall apply the EEP-inequality from Theorem 2.6 to a suitably defined family of non-negative functions $(n_\varepsilon, p_\varepsilon, n_{tr,\varepsilon}) \in L^1(\Omega)^3$ which fulfil $\|n_{tr,\varepsilon}\|_{L^\infty(\Omega)} \le 1$, the L^1-bound $\overline{n_\varepsilon}, \overline{p_\varepsilon} \le M_1$ and the conservation law

$$\overline{n_\varepsilon} - \overline{p_\varepsilon} + \varepsilon\overline{n_{tr,\varepsilon}} = M.$$

A convenient choice is $n_\varepsilon := n$, $p_\varepsilon := p + \varepsilon\overline{n_{tr}}$ and $n_{tr,\varepsilon} := n_{tr}^{eq}$. For this choice, we derive the stated EEP-estimate for the case $\varepsilon = 0$ via the following steps, which are proven below:

$$E_0(n,p) - E_0(n_{\infty,0}, p_{\infty,0}) = \lim_{\varepsilon\to 0}\big(E(n_\varepsilon, p_\varepsilon, n_{tr,\varepsilon}) - E(n_\infty, p_\infty, n_{tr,\infty})\big) \tag{2.64}$$

$$\le \lim_{\varepsilon\to 0}\big(C_{EEP} D(n_\varepsilon, p_\varepsilon, n_{tr,\varepsilon})\big) \tag{2.65}$$

$$= C_{EEP} D(n, p, n_{tr}^{eq}) = C_{EEP} D_0(n,p). \tag{2.66}$$

We recall that n and p are assumed to satisfy $E_0(n,p) < \infty$ and $D_0(n,p), D(n,p,n_{tr}^{eq}) < \infty$, which implies that $D_0(n,p) = D(n,p,n_{tr}^{eq})$ as discussed in the introduction.

Step 1. Proof of (2.64)**:** We first show that

$$E_0(n,p) = \lim_{\varepsilon\to 0} E(n_\varepsilon, p_\varepsilon, n_{tr,\varepsilon}), \tag{2.67}$$

where $(n_\varepsilon, p_\varepsilon, n_{tr,\varepsilon}) = (n, p_\varepsilon, n_{tr}^{eq})$. Recalling that

$$E(n,p_\varepsilon,n_{tr}^{eq}) = \int_\Omega \left(n \ln \frac{n}{n_0\mu_n} - (n - n_0\mu_n) + p_\varepsilon \ln \frac{p_\varepsilon}{p_0\mu_p} - (p_\varepsilon - p_0\mu_p) + \varepsilon \int_{1/2}^{n_{tr}^{eq}} \ln\left(\frac{s}{1-s}\right) ds \right) dx,$$

we notice that $p_\varepsilon = p + \varepsilon\overline{n_{tr}} \to p$ monotonically decreasing for $\varepsilon \to 0$ for all $x \in \Omega$. Thus, by using $\overline{n_{tr}} \le 1$ and the elementary estimate $p_\varepsilon \ln p_\varepsilon \le 2p\,(\ln p + \ln 2)$ for $p \ge \max\{\varepsilon_0, e^{-1}\}$, the Lebesgue dominated convergence theorem and $E_0(n,p) < \infty$ imply the convergence of the p_ε-integral in (2.67). The convergence of the third integral follows directly from

$$\left| \varepsilon \int_{1/2}^{n_{tr}^{eq}(x)} \ln \frac{s}{1-s}\, ds \right| \le \varepsilon \int_{1/2}^{1} \ln \frac{s}{1-s}\, ds \xrightarrow{\varepsilon\to 0} 0.$$

Next, we verify that

$$E_0(n_{\infty,0}, p_{\infty,0}) = \lim_{\varepsilon\to 0} E(n_\infty, p_\infty, n_{tr,\infty}).$$

Due to (2.36) in Proposition 2.10, we know that $n_* \to n_{*,0}$ and $p_* \to p_{*,0}$ for $\varepsilon \to 0$. And as $V_n, V_p \in L^\infty(\Omega)$, equations (2.16) and (2.31) imply that $n_\infty \to n_{\infty,0}$ and $p_\infty \to p_{\infty,0}$ uniformly for $\varepsilon \to 0$. In addition, since n_∞ and p_∞ are uniformly bounded w.r.t. $x \in \Omega$ and $\varepsilon \to 0$, we have that

$$n_\infty \ln \frac{n_\infty}{n_0\mu_n} = n_\infty \ln \frac{n_*}{n_0} \longrightarrow n_{\infty,0} \ln \frac{n_{*,0}}{n_0} = n_{\infty,0} \ln \frac{n_{\infty,0}}{n_0\mu_n}$$

and

$$p_\infty \ln \frac{p_\infty}{p_0\mu_p} = p_\infty \ln \frac{p_*}{p_0} \longrightarrow p_{\infty,0} \ln \frac{p_{*,0}}{p_0} = p_{\infty,0} \ln \frac{p_{\infty,0}}{p_0\mu_p}$$

both uniformly for $\varepsilon \to 0$. Besides, also

$$\left| \varepsilon \int_{1/2}^{n_{tr,\infty}(x)} \ln \frac{s}{1-s}\, ds \right| \le \varepsilon \int_{1/2}^{1} \ln \frac{s}{1-s}\, ds \longrightarrow 0$$

for $\varepsilon \to 0$. Consequently, $E(n_\infty, p_\infty, n_{tr,\infty}) \to E_0(n_{\infty,0}, p_{\infty,0})$ for $\varepsilon \to 0$.

Step 2. Proof of (2.65)**:** The functions $(n_\varepsilon, p_\varepsilon, n_{tr,\varepsilon}) = (n, p+\varepsilon\overline{n_{tr}}, n_{tr}^{eq}) \in L^1(\Omega)^3$ satisfy $\|n_{tr,\varepsilon}\|_{L^\infty(\Omega)} \le 1$, the conservation law

$$\overline{n_\varepsilon} - \overline{p_\varepsilon} + \varepsilon\overline{n_{tr,\varepsilon}} = \overline{n} - \overline{p} = M$$

as well as the L^1-bounds $\overline{n_\varepsilon} \le M_1$ and $\overline{p_\varepsilon} \le \overline{p} + \varepsilon'$ where $\varepsilon \in (0, \varepsilon'] \subset (0, \varepsilon_0]$. Because of $\overline{p} < M_1$, we have $\overline{p_\varepsilon} \le M_1$ for $\varepsilon' > 0$ sufficiently small. As a consequence,

$$E(n, p_\varepsilon, n_{tr}) - E(n_\infty, p_\infty, n_{tr,\infty}) \le C_{EEP} D(n, p_\varepsilon, n_{tr})$$

where $C_{EEP} > 0$ is the same constant as in Theorem 2.6.

Step 3. Proof of (2.66)**:** As the constant $C_{EEP} > 0$ is independent of $\varepsilon \in (0, \varepsilon_0]$, it suffices to show that

$$\lim_{\varepsilon\to 0} D(n_\varepsilon, p_\varepsilon, n_{tr,\varepsilon}) = D(n, p, n_{tr}^{eq}).$$

To this end, we consider the representation

$$D(n_\varepsilon, p_\varepsilon, n_{tr,\varepsilon}) = \int_\Omega \Bigg(\frac{|J_n|^2}{n} + \frac{|\nabla p|^2}{p_\varepsilon} + 2\nabla p \cdot \nabla V_p + p_\varepsilon |\nabla V_p|^2 - R_n \ln\left(\frac{n(1-n_{tr}^{eq})}{n_0\mu_n n_{tr}^{eq}}\right) + \frac{1}{\tau_p}\left(\frac{p_\varepsilon}{p_0\mu_p} n_{tr}^{eq} - (1-n_{tr}^{eq})\right)\left(\ln \frac{p_\varepsilon n_{tr}^{eq}}{p_0\mu_p} - \ln(1-n_{tr}^{eq})\right)\Bigg) dx,$$

where we have already taken into account that $n_\varepsilon = n$, $\nabla p_\varepsilon = \nabla p$ and $n_{tr,\varepsilon} = n_{tr}^{eq}$ for all $\varepsilon > 0$.

We first note that the convergence of the second, third and forth integral follows from the pointwise convergence of p_ε for all $x \in \Omega$ and from the Lebesgue dominated convergence theorem by estimating

$$0 \le \frac{|\nabla p|^2}{p_\varepsilon} + 2\nabla p \cdot \nabla V_p + p_\varepsilon |\nabla V_p|^2 \le \frac{|\nabla p|^2}{p} + 2\nabla p \cdot \nabla V_p + p|\nabla V_p|^2 + (p_\varepsilon - p)|\nabla V_p|^2 \le \frac{|J_p|^2}{p} + \varepsilon_0 |\nabla V_p|^2,$$

where the function on the right hand side is integrable due to the finiteness of $D(n,p,n_{tr}^{eq})$.

Secondly, the product

$$\left(\frac{p_\varepsilon}{p_0\mu_p} n_{tr}^{eq} - (1-n_{tr}^{eq})\right)\left(\ln \frac{p_\varepsilon n_{tr}^{eq}}{p_0\mu_p} - \ln(1-n_{tr}^{eq})\right) \to \left(\frac{p}{p_0\mu_p} n_{tr}^{eq} - (1-n_{tr}^{eq})\right)\left(\ln \frac{p n_{tr}^{eq}}{p_0\mu_p} - \ln(1-n_{tr}^{eq})\right)$$

converges pointwise for all $x \in \Omega$ as $\varepsilon \to 0$. In order to conclude the convergence of the corresponding integral via the Lebesgue dominated convergence theorem, we use similar to Step 1 the elementary inequality $p_\varepsilon \ln p_\varepsilon \le 2p\,(\ln p + \ln 2)$ for $p \ge \max\{\varepsilon_0, e^{-1}\}$ and the finiteness of $D(n,p,n_{tr}^{eq})$. This yields

$$\lim_{\varepsilon\to 0} \int_\Omega \frac{1}{\tau_p} \left(\frac{p_\varepsilon}{p_0\mu_p} n_{tr}^{eq} - (1-n_{tr}^{eq})\right)\left(\ln \frac{p_\varepsilon n_{tr}^{eq}}{p_0\mu_p} - \ln(1-n_{tr}^{eq})\right) dx = -\int_\Omega R_p \ln\left(\frac{p n_{tr}^{eq}}{p_0\mu_p(1-n_{tr}^{eq})}\right) dx$$

and therefore, $D(n_\varepsilon, p_\varepsilon, n_{tr,\varepsilon}) \to D(n,p,n_{tr}^{eq})$ for $\varepsilon \to 0$. □

Proof of Proposition 2.7'. We employ a technique similar to that from the proof of Theorem 2.6'. For $\varepsilon > 0$ sufficiently small, we define $(n_\varepsilon, p_\varepsilon, n_{tr,\varepsilon}) := (n, p + \varepsilon\overline{n_{tr}}, n_{tr})$ and deduce a CKP-estimate for $\varepsilon = 0$ as follows:

$$\begin{aligned} E_0(n,p) - E_0(n_{\infty,0}, p_{\infty,0}) &= \lim_{\varepsilon\to 0} \big(E(n,p_\varepsilon,n_{tr}) - E(n_\infty,p_\infty,n_{tr,\infty})\big) \\ &\ge \lim_{\varepsilon\to 0} C_{\text{CKP}}\big(\|n-n_\infty\|^2_{L^1(\Omega)} + \|p_\varepsilon - p_\infty\|^2_{L^1(\Omega)} + \varepsilon\|n_{tr}-n_{tr,\infty}\|^2_{L^1(\Omega)}\big) \quad (2.68) \\ &= C_{\text{CKP}}\big(\|n-n_{\infty,0}\|^2_{L^1(\Omega)} + \|p-p_{\infty,0}\|^2_{L^1(\Omega)}\big). \end{aligned}$$

The equality in the first line has already been shown within the proof of Theorem 2.6' (Eq. (2.64)). And the last equality essentially follows from arguments within the proof of Theorem 2.6' too: When deriving (2.64), we have seen that $n_\infty \to n_{\infty,0}$ and $p_\infty \to p_{\infty,0}$ both uniformly for $\varepsilon \to 0$. Obviously, also $p_\varepsilon = p + \varepsilon\overline{n_{tr}} \to p$ uniformly for $\varepsilon \to 0$. And due to $0 \le n_{tr}, n_{tr,\infty} \le 1$, we further have $\varepsilon\|n_{tr} - n_{tr,\infty}\|^2_{L^1(\Omega)} \to 0$ as $\varepsilon \to 0$.

Concerning (2.68), we observe that the condition $\|n_{tr}\|_{L^\infty(\Omega)} \le 1$, the L^1-bounds $\overline{n} \le M_1$ and $\overline{p_\varepsilon} \le \overline{p} + \varepsilon \le M_1$ as well as the conservation law $\overline{n} - \overline{p_\varepsilon} + \varepsilon\overline{n_{tr}} = M$ hold true for $\varepsilon > 0$ small enough. Proposition 2.7, thus, results in

$$E(n,p_\varepsilon,n_{tr}) - E(n_\infty,p_\infty,n_{tr,\infty}) \ge C_{\text{CKP}}\big(\|n-n_\infty\|^2_{L^1(\Omega)} + \|p_\varepsilon-p_\infty\|^2_{L^1(\Omega)} + \varepsilon\|n_{tr}-n_{tr,\infty}\|^2_{L^1(\Omega)}\big)$$

where $C_{\text{CKP}} > 0$ equals the constant from Proposition 2.7. □

Proof of Theorem 2.8'. As a consequence of the bounds on n and p from Theorem 2.1', the entropy production law is fulfilled for all $0 < t_0 \le t_1 < \infty$. Besides, the relation describing the exponential decay of the relative entropy is trivially satisfied at time $t = 0$. We are thus left to verify the exponential decay property for times $t > 0$.

We first check that the assumptions on the finiteness of the entropy E and its production D within Theorem 2.6' are satisfied when evaluating them for solutions to (2.25) at $t > 0$. Due to the uniform L^∞-bounds of $n(t)$ and $p(t)$ for all $t \ge 0$, we know that $E_0(n,p) < \infty$ for all $t \ge 0$. Similarly, we deduce that $D_0(n,p)$ and $D(n,p,n_{tr}^{eq})$ are finite for all strictly positive $t > 0$ since then n and p are bounded away from 0 uniformly in Ω. The exponential decay of the relative entropy for $t > 0$ then follows from the EEP-inequality within Theorem 2.6' using the same arguments as in the proof of Theorem 2.8.

Exponential convergence in L^1 now follows from the Csiszár–Kullback–Pinsker inequality stated in Proposition 2.7'. □

Proof of Corollary 2.9'. We are able to derive polynomially growing H^1-bounds and uniform-in-time L^∞-bounds for n and p by following the same strategy as in the proof of Corollary 2.9. Here, we use $z = e^{V_n} n$ and derive (similar to (2.84))

$$\partial_t z - \Delta z = -\nabla V_n \cdot \nabla z + e^{V_n} \frac{1 - e^{V_p} pz}{2 + e^{V_p} p + z} = f_1 + f_2 z + f_3 \nabla z$$

with appropriate $f_i \in L^\infty([0,\infty), L^\infty(\Omega))$ for $i \in \{1,2,3\}$. This allows us to proceed as mentioned above.

The lower bounds n, $p \geq \Gamma$ follow from (2.98) together with the subsequent arguments and the time-independent lower bound $d(t) \geq \gamma$. □

2.7 Proofs of the Existence Theorems

Proof of Theorem 2.1. In order to simplify the notation, we set the parameter $\tau_n := \tau_p := 1$ and $n_0 := p_0 := 1$ throughout the proof. All arguments also apply in the case of arbitrary values for τ_n, τ_p, n_0 and p_0. The structure of system (2.1) can be further simplified via introducing new variables

$$u := e^{\frac{V_n}{2}} n, \qquad v := e^{\frac{V_p}{2}} p.$$

One obtains

$$\nabla u = \frac{1}{2} e^{\frac{V_n}{2}} \nabla V_n n + e^{\frac{V_n}{2}} \nabla n \qquad \text{and} \qquad \Delta u = e^{\frac{V_n}{2}} \Big(\Delta n + \nabla n \cdot \nabla V_n + \frac{1}{4} n |\nabla V_n|^2 + \frac{1}{2} n \Delta V_n \Big)$$

which results in

$$\begin{aligned} \partial_t u = e^{\frac{V_n}{2}} \partial_t n = e^{\frac{V_n}{2}} \Big(\Delta n + \nabla n \cdot \nabla V_n + n \Delta V_n + R_n \Big) = \Delta u - e^{\frac{V_n}{2}} \Big(\frac{1}{4} n |\nabla V_n|^2 - \frac{1}{2} n \Delta V_n \Big) + e^{\frac{V_n}{2}} R_n \\ = \Delta u + \Big(\frac{1}{2} \Delta V_n - \frac{1}{4} |\nabla V_n|^2 \Big) u + e^{\frac{V_n}{2}} n_{tr} - e^{V_n} u (1 - n_{tr}). \end{aligned}$$

Analogously, we derive

$$\partial_t v = \Delta v + \Big(\frac{1}{2} \Delta V_p - \frac{1}{4} |\nabla V_p|^2 \Big) v + e^{\frac{V_p}{2}} (1 - n_{tr}) - e^{V_p} v n_{tr}.$$

For convenience, we also introduce the abbreviations

$$A_n := \frac{1}{2} \Delta V_n - \frac{1}{4} |\nabla V_n|^2 \in L^\infty(\Omega), \qquad A_p := \frac{1}{2} \Delta V_p - \frac{1}{4} |\nabla V_p|^2 \in L^\infty(\Omega)$$

as well as $\alpha, \beta > 0$ such that the following estimates hold true a.e. in Ω:

$$|A_n|, |A_p| \leq \alpha \qquad \text{and} \qquad e^{\frac{V_n}{2}}, e^{\frac{V_p}{2}}, e^{V_n}, e^{V_p} \leq \beta.$$

Next, we introduce the new variable

$$n'_{tr} := 1 - n_{tr} \tag{2.69}$$

for reasons of symmetry. In fact, we can prove the positivity of n'_{tr} in the same way as for n_{tr}, which then implies the desired bound $0 \leq n_{tr} \leq 1$. A further ingredient for establishing the positivity of the variables u, v, n_{tr} and n'_{tr} is to project them onto $[0,\infty)$ and $[0,1]$, respectively, on the right hand side of the PDE-system. In this context, we use $X^+ := \max(X, 0)$ to denote the positive part of an arbitrary function X and $X^{[0,1]} := \min(\max(X,0),1)$ for the projection of X to the interval $[0,1]$. The modified system now reads

$$\begin{cases} \partial_t u - \Delta u = A_n u^+ + e^{\frac{V_n}{2}} n_{tr}^{[0,1]} - e^{V_n} u^+ n_{tr}'^{[0,1]}, \\ \partial_t v - \Delta v = A_p v^+ + e^{\frac{V_p}{2}} n_{tr}'^{[0,1]} - e^{V_p} v^+ n_{tr}^{[0,1]}, \\ \varepsilon\, \partial_t n_{tr} = n_{tr}'^{[0,1]} - e^{\frac{V_p}{2}} v^+ n_{tr}^{[0,1]} - n_{tr}^{[0,1]} + e^{\frac{V_n}{2}} u^+ n_{tr}'^{[0,1]}, \\ \varepsilon\, \partial_t n'_{tr} = n_{tr}^{[0,1]} - e^{\frac{V_n}{2}} u^+ n_{tr}'^{[0,1]} - n_{tr}'^{[0,1]} + e^{\frac{V_p}{2}} v^+ n_{tr}^{[0,1]}. \end{cases} \tag{2.70}$$

The no-flux boundary conditions of (2.1) transfer to similar conditions on u and v. In detail, we have

$$e^{-\frac{V_n}{2}}\nabla u = \nabla n + \frac{1}{2}n\nabla V_n$$

and, hence,

$$\nabla n + n\nabla V_n = e^{-\frac{V_n}{2}}\Big(\nabla u + \frac{1}{2}u\nabla V_n\Big).$$

Therefore, the corresponding boundary conditions for u and v read

$$\hat{n}\cdot\Big(\nabla u + \frac{1}{2}u\nabla V_n\Big) = \hat{n}\cdot\Big(\nabla v + \frac{1}{2}v\nabla V_p\Big) = 0. \tag{2.71}$$

Furthermore, we assume that the corresponding initial states satisfy

$$(u_I, v_I, n_{tr,I}, n'_{tr,I}) \in L^\infty_+(\Omega)^4, \qquad n_{tr,I} + n'_{tr,I} = 1. \tag{2.72}$$

In this situation, $\|n_{tr,I}\|_{L^\infty(\Omega)} + \|n'_{tr,I}\|_{L^\infty(\Omega)} \geq 1$ and we set

$$I := \|u_I\|_{L^\infty(\Omega)} + \|v_I\|_{L^\infty(\Omega)} + \|n_{tr,I}\|_{L^\infty(\Omega)} + \|n'_{tr,I}\|_{L^\infty(\Omega)} \geq 1.$$

We now aim to apply Banach's fixed-point theorem to obtain a solution of (2.70)–(2.72).

Step 1: Definition of the fixed-point iteration. For any time $T > 0$ (to be chosen sufficiently small in the course of the fixed-point argument), we introduce the space

$$X_T := C([0,T], L^2(\Omega))^4$$

and the closed subspace

$$\begin{aligned} M_T := \big\{(u,v,n_{tr},n'_{tr}) \in X_T \,\big|\, &(u(0),v(0),n_{tr}(0),n'_{tr}(0)) = (u_I,v_I,n_{tr,I},n'_{tr,I}) \wedge \\ &\max_{0\le t\le T}\|u(t)\|_{L^2(\Omega)},\ \max_{0\le t\le T}\|v(t)\|_{L^2(\Omega)},\ \max_{0\le t\le T}\|n_{tr}(t)\|_{L^2(\Omega)},\ \max_{0\le t\le T}\|n'_{tr}(t)\|_{L^2(\Omega)} \le 2I \wedge \\ &\|u\|_{L^\infty((0,T)\times\Omega)},\ \|v\|_{L^\infty((0,T)\times\Omega)} \le 2I\big\} \subset X_T. \end{aligned}$$

The fixed-point mapping $\mathcal{S} : X_T \to X_T$ is now defined via

$$\mathcal{S}(\widetilde{u},\widetilde{v},\widetilde{n}_{tr},\widetilde{n}'_{tr}) := (u,v,n_{tr},n'_{tr})$$

where (u,v,n_{tr},n'_{tr}) is the solution of the following PDE-system subject to the boundary and initial conditions specified above:

$$\begin{cases} \partial_t u - \Delta u = A_n\widetilde{u}^+ + e^{\frac{V_n}{2}}\widetilde{n}_{tr}^{[0,1]} - e^{V_n}\widetilde{u}^+\widetilde{n}_{tr}^{\prime[0,1]} & =: \widetilde{f}_1, \\ \partial_t v - \Delta v = A_p\widetilde{v}^+ + e^{\frac{V_p}{2}}\widetilde{n}_{tr}^{\prime[0,1]} - e^{V_p}\widetilde{v}^+\widetilde{n}_{tr}^{[0,1]} & =: \widetilde{f}_2, \\ \varepsilon\,\partial_t n_{tr} = \widetilde{n}_{tr}^{\prime[0,1]} - e^{\frac{V_p}{2}}\widetilde{v}^+\widetilde{n}_{tr}^{[0,1]} - \widetilde{n}_{tr}^{[0,1]} + e^{\frac{V_n}{2}}\widetilde{u}^+\widetilde{n}_{tr}^{\prime[0,1]} & =: \widetilde{f}_3, \\ \varepsilon\,\partial_t n'_{tr} = \widetilde{n}_{tr}^{[0,1]} - e^{\frac{V_n}{2}}\widetilde{u}^+\widetilde{n}_{tr}^{\prime[0,1]} - \widetilde{n}_{tr}^{\prime[0,1]} + e^{\frac{V_p}{2}}\widetilde{v}^+\widetilde{n}_{tr}^{[0,1]} & =: \widetilde{f}_4. \end{cases} \tag{2.73}$$

We first show that $(u,v,n_{tr},n'_{tr}) = \mathcal{S}(\widetilde{u},\widetilde{v},\widetilde{n}_{tr},\widetilde{n}'_{tr}) \in X_T$ provided $(\widetilde{u},\widetilde{v},\widetilde{n}_{tr},\widetilde{n}'_{tr}) \in X_T$. Due to $\widetilde{f}_1$, $\widetilde{f}_2 \in L^2((0,T)\times\Omega)$, it is known from classical PDE-theory (see e.g. [8]) that

$$u, v \in W_2(0,T) = \big\{f \in L^2((0,T),H^1(\Omega)) \,|\, \partial_t f \in L^2((0,T),H^1(\Omega)^*)\big\} \hookrightarrow C([0,T],L^2(\Omega)).$$

And since

$$n_{tr}(t) = n_{tr}(0) + \frac{1}{\varepsilon}\int_0^t \widetilde{f}_3(s)\,ds$$

for all $t \in [0,T]$, we deduce

$$\|n_{tr}(t)\|_{L^2(\Omega)} \le \|n_{tr}(0)\|_{L^2(\Omega)} + \frac{1}{\varepsilon}\int_0^t \|\widetilde{f}_3(s)\|_{L^2(\Omega)}\,ds \le I + \frac{T}{\varepsilon}\max_{0\le t\le T}\|\widetilde{f}_3(s)\|_{L^2(\Omega)}.$$

Hence, $n_{tr} \in L^\infty((0,T),L^2(\Omega))$. And for $[0,T] \ni t_n \to t \in [0,T]$, we observe that

$$\|n_{tr}(t_n) - n_{tr}(t)\|_{L^2(\Omega)} \le \frac{1}{\varepsilon}\left|\int_t^{t_n}\|\widetilde{f}_3(s)\|_{L^2(\Omega)}\,ds\right| \le \frac{|t_n - t|}{\varepsilon}\max_{0\le t\le T}\|\widetilde{f}_3(s)\|_{L^2(\Omega)} \xrightarrow{n\to\infty} 0.$$

This proves $n_{tr} \in C([0,T],L^2(\Omega))$. The same arguments can be applied to n'_{tr}.

Step 2: Invariance of M_T. Now, let $(\widetilde{u}, \widetilde{v}, \widetilde{n}_{tr}, \widetilde{n}'_{tr}) \in M_T$. Similar to the strategy of e.g. [1, 22, 33], we perform the subsequent calculations for any $q \in 2\mathbb{N}_+$ and every $t \in [0,T]$:

$$\int_0^t \frac{d}{ds} \int_\Omega \frac{u^q}{q}\, dx\, ds = \int_0^t \int_\Omega u^{q-1} \partial_t u\, dx\, ds = \int_0^t \int_\Omega u^{q-1} \Delta u\, dx\, ds + \int_0^t \int_\Omega u^{q-1} \widetilde{f}_1\, dx\, ds$$
$$\leq -(q-1) \int_0^t \int_\Omega u^{q-2} |\nabla u|^2\, dx\, ds - \frac{1}{2} \int_0^t \int_{\partial\Omega} u^q\, \hat{n} \cdot \nabla V_n\, d\sigma\, ds + \|\widetilde{f}_1\|_{L^\infty((0,T)\times\Omega)} \int_0^t \int_\Omega |u|^{q-1}\, dx\, ds$$
$$\leq (2\alpha I + \beta + 2\beta I) \int_0^t \|u\|_{L^q(\Omega)}^{q-1}\, ds.$$

Note that the first two terms in the second line are both non-positive due to $q \in 2\mathbb{N}_+$ and assumption (2.3). Introducing $\gamma := 2\alpha I + \beta + 2\beta I$, we obtain

$$\|u(t)\|_{L^q(\Omega)}^q - \|u(0)\|_{L^q(\Omega)}^q \leq q\gamma \int_0^t \|u(s)\|_{L^q(\Omega)}^{q-1}\, ds. \tag{2.74}$$

This inequality already implies a linear bound on the L^∞-norm of u as we shall see below (cf. [14]). We define

$$U(t) := q\gamma \int_0^t \|u(s)\|_{L^q(\Omega)}^{q-1}\, ds$$

and note that $U(0) = 0$. Estimate (2.74) entails

$$U'(t) = q\gamma \Big(\|u(t)\|_{L^q(\Omega)}^q \Big)^{\frac{q-1}{q}} \leq q\gamma \Big(\eta + \|u(0)\|_{L^q(\Omega)}^q + U(t) \Big)^{\frac{q-1}{q}}$$

for all $t \in [0,T]$, where $\eta > 0$ is an arbitrary constant, which guarantees that the expession $X := \eta + \|u(0)\|_{L^q(\Omega)}^q + U(t)$ is strictly positive. Multiplying both sides with $X^{(1-q)/q}$ and integrating from 0 to t gives

$$\int_0^t \Big(\eta + \|u(0)\|_{L^q(\Omega)}^q + U(s) \Big)^{\frac{1-q}{q}} U'(s)\, ds \leq \int_0^t q\gamma\, ds.$$

We now substitute $\sigma := U(s)$ and deduce

$$q\gamma t \geq \int_0^{U(t)} \Big(\eta + \|u(0)\|_{L^q(\Omega)}^q + \sigma \Big)^{\frac{1}{q}-1} d\sigma = q\Big(\eta + \|u(0)\|_{L^q(\Omega)}^q + \sigma \Big)^{\frac{1}{q}} \Big|_0^{U(t)}$$
$$= q\Big(\eta + \|u(0)\|_{L^q(\Omega)}^q + U(t) \Big)^{\frac{1}{q}} - q\Big(\eta + \|u(0)\|_{L^q(\Omega)}^q \Big)^{\frac{1}{q}} \geq q\Big(\|u(t)\|_{L^q(\Omega)}^q \Big)^{\frac{1}{q}} - q\Big(\eta + \|u(0)\|_{L^q(\Omega)}^q \Big)^{\frac{1}{q}}$$

where we have used (2.74) in the last step. Therefore,

$$\|u(t)\|_{L^q(\Omega)} \leq \Big(\eta + \|u(0)\|_{L^q(\Omega)}^q \Big)^{\frac{1}{q}} + \gamma t$$

and, taking the limit $\eta \to 0$,

$$\|u(t)\|_{L^q(\Omega)} \leq \|u(0)\|_{L^q(\Omega)} + \gamma t \leq I + \gamma t.$$

As the bound on the right hand side is independent of q, we even obtain

$$\|u(t)\|_{L^\infty(\Omega)} \leq I + \gamma t, \tag{2.75}$$

for all $t \in [0,T]$. This result naturally gives rise to

$$\|u\|_{L^\infty((0,T)\times\Omega)} \leq I + \gamma T.$$

An analogous estimate is valid for v. As a result, we obtain

$$\|u\|_{L^\infty((0,T)\times\Omega)},\ \|v\|_{L^\infty((0,T)\times\Omega)} \leq 2I$$

for $T > 0$ chosen sufficiently small.

Employing (2.75), we also derive

$$\max_{0\le t\le T}\|u(t)\|_{L^2(\Omega)} \le \max_{0\le t\le T}\|u(t)\|_{L^\infty(\Omega)} \le I + \gamma T.$$

The same argument is applicable to v, which results in

$$\max_{0\le t\le T}\|u(t)\|_{L^2(\Omega)},\ \max_{0\le t\le T}\|v(t)\|_{L^2(\Omega)} \le 2I$$

for sufficiently small $T > 0$. The corresponding bounds on n_{tr} and n'_{tr} can be deduced from the formula

$$n_{tr}(t) = n_{tr}(0) + \frac{1}{\varepsilon}\int_0^t \widetilde{f}_3(s)\,ds$$

and from an analogous one for n'_{tr}. In fact,

$$\|n_{tr}(t)\|_{L^2(\Omega)} \le \|n_{tr}(0)\|_{L^2(\Omega)} + \frac{1}{\varepsilon}\int_0^t \left\|\widetilde{f}_3(s)\right\|_{L^2(\Omega)} ds \le I + \frac{T}{\varepsilon}(2+4\beta I)$$

and, hence,

$$\max_{0\le t\le T}\|n_{tr}(t)\|_{L^2(\Omega)},\ \max_{0\le t\le T}\|n'_{tr}(t)\|_{L^2(\Omega)} \le 2I$$

for $T > 0$ sufficiently small.

Step 3: Contraction property of $\mathcal{S}$. We consider $(\widetilde{u}_1, \widetilde{v}_1, \widetilde{n}_{tr,1}, \widetilde{n}'_{tr,1}), (\widetilde{u}_2, \widetilde{v}_2, \widetilde{n}_{tr,2}, \widetilde{n}'_{tr,2}) \in M_T$ and the corresponding solutions $(u_1, v_1, n_{tr,1}, n'_{tr,1}) = \mathcal{S}(\widetilde{u}_1, \widetilde{v}_1, \widetilde{n}_{tr,1}, \widetilde{n}'_{tr,1}) \in M_T$ and $(u_2, v_2, n_{tr,2}, n'_{tr,2}) = \mathcal{S}(\widetilde{u}_2, \widetilde{v}_2, \widetilde{n}_{tr,2}, \widetilde{n}'_{tr,2}) \in M_T$. We further introduce the notation

$$u := u_1 - u_2, \quad \widetilde{u} := \widetilde{u}_1 - \widetilde{u}_2$$

and similarly v, n_{tr}, n'_{tr}, $\widetilde{v}$, $\widetilde{n}_{tr}$ and $\widetilde{n}'_{tr}$. Then, we have to show that

$$\|(u, v, n_{tr}, n'_{tr})\|_{X_T} \le c\|(\widetilde{u}, \widetilde{v}, \widetilde{n}_{tr}, \widetilde{n}'_{tr})\|_{X_T}$$

with a constant $c \in (0,1)$ on a time interval $[0,T]$ small enough. The norm in X_T is defined as

$$\|(u, v, n_{tr}, n'_{tr})\|_{X_T} := \max_{0\le t\le T}\|u(t)\|_{L^2(\Omega)} + \max_{0\le t\le T}\|v(t)\|_{L^2(\Omega)} + \max_{0\le t\le T}\|n_{tr}(t)\|_{L^2(\Omega)} + \max_{0\le t\le T}\|n'_{tr}(t)\|_{L^2(\Omega)}.$$

We obtain the following system by taking the difference of corresponding equations of the system for the 1- and the 2-variables, respectively:

$$\begin{cases} \partial_t u - \Delta u = A_n\big(\widetilde{u}_1^+ - \widetilde{u}_2^+\big) + e^{\frac{V_n}{2}}\left(\widetilde{n}_{tr,1}^{[0,1]} - \widetilde{n}_{tr,2}^{[0,1]}\right) - e^{V_n}\left(\widetilde{u}_1^+\widetilde{n}'^{[0,1]}_{tr,1} - \widetilde{u}_2^+\widetilde{n}'^{[0,1]}_{tr,2}\right) =: \widetilde{f}_1, \\ \partial_t v - \Delta v = A_p\big(\widetilde{v}_1^+ - \widetilde{v}_2^+\big) + e^{\frac{V_p}{2}}\left(\widetilde{n}'^{[0,1]}_{tr,1} - \widetilde{n}'^{[0,1]}_{tr,2}\right) - e^{V_p}\left(\widetilde{v}_1^+\widetilde{n}_{tr,1}^{[0,1]} - \widetilde{v}_2^+\widetilde{n}_{tr,2}^{[0,1]}\right) =: \widetilde{f}_2, \\ \varepsilon\,\partial_t n_{tr} = \widetilde{n}'^{[0,1]}_{tr,1} - \widetilde{n}'^{[0,1]}_{tr,2} - e^{\frac{V_p}{2}}\left(\widetilde{v}_1^+\widetilde{n}_{tr,1}^{[0,1]} - \widetilde{v}_2^+\widetilde{n}_{tr,2}^{[0,1]}\right) \\ \qquad\qquad - \widetilde{n}_{tr,1}^{[0,1]} + \widetilde{n}_{tr,2}^{[0,1]} + e^{\frac{V_n}{2}}\left(\widetilde{u}_1^+\widetilde{n}'^{[0,1]}_{tr,1} - \widetilde{u}_2^+\widetilde{n}'^{[0,1]}_{tr,2}\right) =: \widetilde{f}_3, \\ \varepsilon\,\partial_t n'_{tr} = \widetilde{n}_{tr,1}^{[0,1]} - \widetilde{n}_{tr,2}^{[0,1]} - e^{\frac{V_n}{2}}\left(\widetilde{u}_1^+\widetilde{n}'^{[0,1]}_{tr,1} - \widetilde{u}_2^+\widetilde{n}'^{[0,1]}_{tr,2}\right) \\ \qquad\qquad - \widetilde{n}'^{[0,1]}_{tr,1} + \widetilde{n}'^{[0,1]}_{tr,2} + e^{\frac{V_p}{2}}\left(\widetilde{v}_1^+\widetilde{n}_{tr,1}^{[0,1]} - \widetilde{v}_2^+\widetilde{n}_{tr,2}^{[0,1]}\right) =: \widetilde{f}_4. \end{cases} \tag{2.76}$$

We mention that u and v are subject to the boundary conditions

$$\hat{n}\cdot\Big(\nabla u + \frac{1}{2}u\nabla V_n\Big) = \hat{n}\cdot\Big(\nabla v + \frac{1}{2}v\nabla V_p\Big) = 0$$

and the homogeneous initial conditions

$$u(0) = v(0) = n_{tr}(0) = n'_{tr}(0) = 0.$$

First, one finds

$$\max_{0\le t\le T} \|u(t)\|_{L^2(\Omega)} \le C_1 \|u\|_{W_2(0,T)} \le C_1 C_2 \|\widetilde{f}_1\|_{L^2((0,T)\times\Omega)}$$

where $C_1 > 0$ is the constant resulting from the embedding $W_2(0,T) \hookrightarrow C([0,T], L^2(\Omega))$. The constant $C_2 > 0$ originates from well-known parabolic regularity estimates for $\|u\|_{W_2(0,T)}$ in terms of the L^2-norms of $\widetilde{f}_1$ and $u(0) = 0$. Therefore,

$$\begin{aligned}\max_{0\le t\le T} \|u(t)\|_{L^2(\Omega)} \le C_1 C_2 \Big(&\alpha\|\widetilde{u}_1^+ - \widetilde{u}_2^+\|_{L^2((0,T)\times\Omega)} + \beta\|\widetilde{n}_{tr,1}^{[0,1]} - \widetilde{n}_{tr,2}^{[0,1]}\|_{L^2((0,T)\times\Omega)} \\ &+ \beta\|\widetilde{u}_1^+ - \widetilde{u}_2^+\|_{L^2((0,T)\times\Omega)} \|\widetilde{n}_{tr,1}'^{[0,1]}\|_{L^\infty((0,T)\times\Omega)} \\ &+ \beta\|\widetilde{u}_2^+\|_{L^\infty((0,T)\times\Omega)} \|\widetilde{n}_{tr,1}'^{[0,1]} - \widetilde{n}_{tr,2}'^{[0,1]}\|_{L^2((0,T)\times\Omega)}\Big) \\ \le C_1 C_2 \big(&\beta\|\widetilde{n}_{tr}\|_{L^2((0,T)\times\Omega)} + (\alpha+\beta)\|\widetilde{u}\|_{L^2((0,T)\times\Omega)} + 2\beta I\|\widetilde{n}_{tr}'\|_{L^2((0,T)\times\Omega)}\big).\end{aligned}$$

Moreover, every $f \in C([0,T], L^2(\Omega))$ fulfills

$$\|f\|^2_{L^2((0,T)\times\Omega)} = \int_0^T \int_\Omega f^2 \, dx \, dt \le \int_0^T dt \max_{0\le t\le T} \|f(t)\|^2_{L^2(\Omega)} = T\|f\|^2_{C([0,T],L^2(\Omega))}$$

and we proceed with the previous estimates to derive

$$\max_{0\le t\le T} \|u(t)\|_{L^2(\Omega)} \le C_1 C_2 (\alpha + 2\beta I)\sqrt{T}\big(\|\widetilde{n}_{tr}\|_{C([0,T],L^2(\Omega))} + \|\widetilde{u}\|_{C([0,T],L^2(\Omega))} + \|\widetilde{n}_{tr}'\|_{C([0,T],L^2(\Omega))}\big).$$

In a similar way, we arrive at

$$\max_{0\le t\le T} \|v(t)\|_{L^2(\Omega)} \le C_1 C_2 (\alpha + 2\beta I)\sqrt{T}\big(\|\widetilde{n}_{tr}'\|_{C([0,T],L^2(\Omega))} + \|\widetilde{v}\|_{C([0,T],L^2(\Omega))} + \|\widetilde{n}_{tr}\|_{C([0,T],L^2(\Omega))}\big).$$

Due to $n_{tr}(0) = 0$, one obtains

$$n_{tr}(t) = \frac{1}{\varepsilon} \int_0^t \widetilde{f}_3 \, ds$$

for $t \in [0,T]$ and, using similar techniques as above,

$$\begin{aligned}\max_{0\le t\le T} \|n_{tr}(t)\|_{L^2(\Omega)} &\le \frac{1}{\varepsilon} \int_0^T \|\widetilde{f}_3\|_{L^2(\Omega)} \, ds \le \frac{\sqrt{T}}{\varepsilon} \|\widetilde{f}_3\|_{L^2((0,T)\times\Omega)} \\ &\le \frac{1+2\beta I}{\varepsilon} \sqrt{T}\big(\|\widetilde{u}\|_{L^2((0,T)\times\Omega)} + \|\widetilde{v}\|_{L^2((0,T)\times\Omega)} + \|\widetilde{n}_{tr}\|_{L^2((0,T)\times\Omega)} + \|\widetilde{n}_{tr}'\|_{L^2((0,T)\times\Omega)}\big) \\ &\le \frac{1+2\beta I}{\varepsilon} T\big(\|\widetilde{u}\|_{C([0,T],L^2(\Omega))} + \|\widetilde{v}\|_{C([0,T],L^2(\Omega))} + \|\widetilde{n}_{tr}\|_{C([0,T],L^2(\Omega))} + \|\widetilde{n}_{tr}'\|_{C([0,T],L^2(\Omega))}\big).\end{aligned}$$

Note that because of $\widetilde{f}_4 = -\widetilde{f}_3$, the last estimate equally serves as an upper bound for $\|n_{tr}'(t)\|_{L^2(\Omega)}$. Taking the sum of the above estimates and choosing $T > 0$ sufficiently small yields

$$\|(u, v, n_{tr}, n_{tr}')\|_{X_T} \le c\,\|(\widetilde{u}, \widetilde{v}, \widetilde{n}_{tr}, \widetilde{n}_{tr}')\|_{X_T}$$

with some $c \in (0,1)$.

Step 4: Solution of (2.1)**.** Step 2 and Step 3 imply that for $T > 0$ sufficiently small the mapping $\mathcal{S} : M_T \to M_T$ is a contraction. Banach's fixed point theorem, thus, guarantees that there exists a unique $(u, v, n_{tr}, n_{tr}') \in M_T$ such that $\mathcal{S}(u, v, n_{tr}, n_{tr}') = (u, v, n_{tr}, n_{tr}')$. Moreover, due to standard parabolic regularity for (u, v), the fixed-point (u, v, n_{tr}, n_{tr}') is the unique weak solution of

$$\begin{cases} \partial_t u - \Delta u = A_n u^+ + e^{\frac{V_n}{2}} n_{tr}^{[0,1]} - e^{V_n} u^+ n_{tr}'^{[0,1]}, \\ \partial_t v - \Delta v = A_p v^+ + e^{\frac{V_p}{2}} n_{tr}'^{[0,1]} - e^{V_p} v^+ n_{tr}^{[0,1]}, \\ \quad \varepsilon\, \partial_t n_{tr} = n_{tr}'^{[0,1]} - e^{\frac{V_p}{2}} v^+ n_{tr}^{[0,1]} - n_{tr}^{[0,1]} + e^{\frac{V_n}{2}} u^+ n_{tr}'^{[0,1]}, \\ \quad \varepsilon\, \partial_t n_{tr}' = n_{tr}^{[0,1]} - e^{\frac{V_n}{2}} u^+ n_{tr}'^{[0,1]} - n_{tr}'^{[0,1]} + e^{\frac{V_p}{2}} v^+ n_{tr}^{[0,1]}. \end{cases} \tag{2.77}$$

In order to prove the non-negativity of u, v, n_{tr} and n'_{tr}, we adapt an argument from [33]. First, we define

$$h := \min(0, u)$$

on $[0, T] \times \Omega$ and notice that $h \leq 0$ and $h(t = 0) = 0$ a.e. since $u(0) \geq 0$ a.e. We now multiply the first equation in (2.77) with h and integrate over $(0, t) \times \Omega$ for $t \in [0, T]$. This yields

$$\int_0^t \int_\Omega \partial_s u\, h\, dx\, ds = \int_0^t \int_\Omega \Delta u\, h\, dx\, ds + \int_0^t \int_\Omega A_n u^+ h\, dx\, ds + \int_0^t \int_\Omega \left(e^{\frac{V_n}{2}} n_{tr}^{[0,1]} - e^{V_n} u^+ n_{tr}'^{[0,1]} \right) h\, dx\, ds. \tag{2.78}$$

The first term on the right hand side of (2.78) can be seen to be non-positive using integration by parts and the boundary condition from (2.71):

$$\begin{aligned} \int_0^t \int_\Omega \Delta u\, h\, dx\, ds &= -\int_0^t \int_\Omega \nabla u \cdot \nabla h\, dx\, ds - \frac{1}{2} \int_0^t \int_{\partial\Omega} u\, h\, \hat{n} \cdot \nabla V_n\, d\sigma\, ds \\ &\leq -\int_0^t \int_\Omega \nabla u \cdot \nabla h\, dx\, ds = -\int_0^t \int_\Omega \nabla h \cdot \nabla h\, dx\, ds \leq 0 \end{aligned}$$

due to $uh \geq 0$, $\hat{n} \cdot \nabla V_n \geq 0$, and since $\nabla h \neq 0$ holds true only in the case $u < 0$, where we have $\nabla u = \nabla h$ in L^2, see e.g. [20]. Moreover,

$$\int_0^t \int_\Omega A_n u^+ h\, dx\, ds = 0,$$

and the third term in (2.78) is again non-positive as an integral over non-positive quantities:

$$\int_0^t \int_\Omega \left(e^{\frac{V_n}{2}} n_{tr}^{[0,1]} - e^{V_n} u^+ n_{tr}'^{[0,1]} \right) h\, dx\, ds = \int_0^t \int_\Omega e^{\frac{V_n}{2}} n_{tr}^{[0,1]}\, h\, dx\, ds \leq 0$$

as a consequence of $u^+ h = 0$ in $L^2(\Omega)$. The left hand side of (2.78) can be reformulated as

$$\int_0^t \int_\Omega \partial_s u\, h\, dx\, ds = \int_0^t \int_\Omega \partial_s h\, h\, dx\, ds = \frac{1}{2} \int_\Omega \int_0^t \left(\frac{d}{ds} h^2 \right) ds\, dx = \frac{1}{2} \|h(t)\|^2_{L^2(\Omega)}.$$

For the first step, we have used that the integrand $\partial_s u\, h$ only contributes to the integral if $h < 0$. But in this case, $u = h$ and, hence, $\partial_s u = \partial_s h$ in L^2, see e.g. [20]. This proves $\|h(t)\|_{L^2(\Omega)} \leq 0$ for all $t \in [0, T]$, which establishes $h(t) = 0$ in $L^2(\Omega)$ for all $t \in [0, T]$, and thus $u(t, x) \geq 0$ for all $t \in [0, T]$ and a.e. $x \in \Omega$. In the same way, one can show that $v(t, x) \geq 0$ for all $t \in [0, T]$ and a.e. $x \in \Omega$.

The non-negativity of n_{tr} follows from a similar idea using

$$h := \min(0, n_{tr}).$$

Again, $h \leq 0$ and $h(t = 0) = 0$ due to $n_{tr}(0) \geq 0$. Multiplying the third equation of (2.77) with h and integrating over $(0, t) \times \Omega$, $t \in [0, T]$, we find

$$\varepsilon \int_0^t \int_\Omega \partial_s n_{tr}\, h\, dx\, ds = \int_0^t \int_\Omega \left(n_{tr}'^{[0,1]} - e^{\frac{V_p}{2}} v^+ n_{tr}^{[0,1]} - n_{tr}^{[0,1]} + e^{\frac{V_n}{2}} u^+ n_{tr}'^{[0,1]} \right) h\, dx\, ds.$$

As before, all terms under the integral on the right hand side involving $n_{tr}^{[0,1]}$ vanish. Consequently,

$$\frac{\varepsilon}{2} \|h(t)\|^2_{L^2(\Omega)} = \varepsilon \int_0^t \int_\Omega \partial_s h\, h\, dx\, ds = \int_0^t \int_\Omega \left(n_{tr}'^{[0,1]} + e^{\frac{V_n}{2}} u^+ n_{tr}'^{[0,1]} \right) h\, dx\, ds \leq 0$$

for all $t \in [0, T]$. The same result holds true for n'_{tr}. Therefore, we have verified that $n_{tr}(t, x), n'_{tr}(t, x) \geq 0$ for all $t \in [0, T]$ and a.e. $x \in \Omega$.

The non-negativity of n_{tr} and n'_{tr} together with $n'_{tr} = 1 - n_{tr}$ from (2.69) now even imply

$$n_{tr}(t, x),\, n'_{tr}(t, x) \in [0, 1], \qquad \text{for all} \quad t \in [0, T] \quad \text{and a.e.} \quad x \in \Omega.$$

This allows us to identify the unique weak solution (u, v, n_{tr}, n'_{tr}) of (2.77) to equally solve

$$\begin{cases} \partial_t u - \Delta u = A_n u + e^{\frac{V_n}{2}} n_{tr} - e^{V_n} u (1 - n_{tr}), \\ \partial_t v - \Delta v = A_p v + e^{\frac{V_p}{2}} (1 - n_{tr}) - e^{V_p} v\, n_{tr}, \\ \quad \varepsilon\, \partial_t n_{tr} = 1 - n_{tr} - e^{\frac{V_p}{2}} v\, n_{tr} - n_{tr} + e^{\frac{V_n}{2}} u (1 - n_{tr}), \end{cases} \tag{2.79}$$

which is the transform version of the original problem (2.1).

Up to now, we have proven that there exists a unique solution $(u, v, n_{tr}) \in C([0,T], L^2(\Omega))^3$ such that $(u, v, n_{tr}, 1 - n_{tr}) \in M_T$ on a sufficiently small time interval $[0, T]$.

Step 5: Global solution. We now fix $T^* > 0$ in such a way that $[0, T^*)$ is the maximal time interval of existence for the solution $(u, v, n_{tr}) \in C([0,T], L^2(\Omega))^3$ of (2.79). Moreover, we choose some arbitrary $q \in \mathbb{N}_{\geq 2}$ and multiply the first equation in (2.79) with u^{q-1}. Integrating over Ω at time $t \in [0, T^*)$ gives

$$\frac{d}{dt}\int_\Omega \frac{u^q}{q}\,dx = \int_\Omega u^{q-1}\partial_t u\,dx = \int_\Omega u^{q-1}\Delta u\,dx + \int_\Omega A_n u^q\,dx + \int_\Omega u^{q-1}\Big(e^{\frac{V_n}{2}} n_{tr} - e^{V_n} u(1-n_{tr})\Big)\,dx.$$

Integration by parts and the estimates $|A_n| \leq \alpha$, $\big|e^{\frac{V_n}{2}} n_{tr} - e^{V_n} u(1 - n_{tr})\big| \leq \beta(1+u)$ further yield

$$\frac{d}{dt}\int_\Omega \frac{u^q}{q}\,dx \leq -(q-1)\int_\Omega u^{q-2}|\nabla u|^2\,dx - \frac{1}{2}\int_0^t\int_{\partial\Omega} u^q\,\hat{n}\cdot\nabla V_n\,d\sigma\,ds + \alpha\int_\Omega u^q\,dx + \beta\int_\Omega (u^{q-1} + u^q)\,dx.$$

Moreover, we derive

$$\int_\Omega u^{q-1}\,dx = \int_{\{u\leq 1\}} u^{q-1}\,dx + \int_{\{u>1\}} \frac{u^q}{u}\,dx \leq \int_\Omega 1\,dx + \int_\Omega u^q\,dx = 1 + \int_\Omega u^q\,dx$$

where we used $|\Omega| = 1$. Hence,

$$\frac{d}{dt}\int_\Omega \frac{u^q}{q}\,dx \leq \beta + (\alpha + 2\beta)\int_\Omega u^q\,dx \leq \gamma\left(1 + \int_\Omega u^q\,dx\right) \tag{2.80}$$

after defining $\gamma := \alpha + 2\beta$. This results in

$$\frac{d}{dt}\int_\Omega u^q\,dx \leq \gamma q\left(1 + \int_\Omega u^q\,dx\right),$$

which can be integrated over time from 0 to t:

$$\|u(t)\|^q_{L^q(\Omega)} \leq \|u(0)\|^q_{L^q(\Omega)} + \gamma q\int_0^t \Big(1 + \|u(s)\|^q_{L^q(\Omega)}\Big)\,ds.$$

From this generalized Gronwall-type inequality, we deduce (cf. [14])

$$\|u(t)\|^q_{L^q(\Omega)} \leq \|u(0)\|^q_{L^q(\Omega)} e^{\gamma q t} + e^{\gamma q t} - 1 < \big(1 + \|u(0)\|^q_{L^q(\Omega)}\big)e^{\gamma q t}$$

and

$$\|u(t)\|_{L^q(\Omega)} \leq \big(1 + \|u(0)\|_{L^q(\Omega)}\big)e^{\gamma t} \leq I e^{\gamma t}$$

since $1 + \|u(0)\|_{L^q(\Omega)} \leq 1 + \|u(0)\|_{L^\infty(\Omega)} \leq I$. As $Ie^{\gamma t}$ is independent of q, we even arrive at

$$\|u(t)\|_{L^\infty(\Omega)} \leq I e^{\gamma t}.$$

In the same way, we can show that $\|v(t)\|_{L^\infty(\Omega)} \leq Ie^{\gamma t}$ for all $t \in [0, T^*)$. As a consequence, we obtain that the solution $(u, v, n_{tr}) \in C([0,T], L^2(\Omega))^3$ can be extended for all times, i.e. $T^* = \infty$.

Step 6: L^∞-bounds for n and p. We now prove the linearly growing L^∞-bounds (2.8) for n and p. We only detail the bound for p and sketch how the bound for n follows in a similar fashion. After recalling (with $\tau_p = 1$ w.l.o.g.)

$$\partial_t p = \nabla\cdot J_p + \left(1 - n_{tr} - \frac{p}{p_0 e^{-V_p}} n_{tr}\right), \qquad J_p = e^{-V_p}\nabla\left(p\,e^{V_p}\right),$$

we introduce the variable $w = p\,e^{V_p}$ and observe that $\nabla\cdot J_p = \nabla\cdot\big(e^{-V_p}\nabla w\big) = e^{-V_p}\left(\Delta w - \nabla V_p\cdot\nabla w\right)$ and thus,

$$\partial_t w = \Delta w - \nabla V_p\cdot\nabla w + e^{V_p}\left(1 - n_{tr} - \frac{n_{tr}}{p_0} w\right), \tag{2.81}$$

while the no-flux boundary condition $\hat{n}\cdot J_p = 0$ on $\partial\Omega$ transforms to the homogeneous Neumann condition $\hat{n}\cdot\nabla w = 0$ on $\partial\Omega$.

Next, by testing (2.81) with the positive part $(w-r-st)_+ := \max\{0, w-r-st\}$ for two constants $r, s > 0$ to be chosen, we calculate by integration by parts in the first two terms

$$\begin{aligned}\frac{d}{dt}\frac{1}{2}\int_\Omega (w-r-st)_+^2\,dx &= \int_\Omega (w-r-st)_+\left(\Delta w - \nabla V_p\cdot\nabla w + e^{V_p}\Big(1-n_{tr}-\frac{n_{tr}}{p_0}w\Big) - s\right)dx\\ &= -\int_\Omega \mathbb{1}_{w\geq r+st}|\nabla w|^2\,dx - \int_\Omega \nabla V_p\cdot\nabla\frac{(w-r-st)_+^2}{2}\,dx\\ &\quad+\int_\Omega (w-r-st)_+\left(e^{V_p}\Big(1-n_{tr}-\frac{n_{tr}}{p_0}w\Big)-s\right)dx\\ &\leq \frac{\|\Delta V_p\|_\infty}{2}\int_\Omega (w-r-st)_+^2\,dx + \int_\Omega (w-r-st)_+\left(e^{V_p}\Big(1-n_{tr}-\frac{n_{tr}}{p_0}w\Big)-s\right)dx,\end{aligned}$$

since $\hat{n}\cdot V_p \geq 0$ by assumption (2.3). Moreover, since $n_{tr}\in[0,1]$ and $w\geq 0$, we have

$$\frac{d}{dt}\frac{1}{2}\int_\Omega (w-r-st)_+^2\,dx \leq \frac{\|\Delta V_p\|_\infty}{2}\int_\Omega (w-r-st)_+^2\,dx + \int_\Omega (w-r-st)_+\Big(\|e^{V_p}\|_\infty - s\Big)dx.$$

Thus, by choosing $s := \|e^{V_p}\|_\infty$ and $r := \|w(\tau,\cdot)\|_\infty$ for some time $\tau\geq 0$, we conclude that

$$\frac{d}{dt}\int_\Omega (w-r-st)_+^2\,dx \leq \|\Delta V_p\|_\infty \int_\Omega (w-r-st)_+^2\,dx,$$

and a Gronwall lemma implies

$$\|w(t,\cdot)\|_\infty \leq \|w(\tau,\cdot)\|_\infty + \|e^{V_p}\|_\infty\, t, \qquad \text{for all } t\geq\tau\geq 0. \tag{2.82}$$

Transforming back, this yields

$$\|p(t,\cdot)\|_\infty \leq \frac{1}{\inf\{e^{V_p}\}}\left(\|p(\tau,\cdot)\|_\infty\|e^{V_p}\|_\infty + \|e^{V_p}\|_\infty\, t\right), \qquad \text{for all } t\geq\tau\geq 0. \tag{2.83}$$

In order to deduce the analog bound for n in (2.8), we consider (with $\tau_n = 1$ w.l.o.g.)

$$\partial_t n = \nabla\cdot J_n + \left(n_{tr} - \frac{n}{n_0 e^{-V_n}}(1-n_{tr})\right), \qquad J_n = e^{-V_n}\nabla\big(n\,e^{V_n}\big).$$

We introduce the variable $z = n\,e^{V_n}$ and observe that $\nabla\cdot J_n = \nabla\cdot\big(e^{-V_n}\nabla z\big) = e^{-V_n}\left(\Delta z - \nabla V_n\cdot\nabla z\right)$ and thus,

$$\partial_t z = \Delta z - \nabla V_n\cdot\nabla z + e^{V_n}\left(n_{tr} - \frac{1-n_{tr}}{n_0}z\right). \tag{2.84}$$

Following the same arguments as above,

$$\|z(t,\cdot)\|_\infty \leq \|z(\tau,\cdot)\|_\infty + \|e^{V_n}\|_\infty\, t, \qquad \text{for all } t\geq\tau\geq 0. \tag{2.85}$$

Transforming back, this yields

$$\|n(t,\cdot)\|_\infty \leq \frac{1}{\inf\{e^{V_n}\}}\left(\|n(\tau,\cdot)\|_\infty\|e^{V_n}\|_\infty + \|e^{V_n}\|_\infty\, t\right), \qquad \text{for all } t\geq\tau\geq 0 \tag{2.86}$$

and thus (2.8).

Step 7: Regularity and bounds for n_{tr}. We still have to verify $n_{tr}\in C([0,T],L^\infty(\Omega))$ for all $T>0$. Now, let $T>0$ and recall that

$$n_{tr}(t) = n_{tr}(0) + \frac{1}{\varepsilon}\int_0^t \big(1 - n_{tr} - e^{V_p}p\,n_{tr} - n_{tr} + e^{V_n}n(1-n_{tr})\big)\,ds$$

in $L^2(\Omega)$ for all $t \in [0,T]$. Considering a sequence $(t_n)_{n\in\mathbb{N}} \subset [0,T]$, $t_n \to t$, we thus arrive at

$$\|n_{tr}(t_n) - n_{tr}(t)\|_{L^\infty(\Omega)} \le \frac{1}{\varepsilon}\left|\int_t^{t_n} \|1 - n_{tr} - e^{V_p} p\, n_{tr} - n_{tr} + e^{V_n} n(1-n_{tr})\|_{L^\infty(\Omega)}\, ds\right| \le \frac{|t_n - t|}{\varepsilon} C_T \to 0$$

for $n \to \infty$. This proves the assertion.

The claim $\partial_t n_{tr} \in C([0,T], L^2(\Omega))$ for all $T > 0$ is an immediate consequence of the last equation in (2.79) together with the L^2-continuity and L^∞-bounds of u, v and n_{tr}.

Next, concerning the bounds (2.9), we recall system (2.1) and observe that for all $\varepsilon \in (0, \varepsilon_0]$

$$\varepsilon \partial_t n_{tr} = h(n_{tr}) := R_p(p, n_{tr}) - R_n(n, n_{tr}),$$

in the sense of $L^2(\Omega)$, where $h(n_{tr} = 0) \ge 1/\tau_p > 0$ and $h(n_{tr} = 1) \le -1/\tau_n < 0$ uniformly for all non-negative n and p. Therefore, wherever $n_{tr,I}(x) = 0$ (or analogous $n_{tr,I}(x) = 1$), an elementary argument proves that $n_{tr}(t,x)$ grows (or decreases) linearly in time and decays back to 0 (or 1) at most like $(a + bt)^{-1}$. More precisely, we reuse the transformed variable $w = p\, e^{V_p}$ and find

$$\varepsilon \partial_t n_{tr} \ge \frac{1}{\tau_p}\left[1 - \left(1 + \frac{\tau_p}{\tau_n} + \frac{\|w\|_\infty}{p_0}\right) n_{tr}\right] \ge \frac{1}{\tau_p}\left[1 - \left(1 + \frac{\tau_p}{\tau_n} + \frac{r + st}{p_0}\right) n_{tr}\right]$$

due to the estimate (2.82). Setting $\tau_n := \tau_p := 1$ w.l.o.g., we have

$$\varepsilon \partial_t n_{tr} \ge 1 - (\widetilde{r} + \widetilde{s}t) n_{tr} \tag{2.87}$$

with appropriate $\widetilde{r}, \widetilde{s} > 0$ independent of ε. This implies, for some fixed time $\tau > 0$,

$$n_{tr}(t,x) \ge \frac{1}{2\widetilde{r} + 2\widetilde{s}t} \quad \text{for all } t \ge \tau \text{ and a.a. } x \in \Omega,$$

as can be seen from the following argument. Assuming that this claim is false, there exists an arbitrarily large $t_0 > 0$ and some $x \in \Omega$ such that

$$n_{tr}(t_0, x) < \frac{1}{2\widetilde{r} + 2\widetilde{s}t_0}.$$

But since $\partial_{-t} n_{tr}(t,x) \le -1/(2\varepsilon_0) < 0$ whenever $n_{tr}(t,x) < 1/(2\widetilde{r} + 2\widetilde{s}t)$, we find by propagating into the negative time direction that $n_{tr}(0,x) < 0$ provided t_0 is chosen large enough. This proves the announced decay property.

For the linear increase, we distinguish two cases. If

$$n_{tr}(0,x) < \frac{1}{2\widetilde{r} + 2\widetilde{s}\tau},$$

then $\partial_t n_{tr}(t,x) \ge 1/(2\varepsilon_0) > 0$ (at least) as long as $n_{tr}(t,x) < 1/(2\widetilde{r} + 2\widetilde{s}\tau)$ and $t \le \tau$. Hence, there exists a $T_x \le \widehat{T} := \min\{\varepsilon_0/(\widetilde{r} + \widetilde{s}\tau), \tau\}$ such that

$$n_{tr}(T_x, x) \ge \frac{1}{2\widetilde{r} + 2\widetilde{s}\tau} \quad \text{and} \quad n_{tr}(t,x) \ge \frac{t}{2\varepsilon_0} \quad \text{for all } t \le T_x.$$

An analogous argument shows that $n_{tr}(t,x) \ge 1/(2\widetilde{r} + 2\widetilde{s}\tau)$ for all $t \in [T_x, \tau]$. As a consequence, we first have that $n_{tr}(t,x) \ge t/(2\varepsilon_0)$ for a.a. $x \in \Omega$ and all $t \in \big[0, \widehat{T}\big]$. And second, $n_{tr}(t,x) \ge 1/(2\widetilde{r} + 2\widetilde{s}\tau)$ for all $t \in [\widehat{T}, \tau]$ and a.a $x \in \Omega$. In the other case, when

$$n_{tr}(0,x) \ge \frac{1}{2\widetilde{r} + 2\widetilde{s}\tau},$$

we directly obtain $n_{tr}(t,x) \ge 1/(2\widetilde{r} + 2\widetilde{s}\tau)$ for all $t \in [0,\tau]$ and a.a. $x \in \Omega$. Adapting the coefficients of the linear increase and the inverse linear decrease appropriately, we obtain bounds which intersect at any prescribed time τ.

Step 8: Lower bounds for n and p. Finally, we prove the bounds (2.10). We will only detail the argument for the lower bound on n, as the bound for p follows in an analog way. Recalling the transformed equation for $u = e^{V_n/2}n$, we estimate

$$\partial_t u - \Delta u = \Big(\frac{1}{2}\Delta V_n - \frac{1}{4}|\nabla V_n|^2 - e^{V_n}\Big)u + e^{\frac{V_n}{2}} n_{tr} + e^{V_n} u n_{tr} \geq cu + dn_{tr}, \tag{2.88}$$

where $c \in \mathbb{R}$ and $d > 0$ are constants due to the assumptions (2.3) and $e^{V_n} u n_{tr} \geq 0$.

Next, we use (2.9), i.e. that for all $\tau > 0$ fixed, there exist constants η, θ and γ such that $n_{tr}(t,x) \geq \eta t$ for all $0 \leq t \leq \tau$ and a.a. $x \in \Omega$, while $n_{tr}(t,x) \geq \gamma/(1+\theta t)$ for all $t \geq \tau$ and a.a. $x \in \Omega$. Then, by introducing the negative part $(u)_- := \min\{u, 0\}$ and testing (2.88) with $\big(u - \frac{\mu t^2}{2}\big)_-$ for a constant $\mu > 0$ to be chosen below, we estimate

$$\begin{aligned}
\frac{d}{dt}\frac{1}{2}\int_\Omega \Big(u - \frac{\mu t^2}{2}\Big)_-^2 dx &= \int_\Omega \Big(u - \frac{\mu t^2}{2}\Big)_- (\partial_t u - \mu t)\, dx = \int_\Omega \Big|\Big(u - \frac{\mu t^2}{2}\Big)_-\Big| (-\partial_t u + \mu t)\, dx \\
&\leq \int_\Omega \Big|\Big(u - \frac{\mu t^2}{2}\Big)_-\Big| (-\Delta u - cu - dn_{tr} + \mu t)\, dx \\
&\leq -\int_\Omega \mathbb{1}_{u \leq \frac{\mu t^2}{2}} |\nabla u|^2\, dx + \int_\Omega \Big|\Big(u - \frac{\mu t^2}{2}\Big)_-\Big| (|c|u - dn_{tr} + \mu t)\, dx.
\end{aligned}$$

Thus, for $0 \leq t \leq \tau$ when $n_{tr}(t,x) \geq \eta t$, we have

$$\frac{d}{dt}\frac{1}{2}\int_\Omega \Big(u - \frac{\mu t^2}{2}\Big)_-^2 dx \leq \int_\Omega \Big|\Big(u - \frac{\mu t^2}{2}\Big)_-\Big| \Big(|c|\frac{\mu t^2}{2} - d\eta t + \mu t\Big)\, dx \leq 0,$$

provided that we choose $\mu(|c|\tau/2 + 1) \leq d\eta$. Hence, since $\int_\Omega \big(u(0,x)\big)_-^2 dx = 0$, we have

$$\int_\Omega \Big(u - \frac{\mu t^2}{2}\Big)_-^2 dx = 0, \qquad \text{for all } 0 \leq t \leq \tau,$$

which yields in particular $u(t,x) \geq \frac{\mu t^2}{2}$ for all $0 \leq t \leq \tau$ and a.a. $x \in \Omega$.

Moreover, for $t \geq \tau$ when $n_{tr}(t,x) \geq \frac{\gamma}{1+\theta t}$, we test (2.88) with $\big(u - \frac{\Gamma}{1+\theta t}\big)_-$ for a constant $\Gamma > 0$ to be chosen below, and estimate similar to above

$$\begin{aligned}
&\frac{d}{dt}\frac{1}{2}\int_\Omega \Big(u - \frac{\Gamma}{1+\theta t}\Big)_-^2 dx = \int_\Omega \Big(u - \frac{\Gamma}{1+\theta t}\Big)_- \Big(\partial_t u + \frac{\Gamma\theta}{(1+\theta t)^2}\Big)\, dx \\
&\leq \int_\Omega \Big(u - \frac{\Gamma}{1+\theta t}\Big)_- \Big(\Delta u + cu + dn_{tr} + \frac{\Gamma\theta}{(1+\theta t)^2}\Big)\, dx \\
&\leq -\int_\Omega \mathbb{1}_{u \leq \frac{\Gamma}{1+\theta t}} |\nabla u|^2\, dx + \int_\Omega \Big|\Big(u - \frac{\Gamma}{1+\theta t}\Big)_-\Big| \Big(|c|\frac{\Gamma}{1+\theta t} - d\frac{\gamma}{1+\theta t} - \frac{\Gamma\theta}{(1+\theta t)^2}\Big)\, dx \leq 0,
\end{aligned}$$

provided that we choose $|c|\Gamma \leq d\gamma$. By further reducing either Γ or μ, we are able to satisfy $\frac{\Gamma}{1+\theta\tau} = \frac{\mu\tau^2}{2}$. On the one hand, this implies that $\int_\Omega \Big(u(\tau,x) - \frac{\Gamma}{1+\theta\tau}\Big)_-^2 dx = 0$, which results in

$$\int_\Omega \Big(u(t,x) - \frac{\Gamma}{1+\theta t}\Big)_-^2 dx = 0, \qquad \text{for all } t \geq \tau,$$

and, hence, $u(t,x) \geq \frac{\Gamma}{1+\theta t}$ for all $t \geq \tau$ and a.a. $x \in \Omega$. On the other hand, the increasing and decreasing bounds now again intersect at time τ as desired. ☐

Proof of Theorem 2.1'. As the major part of the proof is very similar to that of Theorem 2.1, we only detail the relevant differences. We again set the parameter $\tau_n := \tau_p := 1$ and $n_0 := p_0 := 1$ throughout the proof and introduce the variables

$$u := e^{\frac{V_n}{2}} n, \qquad v := e^{\frac{V_p}{2}} p.$$

The equations for u and v then rewrite as

$$\partial_t u = \Delta u + \Big(\frac{1}{2}\Delta V_n - \frac{1}{4}|\nabla V_n|^2\Big)u + e^{\frac{V_n}{2}} \frac{1 - e^{\frac{V_n}{2}} e^{\frac{V_p}{2}} uv}{2 + e^{\frac{V_p}{2}} v + e^{\frac{V_n}{2}} u}$$

and

$$\partial_t v = \Delta v + \Big(\frac{1}{2}\Delta V_p - \frac{1}{4}|\nabla V_p|^2\Big)v + e^{\frac{V_p}{2}} \frac{1 - e^{\frac{V_n}{2}} e^{\frac{V_p}{2}} uv}{2 + e^{\frac{V_p}{2}} v + e^{\frac{V_n}{2}} u}.$$

We also maintain the abbreviations

$$A_n := \frac{1}{2}\Delta V_n - \frac{1}{4}|\nabla V_n|^2 \in L^\infty(\Omega), \qquad A_p := \frac{1}{2}\Delta V_p - \frac{1}{4}|\nabla V_p|^2 \in L^\infty(\Omega)$$

as well as $\alpha, \beta > 0$ where

$$|A_n|, |A_p| \le \alpha \qquad \text{and} \qquad e^{\frac{V_n}{2}}, e^{\frac{V_p}{2}}, e^{V_n}, e^{V_p} \le \beta \qquad \text{a.e. in } \Omega.$$

We shall also recall the notation $X^+ := \max(X, 0)$, which denotes the positive part of an arbitrary function X. We now consider the system

$$\begin{cases} \partial_t u - \Delta u = A_n u^+ + e^{\frac{V_n}{2}} \dfrac{1 - e^{\frac{V_n}{2}} e^{\frac{V_p}{2}} u^+ v^+}{2 + e^{\frac{V_p}{2}} v^+ + e^{\frac{V_n}{2}} u^+}, \\ \partial_t v - \Delta v = A_p v^+ + e^{\frac{V_p}{2}} \dfrac{1 - e^{\frac{V_n}{2}} e^{\frac{V_p}{2}} u^+ v^+}{2 + e^{\frac{V_p}{2}} v^+ + e^{\frac{V_n}{2}} u^+}. \end{cases} \tag{2.89}$$

The corresponding boundary conditions for u and v read

$$\hat{n} \cdot \Big(\nabla u + \frac{1}{2} u \nabla V_n\Big) = \hat{n} \cdot \Big(\nabla v + \frac{1}{2} v \nabla V_p\Big) = 0, \tag{2.90}$$

the initial states are assumed to satisfy

$$(u_I, v_I) \in L^\infty_+(\Omega)^2 \tag{2.91}$$

and we set

$$I := \|u_I\|_{L^\infty(\Omega)} + \|v_I\|_{L^\infty(\Omega)} + 1 \ge 1.$$

Subsequently, we will apply Banach's fixed-point theorem to derive a solution of (2.89)–(2.91).

Step 1: Definition of the fixed-point iteration. We define the space

$$X_T := C([0,T], L^2(\Omega))^2$$

for any $T > 0$ as well as the closed subspace

$$M_T := \big\{(u,v) \in X_T \,\big|\, (u(0), v(0)) = (u_I, v_I) \wedge \max_{0\le t\le T} \|u(t)\|_{L^2(\Omega)}, \max_{0\le t\le T} \|v(t)\|_{L^2(\Omega)} \le 2I \wedge \|u\|_{L^\infty((0,T)\times\Omega)}, \|v\|_{L^\infty((0,T)\times\Omega)} \le 2I\big\} \subset X_T.$$

Here, we define the fixed-point mapping $\mathcal{S} : X_T \to X_T$ via

$$\mathcal{S}(\widetilde{u}, \widetilde{v}) := (u, v)$$

where (u, v) is the unique weak solution of the PDE-system

$$\begin{cases} \partial_t u - \Delta u = A_n \widetilde{u}^+ + e^{\frac{V_n}{2}} \dfrac{1 - e^{\frac{V_n}{2}} e^{\frac{V_p}{2}} \widetilde{u}^+ \widetilde{v}^+}{2 + e^{\frac{V_p}{2}} \widetilde{v}^+ + e^{\frac{V_n}{2}} \widetilde{u}^+} =: \widetilde{f}_1, \\ \partial_t v - \Delta v = A_p \widetilde{v}^+ + e^{\frac{V_p}{2}} \dfrac{1 - e^{\frac{V_n}{2}} e^{\frac{V_p}{2}} \widetilde{u}^+ \widetilde{v}^+}{2 + e^{\frac{V_p}{2}} \widetilde{v}^+ + e^{\frac{V_n}{2}} \widetilde{u}^+} =: \widetilde{f}_2, \end{cases} \tag{2.92}$$

subject to the previously defined boundary and initial conditions. Due to $\widetilde{f}_1,\ \widetilde{f}_2 \in L^2((0,T)\times\Omega)$, we know that

$$u, v \in W_2(0,T) = \big\{f \in L^2((0,T), H^1(\Omega)) \,|\, \partial_t f \in L^2((0,T), H^1(\Omega)^*)\big\} \hookrightarrow C([0,T], L^2(\Omega)).$$

As a result, we have verified that $(u,v) = \mathcal{S}(\widetilde{u}, \widetilde{v}) \in X_T$.

Step 2: Invariance of M_T. In the same way as in the proof of Theorem 2.1, we start with $(\widetilde{u},\widetilde{v})\in M_T$ and calculate for any $q\in 2\mathbb{N}_+$ and every $t\in[0,T]$:

$$\int_0^t \frac{d}{ds}\int_\Omega \frac{u^q}{q}\,dx\,ds \le (2\alpha I+\beta+4\beta^3 I^2)\int_0^t \|u\|_{L^q(\Omega)}^{q-1}\,ds.$$

Introducing $\gamma := 2\alpha I+\beta+4\beta^3I^2$, we have

$$\|u(t)\|_{L^q(\Omega)}^q - \|u(0)\|_{L^q(\Omega)}^q \le q\gamma\int_0^t \|u(s)\|_{L^q(\Omega)}^{q-1}\,ds. \tag{2.93}$$

Using the Gronwall-type reasoning from the proof of Theorem 2.1, we obtain

$$\|u(t)\|_{L^\infty(\Omega)} \le I+\gamma t, \tag{2.94}$$

for all $t\in[0,T]$. Corresponding arguments for v show that

$$\|u\|_{L^\infty((0,T)\times\Omega)},\ \|v\|_{L^\infty((0,T)\times\Omega)} \le I+\gamma T\le 2I$$

for $T>0$ chosen sufficiently small. From the estimate in (2.94), we also get

$$\max_{0\le t\le T}\|u(t)\|_{L^2(\Omega)},\ \max_{0\le t\le T}\|v(t)\|_{L^2(\Omega)} \le I+\gamma T\le 2I.$$

Step 3: Contraction property of $\mathcal{S}$. We take arbitrary $(\widetilde{u}_1,\widetilde{v}_1),(\widetilde{u}_2,\widetilde{v}_2)\in M_T$ and consider the corresponding solutions $(u_1,v_1)=\mathcal{S}(\widetilde{u}_1,\widetilde{v}_1)\in M_T$ and $(u_2,v_2)=\mathcal{S}(\widetilde{u}_2,\widetilde{v}_2)\in M_T$. We recall the notation

$$u := u_1-u_2,\quad \widetilde{u} := \widetilde{u}_1-\widetilde{u}_2$$

and similarly v, $\widetilde{v}$. Then, we want to show that

$$\|(u,v)\|_{X_T}\le c\|(\widetilde{u},\widetilde{v})\|_{X_T}$$

for a constant $c\in(0,1)$ on a time interval $[0,T]$ small enough. The norm $\|\cdot\|_{X_T}$ is defined via

$$\|(u,v)\|_{X_T} := \max_{0\le t\le T}\|u(t)\|_{L^2(\Omega)}+\max_{0\le t\le T}\|v(t)\|_{L^2(\Omega)}.$$

The subsequent system results from taking the differences of corresponding equations for the 1- and 2-variables:

$$\begin{cases} \partial_t u-\Delta u = A_n\big(\widetilde{u}_1^+-\widetilde{u}_2^+\big)+e^{\frac{V_n}{2}}\left(\dfrac{1-e^{\frac{V_n}{2}}e^{\frac{V_p}{2}}\widetilde{u}_1^+\widetilde{v}_1^+}{2+e^{\frac{V_p}{2}}\widetilde{v}_1^+ + e^{\frac{V_n}{2}}\widetilde{u}_1^+} - \dfrac{1-e^{\frac{V_n}{2}}e^{\frac{V_p}{2}}\widetilde{u}_2^+\widetilde{v}_2^+}{2+e^{\frac{V_p}{2}}\widetilde{v}_2^+ + e^{\frac{V_n}{2}}\widetilde{u}_2^+}\right) =: \widetilde{f}_1,\\[2ex] \partial_t v-\Delta v = A_p\big(\widetilde{v}_1^+-\widetilde{v}_2^+\big)+e^{\frac{V_p}{2}}\left(\dfrac{1-e^{\frac{V_n}{2}}e^{\frac{V_p}{2}}\widetilde{u}_1^+\widetilde{v}_1^+}{2+e^{\frac{V_p}{2}}\widetilde{v}_1^+ + e^{\frac{V_n}{2}}\widetilde{u}_1^+} - \dfrac{1-e^{\frac{V_n}{2}}e^{\frac{V_p}{2}}\widetilde{u}_2^+\widetilde{v}_2^+}{2+e^{\frac{V_p}{2}}\widetilde{v}_2^+ + e^{\frac{V_n}{2}}\widetilde{u}_2^+}\right) =: \widetilde{f}_2. \end{cases}$$

The variables u and v are subject to the boundary conditions

$$\hat{n}\cdot\Big(\nabla u+\frac{1}{2}u\nabla V_n\Big) = \hat{n}\cdot\Big(\nabla v+\frac{1}{2}v\nabla V_p\Big)=0$$

and the homogeneous initial conditions

$$u(0)=v(0)=0.$$

We again start with the estimate

$$\max_{0\le t\le T}\|u(t)\|_{L^2(\Omega)}\le C_1\|u\|_{W_2(0,T)}\le C_1C_2\|\widetilde{f}_1\|_{L^2((0,T)\times\Omega)}$$

where $C_1>0$ arises from the embedding $W_2(0,T)\hookrightarrow C([0,T],L^2(\Omega))$ and $C_2>0$ from well-known parabolic regularity estimates for $\|u\|_{W_2(0,T)}$ in terms of the L^2-norms of $\widetilde{f}_1$ and $u(0)=0$. Therefore,

$$\begin{aligned}\max_{0\le t\le T}\|u(t)\|_{L^2(\Omega)} \le C_1C_2\Bigg(&\alpha\big\|\widetilde{u}_1^+-\widetilde{u}_2^+\big\|_{L^2((0,T)\times\Omega)}\\ &+\beta\left\|\frac{1-e^{\frac{V_n}{2}}e^{\frac{V_p}{2}}\widetilde{u}_1^+\widetilde{v}_1^+}{2+e^{\frac{V_p}{2}}\widetilde{v}_1^+ + e^{\frac{V_n}{2}}\widetilde{u}_1^+} - \frac{1-e^{\frac{V_n}{2}}e^{\frac{V_p}{2}}\widetilde{u}_2^+\widetilde{v}_2^+}{2+e^{\frac{V_p}{2}}\widetilde{v}_2^+ + e^{\frac{V_n}{2}}\widetilde{u}_2^+}\right\|_{L^2((0,T)\times\Omega)}\Bigg).\end{aligned} \tag{2.95}$$

The main task is to derive an upper bound for the expression in the second line in terms of $\|\widetilde{u}\|_{L^2((0,T)\times\Omega)}$ and $\|\widetilde{v}\|_{L^2((0,T)\times\Omega)}$. We deduce

$$\begin{aligned}\widetilde{r} &:= \left\| \frac{1-e^{\frac{V_n}{2}}e^{\frac{V_p}{2}}\widetilde{u}_1^+\widetilde{v}_1^+}{2+e^{\frac{V_p}{2}}\widetilde{v}_1^+ + e^{\frac{V_n}{2}}\widetilde{u}_1^+} - \frac{1-e^{\frac{V_n}{2}}e^{\frac{V_p}{2}}\widetilde{u}_2^+\widetilde{v}_2^+}{2+e^{\frac{V_p}{2}}\widetilde{v}_2^+ + e^{\frac{V_n}{2}}\widetilde{u}_2^+}\right\|_{L^2((0,T)\times\Omega)} \\ &= \left\| \frac{(1-e^{\frac{V_n}{2}}e^{\frac{V_p}{2}}\widetilde{u}_1^+\widetilde{v}_1^+)(2+e^{\frac{V_p}{2}}\widetilde{v}_2^+ + e^{\frac{V_n}{2}}\widetilde{u}_2^+) - (1-e^{\frac{V_n}{2}}e^{\frac{V_p}{2}}\widetilde{u}_2^+\widetilde{v}_2^+)(2+e^{\frac{V_p}{2}}\widetilde{v}_1^+ + e^{\frac{V_n}{2}}\widetilde{u}_1^+)}{(2+e^{\frac{V_p}{2}}\widetilde{v}_1^+ + e^{\frac{V_n}{2}}\widetilde{u}_1^+)(2+e^{\frac{V_p}{2}}\widetilde{v}_2^+ + e^{\frac{V_n}{2}}\widetilde{u}_2^+)}\right\|_{L^2((0,T)\times\Omega)}\end{aligned}$$

and define $N := (2+e^{\frac{V_p}{2}}\widetilde{v}_1^+ + e^{\frac{V_n}{2}}\widetilde{u}_1^+)(2+e^{\frac{V_p}{2}}\widetilde{v}_2^+ + e^{\frac{V_n}{2}}\widetilde{u}_2^+)$ as a shorthand notation for the denominator. Expanding the expressions in the numerator yields

$$\begin{aligned}\widetilde{r} = \Bigg\| \frac{1}{N}\Big(& e^{\frac{V_n}{2}}(\widetilde{u}_2^+ - \widetilde{u}_1^+) + e^{\frac{V_p}{2}}(\widetilde{v}_2^+ - \widetilde{v}_1^+) \\ & + 2e^{\frac{V_n}{2}}e^{\frac{V_p}{2}}(\widetilde{u}_2^+\widetilde{v}_2^+ - \widetilde{u}_1^+\widetilde{v}_1^+) + e^{\frac{V_n}{2}}e^{V_p}\widetilde{v}_1^+\widetilde{v}_2^+(\widetilde{u}_2^+ - \widetilde{u}_1^+) + e^{V_n}e^{\frac{V_p}{2}}\widetilde{u}_1^+\widetilde{u}_2^+(\widetilde{v}_2^+ - \widetilde{v}_1^+)\Big)\Bigg\|_{L^2((0,T)\times\Omega)}\end{aligned}$$

and, consequently,

$$\begin{aligned}\widetilde{r} \le & \frac{\beta}{4}\|\widetilde{u}\|_{L^2((0,T)\times\Omega)} + \frac{\beta}{4}\|\widetilde{v}\|_{L^2((0,T)\times\Omega)} \\ & + \beta\|\widetilde{u}\|_{L^2((0,T)\times\Omega)} + \beta\|\widetilde{v}\|_{L^2((0,T)\times\Omega)} + \beta\|\widetilde{u}\|_{L^2((0,T)\times\Omega)} + \beta\|\widetilde{v}\|_{L^2((0,T)\times\Omega)}.\end{aligned}$$

We can now continue the estimate in (2.95):

$$\max_{0\le t\le T}\|u(t)\|_{L^2(\Omega)} \le C_1C_2\left((\alpha+3\beta^2)\big\|\widetilde{u}\big\|_{L^2((0,T)\times\Omega)} + 3\beta^2\big\|\widetilde{v}\big\|_{L^2((0,T)\times\Omega)}\right).$$

And since every $f\in C([0,T],L^2(\Omega))$ fulfills

$$\|f\|^2_{L^2((0,T)\times\Omega)} = \int_0^T\int_\Omega f^2\,dx\,dt \le \int_0^T dt \max_{0\le t\le T}\|f(t)\|^2_{L^2(\Omega)} = T\|f\|^2_{C([0,T],L^2(\Omega))},$$

we may proceed with the previous estimates to arrive at

$$\max_{0\le t\le T}\|u(t)\|_{L^2(\Omega)} \le C_1C_2(\alpha+3\beta^2)\sqrt{T}\Big(\|\widetilde{u}\|_{C([0,T],L^2(\Omega))} + \|\widetilde{v}\|_{C([0,T],L^2(\Omega))}\Big).$$

In the same manner, we obtain

$$\max_{0\le t\le T}\|v(t)\|_{L^2(\Omega)} \le C_1C_2(\alpha+3\beta^2)\sqrt{T}\Big(\|\widetilde{u}\|_{C([0,T],L^2(\Omega))} + \|\widetilde{v}\|_{C([0,T],L^2(\Omega))}\Big).$$

Adding the last two inequalities and choosing $T>0$ sufficiently small gives rise to

$$\|(u,v)\|_{X_T} \le c\,\|(\widetilde{u},\widetilde{v})\|_{X_T}$$

with some $c\in(0,1)$.

Step 4: Solution of (2.25). Step 2 and Step 3 guarantee that $\mathcal{S}: M_T\to M_T$ is a contraction provided that $T>0$ is sufficiently small. Due to Banach's fixed point theorem, there exists a unique $(u,v)\in M_T$ such that $\mathcal{S}(u,v)=(u,v)$. This fixed-point is the unique weak solution of

$$\begin{cases}\partial_t u - \Delta u = A_n u^+ + e^{\frac{V_n}{2}}\dfrac{1-e^{\frac{V_n}{2}}e^{\frac{V_p}{2}}u^+v^+}{2+e^{\frac{V_p}{2}}v^+ + e^{\frac{V_n}{2}}u^+}, \\ \partial_t v - \Delta v = A_p v^+ + e^{\frac{V_p}{2}}\dfrac{1-e^{\frac{V_n}{2}}e^{\frac{V_p}{2}}u^+v^+}{2+e^{\frac{V_p}{2}}v^+ + e^{\frac{V_n}{2}}u^+}.\end{cases} \tag{2.96}$$

The non-negativity of u and v now follows in the same way as in the proof of Theorem 2.1. Consequently, one can identify the unique weak solution (u, v) of (2.96) to equally solve

$$\begin{cases} \partial_t u - \Delta u = A_n u + e^{\frac{V_n}{2}} \dfrac{1 - e^{\frac{V_n}{2}} e^{\frac{V_p}{2}} uv}{2 + e^{\frac{V_p}{2}} v + e^{\frac{V_n}{2}} u}, \\ \partial_t v - \Delta v = A_p v + e^{\frac{V_p}{2}} \dfrac{1 - e^{\frac{V_n}{2}} e^{\frac{V_p}{2}} uv}{2 + e^{\frac{V_p}{2}} v + e^{\frac{V_n}{2}} u}, \end{cases} \tag{2.97}$$

which is the transformed version of the original problem (2.25).

Step 5: Global solution. We notice that the transformed Shockley–Read–Hall reaction term satisfies

$$e^{\frac{V_n}{2}} \left| \frac{1 - e^{\frac{V_n}{2}} e^{\frac{V_p}{2}} uv}{2 + e^{\frac{V_p}{2}} v + e^{\frac{V_n}{2}} u} \right| \le \beta(1 + u),$$

which allows to proceed in analogy to the proof of Theorem 2.1. As a result, the local solutions constructed above may be extended to all times $T > 0$ and satisfy the bounds

$$\|u(t)\|_{L^\infty(\Omega)}, \|v(t)\|_{L^\infty(\Omega)} \le I e^{\gamma t}$$

for $\gamma := \alpha + 2\beta$.

Step 6: L^∞-bounds for n and p. Due to the upper bound

$$\frac{1 - e^{V_n} e^{V_p} np}{2 + e^{V_p} p + e^{V_n} n} \le 1,$$

we can establish linearly growing L^∞-bounds for n and p by applying the same reasoning as in the proof of Theorem 2.1.

Step 7: Lower bounds for n and p. Now, we prove the bounds (2.28), where we will only present the arguments for the lower bound on n, since the bound for p follows analogously. Employing $u = e^{V_n/2} n$, we estimate

$$\partial_t u - \Delta u \ge A_n u - e^{V_n} u + \frac{e^{\frac{V_n}{2}}}{2 + e^{\frac{V_p}{2}} v + e^{\frac{V_n}{2}} u} \ge cu + d(t), \tag{2.98}$$

where $c \in \mathbb{R}$ is a constant and $d(t) \in \mathbb{R}$ for all $t \ge 0$. The L^∞-bounds on n and p tell us that there exist positive constants θ and γ such that $d(t) \ge \gamma/(1 + \theta t)$ for all $t \ge 0$.

We further choose $\tau > 0$ arbitrarily and recall the notation for the negative part $(u)_- = \min\{u, 0\}$. Testing (2.98) with $\big(u - \mu t\big)_-$ for a constant $\mu > 0$ to be chosen below, we estimate

$$\begin{aligned} \frac{d}{dt}\frac{1}{2}\int_\Omega \Big(u - \mu t\Big)_-^2 dx &= \int_\Omega \Big(u - \mu t\Big)_- (\partial_t u - \mu)\, dx = \int_\Omega \Big|\Big(u - \mu t\Big)_-\Big| (-\partial_t u + \mu)\, dx \\ &\le \int_\Omega \Big|\Big(u - \mu t\Big)_-\Big| (-\Delta u - cu - d(t) + \mu)\, dx \\ &\le -\int_\Omega \mathbb{1}_{u \le \mu t} |\nabla u|^2\, dx + \int_\Omega \Big|\Big(u - \mu t\Big)_-\Big| (|c| u - d(t) + \mu)\, dx. \end{aligned}$$

Thus, for $0 \le t \le \tau$ when $d(t) \ge \eta$ for some appropriate $\eta > 0$, we have

$$\frac{d}{dt}\frac{1}{2}\int_\Omega \Big(u - \mu t\Big)_-^2 dx \le \int_\Omega \Big|\Big(u - \mu t\Big)_-\Big| (|c|\mu t - \eta + \mu)\, dx \le 0,$$

provided that we choose $\mu(|c|\tau + 1) \le \eta$. Hence, since $\int_\Omega \big(u(0, x)\big)_-^2 dx = 0$, we arrive at

$$\int_\Omega \Big(u - \mu t\Big)_-^2 dx = 0, \qquad \text{for all } 0 \le t \le \tau,$$

which yields in particular $u(t,x) \geq \mu t$ for all $0 \leq t \leq \tau$ and a.a. $x \in \Omega$.

Furthermore, for $t \geq \tau$ when $d(t) \geq \gamma/(1+\theta t)$, we test (2.98) with $\big(u - \frac{\Gamma}{1+\theta t}\big)_-$ for a constant $\Gamma > 0$ to be chosen below, and estimate similar to above

$$\begin{aligned}
\frac{d}{dt}\frac{1}{2}\int_\Omega \Big(u - \frac{\Gamma}{1+\theta t}\Big)_-^2 dx &= \int_\Omega \Big(u - \frac{\Gamma}{1+\theta t}\Big)_- \left(\partial_t u + \frac{\Gamma\theta}{(1+\theta t)^2}\right) dx \\
&\leq \int_\Omega \Big(u - \frac{\Gamma}{1+\theta t}\Big)_- \left(\Delta u + cu + d(t) + \frac{\Gamma\theta}{(1+\theta t)^2}\right) dx \\
&\leq - \int_\Omega \mathbb{1}_{u \leq \frac{\Gamma}{1+\theta t}} |\nabla u|^2 \, dx + \int_\Omega \left|\Big(u - \frac{\Gamma}{1+\theta t}\Big)_-\right| \left(|c|\frac{\Gamma}{1+\theta t} - \frac{\gamma}{1+\theta t} - \frac{\Gamma\theta}{(1+\theta t)^2}\right) dx \leq 0,
\end{aligned}$$

provided that we choose $|c|\Gamma \leq \gamma$. Reducing either Γ or μ appropriately, we are able to satisfy $\frac{\Gamma}{1+\theta\tau} = \mu\tau$. On the one hand, this implies that $\int_\Omega \Big(u(\tau,x) - \frac{\Gamma}{1+\theta\tau}\Big)_-^2 dx = 0$, which yields

$$\int_\Omega \Big(u(t,x) - \frac{\Gamma}{1+\theta t}\Big)_-^2 dx = 0, \qquad \text{for all } t \geq \tau,$$

and, hence, $u(t,x) \geq \frac{\Gamma}{1+\theta t}$ for all $t \geq \tau$ and a.a. $x \in \Omega$. On the other hand, the increasing and decreasing bounds now again intersect at time τ, which finishes the proof. □

CHAPTER 3

Material Design for Optimal Excitation Induced Charge Transfer in Photovoltaic Devices

The second part of this thesis is devoted to the investigation of a microscopic model for a certain kind of a photovoltaic element. The major part of the work was carried out together with Prof. Dr. Gero Friesecke at the TU Munich.

3.1 Introductory Material

We consider a bounded domain $\Omega \subset \mathbb{R}^3$, which describes the photovoltaic unit, and a compact subset $\Omega_{nuc} \subset \Omega$, wherein the positive nuclear charge is distributed. Our modeling paradigm builds upon the assumption that every nuclear density distribution ρ_{nuc} inside Ω_{nuc} results in a specific distribution ρ_e of the negative electronic charge. Moreover, we will employ the widely-used representation of the electronic charge in terms of occupied and unoccupied orbitals (see e.g. [27]). In a simple picture, one can think of orbitals as predefined spatial distributions according to which an electron is spread over Ω (occupied orbital) or not (unoccupied orbital). These orbitals are solutions to the Kohn–Sham equations

$$H[\varphi_1, \dots, \varphi_n]\varphi_i = \lambda_i \varphi_i$$

which are a coupled system of n nonlinear Schrödinger-type equations in the case of n occupied orbitals. But note that due to the additional spin degree of freedom, every orbital can be occupied by two electrons having opposite spin. As the so-called Kohn–Sham Hamiltonian H is self-adjoint, all eigenvalues λ_i are real. One can, thus, arrange the orbitals φ_i in such a way that the corresponding orbital energies λ_i form an increasing sequence. Let us assume for the remainder of these introductory paragraphs that the sequence $(\lambda_i)_i$ is strictly monotonously increasing.

Our studies shall focus on the structure of the electronic density ρ_e in the ground state and the first excited state of the atomic system. More precisely, we are interested in the change of ρ_e when such an excitation of the system takes place. One may think of a chain of different atoms (sketched as black ticks on the left of Fig. 3.1) whose electrons arrange to electronic orbitals which are possibly distributed over all of Ω. For the subsequent studies, we will restrict ourselves to pairwise occupations of orbitals. Every orbital may thus be unoccupied or twice occupied by two electrons. In the ground state configuration, the lowest n electronic orbitals up to the *highest occupied molecular orbital* (HOMO) are all occupied by two electrons. And the first excited state only differs by the fact that HOMO is unoccupied but the *lowest unoccupied molecular orbital* (LUMO) is now occupied by two electrons (see the right of Fig. 3.1). This excitation can be achieved by an absorption of photons with an appropriate frequency.

The main goal of this chapter is to find a certain nuclear distribution ρ_{nuc} such that the difference between the electronic density in the ground state and the first excited state, respectively, becomes as large as possible. The reason for studying such a situation is motivated by a possible application in photovoltaics. Think of a flux of photons which excites the atomic ground state configuration inside the photovoltaic unit in such a way that the pair of electrons in HOMO is transferred to LUMO, as depicted on the right of Fig. 3.1. If the spatial distributions of HOMO and LUMO are accumulated to different sides of the atomic chain (or different regions of Ω, in general), this excitation simultaneously implies

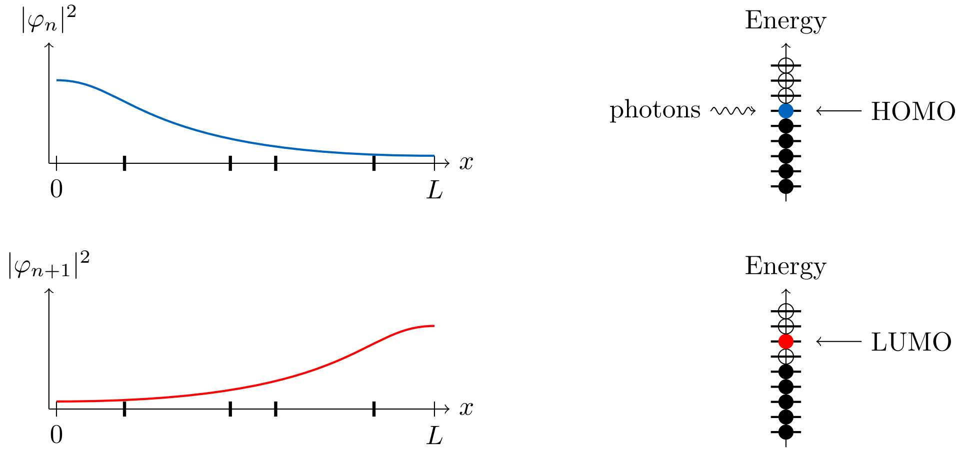

Figure 3.1: Top: The spatial distribution of HOMO and the ground state configuration of occupied orbitals. Bottom: The distribution of LUMO and the orbital configuration of the first excited state.

a transfer of electronic charge, as shown on the left of Fig. 3.1. This charge transfer could then be harvested by embedding the atomic system into an appropriate photovoltaic device to obtain an electric current, but this is beyond the scope of this thesis.

As we want to maximize the electronic charge transfer caused by the excitation itself, we may assume that the distributions of all orbitals φ_i remain unchanged. This approach is justified because we are at this point not interested in any time-dependent relaxation properties of the orbitals but only in the "instantaneous" charge transfer from HOMO to LUMO. Furthermore, we measure the distance between HOMO and LUMO by calculating the difference between the center of mass of HOMO and LUMO. Since we are working in $\mathbb{R}^3$, we additionally prescribe a direction $e \in \mathbb{R}^3$, $\|e\| = 1$, along which we want to determine the charge transfer. We are, therefore, concerned with the following optimization problem:

$$\max\, J[\vec{\varphi}, \rho_{nuc}] := \left| \int_\Omega \left(|\varphi_{n+1}|^2 - |\varphi_n|^2 \right) (x \cdot e)\, dx \right|$$

where we maximize over all admissible ρ_{nuc} specified below and all corresponding ground state orbitals $\vec{\varphi} := (\varphi_1, \ldots, \varphi_{n+1})$. The functional $J[\vec{\varphi}, \rho_{nuc}]$ will be called *charge transfer functional*.

We allow the nuclear density ρ_{nuc} to belong to a certain subset (to be specified below) of $\mathcal{M}(\mathbb{R}^3)$, which is the set of all signed measures $\mu : \mathfrak{B}^3 \to \mathbb{R}$ defined on the Borel-sets $\mathfrak{B}^3$ in $\mathbb{R}^3$. A *signed measure* $\mu : \mathfrak{B}^3 \to \mathbb{R}$ is a function satisfying $\mu(\emptyset) = 0$ and $\mu(\bigcup_{k=1}^\infty A_k) = \sum_{k=1}^\infty \mu(A_k)$ for any family $(A_k)_{k\in\mathbb{N}}$ of pairwise disjoint $A_k \in \mathfrak{B}^3$. A norm on $\mathcal{M}(\mathbb{R}^3)$ can be defined via $\|\mu\|_{\mathcal{M}(\mathbb{R}^3)} := |\mu|(\mathbb{R}^3)$ where $|\mu|$ is the *variation* of μ given by

$$|\mu|(A) := \sup \left\{ \sum_{k=1}^\infty |\mu(A_k)| \;\middle|\; A = \bigcup_{k=1}^\infty A_k,\ (A_k)_{k\in\mathbb{N}} \subset \mathfrak{B}^3 \text{ pairwise disjoint} \right\}$$

for all $A \in \mathfrak{B}^3$. The value $\|\mu\|_{\mathcal{M}(\mathbb{R}^3)}$ is called the *total variation* of μ. The following result [4, 15] will be essential for our subsequent studies.

Theorem. *The mapping $\Phi : \mathcal{M}(\mathbb{R}^3) \to C_0'(\mathbb{R}^3)$,*

$$\Phi(\mu)\, f := \int_{\mathbb{R}^3} f\, d\mu$$

is a norm-perserving isomorphism. Moreover, $\mu \geq 0$ holds true if and only if $\int_{\mathbb{R}^3} f\, d\mu \geq 0$ for all $f \in C_0(\mathbb{R}^3)$, $f \geq 0$.

In this context, $C_0(\mathbb{R}^3)$ denotes the set of all continuous functions $f : \mathbb{R}^3 \to \mathbb{R}$ with the following property: For every $\varepsilon > 0$, there exists a compact set $K \subset \mathbb{R}^3$ such that $|f| < \varepsilon$ holds true on $\mathbb{R}^3 \backslash K$. The fact that $C_0(\mathbb{R}^3)$ is separable allows us to apply the Banach–Alaoglu theorem. This gives rise to another important feature [4] of $\mathcal{M}(\mathbb{R}^3)$.

Theorem. *For every bounded sequence* $(\mu^k)_{k\in\mathbb{N}} \subset \mathcal{M}(\mathbb{R}^3)$*, there exists a subsequence* $(\mu^{k_l})_{l\in\mathbb{N}} \subset (\mu^k)_{k\in\mathbb{N}}$ *and some* $\mu \in \mathcal{M}(\mathbb{R}^3)$ *such that*

$$\int_{\mathbb{R}^3} f\, d\mu^{k_l} \to \int_{\mathbb{R}^3} f\, d\mu$$

for all $f \in C_0(\mathbb{R}^3)$*. In other words,* μ^{k_l} *is weak* convergent to* μ ($\mu^{k_l} \overset{*}{\rightharpoonup} \mu$).

The electronic orbitals $\psi_i(x,s)$ are assumed to belong to $H_0^1(\Omega \times \mathbb{Z}_2)$ and to be pairwise $L^2(\Omega)$-orthonormal. The first component represents the spatial variable x and the second one the spin variable s. The set of admissible electronic orbitals thus reads

$$A_{e,n} := \left\{\vec{\psi} \in H_0^1(\Omega \times \mathbb{Z}_2)^n \,\middle|\, \langle \psi_i(\cdot,s), \psi_j(\cdot,s)\rangle_{L^2(\Omega)} = \delta_{ij} \text{ for all } s \in \mathbb{Z}_2\right\} \tag{3.1}$$

where the subscript n determines the number of orbitals under consideration. Note that Dirichlet boundary conditions for ψ_i are incorporated directly via the function space.

We still have to specify the class of admissible nuclear densities $\rho_{nuc} \in \mathcal{M}(\mathbb{R}^3)$. First, we demand $\rho_{nuc} \geq 0$ as it shall represent a physical charge distribution. Second, we have already mentioned at the beginning of this chapter that the nuclear charges are assumed to be contained in a compact subset $\Omega_{nuc} \subset \Omega$. We, thus, impose the condition $\operatorname{supp} \rho_{nuc} \subset \Omega_{nuc}$ where the *support* [4] of a signed measure $\mu \in \mathcal{M}(\mathbb{R}^3)$, denoted $\operatorname{supp}\mu$, is defined as the smallest closed set $S \subset \mathbb{R}^3$ such that $|\mu|(\mathbb{R}^3 \backslash S) = 0$. And third, we request that $\rho_{nuc}(\mathbb{R}^3) = 2n$, which ensures an electrically neutral system in the case of n twice occupied orbitals and a total number of $2n$ electrons. Therefore, we define the set A_{nuc} of admissible nuclear densities as

$$A_{nuc} := \left\{\rho_{nuc} \in \mathcal{M}(\mathbb{R}^3) \,\middle|\, \rho_{nuc} \geq 0,\ \operatorname{supp} \rho_{nuc} \subset \Omega_{nuc},\ \rho_{nuc}(\mathbb{R}^3) = 2n\right\}. \tag{3.2}$$

In Section 3.2, we will prove the existence of a ground state and derive the Kohn–Sham equations by employing a variational principle. Section 3.3 contains the announced proof for the existence of an optimal nuclear charge distribution which causes a maximal electronic charge transfer by a light-induced excitation. And the simulation of the 1D system describing a chain of atoms is documented in Section 3.4 together with the presentation of the employed algorithms and the obtained results.

3.2 Ground State Orbitals and the Kohn–Sham Equations

As a first step towards investigations of an excitation induced charge transfer, we have to take a closer look at the ground state configuration of the electronic orbitals. More precisely, we shall prove that there exists a collection of occupied orbitals which minimizes a certain energy functional and, hence, represents a ground state configuration. Uniqueness of the ground state orbitals cannot be expected in the general case, as we will discuss below. Nevertheless, we are able to identify at least one of these configurations by solving the optimality system for a minimizer of the energy functional. This gives rise to the famous Kohn–Sham equations.

As explained above, we are given a bounded domain $\Omega \subset \mathbb{R}^3$, which corresponds to the (microscopic) photovoltaic element, and a compact set $\Omega_{nuc} \subset \Omega$, which serves as the admissible set for the distribution of the nuclear charges. We introduce the *electronic energy functional*

$$\mathcal{E}_{\rho_{nuc}}[\vec{\psi}] := \frac{1}{2}\sum_{i=1}^{n} \int_{\mathbb{R}^3\times\mathbb{Z}_2} |\nabla\psi_i|^2 + \frac{1}{2}\int_{\mathbb{R}^3} \Big(\frac{1}{|\cdot|} * \rho_e\Big)\rho_e + \int_{\mathbb{R}^3} e_x[\rho_e] - \int_{\mathbb{R}^3} \Big(\frac{1}{|\cdot|} * \rho_{nuc}\Big)\rho_e. \tag{3.3}$$

In this context, $\vec{\psi} := (\psi_1, \dots, \psi_n) \in A_{e,n}$ (defined in (3.1)) denotes the vector of those n electronic orbitals which are occupied. The electronic density is defined via

$$\rho_e := \rho_e[\vec{\psi}] := \sum_{i=1}^{n} \sum_{s\in\mathbb{Z}_2} |\psi_i(\cdot,s)|^2.$$

This formula is the same as for the density of the Slater-determinant $|\psi_1 \dots \psi_n\rangle$ known from quantum mechanics. Moreover, $\rho_{nuc} \in A_{nuc}$ (defined in (3.2)) represents the nuclear density as discussed above. The last part of the energy functional $\mathcal{E}_{\rho_{nuc}}[\vec{\psi}]$ models the energy due to the interaction between electrons and protons, whereas the first quantity corresponds to the kinetic energy contained in the electronic system. The following two terms represent the electron-electron Coulomb interaction and the ρ-dependent exact Dirac-exchange contribution

$$e_x[\rho_e] := -C_x \rho_e^{\frac{4}{3}}, \quad C_x := \frac{3}{4}\Big(\frac{3}{\pi}\Big)^{\frac{1}{3}}.$$

Lemma 3.1. *The exchange functional $e_x[\rho_e]$ satisfies the following properties:*

1. $L^2(\Omega) \supset \rho_e^k \to \rho_e \in L^2(\Omega) \implies \int_{\mathbb{R}^3} e_x[\rho_e^k] \to \int_{\mathbb{R}^3} e_x[\rho_e]$.
2. $H_0^1(\Omega \times \mathbb{Z}_2)^n \supset \vec{\psi}^k \rightharpoonup \vec{\psi} \in H_0^1(\Omega \times \mathbb{Z}_2)^n \implies \int_{\mathbb{R}^3} e_x[\rho_e^k] \to \int_{\mathbb{R}^3} e_x[\rho_e]$.

Proof. The first statement is obvious due to the continuous embedding $L^2(\Omega) \subset L^{\frac{4}{3}}(\Omega)$. The second claim follows from the first one when using the compact embedding $H_0^1(\Omega) \subset\subset L^4(\Omega)$ for $\Omega \subset \mathbb{R}^3$. □

Lemma 3.2. *Let $m \in \mathbb{N}$, $\vec{\phi} \in A_{e,m}$, $\vec{\psi} \in A_{e,n}$, $\rho_{nuc} \in A_{nuc}$ and $\rho := \sum_{i=1}^m \sum_{s \in \mathbb{Z}_2} |\phi_i(\cdot, s)|^2$.*

1. *The kinetic energy is bounded from below via*

$$\frac{1}{2}\sum_{i=1}^m \int_{\mathbb{R}^3 \times \mathbb{Z}_2} |\nabla \phi_i|^2 \geq \frac{1}{2}\int_{\mathbb{R}^3} |\nabla \sqrt{\rho}|^2.$$

2. *There exists a constant $c(m) > 0$ independent of $\vec{\phi}$ and ρ_{nuc} such that*

$$C_x \int_{\mathbb{R}^3} \rho^{\frac{4}{3}} \leq c(m) + \frac{1}{8}\int_{\mathbb{R}^3} |\nabla \sqrt{\rho}|^2.$$

3. *The electron-proton interaction satisfies the bound*

$$\int_{\mathbb{R}^3} \Big(\frac{1}{|\cdot|} * \rho_{nuc}\Big)\rho \leq 16m(2n)^2 + \frac{1}{8}\int_{\mathbb{R}^3} |\nabla \sqrt{\rho}|^2.$$

4. *As a consequence of the previous bounds, the electronic energy admits the estimate*

$$\mathcal{E}_{\rho_{nuc}}[\vec{\psi}] \geq \frac{1}{4}\sum_{i=1}^n \int_{\mathbb{R}^3 \times \mathbb{Z}_2} |\nabla \psi_i|^2 - c(n) - 8(2n)^3.$$

Proof. 1. We first calculate

$$\int_{\mathbb{R}^3} |\nabla \sqrt{\rho}|^2 = \int_{\mathbb{R}^3} \left|\frac{1}{2}\frac{\nabla \rho}{\sqrt{\rho}}\right|^2 = \frac{1}{4}\int_{\mathbb{R}^3} \frac{|\nabla \rho|^2}{\rho} = \frac{1}{4}\int_{\mathbb{R}^3} \frac{1}{\rho}\left|\sum_{i,s} \phi_i(\cdot, s)^* \nabla \phi_i(\cdot, s) + \phi_i(\cdot, s)\nabla \phi_i(\cdot, s)^*\right|^2.$$

The discrete version of the Cauchy–Schwarz inequality now entails

$$\int_{\mathbb{R}^3} |\nabla \sqrt{\rho}|^2 \leq \int_{\mathbb{R}^3} \frac{1}{\rho}\Big(\sum_{i,s} |\phi_i(\cdot, s)||\nabla \phi_i(\cdot, s)|\Big)^2$$
$$\leq \int_{\mathbb{R}^3} \frac{1}{\rho}\Big(\sum_{i,s} |\phi_i(\cdot, s)|^2\Big)\Big(\sum_{i,s} |\nabla \phi_i(\cdot, s)|^2\Big) = \sum_{i,s}\int_{\mathbb{R}^3} |\nabla \phi_i(\cdot, s)|^2.$$

2. We employ Hölder's interpolation inequality

$$\|f\|_q \leq \|f\|_p^\theta \|f\|_r^{1-\theta}, \qquad \text{where} \quad \frac{1}{q} = \frac{\theta}{p} + \frac{1-\theta}{r},$$

to $p = 1$, $q = 4/3$, $r = 3$ and $f = \rho$. This yields $\theta = 5/8$ and

$$\|\rho\|_{4/3}^{4/3} \leq \|\rho\|_1^{5/6}\|\rho\|_3^{1/2}.$$

We further recall the embedding $H^1(\Omega) \subset L^6(\Omega)$ which gives rise to a constant $C_S > 0$ such that

$$\|\rho\|_3^{1/2} = \|\sqrt{\rho}\|_6 \leq C_S \|\sqrt{\rho}\|_{H^1(\Omega)} \leq C_S C_P \|\nabla \sqrt{\rho}\|_2.$$

The constant $C_P > 0$ results from Poincaré's inequality as $\sqrt{\rho} \in H_0^1(\Omega)$. Together with Young's inequality, we thus obtain

$$C_x \int_{\mathbb{R}^3} \rho^{\frac{4}{3}} \leq C_x (2m)^{\frac{5}{6}} C_S C_P \cdot \|\nabla \sqrt{\rho}\|_2 \leq 2 C_x^2 C_S^2 C_P^2 (2m)^{\frac{5}{3}} + \frac{1}{8} \|\nabla \sqrt{\rho}\|_2^2.$$

3. Applying Fubini's theorem we find

$$\int_{\mathbb{R}^3} \Big(\frac{1}{|\cdot|} * \rho_{nuc} \Big) \rho = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(y)}{|y-x|} \, dy \, d\rho_{nuc}(x) \leq 2n \sup_{x \in \mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(y)}{|y-x|} \, dy = 2n \sup_{x \in \mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho^{(x)}(y)}{|y|} \, dy$$

where $\rho^{(x)}(y) := \rho(y+x)$. Subsequently, we apply the Cauchy–Schwarz inequality and the classical Hardy inequality in $\mathbb{R}^3$. This ensures that for any $x \in \mathbb{R}^3$

$$\int_{\mathbb{R}^3} \frac{\rho^{(x)}(y)}{|y|} \, dy = \int_{\mathbb{R}^3} \frac{\sqrt{\rho^{(x)}(y)}}{|y|} \sqrt{\rho^{(x)}(y)} \, dy \leq \left(\int_{\mathbb{R}^3} \frac{\rho^{(x)}(y)}{|y|^2} \, dy \right)^{\frac{1}{2}} \left(\int_{\mathbb{R}^3} \rho^{(x)}(y) \, dy \right)^{\frac{1}{2}}$$
$$\leq \left(4 \int_{\mathbb{R}^3} \left| \nabla \sqrt{\rho^{(x)}(y)} \right|^2 dy \right)^{\frac{1}{2}} \sqrt{2m} = \sqrt{2m} \left(4 \int_{\mathbb{R}^3} \left| \nabla \sqrt{\rho(y)} \right|^2 dy \right)^{\frac{1}{2}},$$

where the last expression is independent of x. We, finally, derive

$$\int_{\mathbb{R}^3} \Big(\frac{1}{|\cdot|} * \rho_{nuc} \Big) \rho \leq 4n\sqrt{2m} \cdot \left(\int_{\mathbb{R}^3} |\nabla \sqrt{\rho}|^2 \right)^{\frac{1}{2}} \leq 16m(2n)^2 + \frac{1}{8} \int_{\mathbb{R}^3} |\nabla \sqrt{\rho}|^2$$

where we have used Young's inequality in the last step.

4. From the definition of $\mathcal{E}_{\rho_{nuc}}[\vec{\psi}]$ and the lower bound on the kinetic energy, we see that

$$\mathcal{E}_{\rho_{nuc}}[\vec{\psi}] \geq \frac{1}{4} \sum_{i=1}^n \int_{\mathbb{R}^3 \times \mathbb{Z}_2} |\nabla \psi_i|^2 + \frac{1}{4} \int_{\mathbb{R}^3} |\nabla \sqrt{\rho_e}|^2 - C_x \int_{\mathbb{R}^3} \rho_e^{\frac{4}{3}} - \int_{\mathbb{R}^3} \Big(\frac{1}{|\cdot|} * \rho_{nuc} \Big) \rho_e.$$

The previous bounds further imply

$$\mathcal{E}_{\rho_{nuc}}[\vec{\psi}] \geq \frac{1}{4} \sum_{i=1}^n \int_{\mathbb{R}^3 \times \mathbb{Z}_2} |\nabla \psi_i|^2 - c(n) - 8(2n)^3,$$

which proves the claim. □

Up to now, we have not further specified which orbitals ψ_i are occupied in the ground state configuration for a fixed nuclear charge distribution $\rho_{nuc} \in A_{nuc}$, and in general, these orbitals are not uniquely determined. Nevertheless, the characteristic property of ground state orbitals is the minimization of the electronic energy functional $\mathcal{E}_{\rho_{nuc}}[\vec{\psi}]$. One therefore calls a tupel $(\varphi_1, \ldots, \varphi_n) \in A_{e,n}$ *ground state orbitals*, if they satisfy

$$(\varphi_1, \ldots, \varphi_n) \in \operatorname{argmin} \left\{ \mathcal{E}_{\rho_{nuc}}[\vec{\psi}] \,\middle|\, \vec{\psi} \in A_{e,n} \right\}.$$

We will now show that there exists at least one minimizer of $\mathcal{E}_{\rho_{nuc}}[\vec{\psi}]$ by employing a well-known technique in the context of variational problems. First, one ensures that $\mathcal{E}_{\rho_{nuc}}[\vec{\psi}]$ is bounded from below, which enables one to choose a minimizing sequence. Having established boundedness of such a minimizing sequence, we are able to extract a weakly convergent subsequence. This weak limit will then turn out to be a minimizer of the energy functional $\mathcal{E}_{\rho_{nuc}}[\vec{\psi}]$.

Lemma 3.3. *$\mathcal{E}_{\rho_{nuc}}[\vec{\psi}]$ is bounded from below on $A_{e,n}$.*

Proof. This claim is an immediate consequence of Lemma 3.2. □

As a result of the boundedness of $\mathcal{E}_{\rho_{nuc}}$ from below, we can now choose a minimizing sequence $(\vec{\psi}^k) \subset A_{e,n}$. The following Lemma shows that this sequence $(\vec{\psi}^k)$ is bounded in $H_0^1(\Omega \times \mathbb{Z}_2)^n$.

Lemma 3.4. *Minimizing sequences $(\vec{\psi}^k) \subset A_{e,n}$ for $\mathcal{E}_{\rho_{nuc}}$ are bounded in $H_0^1(\Omega \times \mathbb{Z}_2)^n$.*

Proof. Lemma 3.2 guarantees that

$$\mathcal{E}_{\rho_{nuc}}[\vec{\psi}] \geq \frac{1}{4} \sum_{i=1}^{n} \int_{\mathbb{R}^3 \times \mathbb{Z}_2} |\nabla \psi_i|^2 - c(n) - 8(2n)^3.$$

for all $\vec{\psi} \in A_{e,n}$. As the left hand side is bounded along the minimizing sequence $(\vec{\psi}^k)$, this also holds true for the kinetic energy term on the right hand side. □

We are now able to prove the existence of a ground state configuration by showing that the weak limit of an appropriate subsequence of a minimizing sequence is actually a minimizer of $\mathcal{E}_{\rho_{nuc}}$.

Proposition 3.5. *There exists a minimizer $\vec{\varphi} \in A_{e,n}$ for $\mathcal{E}_{\rho_{nuc}}$.*

Proof. From Lemma 3.3, we know that a minimizing sequence $(\vec{\psi}^k) \subset A_{e,n}$ exists, which is even bounded thanks to Lemma 3.4. Due to the reflexivity of $H_0^1(\Omega\times\mathbb{Z}_2)^n$, there exists a weakly convergent subsequence $\vec{\varphi}^k \rightharpoonup \vec{\varphi} \in H_0^1(\Omega\times\mathbb{Z}_2)^n$. The limiting vector $\vec{\varphi}$ again consists of pairwise orthonormal components, which results from the strong convergence of $(\vec{\varphi}^k)$ in $L^2(\Omega \times \mathbb{Z}_2)^n$. Hence, $\vec{\varphi} \in A_{e,n}$. For demonstrating that $\vec{\varphi}$ is a minimizer of $\mathcal{E}_{\rho_{nuc}}$, it suffices to check that

$$\mathcal{E}_{\rho_{nuc}}[\vec{\varphi}] \leq \liminf_{k\to\infty} \mathcal{E}_{\rho_{nuc}}[\vec{\varphi}^k], \tag{3.4}$$

where the electronic energy functional is given by

$$\mathcal{E}_{\rho_{nuc}}[\vec{\varphi}] = \frac{1}{2} \sum_{i=1}^{n} \int_{\mathbb{R}^3 \times \mathbb{Z}_2} |\nabla \varphi_i|^2 + \frac{1}{2} \int_{\mathbb{R}^3} \Big(\frac{1}{|\cdot|} * \rho_e\Big)\rho_e + \int_{\mathbb{R}^3} e_x[\rho_e] - \int_{\mathbb{R}^3} \Big(\frac{1}{|\cdot|} * \rho_{nuc}\Big)\rho_e. \tag{3.5}$$

We know that each summand within the first term is weakly lower semi-continuous as a function of $\varphi_i \in H_0^1(\Omega \times \mathbb{Z}_2)$ since it equals the square of the L^2-norm of $\nabla\varphi_i \in L^2(\Omega \times \mathbb{Z}_2)$. And as Lemma 3.1 shows that the third term is continuous as a function of $\rho_e \in L^2(\Omega)$, both expressions satisfy a relation analog to (3.4).

Concerning the convergence of the second term within (3.5), we keep in mind that $\rho_e^k \to \rho_e$ in $L^2(\Omega)$ because of $\vec{\varphi}^k \rightharpoonup \vec{\varphi}$ in $H_0^1(\Omega\times\mathbb{Z}_2)^n$ and the compact embedding of $H_0^1(\Omega)$ into $L^4(\Omega)$. Hölder's inequality further implies

$$\left\|\frac{1}{|\cdot|} * (\rho_e^k - \rho_e)\right\|_{L^\infty(\mathbb{R}^3)} = \sup_{x\in\mathbb{R}^3} \left|\int_\Omega \frac{1}{|x-\cdot|}(\rho_e^k - \rho_e)\right| \leq \sup_{x\in\mathbb{R}^3} \left\|\frac{1}{|x-\cdot|}\right\|_{L^2(\Omega)} \|\rho_e^k - \rho_e\|_{L^2(\Omega)} \to 0.$$

The desired convergence of the electron-electron Coulomb energy now follows from an additional $L^2(\Omega)$-$L^2(\Omega)$ Hölder estimate:

$$\left|\int_\Omega \Big(\frac{1}{|\cdot|} * \rho_e^k\Big)\rho_e^k - \int_\Omega \Big(\frac{1}{|\cdot|} * \rho_e\Big)\rho_e\right| \leq \left\|\frac{1}{|\cdot|} * \rho_e^k\right\|_{L^2} \|\rho_e^k - \rho_e\|_{L^2} + \left\|\frac{1}{|\cdot|} * (\rho_e^k - \rho_e)\right\|_{L^2} \|\rho_e\|_{L^2} \to 0.$$

We are now left to verify the convergence of the fourth term within (3.5). To this end, we interchange the order of integration using Fubini's theorem and argue that

$$\int_{\mathbb{R}^3} \Big(\frac{1}{|\cdot|} * \rho_e^k\Big) d\rho_{nuc} \to \int_{\mathbb{R}^3} \Big(\frac{1}{|\cdot|} * \rho_e\Big) d\rho_{nuc}.$$

Above, we have already established uniform convergence of the integrand on $\mathbb{R}^3$. This results in

$$\left|\int_{\mathbb{R}^3} \Big(\frac{1}{|\cdot|} * \rho_e^k\Big) d\rho_{nuc} - \int_{\mathbb{R}^3} \Big(\frac{1}{|\cdot|} * \rho_e\Big) d\rho_{nuc}\right| \leq \left\|\frac{1}{|\cdot|} * (\rho_e^k - \rho_e)\right\|_{L^\infty(\mathbb{R}^3)} \int_{\mathbb{R}^3} d\rho_{nuc} \to 0.$$

As a consequence, (3.4) is proven and $\vec{\varphi} \in A_{e,n}$ is a minimizer of $\mathcal{E}_{\rho_{nuc}}$. □

Having demonstrated the existence of ground state orbitals, we will briefly comment on the fact that they are not unique. This is a direct consequence of the unitary invariance of the electronic energy functional $\mathcal{E}_{\rho_{nuc}}$.

Proposition 3.6. *Let $\vec{\psi} \in A_{e,n}$ and $U \in \mathbb{C}^{n\times n}$ be a unitary matrix. Then, $U\vec{\psi} \in A_{e,n}$ and*

$$\mathcal{E}_{\rho_{nuc}}[\vec{\psi}] = \mathcal{E}_{\rho_{nuc}}[U\vec{\psi}].$$

In particular, the set of ground state orbitals is invariant under unitary transformations.

Proof. The unitary invariance of $A_{e,n}$ can be verified by an elementary calculation. A closer look at the definition of $\mathcal{E}_{\rho_{nuc}}[\vec{\psi}]$ in (3.3) reveals that the energy functional is unitary invariant provided the kinetic energy and the electronic density are unitary invariant. Since the reasoning for the kinetic energy is practically the same as for the electronic density, we shall only detail the argument for ρ_e. We set $\vec{\psi}' := U\vec{\psi}$ and find

$$\rho_e' := \sum_{i=1}^{n}\sum_{s\in\mathbb{Z}_2} |\psi_i'(\cdot,s)|^2 = \sum_{s\in\mathbb{Z}_2} (\psi_1^*(\cdot,s),\ldots,\psi_n^*(\cdot,s))U^*U(\psi_1(\cdot,s),\ldots,\psi_n(\cdot,s))^T = \sum_{i=1}^{n}\sum_{s\in\mathbb{Z}_2} |\psi_i(\cdot,s)|^2$$

which is equivalent to $\rho_e' = \rho_e$. □

Despite the lack of uniqueness of ground state orbitals, one can derive optimality conditions for minimizer of $\mathcal{E}_{\rho_{nuc}}$ and solve them for the corresponding orbitals. This approach results in the famous Kohn–Sham equations.

Proposition 3.7. *Let $\vec{\psi} \in A_{e,n}$ be a minimizer of $\mathcal{E}_{\rho_{nuc}}$. Then, there exists a unitary matrix $U \in \mathbb{C}^{n\times n}$ such that $\vec{\varphi} := U\vec{\psi}$ satisfies*

$$H\varphi_i := \Big(-\frac{1}{2}\Delta + \frac{1}{|\cdot|} * \big(\rho_e - \rho_{nuc}\big) + e_x'[\rho_e]\Big)\varphi_i = \lambda_i\varphi_i.$$

The operator H is called the Kohn–Sham Hamiltonian *and the corresponding equations are referred to as the* Kohn–Sham equations*.*

Proof. We start by choosing a vector $\vec{\psi} \in A_{e,n}$ which is a minimizer of

$$\mathcal{E}_{\rho_{nuc}}[\vec{\psi}] = \frac{1}{2}\sum_{i=1}^{n}\int_{\mathbb{R}^3\times\mathbb{Z}_2} |\nabla\psi_i|^2 + \frac{1}{2}\int_{\mathbb{R}^3}\Big(\frac{1}{|\cdot|} * \rho_e\Big)\rho_e + \int_{\mathbb{R}^3} e_x[\rho_e] - \int_{\mathbb{R}^3}\Big(\frac{1}{|\cdot|} * \rho_{nuc}\Big)\rho_e.$$

For each component ψ_i, we now perform a variation $\psi_i \mapsto \psi_i + \varepsilon\chi$ where $\varepsilon \in \mathbb{R}$ and $\chi \in H_0^1(\Omega\times\mathbb{Z}_2)$ fulfills the constraints $\langle\psi_j,\chi\rangle = 0$ for all $1 \le j \le n$. As a result of the orthonormality of $\{\psi_i(\cdot,s)\}_i$ for all $s \in \mathbb{Z}_2$ and the assumption on χ, the norm and orthogonality constraints on $\psi_i + \varepsilon\chi$ are preserved in the following sense for all $s \in \mathbb{Z}_2$:

$$\langle\psi_i + \varepsilon\chi, \psi_i + \varepsilon\chi\rangle_{L^2(\Omega)} = 1 + \mathcal{O}(\varepsilon^2) \quad \text{and} \quad \langle\psi_j, \psi_i + \varepsilon\chi\rangle_{L^2(\Omega)} = 0 \quad \text{for } j \neq i.$$

As $\varepsilon = 0$ is optimal for the mapping $\varepsilon \mapsto \mathcal{E}_{\rho_{nuc}}[\psi_1,\ldots,\psi_i+\varepsilon\chi,\ldots,\psi_n]$, there exist Lagrange multiplier $\Lambda_{ij} \in \mathbb{C}$ such that

$$\frac{d}{d\varepsilon}\Big|_{\varepsilon=0} \mathcal{E}_{\rho_{nuc}}[\psi_1,\ldots,\psi_i+\varepsilon\chi,\ldots,\psi_n] = \Lambda_{ii}^*\frac{d}{d\varepsilon}\Big|_{\varepsilon=0}\langle\psi_i+\varepsilon\chi,\psi_i+\varepsilon\chi\rangle_{L^2(\Omega)} + \sum_{j\neq i}\Lambda_{ij}^*\frac{d}{d\varepsilon}\Big|_{\varepsilon=0}\varepsilon\langle\psi_j,\chi\rangle_{L^2(\Omega)}.$$

A couple of elementary calculations gives rise to

$$\mathrm{Re}\Big(\int_{\mathbb{R}^3\times\mathbb{Z}_2}\nabla\psi_i^*\,\nabla\chi + \int_{\mathbb{R}^3\times\mathbb{Z}_2}\Big(\frac{1}{|\cdot|} * \rho_e\Big)2\psi_i^*\chi + \int_{\mathbb{R}^3\times\mathbb{Z}_2} e_x'[\rho_e]2\psi_i^*\chi - \int_{\mathbb{R}^3\times\mathbb{Z}_2}\Big(\frac{1}{|\cdot|} * \rho_{nuc}\Big)2\psi_i^*\chi\Big) = 2\Lambda_{ii}^*\,\mathrm{Re}\int_{\mathbb{R}^3\times\mathbb{Z}_2}\psi_i^*\chi + \sum_{j\neq i}\Lambda_{ij}^*\int_{\mathbb{R}^3\times\mathbb{Z}_2}\psi_j^*\chi. \quad (3.6)$$

Since $\chi \in H_0^1(\Omega \times \mathbb{Z}_2)$ is arbitrary, we first get rid of the real parts by taking the sum of (3.6) as above and i times (3.6) where χ is replaced by $-i\chi$. Moreover, we integrate by parts the first term on the left hand side and collect the terms on the right hand side. We then arrive at

$$H\psi_i := \Big(-\frac{1}{2}\Delta + \frac{1}{|\cdot|} * \Big(\rho_e - \rho_{nuc}\Big) + e_x'[\rho_e]\Big)\psi_i = \sum_{j=1}^{n} \Lambda_{ij}\psi_j.$$

Due to the self-adjointness of H, we further conclude that $(\Lambda_{ij})_{ij}$ is hermitian:

$$\Lambda_{ij} = \langle \psi_j, H\psi_i \rangle = \langle H\psi_j, \psi_i \rangle = \langle \psi_i, H\psi_j \rangle^* = \Lambda_{ji}^*.$$

As a consequence, there exists a unitary $U \in \mathbb{C}^{n\times n}$ and $\lambda_i \in \mathbb{R}$ such that

$$U^{-1}\Lambda U = \begin{pmatrix} \lambda_1 & & \\ & \ddots & \\ & & \lambda_n \end{pmatrix}.$$

Defining $\vec{\varphi} := U^{-1}\vec{\psi}$ thus gives a solution of the Kohn–Sham equations

$$H\varphi_i = \Big(-\frac{1}{2}\Delta + \frac{1}{|\cdot|} * \Big(\rho_e - \rho_{nuc}\Big) + e_x'[\rho_e]\Big)\varphi_i = \lambda_i\varphi_i.$$

And this $\vec{\varphi}$ is also a minimizer of $\mathcal{E}_{\rho_{nuc}}$ as the electronic energy is invariant under unitary transformations due to Lemma 3.6. □

3.3 Existence of Optimal Nuclear Densities

We now come to the main result of this chapter, which guarantees that there exists a certain distribution of the nuclear charges such that the resulting electronic charge separation between HOMO and LUMO attains its maximal value. As above, we choose a domain $\Omega \subset \mathbb{R}^3$ being open and bounded, as well as a compact subset $\Omega_{nuc} \subset \Omega$. The set of admissible nuclear mass distributions reads

$$A_{nuc} = \Big\{\rho_{nuc} \in \mathcal{M}(\mathbb{R}^3) \;\Big|\; \rho_{nuc} \geq 0,\ \operatorname{supp}\rho_{nuc} \subset \Omega_{nuc},\ \rho_{nuc}(\mathbb{R}^3) = 2n\Big\}.$$

It contains all non-negative, bounded Borel-measures on $\mathbb{R}^3$ which are supported inside Ω_{nuc} and describe a total nuclear mass of $2n$. Additional constraints are possible as long as they do not violate the compactness property from Proposition 3.8 below. In Section 3.4, we will investigate nuclear densities which are the sum of a certain number of Gaussian distributions at fixed positions representing the atomic cores. All subsequent results hold true also for mass distributions of this type (see the discussion at the end of this section).

In the previous section, we have studied the ground state configuration of n orbitals which are all twice occupied. In this situation, we did not pay attention to a specific order of the orbitals. However, if we are dealing with HOMO and LUMO, we have to specify which of the n orbitals corresponds to HOMO. And we also need a condition which characterizes LUMO. We, therefore, consider $n+1$ electronic ground state orbitals $\vec{\varphi} := (\varphi_1, \dots, \varphi_{n+1}) \in A_{e,n+1}$ which satisfy the subsequent conditions (i), (ii) and (iii).

For technical reasons, we introduce the following shorthand notations for certain components and subvectors of *any* $\vec{\varphi} \in H_0^1(\Omega \times \mathbb{Z}_2)^{n+1}$ and related objects like $\vec{\varphi}^k$:

$$\begin{aligned} \vec{\psi} &:= (\varphi_1, \dots, \varphi_n), \\ \vec{v} &:= (\varphi_1, \dots, \varphi_{n-1}), \\ \chi &:= \varphi_n, \quad \omega := \varphi_{n+1}, \end{aligned} \qquad \vec{\varphi} = (\overbrace{\overbrace{\varphi_1, \dots, \varphi_{n-1}}^{\vec{v}}, \underbrace{\varphi_n}_{\chi}}^{\vec{\psi}}, \underbrace{\varphi_{n+1}}_{\omega}). \tag{3.7}$$

The main advantage of this notation consists in preventing additional subindices which determine the components and parts of $\vec{\varphi}$, respectively.

The first condition demands that the orbitals $\varphi_1, \dots, \varphi_n$ are all twice occupied in the ground state. This constraint has already been used in Section 3.2.

(i) $(\varphi_1, \dots, \varphi_n) \in \operatorname{argmin} \left\{ \mathcal{E}_{\rho_{nuc}}[\vec{\phi}] \,\middle|\, \vec{\phi} \in A_{e,n} \right\}$ where

$$\mathcal{E}_{\rho_{nuc}}[\vec{\phi}] = \frac{1}{2} \sum_{i=1}^{n} \int_{\mathbb{R}^3 \times \mathbb{Z}_2} |\nabla \phi_i|^2 + \frac{1}{2} \int_{\mathbb{R}^3} \Big(\frac{1}{|\cdot|} * \rho_e \Big) \rho_e + \int_{\mathbb{R}^3} e_x[\rho_e] - \int_{\mathbb{R}^3} \Big(\frac{1}{|\cdot|} * \rho_{nuc} \Big) \rho_e.$$

We recall that

$$\rho_e = \sum_{i=1}^{n} \sum_{s \in \mathbb{Z}_2} |\phi_i(\cdot, s)|^2.$$

The following constraint guarantees that φ_n is indeed the energetically highest orbital which is occupied in the ground state. Literally, we are looking for that orbital which lowers the electronic energy at most when removing it from the set of occupied orbitals.

(ii) $\varphi_n \in \operatorname{argmin} \left\{ \mathcal{E}^{-}_{\vec{\psi}, \rho_{nuc}}[\phi] \,\middle|\, \phi \in \{\varphi_1, \dots, \varphi_n\} \right\}$ where

$$\mathcal{E}^{-}_{\vec{\psi}, \rho_{nuc}}[\phi] := \mathcal{E}_{\rho_{nuc}}[\vec{\psi}] - \frac{1}{2} \int_{\mathbb{R}^3 \times \mathbb{Z}_2} |\nabla \phi|^2 - \int_{\mathbb{R}^3} e_x[\rho_e] + \int_{\mathbb{R}^3} e_x \Big[\rho_e - \sum_{s \in \mathbb{Z}_2} |\phi(\cdot, s)|^2 \Big] + \int_{\mathbb{R}^3 \times \mathbb{Z}_2} \Big(\frac{1}{|\cdot|} * (\rho_{nuc} - \rho_e) \Big) |\phi|^2 + \frac{1}{2} \int_{\mathbb{R}^3 \times \mathbb{Z}_2} \Big(\frac{1}{|\cdot|} * |\phi|^2 \Big) |\phi|^2.$$

The third condition determines possible choices for LUMO by the solution of another variational problem. In this case, both the electronic potential generated by $\varphi_1, \dots, \varphi_n$ and the nuclear potential serve as external quantities independent of the choice for LUMO. This is also the reason for the factor 1/2 in (i) and the factor 1 in (iii) in front of the electronic potential.

(iii) $\varphi_{n+1} \in \operatorname{argmin} \left\{ \mathcal{E}^{+}_{\rho_e, \rho_{nuc}}[\phi] \,\middle|\, \phi \in A_{e,1},\ \phi(\cdot, s) \perp \{\varphi_i(\cdot, s)\}_{i=1}^{n} \text{ for all } s \in \mathbb{Z}_2 \right\}$ where

$$\mathcal{E}^{+}_{\rho_e, \rho_{nuc}}[\phi] := \frac{1}{2} \int_{\mathbb{R}^3 \times \mathbb{Z}_2} |\nabla \phi|^2 + \int_{\mathbb{R}^3 \times \mathbb{Z}_2} \Big(\frac{1}{|\cdot|} * (\rho_e - \rho_{nuc}) \Big) |\phi|^2 - \int_{\mathbb{R}^3} e_x[\rho_e] + \int_{\mathbb{R}^3} e_x \Big[\rho_e + \sum_{s \in \mathbb{Z}_2} |\phi(\cdot, s)|^2 \Big].$$

We are now able to state the optimization problem which we are going to investigate in this section. Our aim is to maximize the charge transfer functional $J[\vec{\varphi}, \rho_{nuc}]$ as a function of the ground state orbitals $\vec{\varphi} \in A_{e,n+1}$ and the nuclear density $\rho_{nuc} \in A_{nuc}$:

$$\max\ J[\vec{\varphi}, \rho_{nuc}] := \left| \int_{\Omega} \left(|\varphi_{n+1}|^2 - |\varphi_n|^2 \right) (x \cdot e) \, dx \right|.$$

Here, $e \in \mathbb{R}^3$, $\|e\| = 1$ serves as the direction along which we calculate the resulting charge transfer from HOMO to LUMO. The optimization is performed simultaneously over all $(\vec{\varphi}, \rho_{nuc}) \in A_{e,n+1} \times A_{nuc}$ such that (i), (ii) and (iii) are fulfilled. In other words, $(\varphi_1, \dots, \varphi_n)$ are ground state orbitals, φ_n equals HOMO and φ_{n+1} equals LUMO.

In order to prove that there exists an optimal nuclear density resulting in a maximal charge transfer from HOMO to LUMO, we first prove that the set of all pairs $(\vec{\varphi}, \rho_{nuc}) \in A_{e,n+1} \times A_{nuc}$ satisfying (i), (ii) and (iii) is weakly × weak* sequentially compact. Together with the weak × weak* continuity of the charge transfer functional $J[\vec{\varphi}, \rho_{nuc}]$, we are able to deduce the existence of an optimal nuclear charge density. But most of the work is necessary for the subsequent compactness result.

Proposition 3.8. *The subset*

$$A := \{ (\vec{\varphi}, \rho_{nuc}) \in A_{e,n+1} \times A_{nuc} \,|\, \textit{(i), (ii), (iii) are satisfied} \}$$

is weakly × weak sequentially compact in* $H^1_0(\Omega \times \mathbb{Z}_2)^{n+1} \times \mathcal{M}(\mathbb{R}^3)$.

Proof. Let $(\vec{\varphi}^k, \rho^k_{nuc}) \subset A$. We first show that there exists some $C > 0$ such that $\|\vec{\varphi}^k\|_{H^1(\Omega\times\mathbb{Z}_2)^{n+1}} \leq C$ for all k. Besides, we recall the notation $(\vec{\psi}^k, \omega^k) = \vec{\varphi}^k$ with $\vec{\psi}^k \in A_{e,n}$ and $\omega^k \in A_{e,1}$ introduced in (3.7). Thanks to Lemma 3.2, we have

$$\frac{1}{4}\sum_{i=1}^n \int_{\mathbb{R}^3\times\mathbb{Z}_2} |\nabla\varphi_i^k|^2 \leq \mathcal{E}_{\rho^k_{nuc}}[\vec{\psi}^k] + c(n) + 8(2n)^3 \leq \mathcal{E}_{\rho^k_{nuc}}[\vec{\psi}'] + c(n) + 8(2n)^3$$
$$\leq \frac{1}{2}\sum_{i=1}^n \int_{\mathbb{R}^3\times\mathbb{Z}_2} |\nabla\psi_i'|^2 + \frac{1}{2}\int_{\mathbb{R}^3} \Big(\frac{1}{|\cdot|} * \rho_e'\Big)\rho_e' + c(n) + 8(2n)^3, \quad (3.8)$$

where $\vec{\psi}' \in A_{e,n}$ is an arbitrary trial function. As the right hand side is independent of both $\vec{\varphi}^k$ and ρ^k_{nuc}, the bound on $\|\vec{\psi}^k\|_{H^1(\Omega\times\mathbb{Z}_2)^n}$ follows.

Using the elementary inequality $(a+b)^{4/3} \leq 2^{2/3}(a^{4/3} + b^{4/3})$ for all $a, b \geq 0$, we derive the estimate

$$\mathcal{E}^+_{\rho_e,\rho_{nuc}}[\phi] \geq \frac{1}{2}\int_{\mathbb{R}^3\times\mathbb{Z}_2} |\nabla\phi|^2 - \int_{\mathbb{R}^3\times\mathbb{Z}_2} \Big(\frac{1}{|\cdot|} * \rho_{nuc}\Big)|\phi|^2 - C_x\int_{\mathbb{R}^3} \Big(\rho_e + \sum_{s\in\mathbb{Z}_2} |\phi(\cdot,s)|^2\Big)^{\frac{4}{3}}$$
$$\geq \Big(\frac{2}{8} + \frac{1}{5}\Big)\int_{\mathbb{R}^3\times\mathbb{Z}_2} |\nabla\phi|^2 - \int_{\mathbb{R}^3\times\mathbb{Z}_2} \Big(\frac{1}{|\cdot|} * \rho_{nuc}\Big)|\phi|^2 - 2^{\frac{2}{3}}C_x\int_{\mathbb{R}^3} \Big(\sum_{s\in\mathbb{Z}_2} |\phi(\cdot,s)|^2\Big)^{\frac{4}{3}} - 2^{\frac{2}{3}}C_x\int_{\mathbb{R}^3} \rho_e^{\frac{4}{3}}$$
$$\geq \frac{1}{8}\int_{\mathbb{R}^3\times\mathbb{Z}_2} |\nabla\phi|^2 - 16(2n)^2 - 2^{\frac{2}{3}}c(1) - 2^{\frac{2}{3}}\Big(c(n) + \frac{1}{8}\sum_{i=1}^n \int_{\mathbb{R}^3\times\mathbb{Z}_2} |\nabla\varphi_i|^2\Big)$$

where $c(1)$ and $c(n)$ are constants introduced in Lemma 3.2. Evaluated along $(\vec{\varphi}^k, \rho^k_{nuc}) = (\vec{\psi}^k, \omega^k, \rho^k_{nuc})$, the term at the end of the last line above is bounded independent of k due to (3.8). Consequently, there exists a constant $C_1 > 0$ independent of k such that for some trial function $\omega' \in A_{e,1}$ satisfying $\omega(\cdot,s) \perp \{\varphi_i(\cdot,s)\}_{i=1}^n$ for all $s \in \mathbb{Z}_2$ one has

$$\frac{1}{8}\int_{\mathbb{R}^3\times\mathbb{Z}_2} |\nabla\omega^k|^2 \leq \mathcal{E}^+_{\rho_e^k,\rho^k_{nuc}}[\omega^k] + C_1 \leq \mathcal{E}^+_{\rho_e^k,\rho^k_{nuc}}[\omega'] + C_1$$
$$\leq \frac{1}{2}\int_{\mathbb{R}^3\times\mathbb{Z}_2} |\nabla\omega'|^2 + \int_{\mathbb{R}^3\times\mathbb{Z}_2} \Big(\frac{1}{|\cdot|} * \rho_e^k\Big)|\omega'|^2 - \int_{\mathbb{R}^3} e_x[\rho_e^k] + C_1$$
$$\leq \frac{1}{2}\int_{\mathbb{R}^3\times\mathbb{Z}_2} |\nabla\omega'|^2 + \Big\|\frac{1}{|\cdot|}\Big\|_{L^2(\Omega)}\Big\|\sum_{s\in\mathbb{Z}_2} |\omega'(\cdot,s)|^2\Big\|_{L^2(\Omega)} \|\rho_e^k\|_{L^1(\Omega)} + c(n) + \frac{1}{8}\sum_{i=1}^n \int_{\mathbb{R}^3\times\mathbb{Z}_2} |\nabla\varphi_i^k|^2 + C_1$$
$$\leq \frac{1}{2}\int_{\mathbb{R}^3\times\mathbb{Z}_2} |\nabla\omega'|^2 + 2n\Big\|\frac{1}{|\cdot|}\Big\|_{L^2(\Omega)}\Big\|\sum_{s\in\mathbb{Z}_2} |\omega'(\cdot,s)|^2\Big\|_{L^2(\Omega)} + C_2$$

with a constant $C_2 > 0$ independent of k due to (3.8). Here, we have applied Young's inequality for convolutions in the third line. This proves the bound on $\|\omega^k\|_{H^1(\Omega\times\mathbb{Z}_2)}$ and, hence, on $\|\vec{\varphi}^k\|_{H^1(\Omega\times\mathbb{Z}_2)^{n+1}}$ as claimed above.

We further have

$$\|\rho^k_{nuc}\|_{\mathcal{M}(\mathbb{R}^3)} = |\rho^k_{nuc}|(\mathbb{R}^3) = \rho^k_{nuc}(\mathbb{R}^3) = 2n.$$

Due to the Banach–Alaoglu theorem, there exists a subsequence $(\vec{\varphi}^{k_l}, \rho^{k_l}_{nuc}) \subset (\vec{\varphi}^k, \rho^k_{nuc})$ such that

$$\vec{\varphi}^{k_l} \rightharpoonup \vec{\varphi} \in H^1_0(\Omega\times\mathbb{Z}_2)^{n+1} \quad \text{and} \quad \rho^{k_l}_{nuc} \overset{*}{\rightharpoonup} \rho_{nuc} \in \mathcal{M}(\mathbb{R}^3).$$

We show that $\rho_{nuc} \in A_{nuc}$ and $(\vec{\varphi}, \rho_{nuc})$ satisfy (i), (ii), (iii). Concerning $\rho_{nuc} \geq 0$, we take an arbitrary $f \in C_0(\mathbb{R}^3)$, $f \geq 0$, and obtain $\int_{\mathbb{R}^3} f\, d\rho_{nuc} = \lim_{l\to\infty}\int_{\mathbb{R}^3} f\, d\rho^{k_l}_{nuc} \geq 0$ since $\rho^{k_l}_{nuc} \geq 0$ for all l. Next, assume that $\operatorname{supp}\rho_{nuc} \not\subset \Omega_{nuc}$. Then, there exists some $x \in \operatorname{supp}\rho_{nuc}\backslash\Omega_{nuc}$ and a compact neighborhood U of x satisfying $U \subset \mathbb{R}^3\backslash\Omega_{nuc}$ and $\rho_{nuc}(U) > 0$. Besides, there exists some $f \in C_0(\mathbb{R}^3)$ such that $f = 1$ on U, $f = 0$ on Ω_{nuc} and $f \geq 0$. This gives rise to $\int_{\mathbb{R}^3} f\, d\rho_{nuc} \geq \int_U f\, d\rho_{nuc} = \rho_{nuc}(U) > 0$. On the other hand, $\int_{\mathbb{R}^3} f\, d\rho_{nuc} = \lim_{l\to\infty}\int_{\mathbb{R}^3} f\, d\rho^{k_l}_{nuc} = \lim_{l\to\infty}\int_{\Omega_{nuc}} f\, d\rho^{k_l}_{nuc} = 0$ — a contradiction. And for proving $\rho_{nuc}(\mathbb{R}^3) = 2n$, we choose some $f \in C_0(\mathbb{R}^3)$ satisfying $f = 1$ on Ω_{nuc} and calculate

$$\rho_{nuc}(\mathbb{R}^3) = \int_{\mathbb{R}^3} d\rho_{nuc} = \int_{\mathbb{R}^3} f\, d\rho_{nuc} = \lim_{l\to\infty}\int_{\mathbb{R}^3} f\, d\rho^{k_l}_{nuc} = \lim_{l\to\infty}\int_{\mathbb{R}^3} d\rho^{k_l}_{nuc} = \lim_{l\to\infty}\rho^{k_l}_{nuc}(\mathbb{R}^3) = 2n.$$

For proving that $\vec{\varphi} \in A_{e,n+1}$, we only need to show that $\langle \varphi_i(\cdot, s), \varphi_j(\cdot, s)\rangle_{L^2(\Omega)} = \delta_{ij}$ for all $s \in \mathbb{Z}_2$. But this is a trivial consequence of the compact embedding of $H_0^1(\Omega)$ into $L^2(\Omega)$ and the resulting strong convergence $\vec{\varphi}^k \to \vec{\varphi}$ in $L^2(\Omega)$.

It remains to establish (i), (ii) and (iii) for the pair $(\vec{\varphi}, \rho_{nuc}) \in A_{e,n+1} \times A_{nuc}$. This will be done via the subsequent lemmata, which will be proven immediately after the proof of this proposition. We first show that $(\vec{\varphi}, \rho_{nuc})$ satisfies (i). For this reason, we recall the separation $(\vec{\psi}, \omega) = \vec{\varphi}$ with $\vec{\psi} \in A_{e,n}$ and $\omega \in A_{e,1}$ as defined in (3.7). The same notation will be applied to sequences.

Lemma 3.9. *Let $(\vec{\psi}^k, \omega^k, \rho^k_{nuc}) \subset A$, $(\vec{\psi}^k, \omega^k) \rightharpoonup (\vec{\psi}, \omega) \in A_{e,n+1}$, $\rho^k_{nuc} \overset{*}{\rightharpoonup} \rho_{nuc} \in A_{nuc}$. Then,*

$$\mathcal{E}_{\rho_{nuc}}[\vec{\psi}] \leq \liminf_{k\to\infty} \mathcal{E}_{\rho^k_{nuc}}[\vec{\psi}^k].$$

Lemma 3.10. *Let $(\vec{\psi}^k, \omega^k, \rho^k_{nuc}) \subset A$, $(\vec{\psi}^k, \omega^k) \rightharpoonup (\vec{\psi}, \omega) \in A_{e,n+1}$, $\rho^k_{nuc} \overset{*}{\rightharpoonup} \rho_{nuc} \in A_{nuc}$. Then,*

$$\limsup_{k\to\infty} \mathcal{E}_{\rho^k_{nuc}}[\vec{\psi}^k] \leq \mathcal{E}_{\rho_{nuc}}[\vec{\psi}_*]$$

where $\vec{\psi}_* \in A_{e,n}$ is a minimizer of $\mathcal{E}_{\rho_{nuc}}$.

Thus, $\vec{\psi}$ is a minimizer of $\mathcal{E}_{\rho_{nuc}}$ and $(\vec{\psi}, \omega, \rho_{nuc}) = (\vec{\varphi}, \rho_{nuc})$ satisfies (i). One can proceed in a similar way to show that $(\vec{\varphi}, \rho_{nuc})$ also fulfills (ii). In order to prevent confusions with the notation introduced in (3.7), we mention that $(\vec{v}, \chi, \omega) = \vec{\varphi}$ where $\vec{v} \in A_{e,n-1}$ and $\chi, \omega \in A_{e,1}$.

Lemma 3.11. *Let $(\vec{v}^k, \chi^k, \omega^k, \rho^k_{nuc}) \subset A$, $(\vec{v}^k, \chi^k, \omega^k) \rightharpoonup (\vec{v}, \chi, \omega) \in A_{e,n+1}$, $\rho^k_{nuc} \overset{*}{\rightharpoonup} \rho_{nuc} \in A_{nuc}$. Then,*

$$\mathcal{E}^-_{\vec{\psi},\rho_{nuc}}[\chi] \leq \liminf_{k\to\infty} \mathcal{E}^-_{\vec{\psi}^k,\rho^k_{nuc}}[\chi^k].$$

Lemma 3.12. *Let $(\vec{v}^k, \chi^k, \omega^k, \rho^k_{nuc}) \subset A$, $(\vec{v}^k, \chi^k, \omega^k) \rightharpoonup (\vec{v}, \chi, \omega) \in A_{e,n+1}$, $\rho^k_{nuc} \overset{*}{\rightharpoonup} \rho_{nuc} \in A_{nuc}$. Then,*

$$\limsup_{k\to\infty} \mathcal{E}^-_{\vec{\psi}^k,\rho^k_{nuc}}[\chi^k] \leq \mathcal{E}^-_{\vec{\psi},\rho_{nuc}}[\chi_*]$$

where $\chi_* \in A_{e,1}$ is a minimizer of $\mathcal{E}^-_{\vec{\psi},\rho_{nuc}}$.

This proves that χ is a minimizer of $\mathcal{E}^-_{\vec{\psi},\rho_{nuc}}$ and, hence, $(\vec{v}, \chi, \omega, \rho_{nuc}) = (\vec{\varphi}, \rho_{nuc})$ satisfies (ii). Along the same lines of arguments, one can verify that also (iii) is fulfilled by $(\vec{\varphi}, \rho_{nuc})$. Here, we will use the notation $(\vec{\psi}, \omega) = \vec{\varphi}$ as introduced in (3.7), where $\vec{\psi} \in A_{e,n}$ and $\omega \in A_{e,1}$.

Lemma 3.13. *Let $(\vec{\psi}^k, \omega^k, \rho^k_{nuc}) \subset A$, $(\vec{\psi}^k, \omega^k) \rightharpoonup (\vec{\psi}, \omega) \in A_{e,n+1}$, $\rho^k_{nuc} \overset{*}{\rightharpoonup} \rho_{nuc} \in A_{nuc}$. Then,*

$$\mathcal{E}^+_{\rho_e,\rho_{nuc}}[\omega] \leq \liminf_{k\to\infty} \mathcal{E}^+_{\rho^k_e,\rho^k_{nuc}}[\omega^k].$$

Lemma 3.14. *Let $(\vec{\psi}^k, \omega^k, \rho^k_{nuc}) \subset A$, $(\vec{\psi}^k, \omega^k) \rightharpoonup (\vec{\psi}, \omega) \in A_{e,n+1}$, $\rho^k_{nuc} \overset{*}{\rightharpoonup} \rho_{nuc} \in A_{nuc}$. Then,*

$$\limsup_{k\to\infty} \mathcal{E}^+_{\rho^k_e,\rho^k_{nuc}}[\omega^k] \leq \mathcal{E}^+_{\rho_e,\rho_{nuc}}[\omega_*]$$

where $\omega_* \in A_{e,1}$ is a minimizer of $\mathcal{E}^+_{\rho_e,\rho_{nuc}}$.

As a consequence, (iii) holds true for $(\vec{\varphi}, \rho_{nuc}) \in A_{e,n+1} \times A_{nuc}$, which finally proves $(\vec{\varphi}, \rho_{nuc}) \in A$. □

Proof of Lemma 3.9. We recall the electronic energy functional for $(\vec{\psi}^k, \omega^k, \rho^k_{nuc}) \subset A$:

$$\mathcal{E}_{\rho^k_{nuc}}[\vec{\psi}^k] = \frac{1}{2}\sum_{i=1}^n \int_{\mathbb{R}^3\times\mathbb{Z}_2} |\nabla\psi^k_i|^2 + \frac{1}{2}\int_{\mathbb{R}^3} \Big(\frac{1}{|\cdot|} * \rho^k_e\Big)\rho^k_e + \int_{\mathbb{R}^3} e_x[\rho^k_e] - \int_{\mathbb{R}^3} \Big(\frac{1}{|\cdot|} * \rho^k_{nuc}\Big)\rho^k_e.$$

The same arguments as in the proof of Proposition 3.5 show that the first three terms are weakly lower semi-continuous as a function of $\vec{\psi}^k \in H^1_0(\Omega \times \mathbb{Z}_2)^n$. The convergence of the last integral,

$$\int_{\mathbb{R}^3} \Big(\frac{1}{|\cdot|} * \rho^k_e\Big) d\rho^k_{nuc} \to \int_{\mathbb{R}^3} \Big(\frac{1}{|\cdot|} * \rho_e\Big) d\rho_{nuc},$$

where we have already interchanged the order of integration using Fubini's theorem, has to be considered separately due to the simultaneous convergence of ρ_e^k and ρ_{nuc}^k. To this end, we rewrite

$$\begin{aligned}\Big|\int_{\mathbb{R}^3}\Big(\frac{1}{|\cdot|}*\rho_e^k\Big)d\rho_{nuc}^k-\int_{\mathbb{R}^3}\Big(\frac{1}{|\cdot|}*\rho_e\Big)d\rho_{nuc}\Big|\le&\\ \Big|\int_{\mathbb{R}^3}\Big(\frac{1}{|\cdot|}*\rho_e^k\Big)d\rho_{nuc}^k-\int_{\mathbb{R}^3}\Big(\frac{1}{|\cdot|}*\rho_e\Big)d\rho_{nuc}^k\Big|&+\Big|\int_{\mathbb{R}^3}\Big(\frac{1}{|\cdot|}*\rho_e\Big)d\rho_{nuc}^k-\int_{\mathbb{R}^3}\Big(\frac{1}{|\cdot|}*\rho_e\Big)d\rho_{nuc}\Big|\end{aligned}$$

and observe that the first term on the right hand side satisfies

$$\Big|\int_{\mathbb{R}^3}\Big(\frac{1}{|\cdot|}*\rho_e^k\Big)d\rho_{nuc}^k-\int_{\mathbb{R}^3}\Big(\frac{1}{|\cdot|}*\rho_e\Big)d\rho_{nuc}^k\Big|\le\Big\|\frac{1}{|\cdot|}*(\rho_e^k-\rho_e)\Big\|_{L^\infty(\mathbb{R}^3)}\int_{\mathbb{R}^3}d\rho_{nuc}^k\to 0.$$

The employed L^∞-convergence $|\cdot|^{-1}*\rho_e^k\to|\cdot|^{-1}*\rho_e$ follows from the same reasoning as in the proof of Proposition 3.5. It remains to verify that

$$\int_{\mathbb{R}^3}\Big(\frac{1}{|\cdot|}*\rho_e\Big)d\rho_{nuc}^k\to\int_{\mathbb{R}^3}\Big(\frac{1}{|\cdot|}*\rho_e\Big)d\rho_{nuc}.$$

The main part consists of proving that the integrand is in fact continuous. The claim then follows from an additional decay property of the integrand, which allows us to pass to the limit using the weak* convergence $\rho_{nuc}^k\overset{*}{\rightharpoonup}\rho_{nuc}$. First, the embedding $H_0^1(\Omega)\hookrightarrow L^6(\Omega)$ in $\mathbb{R}^3$ implies $\rho_e\in L^3(\Omega)$. Together with Young's inequality for convolutions, we derive $|\cdot|^{-1}*\rho_e\in L^\infty(\mathbb{R}^3)$ since both $|\cdot|^{-1}$ and ρ_e are square-integrable in $\mathbb{R}^3$. Using Hölder's inequality and again Young's inequality, we obtain $\nabla\rho_e\in L^{3/2}(\Omega)$ and, hence, $|\cdot|^{-1}*\nabla\rho_e\in L^p(\mathbb{R}^3)$ for all $p<\infty$. Consequently, $|\cdot|^{-1}*\rho_e\in W^{1,p}(\mathbb{R}^3)$ for all $p<\infty$ and

$$|\cdot|^{-1}*\rho_e\in C^{0,1-\varepsilon}(\mathbb{R}^3)\quad\text{for all }\varepsilon>0.$$

For $x\in\mathbb{R}^3\backslash\overline{\Omega}$, we further calculate

$$\Big(\frac{1}{|\cdot|}*\rho_e\Big)(x)=\int_{\mathbb{R}^3}\frac{1}{|x-y|}\rho_e(y)\,dy=\int_\Omega\frac{1}{|x-y|}\rho_e(y)\,dy\le\frac{1}{\mathrm{dist(x,\Omega)}}\int_\Omega\rho_e(y)\,dy=\frac{2n}{\mathrm{dist(x,\Omega)}}.$$

This proves $|\cdot|^{-1}*\rho_e\in C_0(\mathbb{R}^3)$ and we deduce

$$\int_{\mathbb{R}^3}\Big(\frac{1}{|\cdot|}*\rho_e\Big)d\rho_{nuc}^k\to\int_{\mathbb{R}^3}\Big(\frac{1}{|\cdot|}*\rho_e\Big)d\rho_{nuc}$$

as a consequence of the weak* convergence of ρ_{nuc}^k to ρ_{nuc}. □

Proof of Lemma 3.10. Let $k\in\mathbb{N}$ be arbitrary and $\vec{\psi}_*\in A_{e,n}$ be a minimizer of $\mathcal{E}_{\rho_{nuc}}$. As $\vec{\psi}^k$ is a minimizer of $\mathcal{E}_{\rho_{nuc}^k}$, we obtain

$$\begin{aligned}&\mathcal{E}_{\rho_{nuc}^k}[\vec{\psi}^k]\le\mathcal{E}_{\rho_{nuc}^k}[\vec{\psi}_*]\\&=\frac12\sum_{i=1}^n\int_{\mathbb{R}^3\times\mathbb{Z}_2}|\nabla\psi_{i,*}|^2+\frac12\int_{\mathbb{R}^3}\Big(\frac{1}{|\cdot|}*\rho_{e,*}\Big)\rho_{e,*}+\int_{\mathbb{R}^3}e_x[\rho_{e,*}]-\int_{\mathbb{R}^3}\Big(\frac{1}{|\cdot|}*\rho_{nuc}^k\Big)\rho_{e,*}\\&\to\frac12\sum_{i=1}^n\int_{\mathbb{R}^3\times\mathbb{Z}_2}|\nabla\psi_{i,*}|^2+\frac12\int_{\mathbb{R}^3}\Big(\frac{1}{|\cdot|}*\rho_{e,*}\Big)\rho_{e,*}+\int_{\mathbb{R}^3}e_x[\rho_{e,*}]-\int_{\mathbb{R}^3}\Big(\frac{1}{|\cdot|}*\rho_{nuc}\Big)\rho_{e,*}=\mathcal{E}_{\rho_{nuc}}[\vec{\psi}_*]\end{aligned}$$

where the last integral converges due to the same reasoning as in the proof of Lemma 3.9. □

Proof of Lemma 3.11. A closer look at the energy functional

$$\begin{aligned}\mathcal{E}^-_{\vec{\psi}^k,\rho_{nuc}^k}[\chi^k]=\frac12\sum_{i=1}^{n-1}\int_{\mathbb{R}^3\times\mathbb{Z}_2}|\nabla\psi_i^k|^2-\int_{\mathbb{R}^3}e_x[\rho_e^k]+\int_{\mathbb{R}^3}e_x\Big[\rho_e^k-\sum_{s\in\mathbb{Z}_2}|\chi^k(\cdot,s)|^2\Big]&\\+\int_{\mathbb{R}^3\times\mathbb{Z}_2}\Big(\frac{1}{|\cdot|}*(\rho_{nuc}^k-\rho_e^k)\Big)|\chi^k|^2+\frac12\int_{\mathbb{R}^3\times\mathbb{Z}_2}\Big(\frac{1}{|\cdot|}*|\chi^k|^2\Big)|\chi^k|^2,&\end{aligned}$$

where $(\vec{v}^k, \chi^k, \omega^k, \rho_{nuc}^k) \subset A$, shows that the convergence behavior of all appearing quantities has already been investigated in the proofs of previous lemmata. In detail, the weak H^1-convergence of $\vec{\psi}^k$ and χ^k implies a corresponding strong L^2-convergence of ρ_e^k and $|\chi^k|^2$. The two expressions in the second line above converge to the same expressions but without the index k (see the proof of Lemma 3.9 for details). And both integrals over the exchange energy e_x converge due to Lemma 3.1. The gradient terms, finally, are weakly lower semi-continuous as a function of $\psi_i \in H_0^1(\Omega \times \mathbb{Z}_2)$. □

Proof of Lemma 3.12. Choose some arbitrary $k \in \mathbb{N}$ and let $\chi_* \in A_{e,1}$ be a minimizer of $\mathcal{E}^-_{\vec{\psi},\rho_{nuc}}$. Since χ^k is a minimizer of $\mathcal{E}^-_{\vec{\psi}^k,\rho^k_{nuc}}$, one finds

$$\begin{aligned}\mathcal{E}^-_{\vec{\psi}^k,\rho^k_{nuc}}[\chi^k] &\leq \mathcal{E}^-_{\vec{\psi}^k,\rho^k_{nuc}}[\chi_*]\\ &= \mathcal{E}_{\rho^k_{nuc}}[\vec{\psi}^k] - \frac{1}{2}\int_{\mathbb{R}^3\times\mathbb{Z}_2}|\nabla\chi_*|^2 - \int_{\mathbb{R}^3} e_x[\rho_e^k] + \int_{\mathbb{R}^3} e_x\Big[\rho_e^k - \sum_{s\in\mathbb{Z}_2}|\chi_*(\cdot,s)|^2\Big]\\ &\qquad + \int_{\mathbb{R}^3\times\mathbb{Z}_2}\Big(\frac{1}{|\cdot|}*(\rho^k_{nuc}-\rho^k_e)\Big)|\chi_*|^2 + \frac{1}{2}\int_{\mathbb{R}^3\times\mathbb{Z}_2}\Big(\frac{1}{|\cdot|}*|\chi_*|^2\Big)|\chi_*|^2.\end{aligned}$$

From Lemma 3.10, we deduce

$$\limsup_{k\to\infty}\mathcal{E}_{\rho^k_{nuc}}[\vec{\psi}^k] \leq \mathcal{E}_{\rho_{nuc}}[\vec{\psi}_*] \leq \mathcal{E}_{\rho_{nuc}}[\vec{\psi}]$$

as $\vec{\psi}_* \in A_{e,n}$ is a minimizer of $\mathcal{E}_{\rho_{nuc}}$. Due to the convergence of the remaining terms on the right hand side, we arrive at

$$\limsup_{k\to\infty}\mathcal{E}^-_{\vec{\psi}^k,\rho^k_{nuc}}[\chi^k] \leq \mathcal{E}^-_{\vec{\psi},\rho_{nuc}}[\chi_*],$$

as claimed above. □

Proof of Lemma 3.13. The energy functional

$$\mathcal{E}^+_{\rho^k_e,\rho^k_{nuc}}[\omega^k] = \frac{1}{2}\int_{\mathbb{R}^3\times\mathbb{Z}_2}|\nabla\omega^k|^2 + \int_{\mathbb{R}^3\times\mathbb{Z}_2}\Big(\frac{1}{|\cdot|}*(\rho^k_e-\rho^k_{nuc})\Big)|\omega^k|^2 - \int_{\mathbb{R}^3} e_x[\rho^k_e] + \int_{\mathbb{R}^3} e_x\Big[\rho^k_e + \sum_{s\in\mathbb{Z}_2}|\omega^k(\cdot,s)|^2\Big]$$

evaluated at $(\vec{\psi}^k, \omega^k, \rho^k_{nuc}) \subset A$ is closely related to the energies investigated above. In particular, the first integral term is weakly lower semi-continuous with respect to $\omega \in H_0^1(\Omega \times \mathbb{Z}_2)$. And the remaining three quantities converge to their counterparts without the index k due to the strong L^2-convergence of ρ^k_e, the L^2-continuity of e_x and the weak* convergence of ρ^k_{nuc}. Compare the proof of Lemma 3.9 for further details. □

Proof of Lemma 3.14. We select a minimizer $\omega_* \in A_{e,1}$ of $\mathcal{E}^+_{\rho_e,\rho_{nuc}}$ and pick some arbitrary $k \in \mathbb{N}$. As ω^k is itself a minimizer of $\mathcal{E}^+_{\rho^k_e,\rho^k_{nuc}}$, we deduce

$$\begin{aligned}&\mathcal{E}^+_{\rho^k_e,\rho^k_{nuc}}[\omega^k] \leq \mathcal{E}^+_{\rho^k_e,\rho^k_{nuc}}[\omega_*] =\\ &= \frac{1}{2}\int_{\mathbb{R}^3\times\mathbb{Z}_2}|\nabla\omega_*|^2 + \int_{\mathbb{R}^3\times\mathbb{Z}_2}\Big(\frac{1}{|\cdot|}*(\rho^k_e-\rho^k_{nuc})\Big)|\omega_*|^2 - \int_{\mathbb{R}^3} e_x[\rho^k_e] + \int_{\mathbb{R}^3} e_x\Big[\rho^k_e + \sum_{s\in\mathbb{Z}_2}|\omega_*(\cdot,s)|^2\Big]\\ &\to \frac{1}{2}\int_{\mathbb{R}^3\times\mathbb{Z}_2}|\nabla\omega_*|^2 + \int_{\mathbb{R}^3\times\mathbb{Z}_2}\Big(\frac{1}{|\cdot|}*(\rho_e-\rho_{nuc})\Big)|\omega_*|^2 - \int_{\mathbb{R}^3} e_x[\rho_e] + \int_{\mathbb{R}^3} e_x\Big[\rho_e + \sum_{s\in\mathbb{Z}_2}|\omega_*(\cdot,s)|^2\Big]\\ &= \mathcal{E}^+_{\rho_e,\rho_{nuc}}[\omega_*].\end{aligned}$$

The convergence of the various expressions is a consequence of the reasoning which has already been presented in detail above. □

Proposition 3.15. *$J[\vec{\varphi}, \rho_{nuc}]$ is weakly × weak* sequentially continuous in $H_0^1(\Omega \times \mathbb{Z}_2)^{n+1} \times \mathcal{M}(\mathbb{R}^3)$.*

Proof. Let $(\vec{\varphi}^k, \rho_{nuc}^k) \subset A_{e,n+1} \times A_{nuc}$ and $(\vec{\varphi}, \rho_{nuc}) \in A_{e,n+1} \times A_{nuc}$, where we assume

$$\vec{\varphi}^k \rightharpoonup \vec{\varphi} \text{ in } H_0^1(\Omega \times \mathbb{Z}_2)^{n+1} \quad \text{and} \quad \rho_{nuc}^k \overset{*}{\rightharpoonup} \rho_{nuc} \text{ in } \mathcal{M}(\mathbb{R}^3).$$

The weak convergence $\vec{\varphi}^k \rightharpoonup \vec{\varphi}$ in $H_0^1(\Omega \times \mathbb{Z}_2)^{n+1}$ yields strong convergence $\vec{\varphi}^k \to \vec{\varphi}$ in $L^2(\Omega \times \mathbb{Z}_2)^{n+1}$. This already implies

$$J[\vec{\varphi}^k, \rho_{nuc}^k] = \left| \int_\Omega \left(|\varphi_{n+1}^k|^2 - |\varphi_n^k|^2\right)(x \cdot e)\, dx \right| \to \left| \int_\Omega \left(|\varphi_{n+1}|^2 - |\varphi_n|^2\right)(x \cdot e)\, dx \right| = J[\vec{\varphi}, \rho_{nuc}]$$

and, hence, the announced continuity. □

Theorem 3.16. *There exists a maximizer of $J[\vec{\varphi}, \rho_{nuc}]$ in A. In particular, $\rho_{nuc} \in A_{nuc}$ is an optimal nuclear charge density giving rise to the largest charge transfer possible.*

Proof. As the charge transfer functional J is bounded from above, there exists a maximizing sequence $(\vec{\varphi}^k, \rho_{nuc}^k) \subset A$. Due to Proposition 3.8, there exists a subsequence $(\vec{\varphi}^{k_l}, \rho_{nuc}^{k_l}) \subset (\vec{\varphi}^k, \rho_{nuc}^k)$ and a pair $(\vec{\varphi}, \rho_{nuc}) \in A$ such that $\vec{\varphi}^{k_l} \rightharpoonup \vec{\varphi}$ and $\rho_{nuc}^{k_l} \overset{*}{\rightharpoonup} \rho_{nuc}$. Finally, Proposition 3.15 enables us to conclude that

$$\sup_{(\vec{\phi}, \varrho_{nuc}) \in A} J[\vec{\phi}, \varrho_{nuc}] = \lim_{k\to\infty} J[\vec{\varphi}^k, \rho_{nuc}^k] = \lim_{l\to\infty} J[\vec{\varphi}^{k_l}, \rho_{nuc}^{k_l}] = J[\vec{\varphi}, \rho_{nuc}],$$

which demonstrates that $\rho_{nuc} \in A_{nuc}$ is an optimal nuclear charge density. □

In the next section, we will be concerned with nuclear densities

$$\rho_{nuc} = \sum_{j=1}^N a_j \mathcal{N}(p_j, \sigma^2)$$

where p_j and σ are the fixed positions of N nuclei and the width of the normalized Gaussian distributions, respectively. Thus, ρ_{nuc} only depends on the coefficients a_j. Due to modeling issues explained below, all a_j are integer valued and bounded. The set of admissible nuclear mass densities then reads

$$A'_{nuc} := \left\{ \rho_{nuc} = \sum_{j=1}^N a_j \mathcal{N}(p_j, \sigma^2) \,\middle|\, a_j \in [A_*, A^*] \right\}$$

where $A'_{nuc} \subset A_{nuc}$ is a consequence of the assumptions $0 < A_* < A^* < \infty$, $\sum_{j=1}^N a_j = 2n$ and the fact that the normal distribution can be regarded as numerically zero outside a certain neighborhood of the points p_j (see Fig. 3.3 for a visualization). All results presented above for the set A_{nuc} are equally valid for A'_{nuc}. There is just one point where a careful reconsideration is necessary. In the proof of Proposition 3.8, we choose a subsequence $\rho_{nuc}^{k_l}$ converging weak* to $\rho_{nuc} \in \mathcal{M}(\mathbb{R}^3)$. Here, we have to assure that $\rho_{nuc} \in A'_{nuc}$. We know that

$$\rho_{nuc}^{k_l} = \sum_{j=1}^N a_j^{k_l} \mathcal{N}(p_j, \sigma^2)$$

with $a_j^{k_l} \in [A_*, A^*]$. Therefore, there exists a sub-subsequence

$$\rho_{nuc}^{k_{l_m}} = \sum_{j=1}^N a_j^{k_{l_m}} \mathcal{N}(p_j, \sigma^2)$$

where $a_j^{k_{l_m}} \to a_j^* \in [A_*, A^*]$ holds true for all $1 \le j \le N$. This sub-subsequence $\rho_{nuc}^{k_{l_m}}$ converges uniformly and, hence, weak* towards

$$\rho_{nuc}^* = \sum_{j=1}^N a_j^* \mathcal{N}(p_j, \sigma^2).$$

The uniqueness of weak* limits, finally, implies that $\rho_{nuc} = \rho_{nuc}^* \in A'_{nuc}$.

3.4 Numerical Results for a Chain of Atoms

In order to illustrate the practical applicability of an appropriate nuclear density distribution concerning a significant charge transfer within the material, we investigate the following 1D problem. Consider a chain of 20 atoms where each of them coincides with carbon at the beginning of the optimization procedure. This corresponds to a total number of 120 protons inside the atomic cores and 120 electronic states, which may either be localized to certain atoms or delocalized between the atomic cores. During the subsequent optimization steps we only change the number of protons at the given sites of the chain preserving the total number of 120 protons. Apart from that, we will also have a look at the "continuous" dependence of the charge transfer functional on the atomic configuration. In other words, we calculate the charge transfer also for certain non integer-valued proton numbers in order to study the underlying mechanisms in more detail.

In this simplified one-dimensional setting, the optimization problem reads as follows:

$$\max\ J[\rho_{nuc}] = \left| \int_{-L}^{L} x \left(|\varphi_n|^2 - |\varphi_{n+1}|^2\right)\, dx \right|$$

where $[-L, L]$ is the spatial extent of the system and φ_i — implicitly depending on the nuclear density ρ_{nuc} — is the i-th electronic eigenstate of the Kohn–Sham Hamiltonian $H = -1/2\, d^2/dx^2 + V$ corresponding to the i-th lowest eigenvalue λ_i. Hence,

$$H\varphi_i = \lambda_i \varphi_i.$$

For the following modeling approach, we only take the Coulomb part of the Kohn–Sham potential V into account. We therefore skip the contribution of the exchange-correlation part of V. The state φ_n denotes the *highest occupied molecular orbital* (HOMO) and φ_{n+1} the *lowest unoccupied molecular orbital* (LUMO) in the ground state configuration. Thus, $n = 120$ in our situation. We will subsequently refer to $J[\rho_{nuc}]$ as the charge transfer functional. But we will also encounter the *signed* charge transfer functional

$$I[\rho_{nuc}] = \int_{-L}^{L} x \left(|\varphi_{n+1}|^2 - |\varphi_n|^2\right)\, dx,$$

which can attain both positive and negative values.

In 1D, the Coulomb potential V cannot be obtained by the convolution of $1/|\cdot|$ with the charge density as $1/|\cdot|$ is not integrable in 1D. Instead, we employ an effective potential [5, 6]

$$v_d(x) = \frac{\sqrt{\pi}}{2d} \exp\left(\frac{x^2}{4d^2}\right) \operatorname{erfc}\left(\frac{x}{2d}\right)$$

which results from the integration of $1/|\cdot|$ over the lateral degrees of freedom inside a thin wire. The constant d is related to the diameter of the wire, and erfc denotes the complementary error function. We will set $d = 0.01$ throughout all numerical simulations. The Coulomb potential is then calculated from

$$V = v_d * (\rho_e - \rho_{nuc})$$

where

$$\rho_e = \sum_{i=1}^{n} |\varphi_i|^2$$

is the electron density of the ground state and

$$\rho_{nuc} = \sum_{j=1}^{N} a_j \mathcal{N}(p_j, \sigma^2)$$

defines the nuclear density. Moreover, $N = 20$ equals the number of atoms in the chain and the 20-component vector a contains the proton numbers of the corresponding atoms. The nuclei are modeled as sharply peaked Gaussian distributions of width $\sigma > 0$ at fixed positions $-L < p_1 < \ldots < p_N < L$. For all subsequent simulations we employ $\sigma^2 = 1/2000$. The variables which we aim to optimize are

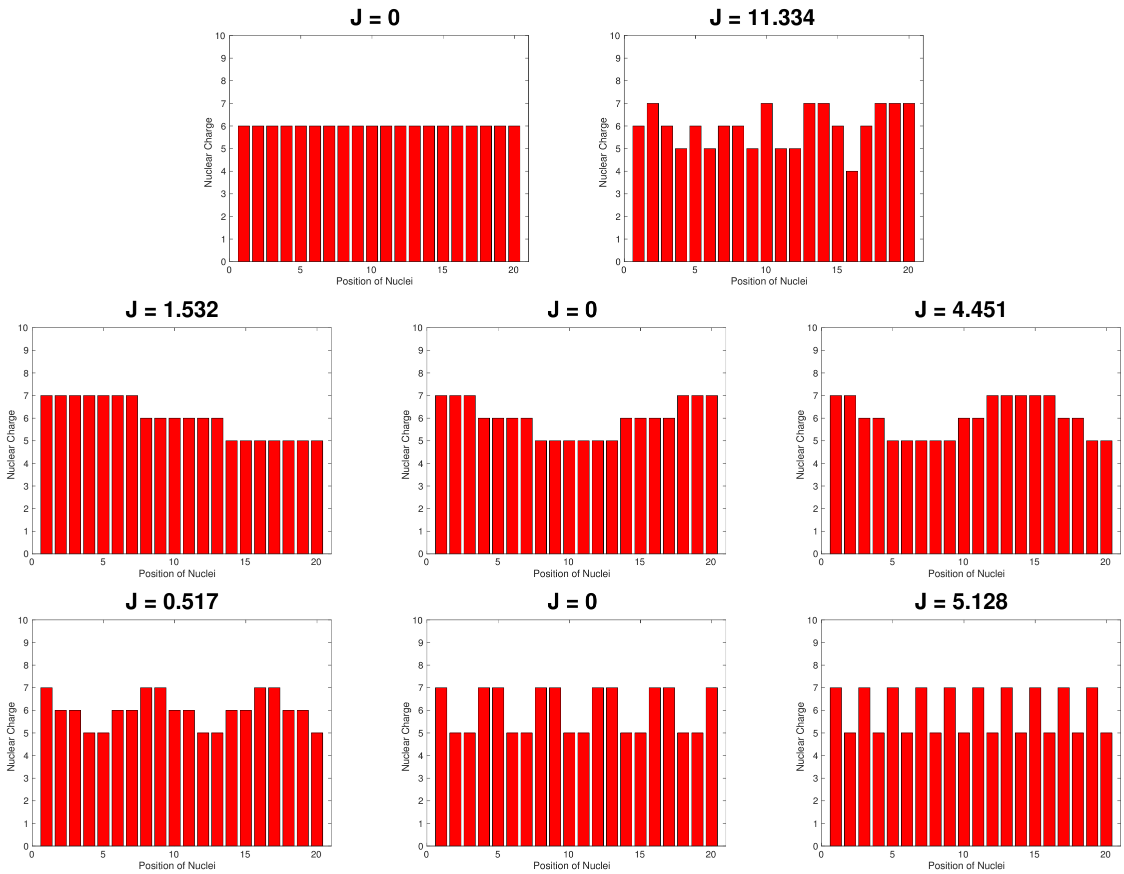

Figure 3.2: Top left: The pure carbon chain does not yield a non-vanishing charge transfer. Top right: The nuclear configuration resulting from our optimization method which generates a significant increase of the charge transfer functional compared to the elementary perturbations below. Middle and bottom: Six phonon-type perturbations of the undoped state and the corresponding value of the charge transfer functional J. Note that $J = 0$ for the two symmetric configurations in the center.

the components of a. In order to conserve the total number of 120 protons and to exclude atomic configurations containing noble gases, we impose the additional constraints

$$\sum_{j=1}^{20} a_j = 120 \quad \text{and} \quad 3 \leq a_j \leq 9.$$

Our approach to construct an atomic configuration a which satisfies the previous constraints and generates a significant difference between φ_n (HOMO) and φ_{n+1} (LUMO) is based on randomly chosen directions $h \in \{-1, 0, 1\}^{20}$. According to these directions, the proton numbers are decreased at certain positions and increased at other sites. If we investigated a chain of only five atoms, a typical configuration may be given by

$$a = (6, 5, 6, 6, 7),$$

which encodes a chain with three carbon, one boron and one nitrogen atom. A generic direction for adapting this configuration could be

$$h = (1, -1, -1, 0, 1).$$

Within the optimization procedure we shall only deal with integer-valued configurations and, hence, restrict ourselves to possible updates $a^{\text{new}} = a^{\text{old}} \pm h$.

Some typical values of the charge transfer functional J when applied to a couple of atomic configurations are shown in Fig. 3.2. Perturbing the undoped carbon chain with a phonon-type pattern of a certain frequency, we are in general not able to clearly exceed a value of $J = 5$. We may even end

Algorithm 1: Optimization method for finding local maxima of the charge transfer functional J

Input: n, p, *iter*
Output: a
begin
  $a \leftarrow (6)_{i=1}^{20}$
  for $i = 1 : iter$ **do**
    generate $n(i)$ random directions $h \in \{-1, 0, 1\}^{20}$ with $P(1) = P(-1) = p(i)$, $\sum_{k=1}^{20} h_k = 0$ and $a + h \in ([3, 9] \cap \mathbb{Z})^{20}$
    $a \leftarrow a + t_* h_*$ where $t_* \in \{-1, 0, 1\}$ and $a + t_* h_*$ yields the maximal $J[a + th]$ amongst all $t \in \{-1, 0, 1\}$ and h generated so far such that $a + th \in ([3, 9] \cap \mathbb{Z})^{20}$

up with a vanishing charge transfer $J = 0$ in case that the resulting configuration of proton numbers is symmetric around $x = 0$. However, if we apply our optimization technique presented subsequently, then we may even obtain configurations which allow for a charge transfer $J > 10$.

The structure of our optimization method is sketched in Algorithm 1. In detail, we start from a chain of 20 carbon atoms and then perform a prescribed number of iterations *iter* giving rise to a final configuration a_*. The fact why the algorithm does not finish due to an a-posteriori stopping criterion but due to an a-priori one will be explained in a moment. In the i-th iteration step, we randomly generate a certain number $n(i)$ of admissible directions for updating the current atomic configuration. Depending on the iteration step, we also impose certain probabilities $p(i)$ that an entry of the update direction equals 1. Increasing the amount of directions allows for a more detailed exploration of the configuration space in a neighborhood of the current iterate, but demands a higher computational effort. And varying the probability of ± 1 influences the step length of an average search direction. At the end, we update the current iterate a by adding $t_* h_*$ where $a + t_* h_*$ gives rise to the largest charge separation under all admissible configurations $a + th$ generated before. We further stress that this optimization algorithm is based on a stochastic approach. Therefore, one can expect to obtain different final configurations a_* in each run of the algorithm.

For our purposes, we decided to set

$$iter = 4, \qquad n = (10, 20, 40, 80), \qquad p = (1/3, 1/6, 1/12, 1/24).$$

The exponentially increasing number of search directions $n(i)$ and the exponentially decreasing probability for ± 1 result in a structure of the algorithm which is similar to simulated annealing. Within the first iteration step we perform 10 quite large steps (corresponding to a relatively high probability of a 1) which allow for a significant change of the pure carbon chain. During the following iterations we then reduce the length of an average step by decreasing the probability for a 1 within the update direction. And we simultaneously increase the number of generated directions in order to approximate the local maximum as close as possible (provided there actually exists one in a neighborhood of the current iterate). Now, it is also clear why we terminate our algorithm after four iterations. The fifth step would generate a 1 within an update direction with a probability of only 1/48, but since we skip all proposed directions being identically zero, there would be almost no difference concerning the sparsity of the search directions compared to the fourth step.

Another essential part of our investigations is the calculation of the orbitals $\varphi_1, \ldots, \varphi_{121}$ in the ground state, i.e. when exactly the orbitals $\varphi_1, \ldots, \varphi_{120}$ are occupied. A possible method which one can apply in this situation is the self-consistent field (SCF) iteration sketched in Algorithm 2. One starts from an initial approximation ρ_{el}^{init} of the electronic density and iteratively improves it until a certain stopping criterion is fulfilled. For our purposes, we terminate the SCF-iteration if the resulting signed charge transfer I changes less than a given threshold ε from one iterate to the other. In each iteration, we first calculate the potential V generated by the electronic and the nuclear density and then determine the 121 lowest eigenfunctions $\varphi_1, \ldots, \varphi_{121}$ of the Hamilton H. We can now easily calculate the new iterates for the electronic density ρ_{el} and the signed charge transfer I. In order to numerically stabilize this method, we also add a small portion of the previous iterates of V and ρ_{el} to the corresponding new ones. Whenever we perform such an SCF-iteration, we use $\varepsilon = 0.0001$ and $\eta = 0.9$.

The outcome of our optimization method is depicted in Fig. 3.3. We start from a pure carbon chain and arrive at an atomic configuration which includes elements from beryllium to nitrogen. In detail, the

Algorithm 2: Self-consistent field (SCF) iteration calculating the ground state electronic density

Input: ρ_{nuc}, ε, η
Output: ρ_{el}
begin
  $\rho_{el} \leftarrow \rho_{el}^{\text{init}}$
  while $|I^{\text{new}} - I^{\text{old}}| > \varepsilon$ **do**
    $V \leftarrow \eta\, v_d * (\rho_{el} - \rho_{nuc}) + (1-\eta)V$
    calculate the 121 lowest eigenstates $\varphi_1, \dots, \varphi_{121}$ of the Hamilton $H = -1/2\, d^2/dx^2 + V$
    $\rho_{el} \leftarrow \eta \sum_{i=1}^{120} |\varphi_i|^2 + (1-\eta)\rho_{el}$
    $I^{\text{old}} \leftarrow I^{\text{new}}$
    $I^{\text{new}} \leftarrow \int_x (|\varphi_{121}|^2 - |\varphi_{120}|^2)\, x\, dx$

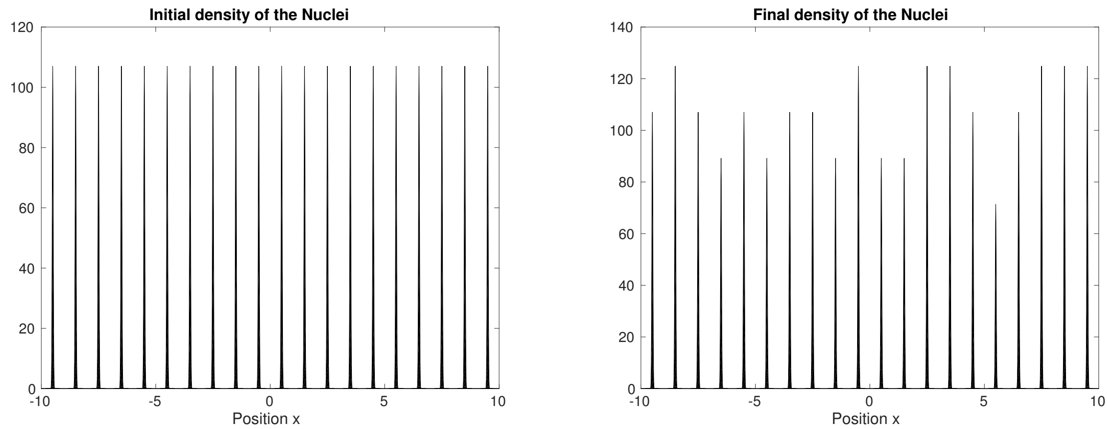

Figure 3.3: Left: The initial nuclear density — a homogeneous chain of 20 carbon atoms. Right: The final nuclear density at the end of the optimization procedure.

resulting vector of proton numbers reads

$$a_* = (6\ 7\ 6\ 5\ 6\ 5\ 6\ 6\ 5\ 7\\ 5\ 5\ 7\ 7\ 6\ 4\ 6\ 7\ 7\ 7).$$

We further mention that the Gaussian charge distributions do not intersect each other from a practical point of view due to the small width of the Gaussian peaks. In the same sense, the nuclear charge is contained in the interval $[-9.9, 9.9]$, which fits to the generic assumption within this chapter that the nuclear charge is supported in a compact subset of the domain under consideration.

Since we are not only interested in time-independent properties of the electronic system but also in the temporal evolution of the excited system, we have to deal with the time-dependent Schrödinger equation

$$i\partial_t \varphi_i = H[\rho_e]\varphi_i$$

applied to the orbitals φ_i. Using the electronic density

$$\rho_e = \sum_{i=1}^{119} |\varphi_i|^2 + |\varphi_{121}|^2$$

within the Hamiltonian H, we are able to determine $\varphi_i(t)$ for $t > 0$, if we employ the initial condition

$$\varphi_i(0) = \varphi_{i,0}$$

where the orbitals $\varphi_{i,0}$ are calculated for the ground state configuration $\rho_e = \sum_{i=1}^{120} |\varphi_i|^2$. Here, we shall apply a Crank–Nicholson scheme to calculate electronic orbitals also for times $t > 0$. Apart from

Spatial meshsize Δx	0.005	0.01	0.02
Charge separation for the ground state	-11.0819	-11.3343	-12.1975

Temporal meshsize Δt	0.001	0.002	0.005
Charge separation at time $T = 5$	-10.8021	-10.0394	-6.0738

Table 3.1: Robustness of charge separation with respect to numerical discretization. For our purposes, we choose $\Delta x = 0.01$ and $\Delta t = 0.002$. See Fig. 3.4 for another comparison of different values for Δt.

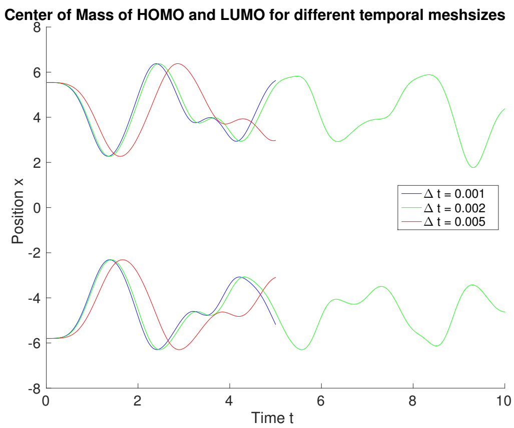

Figure 3.4: A comparison of the temporal evolution of the center of mass of $|\text{HOMO}|^2$ and $|\text{LUMO}|^2$ for different temporal step sizes.

an appropriate choice for the spatial mesh size Δx, we thus have to decide for a reasonable temporal step size Δt too. A comparison between results arising from different values for Δx and Δt is given in Table 3.1. First of all, we notice that the existence of a significant charge separation between HOMO and LUMO is a robust effect independent of minor changes of the spatial mesh size Δx. Similarly, a reduction of the temporal step size Δt only slightly affects the results of the temporal evolution provided Δt is smaller than a certain threshold. For all subsequent numerical implementations we shall use

$$\Delta x = 0.01, \qquad \Delta t = 0.002,$$

which accounts for a reasonable compromise between numerical accuracy and computational effort, which is about four times larger for $\Delta x = 0.005$. Likewise, $\Delta t = 0.001$ increases the number of necessary calculations by a factor 2, while the difference concerning the temporal evolution of the charge separation is almost negligible (cf. Fig. 3.4).

The spatial distribution of the electronic density in the ground state, where all orbitals up to the 120^{th} one are occupied and all higher ones are unoccupied, is depicted on the left of Fig. 3.5. As we would expect, the overall shape of the electronic density resembles the distribution of the nuclear charges. According to the homogeneous Dirichlet boundary conditions, which we imposed to the system, the electron density approaches zero at the boundary. But it is interesting to note that the electron density is bounded far away from zero in the interior of the atomic chain. This shows that a significant number of electronic orbitals is delocalized over the whole range of the system. Only the lower orbitals are typically concentrated around one or several atoms resulting in the peaks of the electron density at the sites of the atomic cores. A remarkable property of HOMO and LUMO is their macroscopic accumulation to the left and the right end of the system, respectively, while being delocalized over the whole atomic chain at the same time. This is depicted on the right side of Fig. 3.5. The physical interest in such a separation of HOMO and LUMO lies in the possible generation of an electric current by an appropriate excitation of the electronic system. In more detail, one might think of a light-induced excitation of the ground state (orbitals 1–120 occupied) to the first excited state (orbitals 1–119 and 121 occupied but not 120). If HOMO and LUMO are now concentrated to different sides of the atomic chain, this excitation also implies a charge transfer from one side to the other, which could be harvested to obtain an electric current. But this is only possible as long as the separation in space is large enough.

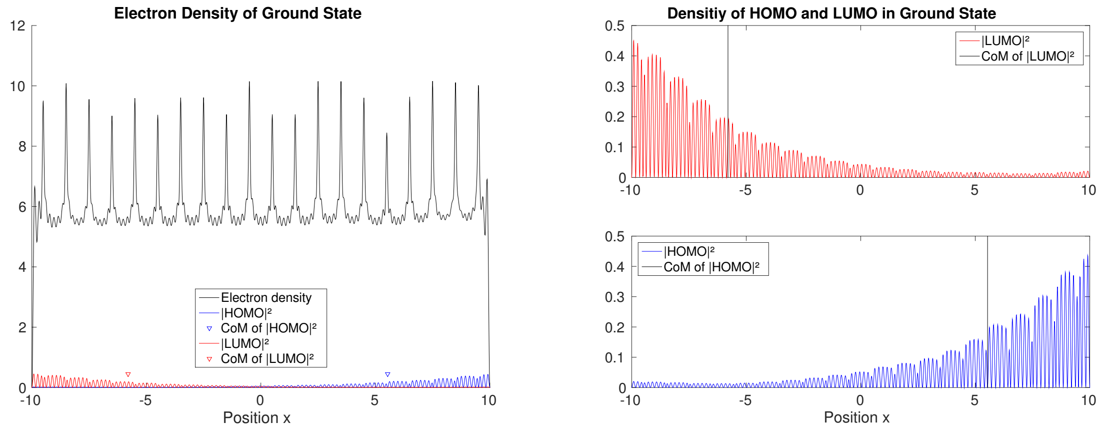

Figure 3.5: Left: The electron density of the ground state (black) together with the density of HOMO (blue) and LUMO (red). Right: A more detailed presentation of the density of HOMO and LUMO. A small triangle and a vertical line indicate the center of mass of $|\text{HOMO}|^2$ and $|\text{LUMO}|^2$ in the two plots.

An interesting theoretical feature of the signed charge transfer functional I can be seen when investigating also configurations with non integer-valued proton numbers. In many cases, the functional I reveals a surprising substructure which cannot be seen when considering only integer-valued atomic numbers. Fig. 3.6 details for a couple of phonon-type perturbations inc the dependence of $I[6+s\cdot inc]$ as a function of s. In other words, we study the sensitivity of I when perturbing the pure carbon chain with certain phonon-type and random patterns. A remarkable property of phonon perturbations with one, three and five half-periods is the suggested inverse correlation between the frequency of the perturbation and the frequency of the signed charge transfer functional along this perturbation. Furthermore, we note that — at least for all numerical examples which we have considered — the charge transfer is identically zero for all atomic configurations being symmetric around $x = 0$.

In order to study the temporal evolution of the system in more detail, we run a simulation over 5000 time steps where each step has a length of $\Delta t = 0.002$ atomic units of time. We thus cover a period of 10 natural units of time (about $2 \cdot 10^{-16}\, s$) in total. Fig. 3.7 depicts on the left side in the first row the electronic density of the atomic chain as a function of time t and position x minus the electron density of the ground state. We clearly notice that the electron density is larger close to $x = -10$ compared to positions near $x = 10$ over the whole range for $T \in [0, 10]$. This shows that one is not forced to harvest the charge transfer instantaneously but only within a certain period of time, which is presumably significantly larger than 10 atomic units of time. The plot on the right in the first row shows the positions of the center of mass for HOMO and LUMO. Despite the significant motion in time of the two center of mass, they never change the relative position to each other. The center of mass of HOMO always stays to the right of the center of mass of LUMO during the first 10 atomic units of time. In addition, the average positions of both center of mass only marginally change over the simulated period of time. The variation around this mean position is the much more relevant process taking place in a different order of magnitude.

The electronic density after 10 atomic units of time is depicted on the left of the bottom row of Fig. 3.7 together with the spatial distribution of HOMO and LUMO at the same time. We notice that there is no distinctive difference between the total charge density at time $T = 10$ and the ground state density. Single orbitals, in contrast, may change their overall shape more visibly, as can be seen from the density of HOMO and LUMO at time $T = 10$ shown on the right of the bottom row. At the (artificial) end of the simulation, these two orbitals reveal a more detailed substructure including kind of a macroscopic plateau around $x = 0$.

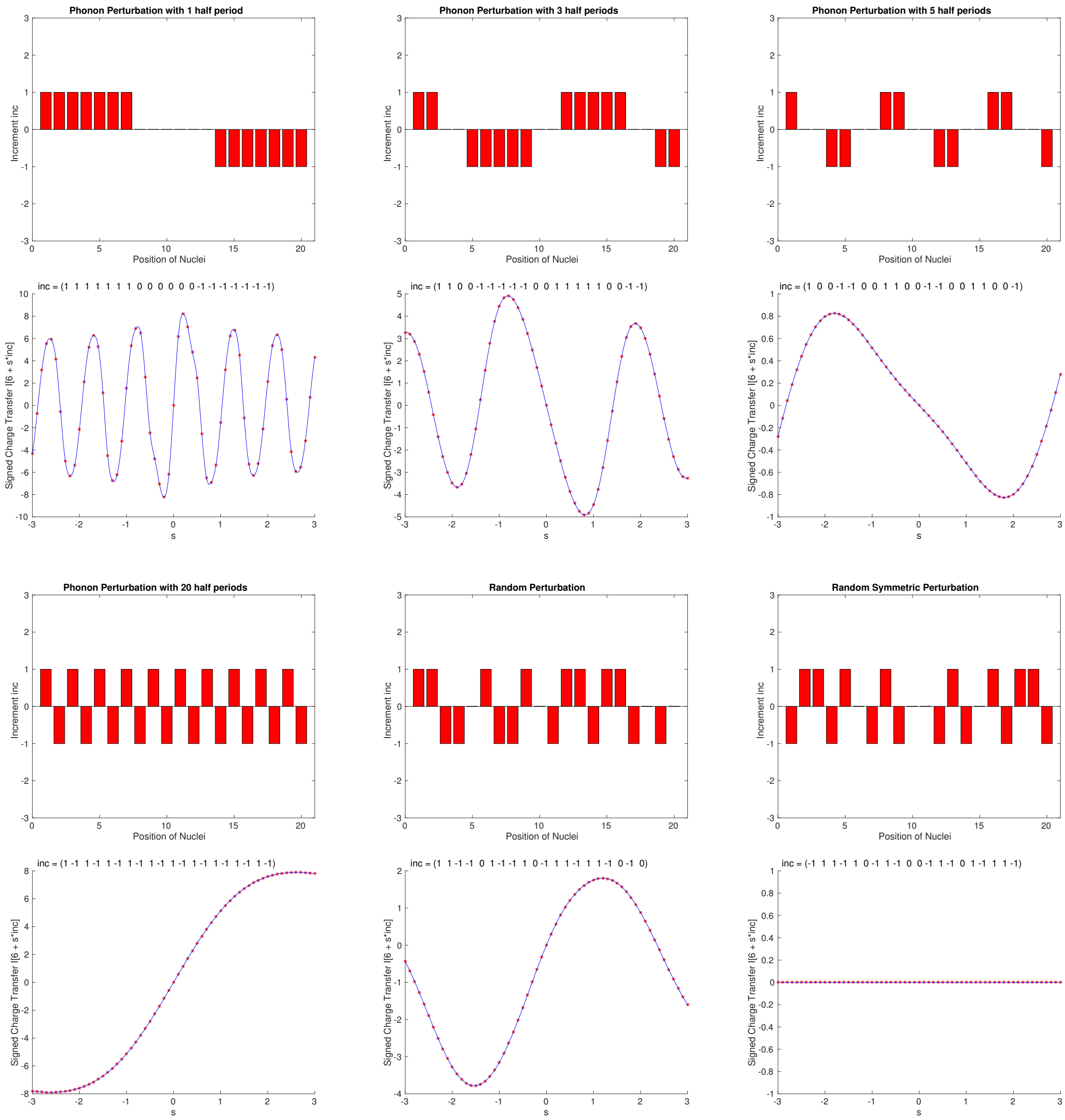

Figure 3.6: The plots in the second and fourth row show the dependence of the signed charge transfer functional I on non integer-valued configurations arising from phonon-type and random perturbations of a carbon chain depicted above within the first and third row. The resulting phonon-type configurations at $s = 1$ and the corresponding value of the charge transfer functional J are shown in Fig. 3.2.

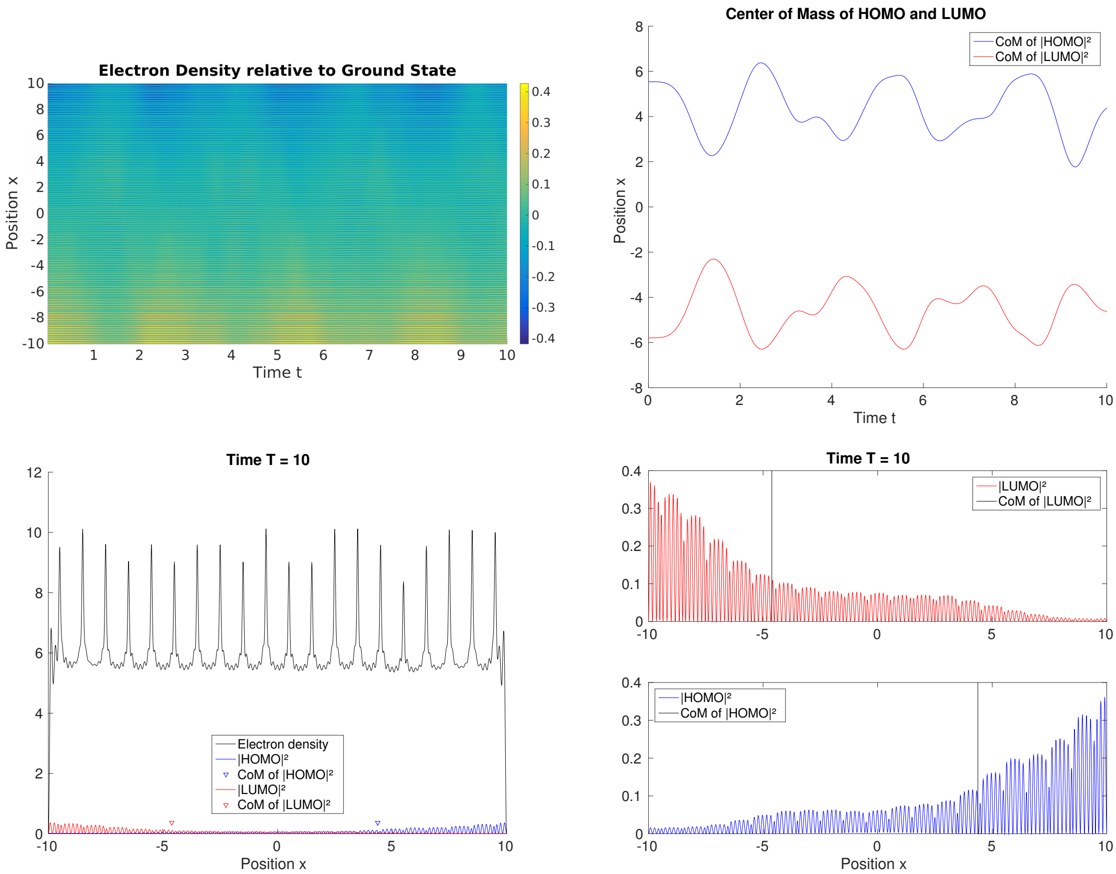

Figure 3.7: Top left: The electron density at time t and position x minus the electron density of the ground state. Top right: The temporal evolution of the center of mass of $|\text{HOMO}|^2$ and $|\text{LUMO}|^2$. Bottom left: The electron density at time $T = 10$ together with the density of HOMO and LUMO. Bottom right: The density of HOMO and LUMO at time $T = 10$.

Chapter 4

A Recombination-Drift-Diffusion System with Selfconsistent Potential

We consider the following recombination-drift-diffusion-Poisson system on a bounded domain $\Omega \subset \mathbb{R}^m$ with sufficiently smooth boundary $\partial\Omega$:

$$\begin{cases} \partial_t n = \nabla \cdot J_n(n,\psi) - R(n,p), \\ \partial_t p = \nabla \cdot J_p(p,\psi) - R(n,p), \\ -\varepsilon \Delta \psi = n - p - C, \end{cases} \tag{4.1}$$

where

$$J_n := \nabla n + n\nabla(\psi + V_n) = n\nabla\Phi_n, \qquad \Phi_n := \psi + V_n + \ln n,$$

$$J_p := \nabla p + p\nabla(-\psi + V_p) = p\nabla\Phi_p, \qquad \Phi_p := -\psi + V_p + \ln p,$$

$$R := F(n,p,x)(np - e^{-V_n - V_p}), \qquad 0 < C_F \le F(n,p,x),$$

$V_n, V_p \in W^{2,\infty}(\Omega)$ are external potentials and $C \in L^\infty(\Omega)$ is the internal doping concentration. We impose homogeneous Neumann boundary conditions for the potential ψ and no-flux boundary conditions for J_n and J_p:

$$\hat{n} \cdot J_n = \hat{n} \cdot J_p = \hat{n} \cdot \nabla\psi = 0 \quad \text{on } \partial\Omega$$

where $\hat{n}$ denotes to outer unit normal vector on $\partial\Omega$. We may also assume that the volume of Ω is normalized, i.e. $|\Omega| = 1$, which can be achieved by an appropriate scaling of the spatial variables.

4.1 Introductory Comments

Remark 4.1. Taking the sum of the dynamic equations for n and p in (4.1), we see that the total charge is conserved as a function of time:

$$\frac{d}{dt}\int_\Omega (n-p)\,dx = 0.$$

Thus, starting with initial concentrations n_I and p_I satisfying $\int_\Omega (n_I - p_I - C)\,dx = 0$, the system features charge neutrality for all times $t \ge 0$:

$$\int_\Omega (n - p - C)\,dx = 0. \tag{4.2}$$

For any function f, we set

$$\overline{f} := \int_\Omega f(x)\,dx$$

which is consistent with the usual definition of the average of f since $|\Omega| = 1$. Using this notation, the conservation law (4.2) rewrites as

$$\overline{n} - \overline{p} = \overline{C} \in \mathbb{R}.$$

Remark 4.2. Consider the homogeneous Neumann-problem

$$\begin{cases} \Delta u = f & \text{in } \Omega, \\ \hat{n} \cdot \nabla u = 0 & \text{on } \partial\Omega, \end{cases}$$

with $f \in L^2(\Omega)$. This system has a weak solution $u \in H^1(\Omega)$ iff $\overline{f} = 0$ (compatibility condition). In this case, there exists a unique solution $u \in H^1(\Omega)$ satisfying $\overline{u} = 0$. Here, we have $\overline{n - p - C} = 0$. Therefore, there exists a unique $\psi \in H^1(\Omega)$ with the following properties:

$$-\varepsilon\Delta\psi = n - p - C \ \text{ in } \Omega, \qquad \hat{n} \cdot \nabla\psi = 0 \ \text{ on } \partial\Omega, \qquad \overline{\psi} = 0. \tag{4.3}$$

In the sequel, the potential ψ always refers to this special solution of the Poisson-equation.

Remark 4.3. Let us assume that there exists a sufficiently smooth global solution of (4.1) corresponding to appropriate initial states (n_I, p_I) (cf. [33] for results in this direction on $\mathbb{R}^3$). Additionally, the stationary system

$$\begin{cases} \nabla \cdot J_n(n, \psi) - R(n, p) = 0, \\ \nabla \cdot J_p(p, \psi) - R(n, p) = 0, \\ -\varepsilon\Delta\psi = n - p - C, \end{cases}$$

together with $\hat{n} \cdot \nabla\psi = 0$ on $\partial\Omega$ and $\overline{\psi_\infty} = 0$, shall have a unique solution $(n_\infty, p_\infty, \psi_\infty)$ which is sufficiently smooth as well (cf. [33] for results concerning solutions to the stationary system in $\mathbb{R}^m$, $m \geq 3$). These equilibrium states n_∞, p_∞ and ψ_∞ satisfy $J_n(n_\infty, \psi_\infty) = J_p(p_\infty, \psi_\infty) = 0$ which implies

$$n_\infty = C_n e^{-\psi_\infty - V_n} \qquad \text{and} \qquad p_\infty = C_p e^{\psi_\infty - V_p}$$

with constants $C_n, C_p > 0$. Moreover $R(n_\infty, p_\infty) = 0$, hence,

$$n_\infty p_\infty = e^{-V_n - V_p}$$

and $C_n C_p = 1$. Uniqueness of the equilibrium states is only achieved if they satisfy the conservation law $\overline{n_\infty} - \overline{p_\infty} = \overline{C}$, or equivalently,

$$C_n \overline{e^{-\psi_\infty - V_n}} - C_p \overline{e^{\psi_\infty - V_p}} = \overline{C}. \tag{4.4}$$

Furthermore, we observe that ψ_∞ is only determined up to an additive constant unless we employ the condition $\overline{\psi_\infty} = 0$. The equilibrium states n_∞ and p_∞, however, are independent of the special choice of $\overline{\psi_\infty} = c \in \mathbb{R}$. This is a consequence of the formulas for C_n and C_p in (4.5) and (4.6) below.

In addition, we assume $\psi_\infty \in L^\infty(\Omega)$ and define

$$K_\infty := \|\psi_\infty\|_{L^\infty(\Omega)} \qquad \text{and} \qquad V_\infty := \max\left\{\|V_n\|_{L^\infty(\Omega)}, \|V_p\|_{L^\infty(\Omega)}\right\}.$$

The boundedness of ψ_∞ follows from a general existence result presented in [31] in the case of bounded Lipschitzian domains $\Omega \subset \mathbb{R}^m$ for $m \geq 2$. Apart from that, there exists a constant $C_P > 0$ such that for all $\phi \in H^1(\Omega)$, $\overline{\phi} = 0$, the Poincaré inequality

$$\|\phi\|_{L^2(\Omega)} \leq C_P \|\nabla\phi\|_{L^2(\Omega)}$$

holds true. Finally, $\|\cdot\|$ without further specification shall always denote the L^2-norm in Ω.

Lemma 4.4. *The following bounds in terms of K_∞, V_∞ and $|\overline{C}|$ hold true:*

$$C_n, C_p \leq e^{K_\infty + V_\infty}\big(1 + |\overline{C}|\big) \qquad \textit{and} \qquad n_\infty, n_\infty^{-1}, p_\infty, p_\infty^{-1} \leq e^{2(K_\infty + V_\infty)}\big(1 + |\overline{C}|\big).$$

Proof. We recall $C_n C_p = 1$ and solve (4.4) for $C_n > 0$:

$$C_n = \frac{\overline{C}}{2\overline{e^{-\psi_\infty - V_n}}} + \sqrt{\frac{\overline{C}^2}{4\overline{e^{-\psi_\infty - V_n}}^2} + \frac{\overline{e^{\psi_\infty - V_p}}}{\overline{e^{-\psi_\infty - V_n}}}} \leq \frac{|\overline{C}|}{\overline{e^{-\psi_\infty - V_n}}} + \sqrt{\frac{\overline{e^{\psi_\infty - V_p}}}{\overline{e^{-\psi_\infty - V_n}}}} \leq e^{K_\infty + V_\infty}(1 + |\overline{C}|). \tag{4.5}$$

Likewise, we can solve (4.4) for $C_p > 0$:

$$C_p = -\frac{\overline{C}}{2\overline{e^{\psi_\infty - V_p}}} + \sqrt{\frac{\overline{C}^2}{4\overline{e^{\psi_\infty - V_p}}^2} + \frac{\overline{e^{-\psi_\infty - V_n}}}{\overline{e^{\psi_\infty - V_p}}}} \leq \frac{|\overline{C}|}{\overline{e^{\psi_\infty - V_p}}} + \sqrt{\frac{\overline{e^{-\psi_\infty - V_n}}}{\overline{e^{\psi_\infty - V_p}}}} \leq e^{K_\infty + V_\infty}(1 + |\overline{C}|). \qquad (4.6)$$

The bounds on n_∞, n_∞^{-1}, p_∞ and p_∞^{-1} directly follow from the bounds on C_n and C_p when keeping in mind that $C_n C_p = 1$. □

Remark 4.5. We introduce the relative entropy

$$E(n, p, \psi) := \int_\Omega \left(n \ln \frac{n}{n_\infty} - (n - n_\infty) + p \ln \frac{p}{p_\infty} - (p - p_\infty) \right) dx + \frac{\varepsilon}{2} \int_\Omega |\nabla(\psi - \psi_\infty)|^2 \, dx$$

and the entropy production

$$D := -\frac{d}{dt} E,$$

which satisfies

$$\begin{aligned} D(n, p, \psi) &= \int_\Omega \left(\frac{|J_n|^2}{n} + \frac{|J_p|^2}{p} + F(n, p, x) \left(np - e^{-V_n - V_p} \right) \ln \left(\frac{np}{e^{-V_n - V_p}} \right) \right) dx \\ &= \int_\Omega \left(n |\nabla \Phi_n|^2 + p |\nabla \Phi_p|^2 + F(n, p, x) \left(np - e^{-V_n - V_p} \right) \ln \left(\frac{np}{e^{-V_n - V_p}} \right) \right) dx. \end{aligned} \qquad (4.7)$$

Both the entropy E and its production D are non-negative functionals.

Consider an arbitrary state (N, P, Ψ) which fulfills $D(N, P, \Psi) = 0$. We conclude that $J_n(N, \Psi) = J_p(P, \Psi) = R(N, P) = 0$ and, hence,

$$N = N_a := a \, e^{-\Psi - V_n}, \qquad P = P_a := \frac{1}{a} \, e^{\Psi - V_p}$$

and

$$-\varepsilon \Delta \Psi = N_a - P_a - C \ \text{ in } \Omega, \qquad \hat{n} \cdot \nabla \Psi = 0 \ \text{ on } \partial\Omega, \qquad \overline{\Psi} = 0.$$

However, none of these intermediate equilibria can be attained by the system unless it equals the equilibrium $(n_\infty, p_\infty, \psi_\infty)$. This fact can be seen from two perspectives. On the one hand, (N_a, P_a, Ψ) necessarily has to satisfy the conservation law $\overline{N_a - P_a - C} = 0$, if the system is able to reach this state. On the other hand, Poisson's equation with homogeneous Neumann boundary condition only admits a solution if the right hand side integrates to zero, i.e. $\overline{N_a - P_a - C} = 0$. But this additional constraint coincides with (4.4) within Remark 4.3. This demonstrates that $(N_a, P_a, \Psi) = (n_\infty, p_\infty, \psi_\infty)$ (provided there exists a unique equilibrium state as assumed in Remark 4.3). In addition, replacing the condition $\overline{\Psi} = 0$ by $\overline{\Psi} = c \in \mathbb{R}$ results in a shift of the potential in terms of the constant c. But the states N and P remain unchanged due to the same reasoning as in Remark 4.3.

Our aim is to prove convergence to equilibrium for system (4.1) and to obtain an explicit bound for the rate of convergence. For this reason, we want to derive an entropy-entropy production inequality of the form

$$E \leq C_{EEP} \, D$$

with some constant $C_{EEP} > 0$. To this end, we define the functional

$$G(n, p) := \int_\Omega \left(\frac{(n - n_\infty)^2}{n_\infty} + \frac{(p - p_\infty)^2}{p_\infty} \right) dx$$

and establish $E \leq c_1 G$ and $G \leq c_2 D$ with explicit constants $c_1, c_2 > 0$. This follows from an adaption of a technique presented in [19].

4.2 Derivation of an EEP-Inequality

Proposition 4.6. *There exists an explicitly computable constant $c_1 > 0$ such that*

$$E(n,p,\psi) \leq c_1 G(n,p)$$

for all $n,p \in L^2(\Omega)$ where $\psi \in H^1(\Omega)$ is the unique solution of (4.3). *More precisely, this inequality holds true for*

$$c_1 := 1 + \frac{C_P}{\varepsilon}\, e^{2(K_\infty+V_\infty)}\big(1+|\overline{C}|\big).$$

Proof. From the elementary inequality $\ln x \leq x-1$ for $x>0$, we derive

$$n\ln\left(\frac{n}{n_\infty}\right) - (n-n_\infty) \leq n\left(\frac{n}{n_\infty}-1\right) - n + n_\infty = \frac{(n-n_\infty)^2}{n_\infty}$$

and an analogous relation involving p and p_∞. Furthermore, we obtain

$$\varepsilon\int_\Omega |\nabla(\psi-\psi_\infty)|^2\,dx = -\varepsilon\int_\Omega (\psi-\psi_\infty)\Delta(\psi-\psi_\infty)\,dx = \int_\Omega \big((n-n_\infty)-(p-p_\infty)\big)(\psi-\psi_\infty)\,dx,$$

which follows from an integration by parts, the homogeneous Neumann boundary conditions for ψ and ψ_∞, as well as from $-\varepsilon\Delta(\psi-\psi_\infty) = (n-n_\infty)-(p-p_\infty)$. Applying Hölder's inequality and Young's inequality with some $\gamma>0$, we find

$$\varepsilon\int_\Omega |\nabla(\psi-\psi_\infty)|^2\,dx \leq \frac{1}{2}\left(\frac{1}{\gamma}\|(n-n_\infty)-(p-p_\infty)\|^2 + \gamma\|\psi-\psi_\infty\|^2\right).$$

As a consequence of $\overline{\psi-\psi_\infty}=0$, we may apply Poincaré's inequality giving rise to

$$\varepsilon\int_\Omega |\nabla(\psi-\psi_\infty)|^2\,dx \leq \frac{1}{\gamma}\Big(\|n-n_\infty\|^2+\|p-p_\infty\|^2\Big) + \frac{\varepsilon}{2}\|\nabla(\psi-\psi_\infty)\|^2$$

if we choose $\gamma := \varepsilon/C_P$. We thus arrive at

$$\begin{aligned}\frac{\varepsilon}{2}\int_\Omega |\nabla(\psi-\psi_\infty)|^2\,dx &\leq \frac{C_P}{\varepsilon}\int_\Omega \Big((n-n_\infty)^2+(p-p_\infty)^2\Big)\,dx \\ &\leq \frac{C_P}{\varepsilon}\,e^{2(K_\infty+V_\infty)}\big(1+|\overline{C}|\big)\int_\Omega\left(\frac{(n-n_\infty)^2}{n_\infty}+\frac{(p-p_\infty)^2}{p_\infty}\right)dx,\end{aligned}$$

where we have employed the bounds from Lemma 4.4. This proves the claim. □

Proposition 4.7. *There exists an explicitly computable constant $c_2>0$ such that*

$$G(n,p) \leq c_2 D(n,p,\psi)$$

for all $n,p\in L^2(\Omega)$ where $\psi\in H^1(\Omega)$ is the unique solution of (4.3). *In detail, this estimate is valid for*

$$c_2 := \frac{1}{2}\,e^{2(K_\infty+V_\infty)}\big(1+|\overline{C}|\big)\max\left\{\varepsilon\, e^{2(K_\infty+V_\infty)}\big(1+|\overline{C}|\big),\,\frac{1}{C_F}\right\}.$$

Proof. From the representation of the entropy production in (4.7) we deduce that

$$D(n,p,\psi) \geq c\int_\Omega\left(\frac{\varepsilon}{2}\Big(\frac{n}{n_\infty}|\nabla\Phi_n|^2 + \frac{p}{p_\infty}|\nabla\Phi_p|^2\Big) + \frac{1}{2}\big(np-e^{-V_n-V_p}\big)\ln\Big(\frac{np}{e^{-V_n-V_p}}\Big)\right)dx \tag{4.8}$$

where

$$c := \min\left\{\frac{2}{\varepsilon}\,e^{-2(K_\infty+V_\infty)}\frac{1}{1+|\overline{C}|},\,2C_F\right\}.$$

A couple of elementary manipulations show that

$$\begin{aligned}\frac{n}{n_\infty}|\nabla\Phi_n|^2 &= \frac{n}{n_\infty}|\nabla(\psi+V_n+\ln n)|^2 = \frac{n}{n_\infty}\Big|\nabla\Big(\psi+V_n+\ln C_n-\psi_\infty-V_n+\ln\Big(\frac{n}{n_\infty}\Big)\Big)\Big|^2\\ &= \frac{n}{n_\infty}\Big|\nabla\Big(\psi-\psi_\infty+\ln\Big(\frac{n}{n_\infty}\Big)\Big)\Big|^2 = \frac{n}{n_\infty}|\nabla(\psi-\psi_\infty)|^2+2\nabla(\psi-\psi_\infty)\cdot\nabla\Big(\frac{n}{n_\infty}\Big)+4\Big|\nabla\sqrt{\frac{n}{n_\infty}}\Big|^2\\ &\geq 2\nabla(\psi-\psi_\infty)\cdot\nabla\Big(\frac{n}{n_\infty}\Big) = 2\nabla(\psi-\psi_\infty)\cdot\nabla\Big(\frac{n}{n_\infty}-1\Big).\end{aligned}$$

Likewise, one finds

$$\begin{aligned}\frac{p}{p_\infty}|\nabla\Phi_p|^2 &= \frac{p}{p_\infty}|\nabla(-\psi+V_p+\ln p)|^2 = \frac{p}{p_\infty}\Big|\nabla\Big(-\psi+V_p+\ln C_p+\psi_\infty-V_p+\ln\Big(\frac{p}{p_\infty}\Big)\Big)\Big|^2\\ &= \frac{p}{p_\infty}\Big|\nabla\Big(\psi-\psi_\infty-\ln\Big(\frac{p}{p_\infty}\Big)\Big)\Big|^2 = \frac{p}{p_\infty}|\nabla(\psi-\psi_\infty)|^2-2\nabla(\psi-\psi_\infty)\cdot\nabla\Big(\frac{p}{p_\infty}\Big)+4\Big|\nabla\sqrt{\frac{p}{p_\infty}}\Big|^2\\ &\geq -2\nabla(\psi-\psi_\infty)\cdot\nabla\Big(\frac{p}{p_\infty}\Big) = -2\nabla(\psi-\psi_\infty)\cdot\nabla\Big(\frac{p}{p_\infty}-1\Big).\end{aligned}$$

Combining the previous estimates results in

$$\frac{\varepsilon}{2}\int_\Omega\Big(\frac{n}{n_\infty}|\nabla\Phi_n|^2+\frac{p}{p_\infty}|\nabla\Phi_p|^2\Big)dx \geq \varepsilon\int_\Omega \nabla(\psi-\psi_\infty)\cdot\nabla\Big(\Big(\frac{n}{n_\infty}-1\Big)-\Big(\frac{p}{p_\infty}-1\Big)\Big)dx.$$

As a result of (4.3), we arrive at

$$\begin{aligned}\frac{\varepsilon}{2}\int_\Omega\Big(\frac{n}{n_\infty}|\nabla\Phi_n|^2+\frac{p}{p_\infty}|\nabla\Phi_p|^2\Big)dx &\geq \int_\Omega\Big((n-n_\infty)-(p-p_\infty)\Big)\Big(\Big(\frac{n}{n_\infty}-1\Big)-\Big(\frac{p}{p_\infty}-1\Big)\Big)dx\\ &= \int_\Omega\Big(\frac{(n-n_\infty)^2}{n_\infty}+\frac{(p-p_\infty)^2}{p_\infty}-(n-n_\infty)(p-p_\infty)\Big(\frac{1}{n_\infty}+\frac{1}{p_\infty}\Big)\Big)dx.\end{aligned}$$

By introducing

$$\Omega^+ := \big\{x\in\Omega\,\big|\,\big(n(x)-n_\infty(x)\big)\big(p(x)-p_\infty(x)\big)>0\big\},$$

we further observe that

$$\frac{\varepsilon}{2}\int_\Omega\Big(\frac{n}{n_\infty}|\nabla\Phi_n|^2+\frac{p}{p_\infty}|\nabla\Phi_p|^2\Big)dx \geq G(n,p)-\int_{\Omega^+}(n-n_\infty)(p-p_\infty)\Big(\frac{1}{n_\infty}+\frac{1}{p_\infty}\Big)\,dx.$$

Due to the bounds on n_∞^{-1} and p_∞^{-1} from Lemma 4.4, this implies

$$G(n,p) \leq \frac{\varepsilon}{2}\int_\Omega\Big(\frac{n}{n_\infty}|\nabla\Phi_n|^2+\frac{p}{p_\infty}|\nabla\Phi_p|^2\Big)dx + 2e^{2(K_\infty+V_\infty)}\big(1+|\overline{C}|\big)\int_{\Omega^+}(n-n_\infty)(p-p_\infty)\,dx. \quad (4.9)$$

Subsequently, we shall prove that

$$4(n-n_\infty)(p-p_\infty) \leq \big(np-e^{-V_n-V_p}\big)\ln\Big(\frac{np}{e^{-V_n-V_p}}\Big).$$

This will follow from the elementary inequality $(x-1)\ln x \geq 4(\sqrt{x}-1)^2$ for all $x>0$ and some careful manipulations of the involved expressions. We first notice that

$$\begin{aligned}\big(np-e^{-V_n-V_p}\big)\ln\Big(\frac{np}{e^{-V_n-V_p}}\Big) &= e^{-V_n-V_p}\Big(\frac{np}{e^{-V_n-V_p}}-1\Big)\ln\Big(\frac{np}{e^{-V_n-V_p}}\Big)\\ &\geq 4e^{-V_n-V_p}\Bigg(\sqrt{\frac{np}{e^{-V_n-V_p}}}-1\Bigg)^2 = 4\big(\sqrt{np}-\sqrt{n_\infty p_\infty}\big)^2.\end{aligned}$$

Following the arguments of [19], we are able to verify that

$$\begin{aligned}\big(np-e^{-V_n-V_p}\big)\ln\Big(\frac{np}{e^{-V_n-V_p}}\Big) &\geq 4\big(\sqrt{np}-\sqrt{n_\infty p_\infty}\big)^2\\ &= \Big((\sqrt{n}-\sqrt{n_\infty})(\sqrt{p}+\sqrt{p_\infty})-(\sqrt{n}+\sqrt{n_\infty})(\sqrt{p}-\sqrt{p_\infty})\Big)^2\\ &\quad+4(\sqrt{n}-\sqrt{n_\infty})(\sqrt{p}-\sqrt{p_\infty})(\sqrt{n}+\sqrt{n_\infty})(\sqrt{p}+\sqrt{p_\infty})\\ &\geq 4(n-n_\infty)(p-p_\infty).\end{aligned}$$

This shows that

$$2\int_{\Omega^+}(n-n_\infty)(p-p_\infty)\,dx \le \frac{1}{2}\int_{\Omega^+}\big(np-e^{-V_n-V_p}\big)\ln\Big(\frac{np}{e^{-V_n-V_p}}\Big)dx$$

which — together with (4.9) and (4.8) — yields

$$\begin{aligned}G(n,p) &\le e^{2(K_\infty+V_\infty)}\big(1+|\overline{C}|\big)\int_\Omega\bigg(\frac{\varepsilon}{2}\Big(\frac{n}{n_\infty}|\nabla\Phi_n|^2+\frac{p}{p_\infty}|\nabla\Phi_p|^2\Big)+\frac{1}{2}\big(np-e^{-V_n-V_p}\big)\ln\Big(\frac{np}{e^{-V_n-V_p}}\Big)\bigg)dx\\ &\le e^{2(K_\infty+V_\infty)}\big(1+|\overline{C}|\big)\max\Big\{\frac{\varepsilon}{2}\,e^{2(K_\infty+V_\infty)}\big(1+|\overline{C}|\big),\,\frac{1}{2C_F}\Big\}D(n,p,\psi)\end{aligned}$$

and, hence, the assertion. □

Theorem 4.8. *There exists an explicitly computable constant $C_{EEP}>0$ such that*

$$E(n,p,\psi)\le C_{EEP}D(n,p,\psi)$$

for all $n,p\in L^2(\Omega)$ where $\psi\in H^1(\Omega)$ is the unique solution of (4.3). In particular, we may employ

$$C_{EEP}:=\frac{1}{2}\,e^{2(K_\infty+V_\infty)}\big(1+|\overline{C}|\big)\max\Big\{\varepsilon\,e^{2(K_\infty+V_\infty)}\big(1+|\overline{C}|\big),\,\frac{1}{C_F}\Big\}\bigg(1+\frac{C_P}{\varepsilon}\,e^{2(K_\infty+V_\infty)}\big(1+|\overline{C}|\big)\bigg).$$

Proof. This is an immediate consequence of Proposition 4.6 and Proposition 4.7. □

4.3 Convergence to the Equilibrium

Lemma 4.9. *Any entropy producing solution of (4.1) satisfies*

$$\forall\, t\ge 0:\quad \overline{n},\,\overline{p}\le\frac{5}{2}\,e^{2(K_\infty+V_\infty)}\big(1+|\overline{C}|\big)+\frac{3}{4}E_I=:M_1$$

where E_I denotes the initial entropy of the system.

Proof. Lemma 2.15 and Young's inequality entail

$$\begin{aligned}\overline{n}&\le\overline{n_\infty}+\|n-n_\infty\|_{L^1(\Omega)}\le\overline{n_\infty}+\sqrt{\frac{2}{3}\overline{n}+\frac{4}{3}\overline{n_\infty}}\sqrt{\int_\Omega\Big(n\ln\Big(\frac{n}{n_\infty}\Big)-(n-n_\infty)\Big)\,dx}\\ &\le\overline{n_\infty}+\frac{1}{3}\overline{n}+\frac{2}{3}\overline{n_\infty}+\frac{1}{2}\int_\Omega\Big(n\ln\Big(\frac{n}{n_\infty}\Big)-(n-n_\infty)\Big)\,dx.\end{aligned}$$

Solving this inequality for $\overline{n}$ yields

$$\overline{n}\le\frac{5}{2}\overline{n_\infty}+\frac{3}{4}\int_\Omega\bigg(n\ln\Big(\frac{n}{n_\infty}\Big)-(n-n_\infty)\bigg)\,dx.$$

Therefore, we arrive at

$$\overline{n}\le\frac{5}{2}\overline{n_\infty}+\frac{3}{4}E(n,p,\psi)\le\frac{5}{2}\,e^{2(K_\infty+V_\infty)}\big(1+|\overline{C}|\big)+\frac{3}{4}E_I$$

where we used Lemma 4.4 and the monotonicity of the entropy functional in the last step. In the same way, we may bound $\overline{p}$ from above. □

Proposition 4.10. *There exists an explicitly computable constant $C_{CKP}>0$ such that*

$$E(n,p,\psi)\ge C_{CKP}\Big(\|n-n_\infty\|^2_{L^1(\Omega)}+\|p-p_\infty\|^2_{L^1(\Omega)}\Big)$$

for all $n,p\in L^2(\Omega)$ satisfying $\overline{n},\overline{p}\le M_1$ where $\psi\in H^1(\Omega)$ is the unique solution of (4.3). More precisely, one can choose

$$C_{CKP}:=\Big(3\,e^{2(K_\infty+V_\infty)}\big(1+|\overline{C}|\big)+\frac{1}{2}E_I\Big)^{-1}.$$

Proof. We observe that

$$E(n,p,\psi) \geq \int_\Omega \left(n \ln \frac{n}{n_\infty} - (n - n_\infty) + p \ln \frac{p}{p_\infty} - (p - p_\infty) \right) dx$$
$$\geq \frac{3}{2\overline{n} + 4\overline{n_\infty}} \|n - n_\infty\|^2_{L^1(\Omega)} + \frac{3}{2\overline{p} + 4\overline{p_\infty}} \|p - p_\infty\|^2_{L^1(\Omega)}$$

thanks to Lemma 2.15. Owing to the assumption $\overline{n}$, $\overline{p} \leq M_1$ and Lemma 4.4, we continue the estimate

$$E(n,p,\psi) \geq 3 \left(9\, e^{2(K_\infty + V_\infty)} \big(1 + |\overline{C}|\big) + \frac{3}{2} E_I \right)^{-1} \Big(\|n - n_\infty\|^2_{L^1(\Omega)} + \|p - p_\infty\|^2_{L^1(\Omega)} \Big),$$

which finishes the proof. □

Theorem 4.11. *Let* (n,p) *be a global solution of system* (4.1) *as assumed to exist in Remark 4.3. Furthermore, we assume that this solution satisfies the weak entropy production law*

$$E(n,p,\psi)(t_1) + \int_{t_0}^{t_1} D(n,p,\psi)(s)\, ds \leq E(n,p,\psi)(t_0)$$

for all $0 < t_0 \leq t_1 < \infty$. *Then, the solution decays exponentially to the equilibrium* (n_∞, p_∞) *as a function of time* $t \geq 0$*:*

$$E(n,p,\psi) \leq (E_I - E_\infty) e^{-Kt}$$

and

$$\|n - n_\infty\|^2_{L^1(\Omega)} + \|p - p_\infty\|^2_{L^1(\Omega)} \leq C(E_I - E_\infty) e^{-Kt}$$

where $C := C_{CKP}^{-1}$ *and* $K := C_{EEP}^{-1}$ *are defined in Theorem 4.8 and Proposition 4.10. In addition,* E_I *and* E_∞ *denote the initial entropy of the system and the entropy of the equilibrium, respectively.*

Proof. The claim of this theorem follows along the same lines as the proof of Theorem 2.8. □

Chapter 5

Remarks and Outlook

Below, we collect a couple of ideas for future research which could be investigated within some follow-up projects. Note that we do not claim the following list of comments to be exhaustive.

In Chapter 2, we studied the PDE-ODE system (2.1) which describes drift, diffusion and recombination of electrons and holes in semiconductors. But since electrons and holes are charged particles, one should also take the electrostatic interaction between them into account when designing a physically more precise model. From a mathematical point of view, this results in an additional Poisson-equation which determines the electrostatic potential ψ generated by electrons and holes. But this Coulomb potential itself influences the motion of the charged particles, which results in a coupling of the Poisson-equation to the dynamic equations of electrons and holes:

$$\begin{cases} \partial_t n = \nabla \cdot J_n(n) + R_n(n, n_{tr}), \\ \partial_t p = \nabla \cdot J_p(p) + R_p(p, n_{tr}), \\ \varepsilon\, \partial_t n_{tr} = R_p(p, n_{tr}) - R_n(n, n_{tr}), \\ -\eta \Delta \psi = n - p + \varepsilon n_{tr}, \end{cases} \tag{5.1}$$

with

$$J_n := \nabla n + n \nabla(\psi + V_n) = \mu_n \nabla \left(\frac{n}{\mu_n} \right), \qquad \mu_n := e^{-\psi - V_n},$$

$$J_p := \nabla p + p \nabla(-\psi + V_p) = \mu_p \nabla \left(\frac{p}{\mu_p} \right), \qquad \mu_p := e^{\psi - V_p},$$

$$R_n := \frac{1}{\tau_n} \left(n_{tr} - \frac{n}{n_0 \mu_n}(1 - n_{tr}) \right), \quad R_p := \frac{1}{\tau_p} \left(1 - n_{tr} - \frac{p}{p_0 \mu_p} n_{tr} \right).$$

Here, we encounter the same quantities as in Chapter 2 plus a constant $\eta > 0$ which encodes the permittivity of the material. However, this additional coupling to the Poisson-equation causes further difficulties regarding the proof of an EEP-inequality with explicit constants. To our knowledge, this problem is still open in the literature. A possible approach could build on an adaption of the strategy from Chapter 4 to system (5.1). But here, we encounter two species of recombination terms, R_n and R_p, and the additional variable n_{tr}. Moreover, R_n and R_p measure differences between time-dependent quantities, whereas the recombination term R in (4.1) is proportional to $np - n_\infty p_\infty$. A thorough investigation of this approach (maybe combined with techniques from Chapter 2) might be the subject of subsequent studies.

Moreover, we assumed initial data $(n_I, p_I) \in L^\infty(\Omega)^3$, an assumption which could possibly be weakened to $(n_I, p_I) \in L^2(\Omega)^3$. For sure, we need the L^∞-assumption within the existence proofs in Section 2.7 to control some nonlinear terms, especially when proving that the fixed-point iteration constitutes a contraction. But one could possibly get around this difficulty by employing more elaborate arguments for proving the contraction property. A completely different approach could be taken by using the concept of *renormalized solutions* introduced in [18] for general reaction-drift-diffusion equations. In this article, renormalized solutions are shown to exist globally in time under some natural assumptions on the structure of the system for initial data $u_0 \in L^1(\Omega)$ satisfying $\int_\Omega u_0 \ln u_0 \, dx < \infty$. Nevertheless, this result is not directly applicable in our situation as we are lacking diffusion for n_{tr}.

At the beginning of Chapter 3, we restricted our considerations to pairwise occupations of orbitals and pairwise excitations of $2n$ electrons. On the one hand, this assumption enabled us to easily identify the ground state configuration and the first excited state. In the former case, all orbitals up to HOMO are twice occupied, and identically in the latter case except that now HOMO is unoccupied but LUMO is twice occupied. This fact further implied a simple structure of the charge transfer functional

$$J[\vec{\varphi}, \rho_{nuc}] = \left| \int_\Omega \left(|\varphi_{n+1}|^2 - |\varphi_n|^2 \right) (x \cdot e) \, dx \right|,$$

which was presumably by far more complicated if we did not stick to pairwise occupations. On the other hand, as this restriction is artificial for the most part, one should remove it in order to obtain physically more relevant results about the process of charge transfer and the corresponding material design problem.

Obviously, there are various directions for generalizations of the 1D simulation in Section 3.4. The extension of our approach to a 3D simulation is, for sure, desirable but probably related to a computational effort which only allows one to study few-electron-configurations. We also plan to investigate the possibility to gain an electric current by harvesting the charge separation appropriately. This demands for certain boundary conditions for the Kohn–Sham equations which model the outflow of the electric charge. Since we have proven the existence of an optimal nuclear charge density in Section 3.3 for orbitals with homogeneous Dirichlet conditions, these more general boundary conditions could also impose a challenge for this existence proof. Furthermore, one could also skip the restriction to a prescribed number of protons and electrons (120 in our simulation) inside the atomic system. Even if we keep this constraint on the particle number, we might try to add the positions of the atoms as additional variables to the optimization procedure. We see there is enough space for future studies on this problem.

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