Dissertation

Derivation, analysis and numerics for diffusive multi-component mixtures

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Dott. Mag. **Annamaria Massimini**

Matr.Nr.: 12142875

President:	Ao.Univ.Prof. Dipl.-Ing. Dr.techn. **Gernot Tragler** Institute of Statistics and Mathematical Methods in Economics, TU Wien
Supervisor:	Univ. Prof. Dr. **Ansgar Jüngel** Institut für Analysis und Scientific Computing, TU Wien
Supervisor:	Univ. Prof. Dr. **Francesco Salvarani** De Vinci Research Center, Pôle Léonard de Vinci
Reviewer:	Univ. Prof. Dr. **Benoît Perthame** Laboratoire Jacques-Louis Lions, Sorbonne Université
Reviewer:	Univ. Prof. Dr. **Jian-Guo Liu** Trinity College of Arts & Sciences (Mathematics and Physics), Duke University
Examiner:	Univ. Prof. Dr. **Frédérique Charles** Laboratoire Jacques-Louis Lions, Sorbonne Université

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Ai curiosi,
A coloro che sanno ancora stupirsi e non smettono di farsi domande.

A mamma e papà, Tommaso e Agata.

"Here, on the edge of what we know, in contact with the ocean of the unknown, shines the mystery and beauty of the world. And it's breathtaking."

Carlo Rovelli

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Abstract

This thesis studies the mathematical and numerical analysis of macroscopic models for multispecies systems. The derivation of a new model will also be part of the manuscript.

Multispecies systems describe real world phenomena in which several entities of different species interact. Importantly, the interactions among species are crucial in determining the behaviour of each species and the system as a whole.

The thesis begins with a study of mixtures of finite-size ions species immersed in a polar solvent. They move through channels or nanopores. The evolution of the ion concentrations is described by systems of partial differential equations of modified Poisson-Nernst-Planck type with mixed Dirichlet-Neumann boundary conditions. Since the ion size is not significantly smaller than the channel diameter, size exclusion effects must be taken into account in the model. The so-called "size exclusion" or "volume filling" constraint is imposed, implying that the sum of the ion and solvent concentrations is constant. This saturation introduces cross-diffusion effects into the system of PDEs. In addition, a drift term, accounting for electrostatic interactions, is contained in the equations' fluxes. It can be expressed in terms of the electric potential gradient, which is coupled to the concentrations via a Poisson-type equation.

This thesis' first work presents two finite volume approaches for a degenerate Poisson-Nernst-Planck system. Both methods employ a two-point flux approximation and belong to the exponentially fitted scheme framework. The two approaches differ in the use of the Stolarsky mean for describing the drift term, derived from a self-consistent electric potential. The first method (SQRA) uses a geometric mean, extending the square-root approximation. In contrast, the second method (SG) employs an inverse logarithmic mean, generalizing the Scharfetter-Gummel scheme. Both approaches ensure the decay of some discrete free energy. Classical numerical analysis results follow, investigating the scheme's long-time behaviour. Numerical simulations show that both schemes are effective for moderate Debye lengths. The SG scheme demonstrates greater robustness in the small Debye length limit. Nevertheless, simulations also point to a possible slow convergence to equilibrium.

The thesis's second work analyses a Poisson–Nernst–Planck–Fermi system. The concentrations solve cross-diffusion equations, which are thermodynamically consistent. In particular, the correlated electric potential depends nonlocally on the electric potential and solves the fourth-order Poisson–Fermi equation. The existence of global bounded weak solutions is proved using the boundedness-by-entropy method. This work's novelty lies in proving the weak–strong uniqueness property. In contrast to the existence proof, the solvent concentration is included in the cross-diffusion system, leading to a diffusion matrix with nontrivial kernel. The proof is based on the relative entropy method for the extended cross-diffusion system and the positive definiteness property of a related diffusion matrix on a subspace.

The final part of the manuscript explores aerosols mixtures. It proposes a non-isothermal kinetic model of the interactions between dust particles and gas molecules. Gas-dust collisions follow a diffuse reflection mechanism on the surface of dust particles. The surface temperature of the particles is treated as a function of time and space, satisfying a transport-like equation.

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The main novelty of this approach lies in two aspects. First, the model allows for the conservation of the total energy of the system. Secondly, the work presents a derivation of an explicit expression for entropy. After an appropriate scaling of the equations, a formal diffusive asymptotics to a two-species Maxwell-Stefan model is carried out. In particular, the case of vanishing mass and velocity ratios between gas and dust, as well as the Knudsen number, are analysed.

Keywords: Ions mixtures; Aerosol mixtures; Cross-diffusion; Boundedness-by-entropy methods; Weak-strong uniqueness; Finite Volume schemes; Exponential fitting; Kinetic theory; Boltzmann equation; Diffusive asymptotic.

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Kurzfassung

Diese Dissertation untersucht die mathematische und numerische Analyse makroskopischer Modelle für Multispezies-Systeme. Die Ableitung eines neuen Modells wird ebenfalls Teil des Manuskripts sein.

Diese Systeme beschreiben reale Phänomene, bei denen mehrere Entitäten verschiedener Spezies interagieren. Wichtig ist, dass die Interaktionen zwischen den Spezies entscheidend für das Verhalten jeder Spezies und des gesamten Systems sind.

Die Dissertation beginnt mit einer Studie über Mischungen von Ionen endlicher Größe, die in einem polaren Lösungsmittel eingetaucht sind. Sie bewegen sich durch Kanäle oder Nanoporen. Die Entwicklung der Ionenkonzentrationen wird durch Systeme von partiellen Differentialgleichungen vom modifizierten Poisson-Nernst-Planck-Typ mit gemischten Dirichlet-Neumann-Randbedingungen beschrieben. Da die Ionengröße nicht wesentlich kleiner als der Kanaldurchmesser ist, müssen Größenausschlusseffekte im Modell berücksichtigt werden. Die sogenannte 'Größenausschluss' oder 'Volumenfüllungs' Beschränkung wird auferlegt, was bedeutet, dass die Summe der Ionenkonzentrationen und der Lösungsmittelkonzentrationen konstant ist. Diese Sättigung führt zu Kreuzdiffusionseffekten im System der PDEs. Zusätzlich ist ein Drifterm enthalten, der elektrostatische Wechselwirkungen berücksichtigt. Dieser kann in Form des elektrischen Potentialgradienten ausgedrückt werden, der über eine Poisson-Gleichung mit den Konzentrationen gekoppelt ist.

Die erste Arbeit dieser Dissertation stellt zwei Finite-Volumen-Ansätze für ein degeneriertes Poisson-Nernst-Planck-System vor. Beide Methoden verwenden eine Zwei-Punkt-Fluss-Approximation und gehören zum Rahmen exponentiell angepasster Schemata. Die Ansätze unterscheiden sich in der Verwendung des Stolarsky-Mittels zur Beschreibung des Drifterms, der aus einem selbstkonsistenten elektrischen Potential abgeleitet wird. Die erste Methode (SQRA) verwendet ein geometrisches Mittel und erweitert die Quadratwurzel-Approximation. Im Gegensatz dazu verwendet die zweite Methode (SG) ein inverses logarithmisches Mittel und verallgemeinert das Scharfetter-Gummel-Schema. Beide Ansätze gewährleisten den Abfall einer diskreten freien Energie. Es folgen klassische numerische Analyseergebnisse, und das Langzeitverhalten des Schemas wird ebenfalls untersucht. Numerische Simulationen zeigen, dass beide Schemata für moderate Debye-Längen effektiv sind, aber auch auf eine möglicherweise sehr langsame Konvergenz zum Gleichgewicht hinweisen. Doch das SG-Schema zeigt eine größere Robustheit im Fall kleiner Debye-Längen.

Die zweite Arbeit der Dissertation analysiert ein Poisson-Nernst-Planck-Fermi-System. Die Konzentrationen lösen thermodynamisch konsistente Kreuzdiffusionsgleichungen. Insbesondere hängt das korrelierte elektrische Potential nichtlokal vom elektrischen Potential ab und löst die Poisson-Fermi-Gleichung vierter Ordnung. Die Existenz global beschränkter schwacher Lösungen wird mit der Entropie-Methode bewiesen. Die Neuheit dieser Arbeit liegt im Nachweis der schwach-starken Eindeutigkeit. Im Gegensatz zum Existenzbeweis wird die Lösungsmittelkonzentration in das Kreuzdiffusionssystem einbezogen, was zu einer Diffusionsmatrix mit nichttrivialem Kern führt. Der Beweis basiert auf der relativen Entropie-Methode für das er-

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weiterte Kreuzdiffusionssystem und der Eigenschaft der positiven Definitheit einer zugehörigen Diffusionsmatrix auf einem Unterraum.

Der letzte Teil des Manuskripts untersucht Aerosolmischungen. Es wird ein nichtisothermes kinetisches Modell der Wechselwirkungen zwischen Staubpartikeln und Gasmolekülen vorgeschlagen. Die Arbeit geht davon aus, dass Kollisionen zwischen Gas und Staub an der Stauboberfläche einer diffusen Reflexion folgen. Die Oberflächentemperatur der Partikel wird als Funktion der Zeit und des Raums behandelt und erfüllt eine transportähnliche Gleichung. Die Hauptneuheit dieses Ansatzes liegt in zwei Aspekten: Zum einen ermöglicht das Modell die Erhaltung der Gesamtenergie des Systems. Zum anderen wird eine explizite Entropieformel abgeleitet. Nach einer geeigneten Skalierung der Gleichungen wird eine formale diffusive Asymptotik zu einem zweispezifischen Maxwell-Stefan-Modell durchgeführt. Insbesondere werden die Fälle verschwindender Massen- und Geschwindigkeitsverhältnisse zwischen Gas und Staub sowie die Knudsen-Zahl analysiert.

Schlüsselwörter: Ionenmischungen; Aerosolmischungen; Kreuzdiffusion; Boundedness-by-Entropy-Methoden; Schwach-starke Eindeutigkeit; Finite-Volumen-Schemata; Exponentiale Anpassung; Kinetische Theorie; Boltzmann-Gleichung; Diffusive Asymptotik.

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Résumé

Cette thèse étudie l'analyse mathématique et numérique des modèles macroscopiques pour les systèmes multi-espèces, y compris la dérivation d'un nouveau modèle.

Ces systèmes décrivent des phénomènes réels où différentes espèces interagissent, et ces interactions sont cruciales pour déterminer le comportement de chaque espèce et du système dans son ensemble.

La thèse commence par une étude des mélanges d'ions de taille finie dans un solvant polaire, se déplaçant à travers des canaux ou nanopores. L'évolution des concentrations d'ions est décrite par des équations aux dérivées partielles de type Poisson-Nernst-Planck modifié avec des conditions aux limites mixtes de Dirichlet-Neumann. Comme la taille des ions n'est pas beaucoup plus petite que le diamètre du canal, les effets d'exclusion par taille doivent être modélisés. La contrainte "d'exclusion par taille" ou "de remplissage de volume" est imposée, signifiant que la somme des concentrations d'ions et de solvant est constante, introduisant des effets de diffusion croisée. Un terme de dérive pour les interactions électrostatiques est également présent dans les flux, exprimé en termes de gradient du potentiel électrique, couplé aux concentrations via une équation de type Poisson.

Le premier travail présente deux approches de volume fini pour un système de Poisson-Nernst-Planck dégénéré. Les deux méthodes utilisent une approximation de flux à deux points et appartiennent au cadre des schémas exponentiellement ajustés, différant par l'utilisation de la moyenne de Stolarsky pour le terme de dérive dérivé d'un potentiel électrique auto-cohérent. La première méthode (SQRA) utilise une moyenne géométrique, étendant l'approximation par racine carrée, tandis que la seconde (SG) emploie une moyenne logarithmique inverse, généralisant le schéma de Scharfetter-Gummel. Les deux approches assurent la décroissance de l'énergie libre discrète. Les résultats classiques de l'analyse numérique suivent, et le comportement à long terme est étudié. Les simulations montrent que les deux schémas sont efficaces pour des longueurs de Debye modérées, mais signalent une convergence possiblement lente vers l'équilibre, le schéma SG montrant une plus grande robustesse pour de petites longueurs de Debye.

Le deuxième travail analyse un système de Poisson-Nernst-Planck-Fermi où les concentrations résolvent des équations de diffusion croisée thermodynamiquement cohérentes. Le potentiel électrique corrélé dépend non localement du potentiel électrique et résout l'équation de Poisson-Fermi du quatrième ordre. L'existence de solutions faibles globales bornées est prouvée en utilisant la méthode de la bornitude par l'entropie. La nouveauté réside dans la preuve de l'unicité faible-forte. Contrairement à la preuve d'existence, la concentration de solvant est incluse dans le système de diffusion croisée, conduisant à une matrice de diffusion avec un noyau non trivial. La preuve repose sur la méthode de l'entropie relative pour le système de diffusion croisée étendu et la positivité définie d'une matrice de diffusion associée sur un sous-espace.

La dernière partie explore les mélanges d'aérosols et propose un modèle cinétique non isotherme des interactions entre particules de poussière et molécules de gaz. Le travail suppose une réflexion diffuse pour les collisions gaz-poussière. La température de surface des particules

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est traitée comme une fonction du temps et de l'espace, satisfaisant une équation de type transport. La principale nouveauté réside en deux aspects : le modèle permet la conservation de l'énergie totale et présente une dérivation explicite de l'entropie. Après une mise à l'échelle des équations, une asymptotique diffusive formelle vers un modèle de Maxwell-Stefan à deux espèces est réalisée, analysant les rapports de masse et de vitesse nuls entre gaz et poussière, ainsi que le nombre de Knudsen.

Mots-clés: Mélanges d'ions ; Aérosols ; Diffusion croisée ; Méthodes d'entropie; Unicité faible-forte ; Schémas de volumes finis ; Exponential fitting ; Théorie cinétique ; Équation de Boltzmann ; Asymptotique diffusive.

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List of Collaborations and Publications

This thesis is the result of the following scientific collaborations carried out during the years 2021-2024:

- A. Jüngel, A. Massimini, *"Analysis of a Poisson-Nernst-Planck-Fermi system for charge transport in ion channels"*, Journal of Differential Equations 395, 38-68 (2024).
- C. Cances, M. Herda, A. Massimini, *"Finite volumes for a generalized Poisson-Nernst-Planck system with cross-diffusion and size exclusion"*, In: Franck, E., Fuhrmann, J., Michel-Dansac, V., Navoret, L. (eds) Finite Volumes for Complex Applications X—Volume 1, Elliptic and Parabolic Problems. FVCA 2023. Springer Proceedings in Mathematics & Statistics, vol 432. Springer, Cham.
- C. Cances, M. Herda, A. Massimini, *"Convergence and long-time behavior of finite volumes for a generalized Poisson-Nernst-Planck system with cross-diffusion and size exclusion"*, work in progress.
- F. Charles, A. Massimini, F. Salvarani, *"Diffusion asymptotic of a kinetic model for gas-particle mixture with energy exchanges"*, work in progress.

Another publication, which was started during my master's thesis in 2021, was finished during my PhD. However, it will not be included in this manuscript:

- F. Charles, A. Massimini, F. Salvarani, *"Mathematical and numerical study of a kinetic model describing the evolution of planetary rings"*, Computers & Mathematics with Applications, 143, 48-56 (2023).

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Part I

Introduction

Summary of Part I - Introduction

This introduction provides the non-mathematical motivations as well as the mathematical tools for the study of multicomponent systems.

Chapter 1 introduces multicomponent systems, focusing on how interactions between species determine their behaviour. Special attention is given to the role of diffusion, which in multicomponent systems does not follow the conventional rule of diffusion 'against the gradient'. Examples will then be presented from the fields of chemistry and physics where there is evidence for such diffusive 'anomalies'. Particular emphasis is placed on the dynamics of gases and ions. This is the main subject of the thesis.

Having provided a framework for the main subject of study, Having provided a framework for the main subject of study, an explanation of the mathematical techniques used to study multicomponent systems is given. In Chapter 2 I will explain what is meant by cross-diffusion systems and the mathematical difficulties encountered in their analysis. Then the boundedness-by-entropy method and the finite volume schemes discretisation will be explored.

The kinetic description of such mixtures is reserved for Chapter 4. I will discuss the concept of the diffusive limit, moving from the mesoscopic to the macroscopic scale of description.

Finally, Chapter 5 will discuss the outlines of the thesis.

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Chapter 1

General Introduction

1.1 Multi-component systems: the role of interactions

Multispecies systems frequently appear in biology and sociology, as well as in engineering. These systems consist of many types of interacting entities, such as communities of organisms including plants, insects, animals or humans. At the microscopic level, they consist in mixtures of gas particles, colonies of bacteria, populations of cells. As one might expect, the individual behaviour of each species changes when considering the species embedded in a community of different entities. Inter-species relationships play a crucial role in determining how species behave. In population dynamics, resource consumption, movement, and inter-species aggression introduce behavioural patterns that are not a priori included in the individual strategies [146], [152], [162]. In a closed market, capital and labour can influence their spatial distribution [15]. Moreover, the so-called "Ouzo effect", observed when water is added to an aniseed-based alcohol, results from the involvement of all the driving forces of the constituents (water, ethanol, trans-anethol) in determining the flux of each constituent species [130]. Therefore, modelling interactions is important.

1.2 Diffusion in multi-component systems

Section 1.1 illustrated how important the role of inter-species interaction in determining the behavior of entities in multicomponent systems is. Explaining more precisely what happens and trying to translate it into mathematical language is the aim of this section.

1.2.1 What does "diffusion" mean?

Diffusion is the tendency of particles, initially concentrated close to a point in space, to *spread out* over time, gradually covering a larger area around their origin [146], [168]. However, this definition is likely to lead to confusion. Particles in uniform rectilinear motion, that is each with its own constant speed and direction, move away from their original point, occupying larger and larger areas. This, however, is not the result of diffusion. Diffusion is a macroscopic phenomenon that results from the irregular motion of each particle at the microscopic level. Thus is related to the concept of randomness. The irregular microscopic motion of each particle gives rise to regularity in the motion of the total group of particles. The phenomenon of diffusion describes this regularity and thus pertains to the macroscopic level.

Diffusion quantities are not confined to particles. In fact, the first studies of diffusion concerned heat, diffusing from hot to cold areas. Spreading quantities can be concentrations, momentum, information, ideas, prices. Every such process can diffuse and its evolution may be governed by mathematical analysis.

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1.2.2 Different scales to describe the problem

As emerged from the previous section, the scale of observation of the interaction between entities plays a crucial role in the observation and study of the phenomenon itself. Consider a flock of birds, the trajectory of each bird may be described. However, it is only when zooming out that one observes the flocking motion of the whole crowd [16] [1] [73]. Depending on the phenomenon of study, one must therefore choose the correct 'position' of observation.

The microscopic description

The microscopic approach uses ordinary differential equations to track the movement of individual particles based on interactions and external forces. In a system of N particles, denoted by $(x_i(t))_{i=1}^N$ and $(v_i(t))_{i=1}^N$ their positions and velocities, respectively, Newton's law [145] describes their evolution by

$$\begin{cases} \frac{d}{dt}x_i(t) = v_i(t), \\ \frac{d}{dt}v_i(t) = \mathcal{F}_i(t), \end{cases} \tag{1.1}$$

where $\mathcal{F}_i$ represents the force acting on the i-th particle. Hence, given the initial position of each particle, the dynamics of the system is described by $6N$ (if in $\mathbb{R}^3$) coupled first-order ordinary differential equations. Although conceptually simple and extremely detailed, this method is computationally demanding for large particle numbers N. In addition, observing the behaviour of particles at the microscopic level does not capture interesting phenomena such as diffusion. This scale is only suitable for describing the dynamics of a system with a few entities. An example is the planets in the Solar System. This approach is not suitable for the motion of fluids or rarefied gases.

The macroscopic description

In this situation, particles are observed from far away. From this reference point, the set of particles appears as a fluid, whose evolution in space and time can thus be described through the concentration variable $u(x,t)$. The evolution of the latter will be dictated by partial differential equations. One of the most basic and classical example of macroscopic model, the main model for diffusion, is the (linear) heat equation

$$\partial_t u - \Delta u = 0. \tag{1.2}$$

It was first proposed by Fourier in 1822 [95] to mathematically model the propagation of heat, described here by the space-time function u. This family of equations also includes the Euler and the Navier-Stokes equations.

The mesoscopic description

The kinetic or mesoscopic description of a particle system, proposed by Boltzmann in the late 19th century, is placed between the micro and macro ones. In this approach, a distribution function $F = F(t,x,v)$ gives the probability of finding a particle with velocity v in the space position x at the time t. In particular the integral

$$\int_{X\times V} F(t,x,v)dxdv$$

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gives the number of particles at the time t in the space-velocity domain $X \times V$. The system's degrees of freedom are significantly reduced compared to the microscopic description, as it focuses on "typical" displacements rather than exact positions and velocities of particles. This approach retains molecular interaction information, that are lost in the macroscopic description. Moreover, it allows physical observables like matter, velocity, and temperature to be interpreted through probabilistic measures on the F density (mass, expectation, and variance).

The kinetic description holds for rarefied particle systems, where the mean free path of a molecule is comparable to a length scale of the problem, i.e. the ratio between the mean free path and the characteristic length (called *Knudsen number* (Kn)) is near or greater than one. The free transport equation, Vlasov and Boltzmann-type equations are classical examples of kinetic equations (see Chapter 4 for an in-depth discussion).

Collisions between particles are usually described by means of an operator, which is usually non-linear and an integral term in velocity. Such collisional kernels, for non-trivial collisional mechanisms are difficult to treat from a mathematically. This is especially true in multi-species dynamics, where multi-species kernels are involved. A macroscopic model is hence preferable to study in this case.

The change of scaling

In many situations, the macroscopic description is the most appropriate scale to capture interesting observable phenomena. It is also the easiest to handle numerically. Unlike the microscopic description, it describes collective behavior without requiring a large number of unknowns. Unlike the mesoscopic description, it does not involve non-trivial collision kernels.

However, it is difficult to write a macroscopic equation at a glance that takes into account observable large-scale effects. One would have to add ad hoc terms without knowing whether these result from the microscopic interaction between the particles. Consequently, the formal way to obtain macroscopic models is to start at the microscopic or mesoscopic level. To pass from the microscopic to the macroscopic scale, one idea is that as $N \to \infty$, the particles behave as "one" and become independent in the limit. Hence, from a microscopic system of ordinary (stochastic) differential equations, we obtain a PDE (mean-field limits). Moreover, we can transition from the mesoscopic to the macroscopic scale by performing a proper dimensionless analysis and then passing to the limit in the Knudsen number ($Kn \to 0$). In this way, "cost effects" can be added to the macroscopic model without altering the macroscopic equations themselves. Instead, one simply analyzes the relationship between particle interactions and the working scale (diffusive limit, hydrodynamic limit, etc.). Furthermore, depending on which parameter we neglect, we obtain different equations in the limit. Thus, the relationship between the kinetic level and the macroscopic description also specifies the range of validity of the target equations as well as the relationship within the model hierarchy. An in-depth discussion of kinetic equations, particularly the passage from the mesoscopic to the macroscopic scale via the *diffusive limit*, can be found in Chapter 4.

Another way to deduce macroscopic equations is to start working on a discrete equidistant spatial grid of mesh size h (*lattice model*). One divides the space into discrete sites and models the movement of the population based on the probability that an individual jumps from its current location to a neighboring site [10, 149, 167]. Here, $u(x,t)$ represents the probability of finding a particle at node x at time t. This description is often referred to as a microscopic description because the pattern of movement of the population emerges from individual-level

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assumptions. By refining the spatial discretization ($h \to 0$), one can obtain, in the limit, a partial differential equation for u. This scaling via a hopping process will be discussed again in Chapter 6. Here the hopping process introduced in [38] will be used as a starting point for the definition of a numerical scheme for the limit (macroscopic) equation.

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Chapter 2

Macroscopic description of multi-species systems

The concept of diffusion, a common denominator throughout this thesis, is the focus of this chapter. The following sections provide a mathematical understanding of mass diffusion at the macroscopic level. Starting with Adolf Fick's first model, experimental data and model inaccuracies when dealing with multi-species systems will be discussed. Then, diffusion will be outlined in a more general sense (not just of matter). Lastly, this chapter presents an explanation of diffusion in thermodynamic terms.

2.1 Fick's laws of mass diffusion

The first qualitative understandings of mass diffusion date back to the first half of the 19th century, when the foundations of cell theory were laid, and the new concept of the *atom* emerged in the scientific community. Chemist Thomas Graham, while studying gases [110, 111], discovered that the effusion rate of a gas[1] is inversely proportional to the square root of its molecular weight (heavier gases diffuse more slowly). Ten years later, physician and physiologist Ernst Wilhelm von Brücke focused on experiments involving liquids passing through a membrane. Graham deduced that

"the flux caused by diffusion is proportional to the concentration difference of the salt."

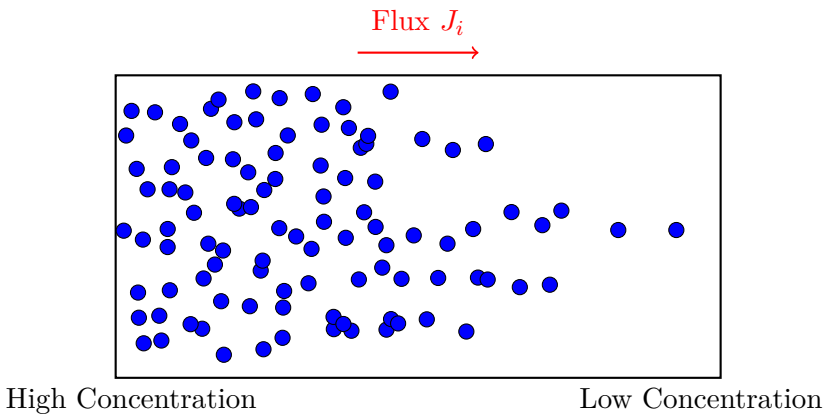

Fig. 2.1: Diffusion of matter

[1]The process in which a gas escapes from a container through a hole of diameter considerably smaller than the mean free path of the molecules.

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However, it was not until 1855 that Adolf Fick [91] translated these experimental results into a mathematical formulation. He stated that diffusion can be described on the same mathematical basis as Fourier's law of heat conductance:

$$Q = -k\nabla T, \tag{2.1}$$

where Q is the heat flux, k is the thermal conductivity, and T is the temperature. Similarly, diffusion can also be described analogously to Ohm's law for electrical conduction:

$$j = -\sigma\nabla\Phi, \tag{2.2}$$

where j is the electric current, σ is the electric conductivity, and Φ is the electric potential [71].

If $\Omega\times(0,T)$ corresponds to the spatio-temporal domain, let $u_i(x,t)$ denote the concentrations or volume fractions of I particle species. In his first law, Fick predicted a linear relationship between the flux of any species and its own concentration gradient. More precisely, species move down their concentration gradient, in a process called *downhill diffusion* (as illustrated in Figure 2.2). Hence, the flux J_i of the i-th species satisfies the equation:

$$J_i = -D_i\nabla u_i, \tag{2.3}$$

where D_i denotes the diffusion coefficient specific to the i-th species.

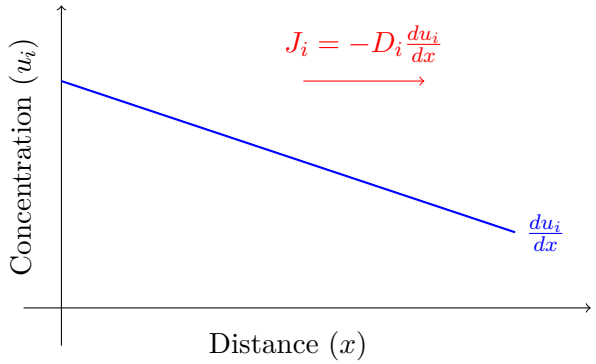

Fig. 2.2: Illustration of the first Fick's law of diffusion in $1D$.

Moreover, with Fick's second law, better known as *conservation of mass equation* in absence of chemical reactions, he describes the evolution in time and space of u_i:

$$\partial_t u_i + \operatorname{div} J_i = r_i(u), \qquad i = 1,\dots,I, \tag{2.4}$$

with $r_i(u)$ representing the reaction rates. If the matrix $A = A(u) \in \mathbb{R}^{I\times I}$ such that $A_{ii} = D_i$ and the vector $u = (u_1,\cdots,u_I)$ are introduced, then

$$J_i = -A_{ii}\nabla u_i, \qquad i = 1,\dots,I. \tag{2.5}$$

The system (2.4) can be rewritten in the vector form as

$$\partial_t u - \operatorname{div}(A\nabla u) = r(u), \tag{2.6}$$

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with r being a vector of all the reaction terms. The matrix A is called *diffusion matrix* and it is diagonal in this case.

Such laws, which work well for single-component problems, encounter inaccuracies when more than one species is involved. The following example is intended to demonstrate the inadequacy of Fick's law to describe multi-component phenomena in gas mixtures.

2.2 Diffusion in gas mixtures: A first experiment highlighting the fallacies of Fick's law

In 1962, Ducan and Toor [84] considered a ternary gas mixture made of hydrogen, nitrogen, and carbon dioxide. Their experiment involves two bulbs connected by a capillary tube with a tap. The latter, when opened, allows the two bulbs to communicate (see Figure 2.3). At the beginning of the experiment, the tap on the capillary is closed. The bulb A contains an equimolar mixture of nitrogen and carbon dioxide, while the bulb B an equimolar mixture of nitrogen and hydrogen. The level of nitrogen in both bulbs is the same. According to

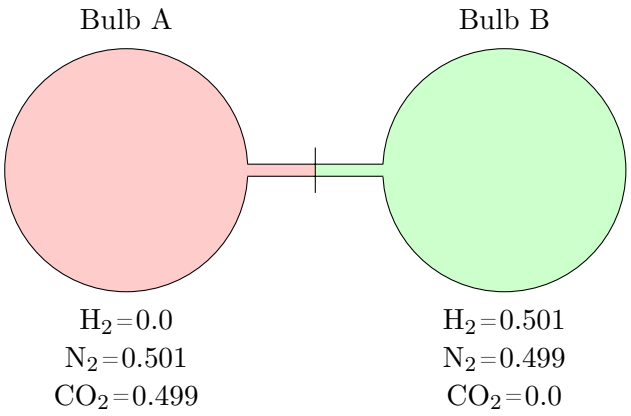

Fig. 2.3: Initial composition of the bulbs

Fick's first law of diffusion (2.3), there should be diffusion of CO_2 from bulb A to bulb B and diffusion of H_2 from B to A. In addition, the nitrogen should not move as its gradient concentration is zero. However, by letting the gases free of moving between the bulbs, one observes that, not only hydrogen and carbon dioxide diffuse till the level of the two gases reaches a plateau, but also nitrogen does. In contrast to the Fickian expectations, the nitrogen composition of bulb A decreases, while the one of bulb B increases (*uphill diffusion*). The nitrogen diffusion continues till the plateau is reached again.

This phenomenon is not unique to hydrogen-nitrogen-carbon dioxide. It usually occurs in any multi-component context, especially when dealing with entities of different sizes: Larger molecules, as in a crowd of people, push smaller ones to move even though they are already in equilibrium. A better understanding of uphill diffusion is relevant in several applied contexts, such as in medicine, where helium is used to facilitate the diffusion of oxygen in patients with chronic obstructive bronchopneumopathy [29, 55, 118]. Further examples can be found in [129, 131].

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2.2.1 The Maxwell-Stefan diffusion

James Maxwell in 1866 [140] and Josef Stefan in 1871 [164] independently suggested a modification of the Fick's laws to account cross-diffusivity effects. Together with the set of equations (2.4), they added the equations

$$\nabla u_i = -\sum_{j\neq i} \frac{u_j J_i - u_i J_j}{D_{ij}}, \quad i = 1, \cdots, I, \tag{2.7}$$

where also $\sum_{i=1}^{I} u_i = 1$, and D_{ij} represents the diffusion coefficient of the species i respect to the j-th one. The linear dependence between flux J_i and concentration gradient ∇u_i for the same species i is broken. The proposed equation (2.7) describes a nonlinear relation between fluxes and concentration gradients. The flux J_i depends not only on ∇u_i, but also on the gradients of the other species, namely ∇u_j with $j \neq i$. In terms of the diffusion matrix A which appears in the vector form of the system (2.4), i.e. in equation (2.6),

$$A(u) = \frac{1}{a(u)} \begin{pmatrix} d_2 + (d_0 - d_2)u_1 & (d_0 - d_1)u_1 \\ (d_0 - d_2)u_2 & d_1 + (d_0 - d_1)u_2 \end{pmatrix}, \tag{2.8}$$

for a mixture of $I = 3$ components, where u_3 and d_{i+j-2} are expressed as $u_3 = 1 - u_1 - u_2$, and $d_{i+j-2} = D_{ij}$, and $a(u) = d_1 d_2(1 - u_1 - u_2) + d_0(d_1 u_1 + d_2 u_2)$ [121]. The first thing to observe is that the off-diagonal elements of the matrix A are no longer zero. The diffusion matrix has lost the diagonal structure predicted by Fick's law (2.6). Note also that A is not symmetric either. Before presenting a second example, a more detailed discussion of the structure of A is given. It is not peculiar to the Maxwell-Stefan system, but common to many other situations of multi-component interactions. Such interactions give rise to cross-diffusion effects, which are well described by *cross-diffusion systems* of equations.

2.3 Cross-diffusion effects and systems

As the previous example shows, in multi-species contexts, entities influence each other's diffusion process. This phenomenon goes by the name of *cross-diffusion*, precisely to emphasise how the diffusion of one component also leads the others to spread. This shows the inadequacy of first Fick's law, which postulates diffusion of each species as non-interacting. Mathematically, cross-diffusion implies that the flux J_i of each species depends not only on ∇u_i, but also on the concentration gradients of all other species ∇u_j, for $j \neq i$. As a consequence, although the structure of these systems is similar to (2.4) or (2.6), the diffusion matrix A, as in Maxwell-Stefan, no longer has a diagonal structure: Non-zero off-diagonal terms represent the cross-diffusivity coefficients. Thus J_i will have a more complicated structure than in (2.5):

$$J_i = -\sum_{j=1}^{I} A_{ij} \nabla u_j. \tag{2.9}$$

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More broadly, given the spatial (bounded) domain $\Omega \subset \mathbb{R}^d$, with Lipschitz boundary, and the time domain $[0, +\infty)$, the general structure of cross-diffusion systems corresponds to

$$\partial_t u_i - \sum_{j=1}^{I} \sum_{k,\ell=1}^{d} \frac{\partial}{\partial x_k} \left(A_{ij}^{k\ell}(x,u) \frac{\partial u_j}{\partial x_\ell} \right) = r_i(u), \quad i = 1, \cdots, I, \tag{2.10}$$

where $u(x,t) = (u_1(x,t), \cdots, u_I(x,t))$ are the unknowns, $A_{ij}^{k\ell}$ are the diffusion coefficients, and $r_i(u)$ the reaction terms. Hence, cross-diffusion equations are quasilinear parabolic equations. To study the system (2.10), we need to provide additional information of the behavior of the solutions on the boundary of Ω and at the initial time. Here, we assume no-flux boundary conditions on the entire boundary to have an easier weak formulation of (2.10) which does not involve boundary integrals. Called $\nu = (\nu_1, \cdots, \nu_d)$ the exterior unit normal vector to the boundary $\partial\Omega$, on $\partial\Omega$, for $t > 0$, they correspond to

$$\sum_{j=1}^{I} \sum_{k,\ell=1}^{d} \nu_k \left(A_{ij}^{k\ell}(x,u) \frac{\partial u_j}{\partial x_\ell} \right) = 0, \quad i = 1, \cdots, I. \tag{2.11}$$

Moreover, for $x \in \Omega$, we take

$$u_i(x,0) = u_i^0(x), \quad i = 1, \cdots, I. \tag{2.12}$$

Usually, the matrix A is not symmetric, nor positive-definite. These characteristics make *cross-diffusion systems* highly nonlinear and entail coupled partial differential equations, posing significant challenges for study, particularly complicating mathematical and numerical analysis, as will be discussed in Chapter 3.

2.4 Diffusion in ion mixtures: A second experiment highlighting the fallacies of Fick's law

A second example [172] of cross-diffusion is now presented by a new particle behaviour. Let us consider a box that is divided into two parts by a membrane, permeable to cations (negative ions) but not to anions (positive ions). A dilute electrolyte solution of sodium chloride (Na^+ and Cl^- plus water) is placed in the right part of the compartment. The left side contains a much more concentrated electrolyte solution of hydrochloric acid (H^+ and Cl^- plus water).

2.4.1 Volume filling constraint: The advection effect of water

The first thing to notice is that the ionic particles of the electrolyte solution are surrounded by a solvent.The solvent, which is not stationary, transports the suspended components (advection). In doing so, it modifies their motion. Therefore, when modifying the fluxes, a drift term due to the water must be included. In dilute solution, this term is relatively easy to define: It will be of the form $u_i v$, where v refers to the velocity of the solvent, which can be assumed to be independent of the ion's motion. However, this velocity becomes more difficult to express when dealing with concentrated solutions or narrow geometries, such as the membrane, or general biological channels or nanopores. If the diameter of the channel and that of the ions are of comparable order of magnitude, ions can no longer be considered points.

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Ions occupy a no-negligible volume, and so the mixture is saturated (*volume filling constraint*). Mathematically, if the volume available is normalised as unity, then the constraint reads

$$u_0 := 1 - \sum_{i=1}^{I} u_i, \tag{2.13}$$

namely the volume fraction of the solvent u_0 corresponds to the remaining volume not occupied by ions. Since the solvent speed v is usually a function of ∇u_0, due to the volume filling constraint (2.13), J_i will also depend on all the ∇u_j, where $j \neq i$, with an expression similar to (2.9). The expression of the diffusion matrix A for this model will hence be similar to the Maxwell-Stefan one (2.8). Modelling concentrated dilute solutions is an active field of research in mathematical modelling. Indeed, such solutions have many applications in physiology, for example to describe the motion of ions through protein channels such as cellular channels, or in electrochemistry modelling batteries. Therefore, several models have been developed, trying to improve the theory or taking into account new phenomena. A significant example, used in [38], is reported. For $I = 2$, the matrix corresponds to

$$A(u) = \begin{pmatrix} D_1(1-u_2) & D_1 u_1 \\ D_2 u_2 & D_2(1-u_1) \end{pmatrix}. \tag{2.14}$$

Again non-diagonal and non-symmetric matrix, encoding cross-interactions is obtained.

For the time being, only the effect of the solvent on the particles has been considered. However, the particles are charged. This influences the definition of the flux, as explained in the next section.

2.4.2 The electromigration effect and the Nernst–Planck equation

Returning to the experiment, at the beginning of the diffusion process, the highly mobile H^+ diffuses ahead of Na^+, creating a positive excess charge in the right compartment. This induces an electrical gradient that maintains electrical neutrality in the box. Consequently, Na^+ diffuses from right to left, but does not stop when its gradient concentration becomes zero. The electrical gradient forces the sodium ions to the left and limits the amount of hydrogen that can be transferred. Thus the Na^+ - attracted by the negative Cl^- on the left - can continue to move until its concentration in the left compartment is many times greater than that in the right (see Figure 2.4). As a result, the transport of ionic species is invariably

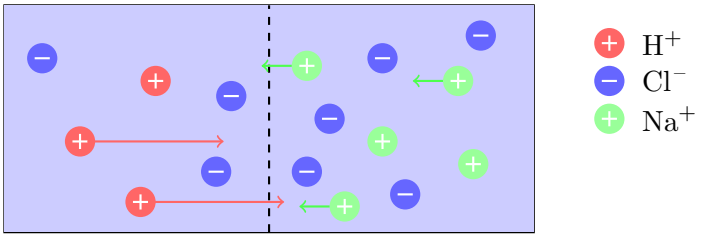

Fig. 2.4: Ions' movement due to electro-neutrality effect.

coupled with partner ions due to electro-neutrality constraints. This in turn accelerates or decelerates a specific ion. Between 1888 and 1890, Nernst [143, 144] and Planck [156, 157]

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refined a new model of Fick's equations to include the effects of charged interactions: The Nernst-Planck equation. Given Φ the electrostatic potential, and $z_i \in \mathbb{Z}$ the ionic valences ($+1$ for Na^+ and H^+, -1 for Cl^-) the expression of the flux results

$$J_i = -D_i \left(\nabla u_i + z_i u_i \nabla \Phi\right). \tag{2.15}$$

This allows to obtain a new drift term describing electromigration. Typically, the electric potential Φ is not provided, as its value over time and space depends on the ions themselves. To close the system, a Poisson-type equation is usually added, as outlined later on.

Considering the two effects together, electromigration and volume filling constraint, the flow becomes cross-diffusion, with an electrical drift term. In the example with the diffusion matrix (2.14), J_i becomes

$$J_i = -\left(\sum_{i,j=1}^{2} A_{ij} \nabla u_j + z_i D_i u_i \nabla \Phi\right),$$

where Φ usually satisfies a Poisson-type equation. This family of new models is called *generalised Poisson-Nernst-Planck*. They better capture phenomena such as current saturation in crowded channels [68]. Generalised Poisson-Nernst-Planck equations will be the argument of Part II of this thesis.

2.5 Thermodynamic definition of diffusion: Onsager's generalisation of Fick's law

Section 2.4 gave an example of the strong correlation between diffusion-type phenomena, such as how matter transport can cause an electromotive force and vice versa. In general, when several irreversible transport processes (e.g. heat conduction, electrical conduction, diffusion) occur in a system, they often interact with each other. One process typically induces others, resulting in 'coupled' transport. For example, a temperature gradient in a solution can create a composition gradient, leading to thermal diffusion and its reverse effect, among other interactions [147]. These considerations illustrate the interdependence of heat, electricity, and matter transport. Without interaction, individual flows follow empirical laws such as Fourier's (2.1), Ohm's (2.2), and Fick's laws (2.3). When interactions are significant, phenomenological relations describe currents as linear combinations of all gradients. For instance, diffusion J and heat flux Q can be expressed as:

$$\begin{aligned} J &= -(D\nabla u + D_T \nabla T), \\ Q &= -(k\nabla T + k_u \nabla u), \end{aligned}$$

where D, D_T, and k are diffusion, thermal diffusion, and thermal conductivity coefficients, respectively. More often, these relationships are expressed in terms of the forces producing such currents. If μ represents the *chemical potential*, namely the energy absorbed or released when the particle number of a given species changes, then J and Q can be rewritten in terms of $\nabla\mu$ and $\nabla(1/T)$, where $\nabla\mu$ represents the force of diffusion. Moreover, as discussed in Sections 2.2 and 2.3, in multi-component solutions, there is also mutual interaction among

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solute transports (cross-diffusion effects). The question of how to interpret and define diffusion in general therefore arises.

Generally speaking, diffusion is an *irreversible process*, in which energy dissipates and entropy grows. It was Lars Onsager [147, 148] who laid the foundations for a rigorous theory of diffusion. For a general flux (of matter, heat, electricity, etc.) J_α, where α encodes the transport phenomenon under consideration, it holds

$$J_\alpha = \sum_\beta L_{\alpha\beta} \nabla f_\beta,$$

where $L_{\alpha\beta}$ encodes the Onsager matrix of transport coefficients, linking the driving forces ∇f_β to the fluxes J_α. The Onsager matrix is symmetric, meaning that

$$L_{\alpha\beta} = L_{\beta\alpha}.$$

Moreover, the entropy production or dissipation associated to the system, can be written in terms of the Onsager matrix as $\sum_\alpha \sum_\beta (\nabla f_\alpha)^T L_{\alpha\beta} \nabla f_\beta$. Since the entropy production cannot be negative, the Onsager matrix is hence positive semi-definite.

Hence, if μ_i represents the potential of the i-th species, which includes all the possible diffusive effects, the flux J_i of the i-th species can be expressed as

$$J_i = -D_i u_i \nabla \mu_i.$$

Explicitly, μ_i reads

$$\mu_i = \mu_i^{diff} + \mu_i^{el} + \cdots = \log u_i + z_i \Phi + \cdots,$$

and depends on the diffusive phenomena involved. In this reformulations of the fluxes, Fick's and Nernst-Planck laws are included. In concentrated solutions, as in the example of Section 2.4, when the finite size of the ions needs to be taken into account, an excess chemical potential μ_i^{ex} must be included in the definition of μ_i. Bikerman [25] suggested the choice $\mu_i^{\text{ex}} = -\log(1 - \sum_{i=1}^n u_i) = -\log u_0$. I find these last remarks extremely interesting, as they seem to bridge the diffusion theory with the *boundedness-by-entropy method* which will be discussed in the next chapter. Here the *entropy variables* are strongly related to the potentials μ_i arising in thermodynamics (see [121, Remark 4.1]).

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Chapter 3

Mathematical and numerical study of cross-diffusion systems

In Section 2.3 the general structure of quasilinear parabolic cross-diffusion systems was shown (Equation (2.10)). In this chapter, and in the rest of the thesis, the focus will be on a simpler structure of the diffusion matrix A. The framework is the same as in Section 2.3. Thus, given the spatial (bounded) domain $\Omega \subset \mathbb{R}^d$ with Lipschitz boundary and the time domain $[0, +\infty)$, the matrix A satisfies

$$A_{ij}^{k\ell}(x,u) = A_{ij}(u)\delta_{k\ell}, \quad i,j = 1,\cdots,I$$

where I is the total number of species. In the examples (2.8) and (2.14) the diffusion matrix has this structure. Hence, being J_i as in (2.9), the cross-diffusion system (2.10) reads

$$\partial_t u_i - \operatorname{div}\left(\sum_{j=1}^{I} A_{ij}(u)\nabla u_j\right) = r_i(u), \quad i = 1,\cdots,I, \tag{3.1}$$

or, written in vector form,

$$\partial_t u - \operatorname{div}\left(A(u)\nabla u\right) = r(u). \tag{3.2}$$

For the sake of simplicity, no-flux boundary conditions are imposed on $\partial\Omega$. Initial conditions are also given. The vector $r(u) = (r_1(u),\cdots,r_I(u))$ encodes the reaction terms. For the cases analysed in this thesis, the unknowns $u(t) = (u_1,\cdots,u_I)(\cdot,t) : \Omega \to \mathbb{R}^I$ have the meaning of concentrations or volume fractions of the components. If u represents the vector of concentrations, it is expected to take values in an open set $\mathcal{D} \subset (0,+\infty)^I$. If it represents the vector of volume fractions, it should take value in $\mathcal{D} \subset (0,1)^I$. While in the first case the unknowns u_i should only be positive, in the second case they should be positive and bounded (not exceeding the maximum available volume, i.e. 1).

The equations studied in Part II include both cross diffusion and drift term. Moreover, an additional unknown is included in the system. This unknown will be called u_0 and will satisfy the *volume filling constraint* (2.13), namely

$$u_0 := 1 - \sum_{i=1}^{I} u_i.$$

The systems considered, with both cross-diffusion and drift, can be summarised by the formula

$$\partial_t u_i - \operatorname{div}\left(\sum_{j=1}^{I} \left(A_{ij}(u)\nabla u_j + Q_{ij}(u)\nabla\Phi\right)\right) = r_i(u), \quad i = 1,\cdots,I,$$

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where Φ represents the electric potential satisfying a Poisson or Poisson–Fermi equation. In the following, the drift coefficients Q_{ij} of the $I \times I$ matrix $Q(u)$ will take the form

$$Q_{ij} = u_i \delta_{ij} \quad \text{or} \quad Q_{ij} = u_0 u_i \delta_{ij}.$$

However, for simplicity sake, this chapter will focus on cross-diffusion system of type (3.1). Yet the case involving a drift term is treated similarly. A more in depth treatment can be found in Part II.

The mathematical analysis of cross-diffusion systems is very difficult. The main difficulties arise from the strong coupling of the equations and their nonlinearity. A standard tool such as the maximum/minimum principle is generally not applicable to show bounds on solutions. Moreover, the fact that the diffusion matrix A is often neither symmetric nor positive semidefinite has made the study of the global-in-time existence of weak solutions a challenge for mathematical research. General regularity results do not apply in this context, so solutions can develop singularities in finite time.

Amann has shown [6] the existence of a unique local-in-time classical solution to quasi-linear parabolic cross-diffusion systems under restrictions on the regularity of the spatial domain Ω and on the spectrum of the diffusion matrix.

Ladyženskaya et al. [132] proved that L^∞ bounds on the local solution u and its gradient, under some growth conditions on the nonlinearities of the model, are enough to obtain global-in-time existence of classical solutions. Amann in [7] formulated the concept of $W^{1,p}$ weak solutions and he showed that, if the local solution u with maximal existence time T satisfies

$$\sup_{0\le t\le T} ||u(t)||_{W^{1,p}(\Omega)} < \infty, \quad \text{for } p > d,$$

then the local solution u can be continued globally in time. However, such conditions are often not fulfilled, in particular when $d \ge 2$. Starà and John in [163] and Pierre and Schmitt in [155] found some examples of parabolic systems with solutions that exhibit blow-up in finite time. In general, therefore, it is not possible to show global solvability for general systems of the cross-diffusion type. Additional conditions are needed to prove that local-in-time weak solutions are bounded and can be continued globally in time. Le and Nguyen in [134] discovered that structural assumptions on the diffusion matrix A are required.

In the next section the existence of global solutions for cross-diffusion systems with an *entropy structure* is discussed. The *boundedness-by-entropy method* is explored to show the global-in-time existence of weak solutions of the system (3.1). Bounds on the solutions can also be derived.

3.1 Boundedness-by-entropy method

The *boundedness-by-entropy method* is a useful tool to show the global-in-time existence of bounded solutions. It is applicable to a large class of physically relevant, strongly coupled parabolic systems such as (3.2), which have a formal *gradient flow structure* or *entropy structure*. To illustrate the method, the concept of (mathematical) *entropy* is first introduced. This discussion is based on the works [46, 121, 123].

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Entropy structure An *entropy density* associated with the system (3.2) is a function $h : \mathcal{D} \subset \mathbb{R}^d \to \mathbb{R}$ satisfying the following hypotheses:

- It is convex and $C^2(\mathcal{D})$;
- Its first derivative $h' : \mathcal{D} \to \mathbb{R}^I$ and the Hessian $h'' : \mathcal{D} \to \mathbb{R}^I \times \mathbb{R}^I$ are invertible,
- The matrix $h''(u)A(u)$ is positive semidefinite for all $u \in \mathcal{D}$.

The functional $H(u) = \int_\Omega h(u)dx$ is its corresponding *entropy*. If we identify the variational derivative of H, namely $\frac{\delta H(u)}{\delta u}$, with its Riesz representative $w := h'(u)$ (*entropy variable*), we can formally rewrite a system (3.2) with an entropy functional in the vector form

$$\partial_t u - \operatorname{div}(B(w)\nabla w) = r(u), \tag{3.3}$$

where $B = B(w) = A(u)h''(u)^{-1}$ is the *mobility matrix*. Structure (3.3) is called *entropy* or *gradient flow*, and has been observed in many cross-diffusion systems.

Remark 3.1 (How to determine if a system has an entropy structure?)**.** For models coming from physics or chemistry, the existence of entropy often follows from physical considerations. However, there seems to be no general strategy for determining whether a cross-diffusion system has an entropy structure or not. In [64] the authors showed that every cross-diffusion system with an entropy structure has a *normally elliptic* diffusion matrix. This means that the real parts of all its eigenvalues are positive. Therefore, if $A(u)$ is *not* normally elliptic, then such an entropy structure cannot exist. If $A(u)$ is normally elliptic for all $u \in \mathcal{D}$ and furthermore $h''(u)A(u)$ is symmetric for some convex function $h(u)$, then the system has an entropy structure. However, the last result does not give an explicit expression of an entropy associated with the system.

Global-in-time existence and boundedness One of the consequences of the gradient flow structure is represented by the following *entropy inequality*. Thanks to (3.3), integration by parts and homogeneous Neumann boundary conditions, the time derivative of the entropy becomes

$$\frac{d}{dt}\int_\Omega h(u)dx = \int_\Omega \partial_t u \cdot h'(u)dx = \int_\Omega \partial_t u \cdot w dx = -\int_\Omega \nabla w : B(w)\nabla w dx + \int_\Omega r(u)\cdot w dx, \tag{3.4}$$

where ":" denotes the Frobenius matrix product. For simplicity, the assumption $r(u)\cdot w \le 0$ is imposed. Thanks to the positive semidefiniteness of $h''(u)A(u)$, and thus of the matrix $B(w)$, the inequality

$$\frac{dH}{dt} \le 0 \tag{3.5}$$

is derived. The functional H is consequently a Lyapunov functional, decreasing in time along the solutions of the system. It is therefore a mathematical entropy. The latter is the same as the physical one, but with the opposite sign.

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The term $\int_\Omega \nabla w : B(w)\nabla w dx$ is called *entropy dissipation*. Under certain conditions on the matrix $h''(u)A(u)$, the entropy dissipation is crucial to deduce uniform estimates on the gradient of u. Indeed, for example, if $h''(u)A(u)$ is positive definite uniformly in u, then

$$\int_\Omega \nabla w : B(w)\nabla w dx = \int_\Omega \nabla u : h''(u)A(u)\nabla u dx \geq c\int_\Omega |\nabla u|^2 dx, \tag{3.6}$$

holds, for some $c > 0$. The positive definiteness of $h''(u)A(u)$, which implies (3.6), can be weakened. Having a positive definite matrix $h''(u)A(u)$ with a constant depending on $u \in \mathcal{D}$ is enough: There exist $m_1, \cdots, m_I \geq 0$ and $c > 0$ such that

$$z^T h''(u)A(u)z \geq \sum_{i=1}^{I} u_i^{2(m_i-1)} z_i^2, \quad \forall z \in \mathbb{R}^I, u \in \mathcal{D}. \tag{3.7}$$

The key idea of the proof is to work with the reformulation (3.3), in the entropy variable w. In particular, the existence proof combines the study of the existence for an approximated problem with compactness result. The main points of the existence proof for the approximated problem are summarised:

- First, the time derivative $\partial_t u(w)$ is replaced by its implicit Euler discretisation to avoid problems with time regularity and to work only with elliptic equations. This introduces a time discretisation parameter $\tau > 0$..
- Since the operator
$$w \mapsto \mathrm{div}(B(w)\nabla w)$$
is not uniformly elliptic, a higher-order regularisation term $\epsilon((-\Delta)^m w + w)$, where $m > d/2$, $\epsilon > 0$ must be added in (3.3). The new operator is thus uniformly elliptic, which guarantees global solvability in $w \in H^m(\Omega)$. The second advantage of this regularisation lies in the choice of $m > d/2$. Indeed, for such m the embedding $H^m(\Omega) \hookrightarrow L^\infty(\Omega)$ holds, and the boundedness of w ensues. As a consequence, the relation $w = h'(w)$ can be inverted, and the inverse $u(w) = (h')^{-1}(w)$ is well defined. Since $h' : \mathcal{D} \to \mathbb{R}^I$, then
$$u(w) = (h')^{-1}(w) \in \mathcal{D}.$$
Therefore, if $\mathcal{D}$ is bounded, the bound on u follows automatically, without using tools like the maximum principle.
- The global-in-time existence of the variable w for the discretised and regularised system is proven by a standard fixed-point argument. Thus, one should linearise the system by "freezing" the non-linearity; show that the linearised problem is well defined (e.g. using Lax-Milgram theorem); prove that the resulting solution operator associated with the linearised equation admits at least one fixed point, namely a solution to the non-linear problem.

At this point, if $w^{(\tau)}$ denotes the constant-time interpolation of the discrete solutions, the goal is to show convergence for $u(w^{(\tau)})$ as $(\epsilon, \tau) \to 0$. Compactness estimates are needed to identify the limit with a weak solution of (3.2). They follow from the lower bounds on entropy dissipation (3.7). The main tool for carrying out this limit is a discrete version of the Aubin-Lions lemma as written in [80]. It provides the almost everywhere convergence of the sequence of discrete solutions (up to subsequences), which allows to identify the nonlinearities.

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Moreover, when passing into the limit $(\tau, \epsilon) \to 0$, the solution varies in $\bar{\mathcal{D}}$. If the latter is bounded, so is $u(w)$.

An illustrative example is the Maxwell-Stefan system discussed in Section 2.2.1, with $I = 3$ species. In the following discussion, $u = (u_1, u_2)$ actually denotes a discrete solution of the approximated problem. The concentration of the third species can be expressed in terms of u_1 and u_2, namely $u_3 = 1 - u_1 - u_2$, then

$$\mathcal{D} := \{u = (u_1, u_2) \in (0,1)^2 : u_1 + u_2 < 1\}.$$

Furthermore, the entropy density for the system is defined as:

$$h(u) = \sum_{i=1}^{2} u_i(\log u_i - 1) + (1 - u_1 - u_2)(\log(1 - u_1 - u_2) - 1), \quad u \in \mathcal{D}.$$

Therefore,

$$w_1 = \frac{\partial h}{\partial u_1} = \log \frac{u_1}{u_3} \quad \text{and} \quad w_2 = \frac{\partial h}{\partial u_2} = \log \frac{u_2}{u_3},$$

implying

$$u_i(w) = \frac{e^{w_i}}{1 + \sum_{i=1}^{2} e^{w_i}},$$

for $i = 1, 2$, which is a function with image $\mathcal{D}$. Therefore, u_i are automatically bounded.

Remark 3.2. *As shown in [77], the regularising term $(-\Delta)^m + Id)$ can be avoided for systems of the form*

$$\partial_t u - \Delta a(u) = r(u),$$

with $a : \mathbb{R}^I \to \mathbb{R}^I$ invertible function, by using instead the operator $(M - \Delta)^{-1} : L^m(\Omega) \to L^\infty(\Omega)$, with $m > d/2$ and $M > 0$. The procedure allows to prove strict positive lower bounds for the solutions and also the study of the limit $\tau \to 0$ only.

3.2 Uniqueness of weak solutions

For strong solutions of cross-diffusion systems, uniqueness follows from standard L^2 estimates. However, the uniqueness of weak solutions remains largely unresolved. From the entropy method presented above, it is usually not possible to deduce the uniqueness of the solution. The fixed point operator defined by the solution of the linearised problem usually only fulfils the assumptions of the Leray-Schauder fixed point theorem. This allows to deduce the existence but not the uniqueness of solutions of the (approximated) nonlinear problem. And even if one could prove uniqueness for the approximate problem, this would not imply uniqueness for the continuous problem. In fact, compactness provides only one convergent subsequence. There may be another that converges to a different limit.

The main problems in proving uniqueness arise from the coupling of the system equations and their nonlinearities. To the best of our knowledge, there is no general uniqueness result for cross-diffusion systems, and only a few partial results have been obtained for specific cases. The first result for diffusive systems was given by Alt and Luckhaus in [5]. They showed uniqueness in the class of weak solutions under the integrability assumption on $\partial_t u_i$ and the linearity of the elliptic operator. A relaxation of these hypotheses can be found in [151] by Otto and in [2] by Agueh. However, both results are only valid for scalar equations. Results

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for cross-diffusion systems can be found for example in [174], for cross-diffusion systems with volume filling, under simplifying assumptions on the nonlinearities, or in [37] and [106] for initial data sufficiently close to the constant steady states.

Another discussion for cross-diffusion equations with drift term is in [64] where they used the H^{-1} method, combined with a Gajewski method, to improve the results of [126] and [174]. The mentioned methods are presented hereafter. Even in the linear diffusion case of the one-species Fokker-Planck equation

$$\partial_t u - \operatorname{div}(\nabla u + u\nabla\Phi) = 0,$$

strong assumptions on the data are required (see [123]). The electric potential Φ should be such that $\nabla\Phi \in L^\infty(0,T;L^d(\Omega))$.

The method of Gajewski and H^{-1} method will be discussed, and later the concept of weak-strong uniqueness will be introduced. The latter is more appropriate to show the uniqueness result in the context of cross-diffusion.

The method of Gajewski Gajewski in [97] developed a method, again based on an entropy method, to obtain uniqueness of weak solutions of drift-diffusion models for semiconductor devices. For the Fokker-Plank equation, this technique allows to obtain uniqueness under a weaker regularity assumption on the potential Φ (namely $\Phi \in L^2(0,T;H^1(\Omega))$).

The idea of the Gajewski's method is to use a semimetric to compare two bounded solutions u and v. Such semimetric is defined in terms of the entropy density h, namely

$$d(u,v) = \int_\Omega \left(h(u) + h(v) - 2h\left(\frac{u+v}{2}\right)\right) dx.$$

The main idea of the method is to show that $t \mapsto d(u(t),v(t))$ is decreasing in time. If u and v are two solutions of the same Cauchy problem, they have the same initial data, i.e. $u(0) = v(0)$. Therefore, $d(u(t),v(t)) \le d(u(0),v(0)) = 0$. Since the semimetric can usually be bounded from below by the difference of u and v in the squared $L^2(\Omega)$-norm, the equality $u(t) = v(t)$ follows for $t > 0$, i.e. in Ω.

Gajewski's method can also be applied in the context of cross-diffusion. For example, in [102] it was used to show the uniqueness of a generalised Poisson-Nernst-Planck model with volume filling constraint (2.13). However, strong assumptions on the diffusion coefficients are needed to rewrite the system in Fokker-Planck form and thus prove uniqueness. Another application in the context of cross-diffusion can be found in[174].

H^{-1} method The H^{-1} method [79, 122, 141, 154] is another technique often applied in this context. This method is a dual approach, which involves choosing a test function χ that satisfies an appropriate elliptic problem. Consequently, uniqueness is reduced to the existence of $\chi \in L^2(0,T;H^1(\Omega))$ for the Poisson problem:

$$-\Delta\chi = u - v, \tag{3.8}$$

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with homogeneous Neumann boundary conditions on $\partial\Omega$, where u and v are solutions of the cross-diffusion system (3.2), starting from the same initial data. If it can be shown that

$$\frac{d}{dt}\int_\Omega |\nabla\chi|^2\,dx \le 0, \tag{3.9}$$

then χ must be constant, leading to the conclusion that $u = v$. However, deriving an inequality like (3.9) typically requires strong assumptions on $A(u)\nabla u =: \Psi(u)$. Specifically, we have:

$$\begin{aligned}\frac{d}{dt}\int_\Omega |\nabla\chi|^2\,dx &= \langle\partial_t(-\Delta\chi),\chi\rangle\\ &= \langle\partial_t(u-v),\chi\rangle\\ &= \langle\nabla\cdot(\nabla\Psi(u)-\nabla\Psi(v)),\chi\rangle\\ &= -\langle\Psi(u)-\Psi(v),\Delta\chi\rangle.\end{aligned}$$

Since χ solves (3.8), we need to assume the monotonicity of Ψ to get:

$$-\langle\Psi(u)-\Psi(v),\Delta\chi\rangle = -\langle\Psi(u)-\Psi(v),u-v\rangle \le 0.$$

The monotonicity assumption on Ψ can often be weakened. However, the new conditions that replace it are still quite restrictive in practice.

Weak-strong uniqueness Many recent works have demonstrated that establishing weak-strong uniqueness appears more feasible. For instance, weak-strong uniqueness has been proven for the compressible Navier-Stokes system [88], the Fourier-Navier-Stokes system [89], and for the (isentropic) Euler equations [34, 112]. For hyperbolic-parabolic systems the result has been shown in [66],whereas [35] and [105] proved it for the Navier-Stokes-Korteweg and Euler-Korteweg systems, respectively. Additionally, this approach has been successful for the Navier-Stokes equation with surface tension [94], reaction-cross-diffusion systems [65, 116, 125, 133], entropy-dissipating reaction-diffusion equations [94], energy-reaction-diffusion systems [115], and Maxwell-Stefan systems [119]. These studies illustrate that weak-strong uniqueness is a viable approach for various complex systems.

The method consists in comparing strong and weak solutions. Strong solutions are weak solutions that are more regular. Weak-strong uniqueness states that if both a *weak* solution u and a *strong* solution v exist for the same initial-boundary value problem with the same initial data, the weak solution must coincide with the strong solution for as long as the strong solution exists. Hence, given a strong solution, it coincides with *any* weak solution. Thus the two classes of solutions coincide. The approach discussed ensures that every strong solution coincides with every weak solution, leading to the uniqueness of solutions in both categories. However, this approach typically involves complex calculations. Additionally, establishing the existence of a strong solution is required.

Sometimes, the comparison between the two kind of solutions can be achieved by working directly with the weak formulation, thanks to linear energy estimates [20]. More often, the weak-strong uniqueness approach relies on employing the relative entropy

$$H(u|v) = \int_\Omega \big(h(u) - h(v) - h'(v)(u-v)\big)\;dx,$$

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where h signifies the entropy density, to compare u and v. Indeed, typically, $H(u|v)$ acts as an upper bound for the $L^2(\Omega)$-distance between the two solutions, and it is better adapted to the equation in consideration. By using a right test function in the weak formulation, a bound like

$$\frac{dH}{dt}(u|v) \leq C(v)H(u|v),$$

with $C(v) > 0$ depending on the strong solution only can be established. This enables the application of Gronwall's lemma, leading to the conclusion $H(u(t)|v(t)) = 0$ and consequently $u(t) = v(t)$, for $t \geq 0$.

Note that the relative entropy has similarities to the Gajewski semimetric. The transition from one expression to the other is still not fully understood. The link between the two expressions is that they are both "nonlinear formulations" of $|u - v|^2$. Some comments are made in [64, Remark 4].

3.3 Finite Volume schemes

The numerical approximation of cross-diffusion systems is also complex due to the non-linearity of the fluxes. Since cross-diffusion systems of parabolic type are studied in this thesis, it is essential to introduce discretization both in time and space.

In the cross-diffusion community, the implicit Euler method is commonly used to discretize the time derivative. For the explicit Euler method, the entropy decay, which provides stability estimates, is subject to a stability constraint (see [92]). Additionally, when physical parameters are considered, this stability condition depends on those parameters. It can happen that these parameters are small, leading to an inefficient scheme (see inequality (2.14) of [17] for the time step, where the bound is proportional to the square of the Debye length parameter $\approx 10^{-6}$). On the other hand, implicit Euler guarantees unconditional stability with respect to the time step.

Regarding space discretization, finite volume and finite element methods are the most popular in the literature on numerical studies of cross-diffusion systems. The main goal is to define schemes that preserve the structure of the continuous problem as much as possible, namely the non-negativity or bounds on the solutions, and the decay of the entropy. Moreover, accurate schemes are sought.

The advantage of finite element methods is that they search for solutions in a finite dimensional subspace of the space where weak solutions of the continuous problem lie. However, these schemes do not encode the physics of the problem and they restrict the space of usable test functions to show properties on the discrete solutions. They are therefore unable to prove important properties such as the non-negativity of solutions.

On the contrary, finite volume approximations are more suitable and attractive methods when dealing with conservation laws, like (3.1) in absence of reactions. They guarantee local and global mass conservation, positivity/bounds of solutions, thermodynamic consistency, which are not always possible to show in the finite element context. On the space-time domain $\Omega \times [0, +\infty)$, a general conservation law reads as

$$\partial_t u + \operatorname{div} J(u, \nabla u) = 0, \tag{3.10}$$

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where the initial condition is set as $u(\cdot,0) := u_0(\cdot)$, and boundary conditions are specified on $\partial\Omega$. For simplicity, no-flux boundary conditions are adopted. It is first noticed that cross-diffusion equations are part of this category. After introducing a partition $\mathcal{T}$ of Ω in polytopes (call *control volumes* or *cells*), the principle of the finite volume method is to approximate the mean value of the fluxes on the edges of each control volume. The scheme is hence based on

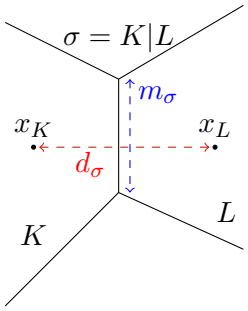

Fig. 3.1: Example of neighbouring cells satisfying the orthogonality condition

local balanced laws. Denoting by $\mathcal{E}_K$ the set of edges of $K \in \mathcal{T}$, one can apply the divergence theorem to obtain:

$$\int_K \partial_t u dx + \sum_{\sigma\in\mathcal{E}_K} \int_\sigma J(u,\nabla u)\cdot\nu_\sigma ds = 0, \tag{3.11}$$

where ν_σ denotes the exterior unit normal vector to the edge σ. As initial data for (3.11), one takes

$$u_K^0 := \frac{1}{m_K}\int_K u_0(x)dx, \quad \forall K \in \mathcal{T},$$

with m_K the Lebesgue measure of K. Moreover, since (3.10) involves also a time derivative, a time discretisation $(t^n)_{n\geq 0}$ of $[0,+\infty)$ is also introduced and the approach proceeds via the implicit Euler method. Consequently, the following finite volume scheme for the unknowns u_K^n is derived:

$$\begin{cases} \frac{m_K}{\Delta t}(u_K^n - u_K^{n-1}) + \sum_{\sigma\in\mathcal{E}_K} F_{K\sigma}^n = 0, & \forall K\in\mathcal{T},\ \forall n\geq 1,\\ u_K^0 := \frac{1}{m_K}\int_K u_0(x)dx, & \forall K\in\mathcal{T}, \end{cases}$$

where Δt is the time step and $F_{K\sigma}^n$ is the numerical flux.

How to define the numerical flux $F_{K\sigma}^n$? It should be *consistent*, namely it should be an approximation of $\int_\sigma J(u,\nabla u)\cdot\nu_\sigma ds$. Moreover, it has to be *conservative*:

$$F_{K\sigma}^n = -F_{L\sigma}^n, \qquad \forall K,L\in\mathcal{T},\ \forall n\in\mathbb{N}.$$

This property is important to conserve the total discrete mass, in absence of reactions. Finally, the flux approximation should ensure that the resulting scheme retains, at the discrete level, several important properties from the continuous level, such as the positivity of concentrations, bounds for volume fractions, decay of free energy, preservation of thermodynamic equilibrium, and long-time behavior of the solutions. Some of these properties are also crucial for proving the convergence of the scheme. The interesting thing to note is that there is no systematic way to define the numerical fluxes for a given equation or system. There may be several definitions of $F_{K\sigma}^n$ that satisfy the above properties. Among these definitions, the choice falls on the flux

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with the highest order of convergence or the one that best suits the properties one wants to study.

In this thesis, the focus is on the two-point flux discretisation method, where, for an edge $\sigma = K|L$, the numerical flux $F^n_{K\sigma}$ depends solely on the discrete values of the variables in the cells K and L. If the flux $J(u, \nabla u)$ is linear, like for example in the case of Fick's law $J(u, \nabla u) = -\nabla u$, then a good approximation of it is provided by finite-difference discretisation of the gradient:

$$F^n_{K\sigma} := \frac{m_\sigma}{d_\sigma}(u^n_K - u^n_L),$$

where m_σ is the $\mathbb{R}^{d-1}-$Hausdorff measure of σ, and $d_\sigma := d(x_K, x_L)$ denotes the distance between the cell centers x_K and x_L. Under the *orthogonality condition* of the mesh, i.e. the vector connecting the center x_K of the cell K to the one of the neighbour cell L, namely x_L, is orthogonal to the shared edge σ, this approximation of the flux is consistent [87]. However, when the flux $J(u, \nabla u)$ includes an advective effect, the numerical fluxes are no longer straightforward to define. For example, consider the drift-diffusion flux $J(u, \nabla u) = -\nabla u - u\nabla\Phi$, where Φ is a given electric potential. The drift term poses the challenge of approximating the value of u over σ. Since the approximation u^n_K is constant over K, and the approximation u^n_L is constant over L, a priori, the value of u over $\sigma = K|L$ is not well defined. Several schemes have been developed in this regard. A simple definition consists in taking u^n_σ as the average between the value of the unknown on both sides of σ, namely u^n_K and u^n_L (*centred scheme*):

$$F^n_{K\sigma} := \frac{m_\sigma}{d_\sigma}(u^n_K - u^n_L) - \frac{m_\sigma}{d_\sigma}\frac{u^n_K + u^n_L}{2}(\Phi_K - \Phi_L), \tag{3.12}$$

where Φ_K represents the discretisation of the electric potential over K. This scheme introduces very little numerical diffusion in the discretization of the drift term, but it is therefore also not very stable if the convection is much stronger than the natural diffusion. When advection is predominant, one of the most natural choice would be the *upwind* scheme. The latter consists in choosing as u^n_σ either u^n_K or u^n_L, depending on the sign of the approximated gradient, namely the versus of the speed flux related to u:

$$F^n_{K\sigma} := \frac{m_\sigma}{d_\sigma}(u^n_K - u^n_L) - \frac{m_\sigma}{d_\sigma}\begin{cases} u^n_K(\Phi_K - \Phi_L), & \text{if } (\Phi_K - \Phi_L) \geq 0, \\ u^n_L(\Phi_K - \Phi_L), & \text{if } (\Phi_K - \Phi_L) \leq 0. \end{cases} \tag{3.13}$$

The resulting scheme is more stable than the centered one, but additional numerical diffusion is introduced.

Both the upwind and centered schemes reproduce a discrete version of the entropy inequality [52]. However, they do not preserve the form of the thermal equilibrium at the discrete level. This means that by substituting the discrete version of the thermal equilibrium $u = e^\Phi$ in the discrete flux of the scheme, one does not obtain $F^n_{K\sigma} = 0$. An interesting scheme that preserve the thermal equilibrium is the *Scharfetter-Gummel scheme* (SG). First proposed in [159] to discretised one-dimensional drift-diffusion equations, it makes use of the Bernoulli function $\mathcal{B}(x) = \frac{x}{e^x - 1}$ to discretise the fluxes:

$$F^n_{K\sigma} := \frac{m_\sigma}{d_\sigma}\left(\mathcal{B}(\Phi_L - \Phi_K)u^n_K - \mathcal{B}(\Phi_K - \Phi_L)u^n_L\right). \tag{3.14}$$

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The latter can be seen as an "interpolation" of the upwind and centered scheme, inheriting the good properties of both schemes. The latter are obtained in the cases of very large or very small advection. In general, both the fluxes (3.12) and (3.13) can be written in the form (3.14) by using an appropriate $\mathcal{B}$-function, see the work [51]. Here the authors proposed a way to unify and simplify the notation. Inspired by the Scharfetter-Gummel scheme, they suggested to write the numerical fluxes via a Lipschitz continuous function $\mathcal{B}$, such that $\mathcal{B}(0) = 1$, $\mathcal{B}(x) \geq 0$, and $\mathcal{B}(x) - \mathcal{B}(-x) = -x$, for all $x \in \mathbb{R}$.

An alternative flux discretisation, which preserves the thermal equilibrium, is the *squareroot approximation scheme* (SQRA), which can be written in the form (3.14) using the function $\mathcal{B}(s) = e^{s/2}$. This choice, however, does not fit the definition of $\mathcal{B}$-functions of [51], as $\mathcal{B}(x) - \mathcal{B}(-x) \neq -x$. In [114], a generalisation of the $\mathcal{B}$-functions was proposed (see Table 1 of [114]). Such function do not have to fulfil the equality $\mathcal{B}(x) - \mathcal{B}(-x) = -x$. The scheme, which is part of *exponentially fitted* schemes, is based on flux reformulation via the Slotboom variable $w := ue^{\Phi}$:

$$J(u, \nabla u) = e^{-\Phi} \nabla w.$$

Finite difference is employed to discretise the gradient, whereas different Stolarsky mean weight functions on the edges, denoted by $\mathfrak{M}$ in Part II, can be used to approximate $e^{-\Phi}$. This family includes both the SG and SQRA schemes. The convergence order mainly depends on mesh quality and, to a lesser extent, on Stolarsky weights. The Scharfetter–Gummel scheme has the best analytical convergence properties, but a range of Stolarsky means offers similar quality.

Thanks to its good properties, the Scharfetter–Gummel method has spread from the semiconductor field into the numerical community to simulate other equations as well. See for example the work [137] for the Keller-Segal equation in $2D$ and the work [4] for the Keller-Segal and Fokker-Planck equations. The flow is reformulated with the variable Slotboom and the SG scheme is used. Recent progresses have been done in the application of the Scharfetter-Gummel scheme for drift-diffusion problems with nonlinear diffusion [23]. The extension to nonlinear diffusive systems with drift term was developed in [39].

In cross-diffusion systems, with pure diffusion, the flux is given by $J(u, \nabla u) = -A(u)\nabla u$. Approximating the diffusion part alone is inherently tricky, even without considering advection. Since u is no longer scalar, the term $A(u)\nabla u = \sum_{i,j} A_{ij}(u)\nabla u_j$ requires careful handling. Specifically, one needs to understand how to approximate $A(u)$ on σ. Reformulation of the flux are sometimes useful in this regard.

The upwind method has been widely employed to express numerical fluxes in terms of $A(u_K^n)$ and $A(u_L^n)$ only, depending on the sign of the discrete gradient of u [3, 14, 45]. As in the discretization of convection, the main limitation is that upwind methods only provide first-order accuracy in space. To achieve second-order accuracy, a natural approach would be to reformulate the flux and use the arithmetic mean to approximate the values on the edges. Hence values on σ are defined as the mean between their values on the cells K and L (centered scheme) [72].

However, this choice may not preserve the entropy inequality at the discrete level when the volume filling constraint (2.13) is enforced. Using the arithmetic mean to define the values over σ does not lead to this deduction. Some studies have utilized the logarithmic mean, as discussed in [44, 127]. With this approximation, the chain rule for entropy density is preserved at the discrete level, allowing for deduction of stability properties while maintaining second-order accuracy.

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This thesis analyses numerical schemes for cross-diffusion systems, with finite volume constraint, that also include a drift term. The first complete study of a nonlinear drift-diffusion system for two species can be found in [50, 53]. The main focus of the thesis is on the definition of good approximations of the flux $J(u, \nabla u) = -(A(u)\nabla u + u\nabla\Phi)$, where both the difficulties of cross-diffusion and advection are involved. The discussion is postponed to Chapter 6.

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Chapter 4

The formal diffusive limit to derive macroscopic systems

As mentioned in Section 1.2.2, writing equations that describe the macroscopic dynamics of a system of interacting agents often involves adding terms that are not justified by the microscopic dynamics of the entities. The derivation of multicomponent equations from a system of Boltzmann equations represents a significant bridge between the microscopic dynamics of molecules and the macroscopic behavior of mixtures. This derivation provides a theoretical framework that explains how interactions at the molecular level lead to observable diffusion phenomena in multicomponent systems.

In this chapter, an overview of the Boltzmann equation for single and multiple species will be given. Then, a general explanation of the hydrodynamic limit in general, and the diffusion limit in particular, will be provided. The main focus will be on deriving diffusion partial differential equations from the Boltzmann equation.

4.1 General introduction to kinetic theory

As already discussed in Section 1.2.2, in this approach, a distribution function $F = F(t, x, v)$ gives the probability of finding a molecule with velocity v at the spatial position x at time t. The integral

$$\int_{X\times V} F(t, x, v)\, dx\, dv$$

gives the number of molecules at time t in the space-velocity domain $X \times V$.

The basic equation of kinetic theory is the free transport equation

$$\partial_t F + v \cdot \nabla_x F = 0, \tag{4.1}$$

which is satisfied by F when no forces are involved. Thus, in the absence of forces, given the initial distribution of the molecules, $F_0(x, v)$, the distribution at time t at position x with velocity v will be the translation of F_0:

$$F(t, x, v) = F_0(x - tv, v).$$

When forces are involved, the motion of molecules is no longer rectilinear, and equation (4.1) needs to be modified accordingly. One type of force that can be involved is those occurring on non-negligible spatial scales relative to the spatial scale of the model. For example, this is the case with the gravitational potential of Saturn acting on the "dust" composing its rings [61]. Other examples include the mutual interaction between the dust molecules themselves or the mutual electric attraction or repulsion between ions in an ion mixture [107].

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Since the force is external, or many entities are involved in determining it, it can be represented via $\mathcal{F} = \mathcal{F}(x, v)$. In the second case, $\mathcal{F}$ will be an average field accounting for the effect of all the entities. This leads to the so-called Vlasov-type equations, where an additional term like $\mathcal{F} \cdot \nabla_v F$ is added to equation (4.1):

$$\partial_t F + v \cdot \nabla_x F + \mathcal{F} \cdot \nabla_v F = 0. \tag{4.2}$$

When molecules interact via forces that occur on spatial scales negligible compared to the spatial scales of these models, the interactions are referred to as collisions. In this case, forces are not modeled by a mean field but are localized. At each instant t and at each fixed point in space x, these interactions depend only on the statistical distribution of velocities at this instant t and at this point in space x, not on those at another point x'. These interactions are encoded in the equation (4.1) via an operator $\mathcal{C}$, and the resulting equation is:

$$\partial_t F + v \cdot \nabla_x F = \mathcal{C}(F(t, x, \cdot))(v). \tag{4.3}$$

The expression of the operator $\mathcal{C}$ depends on the assumptions made for the collisions. In the next section, the Boltzmann collisional operator will be considered and discussed [104, 108].

4.2 The mono-species Boltzmann equation

The Boltzmann equation

$$\partial_t F + v \cdot \nabla_x F = \mathcal{Q}(F, F), \tag{4.4}$$

has the objective to describe a rarefied monoatomic gas, where only binary collisions happen. Such collisions, encoded in the operator $\mathcal{Q}(F, F)$, are also assumed to be elastic, localised in time and space, and micro-reversible (reversible when modelled on a microscopic scale: during a collision, the probability that the velocities of the two molecules (v', v'_*) are exchanged in (v, v_*) is equal to the probability of observing the inverse transformation). Moreover, only decorrelated molecules collide (molecular chaos assumptions: the collision process contains a past-future asymmetry that allows correlations between molecules to increase over time). At the microscopic level, if one molecule with velocity $v' \in \mathbb{R}^3$ collides with another one with velocity v'_*, they change their velocities according to

$$(v', v'_*) = (v - [(v - v_*) \cdot n]\, n,\ v_* + [(v - v_*) \cdot n]\, n)\,. \tag{4.5}$$

In this parametrisation, the post-collisional velocities (v, v_*) are completely determined by the pre-collisional ones and the parameter $n \in \mathbb{S}^2$. In particular, from (4.5), the momentum and the kinetic energy conservation at each collision follow:

$$\begin{cases} v' + v'_* = v + v_* \\ |v'|^2 + |v_*|^2 = |v|^2 + |v'_*|^2. \end{cases}$$

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The operator $\mathcal{Q}(F,F)$ represents the variation of the number of molecules with velocity v. For elastic, localised, micro-reversible collisions of decorrelated molecules, $\mathcal{Q}$ is non-linear and can be defined [49] as

$$Q(F,F)(v) := \int_{\mathbb{R}^3}\int_{\mathbb{S}^2}(F(v'_*)F(v') - F(v_*)F(v))B(v-v_*,n)dndv_*, \tag{4.6}$$

where $B(v-v_*,n)$ is the *collisional kernel*. It encodes, heuristically, the probability that a collision between a molecule with velocity v and one with velocity v_* happens, keeping track of the microscopic interaction. It has the classical form [108]:

$$B(v-v_*,n) = c_{pp}|v-v_*|b\left(|v-v_*|, \left|n\cdot\frac{v-v_*}{|v-v_*|}\right|\right), \tag{4.7}$$

where $b \geq 0$ is the specific differential *cross-section*, which has unit area over mass, and c_{pp} is the scattering cross-section between two colliding molecules.

Hard-sphere kernel For the simplified case of hard sphere collisional kernel, the collision kernel (*hard-sphere kernel*) corresponds to pairwise elastic collisions between such hard spheres:

$$B(v-v_*,n) = c_{pp}|(v-v_*)\cdot n|. \tag{4.8}$$

The reader should note that such an approximation do not account for electrostatic interaction between the constituents.

Maxwell kernel Another particular case of collision kernel is the *Maxwell kernel*. Here, the collision kernel does not depend on the relative velocity, but only on the deviation angle. The Maxwellian kernel is widely used as it simplifies the expression of the collisional operator. However, it does not have a physical justification. It consists in:

$$B(v-v_*,n) = c_{pp}\hat{b}\left(\left|n\cdot\frac{v-v_*}{|v-v_*|}\right|\right), \tag{4.9}$$

with $\hat{b}$ an integrable and nonnegative function.

In the next section the attention is shifted to mixtures. A kinetic description of them will be given in two different circumstances.

4.3 The Boltzmann equations for mixtures

In this section, two cases are treated. The first discussed model is ideal to treat mixtures that collide without exchanging energy. The second one fits more for aerosol mixtures. In this case, indeed, the big difference in size and mass between the species causes exchange of energy between them.

Boltzmann equations for multi-species mixtures of ideal gases To describe multi-species mixtures of ideal monoatomic gases, a Boltzmann-type model was proposed in [33], for a

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mixture of I gases, each described via a distribution $F_i = F_i(t, x, v)$, for $i = 1, \cdots, I$. The system of equations satisfied by the unknowns is hence

$$\partial_t F_i + v \cdot \nabla_x F_i = \mathcal{Q}_i(F_i, F_i) + \sum_{j \neq i} \mathcal{Q}_{ij}(F_i, F_j), \qquad i = 1, \cdots, I. \tag{4.10}$$

The latter is a generalisation of (4.4) for the multi-species case. The operator $\mathcal{Q}_i$ accounts for collisions among the i-th species:

$$Q_i(F, F)(v) := \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} (F(v'_*)F(v') - F(v_*)F(v)) B_i(v - v_*, n) dn dv_*. \tag{4.11}$$

Here, the pre and post collisional velocities still obey (4.5) and B_i represents the collision kernel of the i-th species. On the other hand, the operator $\mathcal{Q}_{ij}$ describes collisions between molecules of the species i and $j \neq i$. For two different functions $F = F(v)$ and $G = G(v_*)$, it can be written as:

$$Q_{ij}(F, G)(v) := \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} (G(v'_*)F(v') - G(v_*)F(v)) B_{ij}(v - v_*, n) dn dv_*, \tag{4.12}$$

where B_{ij} contains information about the cross collisions between a molecule of the species i, with mass m_i and velocity v' and one with velocity v'_* of the species j, with mass m_j. The relation between the pre-collisional velocities and the post collisional one (v, v_*) is

$$\begin{cases} v' = \dfrac{m_i v + m_j v_*}{m_i + m_j} + \dfrac{m_j}{m_i + m_j} T_n(v - v_*), \\ v'_* = \dfrac{m_i v + m_j v_*}{m_i + m_j} - \dfrac{m_i}{m_i + m_j} T_n(v - v_*). \end{cases}$$

where $T_n(z) = z - 2(n \cdot z)n, \forall z \in \mathbb{R}^3$ [31].

Boltzmann equations for aerosol mixtures The collision operators (4.12) do not account for internal energy or chemical reactions among the different species. When dealing with an *aerosol*, i.e., a gas in which solid or liquid microscopic particles are suspended, the nature of the dust cannot be considered solely by introducing different masses for the species. In [59], a novel model for the case of $I = 2$ species was proposed. It has the same structure as (4.10), but with different collision operators. The collisions between dust particles (with mass m_p) and gas molecules (with mass m_g) are assumed to be inelastic and described by a diffuse reflection mechanism (at a fixed temperature) on the surface of dust particles.

This collision mechanism accounts for the macroscopic character of dust particles compared to gas molecules. According to diffuse reflection, gas particles that strike a microscopically rough wall get reflected at some random angle that is uncorrelated with their angle of incidence. This is due to particle-wall interaction, which imparts some information from the wall to the reflected particles. In a collision between a particle and a molecule, the post-collisional relative velocity is picked from a half-Maxwellian distribution at the temperature of the particle surface T_p. The collision mechanism between dust and gas thus introduces, for $n \in \mathbb{S}^2$, the probability density h_n of post-collisional relative velocities, given by:

$$h_n(z) = \frac{1}{2\pi} \frac{m_g^2}{k_B^2 T_p^2} (n \cdot z) \, e^{-\frac{m_g |z|^2}{2 k_B T_p}} \mathbb{1}_{\{z \cdot n \geq 0\}},$$

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where k_B denotes the Boltzmann constant.

The collision operators to describe this mechanism have been derived in [57] for the case of a fixed surface temperature T_p of particles (independent of time and space). Here, hard-sphere kernels $\varsigma(v-w,n) = |(v-w)\cdot n|$, where c_{gp} is the scattering cross-section between the two colliding species, were considered. If $F_1 = F_1(t,x,v)$ represents the distribution of dust particles and $F_2 = F_2(t,x,w)$ represents the distribution of gas molecules, then

$$\mathcal{Q}_{12}\left(F_1,F_2\right)(t,x,v) = c_{gp}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{S}^2}\left[F_2\left(w'\right)F\left(v'\right)e^{\frac{m_g|v'-w'|^2}{2k_BT_p}} - F_2(w)F_1(v)e^{\frac{m_g|v-w|^2}{2k_BT_p}}\right] \times \varsigma(v-w,n)e^{-\frac{m_g|v-w|^2}{2k_BT_p}}h_n(t,x,z)\mathrm{d}z\mathrm{d}n\mathrm{d}w$$

and

$$\mathcal{Q}_{21}(F_1,F_2)(t,x,w) = c_{gp}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{S}^2}\left[F_2\left(w'\right)F_1\left(v'\right)e^{\frac{m_g|v'-w'|^2}{2k_BT_p}} - F_2(w)F_1(v)e^{\frac{m_g|v-w|^2}{2k_BT_p}}\right] \times \varsigma(v-w,n)e^{-\frac{m_g|v-w|^2}{2k_BT_p}}h_n(t,x,z)\mathrm{d}z\mathrm{d}n\mathrm{d}v,$$

where

$$\begin{cases} v' = \dfrac{m_pv+m_gw}{m_p+m_g} - \dfrac{m_g}{m_g+m_p}z, \\ w' = \dfrac{m_pv+m_gw}{m_p+m_g} + \dfrac{m_p}{m_g+m_p}z. \end{cases}$$

Now that the kinetic setting is introduced, the main topic of the chapter can be discussed.

4.4 The hydrodynamic limits of the Boltzmann equation

The problem of the hydrodynamic limit can be described as the transition from the Boltzmann description of dilute gases to a hydrodynamic description on large spatial and temporal scales. Reviews addressing this topic are available in [170] and [108]. Before delving into the subject of hydrodynamic limits, the Boltzmann equation in dimensionless variables is introduced. Subsequently, the attention shifts to the *method of moments*, the *Hilbert expansion*, and the *Chapman-Enskog expansion*.

Collision invariants and conservation laws The connection between kinetic and macroscopic theory relies on local macroscopic quantities such as density, mean velocity, and temperature (referred to as *physical observables*). As noted in Section 1.2.2, these quantities can be

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interpreted as the mass, expectation, and variance of the particle distribution F. For a single species, these quantities are defined as:

$$\begin{aligned}\rho(t,x) &= \int_{\mathbb{R}^3} F(t,x,v)\,dv,\\ u(t,x) &= \frac{1}{\rho(t,x)}\int_{\mathbb{R}^3} F(t,x,v)\,v\,dv,\\ \theta(t,x) &= \frac{m_p}{3k_B\rho(t,x)}\int_{\mathbb{R}^3} F(t,x,v)\,|v-u(t,x)|^2\,dv,\end{aligned} \tag{4.13}$$

where k_B is the Boltzmann constant and m_p is the particle mass.

In the case of multiple species, local macroscopic quantities extend to a family of densities $(\rho_i)_{1\le i\le I}$, velocities $(u_i)_{1\le i\le I}$, and temperatures $(\theta_i)_{1\le i\le I}$, each associated with their respective distribution functions $(F_i)_{1\le i\le I}$. For a detailed discussion on mixtures, readers can refer to [26]. The following discussion, for the sake of simplicity and readability, focus on the mono-species case. Similar considerations hold for mixtures, where the procedure needs to be repeated for each species.

The conservation laws (8.4) are expected to have counterparts at the macroscopic level. One would expect to deduce conservation laws for the macroscopic quantities in (4.13) by integrating the Boltzmann equation (4.4) over velocity, suitably test function $\phi(v)$. These functions are $\phi(v) = 1, v_\ell, \frac{|v|^2}{2}$ for $\ell = 1,2,3$. The first good news is that $\phi(v) = 1, v_\ell, \frac{|v|^2}{2}$ for $\ell = 1,2,3$ are *collisional invariants* for (4.6). This means:

$$\phi(v') + \phi(v'_*) = \phi(v) + \phi(v_*),$$

for every $(v, v_*, n) \in \mathbb{R}^3 \times \mathbb{R}^3 \times \mathbb{S}^2$. Consequently, these invariants imply:

$$\int_{\mathbb{R}^3} \mathcal{Q}(F,F)(v)\phi(v)\,dv = 0, \tag{4.14}$$

where $\mathcal{Q}(F,F)$ represents the collision operator. This equality is derived by using the weak formulation:

$$\int_{\mathbb{R}^3} \mathcal{Q}(F,F)(v)\phi(v)\,dv = \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{S}^2} FF_*(\phi' + \phi'_* - \phi - \phi_*)B(v-v_*,n)\,dv\,dv_*\,dn,$$

where the notation $F = F(v)$, $F_* = F(v_*)$, $F' = F(v')$, and $F'_* = F(v'_*)$ (and similarly for ϕ) is adopted. This notation will be used throughout the rest of the thesis. While integrating the Boltzmann equation (4.4) with these invariants yields local conservation laws for (4.13), the resulting system is not closed. Each equation for the time derivative of a moment involves higher-order moments such as $\nabla_x \cdot (\int_{\mathbb{R}^3} Fv \otimes v\,dv)$ and $\nabla_x \cdot (\int_{\mathbb{R}^3} F|v|^2 v\,dv)$, which are not expressible solely in terms of ρ, u, and θ.

Each equation for the time derivative of a moment involves higher-order moments such as $\nabla_x \cdot (\int_{\mathbb{R}^3} Fv \otimes v\,dv)$ and $\nabla_x \cdot (\int_{\mathbb{R}^3} F|v|^2 v\,dv)$, which are not expressible solely in terms of ρ, u, and θ.

Thus, the central challenge in transitioning from the Boltzmann equation (4.4) to a system of local conservation laws for ρ, u, and θ is: *How can this conservation law system be closed?* One approach is to specify a functional form for the distribution function F, tailored to the

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specific regime of interest. This choice is crucial for accurately closing the conservation laws for the primary variables (ρ, u, θ).

The dimensionless Boltzmann equation To facilitate the closure of the conservation laws, it is necessary to rescale the problem. Let L, t°, T°, and V° the macroscopic length scale, time scale, reference temperature, and reference velocity of the particles. The latter corresponds to the *thermal speed* of the particles with energy $\frac{3}{2}k_B T^\circ$, being k_B the Boltzmann constant. Hence

$$V^\circ = \sqrt{\frac{5}{3}\frac{k_B T^\circ}{m_p}},$$

where m_p corresponds to the particle's mass. One then defines the dimensionless variables

$$\hat{x} = \frac{x}{L} \quad \hat{t} = \frac{t}{t^\circ}, \quad \hat{v} = \frac{v}{V^\circ},$$

and the dimensionless unknown:

$$\hat{F}(\hat{t}, \hat{x}, \hat{v}) = \frac{F(t, x, v)}{F^\circ}, \text{ with } F^\circ = \frac{N_p}{(V^\circ)^3}$$

where N_p is the density of particles in a volume L^3. The collisional kernel, being the relative velocity times the scattering cross-section of the particles, is rescaled as

$$\hat{B}(\hat{z}, n) = \frac{1}{V^\circ} B(z, n), \quad \text{where } \hat{z} = \frac{z}{V^0}.$$

Introducing the Strouhal number γ and the Knudsen number δ_p (mean free path over characteristic length)

$$\gamma = \frac{L}{t^0 V^0}, \quad \text{and} \quad \delta_p = \frac{1}{N_p \sigma_{pp} L},$$

the dimensionless Boltzmann equation takes the form:

$$\gamma \partial_{\hat{t}} \hat{F} + \hat{v} \cdot \nabla_{\hat{x}} \hat{F} = \frac{1}{\delta_p} \hat{\mathcal{Q}}(\hat{F}, \hat{F}), \tag{4.15}$$

where

$$\hat{\mathcal{Q}}(\hat{F}, \hat{F}) = \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} (\hat{F}(\hat{v}'_*)\hat{F}(\hat{v}') - \hat{F}(\hat{v}_*)\hat{F}(\hat{v}))\hat{B}(\hat{v} - \hat{v}_*, n) dn d\hat{v}_*.$$

One needs to clarify what happens when the parameters get small. When δ_p approaches zero, the distance between two collisions will be negligible compared with the spatial scale. Hence the gas can be thought as a fluid. Moreover if the Strouhal number γ is constant, or approaches zero as well, then from (4.15), one can deduce that in the limit also the collisional operator becomes null. Let's try to interpret what $\mathcal{Q}(F, F) = 0$ means. The starting point to do so is the *H-theorem* and the notion of entropy.

Entropy and equilibrium The functional

$$H(F)(t) := \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} F(t, x, v) \log F(t, x, v) dv dx, \tag{4.16}$$

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is called (mathematical) entropy associated to (4.4). The *H-theorem* shows that

$$\frac{d}{dt}H(F)(t) \leq 0, \tag{4.17}$$

meaning that the entropy decreases in time along the solutions of the Boltzmann equation. Indeed, by defining the *dissipation* as the functional

$$\mathbb{D}(F)(t,x) := \int_{\mathbb{R}^3} \mathcal{Q}(F,F)(t,x,v)\log F(t,x,v)dv, \tag{4.18}$$

then

$$\frac{d}{dt}H(F)(t) = -\int_{\mathbb{R}^3} \mathbb{D}(F)(t,x)dx \leq 0,$$

thank to the weak formulation

$$\int_{\mathbb{R}^3} \mathcal{Q}(F,F)(v)\phi(v)dv = \frac{1}{4}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{S}^2}(FF_* - F'F'_*)(\phi' + \phi'_* - \phi - \phi_*)B(v-v_*,n)dvdv_*dn, \tag{4.19}$$

of the collisional operator $\mathcal{Q}(F,F)$. Moreover, another important result stated in this theorem is that [107]

$$\begin{aligned}\int_{\mathbb{R}^3} \mathbb{D}(F)(t,x)dx = 0 &\iff F(t,x,v) = \frac{\rho(t,x)}{(2\pi\theta(t,x))^{3/2}}\exp\left(-\frac{|v-u(t,x)|^2}{2\theta(t,x)}\right) =: \mathcal{M}_{(\rho,u,\theta)}(t,x,v)\\ &\iff \mathcal{Q}(F,F) = 0.\end{aligned}$$

Therefore, even though it is not a solution to the Boltzmann equation, the local Maxwellian is an equilibrium for the Boltzmann equation, in the sense that it is a minimum of the entropy functional. Saying that $\mathcal{Q}(F,F) = 0$ is equivalent to say that F is a local Maxwellian. When δ_p approaches zero, F approaches a local Maxwellian in the parameters (4.13).

Hydrodynamic limits As mentioned in previous discussions, closing the system of local conservation laws requires choosing an expression for F in an appropriate regime. In the fluid regime, i.e., $\delta_p \to 0$, the distribution function approaches the local Maxwellian $\mathcal{M}_{(\rho,u,\theta)}(t,x,v)$. Hence, a proper approximation of F is a perturbation of the local Maxwellian.

Such an approximation is valid when the size of the system and the time scale of interest are large compared with the typical space and time scales of collisions, i.e., the mean free path and the mean time between collisions. In this regime, the role of collisions is considerably enhanced, as their effect is to bring F closer and closer to a local Maxwellian. Moreover, a physical regime with frequent collisions is also where the set of particles can be considered a fluid.

From the previous discussion, it emerges that changing the time-space scale of the problem is necessary to approximate F as a local Maxwellian $\mathcal{M}_{(\rho,u,\theta)}$. This change allows for closing the conservation law system for the primary variables (ρ,u,θ).

One way to perform such a limit is to directly pass into the limit in the conservation laws for the perturbation. Such a method is called *method of moments*. An example will explain better how it works. For example, the compressible Euler equations are obtained in the limit

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$\delta_p =: \epsilon \ll 1$, when $\gamma = 1$. By omitting the hats on the rescaled variables and underling the dependence of the unknown on ϵ, we have that $F^\epsilon = F^\epsilon(t, x, v)$ satisfies

$$\partial_t F^\epsilon + v \cdot \nabla_x F^\epsilon = \frac{1}{\epsilon} \mathcal{Q}(F^\epsilon, F^\epsilon). \tag{4.20}$$

In the limit $\epsilon \to 0$, the distance between two collisions will be negligible compared with the spatial scale considered. The gas can be hence be thought as a fluid. Obviously, one expect that

$$F^\epsilon \to F, \quad \text{while} \quad \mathcal{Q}(F^\epsilon, F^\epsilon) \to 0 = \mathcal{Q}(F, F),$$

in the limit $\epsilon \to 0$. This justifies the assumption of F_ϵ being close to the local Maxwellian $\mathcal{M}(\rho, u, \theta)$. Indeed, as a consequence of the *H-Theorem*, $\mathcal{Q}(F, F) = 0$ implies that the limit F is a local Maxwellian. Hence, under some assumptions on the initial distribution $F^\epsilon|_{t=0}$, we can pass into the limit in the local conservation laws for F^ϵ and obtain the Euler equations satisfied by the Maxwellian's parameters (ρ, u, θ) in the limit.

Another approach to pass to the macroscopic description is to use asymptotic expansions of the function F^ϵ. Namely, one seek solutions of the equation (4.15), with $\epsilon = \delta_p$, as formal power series in ϵ:

$$F^\epsilon(t, x, v) = \sum_{n \geq 0} \epsilon^n F_n(t, x, v).$$

The leading order F_0 is expected to be the hydrodynamic limit, while the successive corrections account for the finite Knudsen effect. Hence, in this way, higher order hydrodynamic corrections to the compressible Euler equation are taken into account.

The diffusive scaling The set of the scaling is relevant to the phenomena one wants to observed. By taking $\gamma = 1$ and $\delta_p = \epsilon \ll 1$, we have seen that hydrodynamics equations can be deduced in the limit. What about diffusion equations? Another example consists in setting $\epsilon := 1/L = F^\circ$, $V^\circ = 1$, and $t^\circ = \epsilon^2$. This scaling is part of the so-called *diffusive scaling*. It consists in taking a time scaling much bigger than the spatial one. Indeed, diffusion occurs on time scales much larger than transport phenomena. Hence the adimensionalised equation becomes

$$\epsilon \partial_t F^\epsilon + v \cdot \nabla_x F^\epsilon = \frac{1}{\epsilon} \mathcal{Q}(F^\epsilon, F^\epsilon). \tag{4.21}$$

In this situation, when $\epsilon \to 0$, on the one hand, the penalisation of the collision term forces the solution F^ϵ to be an equilibrium state. On the other hand, the diffusive scaling allows to obtain a diffusion equation for the macroscopic quantities in the limit. A diffusion equation for equation (4.21) can be obtained by performing a formal expansion of F^ϵ as explained in detail, for example, in [74]. An additional scaling has to be imposed in order to generate velocities of order ϵ. This is achieved by considering initial distributions close to a uniform Maxwellian. Then the moments of F^ϵ converge to the ones of the local Maxwellian. Moreover, under suitable assumptions on the initial (scaled) distributions, it is proved that a similar perturbation of the local Maxwellian, taken for the initial distribution, holds true also for the solution F^ϵ [153].

The convergence in the macroscopic limit to a drift-diffusion model can be found in [54].

Recently, there has also been a strong interest in performing the diffusive limit for multi-species systems of type (4.10). The multispecies interaction would indeed lead to Maxwell-Stefan type systems in the limit [26, 33], which include cross-diffusion (see Section 2.2.1). The

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method used in this context is usually the method of moments. The choice of the perturbation F^ϵ is detailed and discussed in Part III of this thesis.

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Chapter 5

Outlines of the thesis

5.1 Numerics for a generalised Poisson–Nernst–Planck model, Chapter 6

This chapter proposes two finite volume schemes for a generalised Poisson-Nernst-Planck model. The latter is used to describe the evolution of ion mixtures in biological channels or nanopores. As mentioned in Section 2.4, the modelling of ions in narrow geometries requires the size exclusion effect and electrostatic interactions to be taken into account.

The model setting

In this model, I species, the volume fractions of which being denoted by $U = (u_i)_{1\leq i\leq I}$, are subject to diffusion as well as to electric forces induced by a self-consistent electrostatic potential. Denote by $\Omega \subset \mathbb{R}^d$ a bounded connected polyhedral domain, then the conservation of the volume occupied by the species i writes

$$\partial_t u_i + \operatorname{div} F_i = 0, \quad F_i = -D_i \left(u_0 \nabla u_i - u_i \nabla u_0 + u_0 u_i z_i \nabla \phi\right), \tag{5.1}$$

$$-\lambda^2 \Delta \phi = \sum_{i=1}^{I} z_i u_i + f, \quad \text{in } \Omega,\ t > 0,\ i = 1, \dots, I, \tag{5.2}$$

In the above expression $D_i > 0$ denotes the diffusion coefficient and $z_i \in \mathbb{Z}$ the charge of the species i. The (scaled) Debye length is denoted by $\lambda > 0$. The function f is given and represents a prescribed background charge density. The unknown ϕ is the electrostatic potential, which solves the Poisson equation (5.2). The quantity

$$u_0 = 1 - \sum_{i=1}^{I} u_i \tag{5.3}$$

shall be thought as the volume fraction of available space for the ions, possibly occupied by a motile and electro-neutral solvent. The quantity u_0 is then required to remain nonnegative, leading to size exclusion for the other species u_i, $i = 1, \dots, I$. Equality (5.3) is called *volume filling* or *size exclusion* constraint. It transforms (5.1) in cross-diffusion equations, where F_i stays for the i-th flux. Boundary conditions of mixed type for the electric potential are considered, whereas no-flux boundary conditions are taken for the conservation laws (5.1). The system is finally complemented with initial conditions $u_i(t = 0) = u_i^0$. The latter satisfy the volume filling constraint (5.3) and have a strict positive total mass on Ω.

The main advantage of the model (5.1)-(5.2) is its entropy (or formal gradient flow) structure, as defined in Section 3.1. From an analytical point of view, this allows to show existence of

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global-in-time bounded weak solutions [102]. The gradient flow structure of the model can be also used to rewrite the fluxes as

$$F_i = -D_i u_0^2 e^{-z_i\phi}\nabla w_i, \qquad i = 1,\dots,I, \tag{5.4}$$

where $w_i = \frac{u_i}{u_0}e^{z_i\phi}$ are the Slotboom variables. As discussed in Section 3.3, this reformulation is also useful in defining finite volume schemes which preserve the thermal equilibrium.

After introducing a partition $\mathcal{T}$ of Ω in polytopes (*control volumes* or *cells*), and a time discretisation $(t^n)_{n\geq 0}$ of $[0,+\infty)$, the two finite volume schemes are defined. The discretisation of the Poisson equation (5.2) relies on a classical two-point flux approximation. The equation (5.1) is discretized using a backward Euler method in time and finite volume in space, as in Section 3.3. Keeping the same notation of Section 3.3, where subscript i refers to the i-th species, for $\sigma = K|L$ an internal edge, the numerical fluxes of the i-th species are defined as

$$F^n_{i,K\sigma} = \frac{m_\sigma}{d_\sigma} D_i \left(u^n_{i,K} u^n_{0,L} \mathfrak{B}\left(z_i(\phi^n_L - \phi^n_K)\right) - u^n_{i,L} u^n_{0,K} \mathfrak{B}\left(z_i(\phi^n_K - \phi^n_L)\right)\right), \tag{5.5}$$

with

$$u^n_{0,K} = 1 - \sum_{i=1}^{I} u^n_{i,K}, \qquad K \in \mathcal{T}. \tag{5.6}$$

Formula (5.5) involves a function $\mathfrak{B} \in C^1(\mathbb{R};\mathbb{R})$ which is (strictly) positive and satisfies $\mathfrak{B}(0) = 1$ and $\mathfrak{B}'(0) = -1/2$. In the first proposed scheme, the function $\mathfrak{B}$ is defined as:

$$\mathfrak{B}(y) = e^{-y/2}. \tag{SQRA}$$

The resulting scheme corresponds to the SQRA scheme. The design of this scheme take direct inspiration in the hopping process described in [38] (see also [37]). Although this scheme behaves well in many situations, it suffers from robustness issues in the small Debye length regime. This drawback is overcome by mixing some ideas of the SQRA scheme with some features of the Scharfetter-Gummel (SG) scheme [159], for which $\mathfrak{B}$ is the Bernoulli function:

$$\mathfrak{B}(y) = \frac{y}{e^y - 1}. \tag{SG}$$

The SG scheme shows a better behavior (accuracy and robustness) with respect to the SQRA scheme.

Main results

After having proven the existence of bounded discrete solutions (Theorem 6.1), Chapter 6 will be devoted to rigorously establish the convergence of the SG and SQRA schemes towards a weak solution (Theorem 6.2). The convergence's result is based on the free-energy diminishing character of the SG and SQRA schemes.

Other numerical approaches can be found in the literature to simulate the system (5.1)-(5.2). A finite volume scheme was studied in [40], demonstrating practical effectiveness but limited mathematical analysis. The scheme, using upwind for mobilities, shows only first-order spatial convergence. An alternative finite element method using electrochemical potentials, analyzed in [103], diminishes free energy without physical parameter restrictions and converges to a weak solution as the mesh size and time step approach zero. It achieves second-order spatial

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convergence but results in a stiffer nonlinear system compared to the finite volume scheme, offering no clear advantage. The finite volume scheme in [14] also results in singular numerical flux expressions.

The schemes developed in Chapter 6 aim combining the best aspects of previous approaches, ensuring free energy decay, unconditional convergence, second-order spatial accuracy, and a well-behaved nonlinear system for moderately small Debye length.

5.2 Analysis for a Poisson–Nernst–Planck–Fermi model, Chapter 7

Chapter 7 is devoted to the analysis of a new model to describe the evolution of ion mixtures in narrow channels. This model is consistent with the one proposed in [81]. In developing the model, the authors' aim was to improve the predictive capabilities and accuracy of electrolyte modelling, which is crucial for applications in battery technology, fuel cells and other electrochemical systems.

The model setting

The evolution of n ionic species, immersed in a solvent, is assumed to be given by the Poisson–Nernst–Planck–Fermi system

$$\partial_t u_i + \operatorname{div} J_i = r_i(u), \quad J_i = -D_i(\nabla u_i - u_i \nabla \log u_0 + u_i z_i \nabla \Phi), \tag{5.7}$$

$$\lambda^2(\ell^2\Delta - 1)\Delta\Phi = \sum_{j=1}^n z_j u_j + f(x) \quad \text{in } \Omega,\ t > 0,\ i = 1, \ldots, n, \tag{5.8}$$

where $\Omega \subset \mathbb{R}^d$ $(d \geq 1)$ is a bounded Lipschitz domain, $u = (u_1, \ldots, u_n)$ is the concentration vector, supplemented with initial and mixed Dirichlet–Neumann boundary conditions.

The unknowns are the ion concentrations (or volume fractions) $u_i(x,t)$ of the ith ion species and the correlated electric potential $\Phi(x,t)$. The solvent concentration (or volume fraction) $u_0(x,t)$ is given by the volume filling constraint (5.3). Equations (5.7) are cross-diffusion equations with the fluxes J_i and the reaction rates $r_i(u)$. The parameters are the diffusivities $D_i > 0$ and the valences $z_i \in \mathbb{Z}$. Equation (5.8) is the Poisson–Fermi equation with the scaled Debye length $\lambda > 0$, the correlation length $\ell > 0$, and the given background charge density $f(x)$. A derivation of (5.7)–(5.8) using an averaging procedure of a Langevin model can be found in [161].

The model (5.7)-(5.8) has the advantage of being consistent with the thermodynamical model [81]

$$J_i = -\sum_{j=1}^n D_{ij} u_j \nabla(\mu_j - \mu_0), \quad \text{where } \mu_i = \log u_i + z_i\Phi, \quad \mu_0 = \log u_0 + z_0\Phi,$$

assuming that the diffusion matrix is diagonal, $D_{ij} = D_i\delta_{ij}$, and that the solvent is neutral, $z_0 = 0$.

Main results

The first main result of this chapter concern the proofs of existence of global-in-time bounded weak solutions (Theorem 7.1). Under suitable hypotheses, detailed at the beginning of the

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chapter, a bounded weak solution $u_1, \ldots, u_n$ to (5.7)–(5.8), with mixed Dirichlet-Neumann boundary conditions, satisfying $u_i(x,t) \in \overline{\mathcal{D}}$ for a.e. $(x,t) \in \Omega_T$, $i = 1, \ldots, n$,

$$\sqrt{u_i} \in L^2(0,T;H^1(\Omega)), \quad u_i \in H^1(0,T;H_D^1(\Omega)') \cap C^0([0,T];L^2(\Omega)),$$
$$\Phi \in L^2(0,T;H^2(\Omega)), \quad \log u_0 \in L^2(0,T;H^1(\Omega)).$$

Moreover, the solutions satisfy a free energy inequality. The proof uses the boundedness-by-entropy method, following a similar procedure as the one explained in Section 3.1.

The main novelty of this work is actually the second result: The weak-strong uniqueness result (Theorem 7.2). The weak–strong uniqueness property means that any weak solution to system coincides with a strong solution emanating from the same initial conditions as long as the latter exists. A weak solution $(\bar{u}, \bar{\Phi})$ is a *strong solution* if moreover

$$\bar{u}_i \geq c > 0 \text{ in } \Omega_T, \quad \bar{u}_i,\ \bar{\Phi} \in L^\infty(0,T;W^{1,\infty}(\Omega)) \quad \text{for all } i = 1, \ldots, n.$$

Let (u, Φ) be a weak solution and $(\bar{u}, \bar{\Phi})$ be a strong solution to (5.7)–(5.8). Then, under suitable assumptions on the boundary data and the reaction terms, $u(x,t) = \bar{u}(x,t)$, $\Phi(x,t) = \bar{\Phi}(x,t)$ for a.e. $x \in \Omega$ and $t \in (0,T)$. While the existence proof relies on standard entropy methods, a new idea is needed to prove the weak–strong uniqueness result. The key idea of the proof of Theorem 7.2 is to consider the solvent concentration u_0 as an independent variable and to formulate the cross-diffusion system for the extended concentration vector $(u_0, u_1, \ldots, u_n)$. This leads to a diffusion matrix with nontrivial kernel. Then the proof is based on the relative entropy method for the extended cross-diffusion system and the positive definiteness of a related diffusion matrix on a subspace.

5.3 A non-isothermal model for aerosol mixtures, Chapter 8

Aerosol mixtures of gas and dust will be the focus of Chapter 8. The key characteristic to examine is the significant difference in mass between the two species composing the aerosol. Both dust particles and gas molecules are assumed to be identical within their respective categories. However, dust particles are considered to be much larger and more massive than the gas molecules.

The modelling setting

At the kinetic level, both species are supposed to be described by suitable density functions. In what follows, the function $F = F(t,x,v)$ represents the density of particles, whereas $f = f(t,x,w)$ is a function representing the density of gaseous molecules. The gas-dust dynamics satisfies the following system of Boltzmann-like equations

$$\begin{cases} \partial_t F + v \cdot \nabla_x F = \mathcal{D}(F,f) + \mathcal{P}(F) \\ \partial_t f + w \cdot \nabla_x f = \mathcal{R}(F,f) + \mathcal{C}(f). \end{cases} \tag{5.9}$$

The collisional operators $\mathcal{C}$ and $\mathcal{P}$ encode mono-species collisions, represented by classical Boltzmann operators with a structure similar to (4.6). Conversely, the operators $\mathcal{D}$ and $\mathcal{R}$ describe bi-species interactions.

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As discussed in Section 4.3, a diffuse reflection mechanism at the particle surface temperature is more accurate for describing collisions between dust and gas. This is especially true when considering energy exchange between the species. This model accounts for the macroscopic nature of dust particles and assumes that gas molecules thermalize almost instantaneously upon contact with the particle's surface.

Collision operators for this mechanism, with a fixed particle surface temperature T_p, were derived in [57]. These operators were introduced in Section 4.3. However, despite having an explicit expression for entropy, this model does not conserve the system's total energy. An improved model in [60] adjusts the particle's temperature during collisions. This model treats the surface temperature as a variable in the density function F and derives modified collision operators. Nonetheless, deriving an entropy for this improved model remains complex and unresolved.

Main results

The first aim of the work discussed in Chapter 8 is describing non-isothermal dust-gas mixtures via a new kinetic model. Collisions between entities of the same species are assumed elastic, with generic collision kernels. Gas-dust collisions are treated with a diffuse reflection mechanism as in [57], but inspired by porous media literature, the surface temperature is taken as a macroscopic function of time and space $T_p(t,x)$. The latter satisfies a transport-like equation

$$\partial_t T_p \int_{\mathbb{R}^3} F(v)\,\mathrm{d}v + \nabla_x T_p \cdot \int_{\mathbb{R}^3} vF(t,x,v)\,\mathrm{d}v = C_2 I_2(F,f) - C_1 I_1(F,f) T_p,$$

ensuring total energy conservation. The dependence of T_p, F, and f on (t,x) is omitted. The positive constants C_1 and C_2 depend on the dust and gas mass, on the Boltzmann constant and on the particle's mass heat capacity only. The terms $I_1(F,f) = I_1(F,f)(t,x)$ and $I_2(F,f) = I_2(F,f)(t,x)$ are integrals in v and w of F and f. Their expressions depend on the considered collision kernels. The main novelty is thus proposing a model that, in the case of hard-sphere kernels for the bi-species collisions, possesses an explicit entropy structure and also preserves the total energy of the system.

The second aim of Chapter 8 is to perform a formal asymptotic diffusive limit, as discussed in 4.4, to obtain a Maxwell-Stefan-like system. After performing a proper adimensionalisation of the system and introducing small parameters, macroscopic equations for the macroscopic scaled quantities associated to gas and dust are derived. Then a formal macroscopic limit, where all the parameters tend to zero, is carried out. The idea is to take the point of view of the particles. Particles perceive the molecules of the gas as much faster than themselves, but much lighter and smaller. In particular, a fluid model is considered in the limit, since the Knudsen numbers of the gas and the dust go to zero. The Strouhal numbers also vanish in the diffusive asymptotic.

At the time of writing, complete explicit calculations have been performed to obtain a macroscopic model in the case of Maxwell kernels in collisions between different species. Calculations for hard-sphere kernels are currently only partially completed and reported. They will be concluded in a future work.

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Part II

Two cross-diffusion models for ion-mixtures

Chapter 6

Finite volumes for a Poisson–Nernst–Planck system

This chapter is an extension of the article *"Finite volumes for a generalized Poisson-Nernst-Planck system with cross-diffusion and size exclusion"* [42], joint work with Clément Cancès and Maxime Herda and published in *International Conference on Finite Volumes for Complex Applications*, 57-73 (2023).

6.1 Presentation of the problem

6.1.1 The continuous generalized Poisson-Nernst-Planck model

Motivated by the transfer of ions in confined geometries, Burger *et al.* introduced in [37] a model accounting for cross-diffusion and size-exclusion effects. The model [38] further incorporated self-consistent electric interaction. In this model, I species, the volume fractions of which being denoted by $U = (u_i)_{1\leq i\leq I}$, are subject to diffusion as well as to electric forces induced by a self-consistent electrostatic potential. Denote by $\Omega \subset \mathbb{R}^d$ a bounded connected polyhedral domain, then the conservation of the volume occupied by the species i writes

$$\partial_t u_i + \operatorname{div} F_i = 0, \qquad i = 1, \dots, I, \tag{6.1}$$

with the flux of the species i being (formally) given by

$$F_i = -D_i \left(u_0 \nabla u_i - u_i \nabla u_0 + u_0 u_i z_i \nabla \phi\right) = -D_i u_i u_0 \nabla \left(\log\left(\frac{u_i}{u_0}\right) + z_i \phi\right). \tag{6.2}$$

In the above expression, $D_i > 0$ denotes the diffusion coefficient of the species i. The quantity

$$u_0 = 1 - \sum_{i=1}^{I} u_i \tag{6.3}$$

shall be thought as the volume fraction of available space for the ions, possibly occupied by a motile and electro-neutral solvent. The quantity u_0 is then required to remain nonnegative, leading to size exclusion for the other species u_i, $i = 1, \dots, I$. Denoting by $z_i \in \mathbb{Z}$ the charge of species i and by $\lambda > 0$ the (scaled) Debye length, then the electrostatic potential solves the Poisson equation

$$-\lambda^2 \Delta \phi = \sum_{i=1}^{I} z_i u_i + f \tag{6.4}$$

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for some prescribed background charge density f. We consider boundary conditions of mixed type for the electric potential. More precisely, we assume that the boundary $\partial\Omega$ of the domain can be split into a insulator part Γ^N and its complement Γ^D on which Dirichlet boundary condition is imposed:

$$\nabla\phi \cdot n = 0 \quad \text{on } \Gamma^N \qquad \text{and} \quad \phi = \phi^D \text{ on } \Gamma^D. \tag{6.5}$$

Throughout this paper, we will assume that $f \in L^\infty(\Omega)$ and that ϕ^D is the trace of an $L^\infty \cap H^1(\Omega)$ function (which we also denote by ϕ^D). Neither f nor ϕ^D depend on time. Boundary conditions of various types can be considered for the conservation laws (6.1)–(6.2), like for instance Robin type boundary condition modeling electrochemical reaction thanks to Butler-Volmer type formula, see for instance [41], or boundary conditions of mixed Dirichlet-Neumann type as in [102]. In the presentation of the scheme, we assume for simplicity that the system is isolated, in the sense that

$$F_i \cdot n = 0 \quad \text{on } \partial\Omega, \qquad i = 1, \dots, I. \tag{6.6}$$

The system is finally complemented with initial conditions $u_i(t=0) = u_i^0$ with

$$u_i^0 \geq 0 \quad \text{and} \quad \int_\Omega u_i^0 > 0 \quad \text{for} \quad i = 0, \dots, I \quad \text{and} \quad \sum_{i=0}^{I} u_i^0 = 1. \tag{6.7}$$

We then denote by

$$\mathcal{A} = \left\{ U = (u_i)_{1 \leq i \leq I} \in \mathbb{R}_+^I \;\middle|\; \sum_{i=1}^{I} u_i \leq 1 \right\}$$

the set in which the volume fractions have to take their values.

6.1.2 Entropy structure of the model

Let us now described the entropy (or formal gradient flow) structure of the model. Introduce the Slotboom variables $w_i = \frac{u_i}{u_0} e^{z_i \phi}$, then the fluxes (6.2) rewrite as

$$F_i = -D_i u_0^2 e^{-z_i\phi} \nabla w_i, \qquad i = 1, \dots, I. \tag{6.8}$$

Multiplying (6.1) by the so-called electrochemical potentials $\mu_i = \log w_i = \log \frac{u_i}{u_0} + z_i\phi$, integrating over Ω and summing over $i = 1, \dots, I$ yields

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{H} + 4 \int_\Omega \sum_{i=1}^{I} D_i u_0^2 e^{-z_i\phi} |\nabla \sqrt{w_i}|^2 = 0, \tag{6.9}$$

where, denoting the mixing (neg)entropy density function $H : \mathcal{A} \to [-\log(I+1), +\infty)$ by

$$H(U) = u_0 \log(u_0) + \sum_{i=1}^{I} u_i \log(u_i), \tag{6.10}$$

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with u_0 seen as a function of U, the free energy $\mathcal{H}$ is given by

$$\mathcal{H} = \int_\Omega H(U) + \frac{\lambda^2}{2}\int_\Omega |\nabla\phi|^2 - \lambda^2 \int_{\Gamma^D} \phi^D \nabla\phi \cdot n. \tag{6.11}$$

Assume that the u_i are positive for $i = 0, \dots, I$ (as proved in the discrete case later on), then the second term in (6.9) is well-defined and non-negative. As a consequence, the free energy decays along time, as a manifestation of the second principle of thermodynamics. Observe that $\mathcal{H}$ need not be non-negative but may be bounded uniformly from below by a constant depending only on λ, f and ϕ^D.

6.1.3 Weak solution

As we aim to prove rigorously the convergence of the scheme to be presented in Section 6.2, we need a proper notion of solution for the continuous problem (6.1)–(6.7). The volume fractions we seek are such that

$$0 \le u_i \le 1 \text{ for } 0 \le i \le 1 \text{ and a.e. } (t,x) \in \mathbb{R}_+ \times \Omega. \tag{6.12}$$

The electric potential ϕ then solves the Poisson equation (6.4) with a bounded right-hand side and boundary condition, so it satisfies

$$\|\phi\|_{L^\infty(\mathbb{R}_+\times\Omega)} + \|\phi - \phi^D\|_{L^\infty(\mathbb{R}_+;V)} \le C(\lambda, z, \Omega, f), \tag{6.13}$$

where

$$V = \left\{ v \in H^1(\Omega) \;\middle|\; v_{|_{\Gamma^D}} = 0 \right\}$$

is equipped with the $H^1(\Omega)$ semi-norm $\|\nabla v\|_{L^2}$, which is a norm thanks to Poincaré inequality. We have emphasised in the right-hand side of (6.13) the dependence of the bound on the data, especially on the Debye length λ. The estimate (6.9) is the other main estimate on which our study will rely. It provides enough control to define a proper notion of weak solutions, but at the price of a suitable reformulation of the fluxes (6.2). Let us first remark that, since the free energy $\mathcal{H}$ is bounded (see Lemma 6.2), integrating (6.9) over $t \in \mathbb{R}_+$ provides

$$\iint_{\mathbb{R}_+\times\Omega} \sum_{i=1}^{I} D_i u_0^2 e^{-z_i\phi} |\nabla\sqrt{w_i}|^2 \le C. \tag{6.14}$$

As already noticed in [102], the above control yields a control in $L^2_{\mathrm{loc}}(\mathbb{R}_+; H^1(\Omega))$ on $\sqrt{u_0}$ and on u_0 itself, as well as some control on some product terms involving u_0 and u_i for $i \ge 1$. From the numerical analysis exposed hereafter, we derive a $L^2_{\mathrm{loc}}(\mathbb{R}_+; H^1(\Omega))$ estimate on $u_i\sqrt{u_0}$, which, together with (6.12) provides a $L^2_{\mathrm{loc}}(\mathbb{R}_+; H^1(\Omega))$ control on $u_i u_0$ too. Hence, all the terms in the following expression of the fluxes

$$F_i = -D_i\left(\nabla(u_0u_i) - 4u_i\sqrt{u_0}\nabla\sqrt{u_0} + u_iu_0z_i\nabla\phi\right), \qquad 1 \le i \le I, \tag{6.15}$$

have a clear mathematical sense, motivating the following notion of weak solution.

Definition 6.1 (Weak solution)**.** *(U, ϕ) is said to be a weak solution to* (6.1)–(6.7) *if*

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- $u_i \in L^\infty(\mathbb{R}_+ \times \Omega)$ *with* $U \in \mathcal{A}$ *a.e. in* $\mathbb{R}_+ \times \Omega$, *with moreover* $\sqrt{u_0}$ *and* $u_i\sqrt{u_0}$ *belonging to* $L^2_{loc}(\mathbb{R}_+; H^1(\Omega))$ *for* u_0 *defined as in* (6.3);
- $\phi \in L^\infty(\mathbb{R}_+ \times \Omega)$ *with* $\phi - \phi^D \in L^\infty(\mathbb{R}_+; V)$ *satisfies*

$$\int_\Omega \lambda^2 \nabla\phi(t,x)\cdot\nabla\psi(x)\mathrm{d}x = \int_\Omega \left(\sum_{i=1}^I z_i u_i(t,x) + f(x)\right)\psi(x)\mathrm{d}x \tag{6.16}$$

for all $\psi \in C^1_c(\Omega \cup \Gamma^{\mathrm{N}})$ *and a.e.* $t \geq 0$;

- *for all* $\varphi \in C^1_c(\mathbb{R}_+ \times \overline{\Omega})$ *and all* $i = 1, \ldots, I$, *there holds*

$$\iint_{\mathbb{R}_+\times\Omega} u_i\partial_t\varphi + \int_\Omega u_i^0\varphi(0,\cdot) - \iint_{\mathbb{R}_+\times\Omega} D_i(\nabla(u_0u_i) - 4u_i\sqrt{u_0}\nabla\sqrt{u_0} + u_iu_0z_i\nabla\phi)\cdot\nabla\varphi = 0. \tag{6.17}$$

6.1.4 Goal and positioning of the paper

Because of their applications in biology, chemistry and physics, and of their mathematical complexity, cross-diffusion systems for describing mixtures of ions in fluids have been a very active area of research in recent years. The first models to describe ion species in an electro-neutral solvent in the self-consistent field were proposed by Nernst [143, 144] and Planck [156, 157]. Their fluxes F_i obey the first Fick's law in the diffusive part and the Planck's law in the drift. The equations have been derived in [142] from a microscopic particle model via the mean-field limit approach. However, as pointed out in [131], Fick's law, which postulates a linear relationship between the flux of any species and its concentration gradient, is incorrect for describing diffusion in multi-component mixtures in a wide variety of situations. Often the diffusion flux of one species is strongly coupled to that of the partner species, giving rise to what is known as 'uphill diffusion'. This phenomenon occurs when, for example, considering mixtures of ions immersed in a solvent in a very narrow geometry such as that of biological and synthetic channels. In [38], the Poisson–Nernst–Planck model (6.1)-(6.4) has been formally derived from an on-lattice model, including size-exclusion effects. By doing so, it results that the flux of each ion component is induced by the gradient of another component, leading to parabolic cross-diffusion equations.

The mathematical analysis of cross-diffusion systems is very tricky. A standard tool like the maximum principle is in general not applicable to show bounds on the solutions. Moreover also the study of global-existence-in-time weak solutions has been a challenge for the mathematical community. Amann has shown in [6] the existence of a unique local-in-time classical solution to quasi-linear parabolic cross-diffusion systems under restriction on the regularity of the spatial domain Ω and on the spectrum of the diffusion matrix. To conclude global solvability, he has shown in [7] that additional regularity conditions on the solutions in $W^{1,p}$, with $p > d$, are required. However, such conditions are often not fulfilled, in particular when $d \geq 2$. And Starà and John in [163] and Pierre and Schmitt in [155] found some examples of parabolic systems with solutions that exhibit blow-up in finite time. Therefore, one expects that for a general cross-diffusion system it is not possible to show global solvability. Additional conditions are needed to prove that local-in-time weak solutions are bounded and can be continued globally in time. Le and Nguyen in [134] discovered that structural assumption on the diffusion matrix are required.

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It has been observed that many cross-diffusion systems possess an entropic structure. This means that it is possible to define an entropy functional $\mathcal{H}$ that decreases in time along the solutions of the system, i.e. it is a Lyapunov functional. The focus has therefore been on such cross-diffusion systems. In fact, it turned out that thanks to entropy, on one hand, it is possible to perform a change of variables that makes the system's diffusion matrix positive semi-definite. This allows to deduce global-in-time existence of weak solutions. On the other hand, the fact that $\mathcal{H}$ is a Lypaunov functional yields a priori estimates on the solutions. The idea of using the entropy to deduce bounds on the solutions go back to the work [37]. The first mathematical use of such a method can be found in [78], where they applied the method for a triangular reaction cross diffusion system. A general theory to show global existence of bounded weak solutions for a bigger class of cross-diffusion systems was proposed in [123].

In [102], the boundedness-by-entropy method is used to show the existence of a global-in-time bounded weak solution to the system (6.1)-(6.4), with mixed Dirichlet–Neumann boundary conditions (6.6)-(6.5), in the sense of Definition (6.1). They then proved the uniqueness of the weak solutions under moderate regularity assumptions thanks to the uniqueness technique of Gajewski [96, 98].

A different thermodynamical consistent model, hence with different F_i, of Poisson–Nernst–Planck type was proposed in [81]. In [124], the authors coupled such a system with a Poisson–Fermi equation for the electric potential, accounting for polarisation correlations among the polar solvent molecules (see also [139] for more details on the Poisson–Nernst–Planck–Fermi theory). The novelty of the paper is the proof of the weak–strong uniqueness property.

The numerical analysis of cross-diffusion systems is also complex, due to the non-linearity of the fluxes F_i. When dealing with conservation laws like (6.1), finite volume methods are suitable and attractive methods to use, as they guarantees the local conservativity of the fluxes. The application to cross-diffusion system is quite recent. A first work on it can be found in [9]. A discrete counterpart of the boundedness-by-entropy method for finite-volume approximations of cross-diffusion systems was recently developed in [128].

Regarding the discretisation of (6.1)-(6.5), a finite volume scheme has been studied in [40]. Even though the scheme mainly behaves well in practice, its mathematical study is very partial since requiring strong assumptions such as constant diffusion coefficients $D_i = D$ for all i, or no charge $z_i = 0$. Moreover, since the scheme proposed in [40] uses upwinding for the mobilities, numerical experiments exhibit a mere first order convergence in space. An alternative finite element method using the electrochemical potentials μ_i rather than the u_i as primary variables has been analyzed in [103]. This latter scheme is by construction free energy diminishing without further restriction on the physical parameters, and is shown to converge towards a weak solution as the mesh size and the time step tend to 0 (up to quadrature error terms). Second order convergence w.r.t. the mesh size is observed, but the nonlinear system to be solved at each time step is stiffer than for the finite volume scheme because of the use of the electrochemical potentials as variables, so that no clear gain was observed in comparison with the upstream mobility finite volumes. The finite volume scheme proposed in [14], in which the fluxes F_i are approximated thanks to the second expression of (6.2) also leads to singular numerical fluxes expressions.

The first aim of this work [42] is to propose and analyse two schemes for approximating the solutions of the problem. The schemes share the best with the aforementioned approaches present in the literature: decay of the free energy and unconditional convergence are established,

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second order accuracy in space and well-behaved nonlinear system for moderately small Debye length.

The first scheme extended to our setting is the so-called square-root approximation (SQRA) finite volume schemes initially proposed in [135] and further studied for steady Fokker-Planck equations in [113] before being extended to transient non-linear convection diffusion in [43]. The design of this scheme took direct inspiration in the hopping process described in [38] (see also [37]). An explanation of this link can be found in Appendix 6.5.2. Although this scheme behaves well in many situations, it suffers from robustness issues in the small Debye length regime (see Appendix 6.5.2). This drawback was overcome by mixing some ideas of our SQRA scheme with some features of the Scharfetter-Gummel (SG) scheme [159], with the introduction of the Bernoulli function.

After showing the existence of discrete solutions, our goal is to rigorously establish the convergence of the SG and SQRA schemes towards a weak solution. The proof relies on compactness arguments. The key estimate here is the free energy decay at the discrete level, and its consequences following the lines sketched in the continuous setting in Section 6.1.3.

In the following, the convergence proof is reported for the SG scheme only. The one for the SQRA scheme is very similar and can be fully adapted without additional difficulties.

6.2 The finite volume scheme and main results

First, we introduce the time discretization and the spatial mesh of the domain Ω.

6.2.1 Space and time discretizations

The mesh will be assumed to be admissible in the sense of [87], namely it fulfils the so-called *orthogonality condition*, which is usual for two-point flux approximation finite volumes.

Let $\mathcal{T}$ denote a family of non-empty, disjointed, convex, open and polygonal *control volumes* $K \in \mathcal{T}$, whose Lebesgue measure is denoted by m_K. We also assume that control volumes partition the domain in the sense that $\overline{\Omega} = \bigcup_{K\in\mathcal{T}} \overline{K}$. Further, we call $\mathcal{E}$ a *family of edges/faces*, where $\sigma \in \mathcal{E}$ is a closed subset of $\overline{\Omega}$ contained in a hyperplane of $\mathbb{R}^d$. Each σ has a strictly positive $(d-1)$-dimensional Hausdorff (or Lebesgue) measure, denoted by m_σ. We use the abbreviation $K|L = \partial K \cap \partial L$ for the intersection between two distinct control volumes which is either empty or reduces to a face contained in $\mathcal{E}$. The subset of all interior faces is denoted by

$$\mathcal{E}_{\text{int}} = \{\sigma \in \mathcal{E} \text{ s. t. } \sigma = K|L \text{ for some } K, L \in \mathcal{T}\}.$$

For any $K \in \mathcal{T}$, we assume that there exists a subset $\mathcal{E}_K$ of distinct elements of $\mathcal{E}$ such that the boundary of a control volume can be described by $\partial K = \bigcup_{\sigma\in\mathcal{E}_K} \sigma$ and, consequently, it follows that $\mathcal{E} = \bigcup_{K\in\mathcal{T}} \mathcal{E}_K$. Additionally, we assume that boundary edges $\mathcal{E}_{\text{ext}} = \mathcal{E} \setminus \mathcal{E}_{\text{int}}$ are either subsets of Γ^D or Γ^N. To each control volume $K \in \mathcal{T}$ we assign a *cell center* $x_K \in K$ which satisfies the *orthogonality condition*: If K, L share a face $\sigma = K|L$, then the vector $\overline{x_K x_L}$ is orthogonal to $\sigma = K|L$. The triplet $(\mathcal{T}, \mathcal{E}, \{x_K\}_{K\in\mathcal{T}})$ is called an *admissible mesh*.

We introduce the notation d_σ for the Euclidean distance between x_K and x_L if $\sigma = K|L$ or between x_K and the affine hyperplane spanned by σ if $\sigma \subset \partial\Omega$. We also denote by

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$d_{K\sigma} = \mathrm{dist}(x_K, \sigma)$, so that $d_\sigma = d_{K\sigma} + d_{L\sigma}$ if $\sigma = K|L \in \mathcal{E}_{\rm int}$ and $d_\sigma = d_{K\sigma}$ if $\sigma \in \mathcal{E}_K \cap \mathcal{E}_{\rm ext}$. The *transmittivity* of the edge $\sigma \in \mathcal{E}$ is defined by $a_\sigma = \frac{m_\sigma}{d_\sigma}$. The size of the mesh is

$$h_{\mathcal{T}} = \max_{K\in\mathcal{T}} \mathrm{diam}(K)$$

where $\mathrm{diam}(K)$ denotes the diameter of the cell K. The regularity of the mesh is defined by

$$\zeta_{\mathcal{T}} = \max_{K\in\mathcal{T}} \left(\mathrm{card}\ \mathcal{E}_K\ ;\ \max_{\sigma\in\mathcal{E}_K} \frac{\mathrm{diam}(K)}{d_{K\sigma}} \right).$$

For the time discretization we decompose the time interval $\mathbb{R}_+ := [0, +\infty)$ into an unbounded increasing sequence $(t^n)_{n\geq 0}$ with $t^0 = 0$ and possibly non-uniform time steps

$$\tau^n = t^n - t^{n-1} > 0, \qquad n > 0.$$

We finally introduce $\Delta t = \sup_{n\in\mathbb{N}\setminus\{0\}} \tau^n$, which we assume to be finite.

6.2.2 The finite volume schemes

We are now in position to define the finite volume scheme. Let us start with the discretization of the Poisson equation (6.4)–(6.5), which relies on a classical two-point flux approximation

$$\lambda^2 \sum_{\sigma\in\mathcal{E}_K} a_\sigma(\phi_K^n - \phi_{K\sigma}^n) = m_K \left(f_K + \sum_{i=1}^I z_i u_{i,K}^n \right), \qquad K \in \mathcal{T}, \tag{6.18}$$

where f_K is (possibly an approximation of) the mean value of f on the cell K, and where

$$\phi_{K\sigma}^n = \begin{cases} \phi_L^n & \text{if } \sigma = K|L \in \mathcal{E}_{\rm int}, \\ \phi_K^n & \text{if } \sigma \subset \Gamma^N, \\ \phi_\sigma^D = \frac{1}{m_\sigma} \int_\sigma \phi^D & \text{if } \sigma \subset \Gamma^D. \end{cases}$$

The equation (6.1) is discretized using a backward Euler method in time and finite volumes in space, leading to

$$\frac{u_{i,K}^n - u_{i,K}^{n-1}}{\tau^n} m_K + \sum_{\sigma\in\mathcal{E}_K} F_{i,K\sigma}^n = 0, \quad i = 1, \dots, I, \quad K \in \mathcal{T}. \tag{6.19}$$

In accordance with (6.6), we set $F_{i,K\sigma}^n = 0$ if $\sigma \subset \partial\Omega$. For $\sigma = K|L$ an internal edge, then we define

$$F_{i,K\sigma}^n = a_\sigma D_i \left(u_{i,K}^n u_{0,L}^n \mathfrak{B}\left(z_i(\phi_L^n - \phi_K^n)\right) - u_{i,L}^n u_{0,K}^n \mathfrak{B}\left(z_i(\phi_K^n - \phi_L^n)\right) \right), \tag{6.20}$$

with

$$u_{0,K}^n = 1 - \sum_{i=1}^I u_{i,K}^n, \qquad K \in \mathcal{T}. \tag{6.21}$$

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Formula (6.20) involves a function $\mathfrak{B} \in C^1(\mathbb{R};\mathbb{R})$ which is (strictly) positive and satisfies $\mathfrak{B}(0) = 1$ and $\mathfrak{B}'(0) = -1/2$. The continuous system (6.1)–(6.2) was originally derived in [38] thanks to a hopping process, suggesting the choice

$$\mathfrak{B}(y) = e^{-y/2}, \tag{SQRA}$$

leading to a scheme referred to as the square-root approximation (SQRA) scheme in what follows, in reference to [43, 113, 135]. An explanation of how to interpret the scheme in terms of the hopping process can be found in the Appendix 6.5.2. Another natural choice for the function $\mathfrak{B}$ is the Bernoulli function

$$\mathfrak{B}(y) = \frac{y}{e^y - 1}. \tag{SG}$$

The corresponding scheme will be referred to as the Scharfetter-Gummel (SG) scheme.

Remark 6.1. We would like to underline the fact that the construction of the SG scheme is not based on the original idea of [159]. We rather take advantage of the free-energy diminishing character of the SG scheme highlighted in [62] and exploited in [22, 160].

The introduction of the second method lies in its greater robustness for small values of the Debye length, as revealed by numerical simulations. A deeper understanding of the greater robustness of the SG scheme can be found in the Appendix 6.5.2.

In order to close the system, it remains to define the discrete counterpart to u^0 as follows:

$$u^0_{i,K} = \frac{1}{m_K}\int_K u^0_i, \qquad K \in \mathcal{T},\ i = 0,\dots,I. \tag{6.23}$$

Then we infer from (6.7) that

$$\sum_{i=0}^{I} u^0_{i,K} = 1 \text{ for all } K \in \mathcal{T}, \text{ and } \sum_{K\in\mathcal{T}} u^0_{i,K} m_K = \int_\Omega u^0_i > 0 \quad \text{for } i = 0,\dots,I. \tag{6.24}$$

In what follows, we denote by $U^n_K = \left(u^n_{i,K}\right)_{i=0,\dots,I}$ for $K \in \mathcal{T}$ and $n \geq 0$.

The consistency of the discrete fluxes (6.20) with the continuous ones (6.2) might not look completely obvious. It follows from the identity

$$F^n_{i,K\sigma} = a_\sigma\, D_i\, u^n_{0,K}\, u^n_{0,L} \mathfrak{M}(e^{-z_i\phi^n_K}, e^{-z_i\phi^n_L}) \left(w^n_{i,K} - w^n_{i,L}\right) \tag{6.25}$$

where $w^n_{i,K} = \frac{u^n_{i,K}}{u^n_{0,K}} e^{z_i\phi^n_K}$ are the discrete counterpart of the Slotboom variables and $U^n_K \in (0,1)^I$ for assumption (later on, in Proposition 6.1, it will be proven rigorously). The mean function $\mathfrak{M}$ appearing in (6.25) is defined by

$$\mathfrak{M}(a,b) = \sqrt{ab} \quad \text{for (SQRA)}, \quad \text{and} \quad \mathfrak{M}(a,b) = \frac{\log(1/a) - \log(1/b)}{1/a - 1/b} \quad \text{for (SG)},$$

for $a, b > 0$ with $a \neq b$, and $\mathfrak{M}(a,a) = a$.

We refer to [114] for an extensive discussion on the influence of the choice of the Stolarsky mean $\mathfrak{M}$ on the scheme behavior. The consistency of the formula (6.25) with the expression

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(6.8) of the continuous flux is now clear, and assuming the existence of a regular solution to the continuous problem, inserting it in the scheme and performing Taylor expansions as in [43] shows the second order accuracy in space of our scheme on uniform Cartesian grids.

6.2.3 Main results and organisation of the paper

We provide here a simple presentation of our main results, which will be detailed and proven in the following sections.

The first aim of this paper is to show that the nonlinear system corresponding to the scheme (6.18)–(6.21) admits at least one solution, and that beyond local conservativity, this solution preserves at the discrete level some key features of the model, namely the positivity of the volume fractions and the decay of the free energy.

Then, the convergence of the SG scheme is rigorously proven. Numerical results show the second order convergence in space of the two methods and the long-time behavior.

Theorem 6.1 states that, for fixed mesh and time steps, the numerical schemes admit a positive solution and preserves the L^∞ bounds. Furthermore, the discrete version $\mathcal{H}_\mathcal{T}^n$ of the free energy functional (6.11) - rigorously defined in the formula (6.34) - decays with time.

Theorem 6.1. *Given an admissible mesh $(\mathcal{T}, \mathcal{E}, (x_K)_{K\in\mathcal{T}})$ of Ω an a sequence of time steps $(\tau^n)_{n\geq 0}$ as in Section 6.2.1, then there exists (at least) one solution to the scheme* (6.18)–(6.23) *which satisfies*

$$u_{i,K}^n > 0 \qquad \forall i = 0, \dots, I,\ K \in \mathcal{T},\ n \geq 1.$$

Moreover, the discrete free energy $\mathcal{H}_\mathcal{T}^n$ defined later on in (6.34) *is decaying along the time iterations*

$$\mathcal{H}_\mathcal{T}^n + \tau^n \mathcal{D}_\mathcal{T}^n \leq \mathcal{H}_\mathcal{T}^{n-1}, \qquad n \geq 1, \tag{6.26}$$

for some dissipation rate $\mathcal{D}_\mathcal{T}^n \geq 0$ vanishing if and only if $\left((U_K^n)_{K\in\mathcal{T}}, (\phi_K^n)_{K\in\mathcal{T}}\right)$ is the stationary solution to the scheme.

The inequality (6.26) should be thought as a discrete counterpart to (6.9). Schemes verifying (6.26) in addition to more classical properties like mass conservation or positivity preservation are often referred to as thermodynamically consistent or structure preserving in the literature. Our schemes thus enter this class of schemes.

Theorem 6.1 allows to define the so-called approximate solution to the problem, which consists in piecewise constants functions $U_{\mathcal{T},\tau} = (u_{i,\mathcal{T},\tau})_{1\leq i\leq I}$ and $\phi_{\mathcal{T},\tau}$ defined by

$$u_{i,\mathcal{T},\tau}(t,x) = u_{i,K}^n \quad \text{and} \quad \phi_{\mathcal{T},\tau}(t,x) = \phi_K^n \quad \text{if } (t,x) \in K \times (t^{n-1}, t^n]. \tag{6.27}$$

Here again, we reconstruct $u_{0,\mathcal{T},\tau}$ from $U_{\mathcal{T},\tau}$ by setting

$$u_{0,\mathcal{T},\tau} = 1 - \sum_{i=1}^{I} u_{i,\mathcal{T},\tau}. \tag{6.28}$$

Now, let $(\mathcal{T}_\ell, \mathcal{E}_\ell, \{x_K\}_{K\in\mathcal{T}_\ell})_{\ell\geq 1}$ and $(\tau_\ell)_{\ell\geq 1} = \left((\tau_\ell^n)_{n\geq 1}\right)_{\ell\geq 1}$ be respectively a sequence of admissible meshes and a sequence of time steps, in the sense of Section 6.2.1, such that

$$\lim_{\ell\to\infty} h_{\mathcal{T}_\ell} = \lim_{\ell\to\infty} \Delta t_\ell = 0, \qquad \Delta t_\ell = \max_n \tau_\ell^n,$$

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while the mesh regularity factor $\zeta_{\mathcal{T}_\ell}$ remains uniformly bounded w.r.t. ℓ, i.e. $\zeta_{\mathcal{T}_\ell} \le \zeta_\star < +\infty$. The convergence of our schemes can be stated in a very simplified way as follows:

Theorem 6.2. *There exists a weak solution (U, ϕ) in the sense of Definition 6.1 such that, up to the extraction of a subsequence,*

$$\phi_{\mathcal{T}_\ell,\tau_\ell} \underset{\ell\to+\infty}{\longrightarrow} \phi \quad \text{and} \quad u_{0,\mathcal{T}_\ell,\tau_\ell} \underset{\ell\to+\infty}{\longrightarrow} u_0 \quad \text{in } L^p_{loc}(\mathbb{R}_+; L^p(\Omega)) \quad \forall p \in [1, +\infty),$$

and

$$U_{\mathcal{T}_\ell,\tau_\ell} \underset{\ell\to+\infty}{\longrightarrow} U \quad \text{in the } L^\infty(\mathbb{R}_+ \times \Omega)^I \text{ weak-}\star \text{ sense.}$$

More convergence properties have to be established to prove Theorem 6.2. They are detailed in Section 6.4, complementing the sketchy presentation of [42].

The rest of the paper is organized as follows. Section 6.3 is devoted to the proof of Theorem 6.1, as well as to some post-treatment of the energy / energy dissipation inequality (6.26) in order to derive some uniform bounds on quantities to be used in the convergence analysis carried out in Section 6.4, where the proof of Theorem 6.2 is detailed. The numerical results presented in Section 6.5 contain some numerical evidence of the convergence of the schemes. It also illustrates the long-time behavior of the schemes. This first result does not actually cover the behaviour for all Debye lengths and all initial values. The situation is more complex and is currently under investigation. Some comments are made at the end of Section 6.5.

6.3 Uniform a priori bounds and existence of a discrete solution

The goal of this section is to prove Theorem 6.1, i.e. to show that the nonlinear system corresponding to the scheme (6.18)–(6.21) admits at least one solution, and that beyond local conservativity, this solution preserves at the discrete level some key features of the model, namely the positivity of the volume fractions, as well as uniform L^∞ bounds for them, and the decay of the free energy. Furthermore, in this part, precise quantification of the dissipated total free energy supplies enough uniform estimates, in the mesh size $h_{\mathcal{T}}$ and time steps $(\tau_n)_{n\ge1}$, to perform the convergence analysis in Section 6.4. The grid $\mathcal{T}$ and the time steps $(\tau^n)_{n\ge1}$ remain fixed throughout this section.

6.3.1 Uniform a priori bounds and existence of a discrete solution

The first Lemma regards the discrete counterpart of the conservation of the total mass of the system.

Lemma 6.1. *It holds that*

$$\sum_{K\in\mathcal{T}} u^n_{i,K} m_K = \sum_{K\in\mathcal{T}} u^{n-1}_{i,K} m_K = \sum_{K\in\mathcal{T}} u^0_{i,K} m_K = \int_\Omega u^0_i > 0, \qquad 0 \le i \le I. \tag{6.29}$$

Proof. Since our schemes are locally conservative, i.e., $F^n_{K\sigma} + F^n_{L\sigma} = 0$ for all $\sigma = K|L \in \mathcal{E}_{\rm int}$, then summing (6.19) over K shows by induction and thanks to (6.23) the result. □

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Since we are interested in discrete solutions with positive volume fractions $u_{i,K}^n$, we perform an eventually harmless modification of the flux formula (6.20) into

$$F_{i,K\sigma}^n = a_\sigma D_i \left(\left(u_{i,K}^n\right)^+ \left(u_{0,L}^n\right)^+ \mathfrak{B}\left(z_i(\phi_L^n - \phi_K^n)\right) - \left(u_{i,L}^n\right)^+ \left(u_{0,K}^n\right)^+ \mathfrak{B}\left(z_i(\phi_K^n - \phi_L^n)\right) \right). \tag{6.30}$$

Proposition 6.1. *Let $n \geq 1$, and let $\left(U_K^{n-1}\right)_{K\in\mathcal{T}}$ be such that*

$$u_{i,K}^{n-1} \geq 0, \quad \sum_{i=0}^{I} u_{i,K}^{n-1} = 1 \quad \forall\, K \in \mathcal{T}, \quad \text{and} \quad \sum_{K\in\mathcal{T}} u_{i,K}^{n-1} m_K > 0. \tag{6.31}$$

Then any solution $(U_K^n, \phi_K^n)_{K\in\mathcal{T}, n\geq 1}$ to the modified scheme with (6.30) instead of (6.20) satisfies $u_{i,K}^n > 0$ for all $i = 0, \ldots, I$ and all $K \in \mathcal{T}$.

Proof. Let us start by establishing the positivity of $u_{0,K}^n$. Assume for contradiction that there exists a cell $K \in \mathcal{T}$ such that $u_{0,K}^n \leq 0$. Then we deduce from formula (6.30) that $F_{i,K\sigma}^n \geq 0$ for all $\sigma \in \mathcal{E}_K$ and all $i = 1, \ldots, I$. Because of (6.21) and (6.31), this implies that

$$0 \geq u_{0,K}^n = u_{0,K}^{n-1} + \frac{\tau^n}{m_K} \sum_{i=1}^{I} \sum_{\sigma\in\mathcal{E}_K} F_{i,K\sigma}^n \geq 0.$$

In particular, all the fluxes $F_{i,K\sigma}^n$, $i = 1, \ldots, I$ and $\sigma \in \mathcal{E}_K$ are equal to 0. In view of formula (6.30) and of the strict positivity of $\mathfrak{B}$, this implies either that $u_{i,K}^n \leq 0$ for all i, which yields a contradiction with (6.21), or that $u_{0,L}^n \leq 0$ for all the cells L sharing an edge $\sigma = K|L$ with K. Since Ω is connected, one would obtain that $u_{0,K}^n = 0$ for all $K \in \mathcal{T}$ and thus that $\sum_{K\in\mathcal{T}} u_{0,K}^n m_K = 0$. This contradicts (6.29), and thus we necessarily have that $u_{0,K}^n > 0$ for all $K \in \mathcal{T}$.

With the positivity of $u_{0,K}^n$, $K \in \mathcal{T}$, at hand, let us focus on the $u_{i,K}^n$ for an arbitrary $i = 1, \ldots, I$. Similarly, we assume that there exists some $K \in \mathcal{T}$ such that $u_{i,K}^n \leq 0$. Then owing to (6.30), we infer that $F_{i,K\sigma}^n \leq 0$ for all $\sigma \in \mathcal{E}_K$, and then that

$$0 \geq u_{i,K}^n = u_{i,K}^{n-1} - \frac{\tau^n}{m_K} \sum_{\sigma\in\mathcal{E}_K} F_{i,K\sigma}^n \geq 0.$$

This leads to $u_{i,K}^n = 0$ and to $F_{i,K\sigma}^n = 0$ for all $\sigma \in \mathcal{E}_K$. Since we already know that $u_{0,K}^n > 0$, we deduce from (6.30) that $u_{i,L}^n \leq 0$ for all cell L sharing a cell $\sigma = K|L$ with K. As above, this implies as $u_{0,K}^n = 0$ for all $K \in \mathcal{T}$, which contradicts (6.29). Then $u_{i,K}^n > 0$ for all $K \in \mathcal{T}$, concluding the proof of Proposition 6.1. □

A consequence of previous proposition is that a solution to the modified scheme with (6.30) instead of (6.20) is also a solution to the original scheme (6.18)–(6.21).

As we did assume that the background charge density f and thus its discrete counterpart $(f_K)_{K\in\mathcal{T}}$ are uniformly bounded, and that ϕ^D belongs to $L^\infty \cap H^{1/2}(\Gamma^D)$, we deduce a uniform bound for the electric potential.

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Proposition 6.2. *There exists* $C = C(\phi^D, \Omega, \lambda, f, (z_i)_i, \zeta_{\mathcal{T}})$ *such that*

$$\max_{K\in\mathcal{T}} |\phi_K^n| + \left(\sum_{\sigma\in\mathcal{E}} a_\sigma \left(\phi_K^n - \phi_{K\sigma}^n\right)^2 \right)^{1/2} \leq C, \qquad n \geq 1. \tag{6.32}$$

The proof of this result can be found in [39, Proposition A.1] and is a consequence of the uniform boundedness of the right-hand side of the discrete Poisson equation (6.18).

These a priori estimates are sufficient to prove the existence of a solution to the scheme. We end up with the following proposition.

Proposition 6.3. *There exists at least one solution to the numerical scheme* (6.18)–(6.21) *such that* $u_{i,K}^n > 0$ *for all* $i = 0, \dots, I$, *for all* $K \in \mathcal{T}$ *and all* $n \geq 1$.

Proof. The proof is based on an inductive procedure in time. At each time step $n \geq 1$, we use a topological degree argument to show the existence of a solution $(U_K^n, \phi_K^n)_{K\in\mathcal{T}} \in (0,1)^{I\times\mathcal{T}} \times [-C, C]^{\mathcal{T}}$ to (6.18)-(6.19), with the fluxes defined as in (6.30). In fact, the Proposition 6.1, ensures the existence for the scheme (6.18)-(6.20).

Let $n \geq 1$ be such that $(U_K^{n-1}, \phi_K^{n-1})_{K\in\mathcal{T}} \in [0,1]^{I\times\mathcal{T}} \times [-C, C]^{\mathcal{T}}$ is given (that is the case for $n = 1$, thanks to (6.23) and (6.7)). The idea is to deform our non-linear system continuously until it is transformed into a linear one with known solutions. Therefore, let introduce a parameter $s \in [0, \tau^n]$ and define, for every $K \in \mathcal{T}$,

$$\begin{cases} m_K \left(u_{i,K}^{(s)} - u_{i,K}^{n-1}\right) + s \sum_{\sigma\in\mathcal{E}_K} F_{i,K\sigma}^{(s)} = 0, \quad i = 1, \dots, I, \\ \lambda^2 \sum_{\sigma\in\mathcal{E}_K} a_\sigma \left(\phi_K^{(s)} - \phi_{K\sigma}^{(s)}\right) = m_K \left(f_K + \sum_{i=1}^I z_i u_{i,K}^{(s)}\right), \end{cases} \tag{6.33}$$

with $F_{i,K\sigma}^{(s)}$ defined by (6.30), which corresponds to the original schemes when $s = \tau^n$. For $s = 0$, the two equations can be decoupled and the first one can be rewritten in matrix form

$$\mathbb{M}(U^{(0)} - U^{n-1}) = 0,$$

where $U^{(s)} = \left(U_K^{(s)}\right)_{K\in\mathcal{T}}$, for $s \in [0, \tau^n]$, $U^{n-1} = \left(U_K^{n-1}\right)_{K\in\mathcal{T}}$ and $\mathbb{M} = \operatorname{diag}\left((m_K)_{K\in\mathcal{T}}\right)$ is a positive definite matrix. Therefore, there exists a unique solution $U^{(0)} = U^{n-1} \in [0,1]^{I\times\mathcal{T}}$. Via the Proposition 6.2, there also exists a unique $\phi^{(s)} = \left(\phi_K^{(s)}\right)_{K\in\mathcal{T}} \in [-C, C]^{\mathcal{T}}$. Moreover, thanks to the continuity of the discrete fluxes, the functional

$$\mathcal{H} \; : \; \begin{cases} [0, \tau^n] \times [-2, 2]^{I\times\mathcal{T}} \times [-C-1, C+1]^{\mathcal{T}} \to \mathbb{R}^{\mathcal{T}} \times \mathbb{R}^{\mathcal{T}} \\ (s, U, \phi) \mapsto \mathcal{H}(s, U, \phi) \end{cases}$$

whose zeros $(s, U^{(s)}, \phi^{(s)})$ are the solutions of (6.33), is hence an homotopy. Furthermore, all along it, its zeros $(U^{(s)}, \phi^{(s)})$ remain inside the compact subset $[0,1]^{I\times\mathcal{T}} \times [-C, C]^{\mathcal{T}}$.

Thus, the topological degree corresponding to $\mathcal{H}(s, U, \phi) = 0$ is equal to one, all along the homotopy, and hence in particular for $s = \tau^n$. That implies the existence of a solution to the scheme, for both the $\mathfrak{B}$ function (SQRA) and (SG) (but it does not guarantee uniqueness). □

We note that the proof proposed here is simpler than that found in, for example, [39, Proposition 3.2]. The reason lies in the fact that we did not use entropic inequality to derive

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the uniform estimates on volume fractions and, therefore, we do not have to guarantee the validity of it during the homotopy.

6.3.2 Energy dissipation at the discrete level

Next proposition is about the thermodynamical consistency of our schemes and the decay of a discrete counterpart of the free energy.

Proposition 6.4. *Let $(U_K^n, \phi_K^n)_{K\in\mathcal{T}, n\geq 1}$ be a solution to the scheme (6.18)–(6.21) as in Proposition 6.3, then define for $n \geq 0$ the discrete free energy at the n^{th} time step*

$$\mathcal{H}_{\mathcal{T}}^n = \sum_{K\in\mathcal{T}} m_K H(U_K^n) + \frac{\lambda^2}{2} \sum_{\sigma\in\mathcal{E}} a_\sigma (\phi_K^n - \phi_{K\sigma}^n)^2 + \lambda^2 \sum_{\sigma\in\mathcal{E}^D} a_\sigma \phi_\sigma^D (\phi_K^n - \phi_\sigma^D), \tag{6.34}$$

the discrete electrochemical potentials $\mu_{i,K}^n = \log\left(\frac{u_{i,K}^n}{u_{0,K}^n}\right) + z_i \phi_K^n$ of species i, and

$$\mathcal{D}_{\mathcal{T}}^n = \sum_{i=1}^{I} \sum_{\sigma\in\mathcal{E}_{int}} F_{i,K\sigma}^n (\mu_{i,K}^n - \mu_{i,L}^n)$$

the discrete dissipation, which vanishes if and only if $(\mu_{i,K}^n)_{K\in\mathcal{T}}$ is constant for all $i = 1, \dots, I$. Then there holds

$$\mathcal{H}_{\mathcal{T}}^n + \tau^n \mathcal{D}_{\mathcal{T}}^n \leq \mathcal{H}_{\mathcal{T}}^{n-1}, \qquad n \geq 1. \tag{6.35}$$

Proof. As a consequence of the positivity of $u_{0,K}^n$ and of the monotonicity of the exponential function, one then easily infers from reformulation (6.25) of the discrete fluxes that

$$\mathcal{D}_{i,\sigma}^n := F_{i,K\sigma}^n (\mu_{i,K}^n - \mu_{i,L}^n) \geq 0, \qquad \forall i = 1, \dots, I,\ \sigma = K|L \in \mathcal{E}_{\text{int}}, \tag{6.36}$$

whence the nonnegativity of $\mathcal{D}^n$. As $u_{0,K}^n > 0$ for all $K \in \mathcal{T}$ and $n \geq 1$, and as $y \mapsto e^y$ is strictly increasing, one gets that $\mathcal{D}_{i,\sigma}^n = 0$ iff $\mu_{i,K}^n = \mu_{i,L}^n$.

Define by $\mu_{i,K}^n = \log\left(\frac{u_{i,K}^n}{u_{0,K}^n}\right) + z_i\phi_K^n = \log(w_{i,K}^n)$ the electrochemical potential of species i, then multiplying the discrete conservation law (6.19) by $\tau^n \mu_{i,K}^n$, and summing over $i = 1, \dots, I$ and $K \in \mathcal{T}$ provides thanks to discrete integration by parts

$$\mathcal{A}_{\mathcal{T}}^n + \mathcal{B}_{\mathcal{T}}^n + \tau^n \mathcal{D}_{\mathcal{T}}^n = 0, \tag{6.37}$$

where we have set

$$\begin{aligned}\mathcal{A}_{\mathcal{T}}^n &= \sum_{i=1}^{I} \sum_{K\in\mathcal{T}} \left(u_{i,K}^n - u_{i,K}^{n-1}\right) \log\left(\frac{u_{i,K}^n}{u_{0,K}^n}\right) m_K \\ &\overset{(6.21)}{=} \sum_{i=0}^{I} \sum_{K\in\mathcal{T}} \left(u_{i,K}^n - u_{i,K}^{n-1}\right) \log\left(u_{i,K}^n\right) m_K,\end{aligned}$$

and

$$\mathcal{B}_{\mathcal{T}}^n = \sum_{i=1}^{I} \sum_{K\in\mathcal{T}} \left(u_{i,K}^n - u_{i,K}^{n-1}\right) z_i \phi_K^n m_K$$

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$$\overset{(6.18)}{=}\lambda^2\sum_{K\in\mathcal{T}}\phi_K^n\sum_{\sigma\in\mathcal{E}_K}a_\sigma\left(\phi_K^n-\phi_K^{n-1}-(\phi_{K\sigma}^n-\phi_{K\sigma}^{n-1})\right).$$

Then we deduce from the convexity of H that

$$\mathcal{A}_\mathcal{T}^n\geq\sum_{K\in\mathcal{T}}\left(H(U_K^n)-H(U_K^{n-1})\right)m_K, \tag{6.38}$$

while reorganizing the term $\mathcal{B}^n$ gives

$$\begin{aligned}\mathcal{B}_\mathcal{T}^n=\lambda^2\sum_{\sigma\in\mathcal{E}}a_\sigma\left(\phi_K^n-\phi_K^{n-1}-(\phi_{K\sigma}^n-\phi_{K\sigma}^{n-1})\right)(\phi_K^n-\phi_{K\sigma}^n)\\+\lambda^2\sum_{\sigma\in\mathcal{E}^D}a_\sigma\phi_\sigma^D(\phi_K^n-\phi_K^{n-1}).\end{aligned}$$

Then using the elementary convexity inequality $a(a-b)\geq(a^2-b^2)/2$ in the above term and combining the result with (6.38) in (6.37) provides the desired result (6.35). □

Proposition 6.4 allows us to completes the proof of Theorem 6.1, but it also contains important information for proving the convergence of the schemes. Their extraction is the purpose of next section.

6.3.3 Further uniform estimates on the discrete solution

To pass to the limit in the schemes and to identify the limit as a weak solution, we need to extract some further uniform estimates, as in particular the discrete $L^2_{\mathrm{loc}}(H^1)$ estimates on the discrete counterparts of u_0 and $\sqrt{u_iu_0}$. We prove these estimates in Lemma 6.3. As an intermediate result we need a uniform bound on the discrete free energy.

Lemma 6.2. *There exists $C>0$ depending only on Ω, ϕ^D, λ, f, $(z_i)_i$, and $\zeta_\mathcal{T}$ such that, for all $N\geq1$, there holds $|\mathcal{H}_\mathcal{T}^N|\leq C$.*

Proof. Because of the bound $0\leq u_{i,K}^n\leq1$ for all i and K, it is clear that the first two contributions of (6.34) remain uniformly bounded by a constant depending only on Ω. Concerning the last contribution observe that if one defines ϕ_K^D and ϕ_σ^D as the averages of ϕ^D on $K\in\mathcal{T}$ and $\sigma\in\mathcal{E}$ respectively, then a suitable reorganization of the sum shows that

$$\begin{aligned}\sum_{\sigma\in\mathcal{E}^D}a_\sigma\phi_\sigma^D(\phi_K^n-\phi_\sigma^D)&=\sum_{\sigma\in\mathcal{E}}a_\sigma(\phi_\sigma^D-\phi_K^D)(\phi_K^n-\phi_{K\sigma}^n)+\sum_{K\in\mathcal{T}}\phi_K^D\sum_{\sigma\in\mathcal{E}_K}a_\sigma(\phi_K^n-\phi_{K\sigma}^n)\\&\overset{(6.18)}{=}\sum_{\sigma\in\mathcal{E}}a_\sigma(\phi_\sigma^D-\phi_K^D)(\phi_K^n-\phi_{K\sigma}^n)+\frac{1}{\lambda^2}\sum_{K\in\mathcal{T}}m_K\phi_K^D\left(f_K+\sum_{i=1}^I z_iu_{i,K}^n\right).\end{aligned} \tag{6.39}$$

Using Young's inequality and $\mathcal{E}^D\subset\mathcal{E}$ for the first term in the above right-hand side gives

$$\sum_{K\in\mathcal{T}}\sum_{\sigma\in\mathcal{E}^D}a_\sigma(\phi_\sigma^D-\phi_K^D)(\phi_K^n-\phi_{K\sigma}^n)\leq\sum_{\sigma\in\mathcal{E}}a_\sigma(\phi_\sigma^D-\phi_K^D)^2+\frac{1}{4}\sum_{\sigma\in\mathcal{E}}a_\sigma(\phi_K^n-\phi_{K\sigma}^n)^2.$$

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Then Lemma 9.4 of [87] shows that

$$\sum_{K\in\mathcal{T}}\sum_{\sigma\in\mathcal{E}^D} a_\sigma(\phi^D_\sigma-\phi^D_K)^2 \le C(\zeta_\mathcal{T})\|\nabla\phi^D\|^2_{L^2(\Omega)}.$$

Then since f and U are bounded, we deduce from (6.39) that there exists C depending only on $\|f\|_\infty$, $\max_i|z_i|$, Ω, $\|\phi^D\|_{H^1}$, λ and $\zeta_\mathcal{T}$ such that

$$\sum_{\sigma\in\mathcal{E}^D} a_\sigma\phi^D_\sigma(\phi^n_K-\phi^D_\sigma)\le C.$$

The result of the lemma follows. □

Next lemma shows that the control of the energy dissipation $\sum_{n\ge1}\tau^n\mathcal{D}^n_\mathcal{T}$ inferred from Proposition 6.4 gives some $L^2_{\rm loc}(H^1)$ type control on the discrete counterparts of u_0, $\sqrt{u_0}$ and $\sqrt{u_iu_0}$.

Lemma 6.3. *There exists $C>0$ depending only on Ω, ϕ^D, λ, f, $(z_i)_i$, $(D_i)_i$ and $\zeta_\mathcal{T}$ such that, for all $N\ge1$, there holds*

$$\sum_{n=1}^N\tau^n\sum_{i=1}^I\sum_{\sigma\in\mathcal{E}_{int}} a_\sigma\left(\sqrt{u^n_{i,K}u^n_{0,K}}-\sqrt{u^n_{i,L}u^n_{0,L}}\right)^2 + \sum_{n=1}^N\tau^n\sum_{\sigma\in\mathcal{E}_{int}} a_\sigma\left(\sqrt{u^n_{0,K}}-\sqrt{u^n_{0,L}}\right)^2 + \sum_{n=1}^N\tau^n\sum_{\sigma\in\mathcal{E}_{int}} a_\sigma\left(u^n_{0,K}-u^n_{0,L}\right)^2 \le C(1+t^N). \quad (6.40)$$

As a consequence, one also has

$$\sum_{n=1}^N\tau^n\sum_{i=1}^I\sum_{\sigma\in\mathcal{E}_{int}} a_\sigma\left(u^n_{i,K}\sqrt{u^n_{0,K}}-u^n_{i,L}\sqrt{u^n_{0,L}}\right)^2 \le C(1+t^N) \quad (6.41)$$

and

$$\sum_{n=1}^N\tau^n\sum_{i=1}^I\sum_{\sigma\in\mathcal{E}_{int}} a_\sigma\left(u^n_{i,K}u^n_{0,K}-u^n_{i,L}u^n_{0,L}\right)^2 \le C(1+t^N). \quad (6.42)$$

Proof. One gets from the elementary inequality $(a-b)(\log(a)-\log(b))\ge4(\sqrt{a}-\sqrt{b})^2$ applied to (6.36) that

$$\mathcal{D}^n_{i,\sigma}\ge4a_\sigma D_i\mathfrak{R}(e^{-z_i\phi^n_K},e^{-z_i\phi^n_L})\left(\sqrt{u^n_{i,K}u^n_{0,L}}e^{\frac{z_i}{4}(\phi^n_K-\phi^n_L)}-\sqrt{u^n_{i,L}u^n_{0,K}}e^{\frac{z_i}{4}(\phi^n_L-\phi^n_K)}\right)^2$$

with $\mathfrak{R}(e^{-z_i\phi^n_K},e^{-z_i\phi^n_L})=\mathfrak{M}(e^{-z_i\phi^n_K},e^{-z_i\phi^n_L})e^{\frac{z_i}{2}(\phi^n_K+\phi^n_L)}$ being equal to 1 for the choice (SQRA) of $\mathfrak{B}$ but not for (SG). However, thanks to (6.32) and since $D_i>0$ for all i, there holds

$$2D_i\mathfrak{R}(e^{-z_i\phi^n_K},e^{-z_i\phi^n_L})\ge\kappa$$

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for some $\kappa > 0$ uniform w.r.t. K, i and n. As a consequence, using furthermore that $(a+b)^2 \geq \frac{1}{2}a^2 - b^2$,

$$\mathcal{D}_{i,\sigma}^n \geq \kappa a_\sigma \cosh^2\left(\frac{z_i}{4}(\phi_K^n - \phi_L^n)\right)\left(\sqrt{u_{i,K}^n u_{0,L}^n} - \sqrt{u_{i,L}^n u_{0,K}^n}\right)^2 - \kappa a_\sigma \left(\sqrt{u_{i,K}^n u_{0,L}^n} + \sqrt{u_{i,L}^n u_{0,K}^n}\right)^2 \sinh^2\left(\frac{z_i}{4}(\phi_K^n - \phi_L^n)\right).$$

Since $|\phi_K^n| \leq C$ owing to (6.32), one has $\sinh^2\left(\frac{z_i}{4}(\phi_K^n - \phi_L^n)\right) \leq C(\phi_K^n - \phi_L^n)^2$. Using moreover that $0 < u_{i,K}^n, u_{0,K}^n < 1$ and that $\cosh(a) \geq 1$, one gets that

$$\mathcal{D}_{i,\sigma}^n \geq a_\sigma \kappa \left(\sqrt{u_{i,K}^n u_{0,L}^n} - \sqrt{u_{i,L}^n u_{0,K}^n}\right)^2 - C a_\sigma (\phi_K^n - \phi_L^n)^2.$$

Since

$$\left(\sqrt{u_{i,K}^n u_{0,L}^n} - \sqrt{u_{i,L}^n u_{0,K}^n}\right)^2 = \left(\sqrt{u_{i,K}^n u_{0,K}^n} - \sqrt{u_{i,L}^n u_{0,L}^n}\right)^2 - (u_{i,K}^n - u_{i,L}^n)(u_{0,K}^n - u_{0,L}^n), \quad (6.43)$$

then summing over $i = 1, \ldots, I$ and $\sigma = K|L$ and using (6.21) leads to

$$\mathcal{D}_\mathcal{T}^n \geq \kappa \sum_{i=1}^I \sum_{\sigma \in \mathcal{E}_{\rm int}} a_\sigma \left(\sqrt{u_{i,K}^n u_{0,K}^n} - \sqrt{u_{i,L}^n u_{0,L}^n}\right)^2 + \kappa \sum_{\sigma \in \mathcal{E}_{\rm int}} a_\sigma \left(u_{0,K}^n - u_{0,L}^n\right)^2 - C \sum_{\sigma \in \mathcal{E}_{\rm int}} a_\sigma (\phi_K^n - \phi_{K\sigma}^n)^2.$$

Bearing in mind Proposition 6.2, we obtain that

$$\mathcal{D}_\mathcal{T}^n \geq \kappa \sum_{i=1}^I \sum_{\sigma \in \mathcal{E}_{\rm int}} a_\sigma \left(\sqrt{u_{i,K}^n u_{0,K}^n} - \sqrt{u_{i,L}^n u_{0,L}^n}\right)^2 + \kappa \sum_{\sigma \in \mathcal{E}_{\rm int}} a_\sigma \left(u_{0,K}^n - u_{0,L}^n\right)^2 - C. \quad (6.44)$$

Moreover, the inequality $\sum_{i=0}^I \sqrt{u_{i,K}^n u_{i,L}^n} \leq 1$ gives that

$$\begin{aligned}\sum_{i=1}^I \sum_{\sigma \in \mathcal{E}_{\rm int}} a_\sigma \left(\sqrt{u_{i,K}^n u_{0,K}^n} - \sqrt{u_{i,L}^n u_{0,L}^n}\right)^2 &\geq \sum_{\sigma \in \mathcal{E}_{\rm int}} a_\sigma \left((1 - u_{0,K}^n)u_{0,K}^n + (1 - u_{0,L}^n)u_{0,L}^n - 2(1 - \sqrt{u_{0,K}^n u_{0,L}^n})\sqrt{u_{0,K}^n u_{0,L}^n}\right) \\ &= \sum_{\sigma \in \mathcal{E}_{\rm int}} a_\sigma \left(\sqrt{u_{0,K}^n} - \sqrt{u_{0,L}^n}\right)^2 - \sum_{\sigma \in \mathcal{E}_{\rm int}} a_\sigma \left(u_{0,K}^n - u_{0,L}^n\right)^2,\end{aligned}$$

whence we also deduce that

$$\mathcal{D}_\mathcal{T}^n \geq \kappa \sum_{\sigma \in \mathcal{E}_{\rm int}} a_\sigma \left(\sqrt{u_{0,K}^n} - \sqrt{u_{0,L}^n}\right)^2 - C.$$

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To conclude the proof, it eventually remains to remark from (6.35) and Lemma 6.2 that there exists C depending neither on h, Δt, N nor on the initial data $U^0 = (u_i^0)_{0\le i\le I}$ (provided it fulfills (6.7)) such that $\sum_{n=1}^N \tau^n \mathcal{D}_{\mathcal{T}}^n \le C$. Combining this with (6.44) yields (6.40).

To recover estimate (6.41), remark that

$$\begin{aligned}\left(\sqrt{u_{0,K}^n}u_{i,K}^n - \sqrt{u_{0,L}^n}u_{i,L}^n\right) = \Bigg[&\sqrt{u_{i,K}^n}\left(\sqrt{u_{0,K}^n u_{i,K}^n} - \sqrt{u_{0,L}^n u_{i,L}^n}\right)\\ &+ u_{i,L}^n\left(\sqrt{u_{0,K}^n} - \sqrt{u_{0,L}^n}\right)\\ &+ \sqrt{u_{i,L}^n}\left(\sqrt{u_{0,L}^n u_{i,K}^n} - \sqrt{u_{0,K}^n u_{i,L}^n}\right)\Bigg].\end{aligned}$$

As $(a+b+c)^2 \le 3(a^2+b^2+c^2)$, and since $0 \le u_{i,K}^n \le 1$, one gets that

$$\begin{aligned}\frac{1}{3}\left(\sqrt{u_{0,K}^n}u_{i,K}^n - \sqrt{u_{0,L}^n}u_{i,L}^n\right)^2 \le &\left(\sqrt{u_{0,K}^n u_{i,K}^n} - \sqrt{u_{0,L}^n u_{i,L}^n}\right)^2\\ &+ \left(\sqrt{u_{0,K}^n} - \sqrt{u_{0,L}^n}\right)^2\\ &+ \left(\sqrt{u_{0,L}^n u_{i,K}^n} - \sqrt{u_{0,K}^n u_{i,L}^n}\right)^2.\end{aligned}$$

The two first terms in the right-hand side are controlled thanks to (6.40), while, bearing in mind (6.43), the third term can be overestimated as follows:

$$\begin{aligned}\left(\sqrt{u_{0,L}^n u_{i,K}^n} - \sqrt{u_{0,K}^n u_{i,L}^n}\right)^2 &\le \sum_{i=1}^I \left(\sqrt{u_{0,L}^n u_{i,K}^n} - \sqrt{u_{0,K}^n u_{i,L}^n}\right)^2\\ &\le \sum_{i=1}^I \left(\sqrt{u_{0,K}^n u_{i,K}^n} - \sqrt{u_{0,L}^n u_{i,L}^n}\right)^2 + (u_{0,K}^n - u_{0,L}^n)^2,\end{aligned}$$

which again, after summation on $n = 1,\dots,N$ and $\sigma \in \mathcal{E}_{\rm int}$, can be controlled thanks to (6.40).

Finally, to establish (6.42), remark that

$$u_{i,K}^n u_{0,K}^n - u_{i,L}^n u_{0,L}^n = \left(\sqrt{u_{i,K}^n u_{0,K}^n} - \sqrt{u_{i,L}^n u_{0,L}^n}\right)\left(\sqrt{u_{i,K}^n u_{0,K}^n} + \sqrt{u_{i,L}^n u_{0,L}^n}\right).$$

Since $0 \le u_{0,K}^n, u_{i,K}^n \le 1$, one gets that

$$\left(u_{i,K}^n u_{0,K}^n - u_{i,L}^n u_{0,L}^n\right)^2 \le 4\left(\sqrt{u_{i,K}^n u_{0,K}^n} - \sqrt{u_{i,L}^n u_{0,L}^n}\right)^2.$$

Summing over $n = 1,\dots,N$ and $\sigma \in \mathcal{E}_{\rm int}$ and using (6.40) gives the desired result. □

One also deduces the following discrete $L^2_{\rm loc}(L^2)^d$ estimates on the fluxes, which amount to some discrete $L^2_{\rm loc}(H^1)'$ estimate on time increments of the discrete counterpart to $\partial_t u_i$.

Lemma 6.4. *There exists C depending only on Ω, ϕ^D, λ, f, $(z_i)_i$, $(D_i)_i$ and $\zeta_{\mathcal{T}}$ such that*

$$\sum_{i=1}^I \sum_{n=1}^N \tau^n \sum_{\sigma\in\mathcal{E}_{int}} \frac{d_\sigma}{m_\sigma}\left|F_{i,K\sigma}^n\right|^2 \le C(1+t^N). \tag{6.45}$$

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Proof. To obtain discrete $L^2_{\rm loc}(L^2)^d$ estimates on the fluxes, we need to exploit the discrete uniform estimates we have for $(U^n_K, \phi^n_K)_{K\in\mathcal{T},n\geq 1}$. In this regard, we rewrite the fluxes in a different way, so that we can employ what we know on the function $\mathfrak{B}$, both for (SG) and for (SQRA). One splits the flux (6.2) into two parts corresponding to convection and diffusion respectively:

$$F^n_{i,K\sigma} = F^{{\rm conv},n}_{i,K\sigma} + F^{{\rm diff},n}_{i,K\sigma},$$

with

$$\begin{aligned} F^{{\rm conv},n}_{i,K\sigma} &= a_\sigma D_i \frac{u^n_{i,K}u^n_{0,L} + u^n_{i,L}u^n_{0,K}}{2}\left[\mathfrak{B}(z_i(\phi^n_L - \phi^n_K)) - \mathfrak{B}(z_i(\phi^n_K - \phi^n_L))\right], \\ F^{{\rm diff},n}_{i,K\sigma} &= a_\sigma D_i \frac{u^n_{i,K}u^n_{0,L} - u^n_{i,L}u^n_{0,K}}{2}\left[\mathfrak{B}(z_i(\phi^n_L - \phi^n_K)) + \mathfrak{B}(z_i(\phi^n_K - \phi^n_L))\right]. \end{aligned}$$

The flux $(F^n_{i,K\sigma})_{\sigma,n}$ is bounded in $L^2_{\rm loc}(L^2)^d$ in the sense of (6.45) if both $(F^{{\rm conv},n}_{i,K\sigma})_{\sigma,n}$ and $(F^{{\rm diff},n}_{i,K\sigma})_{\sigma,n}$ are.

For the choice (SG) of the function $\mathfrak{B}$, then $\mathfrak{B}(-y) - \mathfrak{B}(y) = y$, while $\mathfrak{B}(-y) - \mathfrak{B}(y) = y + \mathcal{O}(y^2)$ for (SQRA), so that

$$F^{{\rm conv},n}_{i,K\sigma} = a_\sigma D_i \frac{u^n_{i,K}u^n_{0,L} + u^n_{i,L}u^n_{0,K}}{2} z_i(\phi^n_K - \phi^n_L), \tag{6.46}$$

the remainder term being null for (SG). The $L^2_{\rm loc}(L^2)^d$ character of the above expression directly follows from the uniform bound on $u^n_{i,K}$, $0 \leq i \leq I$ and from the discrete $L^\infty(H^1)$ bound on $(\phi^n_K)_{K,n}$ stated in Proposition 6.2. Therefore,

$$\sum_{i=1}^{I}\sum_{n=1}^{N}\tau^n \sum_{\sigma\in\mathcal{E}_{\rm int}} \frac{d_\sigma}{m_\sigma}\left|F^{{\rm conv},n}_{i,K\sigma}\right|^2 \leq Ct^N.$$

Concerning the diffusive term, one has for both choices (SQRA) and (SG) of the function $\mathfrak{B}$ that

$$1 \leq \frac{1}{2}\left[\mathfrak{B}(z_i(\phi^n_L - \phi^n_K)) + \mathfrak{B}(z_i(\phi^n_K - \phi^n_L))\right] \leq 1 + \frac{z_i^2}{12}(\phi^n_K - \phi^n_L)^2.$$

Therefore, one gets that

$$F^{{\rm diff},n}_{i,K\sigma} = a_\sigma D_i\left(u^n_{i,K}u^n_{0,L} - u^n_{i,L}u^n_{0,K}\right)\left(1 + \mathcal{O}\left((\phi^n_K - \phi^n_L)^2\right)\right). \tag{6.47}$$

From the discrete $L^\infty(H^1)$ bound on $(\phi^n_K)_{K,n}$, one can uniformly estimate the reminder. For the other term, since $u^n_{i,K}u^n_{0,L} - u^n_{i,L}u^n_{0,K} = u^n_{i,K}u^n_{0,K} - u^n_{i,L}u^n_{0,L} + (u^n_{i,K} + u^n_{i,L})(u^n_{0,L} - u^n_{0,K})$, then

$$\begin{aligned} |u^n_{i,K}u^n_{0,L} - u^n_{i,L}u^n_{0,K}|^2 &\leq C\left(|u^n_{i,K}u^n_{0,K} - u^n_{i,L}u^n_{0,L}|^2 + |(u^n_{i,K} + u^n_{i,L})(u^n_{0,L} - u^n_{0,K})|^2\right) \\ &\leq C\left(\left|\sqrt{u^n_{i,K}u^n_{0,K}} - \sqrt{u^n_{i,L}u^n_{0,L}}\right|^2 + |u^n_{0,L} - u^n_{0,K}|^2\right), \end{aligned}$$

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so that we obtain

$$\sum_{i=1}^{I}\sum_{n=1}^{N}\tau^n\sum_{\sigma\in\mathcal{E}_{\rm int}}\frac{d_\sigma}{m_\sigma}\left|F_{i,K\sigma}^{{\rm diff},n}\right|^2 \le C\sum_{i=1}^{I}\sum_{n=1}^{N}\tau^n\sum_{\sigma\in\mathcal{E}_{\rm int}}a_\sigma\left|\sqrt{u_{i,K}^n u_{0,K}^n}-\sqrt{u_{i,L}^n u_{0,L}^n}\right|^2 + C\sum_{i=1}^{I}\sum_{n=1}^{N}\tau^n\sum_{\sigma\in\mathcal{E}_{\rm int}}a_\sigma|u_{0,L}^n-u_{0,K}^n|^2,$$

thanks to the uniform bounds on $(U_K^n)_{K\in\mathcal{T},n\le 1}$. Lemma 6.3 provides the desired $L^2_{\rm loc}(L^2)$ bound on $F_{i,K\sigma}^{{\rm diff},n}$, concluding the proof of Lemma 6.4. □

From Lemma 6.4, we deduce the following discrete $L^2_{\rm loc}((H^1)')$ estimate:

Corollary 6.1. *There exists C depending only on Ω, ϕ^D, λ, f, $(z_i)_i$, $(D_i)_i$ and $\zeta_{\mathcal{T}}$ such that, for all $i=0,\dots,I$ and all $\varphi_{\mathcal{T},\tau}=\sum_{K\in\mathcal{T}}\sum_{n=1}^N\varphi_K^n\mathbb{1}_{(t^{n-1},t^n]\times K}$, one has*

$$\sum_{n=1}^{N}\sum_{K\in\mathcal{T}}(u_{i,K}^n-u_{i,K}^{n-1})\varphi_K^n \le C\left(1+t^N\right)^{1/2}\left(\sum_{n=1}^{N}\tau^n\sum_{\sigma\in\mathcal{E}_{int}}a_\sigma\left(\varphi_K^n-\varphi_{K\sigma}^n\right)^2\right)^{1/2}. \tag{6.48}$$

Proof. Let us first establish (6.48) for $i\ge 1$. Multiplying (6.19) by $\tau^n\varphi_K^n$, summing over $K\in\mathcal{T}$ and $n\in\{1,\dots,N\}$, and performing a discrete integration by parts on the contribution of the fluxes provides

$$\sum_{n=1}^{N}\sum_{K\in\mathcal{T}}m_K(u_{i,K}^n-u_{i,K}^{n-1})\varphi_K^n=\sum_{n=1}^{N}\tau^n\sum_{\sigma\in\mathcal{E}_{\rm int}}F_{i,K\sigma}^n(\varphi_{K\sigma}^n-\varphi_K^n). \tag{6.49}$$

Applying Cauchy-Schwarz inequality to the right-hand side then using Lemma 6.4 provides the desired result. The recovery of the estimate for $i=0$ then directly follows from the definition (6.21) of $u_{0,K}^n$ and from (6.48) for $i\ge 1$. □

6.4 Convergence of the schemes

This section is devoted to the proof of Theorem 6.2, which relies on compactness arguments. Given sequences $(\mathcal{T}_\ell,\mathcal{E}_\ell,\{x_K\}_{K\in\mathcal{T}_\ell})_{\ell\ge1}$ and $(\tau_\ell)_{\ell\ge1}=\left((\tau_\ell^n)_{n\ge1}\right)_{\ell\ge1}$ of admissible meshes and a sequence of time steps in the sense of Section 6.2.1, with

$$\lim_{\ell\to\infty}h_{\mathcal{T}_\ell}=\lim_{\ell\to\infty}\Delta t_\ell=0\quad\text{and}\quad\zeta_{\mathcal{T}_\ell}\le\zeta_\star<+\infty, \tag{6.50}$$

we define the sequences $(u_{i,\mathcal{T}_\ell,\tau_\ell})_{\ell\ge1}$ and $(\phi_{\mathcal{T}_\ell,\tau_\ell})_{\ell\ge1}$ as in (6.27)&(6.28). For legibility, the index ℓ will be removed as soon as it does harm comprehension.

As usual in the analysis of finite volume schemes, we also need to handle quantities attaches to the faces $\sigma\in\mathcal{E}$. To this end, we introduce the so-called diamond mesh of Ω by associating a diamond cell ω_σ to all $\sigma\in\mathcal{E}$. More precisely, ω_σ is the convex hull of $\{x_K,x_L,\sigma\}$ if

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$\sigma = K|L \in \mathcal{E}_{\rm int}$, and $\omega_\sigma = {\rm conv}\{x_K, \sigma\}$ if $\sigma \in \mathcal{E}_{\rm ext} \cap \mathcal{E}_K$, see Figure 6.1 for an illustration. The Lebesgue measure m_{ω_σ} of ω_σ is then given by

$$m_{\omega_\sigma} = \frac{m_\sigma d_\sigma}{d}, \qquad \sigma \in \mathcal{E}, \tag{6.51}$$

where d is the ambiant space dimension.

Among other quantities attached to faces, one defines the inflated fluxes $(F_{i,\mathcal{E},\tau})_{1\le i\le I}$ as the piecewise constant in space and time vector fields defined by

$$F_{i,\mathcal{E},\tau}(t,x) = \frac{d}{m_\sigma} F^n_{i,K\sigma} n_{K\sigma} \quad \text{if } (t,x) \in (t^{n-1}, t^n] \times \omega_\sigma,$$

with $n_{K\sigma}$ the normal to σ outward with respect to K. A major part of the analysis carried out in this section consists in showing that, up to the extraction of a subsequence,

$$F_{i,\mathcal{E}_\ell,\tau_\ell}(t,x) \underset{\ell\to+\infty}{\longrightarrow} F_i \quad \text{weakly in } L^2_{\rm loc}(\mathbb{R}_+ \times \overline{\Omega})^d.$$

where we make use of the definition (6.2) of the continuous fluxes.

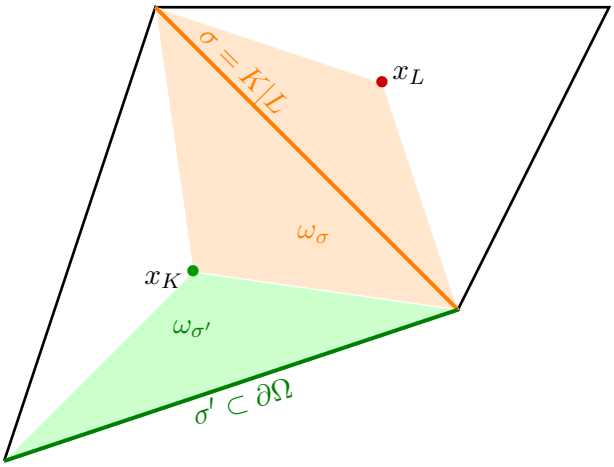

Fig. 6.1: Examples of diamond cells $\omega_\sigma, \omega_{\sigma'}$ for inner and external faces σ and σ'.

Following [50, 86], to a piecewise constant in space function $v_\mathcal{T}(x) = \sum_{K\in\mathcal{T}} v_K \mathbb{1}_K(x)$, we associate the inflated gradient $\nabla_\mathcal{T} v_\mathcal{T} : \Omega \to \mathbb{R}^d$ defined by

$$\nabla_\mathcal{T} v_\mathcal{T}(x) = d\,\frac{v_{K\sigma} - v_K}{d_\sigma} n_{K\sigma} \quad \text{if } x \in \omega_\sigma. \tag{6.52a}$$

This operator straightforwardly extends to piecewise constant functions in space and time:

$$\nabla_\mathcal{T} v_{\mathcal{T},\tau}(t,x) = d\,\frac{v^n_{K\sigma} - v^n_K}{d_\sigma} n_{K\sigma} \quad \text{if } (t,x) \in (t^{n-1}, t^n] \times \omega_\sigma. \tag{6.52b}$$

This section is organized as follows. The needed compactness properties are established in Section 6.4.1, allowing to claim for the existence of (at least) a limit point (U, ϕ) to the sequence $(U_{\mathcal{T}_\ell,\tau_\ell}, \phi_{\mathcal{T}_m,\Delta t_\ell})_{\ell\ge1}$. Section 6.4.2 concludes the proof of Theorem 6.2 by showing

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that the limit value (U, ϕ) is a weak solution of the continuous problem (6.1)–(6.7) in the sense of Definition 6.1.

6.4.1 Compactness of the approximate solutions

We establish here enough compactness properties to pass to the limit in the schemes.

Proposition 6.5 (Compactness results)**.** *There exist functions $u_0 \in L^\infty(\mathbb{R}_+ \times \Omega)$ with $\sqrt{u_0} \in L^2_{loc}(\mathbb{R}_+; H^1(\Omega))$, $u_1, \dots, u_n \in L^\infty(\mathbb{R}_+ \times \Omega)$ with $u_i\sqrt{u_0} \in L^2_{loc}(\mathbb{R}_+; H^1(\Omega))$, and $\phi \in L^\infty(\mathbb{R}_+ \times \Omega)$ with $\phi - \phi^D \in L^\infty(\mathbb{R}_+; V)$ such that, up to a subsequence, as $\ell \to +\infty$, there holds*

$$u_{i,\mathcal{T},\tau} \to u_i \quad \text{in the } L^\infty(\mathbb{R}_+ \times \Omega)\text{-weak-}\star \text{ sense, } 1 \le i \le I, \tag{6.53}$$

$$u_{0,\mathcal{T},\tau} \to u_0 \quad \text{in the } L^\infty(\mathbb{R}_+ \times \Omega)\text{-weak-}\star \text{ sense and a.e. in } \mathbb{R}_+ \times \Omega, \tag{6.54}$$

$$\phi_{\mathcal{T},\tau} \to \phi \quad \text{in the } L^\infty(\mathbb{R}_+ \times \Omega)\text{-weak-}\star \text{ sense and a.e. in } \mathbb{R}_+ \times \Omega. \tag{6.55}$$

Moreover, for $1 \le i \le I$, one has

$$u_{i,\mathcal{T},\tau}\sqrt{u_{0,\mathcal{T},\tau}} \to u_i\sqrt{u_0} \quad \text{a.e. in } \mathbb{R}_+ \times \Omega, \tag{6.56}$$

$$u_{0,\mathcal{T},\tau}u_{i,\mathcal{T},\tau} \to u_0u_i \quad \text{a.e. in } \mathbb{R}_+ \times \Omega, \tag{6.57}$$

and also

$$\nabla_{\mathcal{T},\tau}\sqrt{u_{0,\mathcal{T},\tau}} \rightharpoonup \nabla\sqrt{u_0} \quad \text{weakly in } L^2_{loc}(\mathbb{R}_+; L^2(\Omega)^d), \tag{6.58}$$

$$\nabla_{\mathcal{T},\tau}[u_{0,\mathcal{T},\tau}u_{i,\mathcal{T},\tau}] \rightharpoonup \nabla[u_0u_i] \quad \text{weakly in } L^2_{loc}(\mathbb{R}_+; L^2(\Omega)), \tag{6.59}$$

$$\nabla_{\mathcal{T},\tau}\phi_{\mathcal{T},\tau} \rightharpoonup \nabla\phi \quad \text{weakly in } L^2_{loc}(\mathbb{R}_+; L^2(\Omega)), \tag{6.60}$$

Proof. The $L^\infty(\mathbb{R}_+ \times \Omega)$-weak-$\star$ convergences (6.53)–(6.55) are the consequences of the uniform bounds on $u_{i,\mathcal{T},\tau}$ and $\phi_{\mathcal{T},\tau}$ in $L^\infty(\mathbb{R}_+ \times \Omega)$, thanks to the Banach-Alaoglu Theorem. The strong convergence (6.54) follow directly from the discrete Aubin-Lions lemma, see [99] for a general presentation of the lemma, and [40, Lemma 9] for its application in our context, which can be applied thanks to the uniform estimates of Lemma 6.3 and Corollary 6.1. Furthermore, one obtains the weak convergence in $L^2_{\rm loc}(\mathbb{R}_+; L^2(\Omega))$ of $\nabla_{\mathcal{T},\tau}u_{0,\mathcal{T},\tau}$ towards ∇u_0. Concerning the point-wise convergence of $\phi_{\mathcal{T},\tau}$ towards ϕ, it can be proven by using the discrete $L^2_{\rm loc}((H^1)')$ estimate on time increments of the right-hand side of the discrete Poisson equation (6.18) that follows from Corollary 6.1. As the proof is fully similar to the one of [39, Proposition 4.2], we do not provide details here. The weak compactness property (6.60) is also established in [39, Proposition 4.2].

In order to prove (6.58), one can either make use of the nonlinear Aubin Simon theorem of [8], or directly remark that, thanks to Lemma 6.3, the vector field $\nabla_{\mathcal{T}}\sqrt{u_{0,\mathcal{T},\tau}}$ is uniformly bounded in $L^2_{\rm loc}(\mathbb{R}_+; L^2(\Omega)^d)$. We deduce from this boundedness that there exists $G_0 \in L^2_{\rm loc}(\mathbb{R}_+; L^2(\Omega)^d)$ such that, up to a subsequence, $\nabla_{\mathcal{T}}\sqrt{u_{0,\mathcal{T},\tau}}$ tends to G_0 weakly. As $\sqrt{u_{0,\mathcal{T},\tau}}$ converges point-wise (and thus in $L^1_{\rm loc}(\mathbb{R}_+ \times \Omega)$) towards $\sqrt{u_0}$ owing to (6.54), the weak consistency of the inflated gradient $\nabla_{\mathcal{T}}$, see for instance [50, 82], allows to show that $G_0 = \nabla\sqrt{u_0}$.

Regarding the point-wise convergences (6.56) and (6.57), of $u_{i,\mathcal{T},\tau}\sqrt{u_{0,\mathcal{T},\tau}}$, respectively, we can conclude by applying the discrete Aubin-Lions lemma of "degenerate" type ([40, Lemma 10]). To prove (6.56), we use it with $y_\ell = \sqrt{u_{0,\mathcal{T}_\ell,\tau_\ell}}$ and $z_\ell = u_{i,\mathcal{T}_\ell,\tau_\ell}$, making advantages of the

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uniform estimate (6.48), (6.40) and (6.41). Whereas, with $y_\ell = u_{0,\mathcal{T}_\ell,\tau_\ell}$ and $z_\ell = u_{i,\mathcal{T}_\ell,\tau_\ell}$, we conclude (6.57) similarly, replacing (6.41) by (6.42).

It finally remains to prove (6.59) for $i = 1, \dots, I$. As a consequence of (6.42), $\nabla_{\mathcal{T}}[u_{i,\mathcal{T},\tau} u_{0,\mathcal{T},\tau}]$ is uniformly bounded in $L^2_{\mathrm{loc}}(\mathbb{R}_+ \times \overline{\Omega})^d$. Hence there exists G_i such that, up to a subsequence,

$$\nabla_{\mathcal{T}}[u_{i,\mathcal{T},\tau} u_{0,\mathcal{T},\tau}] \rightharpoonup G_i \quad \text{weakly in } L^2_{\mathrm{loc}}(\mathbb{R}_+ \times \overline{\Omega})^d.$$

As $u_{i,\mathcal{T},\tau} u_{0,\mathcal{T},\tau}$ converges towards $u_i u_0$ thanks to (6.57), we can invoke again the weak consistency of the inflated gradient to conclude that $G_i = \nabla[u_i u_0]$. □

6.4.2 Identification of the limit

In this section, we conclude the proof of Theorem 6.2 by showing the following proposition.

Proposition 6.6. *Let (U, ϕ) be as in Proposition 6.5, then it is a weak solution of the problem* (6.1)–(6.7) *in the sense of Definition 6.1.*

Proof. The regularity requirements on U and ϕ have already been checked in Proposition 6.5. Therefore it only remains to verify that the weak formulations (6.16) and (6.17) hold true. The case of Poisson equation is classical. It will not be detailed here, and we refer to [39, Proposition 4.2] for a synthetic proof. We rather focus our attention on the derivation of (6.17).

Let $\varphi \in C_c^\infty(\mathbb{R}_+ \times \overline{\Omega})$, then, for some admissible mesh $(\mathcal{T}_\ell, \mathcal{E}_\ell, (x_K)_{K\in\mathcal{T}_\ell})$ (we remove the subscript ℓ when possible for legibility), denote by $\varphi_K^n = \varphi(t^n, x_K)$. Multiplying (6.19) by $\tau^n \varphi_K^{n-1}$ and summing over $n \geq 1$ and $K \in \mathcal{T}$ yields, as for (6.49):

$$\sum_{n=1}^{N} \sum_{K\in\mathcal{T}} m_K \, (u_{i,K}^n - u_{i,K}^{n-1}) \varphi_K^{n-1} = \sum_{n=1}^{N} \tau^n \sum_{\sigma\in\mathcal{E}_{\mathrm{int}}} F_{i,K\sigma}^n (\varphi_{K\sigma}^{n-1} - \varphi_K^{n-1}). \tag{6.61}$$

Since φ is compactly supported in time, $\varphi_K^n = 0$ for n large enough. Therefore, the left-hand side of (6.61) rewrites

$$\sum_{n=1}^{N} \sum_{K\in\mathcal{T}} m_K \, (u_{i,K}^n - u_{i,K}^{n-1}) \varphi_K^{n-1} = \sum_{n=1}^{N} \tau^n \sum_{K\in\mathcal{T}} m_K u_{i,K}^n \frac{\varphi_K^{n-1} - \varphi_K^n}{\tau^n} - \sum_{K\in\mathcal{T}} m_K u_{i,K}^0 \varphi_K^0.$$

Since φ is smooth, the approximate time derivative $\delta_\tau \varphi_{\mathcal{T},\tau}$ of φ defined by

$$\delta_\tau \varphi_{\mathcal{T},\tau}(t,x) = \frac{\varphi_K^n - \varphi_K^{n-1}}{\tau^n} \quad \text{if } (t,x) \in (t^{n-1}, t^n] \times K$$

converges in $L^1(\mathbb{R}_+ \times \Omega)$ towards $\partial_t \varphi$. Therefore, using (6.53), we get that

$$\sum_{n=1}^{N} \tau^n \sum_{K\in\mathcal{T}} m_K u_{i,K}^n \frac{\varphi_K^{n-1} - \varphi_K^n}{\tau^n} \underset{\ell\to+\infty}{\longrightarrow} - \iint_{\mathbb{R}_+\times\Omega} u_i \partial_t \varphi. \tag{6.62}$$

The function $u_{i,\mathcal{T}}^0 = \sum_{K\in\mathcal{T}} u_{i,K}^0 \mathbb{1}_K$ converges strongly in $L^1(\Omega)$ towards u_i^0, while $\varphi_{\mathcal{T}}^0 = \sum_{K\in\mathcal{T}} \varphi_K^0 \mathbb{1}_K$ converges uniformly towards $\varphi(0,\cdot)$ thanks to the regularity of φ. Therefore,

$$- \sum_{K\in\mathcal{T}} m_K u_{i,K}^0 \varphi_K^0 \underset{\ell\to+\infty}{\longrightarrow} - \int_\Omega u_i^0 \varphi(0,\cdot), \tag{6.63}$$

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so we can pass to the limit in the left-hand side of (6.61).

Let us now focus on its right-hand side. Define $\tilde{\varphi}_{\mathcal{T},\tau}$ by

$$\tilde{\varphi}_{\mathcal{T},\tau}(t,x) = \varphi(t^{n-1}, x_K) \quad \text{if } (t,x) \in [t^{n-1}, t^n) \times K.$$

Following [83] (see [69] for a practical example), one can reconstruct a second approximate gradient operator $\widehat{\nabla}_{\mathcal{T}}$ mapping the set of piecewise constant functions in space and time to $\mathbb{R}^d$ such that

$$\widehat{\nabla}_{\mathcal{T}}\tilde{\varphi}_{\mathcal{T},\tau}(t,x)\cdot n_{K\sigma} = \frac{\varphi_L^n - \varphi_K^n}{d_\sigma} \quad \text{if } (t,x) \in [t^{n-1}, t^n) \times \omega_\sigma, \quad \sigma = K|L \in \mathcal{E}_{\rm int},$$

and which is strongly consistent, i.e.,

$$\widehat{\nabla}_{\mathcal{T}}\tilde{\varphi}_{\mathcal{T},\tau} \underset{\ell\to+\infty}{\longrightarrow} \nabla\varphi \quad \text{strongly in } L^2(\mathbb{R}_+\times\Omega)^d.$$

The right-had side of (6.61) then simply boils down to

$$\sum_{n=1}^{N}\tau^n \sum_{\sigma\in\mathcal{E}_{\rm int}} F_{i,K\sigma}^n(\varphi_{K\sigma}^{n-1} - \varphi_K^{n-1}) = \iint_{\mathbb{R}_+\times\Omega} F_{i,\mathcal{E},\tau}\cdot\widehat{\nabla}_{\mathcal{T}}\tilde{\varphi}_{\mathcal{T},\tau}.$$

We have shown in Lemma 6.4 that $(F_{i,\mathcal{E}_\ell,\tau_\ell})_{\ell\geq 1}$ is uniformly bounded in $L^2_{\rm loc}(\mathbb{R}_+\times\overline{\Omega})^d$. Therefore, it converges (up to a subsequence) towards some vector field F_i weakly in $L^2_{\rm loc}(\mathbb{R}_+\times\overline{\Omega})$. We can then pass to the limit in the right-hand side of (6.61) to obtain

$$\sum_{n=1}^{N}\tau^n \sum_{\sigma\in\mathcal{E}_{\rm int}} F_{i,K\sigma}^n(\varphi_{K\sigma}^{n-1} - \varphi_K^{n-1}) \underset{\ell\to+\infty}{\longrightarrow} \iint_{\mathbb{R}_+\times\Omega} F_i\cdot\nabla\varphi. \tag{6.64}$$

To conclude the proof of Proposition 6.6, we still have to identify the limiting flux F_i under the form (6.15). To this end, we split the inflated fluxes into a convective and diffusive part,

$$\begin{aligned} F_{i,\mathcal{E},\tau}^{\rm conv}(t,x) &= \frac{d}{m_\sigma} F_{i,K\sigma}^{{\rm conv},n} n_{K\sigma} \quad \text{if } (t,x)\in(t^{n-1},t^n]\times\omega_\sigma,\\ F_{i,\mathcal{E},\tau}^{\rm diff}(t,x) &= \frac{d}{m_\sigma} F_{i,K\sigma}^{{\rm diff},n} n_{K\sigma} \quad \text{if } (t,x)\in(t^{n-1},t^n]\times\omega_\sigma, \end{aligned}$$

where $F_{i,K\sigma}^{{\rm conv},n}$ and $F_{i,K\sigma}^{{\rm diff},n}$ are as in the proof of Lemma 6.4. As both $F_{i,\mathcal{E},\tau}^{\rm conv}$ and $F_{i,\mathcal{E},\tau}^{\rm text}$ have been shown to be bounded in $L^2_{\rm loc}(\mathbb{R}_+\times\overline{\Omega})^d$, one has, up to a subsequence,

$$F_{i,\mathcal{E},\tau}^{\rm diff} \underset{\ell\to+\infty}{\longrightarrow} F_i^{\rm diff} \quad \text{and} \quad F_{i,\mathcal{E},\tau}^{\rm conv} \underset{\ell\to+\infty}{\longrightarrow} F_i^{\rm conv} \quad \text{weakly in } L^2_{\rm loc}(\mathbb{R}_+\times\overline{\Omega})^d. \tag{6.65}$$

Let us first focus on the convective part $F_{i,\mathcal{E},\tau}^{\rm conv}$. For $i=1,\dots,I$, $\sigma\in\mathcal{E}$ and $n\geq 1$, define

$$\eta_{i,\sigma}^n = \begin{cases} \frac{u_{i,K}^n u_{0,L}^n + u_{i,L}^n u_{0,K}^n}{2} & \text{if } \sigma = K|L\in\mathcal{E}_{\rm int},\\ u_{i,K}^n u_{0,K}^n & \text{if } \sigma\in\mathcal{E}_K\cap\mathcal{E}_{\rm ext}, \end{cases}$$

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and

$$\tilde{\eta}_{i,\sigma}^n = \begin{cases} \frac{u_{i,K}^n u_{0,K}^n + u_{i,L}^n u_{0,L}^n}{2} & \text{if } \sigma = K|L \in \mathcal{E}_{\rm int}, \\ u_{i,K}^n u_{0,K}^n & \text{if } \sigma \in \mathcal{E}_K \cap \mathcal{E}_{\rm ext}, \end{cases}$$

and then $\eta_{i,\mathcal{E},\tau}(t,x) = \eta_{i,\sigma}^n$ and $\tilde{\eta}_{i,\mathcal{E},\tau}(t,x) = \eta_{i,\sigma}^n$ if $(t,x) \in (t^{n-1},t^n] \times \omega_\sigma$. In view of (6.46) and of the definition (6.52) of the inflated gradient, the convective part of the inflated approximate flux rewrites

$$F_{i,\mathcal{E},\tau}^{\rm conv} = -D_i\, \eta_{i,\mathcal{E},\tau}\, z_i\, \nabla_{\mathcal{T}} \phi_{\mathcal{T},\tau}. \tag{6.66}$$

Thanks to (6.57), proving that

$$\eta_{i,\mathcal{E},\tau} - \tilde{\eta}_{i,\mathcal{E},\tau} \underset{\ell \to +\infty}{\longrightarrow} 0 \quad \text{a.e. in } \mathbb{R}_+ \times \Omega \tag{6.67}$$

and

$$\tilde{\eta}_{i,\mathcal{E},\tau} - u_{0,\mathcal{T},\tau} u_{i,\mathcal{T},\tau} \underset{\ell \to +\infty}{\longrightarrow} 0 \quad \text{a.e. in } \mathbb{R}_+ \times \Omega \tag{6.68}$$

is equivalent to showing that

$$\eta_{i,\mathcal{E},\tau} \underset{\ell \to +\infty}{\longrightarrow} u_0 u_i \quad \text{a.e. in } \mathbb{R}_+ \times \Omega,$$

and thus strongly in $L^2_{\rm loc}(\mathbb{R}_+ \times \overline{\Omega})$ thanks to the uniform bound $0 \le u_{i,\mathcal{T},\tau} \le 1$. Bearing in mind (6.60), this allows to pass to the weak limit in (6.66) and to recover that

$$F_i^{\rm conv} = -D_i\, u_0 u_i\, z_i\, \nabla \phi. \tag{6.69}$$

To establish (6.67), remark that

$$\left\| \eta_{i,\mathcal{E},\tau} - \tilde{\eta}_{i,\mathcal{E},\tau} \right\|^2_{L^2((0,t^N)\times\Omega)} = \frac{1}{4} \sum_{n=1}^N \tau^n \sum_{\sigma \in \mathcal{E}_{\rm int}} m_{\omega_\sigma} (u_{i,K}^n - u_{i,L}^n)^2 (u_{0,K}^n - u_{0,L}^n)^2.$$

Since $0 \le u_{i,K}^n \le 1$, owing to (6.51), and since $d_\sigma \le 2h_{\mathcal{T}}$ this gives

$$\left\| \eta_{i,\mathcal{E},\tau} - \tilde{\eta}_{i,\mathcal{E},\tau} \right\|^2_{L^2((0,t^N)\times\Omega)} \le \frac{h_{\mathcal{T}}^2}{d} \sum_{n=1}^N \tau^n \sum_{\sigma \in \mathcal{E}_{\rm int}} a_\sigma (u_{0,K}^n - u_{0,L}^n)^2.$$

We can make use of estimate (6.40) to get that $\eta_{i,\mathcal{E},\tau} - \tilde{\eta}_{i,\mathcal{E},\tau}$ tends to 0 in $L^2_{\rm loc}(\mathbb{R}_+ \times \overline{\Omega})$, hence almost everywhere up to the extraction of yet another subsequence, whence (6.67).

Concerning (6.68), we can proceed similarly to obtain

$$\left\| \tilde{\eta}_{i,\mathcal{E},\tau} - u_{0,\mathcal{T},\tau} u_{i,\mathcal{T},\tau} \right\|^2_{L^2((0,t^N)\times\Omega)} = \frac{h_{\mathcal{T}}^2}{d} \sum_{n=1}^N \tau^n \sum_{\sigma \in \mathcal{E}_{\rm int}} a_\sigma \left(u_{0,K}^n u_{i,K}^n - u_{0,L}^n u_{i,L}^n \right)^2$$

which tends to 0 thanks to (6.42).

It finally remains to identify the limit of $F_{i,\mathcal{E},\tau}^{\rm diff}$ as $F_i^{\rm diff}$. To this end, remark first that, for $\sigma = K|L \in \mathcal{E}_{\rm int}$ and $n \ge 1$, one has

$$u_{i,K}^n u_{0,L}^n - u_{i,L}^n u_{0,K}^n = T_{1,\sigma}^n + T_{2,\sigma}^n + T_{3,\sigma}^n$$

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with

$$\begin{aligned} T^n_{1,\sigma} &= u^n_{i,K}u^n_{0,K} - u^n_{i,L}u^n_{0,L},\\ T^n_{2,\sigma} &= 2\left(u^n_{i,K}\sqrt{u^n_{0,K}} + u^n_{i,L}\sqrt{u^n_{0,L}}\right)\left(\sqrt{u^n_{0,K}} - \sqrt{u^n_{0,L}}\right),\\ T^n_{2,\sigma} &= \left(u^n_{i,K} - u^n_{i,L}\right)\left(\sqrt{u^n_{0,K}} - \sqrt{u^n_{0,L}}\right)^2. \end{aligned}$$

Therefore, in view of (6.47), we can split

$$F^{\rm diff}_{i,\mathcal{E},\tau} = -D_i\nabla_{\mathcal{T}}[u_{i,\mathcal{T},\tau}u_{0,\mathcal{T},\tau}] - 4D_i\gamma_{i,\mathcal{E},\tau}\nabla_{\mathcal{T}}\sqrt{u_{0,\mathcal{T},\tau}} + \mathcal{R}_{i,\mathcal{E},\tau} + \mathcal{S}_{i,\mathcal{E},\tau}, \tag{6.70}$$

where we have set

$$\gamma_{i,\mathcal{E},\tau}(t,x) = \begin{cases} \frac{1}{2}\left(u^n_{i,K}\sqrt{u^n_{0,K}} + u^n_{i,L}\sqrt{u^n_{0,L}}\right) & \text{if } (t,x)\in(t^{n-1},t^n]\times\omega_\sigma,\ \sigma = K|L\in\mathcal{E}_{\rm int},\\ u^n_{i,K}\sqrt{u^n_{0,K}} & \text{if } (t,x)\in(t^{n-1},t^n]\times\omega_\sigma,\ \sigma\in\mathcal{E}_K\cap\mathcal{E}_{\rm ext}, \end{cases}$$

and where, for $(t,x)\in(t^{n-1},t^n]\times\omega_\sigma$, $\sigma = K|L\in\mathcal{E}_{\rm int}$,

$$\mathcal{R}_{i,\mathcal{E},\tau}(t,x) = d\,D_i\left(u^n_{i,K} - u^n_{i,L}\right)\left(\sqrt{u^n_{0,K}} - \sqrt{u^n_{0,L}}\right)^2 n_{K\sigma},$$

and, in view of (6.47),

$$|\mathcal{S}_{i,\mathcal{E},\tau}(t,x)| \le \frac{C}{d_\sigma}\left(\phi^n_K - \phi^n_L\right)^2.$$

Both $\mathcal{R}_{i,\mathcal{E},\tau}$ and $\mathcal{S}_{i,\mathcal{E},\tau}$ are assumed to vanish on $\mathbb{R}_+\times\omega_\sigma$ for all $\sigma\in\mathcal{E}_{\rm ext}$. Then thanks to Proposition 6.2, one has

$$\|\mathcal{S}_{i,\mathcal{E},\tau}\|_{L^1((0,t^N)\times\Omega)^d} \le C\sum_{n=1}^N \tau^n \sum_{\sigma\in\mathcal{E}_{\rm int}} m_\sigma\left(\phi^n_K - \phi^n_L\right)^2 \le Ch_{\mathcal{T}}t^N.$$

On the other hand, since $0\le u^n_{i,K}\le 1$, we deduce from (6.40) that

$$\|\mathcal{R}_{i,\mathcal{E},\tau}\|_{L^1((0,t^N)\times\Omega)^d} \le D_i\sum_{n=1}^N \tau^n \sum_{\sigma\in\mathcal{E}_{\rm int}} m_\sigma\left(\sqrt{u^n_{0,K}} - \sqrt{u^n_{0,L}}\right)^2 \le Ch_{\mathcal{T}}(1+t^N).$$

The two last terms in (6.70) then tend to 0, while the first term tends to $-D_i\nabla[u_0u_i]$ thanks to (6.59). In view of the weak $L^2_{\rm loc}(L^2)$ convergence of $\nabla_{\mathcal{T}}\sqrt{u_{0,\mathcal{T},\tau}}$ towards $\nabla\sqrt{u_0}$, cf. (6.58), then it suffices to show that

$$\gamma_{i,\mathcal{E},\tau} \underset{\ell\to+\infty}{\longrightarrow} u_i\sqrt{u_0} \quad \text{strongly in} \quad L^2_{\rm loc}(\mathbb{R}_+\times\overline{\Omega})$$

to pass to the limit in (6.70). As $u_{i,\mathcal{T},\tau}\sqrt{u_{0,\mathcal{T},\tau}}$ converges strongly towards $u_i\sqrt{u_0}$, see (6.56), then

$$\|\gamma_{i,\mathcal{E},\tau} - u_{i,\mathcal{T},\tau}\sqrt{u_{0,\mathcal{T},\tau}}\|^2_{L^2((0,t^N)\times\Omega)} = \frac{1}{2}\sum_{n=1}^N \tau^n \sum_{\sigma\in\mathcal{E}_{\rm int}} m_{\omega_\sigma}\left(u^n_{i,K}\sqrt{u^n_{0,K}} - u^n_{i,L}\sqrt{u^n_{0,L}}\right)^2$$

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$$\leq \frac{h_{\mathcal{T}}^2}{d} \sum_{n=1}^{N} \tau^n \sum_{\sigma \in \mathcal{E}_{\text{int}}} a_\sigma \left(u_{i,K}^n \sqrt{u_{0,K}^n} - u_{i,L}^n \sqrt{u_{0,L}^n} \right)^2$$

$$\overset{(6.41)}{\leq} \frac{h_{\mathcal{T}}^2}{d} (1 + t^N) \underset{\ell \to +\infty}{\longrightarrow} 0.$$

This completes the proof of (6.65), thus the ones of Proposition 6.6 and Theorem 6.2. □

6.5 Numerical results

The nonlinear system corresponding to the schemes is solved thanks to a Newton-Raphson method with stopping criterion $\|\mathcal{F}_{\mathcal{T}}^n((U_K^n)_{K\in\mathcal{T}}, (\phi_K^n)_{K\in\mathcal{T}})\|_\infty \leq 10^{-8}$, the components of $\mathcal{F}_{\mathcal{T}}^n$ being given by the left-hand side of (6.19).

6.5.1 Convergence under grid refinement

The goal of our first numerical test is to show that both schemes corresponding to (SQRA) and (SG) are second order accurate w.r.t. the mesh size. To this end, we consider the one-dimensional domain $\Omega = (0, 1)$, in which $I = 2$ different ions evolve, both with the same diffusion coefficient $D_1 = D_2 = 1$. Their (normalized) charge is set to $z_1 = 2$ and $z_2 = 1$, yielding repulsive interaction. No background charge is considered, i.e. $f = 0$, whereas Dirichlet boundary conditions are imposed for the electric potentiel on both sides of the interval, that are $\phi^D(t, 0) = 10$ and $\phi^D(t, 1) = 0$. We consider a moderately small Debye length $\lambda^2 = 10^{-2}$. We start at initial time $t = 0$ with the following configurations: $u_1^0(x) = 0.2 + 0.1(x - 1)$ and $u_2^0 \equiv 0.4$.

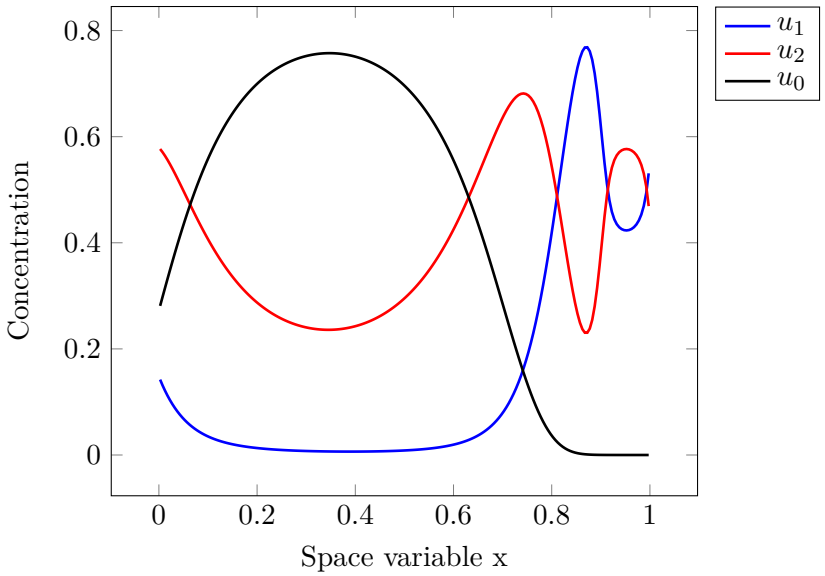

Fig. 6.2: Concentration profiles $u_1(T, x), u_2(T, x)$ and $u_0(T, x)$ at time $T = 1$, $\lambda^2 = 10^{-2}$.

A reference solution is computed on a grid made of 1638400 cells and with a constant time step $\tau = 10^{-3}$, to which we compare solutions computed on successively refined grids but

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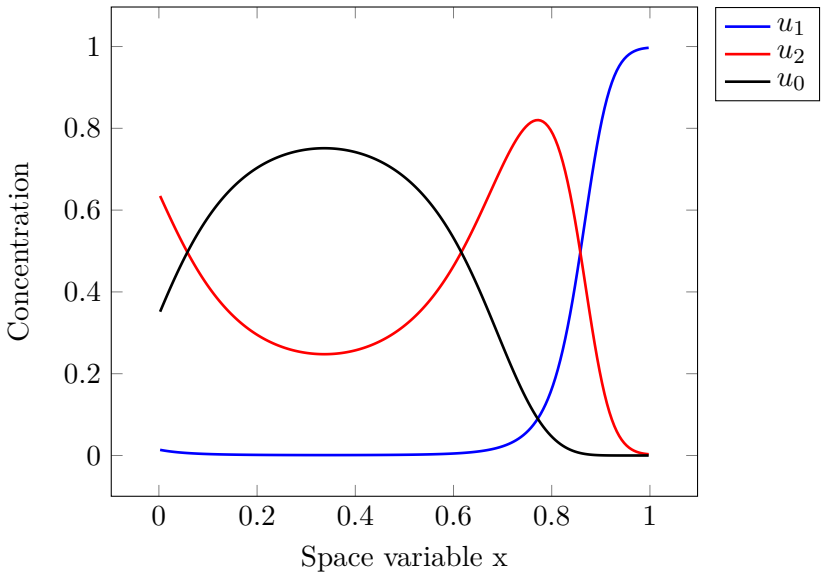

Fig. 6.3: Concentration profiles at time $T = 5000$ for $\lambda^2 = 10^{-2}$.

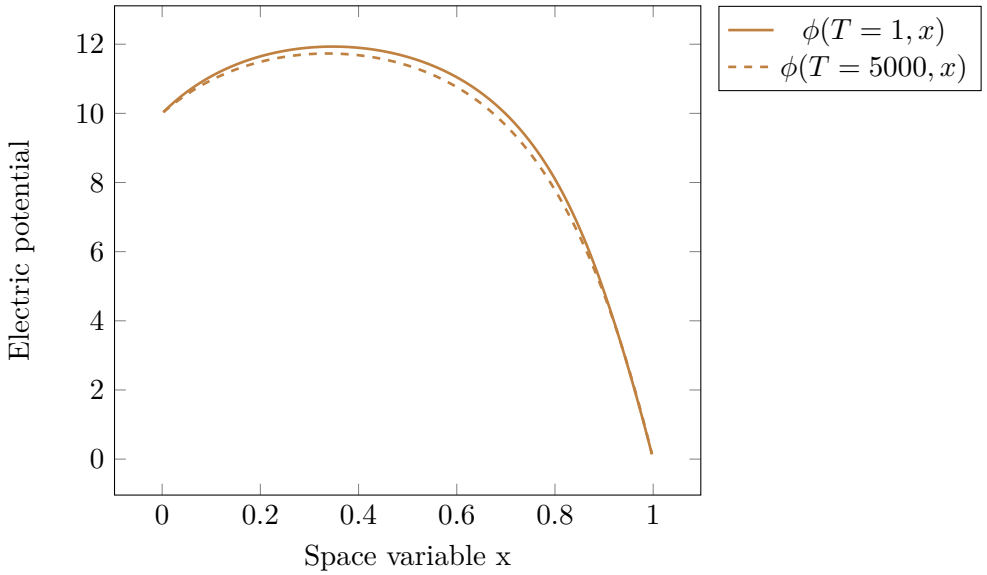

Fig. 6.4: Electric potential profile at times $T = 1$ (solid) and $T = 5000$ (dashed)for $\lambda^2 = 10^{-2}$.

with the same constant time step. The profile of the solution at times $T = 1$ and $T = 5000$ is depicted on Figures 6.2, 6.3 and 6.4 . The relative space-time L^1 error is plotted as a function of the number of cells on Figure 6.5, showing some second order accuracy in space, as specified in the introductory discussion. For such a moderately small value of $\lambda^2 = 10^{-2}$, both schemes exhibit a very similar behavior in terms of accuracy, but also in terms of nonlinear resolution. More precisely, the number of Newton iterations required to solve a time step remains between 6 for the very first iterations and 2 for larger times is mainly insensitive to the mesh size.

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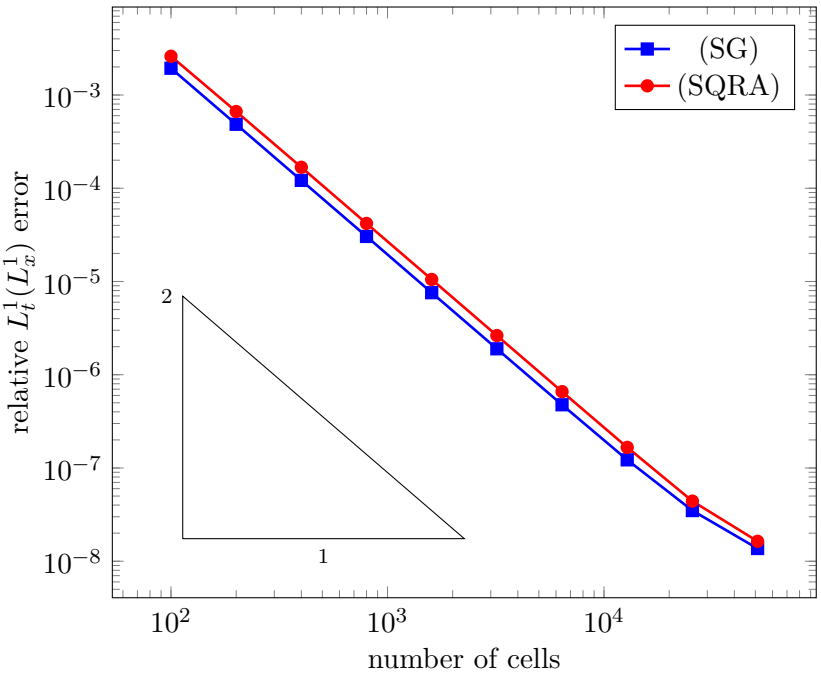

Fig. 6.5: Convergence of the schemes under space grid refinement,($\lambda^2 = 10^{-2}$).

Nevertheless, there is an important difference in the numerical behavior of the two schemes in the small Debye length regime. Indeed, when λ^2 become small, then excepted for very particular values of the data, the variations of $\phi_{\mathcal{T},\tau}$ across the interfaces $\mathcal{E}$ become very large because of (6.18). Therefore, the drift becomes too large to evaluate its exponential, making the computation with the (SQRA) scheme fail. Since $B(y) \sim -y$ as y tends to $-\infty$, the situation is much less problematic with the (SG) scheme, for which computation of the solution corresponding to $\lambda = 10^{-6}$ is feasible without any specific treatment. However, since the drift becomes large, the use of a reduce time step is required to ensure the convergence of Newton's methods.

6.5.2 Long-time behavior of the schemes

We now focus on the long-time behavior of the schemes. The long-time limit of the continuous model has been exhibited in [38]. The model reduces to a nonlinear elliptic equation on the electric potential ϕ, from which one deduces the concentration profiles. However, no quantitative estimate concerning the convergence towards equilibrium. We then perform a numerical study still with the same parameters as previsously (in particular with $\lambda^2 = 10^{-2}$). The steady solution is computed by choosing a very large final time $T_\infty = 5.10^5$ in the simulation. We denote by $\mathcal{H}^\infty_\mathcal{T}$ the corresponding discrete free energy. The relative energy a time t^n is the defined as $\mathcal{H}^{\mathrm{rel},n}_\mathcal{T} = \mathcal{H}^n_\mathcal{T} - \mathcal{H}^\infty_\mathcal{T}$. The energy decay stated in Proposition 6.4 ensures that $\mathcal{H}^{\mathrm{rel},n}_\mathcal{T} \geq 0$ up to numerical errors related to the resolution of the nonlinear systems. One observes on Figure 6.6 that the (SQRA) scheme dissipates faster energy than the (SG) scheme, the latter exhibiting an almost perfect but rather slow exponential convergence towards the steady state as long as the numerical precision has not been reached. The rigorous

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proof of such an exponential convergence in the continuous setting can be deduced from [174]. Its discrete counterpart should be investigated in future works building on the methodology presented in [21].

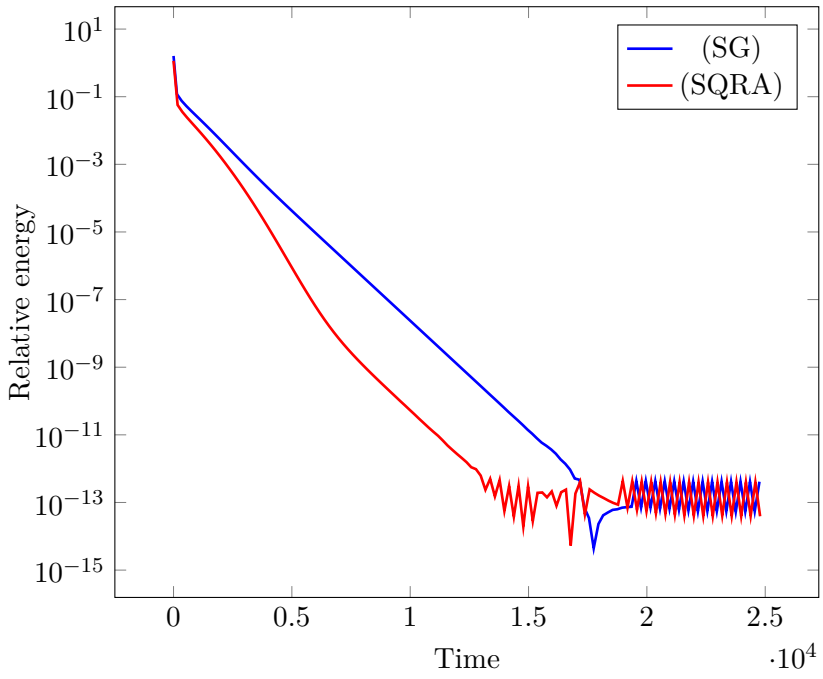

Fig. 6.6: Convergence towards the steady long-time behavior in terms of relative energy $\mathcal{H}_{\mathcal{T}}^{\mathrm{rel},n}$ for $\lambda^2 = 10^{-2}$.

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Appendix A

The continuous model (6.1)–(6.7) was originally derived thanks to a hopping process [38], suggesting the choice

$$F^n_{i,K\sigma} = a_\sigma D_i \left(u^n_{i,K} u^n_{0,L} e^{\frac{1}{2} z_i (\phi^n_K - \phi^n_L)} - u^n_{i,L} u^n_{0,K} e^{\frac{1}{2} z_i (\phi^n_L - \phi^n_K)} \right), \tag{6.71}$$

in the paper [42]. This lead to the *square-root approximation scheme* (SQRA) [43, 113, 135], as introduced in Section 3.3. The flux can be interpreted as a Butler-Volmer law located at the interface between the cells K and L. The probability that a particle of the i-th species jumps from K to L is proportional to the number $u^n_{i,K}$ of candidates in K for a jump as well as to the number of available sites $u^n_{0,L}$ to host the particle in cell L. Whereas the probability that a $i-$particle jumps from L to K is proportional to $u^n_{i,L} u^n_{0,K}$, namely the product between the number of candidates in L for a jump and the number of available sites to host the particle of the i-th species in the cell K. The drift $\phi_K - \phi_L$ appears in an exponential with balanced prefactors $1/2$, which is natural since K and L play symmetric roles in the formula (see Figure 6.7).

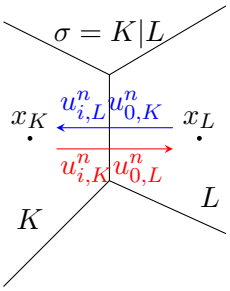

Fig. 6.7: Interpretation of the SQRA scheme (6.71) via the hopping process [38].

The scheme (6.71) appears to be quite intuitive. Nevertheless, as λ^2 diminishes, an analysis of the discretization of the Poisson equation (6.18) reveals a significant amplification in the discrete gradient of the electric potential:

$$\sum_{\sigma \in \mathcal{E}_K} \frac{m_\sigma}{d_\sigma} (\phi^n_K - \phi^n_{K\sigma}) = \frac{1}{\lambda^2} m_K \sum_{i=1}^{I} z_i u^n_{i,K},$$

This substantial growth in the drift term corresponds to an exponential increase $e^{\frac{1}{2} z_i (\phi^n_K - \phi^n_L)}$. Therefore, instead of using the function

$$\mathfrak{B}(y) = e^{-y/2},$$

another natural choice for the drift term is the Bernoulli function

$$\mathfrak{B}(y) = \frac{y}{e^y - 1}.$$

The main advantage of using the Bernoulli function lies in its behaviour for large negative

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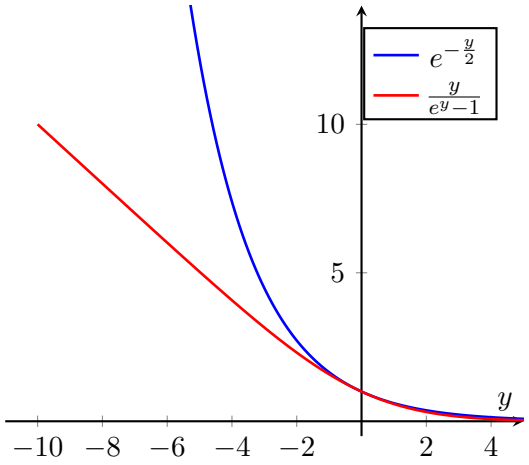

Fig. 6.8: Comparison between the two $\mathfrak{B}$ functions.

values, as one can observe in Figure 6.8. The Bernoulli function $\mathfrak{B}$ leads to the *Scharfetter-Gummel scheme*, with fluxes:

$$F^n_{i,K\sigma} = a_\sigma D_i \left(u^n_{i,K} u^n_{0,L} \frac{z_i(\phi^n_L - \phi^n_K)}{e^{z_i(\phi^n_L - \phi^n_K)} - 1} - u^n_{i,L} u^n_{0,K} \frac{z_i(\phi^n_K - \phi^n_L)}{e^{z_i(\phi^n_K - \phi^n_L)} - 1} \right),$$

as defined in Section 6.2.2.

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Chapter 7

Analysis for a Poisson-Nernst-Planck-Fermi system

This chapter is taken from the article *"Analysis of a Poisson–Nernst–Planck–Fermi system for charge transport in ion channels"* [124], joint work with Ansgar Jüngel and published in *Journal of Differential Equations* 395, 38-68 (2024).

7.1 Introduction

The modeling of the transport of ions through biological channels is of fundamental importance in cell biology. Several strategies have been developed in past decades, using molecular or Brownian dynamics or the Poisson–Nernst–Planck theory. This theory relies on the assumptions that the dynamics of ion transport is based on diffusion and electrostatic interaction only and that the solution is dilute. However, the presence of narrow channel pores requires a more sophisticated modeling. In particular, the ion size is not small compared to the biological channel diameter, and many-particle interactions due to the confined geometry need to be taken into account. In this paper, we analyze a modified Poisson–Nernst–Planck system modeling ion–water interactions and finite ion size constraints. We prove the existence of global weak solutions and, as the main novelty, the weak–strong uniqueness property using entropy methods.

7.1.1 The model setting

The evolution of n ionic species, immersed in a solvent (like water), is assumed to be given by the equations

$$\partial_t u_i + \operatorname{div} J_i = r_i(u), \quad J_i = -D_i(\nabla u_i - u_i \nabla \log u_0 + u_i z_i \nabla \Phi), \tag{7.1}$$

$$\lambda^2(\ell^2\Delta - 1)\Delta\Phi = \sum_{j=1}^n z_j u_j + f(x) \quad \text{in } \Omega,\ t > 0,\ i = 1, \ldots, n, \tag{7.2}$$

where $\Omega \subset \mathbb{R}^d$ $(d \geq 1)$ is a bounded Lipschitz domain, $u = (u_1, \ldots, u_n)$ is the concentration vector, supplemented with initial and mixed Dirichlet–Neumann boundary conditions,

$$u_i(\cdot, 0) = u_i^0 \quad \text{in } \Omega, \quad i = 1, \ldots, n, \tag{7.3}$$

$$J_i \cdot \nu = 0 \text{ on } \Gamma_N, \quad u_i = u_i^D \text{ on } \Gamma_D,\ t > 0, \tag{7.4}$$

$$\nabla\Phi \cdot \nu = \nabla\Delta\Phi \cdot \nu = 0 \text{ on } \Gamma_N, \quad \Phi = \Phi^D,\ \Delta\Phi = 0 \text{ on } \Gamma_D,\ t > 0, \tag{7.5}$$

where $\partial\Omega = \Gamma_D \cup \Gamma_N$, $\Gamma_D \cap \Gamma_N = \emptyset$, and ν is the exterior unit normal vector to $\partial\Omega$.

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The unknowns are the ion concentrations (or volume fractions) $u_i(x,t)$ of the ith ion species and the correlated electric potential $\Phi(x,t)$. The solvent concentration (or volume fraction) $u_0(x,t)$ is given by $u_0 = 1 - \sum_{i=1}^n u_i$, which means that the mixture is saturated. Equations (7.1) are cross-diffusion equations with the fluxes J_i and the reaction rates $r_i(u)$. The parameters are the diffusivities $D_i > 0$ and the valences $z_i \in \mathbb{Z}$. Equation (7.2) is the Poisson–Fermi equation with the scaled Debye length $\lambda > 0$, the correlation length $\ell > 0$, and the given background charge density $f(x)$. We assume that the domain is isolated on the Neumann boundary, while the concentrations and the electric potential are prescribed on the Dirichlet boundary. We refer to [161] for a derivation of (7.1)–(7.2) using an averaging procedure of a Langevin model.

In the following, we discuss definition (7.1) of the fluxes and equation (7.2) for the correlated electric potential. We recover the classical Poisson–Nernst–Planck equations if $u_0 = \text{const.}$ and $\ell = 0$. In this situation, we can write $J_i^{\mathrm{id}} = -D_i u_i \nabla \mu_i^{\mathrm{id}}$ with the electrochemical potential $\mu_i^{\mathrm{id}} = \log u_i + z_i \Phi$ of an ideal dilute solution. In concentrated solutions, the finite size of the ions needs to be taken into account, expressed by the excess chemical potential μ_i^{ex}, so that the electrochemical potential becomes $\mu_i = \mu_i^{\mathrm{id}} + \mu_i^{\mathrm{ex}}$. Bikerman [25] suggested the choice $\mu_i^{\mathrm{ex}} = -\log(1 - \sum_{i=1}^n u_i) = -\log u_0$; also see [18, Sec. 3.1.2]. Then $J_i = -D_i u_i \nabla \mu_i$ coincides with the flux adopted in our model (7.1). Note that solving $\mu_i = \log(u_i/u_0) + z_i\Phi$ for the concentrations, we find that the ion profiles obey the Fermi–Dirac statistics

$$u_i = \frac{\exp(\mu_i - z_i\Phi)}{1 + \sum_{j=1}^n \exp(\mu_j - z_j\Phi)}, \quad i = 1, \ldots, n.$$

Then, given μ_i and Φ, the bounds $0 \le u_i \le 1$ are automatically satisfied. Other choices of the excess chemical potential were suggested in [24, Sec. 2.1].

In the literature, there exist also other approaches to define the fluxes J_i under finite size constraints. The diffusion limit of an on-lattice model, which takes into account that neighboring sites may be occupied (modeling size exclusion), was performed in [38], analyzed in [102], and numerically solved in [42], resulting to

$$J_i^{(1)} = -D_i(u_0 \nabla u_i - u_i \nabla u_0 + u_0 u_i z_i \nabla \Phi), \quad i = 1, \ldots, n. \tag{7.6}$$

This model avoids the singular term $\nabla \log u_0$, which is delicate near $u_0 = 0$, but it introduces the diffusion term $u_0 \nabla u_i$, which degenerates at $u_0 = 0$. Another flux definition was suggested in [109],

$$J_i^{(2)} = -D_i\bigg(\nabla u_i + u_i z_i \nabla \Phi - \sum_{j=1}^n z_j u_j \nabla \Phi\bigg), \quad i = 1, \ldots, n.$$

The additional term $-\sum_{j=1}^n z_j u_j \nabla \Phi$ comes from the force balance in the Euler momentum equation for zero fluid velocity. The ion–water interaction is described in [63] by

$$J_i^{(3)} = -D_i\bigg(\nabla u_i + u_i z_i \nabla \Phi - \frac{\partial \varepsilon_0}{\partial u_i} |\nabla \Phi|^2\bigg), \quad i = 1, \ldots, n,$$

where the dielectricity $\varepsilon_0 = \lambda^2$, instead of being constant, depends on u. This assumption is based on the experimental observation that the dielectric response of water decreases as ion concentrations increase [63]. Thus, $\partial \varepsilon_0 / \partial u_i < 0$, showing that the ion–water interaction

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energy is always nonnegative. Finite ion size effects are modeled in [136] by including an approximation of the Lennard–Jones potential in the energy functional, leading to

$$J_i^{(4)} = -D_i\bigg(\nabla u_i + u_i\nabla\sum_{j=1}^n a_{ij}u_i + z_i\nabla\Phi\bigg), \quad i=1,\ldots,n.$$

Assuming that (a_{ij}) is positive definite, the global existence of weak solutions for two species was proved in [117]. For the analysis of the stationary equations, see [101]. Finally, excluded volume effects can be included by considering nonlinear diffusivities $D_i(u_i) = 1+\alpha u_i$, where $\alpha > 0$ is a measure of the volume exclusion interactions [36].

Our model has the advantage of being consistent with the thermodynamical model [81]

$$J_i = -\sum_{j=1}^n D_{ij}u_j\nabla(\mu_j-\mu_0), \quad \text{where } \mu_i = \log u_i + z_i\Phi, \quad \mu_0 = \log u_0 + z_0\Phi,$$

assuming that the diffusion matrix is diagonal, $D_{ij} = D_i\delta_{ij}$, and that the solvent is neutral, $z_0 = 0$.

The interaction of the ions with polar solvents like water is modeled by the potential in (7.2). Indeed, let ϕ be the electric potential of free ions, given by $-\lambda^2\Delta\phi = \rho$, where ρ is the total charge density. Then the correlated potential $\Phi = \ell^{-2}Y_\ell * \phi$ is the convolution between the Yukawa potential $Y_\ell(x) = (|x|/\ell)^{-1}\exp(-|x|/\ell)$ [138] and the electric potential, where $\ell > 0$ is the correlation length of the screening by ions and water [173]. As this potential satisfies $-\ell^2\Delta\Phi + \Phi = \phi$, we recover (7.2) with $\rho = \sum_{j=1}^n z_j u_j + f(x)$. Thus, the Poisson–Fermi equation (7.2) includes finite ion size effects and polarization correlations among water molecules. It generalizes the fourth-order differential permittivity operator of [158] and the nonlocal permittivity in ionic liquids of [19]. If there are no correlation and polarization effects ($\ell = 0$), we recover the standard Poisson equation for the electric potential. The expression $\varepsilon_0 = \lambda^2(\ell^2\Delta - 1)$ can be interpreted as a dielectric differential operator.

7.1.2 Entropy structure

System (7.1) can be written as a cross-diffusion system with a diffusion matrix which is neither symmetric nor positive definite. This issue is overcome by exploiting the entropy (or free energy) structure and using the boundedness-by-entropy method [123]. The free energy associated to (7.1)–(7.2) is given by [19, 139]

$$H(u) = \int_\Omega h(u)dx, \quad \text{where} \tag{7.7}$$
$$h(u) = \sum_{i=0}^n\int_{u_i^D}^{u_i}\log\frac{s}{u_i^D}ds + \frac{\lambda^2}{2}|\nabla(\Phi-\Phi^D)|^2 + \frac{(\lambda\ell)^2}{2}|\Delta(\Phi-\Phi^D)|^2.$$

The energy density $h(u)$ consists of the internal, free-ion electric, and correlation electric energies. The free energy allows us to formulate equations (7.1) as a diffusion system with a positive semidefinite diffusion matrix. Indeed, we introduce the electrochemical potentials

$$\widetilde{\mu}_i = \frac{\partial h}{\partial u_i} = \log\frac{u_i}{u_0} - \log\frac{u_i^D}{u_0^D} + z_i(\Phi-\Phi^D), \quad i=1,\ldots,n,$$

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where $\partial h/\partial u_i$ denotes the variational derivative of h with respect to u_i (see [102, Lemma 7]) and $u_0^D = 1 - \sum_{i=1}^n u_i^D$. As in [102], we split the electrochemical potentials into the entropy variables w_i and the boundary contributions w_i^D by

$$w_i := \log\frac{u_i}{u_0} + z_i\Phi, \quad w_i^D := \log\frac{u_i^D}{u_0^D} + z_i\Phi^D. \tag{7.8}$$

Then equations (7.1) can be written as

$$\partial_t u_i - \operatorname{div}\sum_{j=1}^n B_{ij}(w,\Phi)\nabla w_j = r_i(u), \quad i = 1,\ldots,n, \tag{7.9}$$

where $B_{ij} = D_i u_i \delta_{ij}$ and $u_i = u_i(w,\Phi)$ is interpreted as a function of $w = (w_1,\ldots,w_n)$ and Φ according to

$$u_i(w,\Phi) = \frac{\exp(w_i - z_i\Phi)}{1 + \sum_{j=1}^n \exp(w_i - z_j\Phi)}. \tag{7.10}$$

The advantage of formulation (7.9) is that the new diffusion matrix $B = (B_{ij})$ is symmetric and positive semidefinite. Observe that system (7.9) is of degenerate type since $u_i = 0$ is possible, and $\det B = 0$ in this case. The formulation in terms of entropy variables has the further advantage that the ion concentrations u_i, defined by (7.10), are nonnegative and satisfy $\sum_{i=1}^n u_i \le 1$, thus fulfilling the saturation assumption.

7.1.3 Main results

We introduce the simplex $\mathcal{D} = \{u = (u_1,\ldots,u_n) \in (0,1)^n : \sum_{i=1}^n u_i < 1\}$ and set $\Omega_T = \Omega\times(0,T)$. The following hypotheses are imposed:

(H1) Domain: $\Omega \subset \mathbb{R}^d$ $(1 \le d \le 3)$ is a bounded Lipschitz domain with $\partial\Omega = \Gamma_D \cup \Gamma_N$, $\Gamma_D \cap \Gamma_N = \emptyset$, Γ_N is open in $\partial\Omega$, and $\operatorname{meas}(\Gamma_D) > 0$.

(H2) Data: $T > 0$, $D_i > 0$, $z_i \in \mathbb{R}$ for $i = 1,\ldots,n$, $f \in L^2(\Omega)$.

(H3) Initial data: $u^0 = (u_1^0,\ldots,u_n^0) \in L^1(\Omega;\mathbb{R}^n)$ satisfies $u^0(x) \in \overline{\mathcal{D}}$ for a.e. $x \in \Omega$.

(H4) Boundary data: $u^D = (u_1^D,\ldots,u_n^D) \in H^1(\Omega;\mathbb{R}^n)$ satisfies $u^D(x) \in \mathcal{D}$ for $x \in \Omega$, $\log u_0^D \in L^2(\Omega)$, and $\Phi^D \in H^2(\Omega)$ solves

$$\begin{aligned} &\lambda^2(\ell^2\Delta - 1)\Delta\Phi^D = f(x) \text{ in } \Omega, \\ &\nabla\Phi^D\cdot\nu = \nabla\Delta\Phi^D\cdot\nu = 0 \text{ on } \Gamma_N, \quad \Delta\Phi^D = 0 \text{ on } \Gamma_D. \end{aligned} \tag{7.11}$$

(H5) Reaction rates: $r_i \in C^0([0,1]^n;\mathbb{R})$ for $i = 1,\ldots,n$, and there exists $C_r > 0$ such that for all $u \in L^\infty(\Omega_T;\mathcal{D})$ and Φ, given by (7.2) and (7.5),

$$\int_\Omega \sum_{i=1}^n r_i(u)\frac{\partial h}{\partial u_i}dx \le C_r(1 + H(u)). \tag{7.12}$$

The restriction to three space dimensions in Hypothesis (H1) is not needed. It can be removed by regularizing the Poisson–Fermi equation (7.2) to ensure that $\Phi \in L^\infty(\Omega)$; see

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Remark 7.1 below. In Hypothesis (H4), it is sufficient to define the boundary data on Γ_D. We have extended them to Ω with the special extention of Φ^D, fulfilling the fourth-order elliptic problem (7.11). This extension is needed to be consistent with the definition of the free energy and the entropy variables; see [102, Lemma 7]. The bound in Hypothesis (H5) is needed to derive gradient bounds on the concentrations from the free energy inequality; see (7.16) below. Since $\partial h/\partial u_i$ contains the logarithm, $r_i(u)$ needs to cancel the singularity in $\partial h/\partial u_i$ at $u_i = 0$. It is sufficient to require Hypothesis (H5) for the logarithmic part of $\partial h/\partial u_i$. Indeed, since r_i is continuous, $r_i(u)$ is bounded for $u \in [0,1]^n$, and we infer from Poincaré's inequality that

$$\begin{aligned}\int_\Omega \sum_{i=1}^n r_i(u)(\Phi - \Phi^D)dx &\le C\|\Phi - \Phi^D\|_{L^1(\Omega)} \\ &\le C + C\|\nabla(\Phi - \Phi^D)\|^2_{l^2(\Omega)} \le C(1 + H(u)).\end{aligned}$$

Therefore, we need the integrated version (7.12) instead of the pointwise inequality assumed in [123, Sec. 1.4].

We introduce the test spaces

$$\begin{aligned}H^1_D(\Omega) &= \{v \in H^1(\Omega) : v = 0 \text{ on } \Gamma_D\}, \\ H^2_{D,N}(\Omega) &= \{v \in H^2(\Omega) : v = 0 \text{ on } \Gamma_D,\ \nabla v \cdot \nu = 0 \text{ on } \Gamma_N\}.\end{aligned}$$

Our first main result is as follows.

Theorem 7.1 (Global existence of solutions)**.** *Let Hypotheses (H1)–(H5) hold and let $T > 0$ be an arbitrary time end point. Then there exists a bounded weak solution $u_1, \dots, u_n$ to (7.1)–(7.5) satisfying $u_i(x,t) \in \overline{\mathcal{D}}$ for a.e. $(x,t) \in \Omega_T$, $i = 1, \dots, n$,*

$$\begin{aligned}&\sqrt{u_i} \in L^2(0,T;H^1(\Omega)), \quad u_i \in H^1(0,T;H^1_D(\Omega)') \cap C^0([0,T];L^2(\Omega)), \\ &\Phi \in L^2(0,T;H^2(\Omega)), \quad \log u_0 \in L^2(0,T;H^1(\Omega)),\end{aligned}$$

the weak formulation

$$\int_0^T \langle \partial_t u_i, \phi_i\rangle dt - \int_0^T \int_\Omega J_i \cdot \nabla\phi_i dxdt = \int_0^T \int_\Omega r_i(u)\phi_i dxdt, \tag{7.13}$$

$$\lambda^2 \int_0^T \int_\Omega (\ell^2 \Delta\Phi\Delta\theta + \nabla\Phi\cdot\nabla\theta)dxdt = \int_0^T \int_\Omega \Big(\sum_{i=1}^n z_i u_i + f\Big)\theta dxdt \tag{7.14}$$

for all $\phi_i \in L^2(0,T;H^1_D(\Omega))$ and $\theta \in L^2(0,T;H^2_{D,N}(\Omega))$, where J_i is given by (7.1) and $\langle\cdot,\cdot\rangle$ is the dual product between $H^1_D(\Omega)'$ and $H^1_D(\Omega)$. The initial conditions (7.3) are satisfied a.e. in Ω, and the Dirichlet boundary conditions are fulfilled in the sense of traces in $L^2(\Gamma_D)$. Furthermore, if $r_i(u) = 0$ for all $i = 1, \dots, n$ and the Dirichlet boundary conditions are in thermal equilibrium (e.g. $w_i^D := \log(u_i^D/u_0^D) + z_i\Phi^D = const.$ in Ω), the solution satisfies for $0 < s < t < T$ the free energy inequality

$$H(u(t)) + \int_s^t \int_\Omega \sum_{i=1}^n D_i u_i \left|\nabla\Big(\log\frac{u_i}{u_0} + z_i\Phi\Big)\right|^2 dxd\sigma \le H(u(s)). \tag{7.15}$$

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The energy dissipation is understood in the sense

$$u_i\left|\nabla\left(\log\frac{u_i}{u_0}+z_i\Phi\right)\right|^2 = \left|2\nabla\sqrt{u_i}-\sqrt{u_i}\nabla\log u_0+\sqrt{u_i}z_i\nabla\Phi\right|^2.$$

We stress the fact that the solutions are nonnegative, have an upper bound, and conserve mass in the absence of reactions. More precisely, the solution of Theorem 7.1 satisfies:

- $u_0(x,t),u_1(x,t),\ldots,u_n(x,t)\in[0,1]$ and $\sum_{i=0}^n u_i(x,t)=1$ for a.e. $x\in\Omega$, $t>0$;
- the solvent concentration u_0 is positive a.e. in $\Omega\times(0,\infty)$;
- if $r_i(u)=0$ then $\int_\Omega u_i(x,t)dx=\int_\Omega u_i^0(x)dx$ for $t>0$, $i=1,\ldots,n$.

The second point is a consequence of the integrability of $\log u_0$ ensured in Theorem 7.1.

The assumption of thermal equilibrium at the Dirichlet boundary, also required in [102], is needed to avoid expressions involving ∇w_i^D in the free energy inequality. Thus, this condition, together with vanishing reactions, is natural to obtain the monotonicity of the free energy. The hypothesis of vanishing reactions is only required to derive the entropy inequality (7.15) and can be weakened. In fact, we may allow for nonnegative and quasipositive reaction terms; see Remark 7.4 for details. In Remark 7.3, we explain how the uniqueness of weak solutions can be proved under restrictive conditions on the parameters. Moreover, we refer to Remark 7.2 for the extension of the free energy inequality (7.15) to the case of nonzero reaction terms r_i.

The proof of Theorem 7.1 is, similarly as in [102], based on an approximation procedure, where we regularize (7.9) by an implicit Euler approximation and higher-order terms in the entropy variables. The uniform estimates that are needed to perform the de-regularization limit are derived from the free energy inequality, which (without regularization) reads as

$$\frac{dH}{dt}+\int_\Omega\sum_{i=1}^n D_iu_i|\nabla w_i|^2dx\le\int_\Omega\sum_{i=1}^n r_i(u)\cdot\frac{\partial h}{\partial u_i}dx\le C_r(1+H(u)), \tag{7.16}$$

recalling definition (7.8) of w_i, and we can conclude by Gronwall's lemma. The free energy dissipation term on the left-hand side can be estimated from above by (see Lemma 7.3)

$$\int_\Omega u_i|\nabla w_i|^2dx\ge\frac12\int_\Omega(|\nabla\sqrt{u_i}|^2+|\nabla\log u_0|^2+|\nabla u_0|^2)dx-C\int_\Omega|\nabla\Phi|^2dx.$$

The last term is bounded by the electric energy part in $H(u)$, thus giving $H^1(\Omega)$ bounds for u_i for $i=0,\ldots,n$ and $\log u_0$. Compared to [102], we obtain gradient estimates for all the ion concentrations, but we have to deal with the singular term $\nabla\log u_0$ in (7.1). Moreover, compared to [100], where a similar Nernst–Planck system (with $\ell=0$) was investigated, we do not need any positivity condition on the initial solvent concentration.

While the existence proof relies on standard entropy methods, we need a new idea to prove the weak–strong uniqueness result. The uniqueness of *weak* solutions is an intricate problem. A uniqueness result for (7.1) with the fluxes (7.6) was shown in [102] for the case $D_i=D$ and $z_i=z$ for all i. In this simplified situation, the solvent concentration solves a Poisson–Nernst–Planck system for which the uniqueness of bounded weak solutions can be proved by a combination of $L^2(\Omega)$ estimates and Gajewski's entropy method. This strategy cannot be used for our system; see Remark 7.3 in Section 7.4. In fact, we need the $H^{-1}(\Omega)$ method and

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a strong regularity condition for $\nabla\Phi$, which restricts the geometry of the Dirichlet–Neumann boundary conditions. Therefore, we do not aim to prove the uniqueness of weak solutions but the weak–strong uniqueness property only, which has the advantage that we may allow for different coefficients D_i and z_i. The weak–strong uniqueness property means that any weak solution to system (7.1)–(7.5) coincides with a strong solution emanating from the same initial conditions as long as the latter exists. We say that $(\bar{u},\bar{\Phi})$ is a *strong solution* to (7.1)–(7.5) if it is a weak solution and

$$\bar{u}_i \geq c > 0 \text{ in } \Omega_T, \quad \bar{u}_i,\ \Phi \in L^\infty(0,T;W^{1,\infty}(\Omega)) \quad \text{for all } i=1,\ldots,n.$$

Our second main result is contained in the following theorem.

Theorem 7.2 (Weak–strong uniqueness)**.** *Let the Dirichlet boundary data be in thermal equilibrium in the sense of Theorem 7.1 and let $r_i = 0$ for $i = 1,\ldots,n$. Let (u,Φ) be a weak solution and $(\bar{u},\bar{\Phi})$ be a strong solution to* (7.1)–(7.5)*. Then $u(x,t) = \bar{u}(x,t)$, $\Phi(x,t) = \bar{\Phi}(x,t)$ for a.e. $x \in \Omega$ and $t \in (0,T)$.*

If the reaction rates are Lipschitz continuous and satisfy some sign conditions, Theorem 7.2 still holds. An exhaustive discussion on this point can be found in Remark 7.4. The condition that the Dirichlet boundary data are in thermal equilibrium is actually not needed, since in contrast to (7.15), the terms involving ∇w_i^D cancel out in the computations for the relative free energy

$$\begin{aligned}
H(u,\Phi|\bar{u},\bar{\Phi}) &= \int_\Omega (h_1(u|\bar{u}) + h_2(\Phi|\bar{\Phi}))dx, \quad \text{where} \\
h_1(u|\bar{u}) &= \sum_{i=0}^n \left(u_i \log\frac{u_i}{\bar{u}_i} - (u_i-\bar{u}_i)\right), \\
h_2(\Phi|\bar{\Phi}) &= \frac{\lambda^2}{2}(|\nabla(\Phi-\bar{\Phi})|^2 + \ell^2|\Delta(\Phi-\bar{\Phi})|^2),
\end{aligned}$$

which can be identified as the Bregman distance of the free energy. The key idea of the proof of Theorem 7.2 is to consider the solvent concentration u_0 as an independent variable and to formulate the parabolic equations for the extended concentration vector $U = (u_0,u_1,\ldots,u_n)$, leading to

$$\partial_t u_i = \operatorname{div}\sum_{j=0}^n (A_{ij}(U)\nabla\log u_j + Q_{ij}(U)\nabla\Phi), \quad i=0,\ldots,n,$$

where $A_{ij}(U)$ and $Q_{ij}(U)$ depend linearly on U and

$$\begin{aligned}
A = (A_{ij}) &= \begin{pmatrix} \sum_{i=1}^n D_i u_i & -D_1u_1 & \cdots & -D_nu_n \\ -D_1u_1 & D_1u_1 & & 0 \\ \vdots & 0 & \ddots & 0 \\ -D_nu_n & 0 & & D_nu_n \end{pmatrix}, \\
Q = (Q_{ij}) &= \begin{pmatrix} -\sum_{i=1}^n D_i z_i u_i & 0 & \cdots & 0 \\ 0 & D_1z_1u_1 & & 0 \\ \vdots & 0 & \ddots & 0 \\ 0 & 0 & & D_nz_nu_n \end{pmatrix},
\end{aligned} \tag{7.17}$$

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setting $z_0 := 0$. The matrix $(A_{ij}/\sqrt{u_i u_j}) \in \mathbb{R}^{(n+1)\times(n+1)}$ is positive definite only on the subspace $L = \{y \in \mathbb{R}^{n+1} : \sum_{i=0}^n \sqrt{u_i} y_i = 0\}$; see Lemma 7.6. This situation is similar to the Maxwell–Stefan system; see [119]. The time derivative of the relative free energy equals

$$\frac{dH}{dt}(u,\Phi|\bar{u},\bar{\Phi}) = K_1 + K_2, \quad \text{where } K_1 = -\int_\Omega \sum_{j=0}^n A_{ij}\nabla\log\frac{u_i}{\bar{u}_i}\cdot\nabla\log\frac{u_j}{\bar{u}_j}dx,$$

and K_2 contains differences like $U_i - \bar{U}_i$ and $\Phi - \bar{\Phi}$. The properties of the matrices (A_{ij}) and (Q_{ij}) imply that

$$K_1 \le -\min_{i=1,\ldots,n} D_i \int_\Omega \left(\frac{1}{u_0}|(P_L Y)_0|^2 + \sum_{i=1}^n |(P_L Y)_i|^2\right)dx,$$

where P_L is the projection on L and $Y_i = \sqrt{u_i}\nabla\log(u_i/\bar{u}_i)$, as well as for any $\delta > 0$,

$$\begin{aligned} K_2 &\le \delta\int_\Omega \left(\frac{1}{u_0}|(P_L Y)_0|^2 + \sum_{i=1}^n |(P_L Y)_i|^2\right)dx \\ &\quad + C(\delta)\left(\sum_{i=0}^n \|u_i - \bar{u}_i\|_{L^2(\Omega)}^2 + \|\nabla(\Phi-\bar{\Phi})\|_{L^2(\Omega)}^2\right). \end{aligned}$$

Consequently, choosing $\delta > 0$ sufficiently small,

$$\frac{dH}{dt}(u,\Phi|\bar{u},\bar{\Phi}) \le C\left(\sum_{i=0}^n \|u_i - \bar{u}_i\|_{L^2(\Omega)}^2 + \|\nabla(\Phi-\bar{\Phi})\|_{L^2(\Omega)}^2\right) \le CH(u,\Phi|\bar{u},\bar{\Phi})$$

for some constant $C > 0$. Since the initial data of u and $\bar{u}$ coincide, we have $H((u,\Phi)(t)|(\bar{u},\bar{\Phi})(t)) = 0$ and finally $u(t) = \bar{u}(t)$ and $\Phi(t) = \bar{\Phi}(t)$ for all $t > 0$. The idea to consider the parabolic system for the extended solution vector $U = (u_0,\ldots,u_n)$ instead of $u = (u_1,\ldots,u_n)$ is the main novelty of this paper. The Maxwell–Stefan equations can also be written as an extended system for U [119], but we are not aware of further volume-filling models with such a property. The understanding of volume-filling systems and mobility matrices with nontrivial kernels is a current field of research.

The article is organized as follows. The proof of Theorem 7.1 is presented in Section 7.2, while Section 7.3 contains the proof of Theorem 7.2. We make some remarks on the uniqueness of solutions in Section 7.4.

7.2 Proof of Theorem 7.1

We assume throughout this section that Hypotheses (H1)–(H5) hold.

7.2.1 Solution of an approximate system

We define the approximate problem by the implicit Euler scheme and using a higher-order regularization. Let $T > 0$, $N \in \mathbb{N}$, $\tau = T/N$, and $m \in \mathbb{N}$ with $m > d/2$. We assume that $u_i^D \ge \eta > 0$ for $i = 0,\ldots,n$. Then $w_i^D = \log(u_i^D/u_0^D) + z_i\Phi^D \in H^1(\Omega;\mathbb{R}^n)\cap L^\infty(\Omega;\mathbb{R}^n)$. Since the entropy variables are not needed in the weak formulation (7.13)–(7.14), we can pass to the limit $\eta \to 0$ at the end of the proof, thus requiring only $u_i^D > 0$. Let $k \ge 1$ and

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let $u^{k-1} - u^D \in H^1_D(\Omega;\mathbb{R}^n) \cap L^\infty(\Omega;\mathbb{R}^n)$ and $\Phi^{k-1} - \Phi^D \in H^2_{D,N}(\Omega)$ be given. If $k = 1$, $\Phi^0 \in H^2(\Omega)$ is the unique solution to (7.2) with u_j^0 instead of u_j on the right-hand side and satisfying the corresponding boundary conditions in (7.4)–(7.5). We wish to find a solution $v^k \in X := H^m(\Omega;\mathbb{R}^n) \cap H^1_D(\Omega;\mathbb{R}^n)$ and $\Phi^k - \Phi^D \in H^2_{D,N}(\Omega)$ to

$$\begin{aligned}\frac{1}{\tau}\int_\Omega (u^k - u^{k-1})\cdot\phi dx + \int_\Omega \nabla\phi : B(v^k + w^D, \Phi^k)\nabla(v^k + w^D)dx \\ + \varepsilon\int_\Omega \Big(\sum_{|\alpha|=m} D^\alpha v^k \cdot D^\alpha\phi + v^k\cdot\phi\Big)dx = \int_\Omega r(u^k)\cdot\phi dx,\end{aligned} \tag{7.18}$$

$$\lambda^2\int_\Omega (\ell^2\Delta\Phi^k\Delta\theta + \nabla\Phi^k\cdot\nabla\theta)dx = \int_\Omega\Big(\sum_{i=1}^n z_i u_i^k + f\Big)\theta dx \tag{7.19}$$

for all $\phi \in X$ and $\theta \in H^2_{D,N}(\Omega)$. Here, we have set $u^k := u(v^k + w^D, \Phi^k)$, where $u(w,\Phi)$ is defined by (7.10), $B_{ij}(w,\Phi) = D_i u_i(w,\Phi)\delta_{ij}$, $r(u) = (r_1(u),\ldots,r_n(u))$, and $D^\alpha = \partial^{|\alpha|}/\partial x_1^{\alpha_1}\cdots\partial x_d^{\alpha_d}$ is a partial derivative of order $|\alpha| = \alpha_1 + \cdots + \alpha_d$. Thanks to the higher-order regularization, we obtain approximate solutions $w^k := v^k + w^D \in H^m(\Omega;\mathbb{R}^n) \hookrightarrow L^\infty(\Omega;\mathbb{R}^n)$. Moreover, since $d \le 3$, we have $\Phi^k \in H^2(\Omega) \hookrightarrow L^\infty(\Omega)$. Hence, $u_i(w^k,\Phi^k)$ is well defined and integrable.

Remark 7.1. Adding a higher-order regularization to the Poisson–Fermi equation (7.19), we may obtain $\Phi^k \in L^\infty(\Omega)$ by a Sobolev embedding similarly as for w^k. This allows us to remove the restriction $d \le 3$ in Hypothesis (H1). □

Lemma 7.1. *There exists a unique solution $v^k \in H^m(\Omega;\mathbb{R}^n) \cap H^1_D(\Omega;\mathbb{R}^n)$ and $\Phi^k - \Phi^D \in H^2_{D,N}(\Omega)$ to* (7.18)–(7.19).

Proof. The proof is similar to that one of Lemma 5 in [102], therefore we give a sketch only. Let $y \in L^\infty(\Omega;\mathbb{R}^n)$ and $\sigma \in [0,1]$. Let $\Phi^k \in H^2(\Omega)$ be the unique solution to

$$\lambda^2(\ell^2\Delta - 1)\Delta\Phi^k = \sum_{i=1}^n z_i u_i(y + w^D, \Phi^k) + f(x) \quad \text{in } \Omega$$

subject to the boundary conditions (7.5). This follows from the fact that the function $(x,\Phi) \mapsto u_i(w(x),\Phi)$ is bounded with values in $(0,1)$ and Lipschitz continuous in Φ. By the Lax–Milgram lemma, there exists a unique solution $v \in X$ to the linear problem

$$\begin{aligned}\varepsilon\int_\Omega\Big(\sum_{|\alpha|=m} D^\alpha v\cdot D^\alpha\phi + v\cdot\phi\Big)ds + \int_\Omega \nabla\phi : B(y + w^D,\Phi^k)\nabla v dx \\ = \delta\int_\Omega r(u(y + w^D,\Phi^k))\cdot\phi dx - \delta\int_\Omega \nabla\phi : B(y + w^D,\Phi^k)\nabla w^D dx \\ - \frac{\delta}{\tau}\int_\Omega (u(y + w^D,\Phi^k) - u^{k-1})\cdot\phi dx.\end{aligned} \tag{7.20}$$

Indeed, as B is positive semidefinite, the left-hand side is coercive in $H^m(\Omega;\mathbb{R}^n)$.

This defines the fixed-point operator $S : L^\infty(\Omega;\mathbb{R}^n)\times[0,1] \to L^\infty(\Omega;\mathbb{R}^n)$, $S(y,\delta) = v$. Then $S(y,0) = 0$, S is continuous and, because of the compact embedding $H^m(\Omega;\mathbb{R}^n) \hookrightarrow L^\infty(\Omega;\mathbb{R}^n)$, also compact. Using $\phi = v$ as a test function in (7.20), standard estimates lead to $\varepsilon\|v\|^2_{H^m(\Omega)} \le C(\tau)\|v\|_{H^m(\Omega)}$, giving a bound for v in $H^m(\Omega;\mathbb{R}^n)$ uniform in δ. Hence, all

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fixed points of $S(\cdot,\delta)$ are uniformly bounded in $L^\infty(\Omega;\mathbb{R}^n)$. We infer from the Leray–Schauder fixed-point theorem that there exists $v^k \in X$ such that $S(v^k,1) = v^k$. Then (v^k,Φ^k) is a solution to (7.18)–(7.19). □

7.2.2 Uniform estimates

We deduce estimates uniform in (ε,τ) from the following free energy inequality.

Lemma 7.2 (Discrete free energy inequality)**.** *Let (v^k,Φ^k) be a solution to* (7.18)–(7.19) *and set $w^k := v^k + w^D$ and $u^k := u(w^k,\Phi^k)$. Then*

$$H(u^k) - H(u^{k-1}) + \frac{\tau}{2}\int_\Omega \sum_{i=1}^n D_i u_i^k |\nabla w_i^k|^2 dx + \varepsilon\tau\|w^k - w^D\|_{H^m(\Omega)}^2 \tag{7.21}$$
$$\le \tau C_r(1+H(u^k)) + \frac{\tau}{2}\int_\Omega \sum_{i=1}^n D_i|\nabla w_i^D|^2 dx,$$

where H is defined in (7.7) *and $C_r > 0$ is introduced in Hypothesis (H5).*

Proof. We choose $\phi = \tau v^k = \tau(w^k - w^D) \in X$ as a test function in (7.18). Using the generalized Poincaré inequality to estimate the ε-regularization and Hypothesis (H5) to estimate the reaction rates, we find that

$$\int_\Omega (u^k - u^{k-1})\cdot(w^k - w^D)dx + \tau\int_\Omega \nabla(w^k - w^D) : B(w^k,\Phi^k)\nabla w^k dx$$
$$+ \varepsilon\tau C\|w^k - w^D\|_{H^m(\Omega)}^2 \le \tau C_r(1+H(u^k)).$$

It follows from the convexity of the function $g(u) = \sum_{i=0}^n \int_{u_i^D}^{u_i} \log(s/u_i^D)ds$ and the Poisson–Fermi equation (7.2) as in [102, Section 2] that

$$\int_\Omega (u^k - u^{k-1})\cdot(w^k - w^D)dx = \int_\Omega \sum_{i=1}^n (u_i^k - u_i^{k-1})\bigg(\log\frac{u_i^k}{u_0^k} - \log\frac{u_i^D}{u_0^D}\bigg)dx$$
$$+ \int_\Omega \sum_{i=1}^n z_i(u_i^k - u_i^{k-1})(\Phi^k - \Phi^D)dx$$
$$\ge \int_\Omega (g(u^k) - g(u^{k-1}))dx + \frac{\lambda^2}{2}\int_\Omega (\ell^2|\Delta(\Phi^k - \Phi^D)|^2 + |\nabla(\Phi^k - \Phi^D)|^2)dx$$
$$- \frac{\lambda^2}{2}\int_\Omega (\ell^2|\Delta(\Phi^{k-1} - \Phi^D)|^2 + |\nabla(\Phi^{k-1} - \Phi^D)|^2)dx = H(u^k) - H(u^{k-1}).$$

Inserting the definition $B_{ij}(w^k,\Phi^k) = D_i u_i^k \delta_{ij}$, we infer from Young's inequality that

$$\nabla(w^k - w^D) : B(w^k,\Phi^k)\nabla w^k = \sum_{i=1}^n D_i u_i^k \nabla(w_i^k - w_i^D)\cdot\nabla w_i^k$$
$$\ge \frac{1}{2}\sum_{i=1}^n D_i u_i^k |\nabla w_i^k|^2 - \frac{1}{2}\sum_{i=1}^n D_i u_i^k |\nabla w_i^D|^2.$$

Collecting these estimates and observing that $u_i^k \le 1$ concludes the proof. □

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We sum (7.21) over $k = 1, \ldots, j$,

$$(1-\tau C_r)H(u^j) + \frac{\tau}{2}\sum_{k=1}^j\int_\Omega\sum_{i=1}^n D_i u_i^k|\nabla w_i^k|^2 dx + \varepsilon\tau\sum_{k=1}^j \|w^k - w^D\|_{H^m(\Omega)}^2$$
$$\le \tau C_r\sum_{k=1}^{j-1} H(u^k) + H(u^0) + j\tau C_r + \frac{\tau}{2}\sum_{k=1}^j\int_\Omega\sum_{i=1}^n D_i|\nabla w_i^D|^2 dx,$$

and, assuming $\tau < 1/C_r$, apply the discrete Gronwall inequality [67]:

$$H(u^j) + \frac{\tau}{2}\Big(\min_{i=1,\ldots,n} D_i\Big)\sum_{k=1}^j\int_\Omega\sum_{i=1}^n u_i^k|\nabla w_i^k|^2 dx + \varepsilon\tau\sum_{k=1}^j\|w^k - w^D\|_{H^m(\Omega)}^2 \le C(T),$$

where $C(T) > 0$ does not depend on (ε, τ). We still need to bound the second term on the left-hand side from below.

Lemma 7.3. *It holds that*

$$\sum_{k=1}^N\tau\int_\Omega\sum_{i=1}^n u_i^k|\nabla w_i^k|^2 dx \ge \frac{1}{2}\sum_{k=1}^N\tau\int_\Omega\Big(\sum_{i=1}^n|\nabla(u_i^k)^{1/2}|^2 + |\nabla\log u_0^k|^2 + |\nabla u_0^k|^2\Big)dx$$
$$- C\sum_{k=1}^N\tau\int_\Omega|\nabla\Phi^k|^2 dx,$$

where $C > 0$ depends on (D_i) and (z_i).

Proof. We infer from Young's inequality and the bound $u_i^k \le 1$ that

$$u_i^k|\nabla w_i^k|^2 = u_i^k\left|\nabla\log\frac{u_i^k}{u_0^k} + z_i\nabla\Phi^k\right|^2 \ge \frac{1}{2}u_i^k\left|\nabla\log\frac{u_i^k}{u_0^k}\right|^2 - |z_i\nabla\Phi^k|^2.$$

The first term on the right-hand side is rewritten as

$$\frac{1}{2}u_i^k\left|\nabla\log\frac{u_i^k}{u_0^k}\right|^2 = \frac{1}{2}\sum_{i=1}^n\frac{|\nabla u_i^k|^2}{u_i^k} + \frac{1}{2}\sum_{i=1}^n u_i^k|\nabla\log u_0^k|^2 - \sum_{i=1}^n\nabla u_i^k\cdot\nabla\log u_0^k$$
$$= \frac{1}{2}\sum_{i=1}^n\frac{|\nabla u_i^k|^2}{u_i^k} + \frac{1}{2}(1-u_0^k)|\nabla\log u_0^k|^2 - \nabla(1-u_0^k)\cdot\nabla\log u_0^k$$
$$= \frac{1}{2}\sum_{i=1}^n\frac{|\nabla u_i^k|^2}{u_i^k} + \frac{1}{2}|\nabla\log u_0^k|^2 + \frac{|\nabla u_0^k|^2}{2u_0^k}$$
$$\ge 2\sum_{i=1}^n|\nabla(u_i^k)^{1/2}|^2 + \frac{1}{2}|\nabla\log u_0^k|^2 + \frac{1}{2}|\nabla u_0^k|^2,$$

using $u_0^k \le 1$ in the last step. □

Since the free energy is bounded from below, we conclude the following uniform bounds.

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Lemma 7.4. *There exists $C>0$ not depending on (ε,τ) such that for $i=1,\ldots,n$,*

$$\sum_{k=1}^N \tau(\|(u_i^k)^{1/2}\|_{H^1(\Omega)}^2+\|u_i^k\|_{H^1(\Omega)}^2+\|u_0^k\|_{H^1(\Omega)}^2+\|\log u_0^k\|_{H^1(\Omega)}^2)\le C,$$

$$\varepsilon\sum_{k=1}^N \tau\|w_i^k\|_{H^m(\Omega)}^2+\sum_{k=1}^N\tau\|\Phi^k\|_{H^2(\Omega)}^2\le C.$$

Proof. The inequality

$$\|\nabla u_i^k\|_{L^2(\Omega)}\le 2\|(u_i^k)^{1/2}\|_{L^\infty(\Omega)}\|\nabla(u_i^k)^{1/2}\|_{L^2(\Omega)}\le 2\|\nabla(u_i^k)^{1/2}\|_{L^2(\Omega)}$$

shows that $\sum_{k=1}^N\tau\|\nabla u_i^k\|_{L^2(\Omega)}^2\le C$. The $H^2(\Omega)$ bound for Φ^k follows immediately from the Poisson–Fermi equation as its right-hand side is bounded in $L^2(\Omega)$. The $H^1(\Omega)$ bound for $\log u_0^k$ is a consequence of the $L^2(\Omega)$ bound for $\nabla\log u_0^k$ and the Poincaré inequality, using the fact that $\log u_0^D\in L^2(\Omega)$ by Hypothesis (H4). □

7.2.3 Limit $(\varepsilon,\tau)\to 0$

We introduce the piecewise constant in time functions $u_i^{(\tau)}(x,t)=u_i^k(x)$, $w_i^{(\tau)}(x,t)=w_i^k(x)$, and $\Phi^{(\tau)}(x,t)=\Phi^k(x)$ for $x\in\Omega$, $t\in((k-1)\tau,k\tau]$. At time $t=0$, we set $w^{(\tau)}(\cdot,0)=h'(u^0)$ and $u_i^{(\tau)}(\cdot,0)=u_i^0$. Furthermore, we introduce the shift operator $(\sigma_\tau u^{(\tau)})(\cdot,t)=u^{k-1}$ for $t\in((k-1)\tau,k\tau]$. Then, summing (7.18)–(7.19) over $k=1,\ldots,N$, we see that $(u^{(\tau)},\Phi^{(\tau)})$ solves

$$\begin{aligned}\frac{1}{\tau}\int_0^T\int_\Omega(u^{(\tau)}-\sigma_\tau u^{(\tau)})\cdot\phi dxdt+\int_0^T\int_\Omega\nabla\phi:B(w^{(\tau)},\Phi^{(\tau)})\nabla w^{(\tau)}dxdt \\ +\varepsilon\int_0^T\int_\Omega\Big(\sum_{|\alpha|=m}D^\alpha(w^{(\tau)}-w^D)\cdot D^\alpha\phi+(w^{(\tau)}-w^D)\cdot\phi\Big)dxdt \\ =\int_0^T\int_\Omega r(u^{(\tau)})\cdot\phi dxdt,\end{aligned}\tag{7.22}$$

$$\lambda^2\int_0^T\int_\Omega(\ell^2\Delta\Phi^{(\tau)}\Delta\theta+\nabla\Phi^{(\tau)}\cdot\nabla\theta)dxdt=\int_0^T\int_\Omega\Big(\sum_{i=1}^n z_iu_i^{(\tau)}+f\Big)\theta dxdt\tag{7.23}$$

for piecewise constant in time functions $\phi:(0,T)\to X$ and $\theta:(0,T)\to H^2_{D,N}(\Omega)$, recalling that $X=H^m(\Omega;\mathbb{R}^n)\cap H^1_D(\Omega;\mathbb{R}^n)$. Lemma 7.4 and the $L^\infty(\Omega)$ estimate of u_i^k imply the uniform bounds

$$\|(u_i^{(\tau)})^{1/2}\|_{L^2(0,T;H^1(\Omega))}+\|u_i^{(\tau)}\|_{L^2(0,T;H^1(\Omega))}+\|u_i^{(\tau)}\|_{L^\infty(\Omega_T)}\le C,\tag{7.24}$$

$$\|u_0^{(\tau)}\|_{L^2(0,T;H^1(\Omega))}+\|u_0^{(\tau)}\|_{L^\infty(\Omega_T)}+\|\log u_0^{(\tau)}\|_{L^2(0,T;H^1(\Omega))}\le C,\tag{7.25}$$

$$\sqrt{\varepsilon}\|w_i^{(\tau)}\|_{L^2(0,T;H^m(\Omega))}+\|\Phi^{(\tau)}\|_{L^2(0,T;H^2(\Omega))}\le C,\tag{7.26}$$

where $i=1,\ldots,n$. We also need a uniform bound for the discrete time derivative.

Lemma 7.5. *There exists a constant $C>0$ independent of (ε,τ) such that for all $i=1,\ldots,n$,*

$$\tau^{-1}\|u_i^{(\tau)}-\sigma_\tau u_i^{(\tau)}\|_{L^2(0,T;X')}+\tau^{-1}\|u_0^{(\tau)}-\sigma_\tau u_0^{(\tau)}\|_{L^2(0,T;X')}\le C.$$

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Proof. Let $\phi : (0,T) \to X$ be piecewise constant. Since

$$\int_0^T \int_\Omega \nabla\phi : B(u^{(\tau)}, \Phi^{(\tau)}) \nabla w^{(\tau)} dxdt$$
$$= \sum_{i=1}^n D_i \int_0^T \int_\Omega (\nabla u_i^{(\tau)} - u_i^{(\tau)} \nabla \log u_0^{(\tau)} + z_i u_i^{(\tau)} \nabla \Phi^{(\tau)}) \cdot \nabla \phi_i dxdt,$$

we find that

$$\begin{aligned}
\frac{1}{\tau}\left| \int_0^T \int_\Omega (u_i^{(\tau)} - \sigma_\tau u_i^{(\tau)}) \phi_i dxdt \right| &\le \varepsilon \|w_i^{(\tau)} - w_i^D\|_{L^2(0,T;H^m(\Omega))} \|\phi_i\|_{L^2(0,T;H^m(\Omega))} \\
&\quad + C(\|\nabla u_i^{(\tau)}\|_{L^2(\Omega_T)} + \|\nabla \log u_0^{(\tau)}\|_{L^2(\Omega_T)} + \|\nabla \Phi^{(\tau)}\|_{L^2(\Omega_T)}) \|\nabla \phi_i\|_{L^2(\Omega_T)} \\
&\quad + \|r_i(u^{(\tau)})\|_{L^2(\Omega_T)} \|\phi_i\|_{L^2(\Omega_T)} \\
&\le C \|\phi_i\|_{L^2(0,T;H^m(\Omega))}.
\end{aligned}$$

By a density argument, this inequality holds for all $\phi_i \in L^2(0,T;X)$, showing the desired bound for the discrete time derivative of $u_i^{(\tau)}$. Summing the bounds over $i = 1, \dots, n$ yields the bound for $u_0^{(\tau)}$. □

Estimates (7.24)–(7.25) and Lemma 7.5 allow us to apply the Aubin–Lions lemma in the version of [80] to conclude the existence of a subsequence, which is not relabeled, such that for $i = 1, \dots, n$, as $(\varepsilon, \tau) \to 0$,

$$u_i^{(\tau)} \to u_i, \quad u_0^{(\tau)} \to u_0 \quad \text{strongly in } L^2(\Omega_T).$$

In view of the uniform $L^\infty(\Omega_T)$ bound for $u_i^{(\tau)}$ and $u_0^{(\tau)}$, these convergences hold in $L^p(\Omega_T)$ for all $p < \infty$. Moreover, by (7.26) and Lemma 7.5, up to a subsequence,

$$\begin{aligned}
\varepsilon w_i^{(\tau)} &\to 0 \quad \text{strongly in } L^2(0,T;H^m(\Omega)), \\
\Phi^{(\tau)} &\rightharpoonup \Phi \quad \text{weakly in } L^2(0,T;H^2(\Omega)), \\
\tau^{-1}(u_i^{(\tau)} - \sigma_\tau u_i^{(\tau)}) &\rightharpoonup \partial_t u_i \quad \text{weakly in } L^2(0,T;X'),\ i = 1, \dots, n.
\end{aligned}$$

We claim that $\nabla \log u_0^{(\tau)} \rightharpoonup \nabla \log u_0$ weakly in $L^2(\Omega_T)$. It follows from (7.25) that (for a subsequence) $\nabla \log u_0^{(\tau)} \rightharpoonup v$ weakly in $L^2(\Omega_T)$. We need to identify $v = \nabla \log u_0$. We know that (again for a subsequence) $u_0^{(\tau)} \to u_0$ a.e. in Ω_T. Therefore $\log u_0^{(\tau)} \to \log u_0$ a.e. in Ω_T, since u_0 can vanish at most on a set of measure zero. The $L^2(\Omega_T)$ bound for $\log u_0^{(\tau)}$ shows that $\log u_0^{(\tau)} \to \log u_0$ strongly in $L^2(\Omega_T)$. Hence, we conclude that $v = \nabla \log u_0$, proving the claim.

These convergences are sufficient to pass to the limit $(\varepsilon, \tau) \to 0$ in (7.22)–(7.23) to find that (u, Φ) solves (7.13)–(7.14) for smooth test functions. By a density argument, we may choose test functions from $L^2(0,T;H_D^1(\Omega))$ and $L^2(0,T;H_{D,N}^2(\Omega))$, respectively. The validity of the initial and Dirichlet boundary conditions is shown as in [102]. Estimates similar as in the proof of Lemma 7.5 (with $\varepsilon = 0$) show that $\partial_t u_i \in L^2(0,T;H_D^1(\Omega)')$ for $i = 1, \dots, n$. Then we conclude from $u_i \in L^2(0,T;H^1(\Omega))$ that $u_i \in C^0([0,T];L^2(\Omega))$. Thus, the initial datum is satisfied in the sense of $L^2(\Omega)$.

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It remains to verify the free energy inequality (7.15) under the assumptions $r_i(u) = 0$ and $\log(u_i^D/u_0^D) + z_i\Phi^D = c_i \in \mathbb{R}$ for $i = 1, \ldots, n$. By definition of w_i^D, this implies that $\nabla w_i^D = 0$. Then (7.21) becomes

$$H(u^k) - H(u^{k-1}) + \tau \int_\Omega \sum_{i=1}^n D_i u_i^k \left|\nabla\left(\log\frac{u_i^k}{u_0^k} + z_i\Phi^k\right)\right|^2 dx + \varepsilon\tau\|w^k - w^D\|_{H^m(\Omega)}^2 \le 0.$$

A summation over $k = j, \ldots, J$ gives

$$\begin{aligned} H(u^{(\tau)}(t)) - H(u^{(\tau)}(s)) + \int_s^t \int_\Omega \sum_{i=1}^n D_i u_i^{(\tau)} \left|\nabla\left(\log\frac{u_i^{(\tau)}}{u_0^{(\tau)}} + z_i\Phi^{(\tau)}\right)\right|^2 dx d\sigma \\ + \varepsilon\int_s^t \|w^{(\tau)} - w^D\|_{H^m(\Omega)}^2 d\sigma \le 0, \end{aligned} \tag{7.27}$$

where $s \in ((j-1)\tau, j\tau]$ and $t \in ((J-1)\tau, J\tau]$. We wish to pass to the limit $(\varepsilon, \tau) \to 0$ in this inequality.

The a.e. convergence of $u_i^{(\tau)}$ implies that $H(u^{(\tau)}(t)) \to H(u(t))$ for a.e. $t \in (0,T)$ and, since $u_i \in C^0([0,T]; L^2(\Omega))$, this convergence holds in fact for all $t \in [0,T]$. Moreover, $\varepsilon(w^{(\tau)} - w^D) \to 0$ strongly $L^2(0,T; H^m(\Omega))$. It follows from the strong convergence of $u_i^{(\tau)}$ in $L^2(\Omega_T)$ that $(u_i^{(\tau)})^{1/2} \to \sqrt{u_i}$ strongly in $L^4(\Omega_T)$. Hence, together with the weak convergence of $\nabla\Phi^{(\tau)}$ in $L^2(\Omega_T)$, we have

$$(u_i^{(\tau)})^{1/2}\nabla\Phi^{(\tau)} \rightharpoonup \sqrt{u_i}\nabla\Phi \quad \text{weakly in } L^{4/3}(\Omega_T).$$

Furthermore, since $\nabla \log u_0^{(\tau)} \rightharpoonup \nabla \log u_0$ weakly in $L^2(\Omega_T)$,

$$\begin{aligned} (u_i^{(\tau)})^{1/2}\nabla\log\frac{u_i^{(\tau)}}{u_0^{(\tau)}} &= 2\nabla(u_i^{(\tau)})^{1/2} - (u_i^{(\tau)})^{1/2}\nabla\log u_0^{(\tau)} \\ &\rightharpoonup 2\nabla\sqrt{u_i} - \sqrt{u_i}\nabla\log u_0 =: \sqrt{u_i}\nabla\log\frac{u_i}{u_0} \quad \text{weakly in } L^{4/3}(\Omega_T). \end{aligned} \tag{7.28}$$

On the other hand, the sequences $\nabla(u_i^{(\tau)})^{1/2}$ and $(u_i^{(\tau)})^{1/2}\nabla\log u_0^{(\tau)}$ are uniformly bounded in $L^2(\Omega_T)$. Therefore, convergence (7.28) also holds in $L^2(\Omega_T)$. Consequently,

$$\begin{aligned} \int_\Omega u_i\left|\nabla\left(\log\frac{u_i}{u_0} + z_i\Phi\right)\right|^2 dx &= \int_\Omega \left|2\nabla\sqrt{u_i} - \sqrt{u_i}\nabla\log u_0 + \sqrt{u_i}z_i\nabla\Phi\right|^2 dx \\ &\le \liminf_{(\varepsilon,\tau)\to 0} \int_\Omega u_i^{(\tau)}\left|\nabla\left(\log\frac{u_i^{(\tau)}}{u_0^{(\tau)}} + z_i\Phi^{(\tau)}\right)\right|^2 dx. \end{aligned}$$

Then (7.15) follows after passing to the limit inferior $(\varepsilon, \tau) \to 0$ in (7.27), completing the proof of Theorem 7.1.

Remark 7.2. Let the reaction rates $r_i : \overline{\mathcal{D}} \to \mathbb{R}$ be Lipschitz continuous and quasi-positive, i.e. $r_i(u) \ge 0$ for all $u \in \mathcal{D}$ with $u_i = 0$. We assume that the total reaction rate is nonnegative,

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i.e. $\sum_{i=1}^n r_i(u) \le 0$ for all $u \in \mathcal{D}$, and that $r_i(u)\log u_i = 0$ if $u_i = 0$. This assumption is only needed to derive the free energy inequality. We claim that it becomes

$$H(u(t)) + \int_s^t \int_\Omega \sum_{i=1}^n D_i u_i |\nabla w_i|^2 dx d\sigma \le H(u(s)) + \int_s^t \int_\Omega \sum_{i=1}^n r_i(u)(w_i - w_i^D) dx d\sigma. \quad (7.29)$$

This inequality follows from (7.27) after including the reaction rates and taking the limit (ε,τ) in

$$\begin{aligned}\int_s^t \int_\Omega \sum_{i=1}^n & r_i(u^{(\tau)})(w_i^{(\tau)} - w_i^D) dx d\sigma \\ &= \int_s^t \int_\Omega \sum_{i=1}^n r_i(u^{(\tau)})(\log u_i^{(\tau)} - \log u_0^{(\tau)} + z_i\Phi^{(\tau)} - w_i^D) dx d\sigma.\end{aligned}$$

Indeed, the strong limit $u_i^{(\tau)} \to u_i$ in $L^2(\Omega_T)$ shows that $r_i(u^{(\tau)})w_i^D \to r_i(u)w_i^D$ strongly in $L^1(\Omega_T)$ as $(\varepsilon,\tau) \to 0$. Moreover, since $\log u_0^{(\tau)} \to \log u_0$ strongly in $L^2(\Omega)$, we have $r_i(u^{(\tau)})\log u_0^{(\tau)} \to r_i(u)\log u_0$ strongly in $L^1(\Omega_T)$. It remains to show that $r_i(u^{(\tau)})\log u_i^{(\tau)} \to r_i(u)\log u_i$ strongly in $L^1(\Omega_T)$. We have $r_i(u^{(\tau)})\log u_i^{(\tau)} \to r_i(u)\log u_i$ a.e. in Ω_T if $u_i > 0$. If $u_i = 0$, by assumption, we have $r_i(u)\log u_i = 0$ and therefore $r_i(u^{(\tau)})\log u_i^{(\tau)} \to r_i(u)\log u_i$ a.e. in Ω_T as well. Moreover, $r_i(u)\log u_i$ is bounded. Hence, by dominated convergence, $r_i(u^{(\tau)})\log u_i^{(\tau)} \to r_i(u)\log u_i$ strongly in $L^1(\Omega_T)$, and the claim follows. □

7.3 Proof of Theorem 7.2

Let (u,Φ) be a weak solution and $(\bar u,\bar\Phi)$ be a strong solution to (7.1)–(7.5). In this section, we interpret $H(u)$ and $H(\bar u)$ as functionals depending on $u = (u_0,\dots,u_n)$ and $\bar u = (\bar u_0,\dots,\bar u_n)$. This notation is only needed to determine the variational derivative of H and will not lead to any confusion in the following computations. We split the lengthy proof in several steps.

Step 1: Calculation of the time derivative of $H(u,\Phi|\bar u,\bar\Phi)$. In the following, we write

$$\begin{aligned}&H(u,\Phi|\bar u,\bar\Phi) = H_1(u|\bar u) + H_2(\Phi|\bar\Phi), \quad \text{where}\\ &H_1(u|\bar u) = H_1(u) - H_1(\bar u) - H_1'(\bar u)(u-\bar u),\\ &H_2(\Phi|\bar\Phi) = H_2(\Phi) - H_2(\bar\Phi) - H_2'(\bar\Phi)(\Phi-\bar\Phi),\end{aligned}$$

where $H_1(u) = \int_\Omega h_1(u)dx$ with $h_1(u) = \sum_{i=0}^n \int_{u_i^D}^{u_i} \log(s/u_i^D)ds$, $H_2(\Phi) = \frac12\lambda^2\int_\Omega(\ell^2|\Delta(\Phi - \Phi^D)|^2 + |\nabla(\Phi-\Phi^D)|^2)dx$, and $H_1'(\bar u)(u-\bar u)$ is the variational derivative of H_1 at $\bar u$ in the direction of $u-\bar u$ (similarly for $H_2'(\bar\Phi)(\Phi-\bar\Phi)$). We compute the time derivative of $H_1(u|\bar u)$, split the sum over $i = 0,\dots,n$ into $i = 0$ and the sum over $i = 1,\dots,n$, and insert $\partial_t u_0 = -\sum_{i=1}^n \partial_t u_i$, $\partial_t \bar u_0 = -\sum_{i=1}^n \partial_t \bar u_i$:

$$\begin{aligned}\frac{dH_1}{dt}(u|\bar u) &= \frac{dH_1}{dt}(u) - \frac{dH_1}{dt}(\bar u) - \frac{d}{dt}\int_\Omega \sum_{i=0}^n \frac{\partial h_1}{\partial u_i}(\bar u)(u_i - \bar u_i)dx\\ &= \frac{dH_1}{dt}(u) - \sum_{i=0}^n \left(\left\langle \partial_t u_i, \frac{\partial h_1}{\partial u_i}(\bar u)\right\rangle + \left\langle \partial_t \bar u_i, \frac{u_i}{\bar u_i} - 1\right\rangle\right)\end{aligned}$$

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$$= \frac{dH_1}{dt}(u) - \sum_{i=1}^n \left(\left\langle \partial_t u_i, \frac{\partial h_1}{\partial u_i}(\bar{u}) - \frac{\partial h_1}{\partial u_0}(\bar{u}) \right\rangle + \left\langle \partial_t \bar{u}_i, \frac{u_i}{\bar{u}_i} - \frac{u_0}{\bar{u}_0} \right\rangle \right).$$

Next, we insert equation (7.1) for u_i and $\bar{u}_i$ and use $(\partial h_1/\partial u_i)(\bar{u}) = \log(\bar{u}_i/u_i^D)$:

$$\begin{aligned}\frac{dH_1}{dt}(u|\bar{u}) &= \frac{dH_1}{dt}(u) + \int_\Omega \sum_{i=1}^n D_i u_i \nabla w_i \cdot \nabla \bigg(\log \frac{\bar{u}_i}{\bar{u}_0} - \log \frac{u_i^D}{u_0^D} dx \bigg) dx \\ &\quad + \int_\Omega \sum_{i=1}^n D_i \bar{u}_i \nabla \bar{w}_i \cdot \bigg(\frac{u_i}{\bar{u}_i} \nabla \log \frac{u_i}{\bar{u}_i} - \frac{u_0}{\bar{u}_0} \nabla \log \frac{u_0}{\bar{u}_0} \bigg) dx.\end{aligned}$$

A similar computation for $H_2(\Phi|\bar{\Phi})$ leads to

$$\begin{aligned}\frac{dH_2}{dt}(\Phi|\bar{\Phi}) &= \lambda^2 \langle (\ell^2 \Delta - 1) \Delta \partial_t (\Phi - \bar{\Phi}), \Phi - \bar{\Phi} \rangle = \sum_{i=1}^n \langle z_i \partial_t (u_i - \bar{u}_i), \Phi - \bar{\Phi} \rangle \\ &= -\int_\Omega \sum_{i=1}^n D_i z_i (u_i \nabla w_i - \bar{u}_i \nabla \bar{w}_i) \cdot \nabla (\Phi - \bar{\Phi}) dx \\ &= \frac{dH_2}{dt}(\Phi) + \int_\Omega \sum_{i=1}^n D_i z_i (u_i \nabla w_i \cdot \nabla \bar{\Phi} - u_i \nabla w_i \cdot \nabla \Phi^D + \bar{u}_i \nabla \bar{w}_i \cdot \nabla (\Phi - \bar{\Phi})) dx,\end{aligned}$$

where we abbreviated $\bar{w}_i = \log(\bar{u}_i/\bar{u}_0) + z_i \bar{\Phi}$. As u_i is only nonnegative, the expression $\nabla \log u_i$ may be not integrable. Therefore, we define $\nabla \log(u_i/u_0) := (2\nabla \sqrt{u_i} - \sqrt{u_i} \nabla \log u_0)/\sqrt{u_i}$ if $u_i > 0$ and $\nabla \log(u_i/u_0) := 0$ else. This expression may be still not integrable, but $\sqrt{u_i} \nabla \log(u_i/u_0)$ lies in $L^2(\Omega_T)$, since $\nabla \sqrt{u_i}$, $\nabla \log u_0 \in L^2(\Omega_T)$. Thus, the expression $\sqrt{u_i} \nabla w_i = u_i \nabla \log(u_i/u_0) + u_i z_i \nabla \Phi \in L^2(\Omega_T)$ is well defined. In a similar way, we define $\nabla \log(u_i/\bar{u}_i)$, which is possible since $\bar{u}_i$ is strictly positive, and we have $\sqrt{u_i} \nabla \log(u_i/\bar{u}_i) \in L^2(\Omega_T)$.

We insert the free energy inequality (7.15), namely

$$\frac{dH_1}{dt}(u) + \frac{dH_2}{dt}(\Phi) \le -\int_\Omega \sum_{i=1}^n D_i u_i |\nabla w_i|^2 dx,$$

and rearrange the terms,

$$\begin{aligned}\frac{dH}{dt}(u, \Phi|\bar{u}, \bar{\Phi}) &= \frac{dH_1}{dt}(u|\bar{u}) + \frac{dH_2}{dt}(\Phi|\bar{\Phi}) \\ &\le -\int_\Omega \sum_{i=1}^n D_i u_i \nabla w_i \cdot \bigg(\nabla \log \frac{u_i}{\bar{u}_i} - \nabla \log \frac{u_0}{\bar{u}_0} + z_i \nabla (\Phi - \bar{\Phi}) \bigg) dx \\ &\quad + \int_\Omega \sum_{i=1}^n D_i \bar{u}_i \nabla \bar{w}_i \cdot \bigg(\frac{u_i}{\bar{u}_i} \nabla \log \frac{u_i}{\bar{u}_i} - \frac{u_0}{\bar{u}_0} \nabla \log \frac{u_0}{\bar{u}_0} + z_i \nabla (\Phi - \bar{\Phi}) \bigg) dx.\end{aligned} \tag{7.30}$$

At this point, we observe that the terms involving ∇w_i^D cancel even if ∇w_i^D does not vanish, since they also appear in the free energy inequality (7.15).

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The terms involving the solvent concentrations u_0 and $\bar{u}_0$ can be integrated into the sum over i if we interpret system (7.1) as equations for $u_0, u_1, \ldots, u_n$. For this, we observe that u_0 solves

$$\partial_t u_0 = -\operatorname{div}\sum_{i=1}^n D_i u_i \nabla w_i = -\operatorname{div}\left\{\sum_{i=1}^n D_i u_i \nabla \log\frac{u_i}{u_0} + \left(\sum_{i=1}^n D_i z_i u_i\right)\nabla\Phi\right\}.$$

Then (7.1) reads as

$$\partial_t u_i = \operatorname{div}\sum_{j=0}^n (A_{ij}\nabla \log u_j + Q_{ij}\nabla\Phi), \quad i = 0, \ldots, n, \tag{7.31}$$

where A_{ij} and Q_{ij} are defined in (7.17). Recall that $z_0 := 0$. We define in a similar way $\bar{A}$ and $\bar{Q}$. With this notation, (7.30) becomes

$$\begin{aligned}\frac{dH}{dt}(u,\Phi|\bar{u},\bar{\Phi}) \le &-\int_\Omega \sum_{i,j=0}^n (A_{ij}\nabla\log u_j + Q_{ij}\nabla\Phi)\cdot\left(\nabla\log\frac{u_i}{\bar{u}_i} + z_i\nabla(\Phi-\bar{\Phi})\right)dx \\ &+\int_\Omega \sum_{i,j=0}^n (\bar{A}_{ij}\nabla\log\bar{u}_j + \bar{Q}_{ij}\nabla\bar{\Phi})\cdot\left(\frac{u_i}{\bar{u}_i}\nabla\log\frac{u_i}{\bar{u}_i} + z_i\nabla(\Phi-\bar{\Phi})\right)dx.\end{aligned}$$

We add and subtract the integral

$$\int_\Omega \sum_{i,j=0}^n (A_{ij}\nabla\log\bar{u}_j + Q_{ij}\nabla\bar{\Phi})\cdot\left(\nabla\log\frac{u_i}{\bar{u}_i} + z_i\nabla(\Phi-\bar{\Phi})\right)dx$$

and integrate over $(0,t)$:

$$H((u,\Phi)(t)|(\bar{u},\bar{\Phi})(t)) - H((u,\Phi)(0)|(\bar{u},\bar{\Phi})(0)) \le I_1 + I_2 + I_3, \quad \text{where} \tag{7.32}$$

$$I_1 = -\int_0^t\int_\Omega \sum_{i,j=0}^n \left(A_{ij}\nabla\log\frac{u_j}{\bar{u}_j} + Q_{ij}\nabla(\Phi-\bar{\Phi})\right)\cdot\left(\nabla\log\frac{u_i}{\bar{u}_i} + z_i\nabla(\Phi-\bar{\Phi})\right)dxds,$$

$$I_2 = -\int_0^t\int_\Omega \sum_{i,j=0}^n u_i\left\{\left(\frac{A_{ij}}{u_i} - \frac{\bar{A}_{ij}}{\bar{u}_i}\right)\nabla\log\bar{u}_j + \left(\frac{Q_{ij}}{u_i} - \frac{\bar{Q}_{ij}}{\bar{u}_i}\right)\nabla\bar{\Phi}\right\}\cdot\nabla\log\frac{u_i}{\bar{u}_i}dxds,$$

$$I_3 = -\int_0^t\int_\Omega \sum_{i,j=0}^n ((A_{ij}-\bar{A}_{ij})\nabla\log\bar{u}_j + (Q_{ij}-\bar{Q}_{ij})\nabla\bar{\Phi})\cdot z_i\nabla(\Phi-\bar{\Phi})dxds.$$

Observe that $u(0) = \bar{u}(0)$, implying that $H((u,\Phi)(0)|(\bar{u},\bar{\Phi})(0)) = 0$.

Step 2: Estimation of I_3. By Young's inequality, we have

$$I_3 \le C\int_0^t \sum_{i=1}^n (\|u_i-\bar{u}_i\|^2_{L^2(\Omega)} + \|\nabla(\Phi-\bar{\Phi})\|^2_{L^2(\Omega)})ds, \tag{7.33}$$

where $C > 0$ depends on the $L^\infty(\Omega_T)$ norms of $\nabla\log\bar{u}_j$ and $\nabla\bar{\Phi}$.

The treatment of I_1 and I_2 is more delicate.

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Step 3: Estimation of I_1. We write $I_1 = I_{11} + I_{12} + I_{13}$, where

$$I_{11} = -\int_0^t \int_\Omega \sum_{i,j=0}^n A_{ij} \nabla \log \frac{u_j}{\bar{u}_j} \cdot \nabla \log \frac{u_i}{\bar{u}_i} dxds,$$

$$I_{12} = -\int_0^t \int_\Omega \sum_{i,j=0}^n z_i Q_{ij} |\nabla(\Phi - \bar{\Phi})|^2 dxds,$$

$$I_{13} = -\int_0^t \int_\Omega \sum_{i,j=0}^n z_i A_{ij} \nabla \log \frac{u_j}{\bar{u}_j} \cdot \nabla(\Phi - \bar{\Phi}) dxds$$
$$- \int_0^t \int_\Omega \sum_{i,j=0}^n Q_{ij} \nabla \log \frac{u_i}{\bar{u}_i} \cdot \nabla(\Phi - \bar{\Phi}) dxds.$$

It follows from $0 \le u_i \le 1$ that $|Q_{ij}| \le C$ and consequently

$$I_{12} \le C \int_0^t \|\nabla(\Phi - \bar{\Phi})\|^2_{L^2(\Omega)} ds.$$

The matrix A is not positive definite since $u_i = 0$ is possible. However, a modified matrix is positive definite on the subspace L, as shown in the following lemma.

Lemma 7.6. *The matrix G, defined by*

$$G_{ij} = \begin{cases} A_{ij}/\sqrt{u_i u_j} & \text{if } u_i u_j > 0, \\ 0 & \text{else,} \end{cases} \qquad i,j = 0, \ldots, n, \tag{7.34}$$

is positive definite on the subspace $L = \{z \in \mathbb{R}^{n+1} : \sum_{i=0}^n \sqrt{u_i} z_i = 0\}$, namely

$$z^T G z \ge D_* \left(\frac{z_0^2}{u_0} + \sum_{i=1}^n z_i^2 \right) \quad \text{for every } z \in L, \tag{7.35}$$

where $D_* = \min_{i=1,\ldots,n} D_i > 0$.

Proof. We start by considering the matrix

$$G_* = D_* \begin{pmatrix} u_0^{-1} \sum_{i=1}^n u_i & -\sqrt{u_1/u_0} & \cdots & -\sqrt{u_n/u_0} \\ -\sqrt{u_1/u_0} & 1 & & 0 \\ \vdots & 0 & \ddots & 0 \\ -\sqrt{u_n/u_0} & 0 & & 1 \end{pmatrix},$$

where $D_* = \min_{i=1,\ldots,n} D_i > 0$. For every $\xi \in L$, we have $\sum_{i=1}^n \sqrt{u_i}\xi_i = -\sqrt{u_0}\xi_0$. Therefore, together with the size-exclusion constraint $\sum_{i=1}^n u_i = 1 - u_0$, we obtain

$$\xi^T G_* \xi = D_* \frac{\xi_0^2}{u_0} \sum_{i=1}^n u_i - 2D_* \frac{\xi_0}{\sqrt{u_0}} \sum_{i=1}^n \sqrt{u_i}\xi_i + D_* \sum_{i=1}^n \xi_i^2$$
$$= D_* \frac{\xi_0^2}{u_0}(1 - u_0) + 2D_* \frac{\xi_0}{\sqrt{u_0}} \sqrt{u_0}\xi_0 + D_* \sum_{i=1}^n \xi_i^2$$

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$$= D_*\bigg\{\Big(\frac{1}{u_0}+1\Big)\xi_0^2 + \sum_{i=1}^n \xi_i^2\bigg\} \geq D_*\Big(\frac{\xi_0^2}{u_0} + \sum_{i=1}^n \xi_i^2\Big).$$

This implies that

$$\begin{aligned}\xi^T(G-G_*)\xi &= \frac{\xi_0^2}{u_0}\sum_{i=1}^n (D_i-D_*)u_i - 2\frac{\xi_0}{\sqrt{u_0}}\sum_{i=1}^n (D_i-D_*)\sqrt{u_i}\xi_i + \sum_{i=1}^n (D_i-D_*)\xi_i^2 \\ &= \sum_{i=1}^n (D_i-D_*)\Big(\frac{\xi_0}{\sqrt{u_0}}\sqrt{u_i}-\xi_i\Big)^2 \geq 0,\end{aligned}$$

and we infer that $\xi^T G z \geq \xi^T G_* \xi$, which ends the proof. □

Lemma 7.6 is crucial in the weak–strong uniqueness proof. The corresponding positive bound helps us to conclude a negative upper estimate for I_{11}, which is used to absorb the contributions from I_{13} and I_2. We introduce the projections

$$(P_L Y)_i = Y_i - \sqrt{u_i}\sum_{j=0}^n \sqrt{u_j}Y_j, \quad (P_{L^\perp} Y)_i = \sqrt{u_i}\sum_{j=0}^n \sqrt{u_j}Y_j,$$

for all $i = 0,\ldots,n$ and $Y \in \mathbb{R}^{n+1}$.

Lemma 7.7. *Let $Y_i = \sqrt{u_i}\nabla\log(u_i/\bar{u}_i) \in L^2(\Omega_T)$ for $i = 0,\ldots,n$. Then*

$$I_{11} \leq -D_* \int_0^t \int_\Omega \Big(\frac{|(P_L Y)_0|^2}{u_0} + \sum_{i=1}^n |(P_L Y)_i|^2\Big) dxds,$$

where $D_* = \min_{i=1,\ldots,n} D_i > 0$.

Proof. Recall that by definition, $\nabla\log(u_i/\bar{u}_i) = (2\nabla\sqrt{u_i} - \sqrt{u_i}\nabla\log\bar{u}_i)/\sqrt{u_i} = Y_i/\sqrt{u_i}$ if $u_i > 0$. In this case,

$$A_{ij}\nabla\log\frac{u_i}{\bar{u}_i}\cdot\nabla\log\frac{u_j}{\bar{u}_j} = G_{ij}Y_iY_j,$$

where the matrix G is defined in (7.34). If $u_i = 0$ or $u_j = 0$, either $Y_i = 0$ or $Y_j = 0$ and hence, the previous expression vanishes. Therefore, we rewrite I_{11} as

$$I_{11} = -\int_0^t \int_\Omega \sum_{i,j=0}^n G_{ij}Y_iY_j dxds.$$

A straightforward computation shows that $\operatorname{ran} G = L$, implying that $\ker G = L^\perp$. Hence, for every $Y \in \mathbb{R}^{n+1}$,

$$Y^T G Y = (P_L Y)^T G (P_L Y),$$

where $(P_L Y)_i = Y_i - \sqrt{u_i}\sum_{j=0}^n \sqrt{u_j}Y_j$. Define $\xi_i := (P_L Y)_i = Y_i - \sqrt{u_i}\sum_{j=0}^n \sqrt{u_j}Y_j$ for $i = 0,\ldots,n$. Then $\xi \in L$, since

$$\sum_{i=0}^n \sqrt{u_i}(P_L Y)_i = \sum_{i=0}^n \sqrt{u_i}Y_i - \Big(\sum_{i=0}^n u_i\Big)\sum_{j=0}^n \sqrt{u_j}Y_j = 0.$$

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The inequality

$$(P_L Y)^T G(P_L Y) \geq \frac{|(P_L Y)_0|^2}{u_0} + \sum_{i=1}^n |(P_L Y)_i|^2, \tag{7.36}$$

follows directly from (7.35), applied to $\xi = P_L Y$. Recall that $u_0 > 0$ a.e. in Ω_T.

We choose now $Y_i = \sqrt{u_i}\nabla \log(u_i/\bar{u}_i)$. The expression

$$\frac{|(P_L Y)_0|^2}{u_0} = \left|\nabla \log \frac{u_0}{\bar{u}_0} - \sum_{j=0}^n \sqrt{u_j} Y_j\right|^2$$

is integrable in Ω_T since $\nabla \log u_0 \in L^2(\Omega_T)$, and $\sqrt{u_j}Y_j \in L^2(\Omega_T)$. Therefore, we can integrate inequality (7.36) to obtain

$$\begin{aligned} I_{11} &= -\int_0^t \int_\Omega Y^T G Y dxds = -\int_0^t \int_\Omega (P_L Y)^T G (P_L Y) dxds \\ &\leq -D_* \int_0^t \int_\Omega \left(\frac{|(P_L Y)_0|^2}{u_0} + \sum_{i=1}^n |(P_L Y)_i|^2 \right) dxds, \end{aligned}$$

which finishes the proof. □

Lemma 7.8. *Let $Y_i = \sqrt{u_i}\nabla \log(u_i/\bar{u}_i)$ for $i = 0, \ldots, n$. For any $\varepsilon > 0$, there exists $C(\varepsilon) > 0$ such that*

$$I_{13} \leq \varepsilon \int_0^t \int_\Omega \left(\frac{|(P_L Y)_0|^2}{u_0} + \sum_{i=1}^n |(P_L Y)_i|^2 \right) dxds + C(\varepsilon) \int_0^t \|\nabla(\Phi - \bar{\Phi})\|^2_{L^2(\Omega)} ds.$$

Proof. We take into account the structures of the matrices A and Q:

$$\begin{aligned} I_{13} = &-\int_0^t \int_\Omega \sum_{i=1}^n z_i \left(A_{i0} \nabla \log \frac{u_0}{\bar{u}_0} + A_{ii} \nabla \log \frac{u_i}{\bar{u}_i} \right) \cdot \nabla(\Phi - \bar{\Phi}) dxds \\ &-\int_0^t \int_\Omega \left(Q_{00} \nabla \log \frac{u_0}{\bar{u}_0} + \sum_{i=1}^n Q_{ii} \nabla \log \frac{u_i}{\bar{u}_i} \right) \cdot \nabla(\Phi - \bar{\Phi}) dxds. \end{aligned}$$

Since $Q_{00} = -\sum_{i=1}^n D_i z_i u_i$ and $Q_{ii} = D_i z_i u_i$, we have

$$Q_{00} \nabla \log \frac{u_0}{\bar{u}_0} + \sum_{i=1}^n Q_{ii} \nabla \log \frac{u_i}{\bar{u}_i} = -\sum_{i=1}^n D_i z_i u_i \nabla \left(\log \frac{u_0}{\bar{u}_0} - \log \frac{u_i}{\bar{u}_i} \right) dx.$$

Furthermore, because of $A_{i0} = -D_i u_i$ and $A_{ii} = D_i u_i$,

$$\sum_{i=1}^n z_i \left(A_{i0} \nabla \log \frac{u_0}{\bar{u}_0} + A_{ii} \nabla \log \frac{u_i}{\bar{u}_i} \right) = -\sum_{i=1}^n D_i z_i u_i \nabla \left(\log \frac{u_0}{\bar{u}_0} - \log \frac{u_i}{\bar{u}_i} \right) dx.$$

This gives

$$I_{13} = 2 \int_0^t \int_\Omega \sum_{i=1}^n D_i z_i u_i \nabla \left(\log \frac{u_0}{\bar{u}_0} - \log \frac{u_i}{\bar{u}_i} \right) \cdot \nabla(\Phi - \bar{\Phi}) dxds$$

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$$= 2\int_0^t\int_\Omega \sum_{i=1}^n D_i z_i\bigg(u_i\frac{Y_0}{\sqrt{u_0}} - \sqrt{u_i}Y_i\bigg)\cdot\nabla(\Phi-\bar\Phi)dxds.$$

Next, we calculate for $i=0,\ldots,n$,

$$\begin{aligned}(P_{L^\perp}Y)_i &= \sqrt{u_i}\sum_{j=0}^n u_j\nabla\log\frac{u_j}{\bar u_j} = \sqrt{u_i}\sum_{j=0}^n(\nabla u_j - u_j\nabla\log\bar u_j)\\ &= -\sqrt{u_i}\sum_{j=0}^n u_j\nabla\log\bar u_j = \sqrt{u_i}\sum_{j=0}^n(\bar u_j - u_j)\nabla\log\bar u_j,\end{aligned} \tag{7.37}$$

where we used the constraint $\sum_{i=0}^n u_i = 1$ to cancel the term $\sum_{j=0}^n\nabla u_j$ in the third equality and we added $0 = \sum_{j=0}^n\nabla\bar u_j = \sum_{j=0}^n\bar u_j\nabla\log\bar u_j$ in the last equality. Hence,

$$\begin{aligned}u_i\frac{(P_{L^\perp}Y)_0}{\sqrt{u_0}} - \sqrt{u_i}(P_{L^\perp}Y)_i &= \frac{u_i}{\sqrt{u_0}}\bigg(\sqrt{u_0}\sum_{j=0}^n(\bar u_j-u_j)\nabla\log\bar u_j\bigg)\\ &\quad - \sqrt{u_i}\bigg(\sqrt{u_i}\sum_{j=0}^n(\bar u_j-u_j)\nabla\log\bar u_j\bigg) = 0.\end{aligned}$$

We split $Y_i = (P_LY)_i + (P_{L^\perp}Y)_i$ in I_{13}, which leads to

$$I_{13} = 2\int_0^t\int_\Omega\sum_{i=1}^n D_iz_i\bigg(u_i\frac{(P_LY)_0}{\sqrt{u_0}} - \sqrt{u_i}(P_LY)_i\bigg)\cdot\nabla(\Phi-\bar\Phi)dxds.$$

An application of Young's lemma finishes the proof. □

The previous lemmas show that

$$I_1 \le (\varepsilon - D_*)\int_0^t\int_\Omega\bigg(\frac{|(P_LY)_0|^2}{u_0} + \sum_{i=1}^n|(P_LY)_i|^2\bigg)dxds + C(\varepsilon)\int_0^t\|\nabla(\Phi-\bar\Phi)\|_{L^2(\Omega)}^2ds. \tag{7.38}$$

Step 4: Estimation of I_2. We split $I_2 = I_{21} + I_{22}$, where

$$\begin{aligned}I_{21} &= -\int_0^t\int_\Omega\sum_{i,j=0}^n u_i\bigg(\frac{A_{ij}}{u_i} - \frac{\bar A_{ij}}{\bar u_i}\bigg)\nabla\log\bar u_j\cdot\nabla\log\frac{u_i}{\bar u_i}dxds,\\ I_{22} &= -\int_0^t\int_\Omega\sum_{i,j=0}^n u_i\bigg(\frac{Q_{ij}}{u_i} - \frac{\bar Q_{ij}}{\bar u_i}\bigg)\nabla\bar\Phi\cdot\nabla\log\frac{u_i}{\bar u_i}dxds.\end{aligned} \tag{7.39}$$

Lemma 7.9. *For any $\varepsilon>0$, there exists $C(\varepsilon)>0$ such that*

$$I_{21} \le \varepsilon\int_0^t\int_\Omega\frac{|(P_LY)_0|^2}{u_0}dxds + C(\varepsilon)\int_0^t\sum_{i=0}^n\|u_i-\bar u_i\|_{L^2(\Omega)}^2ds.$$

Proof. Recalling that $Y_i = \sqrt{u_i}\nabla\log(u_i/\bar u_i)$, we reformulate I_{21} as

$$I_{21} = -\int_0^t\int_\Omega\sum_{i,j=0}^n u_i\bigg(\frac{A_{ij}}{u_i} - \frac{\bar A_{ij}}{\bar u_i}\bigg)\frac{Y_i}{\sqrt{u_i}}\cdot\nabla\log\bar u_jdxds.$$

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All rows of the matrix $(A_{ij}/u_i - \bar{A}_{ij}/\bar{u}_i)$ vanish except the first one,

$$\frac{A_{00}}{u_0} - \frac{\bar{A}_{00}}{\bar{u}_0} = \sum_{i=1}^n D_i\Big(\frac{u_i}{u_0} - \frac{\bar{u}_i}{\bar{u}_0}\Big), \quad \frac{A_{0j}}{u_0} - \frac{\bar{A}_{0j}}{\bar{u}_0} = -D_i\Big(\frac{u_j}{u_0} - \frac{\bar{u}_j}{\bar{u}_0}\Big) \text{ for } j = 1, \ldots, n.$$

This shows that

$$\begin{aligned} I_{21} &= -\int_0^t \int_\Omega \sum_{j=0}^n u_0\Big(\frac{A_{0j}}{u_0} - \frac{\bar{A}_{0j}}{\bar{u}_0}\Big)\frac{Y_0}{\sqrt{u_0}} \cdot \nabla \log \bar{u}_j dxds \\ &= -\int_0^t \int_\Omega M \cdot \Big(\frac{(P_L Y)_0}{\sqrt{u_0}} + \frac{(P_{L^\perp} Y)_0}{\sqrt{u_0}}\Big) dxds, \end{aligned} \tag{7.40}$$

where

$$\begin{aligned} M &= \sum_{j=0}^n \Big(A_{0j} - \frac{u_0}{\bar{u}_0}\bar{A}_{0j}\Big)\nabla \log \bar{u}_j \\ &= \sum_{i=1}^n D_i\Big(u_i - \frac{u_0}{\bar{u}_0}\bar{u}_i\Big)\nabla \log \bar{u}_0 - \sum_{i=1}^n D_i\Big(u_i - \frac{u_0}{\bar{u}_0}\bar{u}_i\Big)\nabla \log \bar{u}_i \\ &= \sum_{i=1}^n D_i(u_i - \bar{u}_i)\nabla \log \bar{u}_0 + \Big(1 - \frac{u_0}{\bar{u}_0}\Big)\sum_{i=1}^n D_i \bar{u}_i \nabla \log \bar{u}_0 \\ &\quad - \sum_{i=1}^n D_i(u_i - \bar{u}_i)\nabla \log \bar{u}_i - \Big(1 - \frac{u_0}{\bar{u}_0}\Big)\sum_{i=1}^n D_i \bar{u}_i \nabla \log \bar{u}_i \\ &= \sum_{i=1}^n D_i(u_i - \bar{u}_i)\nabla \log \frac{\bar{u}_0}{\bar{u}_i} + (u_0 - \bar{u}_0)\sum_{i=1}^n D_i \frac{\bar{u}_i}{\bar{u}_0}\nabla \log \frac{\bar{u}_0}{\bar{u}_i}. \end{aligned}$$

Since $\nabla \log \bar{u}_i$ is bounded in $L^\infty(\Omega_T)$, we can bound the first term in I_{21}:

$$\begin{aligned} -\int_0^t \int_\Omega M \cdot \frac{(P_L Y)_0}{\sqrt{u_0}} dxds &\le C\int_0^t \int_\Omega \sum_{i=0}^n |u_i - \bar{u}_i| \frac{|(P_L Y)_0|}{\sqrt{u_0}} dxds \\ &\le \varepsilon \int_0^t \int_\Omega \frac{|(P_L Y)_0|^2}{u_0} dxds + C(\varepsilon)\int_0^t \sum_{i=0}^n \|u_i - \bar{u}_i\|_{L^2(\Omega)}^2 ds, \end{aligned} \tag{7.41}$$

where $\varepsilon > 0$ is arbitrary. To estimate the second term in I_{21}, we use (7.37) and the elementary inequality $(\sum_{i=0}^n |u_i - \bar{u}_i|)^2 \le (n+1)\sum_{i=0}^n |u_i - \bar{u}_i|^2$:

$$\begin{aligned} -\int_0^t \int_\Omega M \cdot \frac{(P_{L^\perp} Y)_0}{\sqrt{u_0}} dxds &\le C\int_0^t \int_\Omega \sum_{i=0}^n |u_i - \bar{u}_i| \sum_{j=0}^n |\bar{u}_j - u_j| dxds \\ &\le C(n+1)\int_0^t \int_\Omega \sum_{i=0}^n |u_i - \bar{u}_i|^2 dxds. \end{aligned} \tag{7.42}$$

The lemma follows after inserting (7.41) and (7.42) into (7.40). □

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Lemma 7.10. *For any $\varepsilon > 0$, there exists $C(\varepsilon) > 0$ such that*

$$I_{22} \le \varepsilon \int_0^t \int_\Omega \frac{|(P_L Y)_0|^2}{u_0} dxds + C(\varepsilon) \int_0^t \sum_{i=0}^n \|u_i - \bar{u}_i\|^2_{L^2(\Omega)},$$

recalling definition (7.39) *of* I_{22}.

Proof. All entries of the matrix $(Q_{ij}/u_i - \bar{Q}_{ij}/\bar{u}_i)$ vanish except the element $Q_{00}/u_0 - \bar{Q}_{00}/\bar{u}_0 = -\sum_{i=1}^n D_i z_i (u_i/u_0 - \bar{u}_i/\bar{u}_0)$. This leads to

$$\begin{aligned}
I_{22} &= \int_0^t \int_\Omega \sum_{i=1}^n D_i z_i u_0 \Big(\frac{u_i}{u_0} - \frac{\bar{u}_i}{\bar{u}_0} \Big) \nabla \bar{\Phi} \cdot \nabla \log \frac{u_0}{\bar{u}_0} dxds \\
&= \int_0^t \int_\Omega \sum_{i=1}^n D_i z_i \Big((u_i - \bar{u}_i) + \frac{\bar{u}_i}{\bar{u}_0}(\bar{u}_0 - u_0) \Big) \nabla \bar{\Phi} \cdot \frac{Y_0}{\sqrt{u_0}} dxds \\
&= \int_0^t \int_\Omega \sum_{i=1}^n D_i z_i \Big((u_i - \bar{u}_i) + \frac{\bar{u}_i}{\bar{u}_0}(\bar{u}_0 - u_0) \Big) \Big(\frac{(P_L Y)_0}{\sqrt{u_0}} + \frac{(P_{L^\perp} Y)_0}{\sqrt{u_0}} \Big) \cdot \nabla \bar{\Phi} dxds \\
&\le C \int_0^t \int_\Omega \sum_{j=0}^n |u_j - \bar{u}_j| \Big(\frac{|(P_L Y)_0|}{\sqrt{u_0}} + \frac{|(P_{L^\perp} Y)_0|}{\sqrt{u_0}} \Big) |\nabla \bar{\Phi}| dsdx.
\end{aligned}$$

It follows from (7.37) that

$$\frac{|(P_{L^\perp} Y)_0|}{\sqrt{u_0}} = \Big| \sum_{j=0} (\bar{u}_j - u_j) \nabla \log \bar{u}_j \Big| \le C \sum_{j=0}^n |\bar{u}_j - u_j|.$$

Hence, Young's inequality completes the proof. □

We conclude that

$$I_2 \le 2\varepsilon \int_0^t \int_\Omega \frac{|(P_L Y)_0|^2}{u_0} dxds + C(\varepsilon) \int_0^t \sum_{i=0}^n \|u_i - \bar{u}_i\|^2_{L^2(\Omega)} ds. \tag{7.43}$$

Step 5: End of the proof. We collect (7.33), (7.38), and (7.43):

$$\begin{aligned}
I_1 + I_2 + I_3 \le (3\varepsilon - D_*) \int_0^t \int_\Omega \Big(\frac{|(P_L Y)_0|^2}{u_0} + \sum_{i=1}^n |(P_L Y)_i|^2 \Big) dxds \\
+ C(\varepsilon) \int_0^t \Big(\sum_{i=0}^n \|u_i - \bar{u}_i\|^2_{L^2(\Omega)} + \|\nabla(\Phi - \bar{\Phi})\|^2_{L^2(\Omega)} \Big) ds.
\end{aligned}$$

Thus, choosing $\varepsilon \le D_*/3$, we conclude from (7.32) that

$$H((u,\Phi)(t)|(\bar{u},\bar{\Phi})(t)) \le C \int_0^t \Big(\sum_{i=0}^n \|u_i - \bar{u}_i\|^2_{L^2(\Omega)} + \|\nabla(\Phi - \bar{\Phi})\|^2_{L^2(\Omega)} \Big) ds. \tag{7.44}$$

The first term on the right-hand side of (7.44) can be bounded by the relative entropy, as shown in the following lemma.

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Lemma 7.11. *It holds for any $u, \bar{u} \in (0,1)$ that*

$$u \log \frac{u}{\bar{u}} \geq \frac{1}{2}(u-\bar{u})^2.$$

Proof. The lemma has been proved in [119, Lemma 16]. For the convenience of the reader, we recall the short proof. Let $f(u) = u \log u$. Then, for $u, \bar{u} \in (0,1)$,

$$\begin{aligned} u \log\frac{u}{\bar{u}} - (u-\bar{u}) &= f(u) - f(\bar{u}) - f'(\bar{u})(u-\bar{u}) = f(\theta(u-\bar{u})+\bar{u})\big|_{\theta=0}^1 - f'(\bar{u})(u-\bar{u}) \\ &= (u-\bar{u})\int_0^t (f'(\theta(u-\bar{u})+\bar{u}) - f'(\bar{u}))d\theta = (u-\bar{u})\int_0^1 f'(s(u-\bar{u})+\bar{u})\big|_{s=0}^{\theta} d\theta \\ &= (u-\bar{u})^2 \int_0^1 \int_0^\theta f''(s(u-\bar{u})+\bar{u}) ds d\theta. \end{aligned}$$

The result follows from the observation $f''(s(u-\bar{u})+\bar{u}) = (s(u-\bar{u})+\bar{u})^{-1} \geq 1$. □

The previous lemma shows that

$$\sum_{i=0}^n \int_\Omega u_i \log \frac{u_i}{\bar{u}_i} dx \geq \frac{1}{2}\sum_{i=0}^n \int_\Omega (u_i - \bar{u}_i)^2 dx \tag{7.45}$$

and hence,

$$2H(u,\Phi|\bar{u},\bar{\Phi}) \geq \sum_{i=0}^n \|u_i - \bar{u}_i\|_{L^2(\Omega)}^2 + \lambda^2 \|\nabla(\Phi - \bar{\Phi})\|_{L^2(\Omega)}^2.$$

Consequently, we obtain from (7.44):

$$H((u,\Phi)(t)|(\bar{u},\bar{\Phi})(t)) \leq C\int_0^t H(u,\Phi|\bar{u},\bar{\Phi})ds,$$

and Gronwall's lemma finishes the proof.

7.4 Remarks on the uniqueness of solutions

Remark 7.3 (Uniqueness of weak solutions)**.** The uniqueness of weak solutions for our model is more delicate than for the model of [102], even in the case $D_i = z_i = 1$ for $i = 1, \ldots, n$. The reason is that we cannot use simple $L^2(\Omega)$ estimations. Instead, we use the $H^{-1}(\Omega)$ method under the (restrictive) condition that $\nabla\Phi \in L^\infty(\Omega_T)$. This regularity holds if the Dirichlet and Neumann boundaries do not intersect and if $\partial\Omega \in C^{1,1}$, $f \in L^p(\Omega)$, and $\Phi^D \in W^{2,p}(\Omega)$ for some $p > 3$. Indeed, we conclude from elliptic regularity [166, Theorem 3.17] that $\Phi \in L^\infty(0,T;W^{2,p}(\Omega)) \hookrightarrow L^\infty(0,T;W^{1,\infty}(\Omega))$. We also assume that $\sum_{i=1}^n r_i(u) = 0$. Summing (7.1) over $i = 1\ldots, n$, the pair (u_0, Φ) solves

$$\partial_t u_0 = \operatorname{div}(\nabla \log u_0 - (1-u_0)\nabla\Phi), \quad \lambda^2(\ell^2\Delta - 1)\Delta\Phi = 1 - u_0 + f(x) \quad \text{in } \Omega, \tag{7.46}$$

together with the corresponding initial and boundary conditions (7.3)–(7.5). We claim that this system has at most one solution. Let (u_0, Φ) and (v_0, Ψ) be two weak solutions to this problem and let $\chi \in L^2(0,T;H^1(\Omega))$ be the unique solution to $-\Delta\chi = u_0 - v_0$ in Ω, $\nabla\chi\cdot\nu = 0$

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on $\partial\Omega$. This solution exists since $\int_\Omega (u_0 - v_0)dx = 0$ because of mass conservation. We use χ as a test function in the first equation of (7.46):

$$\frac{1}{2}\frac{d}{dt}\int_\Omega |\nabla\chi|^2 dx + \int_\Omega (\log u_0 - \log v_0)(u_0 - v_0)dx$$
$$= \int_\Omega \big(-(u_0 - v_0)\nabla\Phi + (1 - v_0)\nabla(\Phi - \Psi)\big)\cdot\nabla\chi dx.$$

Using $(\log u_0 - \log v_0)(u_0 - v_0) \geq 4(\sqrt{u_0} - \sqrt{v_0})^2$ and $|u_0 - v_0| = |\sqrt{u_0} + \sqrt{v_0}||\sqrt{u_0} - \sqrt{v_0}| \leq 2|\sqrt{u_0} - \sqrt{v_0}|$, we find that

$$\begin{aligned}\frac{1}{2}\frac{d}{dt}\int_\Omega |\nabla\chi|^2 dx + 4\int_\Omega (\sqrt{u_0} - \sqrt{v_0})^2 dx &\leq C\|\sqrt{u_0} - \sqrt{v_0}\|_{L^2(\Omega_T)}\|\nabla\Phi\|_{L^\infty(\Omega_T)}\|\nabla\chi\|_{L^2(\Omega_T)} \\ &\quad + C\|\nabla(\Phi - \Psi)\|_{L^2(\Omega_T)}\|\nabla\chi\|_{L^2(\Omega_T)} \\ &\leq 2\|\sqrt{u_0} - \sqrt{v_0}\|^2_{L^2(\Omega_T)} + C\|\nabla\chi\|^2_{L^2(\Omega_T)},\end{aligned}$$

where we used the elliptic estimate $\|\nabla(\Phi - \Psi)\|_{L^2(\Omega_T)} \leq C\|u_0 - v_0\|_{L^2(\Omega_T)}$ and the assumption $\|\nabla\Phi\|_{L^\infty(\Omega_T)} \leq C$. We conclude from Gronwall's lemma that $\nabla\chi(t) = 0$ and consequently $u_0(t) = v_0(t)$ and $\Phi(t) = \Psi(t)$ for $t > 0$. Now, the equation

$$\partial_t u_i = \operatorname{div}(\nabla u_i - u_i\nabla(\log u_0 - \Phi)) \tag{7.47}$$

can be interpreted as a drift-diffusion equation for u_i with given (u_0, Φ). The regularity $\nabla \log u_0 - \Phi \in L^2(\Omega_T)$ is sufficient for the application of Gajewski's entropy method; see [102, Sec. 3]. Thus, there exists at most one solution u_i to (7.47) with the corresponding initial and boundary conditions. □

Remark 7.4 (Weak–strong uniqueness in the presence of reaction terms)**.** We claim that Theorem 7.2 holds for reaction rates $r_i : \overline{\mathcal{D}} \to \mathbb{R}$, which are Lipschitz continuous and quasi-positive (i.e. $r_i(u) \geq 0$ for all $u \in \mathcal{D}$ with $u_i = 0$) such that the total reaction rate is nonnegative, i.e. $\sum_{i=1}^n r_i(u) \leq 0$ for all $u \in \mathcal{D}$, and that $r_i(u)\log u_i = 0$ if $u_i = 0$. Proceeding as in Step 1 of the proof of Theorem 7.2 and taking into account Remark 7.2, we need to estimate additionally the expression

$$R = \int_\Omega \sum_{i=1}^n r_i(u)(w_i - \bar{w}_i)dx =: R_1 + R_2, \quad \text{where}$$
$$R_1 = \int_\Omega \sum_{i=1}^n \left\{ r_i(u)\left(\log\frac{u_i}{\bar{u}_i} - \log\frac{u_0}{\bar{u}_0}\right) - r_i(\bar{u})\left(\frac{u_i}{\bar{u}_i} - \frac{u_0}{\bar{u}_0}\right)\right\}dx,$$
$$R_2 = \int_\Omega \sum_{i=1}^n z_i(r_i(u) - r_i(\bar{u}))(\Phi - \bar{\Phi})dx.$$

The assumptions on r_i imply that $r_i(u)\log u_i$ is integrable. Therefore, following [93, p. 202f],

$$R_1 = \int_\Omega \sum_{i=1}^n \left\{ r_i(u)\left(\log\frac{u_i}{\bar{u}_i} - \frac{u_i}{\bar{u}_i} + 1\right) - (r_i(u) - r_i(\bar{u}))\left(\frac{u_i}{\bar{u}_i} - 1\right)\right.$$
$$\left. - r_i(u)\left(\log\frac{u_0}{\bar{u}_0} - \frac{u_0}{\bar{u}_0} + 1\right) + (r_i(\bar{u}) - r_i(\bar{u}))\left(\frac{u_0}{\bar{u}_0} - 1\right)\right\}dx.$$

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We deduce from $0 \ge \log z - z + 1 \ge -|z-1|^2/\min\{1,z\}$ for $z > 0$ that

$$\begin{aligned}
R_2 &\le \int_\Omega \sum_{i=1}^n \bigg\{ C_R u_i \frac{|u_i - \bar{u}_i|^2}{\bar{u}_i \min\{u_i, \bar{u}_i\}} + \frac{C}{\bar{u}_i} |r_i(u) - r_i(\bar{u})||u_i - \bar{u}_i| \\
&\quad - r_i(u)\bigg(\log\frac{u_0}{\bar{u}_0} - \frac{u_0}{\bar{u}_0} + 1\bigg) + \frac{C}{\bar{u}_0}|r_i(\bar{u}) - r_i(\bar{u})||u_0 - \bar{u}_0|\bigg\} dx \\
&\le C\int_\Omega \sum_{i=1}^n |u_i - \bar{u}_i|^2 dx - \int_\Omega \sum_{i=1}^n r_i(u)\bigg(\log\frac{u_0}{\bar{u}_0} - \frac{u_0}{\bar{u}_0} + 1\bigg) dx \\
&\le C\int_\Omega \sum_{i=1}^n |u_i - \bar{u}_i|^2 dx.
\end{aligned}$$

where we used in the last step the assumption $\sum_{i=1}^n r_i(u) \le 0$. Furthermore, by the Lipschitz continuity of r_i, the Poincaré inequality, and the elliptic estimate for the Poisson–Fermi equation,

$$R_2 \le C\sum_{i=1}^n \|u_i - \bar{u}_i\|_{L^2(\Omega)} \|\nabla(\Phi - \bar{\Phi})\|_{L^2(\Omega)} \le C\sum_{i=1}^n \|u_i - \bar{u}_i\|_{L^2(\Omega)}^2.$$

Thus, estimate (7.44) is still valid with another constant, and Theorem 7.2 follows. □

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Part III

A non-isothermal models for gas-particles mixtures

Chapter 8

Diffusion asymptotic for a kinetic model for gas-particle mixtures with energy exchanges

This chapter is a work in progress, resulting from a collaboration with Frédérique Charles and Francesco Salvarani.

8.1 Introduction

The study of gas-dust mixtures at the mathematical level is fundamentally important in several fields, such as astrophysics, environmental science and industrial processes. At its core, this importance stems from the intricate and often nonlinear interactions between gas and dust particles, which can lead to complex dynamics and phenomena that are critical to understand the behavior and evolution of various systems.

For example, in astrophysics, gas-dust mixtures play a pivotal role in the formation of stars, planets, and other celestial bodies. In environmental science, understanding the dynamics of gas-dust mixtures is essential for modeling atmospheric phenomena, such as the dispersion of pollutants, sandstorms, and the formation of clouds. These mixtures impact air quality, weather patterns, and climate change. In various industrial processes, such as pharmaceutical manufacturing, mining, and chemical processing, controlling the behavior of gas-dust mixtures is vital for efficiency, safety, and environmental compliance. In reactive gas-dust systems, the presence of solid particles can catalyze chemical reactions or alter the heat transfer properties of the gas. This is particularly relevant in combustion processes, where dust can either inhibit or enhance combustion depending on the conditions. Mathematical modeling of these processes is essential for the design and optimization of reactors, combustion engines, and pollution control systems.

When dealing with diffusive phenomena, the basic model in the framework of multicomponent mixture is given by the Maxwell-Stefan equations. Originating from the foundational works of James Clerk Maxwell and Josef Stefan in the 19th century [140, 164], these equations have become instrumental in the study and modeling of diffusion processes. The equations offer a more detailed and accurate description of mass transport in mixtures than classical Fickian diffusion models [90, 91], especially when dealing with high concentration gradients and non-ideal mixtures.

While very popular in the context of chemical engineering [165], the mathematical study of the Maxwell-Stefan system or of some variants has been studied in the 20th century at the numerical level [85, 106]. However, starting from [28] and [32], the literature has shown a renewed interest in these equations in the mathematical community.

In particular, the derivation of multicomponent equations from a system of Boltzmann equations represents a significant bridge between the microscopic dynamics of particles and the

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macroscopic behavior of gaseous mixtures. This derivation provides a theoretical framework that explains how interactions at the particle level lead to observable diffusion phenomena in multicomponent systems. A key assumption in the derivation is that of local equilibrium, where it is assumed that over small enough scales, the system can be described by a local Maxwell-Boltzmann distribution. This assumption is justified when the mean free path of the particles is much smaller than the characteristic length scale over which macroscopic gradients (e.g., concentration gradients) develop.

The scaling has been extensively studied, for example, in [27, 30, 33, 120] in the case of non-reacting mixtures, whereas [11], [13] and [12] have considered the reactive case in different frameworks.

In the case of models for gas-particle mixtures, the starting point is again a system of two Boltzmann equations (one for the evolution of gas molecules, and one for the evolution of dust particles). The interaction between the particles and the surrounding gas has to be described through specific collisional operators, which take into account the macroscopic character of the particles compared to the gas molecules. In [57], the collisional mechanism is based on the hypothesis of diffuse reflection (at a fixed and constant temperature) of the molecules on the surface of the particles. Collisions preserves the total momentum, but not the kinetic energy. However, the model has an entropy [56] (different from the classical Boltzmann entropy). In order to take into account heat exchanges between the gas and the dispersed phase, in [60], the authors modify the model of [57], introducing the surface temperature of the particles as a variable. The model preserves the total energy of the system, but we do not have an explicit expression of the entropy anymore.

Asymptotic models can be derived by letting the mass ratio between a gas molecule and a particle go to 0. They are very interesting for numerical simulation purposes, the discretization of first model being very costly when the mass ratio is weak [58]. In the asymptotic model proposed in [59], the evolution of the density of particles is described by the Vlasov equation with a term which can be interpreted as a drag force exerted by the gas on the particles. This term has some similarities with existing models of drag force, such as Otterman and Levinet's formula [150] (for a two-phase fluid model), or that of [70] which proposes a correction of the Stokes drag force to extend its validity when the Knudsen number increases. The derivation of macroscopic models for disparate mass binary mixtures is also studied in [75], which is devoted to the study of Grad's epochal relaxation phenomenon. When the gas and dispersed phase are linked not just through drag force but also via temperature exchange between the gas and droplets/dust particles, the asymptotic model involves also a term describing the internal energy exchange between the species [60].

In the case of a porous media, [169] homogenized kinetic equations to derive effective transport properties (such as permeability, Knudsen diffusivity, and thermal transpiration ratio) has been investigated. The authors describe the evolution of the gas via a Boltzmann equation, while the dust is fixed in space and is assume to the part of the spacial domain. The interaction of the gas with the solid surface is described via diffuse reflection boundary conditions, where the surface temperature of the dust is consider as a function of time and space. In particular it satisfies a classical heat equation.

The first aim of our paper is to describe non-isothermal dust-gas mixtures via a model possessing an explicit entropy structure. As in [57], we treat the gas-dust collisions with a diffuse reflection mechanism. Instead of proceeding as in [60], we take inspiration from the porous media literature to treat the surface temperature as a macroscopic quantity. The latter satisfies a transport-like equation, that guarantees the conservation of the total energy of the

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system. The model posses an explicit entropy structure in the case of hard-sphere kernels for the bi-species collisional operators. The second aim of our paper is to perform a formal asymptotic diffusive limit to obtain a Maxwell-Stefan-like system. The technical parts used to prove the results presented depend strongly on the form of the kernel of the bi-species collision operators. Having introduced results valid for general collision kernels, we restrict ourselves to analysing the case of Maxwellian kernels and the hard sphere. Explicit calculations are shown when the bi-species collision operators have Maxwellian kernels. The diffusive limit in the case of hard sphere kernels is only partially shown.

In Section 8.2 and 8.3, we introduce the model and detail its properties. In Section 8.4 we perform the adimensionalisation of the system and introduce small parameters. Macroscopic equations for the macroscopic scaled quantities can be found in Section 8.5. The main results of our paper are the following, proved in Section 8.6.

8.2 The model

Consider a binary aerosol mixture consisting of solid dust particles or liquid droplets in a monatomic carrier gas. Dust particles are assumed to be identical, i.e. all with the same radius and mass, and to be much larger and more massive than the gas molecules. Both species are supposed to be described by suitable density functions. In what follows, the function $F = F(t, x, v)$ represents the density of particles, whereas $f = f(t, x, w)$ is a function representing the density of gaseous atoms (for example, a noble gas, such has Helium or Neon).

8.2.1 Boltzmann system

At the kinetic level, we describe the gas-particle system by the following system of Boltzmann-like equations

$$\begin{cases} \partial_t F + v \cdot \nabla_x F = \mathcal{D}(F, f) + \mathcal{P}(F) \\ \partial_t f + w \cdot \nabla_x f = \mathcal{R}(F, f) + \mathcal{C}(f), \end{cases} \tag{8.1}$$

where the precise form of the four collisional operators $\mathcal{P}$, $\mathcal{D}$, $\mathcal{C}$ and $\mathcal{R}$ depends on the precise microscopic behavior of the collisions. It is worth noticing that the form of the collision kernel may have a main influence in the mathematical properties of the system, even if it does not modify the bilinear structure of the collisional operator.

8.2.2 Mono-species collision operators

In (8.1), $\mathcal{C}(f)$ is the classical Boltzmann operator for monoatomic gases, describing interactions between molecules [48]:

$$\mathcal{C}(f)(w) = \sigma_{gg} \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} \left[f(w'') f(w_*'') - f(w) f(w_*) \right] c\,(w - w_*, n)\, \mathrm{d}n \mathrm{d}w_*, \tag{8.2}$$

where σ_{gg} is a physical constant of the order of magnitude of r_g^2, and the pre-post collisional velocity rules are the following:

$$(w'', w_*'') = (w - [(w - w_*) \cdot n]\, n,\ w_* + [(w - w_*) \cdot n]\, n)\,. \tag{8.3}$$

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In particular, we see from (8.3) that the momentum and the kinetic energy are preserved at each collision:

$$\begin{cases} w' + w'_* = w + w_* \\ |w'|^2 + |w_*|^2 = |w|^2 + |w'_*|^2. \end{cases} \tag{8.4}$$

The nonnegative function c (collision kernel) in (8.2) describes the interactions between molecules and can be written as

$$c\,(w - w_*, n) = |w - w_*|\, q\left(|w - w_*|, \frac{w - w_*}{|w - w_*|} \cdot n\right),$$

where q is a dimensionless function. This operator have the following weak formulations : for any test function $\psi \in L^\infty(\mathbb{R}^3)$, we have (see [48])

$$\int_{\mathbb{R}^3} \mathcal{C}(f)(w)\psi(w)dw = \sigma_{gg} \int_{\mathbb{R}^3} (\psi(w') - \psi(w)) f(w) f(w_*) c\,(w - w_*, n)\, dw\mathrm{d}n\mathrm{d}w_* \tag{8.5}$$

and

$$\int_{\mathbb{R}^3} \mathcal{C}(f)(w)\psi(w)dw = -\frac{\sigma_{gg}}{2} \int_{\mathbb{R}^3} [\psi(w') - \psi(w)] \left[f(w'')f(w_*'') - f(w)f\,(w_*)\right] c\,(w - w_*, n)\, dw\mathrm{d}n\mathrm{d}w_* \tag{8.6}$$

We assume that $\mathcal{P}(F)$ is also a Boltzmann operator with elastic collisions. The expression of $\mathcal{P}(F)(v)$ is similar to (8.2), where we replace σ_{gg} by σ_{pp} (of order of magnitude r_p^2) and q by another dimensionless function p ; we also have similar weak formulation as (8.5), (8.6). We recall the properties of $\mathcal{C}(f)$ and $\mathcal{P}(F)(v)$ concerning the conservation of mass, momentum and kinetic energy, which are a direct consequence of (8.5) and (8.4):

$$\int_{\mathbb{R}^3} \mathcal{C}(f)(w) \begin{pmatrix} 1 \\ w \\ |w|^2/2 \end{pmatrix} dw = \int_{\mathbb{R}^3} \mathcal{P}(f)(v) \begin{pmatrix} 1 \\ v \\ |v|^2/2 \end{pmatrix} dv = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}, \tag{8.7}$$

8.2.3 Bi-species collision operators

In gas mixtures, the collision mechanism between two molecules of different masses can be described, when there is no internal energy or chemical reactions involved, by elastic collisions (see [47] and [58] for instance). In [59], a novel model was proposed, where collisions between dust particles and gas molecules are supposed to be inelastic and given by a diffuse reflection mechanism (at a fixed temperature) on the surface of dust particles. This collision mechanism allows to take into account the macroscopic character of dust particles compared to gas molecules. In a collision between a particle and a molecule, the postcollisional relative velocity was picked from a half-Maxwellian distribution at the temperature of surface of the particle. This amounts to assume that a molecule touching a particle thermalizes with the molecules constituting the surface of the particle within a negligible time with respect to the other characteristic time scales. Then the post-collisional relative velocity is in the half space delimited by the tangent plane to the surface of the particle (see Figure 8.1).

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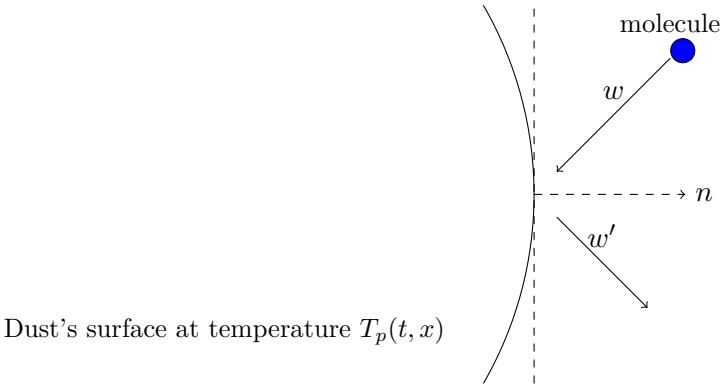

Fig. 8.1: Diffuse reflection mechanism.

Collision operators to describe such mechanism have been derived in [57] for the case of fixed surface temperature T_p of particles (independent of time and space). However, this model is not completely satisfactory, because the total energy of the system is not conserved. In [60] an improvement of the modelling has been proposed, based on the modification of the temperature of a dust particle during a collision. This was done by introducing the temperature of the dust surface as a variable in the density function F. Modified collision operators have been derived according to this mechanism. However, it seems complicated to obtain an entropy for this model.

Here we propose another model, in which the surface temperature of the dust is this time considered as a function of t and x, and where the conservation of total energy is ensured by an equation on this temperature. We assume that at position x and time t the particles have the same surface temperature $T_p(t,x) > 0$ and, as in the previous models, the post-collision relative velocity is given by a diffuse reflection at temperature $T_p(t,x)$. Let $m_g \in \mathbb{R}_+^*$ and $m_p \in \mathbb{R}_+^*$ be the masses of the gas molecules and the particles, respectively. The collision mechanism between dust and gas thus leads to the introduction, for $n \in \mathbb{S}^2$, of the probability density h_n of the post-collision relative velocities, given by

$$h_n(t,x,z) = \frac{1}{2\pi} \frac{m_g^2}{k_B^2 T_p(t,x)^2} (n \cdot z)\, e^{-\frac{m_g |z|^2}{2k_B T_p(t,x)}} \mathbb{1}_{\{z \cdot n \geq 0\}}, \tag{8.8}$$

where k_B denotes the Boltzmann constant.

The expression of the collisional operators derived in [58] can be directly extended to the context of time- and space-dependent surface temperature for particles. Hence, the operators $\mathcal{D}$ and $\mathcal{R}$ can be written in the following form (where we omit the dependence on t and x in f and F, for simplicity)

$$\begin{aligned}
&\mathcal{D}(F,f)(t,x,v) = \\
&\sigma_{gp} \left(\frac{m_g + m_p}{m_g}\right)^3 \int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{S}^2} f(w^\circ)\, F(v^\circ)\, h_n\left(t,x,\frac{m_g+m_p}{m_g}(v_B - v)\right) \varsigma(v^\circ - w^\circ, n) \mathrm{d}n \mathrm{d}v^\circ \mathrm{d}w^\circ \\
&- \sigma_{gp} \int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{S}^2} f(w)\, F(v)\, \varsigma(v-w,n) \mathrm{d}n \mathrm{d}w
\end{aligned} \tag{8.9}$$

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and

$$\mathcal{R}(F,f)(t,x,w) = \sigma_{gp}\left(\frac{m_g+m_p}{m_p}\right)^3 \int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{S}^2} f(w^\circ)\,F(v^\circ)\,h_n\left(t,x,\frac{m_g+m_p}{m_p}(v_B-w)\right)\varsigma(w^\circ-v^\circ,n)\mathrm{d}n\mathrm{d}v^\circ\mathrm{d}w^\circ - \sigma_{gp}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{S}^2} f(w)\,F(v)\,\varsigma(w-v,n)\mathrm{d}n\mathrm{d}v \tag{8.10}$$

where the collision kernel σ_{gp} is of order of magnitude $(r_p+r_g)^2$,

$$v_B = \frac{m_g w^\circ + m_p v^\circ}{m_g+m_p} \tag{8.11}$$

and $\varsigma(\cdot,\cdot)$ encodes the inter-species collision kernel. For the general case, this collision kernel has the following form:

$$\varsigma(v-w,n) = |v-w| b\left(|v-w|, \frac{(v-w)\cdot n}{|v-w|}\right), \tag{8.12}$$

where b is a dimensionless function. We are particularly interested here in the following two cases:

- The hard sphere collision kernel, which correspond to the case where the particles collide like billiard balls:
$$\varsigma(v-w,n) = [(v-w)\cdot n]_+, \tag{8.13}$$
where we denote $s_+ = s\mathbb{1}_{\{s\geq 0\}}$.
- The Maxwellian collision kernel, which is a particular case in which the collision kernel does not depend on the relative velocity, but only on the deviation angle:
$$\varsigma(v-w,n) = b\left(\frac{(v-w)\cdot n}{|v-w|}\right). \tag{8.14}$$
It is a theoretical model rather than a model describing a precise physical situation. However, it could lead to many explicit calculations that are fairly consistent with physical observations [170, 171].

In the following, we denote by

$$\Sigma(v-w) := \int_{\mathbb{S}^2} \varsigma(v-w,n)\mathrm{d}n \tag{8.15}$$

the integral of the collision kernel $\varsigma(\cdot,n)$ respect to n.

We have the following weak formulations of operators $\mathcal{D}(F,f)$ and $\mathcal{R}(F,f)$ [58].

Lemma 8.1. *Let $\varphi \in L^\infty_{\mathrm{loc}}(\mathbb{R}^3)$ and $\psi \in L^\infty_{\mathrm{loc}}(\mathbb{R}^3)$ test functions, and $\mathcal{D}(F,f)$ and $\mathcal{R}(F,f)$ given by* (8.9) *and* (8.10)*. We have*

$$\int_{\mathbb{R}^3}\mathcal{D}(F,f)\varphi(v)\mathrm{d}v = \sigma_{gp}\iiiint (\varphi(v')-\varphi(v))\,F(v)f(w)h_n(z)\varsigma(v-w,n)\,\mathrm{d}n\mathrm{d}z\mathrm{d}w\mathrm{d}v, \tag{8.16}$$

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where

$$v' = \frac{m_g w + m_p v}{m_g + m_p} - \frac{m_g}{m_g + m_p} z \tag{8.17}$$

and

$$\int_{\mathbb{R}^3} \mathcal{R}(F,f)(w)\psi(w)\mathrm{d}w = \sigma_{gp} \iiiint \left(\psi(w') - \psi(w)\right) F(v) f(w) h_n(z) \varsigma(v-w,n)\, \mathrm{d}n\mathrm{d}z\mathrm{d}w\mathrm{d}v, \tag{8.18}$$

where

$$w' = \frac{m_g w + m_p v}{m_g + m_p} + \frac{m_p}{m_g + m_p} z \tag{8.19}$$

Remark 8.1. *Note that the total momentum is conserved during a collision:*

$$m_p v' + m_g w' = m_p v + m_g w. \tag{8.20}$$

Proof. Thanks to (8.9) and to the change of variable $v \to z = \frac{m_g+m_p}{m_g}(v_B - v)$, where v_B is defined by (8.11) (of Jacobian $(\frac{m_g}{m_g})^3$), we have:

$$\begin{aligned}
&\int_{\mathbb{R}^3} \mathcal{D}(F,f)(t,x,v)\varphi(v)\mathrm{d}v \\
&= \sigma_{gp} \left(\frac{m_g+m_p}{m_g}\right)^3 \int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{S}^2} f\left(w^\circ\right) F\left(v^\circ\right) h_n\left(t,x,\frac{m_g+m_p}{m_g}(v_B - v)\right) \varsigma(v^\circ - w^\circ, n)\varphi(v)\mathrm{d}n\mathrm{d}v^\circ\mathrm{d}w^\circ\mathrm{d}v \\
&- \sigma_{gp} \int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{S}^2} f\left(w\right) F\left(v\right) \varsigma(v-w,n)\varphi(v)\mathrm{d}v\mathrm{d}n\mathrm{d}w \\
&= \sigma_{gp} \int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{S}^2} f\left(w^\circ\right) F\left(v^\circ\right) h_n\left(z\right) \varsigma(v^\circ - w^\circ, n)\varphi(v')\mathrm{d}n\mathrm{d}v^\circ\mathrm{d}w^\circ dz \\
&- \sigma_{gp} \int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{S}^2} f\left(w\right) F\left(v\right) \varsigma(v-w,n) h_n\left(t,x,z\right) \varphi(v)\mathrm{d}z\mathrm{d}v\mathrm{d}n\mathrm{d}w
\end{aligned}$$

using that $\int h_n(t,x,z)dz = 1$ for the second integral. We then obtain (8.16). Moreover, the change of variable $(w,n) \to (z = -\frac{m_g+m_p}{m_p}(v_B - w), n)$ in the first integral, and $n \to -n$ in the second integral yield

$$\begin{aligned}
&\int_{\mathbb{R}^3} \mathcal{R}\left(F,f\right)(t,x,w)\psi(w)\mathrm{d}w \\
&= \sigma_{gp} \left(\frac{m_g+m_p}{m_p}\right)^3 \int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{S}^2} f\left(w^\circ\right) F\left(v^\circ\right) h_n\left(\frac{m_g+m_p}{m_p}(v_B - w)\right) \varsigma(w^\circ - v^\circ, n)\psi(w)\mathrm{d}n\mathrm{d}v^\circ\mathrm{d}w^\circ\mathrm{d}w \\
&- \sigma_{gp} \int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{S}^2} f\left(w\right) F\left(v\right) \varsigma(w-v,n)\psi(w)\mathrm{d}n\mathrm{d}v\mathrm{d}w \\
&= \sigma_{gp} \int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{S}^2} f\left(w^\circ\right) F\left(v^\circ\right) h_{-n}\left(t,x,-z\right) \varsigma(w^\circ - v^\circ, -n)\psi(w)\mathrm{d}n\mathrm{d}v^\circ\mathrm{d}w^\circ\mathrm{d}w \\
&- \sigma_{gp} \int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{S}^2} f\left(w\right) F\left(v\right) \varsigma(w-v,-n)\psi(w)\mathrm{d}n\mathrm{d}v\mathrm{d}w
\end{aligned}$$

Expression (8.18) is obtained by observing in (8.8) that $h_{-n}(t,x,-z) = h_n(t,x,z)$ and $\varsigma(w - v, -n) = \varsigma(v - w, n)$. □

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In [58], other expressions of the operators $\mathcal{D}$ and $\mathcal{R}$ have been established in the case of a hard-sphere collision kernel. We extend here these expressions in the case of a general collision kernel $\varsigma(v-w,n)$.

Lemma 8.2. *Operators $\mathcal{D}(F,f)$ and $\mathcal{R}(F,f)$ given by* (8.9) *and* (8.10) *can be written in the following form (where we omit the t and x variables to simplify)*

$$\mathcal{D}(F,f)(v) = \sigma_{gp}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{S}^2}\left[f(w')F(v')h_n(v-w)\varsigma(z,n) - f(w)F(v)h_n(z)\varsigma(v-w,n)\right]\mathrm{d}z\mathrm{d}n\mathrm{d}w \tag{8.21}$$

and

$$\mathcal{R}(F,f)(w) = \sigma_{gp}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{S}^2}\left[F(v')f(w')h_n(v-w)\varsigma(z,n) - F(v)f(w)h_n(z)\varsigma(v-w,n)\right]\mathrm{d}z\mathrm{d}n\mathrm{d}w \tag{8.22}$$

where v' and w' are given by (8.17) *and* (8.19) *respectively.*

Proof. We do the change of variable $(v,w,z,n)\to(v',w',u=w-v,-n)$, where v' and w' are given by (8.17) and (8.19) respectively, in the gain term of (8.16). This transformation is an involution, since $w'-v'=z$, and has consequently a Jacobian equal to 1.

$$\begin{aligned}&\iiiint \varphi(v')F(v)f(w)h_n(z)\varsigma(v-w,n)\,\mathrm{d}n\mathrm{d}z\mathrm{d}w\mathrm{d}v,\\ &=\iiiint \varphi(v)F(v')f(w')h_{-n}(w-v)\varsigma(-z,-n)\,\mathrm{d}n\mathrm{d}z\mathrm{d}w\mathrm{d}v\end{aligned}$$

and we see from (8.12) $\varsigma(-z,-n)=\varsigma(z,n)$ and from (8.8) that $h_{-n}(w-v)=h_n(v-w)$. This allow to obtain (8.21). We then do the change of variable change of variable $(v,w,z,n)\to(v',w',u=w-v,-n)$ in in the gain term of (8.18):

$$\begin{aligned}&\iiiint \psi(w')F(v)f(w)h_n(z)\varsigma(v-w,-n)\,\mathrm{d}n\mathrm{d}z\mathrm{d}w\mathrm{d}v,\\ &=\iiiint \psi(w)F(v')f(w')h_{-n}(w-v)\varsigma(-z,-n)\,\mathrm{d}n\mathrm{d}z\mathrm{d}w\mathrm{d}v\\ &=\iiiint \psi(w)F(v')f(w')h_n(v-w)\varsigma(z,n)\,\mathrm{d}n\mathrm{d}z\mathrm{d}w\mathrm{d}v\end{aligned}$$

to get (8.22). □

We also have the following weak forms of the operators, that we shall use later to show the entropy inequality.

Lemma 8.3. *Let $\varphi\in L^\infty_{\mathrm{loc}}(\mathbb{R}^3)$ and $\psi\in L^\infty_{\mathrm{loc}}(\mathbb{R}^3)$ test functions, and $\mathcal{D}(F,f)$ and $\mathcal{R}(F,f)$ given by* (8.9) *and* (8.10)*. We have*

$$\begin{aligned}&\int_{\mathbb{R}^3}\mathcal{D}(F,f)\varphi(v)\mathrm{d}v+\int_{\mathbb{R}^3}\mathcal{R}(F,f)\psi(w)\mathrm{d}w\\ &=-\frac{\sigma_{gp}}{2}\iiiint\left(\varphi(v')+\psi(w')-\varphi(v)-\psi(w)\right)\\ &\qquad\times\left[F(v')f(w')h_n(v-w)\varsigma(z,n)-F(v)f(w)h_n(z)\varsigma(v-w,n)\right]\mathrm{d}n\mathrm{d}z\mathrm{d}w\mathrm{d}v,\end{aligned} \tag{8.23}$$

where v' and w' are given by (8.17) *and* (8.19) *respectively.*

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Proof. The proof is a direct consequence of the relationships (8.17) and (8.19). □

Lemma 8.4. *Let v' and w' the post-collision velocities, given by* (8.17) *and* (8.19) *respectively. Then we have the following relation*

$$m_p|v'|^2 - m_p|v|^2 + m_g|w'|^2 - m_g|w|^2 = \frac{m_p m_g}{m_p + m_g}\left(|z|^2 - |v-w|^2\right), \tag{8.24}$$

Proof. If we replace $(m_1v_1 + m_2v_2)/(m_1 + m_2)$ by v_B in (8.17) and (8.19), we get:

$$\begin{aligned} m_1|v_1'|^2 + m_2|v_2'|^2 &= m_1\left|v_B - \frac{m_2}{m_1+m_2}z\right|^2 + m_2\left|p + \frac{m_1}{m_1+m_2}z\right|^2 \\ &= (m_1+m_2)|v_B|^2 + \frac{m_1m_2}{m_1+m_2}|z|^2. \end{aligned} \tag{8.25}$$

Using the involutive character of transformation $(v, w, z) \to (v', w', w-v)$, and the conservation of the momentum (8.20), we deduce from (8.25) that

$$m_1|v_1|^2 + m_2|v_2|^2 = (m_1+m_2)|v_B|^2 + \frac{m_1m_2}{m_1+m_2}|v_2 - v_1|^2$$

By subtracting the latter relation and relation (8.25), we obtain (8.24). □

Proposition 8.1. *In the case of a hard sphere collision kernel, that is $\varsigma(v-w, n) = [(v-w)\cdot n]_+$, we have the following weak form, for $\varphi \in L^\infty_{\mathrm{loc}}(\mathbb{R}^3)$ and $\psi \in L^\infty_{\mathrm{loc}}(\mathbb{R}^3)$ test functions:*

$$\begin{aligned} &\int_{\mathbb{R}^3} \mathcal{D}(F,f)\varphi(v)\mathrm{d}v + \int_{\mathbb{R}^3} \mathcal{R}(F,f)\psi(w)\mathrm{d}w \\ &= -\frac{\sigma_{gp}}{2}\iiiint \left[\varphi(v') + \psi(w') - \varphi(v) - \psi(w)\right][(v-w)\cdot n]_+ h_n(z) e^{-\frac{\mu_{gp}}{2k_BT_p}\left(m_p|v|^2 + m_g|w|^2\right)} \\ &\quad \times \left[F(v')e^{\frac{\mu_{gp}}{2k_BT_p}m_p|v'|^2} f(w')e^{\frac{\mu_{gp}}{2k_BT_p}m_g|w'|^2} - F(v)e^{\frac{\mu_{gp}}{2k_BT_p}m_p|v|^2} f(w)e^{\frac{\mu_{gp}}{2k_BT_p}m_g|w|^2}\right]\mathrm{d}n\mathrm{d}z\mathrm{d}w\mathrm{d}v \end{aligned} \tag{8.26}$$

where we denote $\mu_{gp} = (m_p + m_g)/m_p$.

Proof. From (8.23) and the definition (8.8) of h_n, we get

$$\begin{aligned} &\int_{\mathbb{R}^3} \mathcal{D}(F,f)\varphi(v)\mathrm{d}v \\ &= -\frac{\sigma_{gp}}{2}\iiiint \left(\varphi(v') - \varphi(v)\right)[(v-w)\cdot n]_+ h_n(z) \\ &\quad \times \left[F(v')f(w')e^{-\frac{m_g}{2k_BT_p}|v-w|^2} e^{\frac{m_g}{2k_BT_p}|z|^2} - F(v)f(w)\right]\mathrm{d}n\mathrm{d}z\mathrm{d}w\mathrm{d}v, \\ &= -\frac{\sigma_{gp}}{2}\iiiint \left(\varphi(v') - \varphi(v)\right)[(v-w)\cdot n]_+ h_n(z) \\ &\quad \times \left[F(v')f(w')e^{\frac{1}{2k_BT_p}\frac{m_g+m_p}{m_p}\left(m_p|v'|^2 - m_p|v|^2 + m_g|w'|^2 - m_g|w|^2\right)} - F(v)f(w)\right]\mathrm{d}n\mathrm{d}z\mathrm{d}w\mathrm{d}v, \end{aligned}$$

thanks to (8.24). The proof for the part $\int_{\mathbb{R}^3}\mathcal{R}(F,f)\psi(w)\mathrm{d}w$ is similar. We finally get (8.26). □

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8.2.4 Evolution of the surface temperature

The particles' surface temperature $T_p(t,x)$ solves the following PDE, which allows the system to conserve the total energy, as we will show in Proposition 8.2:

$$2c_p\left(\partial_t T_p(t,x)\int_{\mathbb{R}^3}F(t,x,v)\,\mathrm{d}v+\nabla_x T_p(t,x)\cdot\int_{\mathbb{R}^3}vF(t,x,v)\,\mathrm{d}v\right)+\frac{4k_b}{m_p+m_g}I_1(F,f)(t,x)T_p(t,x)$$
$$=\frac{m_g}{m_p+m_g}I_2(F,f)(t,x), \tag{8.27}$$

where c_p is the particle mass heat capacity, and

$$I_1(F,f)(t,x):=\sigma_{gp}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}F(t,x,v)f(t,x,w)\Sigma(v-w)\mathrm{d}v\mathrm{d}w, \tag{8.28}$$

$$I_2(F,f)(t,x):=\sigma_{gp}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}F(t,x,v)f(t,x,w)\Sigma(v-w)|v-w|^2\mathrm{d}v\mathrm{d}w. \tag{8.29}$$

Proposition 8.2. *Let (F,f,T_p) satisfy the system (8.1) and (8.27) in $\mathbb{R}^3$, with with $\mathcal{D}(F,f)$ and $\mathcal{R}(F,f)$ given by (8.9) and (8.10), and $\lim_{|x|\to+\infty}F(t,x,v)=\lim_{|x|\to+\infty}f(t,x,w)=0$. If (F,f,T_p) are smooth enough, then, at a formal level, we have conservation of the total energy of the system*

$$\frac{d}{dt}\int_{\mathbb{R}^3}E_T(t,x)\,\mathrm{d}x=0, \tag{8.30}$$

where

$$E_T(t,x)=m_pc_pT_p(t,x)\int_{\mathbb{R}^3}F(t,x,v)\,\mathrm{d}v+\frac{m_p}{2}\int_{\mathbb{R}^3}F(t,x,v)|v|^2\,\mathrm{d}v+\frac{m_g}{2}\int_{\mathbb{R}^3}f(t,x,w)|w|^2\,\mathrm{d}w. \tag{8.31}$$

Proof. Let's write

$$\partial_t E_T(t,x)=A+B,$$

where

$$A=m_pc_p\partial_tT_p(t,x)\int_{\mathbb{R}^3}F(t,x,v)\,\mathrm{d}v+m_pc_pT_p(t,x)\partial_t\int_{\mathbb{R}^3}F(t,x,v)\,\mathrm{d}v,$$

$$B=\frac{m_p}{2}\partial_t\int_{\mathbb{R}^3}F(t,x,v)|v|^2\,\mathrm{d}v+\frac{m_g}{2}\partial_t\int_{\mathbb{R}^3}f(t,x,w)|w|^2\,\mathrm{d}w.$$

Since 1 is a collisional invariant of $\mathcal{P}(F)$ and $\mathcal{D}(F,f)$, $F(t,x,v)$ satisfies the conservation equation

$$\partial_t\int_{\mathbb{R}^3}F(t,x,v)\,\mathrm{d}v+\nabla_x\cdot\left(\int_{\mathbb{R}^3}F(t,x,v)v\,\mathrm{d}v\right)=0.$$

Then

$$\int_{\mathbb{R}^3}T_p(t,x)\partial_t\int_{\mathbb{R}^3}F(t,x,v)\,\mathrm{d}v\,\mathrm{d}x=-\int_{\mathbb{R}^3}T_p(t,x)\nabla_x\cdot\left(\int_{\mathbb{R}^3}F(t,x,v)v\,\mathrm{d}v\right)\mathrm{d}x$$
$$=\int_{\mathbb{R}^3}\nabla_xT_p(t,x)\cdot\left(\int_{\mathbb{R}^3}F(t,x,v)v\,\mathrm{d}v\right)\mathrm{d}x.$$

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Moreover, since $|v|^2$ is a collisional invariant of $\mathcal{P}(F)$ and $\mathcal{C}(f)$ (equation (8.7)) and thanks to the weak formulations (8.16) and (8.18) of $\mathcal{D}(F,f)$ and $\mathcal{R}(F,f)$, we deduce that

$$\begin{aligned} B =& \frac{m_p}{2}\int_{\mathbb{R}^3}\left(-v\cdot\nabla_x F + \mathcal{D}(F,f) + \mathcal{P}(F)\right)|v|^2\,\mathrm{d}v \\ &+ \frac{m_g}{2}\int_{\mathbb{R}^3}\left(-w\cdot\nabla_x f + \mathcal{R}(F,f) + \mathcal{C}(f)\right)|w|^2\,\mathrm{d}w \\ =& -\frac{m_p}{2}\nabla_x\cdot\left(\int_{\mathbb{R}^3} vF|v|^2\,\mathrm{d}v\right) - \frac{m_g}{2}\nabla_x\cdot\left(\int_{\mathbb{R}^3} wf|w|^2\,\mathrm{d}w\right) \\ &+ \frac{1}{2}\sigma_{gp}\iiiint F(t,x,v)f(t,x,w)h_n(t,x,z)\varsigma(v-w,n) \\ &\qquad \left[m_p|v'|^2 - m_p|v|^2 + m_g|w'|^2 - m_g|w|^2\right]\mathrm{d}n\mathrm{d}z\mathrm{d}v\mathrm{d}w. \end{aligned}$$

Using (8.24) and

$$\int_{\mathbb{R}^3} h_n(t,x,z)\mathrm{d}z = 1, \qquad \int_{\mathbb{R}^3} h_n(t,x,z)|z|^2\mathrm{d}z = \frac{4k_b}{m_g}T_p(t,x), \tag{8.32}$$

(see Equations (8.116) and (8.118) for h_n, with $c = \sqrt{\frac{1}{T_p(t,x)}}$ in the Appendix), then

$$\begin{aligned} B =& -\frac{m_p}{2}\nabla_x\cdot\left(\int_{\mathbb{R}^3} vF|v|^2\,\mathrm{d}v\right) - \frac{m_g}{2}\nabla_x\cdot\left(\int_{\mathbb{R}^3} wf|w|^2\,\mathrm{d}w\right) \\ &+ 2k_b\frac{m_p}{m_p+m_g}T_p(t,x)\sigma_{gp}\iint F(t,x,v)f(t,x,w)\Sigma(v-w)\mathrm{d}v\mathrm{d}w \\ &- \frac{1}{2}\frac{m_p m_g}{m_p+m_g}\sigma_{gp}\iint F(t,x,v)f(t,x,w)\Sigma(v-w)|v-w|^2\mathrm{d}v\mathrm{d}w. \end{aligned}$$

Since, thanks to the hypotheses on the F and f tails, we have

$$\int_{\mathbb{R}^3}\nabla_x\cdot\left(\int_{\mathbb{R}^3} vF|v|^2\,\mathrm{d}v\right)\mathrm{d}x = 0 \qquad \text{and} \qquad \int_{\mathbb{R}^3}\nabla_x\cdot\left(\int_{\mathbb{R}^3} wf|w|^2\,\mathrm{d}w\right)\mathrm{d}x = 0,$$

we get (8.30). □

8.3 Collision invariants and entropy

The goal of the paper is to derive macroscopic equations of diffusive type, starting from the kinetic system (8.1), using the *method of moments*, that we are going to detail later on.

8.3.1 Collision invariants

We recall that property (8.7) of conservation of mass, momentum and energy holds for operators $\mathcal{C}$ and $\mathcal{P}$. For operators $\mathcal{D}$ and $\mathcal{R}$, the following Lemma hold.

Lemma 8.5. *The operators $\mathcal{D}$ and $\mathcal{R}$ defined by* (8.9) *and* (8.10) *satisfy*

$$\int \mathcal{R}(F,f)(w)\begin{pmatrix}1\\ \eta w\end{pmatrix}dw + \int \mathcal{D}(F,f)(v)\begin{pmatrix}1\\ v\end{pmatrix}dv = \begin{pmatrix}0\\ 0\end{pmatrix}. \tag{8.33}$$

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Proof. The starting point is given by the weak formulations (8.16) and (8.18) of the operators $\mathcal{D}$ and $\mathcal{R}$, respectively. Thanks to the pre-post interaction rule (8.17) and (8.19), by taking $\varphi = \psi = 1$ and $\varphi = \psi = v$, the thesis of the Lemma immediately follows. □

Remark 8.2. *The collisions between a gas particle and a dust particle do not conserve the kinetic energy.*

8.3.2 Entropy decay

A key quantity associated to the System (8.1) is the *entropy*

$$\mathbb{H}(F,f)(t) = \int h_1(t,x)\mathrm{d}x + \int h_2(t,x)\mathrm{d}x \tag{8.34}$$

where

$$\begin{aligned} h_1(t,x) &= \int f(t,x,w)\ln f(t,x,w)\mathrm{d}w + \int F(t,x,v)\ln F(t,x,v)\mathrm{d}v \\ h_2(t,x) &= -\frac{m_g+m_p}{k_B}c_p \ln T_p(t,x)\int F(t,x,v)\mathrm{d}v \end{aligned} \tag{8.35}$$

define the *entropy density*. To show that the functional $\mathbb{H}(F,f)$ has the property to be chosen as an entropy for the System (8.1), i.e. it decreases in time along the solution of the system, we start by defining the *entropy dissipation* functional:

$$\mathbb{D}(F,f)(t,x) = \mathbb{D}^d(F,f)(t,x) + \mathbb{D}^e(F,f)(t,x), \tag{8.36}$$

where

$$\begin{aligned} \mathbb{D}^d(F,f)(t,x) &= \int \mathcal{R}(F,f)(t,x,w)\ln\left(f(t,x,w)e^{\frac{\mu_{gp}}{2k_BT_p(t,x)}m_g|w|^2}\right)\mathrm{d}w \\ &\quad + \int \mathcal{D}(F,f)(t,x,v)\ln\left(F(t,x,v)e^{\frac{\mu_{gp}}{2k_BT_p(t,x)}m_p|v|^2}\right)\mathrm{d}v, \\ &= \int \mathcal{R}(F,f)(t,x,w)\ln f(t,x,w)\mathrm{d}w + \int \mathcal{D}(F,f)(t,x,v)\ln F(t,x,v)\mathrm{d}v \\ &\quad + \frac{\mu_{gp}}{2k_BT_p(t,x)}\left(m_g\int \mathcal{R}(F,f)(t,x,w)|w|^2\mathrm{d}w + m_p\int \mathcal{D}(F,f)(t,x,v)|v|^2\mathrm{d}v\right) \end{aligned} \tag{8.37}$$

and

$$\mathbb{D}^e(F,f)(t,x) = \int \mathcal{C}(f)(t,x,w)\ln f(t,x,w)\mathrm{d}w + \int \mathcal{P}(F)(t,x,v)\ln F(t,x,v)\mathrm{d}v. \tag{8.38}$$

Lemma 8.6. *Assume that ς is given by* (8.13)*. The entropy dissipation* (8.36)*, in the case of hard-sphere kernels for the bi-species collisional operators, is such that*

$$\mathbb{D}(F,f)(t,x) \le 0 \qquad \textit{for all } (t,x) \in \mathbb{R}^+ \times \mathbb{R}^3.$$

Proof. To show that the dissipation functional $\mathbb{D}(F,f)$ is negative, we study separately the sign of $\mathbb{D}^e(F,f)$ and $\mathbb{D}^d(F,f)$. The negativity of dissipation functional $\mathbb{D}^e(F,f)$ associated to

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the Boltzmann operators is usual : using $\psi(w) = \ln(f(w))$ and $\varphi(v) = \ln(F(v))$ in the weak formulation (8.6), we get:

$$\begin{aligned}\mathbb{D}^e(F,f)(t,x) = &-\frac{\sigma_{gg}}{4}\iiint \left[f'f'_* - ff_*\right]\left[\ln\left(f'f'_*\right) - \ln\left(ff_*\right)\right] c\left(w-w_*,n\right)\mathrm{d}n\mathrm{d}w_*\mathrm{d}w \\ &-\frac{\sigma_{pp}}{4}\iiint \left[F'F'_* - FF_*\right]\left[\ln\left(F'F'_*\right) - \ln\left(FF_*\right)\right] p\left(v-v_*,n\right)\mathrm{d}n\mathrm{d}v_*\mathrm{d}v.\end{aligned}$$

The algebraic inequality $(y_1-y_2)(\ln(y_1)-\ln(y_2)) \geq 0$ then show that $\mathbb{D}^e(F,f)(t,x) \geq 0$. Then using $\varphi(t,x,v) = \ln\left(F(t,x,v)e^{\frac{\mu_{gp}}{2k_B T_p(t,x)}m_p|v|^2}\right)$ and $\psi(t,x,w) = \ln\left(f(t,x,w)e^{\frac{\mu_{gp}}{2k_B T_p(t,x)}m_g|w|^2}\right)$ in weak formulations (8.26), we get:

$$\begin{aligned}&\mathbb{D}^d(F,f)(t,x) \\ &= -\frac{\sigma_{gp}}{2}\iiiint [(v-w)\cdot n]_+ h_n(z)e^{-\frac{\mu_{gp}}{2k_B T_p}\left(m_p|v|^2+m_g|w|^2\right)} \\ &\quad\times\left[\ln\left(F(v')e^{\frac{\mu_{gp}}{2k_B T_p}m_p|v'|^2}f(w')e^{\frac{\mu_{gp}}{2k_B T_p}m_g|w'|^2}\right) - \ln\left(F(v)e^{\frac{\mu_{gp}}{2k_B T_p}m_p|v|^2}f(w)e^{\frac{\mu_{gp}}{2k_B T_p}m_g|w|^2}\right)\right] \\ &\quad\times\left[F(v')e^{\frac{\mu_{gp}}{2k_B T_p}m_p|v'|^2}f(w')e^{\frac{\mu_{gp}}{2k_B T_p}m_g|w'|^2} - F(v)e^{\frac{\mu_{gp}}{2k_B T_p}m_p|v|^2}f(w)e^{\frac{\mu_{gp}}{2k_B T_p}m_g|w|^2}\right]\mathrm{d}n\mathrm{d}z\mathrm{d}w\mathrm{d}v \\ &\leq 0.\end{aligned}$$

□

We can now state, and prove, the following result:

Proposition 8.3. *Let assume that the collision kernel is an hard sphere collision kernel, given by* (8.13)*. Then the functional* $\mathbb{H}(F,f)$ *defined in* (8.34) *does not increase in time.*

Proof. We start considering $h_1(t,x)$, and we will omit the dependence of f and F on (t,x) for lightning the notation:

$$\begin{aligned}\partial_t h_1(t,x) &= \int \partial_t f(w)\left(\ln f(w)+1\right)\mathrm{d}w + \int \partial_t F(v)\left(\ln F(v)+1\right)\mathrm{d}v \\ &= -\nabla_x\cdot\int w f(w)\ln f(w)\mathrm{d}w - \nabla_x\cdot\int vF(v)\ln F(v)\mathrm{d}v \\ &\quad+\int\left(\mathcal{R}(F,f)(w)+\mathcal{C}(f)(w)\right)\ln f(w)\mathrm{d}w + \int\left(\mathcal{D}(F,f)(v)+\mathcal{P}(F)(v)\right)\ln F(v)\mathrm{d}v\end{aligned}$$

where we made use of the Boltzmann system (8.1) and Lemma 8.5. Using the hypothesis on the F and f tails we have

$$\int\nabla_x\cdot\int w f(w)\ln f(w)\mathrm{d}w\mathrm{d}x = 0 \text{ and } \int\nabla_x\cdot\int vF(v)\ln F(v)\mathrm{d}v\mathrm{d}x = 0.$$

Moreover, using the second line of (8.37), we deduce the following equality:

$$\begin{aligned}&\int\partial_t h_1(t,x)\mathrm{d}x \\ &= \int\mathbb{D}(F,f)(t,x)\mathrm{d}x - \frac{\mu_{gp}}{k_B}\int\frac{1}{T_p(t,x)}\left(\frac{m_g}{2}\int\mathcal{R}(F,f)|w|^2\mathrm{d}w + \frac{m_p}{2}\int\mathcal{D}(F,f)|v|^2\mathrm{d}v\right)\mathrm{d}x.\end{aligned}$$

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If now we use the weak formulations (8.16) and (8.18) for $\mathcal{D}(F,f)$ and $\mathcal{R}(F,f)$ respectively, we can proceed in the same way as in the proof of Proposition 8.2. It follows, thanks to (8.24) and (8.32)

$$\begin{aligned}
&\frac{m_g}{2}\int \mathcal{R}(F,f)|w|^2\mathrm{d}w + \frac{m_p}{2}\int \mathcal{D}(F,f)|v|^2\mathrm{d}v \\
&= \frac{\sigma_{gp}}{2}\iiiint F(t,x,v)f(t,x,w)h_n(t,x,z)\varsigma(v-w,n)\left[m_p|v'|^2 - m_p|v|^2 + m_g|w'|^2 - m_g|w|^2\right]\mathrm{d}n\mathrm{d}z\mathrm{d}v\mathrm{d}w \\
&= \frac{\sigma_{gp}}{2}\frac{m_p m_g}{(m_p+m_g)}\iiiint F(t,x,v)f(t,x,w)h_n(t,x,z)\varsigma(v-w,n)\left[|z|^2 - |v-w|^2\right]\mathrm{d}n\mathrm{d}z\mathrm{d}v\mathrm{d}w \\
&= \frac{\sigma_{gp}}{2}\frac{m_p m_g}{(m_p+m_g)}\left(\frac{4k_B T_p(t,x)}{m_g}I_1(F,f)(t,x) - I_2(F,f)(t,x)\right)
\end{aligned}$$

where $I_1(F,f)$ and $I_2(F,f)$ are defined by (8.28) and (8.29) respectively. Then, using that we have set $\mu_{gp} = (m_p+m_g)/m_p$ and thanks to the surface temperature equation (8.27), we obtain

$$\begin{aligned}
&\int \partial_t h_1(t,x)\mathrm{d}x \\
&= \int \mathbb{D}(F,f)(t,x)\mathrm{d}x - \frac{\mu_{gp}}{2k_B}m_p\int \frac{1}{T_p(t,x)}\left(\frac{4k_B T_p(t,x)}{m_p+m_g}I_1(F,f)(t,x) - \frac{m_g}{m_p+m_g}I_2(F,f)(t,x)\right)\mathrm{d}x. \\
&= \int \mathbb{D}(F,f)(t,x)\mathrm{d}x + \frac{(m_g+m_p)}{k_B}c_p\int \frac{1}{T_p(t,x)}\left(\partial_t T_p(t,x)\int_{\mathbb{R}^3} F(t,x,v)dv + \nabla_x T_p(t,x)\int F(v)v\mathrm{d}v\right)\mathrm{d}x \\
&= \int \mathbb{D}(F,f)(t,x)\mathrm{d}x + \frac{(m_g+m_p)}{k_B}c_p\int \left(\partial_t(\ln(T_p(t,x))\int F(v)\mathrm{d}v + \nabla_x(\ln(T_p(t,x)))\cdot\int F(v)v\mathrm{d}v\right)\mathrm{d}x
\end{aligned}$$

Moreover, since 1 is a collision invariant of $\mathcal{D}(F,f)$ and $\mathcal{P}(F,f)$, we deduce from (8.1) equation

$$\int \partial_t F(t,x,v)\mathrm{d}v + \int \nabla_x\cdot(F(t,x,v)v)\mathrm{d}v = 0$$

and thus

$$\begin{aligned}
&\int \partial_t h_2(t,x)\mathrm{d}x \\
&= -\frac{m_g+m_p}{k_B}c_p\int \partial_t\left(\ln T_p(t,x)\int F(t,x,v)\right)\mathrm{d}v\mathrm{d}x \\
&= -\frac{m_g+m_p}{k_B}c_p\int \left(\partial_t\left(\ln T_p(t,x)\right)\int F(t,x,v)\mathrm{d}v - \ln T_p(t,x)\int \nabla_x\cdot(F(t,x,v)v)\mathrm{d}v\right)\mathrm{d}x \\
&= -\frac{m_g+m_p}{k_B}c_p\left(\int \partial_t\left(\ln T_p(t,x)\right)\int F(t,x,v)\mathrm{d}v\mathrm{d}x + \int \nabla_x(\ln T_p(t,x))\cdot\int F(t,x,v)v\mathrm{d}v\mathrm{d}x\right)
\end{aligned}$$

from the divergence theorem. We finally obtain

$$\int \partial_t h_1(t,x)\mathrm{d}x + \int \partial_t h_2(t,x)\mathrm{d}x = \int \mathbb{D}(F,f)(t,x)\mathrm{d}x,$$

and so, by Lemma 8.6, the thesis. □

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Remark 8.3. *For a Maxwellian collision kernel ς, providing an explicit expression for the entropy of the system looks more complicated. In fact, it is not possible to rewrite $\mathbb{D}^d$, defined in (8.37), as in the proof of Lemma 8.6. In the case of a Maxwellian kernel, the equality $h_n(v-w)\varsigma(z,n) = h_n(z)\varsigma(v-w,n)$ is no longer available as a tool to show the non-negativity of $\mathbb{D}^d$.*

8.3.3 Equilibrium states

We first recall the case of the Boltzmann operator $\mathcal{C}(f)$. We have the following Theorem [107]:

Theorem 8.1 (Boltzmann Theorem)**.** *Let $f : \mathbb{R}^3 \mapsto \mathbb{R}^+$ be a smooth positive solution of the functional equation*

$$\forall (w, w_*, n) \in \mathbb{R}^3 \times \mathbb{R}^3 \times \mathbb{S}^2, \qquad f(w'')f(w_*'') = f(w)f(w_*),$$

where w'' and w_*'' are given by (8.3). Then there exists n_g, u_g, $\theta_g > 0$ such that $f = \mathcal{M}[n_g, u_g, \theta_g]$, where

$$\mathcal{M}[n_g, u_g, \theta_g](w) := \frac{n_g m_g^{3/2}}{(2\pi k_B \theta_g)^{3/2}} e^{-\frac{m_g |w-u_g|^2}{2k_B\theta_g}}, \tag{8.39}$$

It follows that in case of equilibrium

$$\int_{\mathbb{R}^3} \ln f(w) C(f)(w) \mathrm{d}w = 0 \Leftrightarrow f = \mathcal{M}[n_g, u_g, \theta_g],$$

with

$$\rho_g(t,x) := \int_{\mathbb{R}^3} f(t,x,w)\mathrm{d}w, \qquad u_g(t,x) := \frac{1}{n_g(t,x)} \int_{\mathbb{R}^3} f(t,x,w) w \mathrm{d}w,$$

$$\theta_g(t,x) := \frac{m_g}{3k_B n_g(t,x)} \int_{\mathbb{R}^3} f(t,x,w)|w - u_g(t,x)|^2 \mathrm{d}w.$$

We also have

$$\int_{\mathbb{R}^3} \ln F(v) \mathcal{P}(F)(v) \mathrm{d}v = 0 \Leftrightarrow F = \mathcal{M}[n_p, u_p, \theta_p],$$

with

$$\rho_p(t,x) := \int_{\mathbb{R}^3} F(t,x,v)\mathrm{d}v, \qquad u_p(t,x) := \frac{1}{n_p(t,x)} \int_{\mathbb{R}^3} F(t,x,v) v \mathrm{d}v,$$

$$\theta_p(t,x) := \frac{m_p}{3k_B n_p(t,x)} \int_{\mathbb{R}^3} F(t,x,v)|v - u_p(t,x)|^2 \mathrm{d}v.$$

We now extend this result to the case of operators $\mathcal{D}(F,f)$ and $\mathcal{R}(F,f)$.

Lemma 8.7. *Let F and f in $\mathcal{C}^1(\mathbb{R}^3) \cap L^1(\mathbb{R}^3)$, such that*

$$\forall (v,w,z) \in \mathbb{R}^3 \times \mathbb{R}^3 \times \mathbb{R}^3, \qquad F(v')f(w')e^{c(m_p|v'|^2 + m_g|w'|^2)} = F(v)f(w)e^{c(m_p|v|^2 + m_g|w|^2)}, \tag{8.40}$$

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where v' and w' are given by (8.17) *and* (8.19)*, where c is a given constant. Then F and f are Maxwellien states. More precisely there exist $u \in \mathbb{R}^3$, $N_f > 0$, $N_F > 0$ such that*

$$\begin{cases} F(v) = N_f e^{-c(m_p|v-u|^2)} \\ f(w) = N_F e^{-c(m_g|w-u|^2)}. \end{cases} \tag{8.41}$$

Proof. The proof follows the same idea as in [171], but adapted to the particular collision mechanism that we consider here. We multiply equation (8.40) by $h_n(z)$ and integrate over the parameters $z \in \mathbb{R}^3$ and $n \in \mathbf{S}$. Then we get

$$\begin{aligned} &\int_{\mathbb{S}^2}\int_{\mathbb{R}^3} F(v)f(w)e^{c(m_p|v|^2+m_g|w|^2)}h_n(z)\mathrm{d}z\mathrm{d}n \\ &= \int_{\mathbb{S}^2}\int_{\mathbb{R}^3} F(v')f(w')e^{c(m_p|v'|^2+m_g|w'|^2)}h_n(z)\mathrm{d}z\mathrm{d}n. \end{aligned}$$

Let $v_B = \frac{m_p v + m_g w}{m_p+m_g}$. Thanks to relations (8.17) and (8.19), we have

$$m_p|v'|^2 + m_g|w'|^2 = (m_p+m_g)|v_B|^2 + \frac{m_p m_g}{m_p+m_g}|z|^2.$$

Then

$$\begin{aligned} &4\pi F(v)f(w)e^{c(m_p|v|^2+m_g|w|^2)} \\ &= \int_{\mathbb{R}^3}\int_{\mathbb{S}^2} F\left(v_B - \frac{m_g}{m_p+m_g}z\right) f\left(v_B + \frac{m_p}{m_p+m_g}z\right) e^{c((m_p+m_g)|v_B|^2+\frac{m_p m_g}{m_p+m_g}|z|^2)}h_n(z)\mathrm{d}n\mathrm{d}z \\ &= \frac{1}{2\pi}\frac{m_g^2}{2k_B^2T_p}\int_{\mathbb{S}^2}[n\cdot z]_+ dn \\ &\qquad \times \int_{\mathbb{R}^3} F\left(v_B - \frac{m_g}{m_p+m_g}z\right) f\left(v_B + \frac{m_p}{m_p+m_g}z\right) e^{c((m_p+m_g)|v_B|^2+\frac{m_p m_g}{m_p+m_g}|z|^2} e^{-\frac{m_g^2}{2k_B^2T_p}|z|^2} dz \\ &\frac{1}{2\pi}\frac{m_g^2}{2k_B^2T_p}\int_{\mathbb{R}^3} F\left(v_B - \frac{m_g}{m_p+m_g}z\right) f\left(v_B + \frac{m_p}{m_p+m_g}z\right) e^{c((m_p+m_g)|v_B|^2+\frac{m_p m_g}{m_p+m_g}|z|^2} e^{-\frac{m_g^2}{2k_B^2T_p}|z|^2} |z| dz \end{aligned}$$

It follows that

$$\Psi(v_B) := F(v)f(w)e^{c(m_p|v|^2+m_g|w|^2)}$$

is a (smooth) function of the only vector only v_B. Then, if we denote $E = m_p|v|^2 + m_g|w|^2$, we have

$$\ln F(v) + \ln f(w) = \ln \Psi(v_B) - cE.$$

This allows to obtain that

$$\begin{aligned} \nabla_v \ln F(v) &= \frac{m_p}{m_g+m_p}\Psi'\left(\frac{m_p v + m_g w}{m_p+m_g}\right) - 2m_p v \\ \nabla_w \ln f(w) &= \frac{m_p}{m_g+m_p}\Psi'\left(\frac{m_p v + m_g w}{m_p+m_g}\right) - 2m_g w \end{aligned}$$

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and then that $m_g \nabla_v \ln F(v) - m_p \nabla_w \ln f(w)$ is colinear to $v - w$:

$$m_g \nabla_v \ln F(v) - m_p \nabla_w \ln f(w) = -2c\, m_p m_g (v - w) \qquad \forall (v, w) \in \mathbb{R}^3 \times \mathbb{R}^3.$$

Finally we can conclude that there exist $u \in \mathbb{R}^3$ such that

$$\begin{cases} \nabla_v \ln F(v) = -2c\, m_p (v - u) \\ \nabla_w \ln f(w) = -2c\, m_g (w - u) \end{cases}$$

and thus that there exists also $\lambda_1 \in \mathbb{R}$, $\lambda \in \mathbb{R}$ such that

$$\begin{cases} F(v) = e^{-c(m_p |v-u|^2 + \lambda_1)} \\ f(w) = e^{-c(m_g |w-u|^2 + \lambda_2)}. \end{cases}$$

which proves (8.41). □

This lead to the following (formal) characterisation of the equilibrium states of system (8.1).

Proposition 8.4. *Let f and F smooth functions that verify* (8.1)*, with ς given by* (8.13)*. Then*

$$\mathbb{D}(F, f)(t, x) = 0 \text{ for any } (t, x) \in \mathbb{R}^+ \times \mathbb{R}^3$$

if and only if there exists $u^{eq} = u^{eq}(t, x) \in \mathbb{R}^3$, $N_f = N_f(t, x) \geq 0$ and $N_F = N_F(t, x) \geq 0$ such that

$$\begin{cases} f(t, x, w) = N_f(t, x) \exp\left(-\dfrac{\mu_{gp}}{2k_B T_p(t, x)} m_g |w - u^{eq}(t, x)|^2 \right) =: f^{\mathrm{eq}}(t, x, w), \\ F(t, x, v) = N_F(t, x) \exp\left(-\dfrac{\mu_{gp}}{2k_B T_p(t, x)} m_p |v - u^{eq}(t, x)|^2 \right) =: F^{\mathrm{eq}}(t, x, v). \end{cases} \tag{8.42}$$

where $\mu_{gp} = \frac{m_p + m_g}{m_p}$.

Proof. The proof is similar to that of [56, Théorème 2.1]. On the one hand, since both $\mathbb{D}^e(F, f)$ and $\mathbb{D}^d(F, f)$ are non-negative, they must both be zero if $\mathbb{D}(F, f)$ is zero. Therefore, by applying Lemma 8.7 with the choice $c = \mu_{gp}/(2k_B T_p)$, the expressions for the equilibria (8.42) follow. On the other hand, if the equilibria are given by (8.42), then $\mathbb{D}^d(F, f) = 0$. Indeed, substituting the expressions (8.42) into equation (8.37), and using the conservation of mass and momentum (8.33), leads to the conclusion that $\mathbb{D}^d(F, f) = 0$. Furthermore, $\mathbb{D}^e(F, f) = 0$ as well, by applying the conservation of mass, momentum, and energy for the monospecies collisional operators (8.7). □

Remark 8.4. *We emphasise the importance of considering temperature $T_p(t, x)$ as a time and space variable, as opposed to as a microscopic variable as done in [60]. In fact, thanks to this expedient, we are able to provide an expression for the system's entropy* (8.34)*, which is fundamental for deriving the system's equilibria and for the analytical study of the model itself, which will be the subject of a future work.*

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8.4 Adimensionalization

Macroscopic quantities such as density, momentum and energy, for both gases and dust, can be constructed from integrals of the distribution functions f and F with respect to velocities v and w, respectively. These quantities are called 'moments' and their equations can be derived by directly integrating the first equation of the System (8.1) with respect to w, after multiplying by $1, w, |w|^2$, and the second with respect to v, after multiplying by $1, v, |v|^2$. However, the resulting system involves integrals of f and F that cannot be expressed in terms of the macroscopic quantities mass, momentum and energy, unless f and F have a particular expression, given a priori. In fact, the resulting system is not *closed* in general. To close it, it is necessary to specify a form of the distribution functions that depend on the primary variables. This cannot be done in a completely generic manner, but requires specifying a *regime* in which this approximate form of the distribution function is valid. Hence, it is necessary to adimensionalize the equations through a correct scaling.

8.4.1 Scaling units and main hypothesis

Scaling of variables We first introduce some quantities in Table 8.1.

Scaling unit	Meaning
L	macroscopic length scale
t°	macroscopic time scale
V°	reference velocity of particles
W°	reference velocity of molecules
$V_{\text{rel}} = \max\{V^\circ, W^\circ\}$	scaling of the relative velocity
N_g	order of magnitude of the number density in molecules
N_p	order of magnitude of the number density in particles
m_g	mass of the molecules
m_p	mass of the particles
r_g	radius of the molecules
r_p	radius of the particles
T°	reference temperature

Tab. 8.1: Scaling units

We then make the following change of space, time, and velocities coordinates

$$\hat{x} = \frac{x}{L} \quad \hat{t} = \frac{t}{t^\circ}, \quad \hat{v} = \frac{v}{V^\circ} \quad \hat{w} = \frac{w}{W^\circ} \quad \hat{z} = \frac{z}{V_{\text{rel}}},$$

and the dimensionless unknowns:

$$\hat{F}(\hat{t}, \hat{x}, \hat{v}) = \frac{F(t, x, v)}{F^\circ}, \quad \text{with } F^\circ = \frac{N_p}{(V^\circ)^3}$$

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$$\hat{f}(\hat{t},\hat{x},\hat{w}) = \frac{f(t,x,w)}{f^\circ}, \quad \text{with } f^\circ = \frac{N_g}{(W^\circ)^3},$$
$$\hat{T}_p(\hat{t},\hat{x}) = \frac{T_p(t,x)}{T^\circ}.$$

Small parameters We introduce the following small parameters

- η the mass ratio between a molecule and a particle,
$$\eta = \frac{m_g}{m_p}, \tag{8.43}$$
- ν the ratio of gas and dust radius
$$\nu := \frac{r_g}{r_p} \ll 1, \tag{8.44}$$
- δ the Knudsen number related to the gas:
$$\delta = \frac{1}{N_g \sigma_{gg} L},$$
- γ the Strouhal number of the gas
$$\gamma := \frac{L}{W^\circ t^\circ}.$$

Remark 8.5. *We note that the Knudsen number of the dust δ_p depends on that of the gas and the ratio of radii. In fact*
$$\delta_p = \frac{1}{N_p \sigma_{pp} L} \sim \delta\nu^2.$$
Moreover, we have
$$\frac{\sigma_{gg}}{\sigma_{pp}} \sim \nu^2; \qquad \frac{\sigma_{gg}}{\sigma_{gp}} \sim \frac{\nu^2}{(1+\nu)^2} \sim \nu^2.$$

Hypothesis on the order of magnitude

Hypothesis 8.1. *We assume that*
$$\eta \ll 1, \qquad \nu \ll 1, \qquad \delta \ll 1, \qquad \gamma \ll 1$$

Hypothesis 8.2 (Order of magnitude of the kinetic temperatures)**.** *We assume that the velocity scales V° and W° of dust and gas are given by their thermal velocities, and that the orders of magnitude of the kinetic temperatures of gas and dust are T°:*
$$V^\circ = \sqrt{\frac{2k_B T^\circ}{m_p}}, \qquad W^\circ = \sqrt{\frac{2k_B T^\circ}{m_g}}.$$

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Consequently, these velocities depend only on the masses, and the relation

$$\frac{V^\circ}{W^\circ} \sim \sqrt{\eta}$$

holds, where η is the mass ratio (8.43).

Remark 8.6. *As a consequence, we note that the Strouhal number of the dust is related to the one of the gas via the equality*

$$\gamma_p = \frac{L}{V^\circ t^\circ} = \frac{\gamma}{\sqrt{\eta}}.$$

Remark 8.7. *Hypothesis 8.2 explains the introduction of two different scales for the dust and gas velocities, as - from the latter - it follows that*

$$V^\circ = \sqrt{\eta} W^\circ \ll W^\circ.$$

In particular, it follows that

$$V_{\mathrm{rel}} = W^\circ.$$

Hypothesis 8.3 (Order of magnitude of the number densities)**.** *We assume that the quantity*

$$\frac{N_p}{N_g} \sim 1,$$

meaning that the quotient of the order of magnitude of the number density in particles to that of the number density in molecules behaves as a constant, independent of the parameter η.

8.4.2 Adimensionalized Boltzmann system

Through considerations of physical dimension [49], the collision kernels $c(w-w_*, n)$, $p(v-v_*, n)$ and $\varsigma(v-w, n)$ are scaled in the following way:

$$\begin{aligned}
\varsigma(v-w, n) &= W^\circ \hat{\varsigma}\left(\sqrt{\eta}\hat{v} - \hat{w}, n\right), \\
c(w-w_*, n) &= W^\circ \hat{c}(\hat{w} - \hat{w}_*), \\
p(v-v_*, n) &= V^\circ \hat{p}(\hat{v} - \hat{v}_*).
\end{aligned}$$

The dimensionless operators are then deduced by means of the following formulas:

$$\begin{aligned}
\mathcal{D}(F, f) &= \sigma_{gp} F^\circ f^\circ (W^\circ)^4 \hat{\mathcal{D}}(\hat{F}\hat{f}) \\
\mathcal{P}(F) &= \sigma_{pp} \left(F^\circ\right)^2 (V^\circ)^4 \hat{\mathcal{P}}(\hat{F}) \\
\mathcal{R}(F, f) &= \sigma_{gp} F^\circ f^\circ W^\circ (V^\circ)^3 \hat{\mathcal{R}}(\hat{F}, \hat{f}) \\
\mathcal{C}(f) &= \sigma_{gg} \left(f^\circ\right)^2 (W^\circ)^4 \hat{\mathcal{C}}(\hat{f})
\end{aligned}$$

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where $\hat{\mathcal{D}}(\hat{F},\hat{f})$, $\hat{\mathcal{P}}(\hat{F})$, $\hat{\mathcal{R}}(\hat{F},\hat{f})$, and $\hat{\mathcal{C}}(\hat{f})$ are the dimensionless version of $\mathcal{C}(f)$, $\mathcal{P}(F)$, $\mathcal{D}(F,f)$ and $\mathcal{R}(F,f)$, given by:

$$\hat{\mathcal{C}}(\hat{f})(\hat{w}) = \int_{\mathbb{R}^3}\int_{\mathbb{S}^2}\left[\hat{f}(\hat{w}')\hat{f}(\hat{w}'_*) - \hat{f}(\hat{w})\hat{f}\,(\hat{w}_*)\right]\hat{c}\,(\hat{w}-\hat{w}_*,n)\,\mathrm{d}n\mathrm{d}\hat{w}_*, \tag{8.45}$$

$$\hat{\mathcal{P}}(\hat{F})(\hat{v}) = \int_{\mathbb{R}^3}\int_{\mathbb{S}^2}\left[\hat{F}(\hat{v}')\hat{F}(\hat{v}'_*) - \hat{F}(\hat{v})\hat{F}\,(\hat{v}_*)\right]\hat{p}\,(\hat{v}-\hat{v}_*,n)\,\mathrm{d}n\mathrm{d}\hat{v}_*, \tag{8.46}$$

$$\hat{\mathcal{D}}(\hat{F},\hat{f})(\hat{t},\hat{x},\hat{v}) =$$
$$\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{S}^2}\left[\hat{f}\,(\hat{w}')\,\hat{F}\,(\hat{v}')\,h_n(\hat{t},\hat{x},\sqrt{\eta}\hat{v}-\hat{w})\hat{\varsigma}(\hat{z},n) - \hat{f}(\hat{w})\hat{F}(\hat{v})\hat{h}_n(\hat{t},\hat{x},\hat{z})\hat{\varsigma}(\sqrt{\eta}\hat{v}-\hat{w},n)\right]\mathrm{d}\hat{z}\mathrm{d}n\mathrm{d}\hat{w}, \tag{8.47}$$

and

$$\hat{\mathcal{R}}(\hat{F},\hat{f})(\hat{t},\hat{x},\hat{w}) =$$
$$\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{S}^2}\left[\hat{f}\,(\hat{w}')\,\hat{F}\,(\hat{v}')\,h_n(\hat{t},\hat{x},\sqrt{\eta}\hat{v}-\hat{w})\hat{\varsigma}(\hat{z},n) - \hat{f}(\hat{w})\hat{F}(\hat{v})\hat{h}_n(\hat{t},\hat{x},\hat{z})\hat{\varsigma}(\sqrt{\eta}\hat{v}-\hat{w},n)\right]\mathrm{d}\hat{z}\mathrm{d}n\mathrm{d}\hat{v}, \tag{8.48}$$

with

$$\begin{cases}\hat{v}' = \dfrac{\hat{v}+\sqrt{\eta}\hat{w}}{1+\eta} - \dfrac{\sqrt{\eta}}{1+\eta}\hat{z}\\[2ex] \hat{w}' = \dfrac{\sqrt{\eta}\hat{v}+\eta\hat{w}}{1+\eta} + \dfrac{1}{1+\eta}\hat{z}\end{cases} \tag{8.49}$$

and

$$\hat{h}_n(\hat{t},\hat{x},\hat{z}) = \frac{2}{\pi\hat{T}_p(\hat{t},\hat{x})^2}\,(n\cdot\hat{z})\,e^{-\frac{|\hat{z}|^2}{\hat{T}_p}}\mathbb{1}_{\{\hat{z}\cdot n\geq 0\}}.$$

For the collisional operators $\hat{\mathcal{D}}$ and $\hat{\mathcal{R}}$, we have made the dependence on $\hat{t}$ and $\hat{x}$ explicit, although we have only expressed it in $\hat{T}_p$ and $\hat{h}_n$, and not in $\hat{F}$ and $\hat{f}$. This choice is merely to remind the reader of the dependence of the surface temperature on the space-time variables.

System (8.1) is then written as

$$\begin{cases}\partial_{\hat{t}}\hat{F} + \dfrac{V^\circ t^\circ}{L}\hat{v}\cdot\nabla_{\hat{x}}\hat{F} = N_g\sigma_{gp}W^\circ t^\circ\hat{\mathcal{D}}(\hat{F},\hat{f}) + N_p\sigma_{pp}V^\circ t^\circ\hat{\mathcal{P}}(\hat{F})\\[2ex] \partial_{\hat{t}}\hat{f} + \dfrac{W^\circ t^\circ}{L}\hat{w}\cdot\nabla_{\hat{x}}\hat{f} = N_p\sigma_{gp}W^\circ t^\circ\hat{\mathcal{R}}(\hat{F},\hat{f}) + N_g\sigma_{gg}W^\circ t^\circ\hat{\mathcal{C}}(\hat{f}),\end{cases}$$

8.4.3 Adimensionalized surface temperature's equation

Expressions $I_1(F,f)$ and $I_2(F,f)$ defined by (8.28) and (8.29) are scaled in the following way

$$I_1(F,f) = N_pN_g\sigma_{gp}W^\circ\hat{I}_1(\hat{F},\hat{f}), \qquad I_2(F,f) = N_pN_g\sigma_{gp}(W^\circ)^3\hat{I}_2(\hat{F},\hat{f})$$

with

$$\begin{cases}\hat{I}_1(\hat{F},\hat{f}) = \displaystyle\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\hat{F}(\hat{v})\hat{f}(\hat{w})\hat{\Sigma}(\sqrt{\eta}\hat{v}-\hat{w})\mathrm{d}\hat{v}\mathrm{d}\hat{w},\\[2ex] \hat{I}_2(\hat{F},\hat{f}) = \displaystyle\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\hat{F}(\hat{v})\hat{f}(\hat{w})\hat{\Sigma}(\sqrt{\eta}\hat{v}-\hat{w})|\sqrt{\eta}\hat{v}-\hat{w}|^2\mathrm{d}\hat{v}\mathrm{d}\hat{w}.\end{cases} \tag{8.50}$$

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Therefore, the adimensionalised form of (8.27) is

$$c_p\frac{T^\circ N_p}{T^\circ}\left[\partial_{\hat t}\hat T_p\int_{\mathbb{R}^3}\hat F(\hat v)\mathrm{d}\hat v+\frac{\sqrt{\eta}}{\gamma}\nabla_{\hat x}\hat T_p\cdot\int_{\mathbb{R}^3}\hat F(\hat v)\hat v\mathrm{d}\hat v\right]+\frac{1}{2}\frac{m_g}{(m_g+m_p)}2N_pN_g\sigma_{gp}(W^\circ)^3\hat T_p\hat I_1(\hat F,\hat f)$$
$$=\frac{1}{2}\frac{m_g}{(m_g+m_p)}N_pN_g\sigma_{gp}(W^\circ)^3\hat I_2(\hat F,\hat f).$$

8.4.4 Summary of the dimensionless equations

We now remove all hats in the dimensionless formulas, and thanks to Hypothesis 8.1 (we are interessed in the limit $\eta,\nu\to 0$) we replace $1+\eta$ and $1+\nu$ by 1. We then consider the system made up of the following integro-differential coupled system:

$$\begin{cases}\dfrac{\gamma}{\sqrt{\eta}}\partial_t F+v\cdot\nabla_x F=\dfrac{1}{\delta\nu^2\sqrt{\eta}}\mathcal{D}(F,f)+\dfrac{1}{\delta\nu^2}\mathcal{P}(F),\\ \gamma\partial_t f+w\cdot\nabla_x f=\dfrac{1}{\delta\nu^2}\mathcal{R}(F,f)+\dfrac{1}{\delta}\mathcal{C}(f),\end{cases}\tag{8.51}$$

where $\mathcal{D}$, $\mathcal{P}$, $\mathcal{R}$, and $\mathcal{C}$ are the dimensionless operators (8.47), (8.46), (8.48), and (8.45), and the non-linear transport equation for T_p:

$$\tau\Big(\gamma\partial_t T_p(t,x)\int F(t,x)\mathrm{d}v+\sqrt{\eta}\nabla_x T_p(t,x)\cdot\int vF(t,x)\mathrm{d}v\Big)+\frac{1}{\delta\nu^2}\frac{1}{1+\eta}2I_1(F,f)(t,x)T_p(t,x)$$
$$=\frac{1}{\delta\nu^2}\frac{1}{1+\eta}I_2(F,f)(t,x),\tag{8.52}$$

with

$$I_1(F,f)(t,x)=\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}F(v)f(w)\Sigma(\eta v-w)\mathrm{d}v\mathrm{d}w,\tag{8.53}$$

$$I_2(F,f)(t,x)=\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}F(v)f(w)\Sigma(\eta v-w)|\eta v-w|^2\mathrm{d}v\mathrm{d}w.\tag{8.54}$$

The constant

$$\tau:=\frac{2m_pc_p}{k_B},\tag{8.55}$$

thanks to Hypothesis 8.2, can be interpreted as the ratio between the order of magnitude of the internal energy of the dust ($m_pc_pT^\circ$) and the one of the kinetic temperature of the gas, i.e. $\frac{1}{2}m_g(W^\circ)^2$. It depends only of the gas and the material which constitute the particles (but not on the size or the quantity of particles) and it has no unit of measure.

8.4.5 Dimensionless equilibrium states and entropy dissipation

With such scaling, also considering that $\hat u^{eq}=W^\circ u^{eq}$, we obtain the following forms for entropy dissipation and equilibrium, whose expressions can be derived directly from Lemma 8.6:

Lemma 8.8. *The re-scaled equilibrium states have the following shape:*

$$\begin{cases}f^{\mathrm{eq}}(t,x,w) &= n_g(t,x)\exp\left(-\frac{(1+\eta)}{T_p(t,x)}|w-u^{eq}(t,x)|^2\right),\\ F^{\mathrm{eq}}(t,x,v) &= n_p(t,x)\exp\left(-\frac{(1+\eta)}{T_p(t,x)}|v-\frac{1}{\sqrt{\eta}}u^{eq}(t,x)|^2\right).\end{cases}\tag{8.56}$$

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8.5 Diffusive scaling and balance laws

We want to study the diffusion limit of the Boltzmann system (8.51) coupled with equation (8.52), that is when the small parameters δ and γ tend to 0. In addition, we also simultaneously consider the asymptotic of the mass and size ratios between the two species towards 0, that is $\eta \to 0$ and $\nu \to 0$.

We denote $\epsilon = (\gamma, \varepsilon, \delta, \eta)$ and we consider $(f^\epsilon, F^\epsilon, T_p^\epsilon)$ solution of (8.51)-(8.52). We introduce the macroscopic densities of f^ϵ and F^ϵ defined by.

$$\rho_F^\epsilon(t,x) = \int F^\epsilon(t,x,v)\mathrm{d}v, \qquad \rho_f^\epsilon(t,x) = \int f^\epsilon(t,x,w)\mathrm{d}w, \tag{8.57}$$

Since we are interested in a diffusive behaviour, we make, as in [33], the following additional Hypothesis:

Hypothesis 8.4. *The bulk velocity is small and it goes to zero in the vanishing Strouhal number limit.*

Taking into account the different speed scaling of two species, Hypothesis 8.4 lead to define

$$u_F^\epsilon(t,x) = \frac{\sqrt{\eta}}{\gamma\rho_F^\epsilon(t,x)} \int F^\epsilon(t,x,v)v\mathrm{d}v, \qquad u_f^\epsilon(t,x) = \frac{1}{\gamma\rho_f^\epsilon(t,x)} \int f^\epsilon(t,x,w)w\mathrm{d}w. \tag{8.58}$$

Remark 8.8. *Note that u_F^ϵ and u_f^ϵ do not correspond to the macroscopic velocities as they are usually defined, but rather to the first-order term in $\frac{\gamma}{\sqrt{\eta}}$ (respectively γ) of the asymptotic expansion of these macroscopic velocities.*

We also define the kinetic temperature of the species:

$$\theta_F^\epsilon(t,x) = \frac{1}{3\rho_F^\epsilon} \int F^\epsilon(v) \left| v - \frac{\gamma}{\sqrt{\eta}} u_F^\epsilon \right|^2 \mathrm{d}v, \qquad \theta_f^\epsilon(t,x) = \frac{1}{3\rho_f^\epsilon} \int f^\epsilon(w)|w - \gamma u_f^\epsilon|^2 \mathrm{d}w, \tag{8.59}$$

According to definitions (8.57), (8.58) and (8.59), we have for the 0, 1 and 2 moment of F^ϵ:

$$\int_{\mathbb{R}^3} F^\epsilon(t,x,v) \begin{pmatrix} 1 \\ v \\ |v|^2 \end{pmatrix} \mathrm{d}v = \begin{pmatrix} \rho_F^\epsilon \\ \frac{\gamma}{\sqrt{\eta}}\rho_F^\epsilon u_F^\epsilon \\ 3\rho_F^\epsilon\theta_F^\epsilon + \frac{\gamma^2}{\eta}|u_F^\epsilon|^2\rho_F^\epsilon \end{pmatrix}, \tag{8.60}$$

and for the 0, 1 and 2 moment of f^ϵ:

$$\int_{\mathbb{R}^3} f^\epsilon(t,x,w) \begin{pmatrix} 1 \\ w \\ |w|^2 \end{pmatrix} \mathrm{d}w = \begin{pmatrix} \rho_f^\epsilon \\ \gamma\rho_f^\epsilon u_f^\epsilon \\ 3\rho_f^\epsilon\theta_f^\epsilon + \gamma^2|u_f^\epsilon|^2\rho_f^\epsilon \end{pmatrix}. \tag{8.61}$$

8.5.1 Ansatz

The main hypothesis of our work is that the initial distributions $(f^\epsilon(0,\cdot,\cdot), F^\epsilon(0,\cdot,\cdot))$ are local Maxwellian states, and that the evolution following (8.51) and (8.52) maintains the distribution functions in local Maxwellian states. From a physical point of view, it corresponds to assume that the mixtures has reached its global mechanical equilibrium. This approximation

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is justified when the vector parameter ϵ approaches zero, as we will see in the next Section. We then have

$$F^\epsilon(t,x,v) = \rho_F^\epsilon(t,x)\left(\frac{1}{2\pi\theta_F^\epsilon(t,x)}\right)^{\frac{3}{2}}\exp\left(-\frac{1}{2\theta_F^\epsilon(t,x)}|v-\frac{\gamma}{\sqrt{\eta}}u_F^\epsilon(t,x)|^2\right), \tag{8.62}$$

$$f^\epsilon(t,x,w) = \rho_f^\epsilon(t,x)\left(\frac{1}{2\pi\theta_f^\epsilon(t,x)}\right)^{\frac{3}{2}}\exp\left(-\frac{1}{2\theta_f^\epsilon(t,x)}|w-\gamma u_f^\epsilon(t,x)|^2\right), \tag{8.63}$$

where $\rho_F^\epsilon, \rho_f^\epsilon$, $u_F^\epsilon, u_f^\epsilon$, $\theta_F^\epsilon, \theta_f^\epsilon$ are defined by (8.57), (8.58), (8.59). The choice of ansatz (8.62) and (8.63) is the usual line of attack to address diffusion limit procedures in the context of Boltzmann models (see for instance [33] and [120]).

8.5.2 Balance laws

To obtain a macroscopic description of the gas-dust aerosol mixture, we hence start with the kinetic description (8.51), combined with equation (8.52) for the description of the surface temperature of the dust, and integrate them with respect to the velocity variables v and w only.

8.5.2.1 Conservation of mass

Proposition 8.5. *Let (f^ϵ, F^ϵ) solution of system (8.51), and ρ_F^ϵ, ρ_f^ϵ, u_F^ϵ, u_f^ϵ defined by (8.57) and (8.58). We have the mass balance equations:*

$$\begin{cases} \partial_t\rho_F^\epsilon + \nabla_x\cdot(\rho_F^\epsilon u_F^\epsilon) = 0 \\ \partial_t\rho_f^\epsilon + \nabla_x\cdot\left(\rho_f^\epsilon u_f^\epsilon\right) = 0. \end{cases} \tag{8.64}$$

Proof. It follows directly by integrating the first and second equations of (8.51) in v and w respectively, since 1 is a collision invariant for all $\mathcal{D}, \mathcal{P}, \mathcal{R}$ and $\mathcal{C}$, and we can explicitly compute the momentum of order 0 and 1 of F^ϵ and f^ϵ. □

8.5.2.2 Balance of momentum

Proposition 8.6. *Under the same assumptions of Proposition 8.5, we further have the momentum balance:*

$$\begin{cases} \dfrac{\gamma^2}{\eta}\left[\partial_t\left(\rho_F^\epsilon u_F^\epsilon\right) + \nabla_x\cdot\left(u_F^\epsilon\otimes u_F^\epsilon\rho_F^\epsilon\right)\right] + \nabla_x\left(\rho_F^\epsilon\theta_F^\epsilon\right) = \dfrac{1}{\delta\nu^2\sqrt{\eta}}\Theta_F^\epsilon \\ \gamma^2\left[\partial_t\left(\rho_f^\epsilon u_f^\epsilon\right) + \nabla_x\cdot\left(u_f^\epsilon\otimes u_f^\epsilon\rho_f^\epsilon\right)\right] + \nabla_x\left(\rho_f^\epsilon\theta_f^\epsilon\right) = \dfrac{1}{\delta\nu^2}\Theta_f^\epsilon, \end{cases} \tag{8.65}$$

where

$$\Theta_F^\epsilon(t,x) := \int_{\mathbb{R}^3} v\mathcal{D}(F^\epsilon,f^\epsilon)(t,x,v)\,\mathrm{d}v, \qquad \Theta_f^\epsilon(t,x) := \int_{\mathbb{R}^3} w\mathcal{R}(F^\epsilon,f^\epsilon)(t,x,w)\,\mathrm{d}w.$$

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Proof. To deduce (8.65), we first multiply the first and second equations of (8.51) by $w_{(\ell)}$ and $v_{(\ell)}$, respectively, for $\ell = 1, 2, 3$, and then we integrate the first equation of (8.51) respect to v and the second one respect to w. The resulting system is:

$$\begin{cases} \dfrac{\gamma^2}{\eta}\partial_t\left(\rho_F^\epsilon(u_F^\epsilon)_{(\ell)}\right) + \nabla_x \cdot \left(\displaystyle\int_{\mathbb{R}^3} v_{(\ell)} F^\epsilon(v) v \, \mathrm{d}v\right) = \dfrac{1}{\delta\nu^2\sqrt{\eta}}(\Theta_F^\epsilon)_{(\ell)} \\ \gamma^2\partial_t\left(\rho_f^\epsilon(u_f^\epsilon)_{(\ell)}\right) + \nabla_x \cdot \left(\displaystyle\int_{\mathbb{R}^3} w_{(\ell)} f^\epsilon(w) w \, \mathrm{d}w\right) = \dfrac{1}{\delta\nu^2}(\Theta_f^\epsilon)_{(\ell)}, \end{cases} \tag{8.66}$$

We first study the divergence term appearing in the equation for the dust. For $k = 1, 2, 3$, we have that:

$$\begin{aligned} \int_{\mathbb{R}^3} v_{(\ell)} F^\epsilon(v) v_{(k)} \, \mathrm{d}v &= \left(\frac{1}{2\pi\theta_F^\epsilon}\right)^{\frac{3}{2}} \rho_F^\epsilon \int_{\mathbb{R}^3} v_{(\ell)} v_{(k)} \exp\left(-\frac{1}{2\theta_F^\epsilon}\left|v - \frac{\gamma}{\sqrt{\eta}} u_F^\epsilon\right|^2\right) \mathrm{d}v \\ &= \left(\frac{1}{2\pi\theta_F^\epsilon}\right)^{\frac{3}{2}} \rho_F^\epsilon \int_{\mathbb{R}^3} \left(v_{(\ell)} + \frac{\gamma}{\sqrt{\eta}}(u_F^\epsilon)_{(\ell)}\right)\left(v_{(k)} + \frac{\gamma}{\sqrt{\eta}}(u_F^\epsilon)_{(k)}\right) \exp\left(-\frac{|v|^2}{2\theta_F^\epsilon}\right) \mathrm{d}v \\ &= \left(\frac{1}{2\pi\theta_F^\epsilon}\right)^{\frac{3}{2}} \rho_F^\epsilon \int_{\mathbb{R}^3} \left(\frac{\gamma^2}{\eta}(u_F^\epsilon)_{(\ell)}(u_F^\epsilon)_{(k)} + v_{(\ell)}^2\delta_{k\ell}\right) \exp\left(-\frac{|v|^2}{2\theta_F^\epsilon}\right) \mathrm{d}v \\ &= \frac{\gamma^2}{\eta}(u_F^\epsilon)_{(\ell)}(u_F^\epsilon)_{(k)}\rho_F^\epsilon + \rho_F^\epsilon\theta_F^\epsilon, \end{aligned} \tag{8.67}$$

thanks to the change of variables $v \mapsto z := v - \frac{\gamma}{\sqrt{\eta}}u_F^\epsilon$, and by noticing that the following integrals are null

$$\begin{cases} \displaystyle\int_{\mathbb{R}^3} v_{(k)} v_{(\ell)} \exp\left(-\frac{|v|^2}{2\theta_F^\epsilon}\right) \mathrm{d}v = 0 \qquad \text{for all } k \neq \ell, \\ \displaystyle\int_{\mathbb{R}^3} v_{(k)} \exp\left(-\frac{|v|^2}{2\theta_F^\epsilon}\right) \mathrm{d}v = 0 \qquad \text{for all } k. \end{cases}$$

Regarding the divergence term appearing in the equation for the gas, following the same procedure, we deduce that

$$\int_{\mathbb{R}^3} w_{(\ell)} f^\epsilon(w) w_{(k)} \, \mathrm{d}w = \gamma^2 (u_f^\epsilon)_{(\ell)}(u_f^\epsilon)_{(k)}\rho_f^\epsilon + \rho_f^\epsilon\theta_f^\epsilon. \tag{8.68}$$

□

Proposition 8.7. *For a general collision kernel, the operators Θ_F^ϵ and Θ_f^ϵ of the momentum balance System* (8.65) *can explicitly be written as*

$$\begin{aligned} \Theta_F^\epsilon = \frac{-\sqrt{\eta}}{1+\eta}\Bigg[&\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} (\sqrt{\eta}v - w)\, F^\epsilon(v) f^\epsilon(w) \Sigma(\sqrt{\eta}v - w) \mathrm{d}w\mathrm{d}v \\ &+ \frac{\sqrt{\pi}}{2}\sqrt{T_p^\epsilon}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} F^\epsilon(v) f^\epsilon(w) \int_{\mathbb{S}^2} n\varsigma(\sqrt{\eta}v - w, n) \, \mathrm{d}n\mathrm{d}w\mathrm{d}v\Bigg], \end{aligned} \tag{8.69}$$

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and

$$\Theta_f^\epsilon = \frac{1}{1+\eta}\left[\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}(\sqrt{\eta}v-w)\,F^\epsilon(v)f^\epsilon(w)\Sigma(\sqrt{\eta}v-w)\mathrm{d}w\mathrm{d}v\right.$$
$$\left.+\frac{\sqrt{\pi}}{2}\sqrt{T_p^\epsilon}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}F^\epsilon(v)f^\epsilon(w)\int_{\mathbb{S}^2}n\varsigma(\sqrt{\eta}v-w,n)\,\mathrm{d}n\mathrm{d}w\mathrm{d}v\right]. \tag{8.70}$$

Proof. Via the weak formulations (8.16), we can rewrite Θ_F^ϵ as

$$\Theta_F^\epsilon = \int_{\mathbb{R}^3} v\mathcal{D}(F^\epsilon,f^\epsilon)\,\mathrm{d}v = \int_{\mathbb{S}^2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}(v'-v)\,F^\epsilon(v)f^\epsilon(w)h_n(z)\varsigma(\sqrt{\eta}v-w,n)\,\mathrm{d}n\mathrm{d}z\mathrm{d}w\mathrm{d}v,$$

while Θ_f^ϵ can be treated in a similar manner, starting by using the weak formulation (8.18)

$$\Theta_f^\epsilon = \int_{\mathbb{R}^3} w\mathcal{R}(F^\epsilon,f^\epsilon)\,\mathrm{d}w = \int_{\mathbb{S}^2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}(w'-w)\,F^\epsilon(v)f^\epsilon(w)h_n(z)\varsigma(\sqrt{\eta}v-w,n)\,\mathrm{d}n\mathrm{d}z\mathrm{d}w\mathrm{d}v.$$

Thanks to (8.49) we have for the rescaled variables:

$$\begin{cases} v'-v = \frac{-\sqrt{\eta}}{1+\eta}\left(\sqrt{\eta}v-w+z\right), \\ w'-w = \frac{1}{1+\eta}\left(\sqrt{\eta}v-w+z\right). \end{cases}$$

Hence, the expressions (8.69) and (8.70) follows directly from computations (8.116) and (8.117) of Lemma B.11, with $c = \sqrt{\frac{1}{T_p^\epsilon(t,x)}}$. □

8.5.2.3 Balance of energy

Proposition 8.8. *Under the same assumptions of Proposition 8.5, also the energy balance holds:*

$$\begin{cases} \partial_t\left(3\rho_F^\epsilon\theta_F^\epsilon\right)+\nabla_x\cdot\left(5u_F^\epsilon\theta_F^\epsilon\rho_F^\epsilon\right)+\dfrac{\gamma^2}{\eta}\left(\partial_t\left(|u_f^\epsilon|^2\rho_F^\epsilon\right)+\nabla_x\cdot\left(|u_F^\epsilon|^2u_F^\epsilon\rho_F^\epsilon\right)\right)=\dfrac{1}{\gamma\delta\nu^2}\Xi_F^\epsilon, \\ \partial_t\left(3\rho_f^\epsilon\theta_f^\epsilon\right)+\nabla_x\cdot\left(5u_f^\epsilon\theta_f^\epsilon\rho_f^\epsilon\right)+\gamma^2\left(\partial_t\left(|u_f^\epsilon|^2\rho_f^\epsilon\right)+\nabla_x\cdot\left(|u_f^\epsilon|^2u_f^\epsilon\rho_f^\epsilon\right)\right)=\dfrac{1}{\gamma\delta\nu^2}\Xi_f^\epsilon, \end{cases} \tag{8.71}$$

where

$$\Xi_F^\epsilon := \int_{\mathbb{R}^3}|v|^2\mathcal{D}(F^\epsilon,f^\epsilon)\,\mathrm{d}v, \qquad \Xi_f^\epsilon := \int_{\mathbb{R}^3}|w|^2\mathcal{R}(F^\epsilon,f^\epsilon)\,\mathrm{d}w. \tag{8.72}$$

Proof. We now integrate the first equation of (8.51) respect to v, after having multiplied it by $|v|^2$, and the second one respect to w, after having multiplied it by $|w|^2$. The system we obtain has the form:

$$\begin{cases} \dfrac{\gamma}{\sqrt{\eta}}\partial_t\left(3\rho_F^\epsilon\theta_F^\epsilon+\dfrac{\gamma^2}{\eta}|u_f^\epsilon|^2\rho_F^\epsilon\right)+\nabla_x\cdot\left(\displaystyle\int_{\mathbb{R}^3}|v|^2F^\epsilon(v)v\,\mathrm{d}v\right)=\dfrac{1}{\delta\nu^2\sqrt{\eta}}\Xi_F^\epsilon, \\ \gamma\partial_t\left(3\rho_f^\epsilon\theta_f^\epsilon+\gamma^2|u_f^\epsilon|^2\rho_f^\epsilon\right)+\nabla_x\cdot\left(\displaystyle\int_{\mathbb{R}^3}|w|^2f^\epsilon(w)w\,\mathrm{d}w\right)=\dfrac{1}{\delta\nu^2}\Xi_f^\epsilon, \end{cases} \tag{8.73}$$

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For every $k = 1, 2, 3$,

$$\begin{aligned}
\int_{\mathbb{R}^3} |v|^2 F^\epsilon(v) v_{(k)}\, \mathrm{d}v &= \left(\frac{1}{2\pi\theta_F^\epsilon}\right)^{\frac{3}{2}} \rho_F^\epsilon \int_{\mathbb{R}^3} |v|^2 v_{(k)} \exp\left(-\frac{1}{2\theta_F^\epsilon}\left|v - \frac{\gamma}{\sqrt{\eta}} u_F^\epsilon\right|^2\right)\, \mathrm{d}v \\
&= \left(\frac{1}{2\pi\theta_F^\epsilon}\right)^{\frac{3}{2}} \rho_F^\epsilon \int_{\mathbb{R}^3} \left|v + \frac{\gamma}{\sqrt{\eta}} u_F^\epsilon\right|^2 \left(v_{(k)} + \frac{\gamma}{\sqrt{\eta}} (u_F^\epsilon)_{(k)}\right) \exp\left(-\frac{|v|^2}{2\theta_F^\epsilon}\right)\, \mathrm{d}v \\
&= \left(\frac{1}{2\pi\theta_F^\epsilon}\right)^{\frac{3}{2}} \rho_F^\epsilon \int_{\mathbb{R}^3} |v|^2 \left(v_{(k)} + \frac{\gamma}{\sqrt{\eta}} (u_F^\epsilon)_{(k)}\right) \exp\left(-\frac{|v|^2}{2\theta_F^\epsilon}\right)\, \mathrm{d}v \\
&\quad + \frac{\gamma^2}{\eta} \left(\frac{1}{2\pi\theta_F^\epsilon}\right)^{\frac{3}{2}} \rho_F^\epsilon |u_F^\epsilon|^2 \int_{\mathbb{R}^3} \left(v_{(k)} + \frac{\gamma}{\sqrt{\eta}} (u_F^\epsilon)_{(k)}\right) \exp\left(-\frac{|v|^2}{2\theta_F^\epsilon}\right)\, \mathrm{d}v \\
&\quad + 2\frac{\gamma}{\sqrt{\eta}} \left(\frac{1}{2\pi\theta_F^\epsilon}\right)^{\frac{3}{2}} \rho_F^\epsilon \int_{\mathbb{R}^3} \sum_{\ell=1}^{3} v_{(\ell)} (u_F^\epsilon)_{(\ell)} \left(v_{(k)} + \frac{\gamma}{\sqrt{\eta}} (u_F^\epsilon)_{(k)}\right) \exp\left(-\frac{|v|^2}{2\theta_F^\epsilon}\right)\, \mathrm{d}v \\
&= \frac{\gamma}{\sqrt{\eta}} (u_F^\epsilon)_{(k)} \rho_F^\epsilon \left(\frac{1}{2\pi\theta_F^\epsilon}\right)^{\frac{3}{2}} \int_{\mathbb{R}^3} |v|^2 \exp\left(-\frac{|v|^2}{2\theta_F^\epsilon}\right)\, \mathrm{d}v \\
&\quad + \frac{\gamma^3}{\eta^{3/2}} |u_F^\epsilon|^2 (u_F^\epsilon)_{(k)} \rho_F^\epsilon \left(\frac{1}{2\pi\theta_F^\epsilon}\right)^{\frac{3}{2}} \int_{\mathbb{R}^3} \exp\left(-\frac{|v|^2}{2\theta_F^\epsilon}\right)\, \mathrm{d}v \\
&\quad + 2\frac{\gamma}{\sqrt{\eta}} (u_F^\epsilon)_{(\ell)} \rho_F^\epsilon \left(\frac{1}{2\pi\theta_F^\epsilon}\right)^{\frac{3}{2}} \int_{\mathbb{R}^3} (v_{(\ell)})^2 \delta_{k\ell} \exp\left(-\frac{|v|^2}{2\theta_F^\epsilon}\right)\, \mathrm{d}v \\
&= 5\frac{\gamma}{\sqrt{\eta}} (u_F^\epsilon)_{(k)} \theta_F^\epsilon \rho_F^\epsilon + \frac{\gamma^3}{\eta^{3/2}} |u_F^\epsilon|^2 (u_F^\epsilon)_{(k)} \rho_F^\epsilon,
\end{aligned}$$

where we, first, perform the change of variable $z := v - \frac{\gamma}{\sqrt{\eta}} u_F^\epsilon$, then rename z as v and conclude by using the properties of the Maxwellian. In a similar way, we can express the divergence term appearing in the equation for the gas. We conclude by multiplying the first equation of (8.73) by $\frac{\sqrt{\eta}}{\gamma}$ and the second one by $\frac{1}{\gamma}$. □

Proposition 8.9. *For a general collision kernel, we have*

$$\Xi_F^\epsilon + \Xi_f^\epsilon = \frac{1}{1+\eta} \left(2T_p^\epsilon I_1(F^\epsilon, f^\epsilon) - I_2(F^\epsilon, f^\epsilon)\right). \tag{8.74}$$

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Moreover, the operators Ξ_F^ϵ and Ξ_f^ϵ can explicitly be written as

$$\begin{aligned}\Xi_F^\epsilon = \frac{1}{(1+\eta)^2}\Bigg[&\left(-\eta^2-2\eta\right)\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}|v|^2F^\epsilon(v)f^\epsilon(w)\Sigma(\sqrt{\eta}v-w)\,\mathrm{d}w\mathrm{d}v\\ &+\eta\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}|w|^2F^\epsilon(v)f^\epsilon(w)\Sigma(\sqrt{\eta}v-w)\,\mathrm{d}w\mathrm{d}v\\ &+2T_p^\epsilon\eta\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}F^\epsilon(v)f^\epsilon(w)\Sigma(\sqrt{\eta}v-w)\,\mathrm{d}w\mathrm{d}v\\ &+2\sqrt{\eta}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}v\cdot wF^\epsilon(v)f^\epsilon(w)\Sigma(\sqrt{\eta}v-w)\,\mathrm{d}w\mathrm{d}v\\ &-\sqrt{\pi T_p^\epsilon}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}(\sqrt{\eta}v+\eta w)\,F^\epsilon(v)f^\epsilon(w)\cdot\int_{\mathbb{S}^2}n\varsigma(\sqrt{\eta}v-w,n)\,\mathrm{d}n\mathrm{d}w\mathrm{d}v\Bigg],\end{aligned}\tag{8.75}$$

and

$$\begin{aligned}\Xi_f^\epsilon = \frac{1}{(1+\eta)^2}\Bigg[&(-1-2\eta)\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}|w|^2F^\epsilon(v)f^\epsilon(w)\Sigma(\sqrt{\eta}v-w)\,\mathrm{d}w\mathrm{d}v\\ &+\eta\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}|v|^2F^\epsilon(v)f^\epsilon(w)\Sigma(\sqrt{\eta}v-w)\,\mathrm{d}w\mathrm{d}v\\ &+2T_p^\epsilon\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}F^\epsilon(v)f^\epsilon(w)\Sigma(\sqrt{\eta}v-w)\,\mathrm{d}w\mathrm{d}v\\ &+2\eta\sqrt{\eta}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}v\cdot wF^\epsilon(v)f^\epsilon(w)\Sigma(\sqrt{\eta}v-w)\,\mathrm{d}w\mathrm{d}v\\ &+\sqrt{\pi T_p^\epsilon}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}(\sqrt{\eta}v+\eta w)F^\epsilon(v)f^\epsilon(w)\cdot\int_{\mathbb{S}^2}n\varsigma(\sqrt{\eta}v-w,n)\,\mathrm{d}n\mathrm{d}w\mathrm{d}v\Bigg].\end{aligned}\tag{8.76}$$

Proof. The operators Ξ_F^ϵ and Ξ_f^ϵ can be rewritten using the weak formulations (8.16) and (8.18), respectively. In particular,

$$\Xi_F^\epsilon=\int_{\mathbb{R}^3}|v|^2\mathcal{D}(F^\epsilon,f^\epsilon)(v)\,\mathrm{d}v=\int_{\mathbb{S}^2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\left(|v'|^2-|v|^2\right)F^\epsilon(v)f^\epsilon(w)h_n(z)\varsigma(\sqrt{\eta}v-w,n)\,\mathrm{d}n\mathrm{d}z\mathrm{d}w\mathrm{d}v,$$

and

$$\Xi_f^\epsilon=\int_{\mathbb{R}^3}|w|^2\mathcal{R}(F^\epsilon,f^\epsilon)(w)\,\mathrm{d}w=\int_{\mathbb{S}^2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\left(|w'|^2-|w|^2\right)F^\epsilon(v)f^\epsilon(w)h_n(z)\varsigma(\sqrt{\eta}v-w,n)\,\mathrm{d}n\mathrm{d}z\mathrm{d}w\mathrm{d}v.$$

Using the dimensionless version of relation (8.24), which is

$$|v'|^2+|w'|^2-|v|^2-|w|^2=\frac{1}{1+\eta}(|z|^2-|\sqrt{\eta}v-w|^2),$$

we get

$$\begin{aligned}&\Xi_F^\epsilon+\Xi_f^\epsilon\\ &=\frac{1}{1+\eta}\int_{\mathbb{S}^2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}(|z|^2-|\sqrt{\eta}v-w|^2)F^\epsilon(v)f^\epsilon(w)h_n(z)\varsigma(\sqrt{\eta}v-w,n)\,\mathrm{d}n\mathrm{d}z\mathrm{d}w\mathrm{d}v,\end{aligned}$$

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which directly gives (8.74), using (8.118) of Lemma B.11, with $c = \sqrt{\frac{1}{T_p^\epsilon(t,x)}}$.

Via (8.49), we know that for the rescaled variables

$$\begin{cases} |v'|^2 - |v|^2 = \frac{1}{(1+\eta)^2}\left(\eta|w|^2 + \eta|z|^2 + 2\sqrt{\eta}v\cdot w - 2\sqrt{\eta}v\cdot z - 2\eta w\cdot z\right) + \left(\frac{1}{(1+\eta)^2} - 1\right)|v|^2, \\ |w'|^2 - |w|^2 = \frac{1}{(1+\eta)^2}\left(\eta|v|^2 + |z|^2 + 2\sqrt{\eta}\eta v\cdot w + 2\sqrt{\eta}v\cdot z + 2\eta w\cdot z\right) + \left(\frac{\eta^2}{(1+\eta)^2} - 1\right)|w|^2. \end{cases}$$

Hence, thanks to computations (8.116), (8.117) and (8.118) of Lemma B.11, with $c = \sqrt{\frac{1}{T_p^\epsilon(t,x)}}$, we can conclude. □

8.5.2.4 Surface temperature's equation

Remark 8.9. *If the functions F^ϵ and f^ϵ are given by the ansatzs (8.62) and (8.63), respectively, than the dust surface temperature T_p^ϵ satisfies the following equation:*

$$\rho_F^\epsilon \tau\gamma\left(\partial_t T_p^\epsilon + u_F^\epsilon\cdot\nabla_x T_p^\epsilon\right) + \frac{1}{\delta\nu^2}\frac{1}{(1+\eta)}2I_1(F^\epsilon,f^\epsilon)T_p^\epsilon = \frac{1}{\delta\nu^2}\frac{1}{(1+\eta)}I_2(F^\epsilon,f^\epsilon), \tag{8.77}$$

where $I_1(F^\epsilon,f^\epsilon)$ and $I_2(F^\epsilon,f^\epsilon)$ are given by

$$\begin{cases} I_1(F^\epsilon,f^\epsilon) = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} F^\epsilon(v)f^\epsilon(w)\Sigma(\sqrt{\eta}v - w)\mathrm{d}v\mathrm{d}w, \\ I_2(F^\epsilon,f^\epsilon) = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} F^\epsilon(v)f^\epsilon(w)\Sigma(\sqrt{\eta}v - w)|\sqrt{\eta}v - w|^2\mathrm{d}v\mathrm{d}w. \end{cases} \tag{8.78}$$

8.5.3 Maxwellian collision kernel

For a Maxwellian molecule case, the collision kernel ς depends on v, w and n only trough the deviation angle $\theta\in[0,\pi]$ between $v-w$ and n and it does not depend on $|v-w|$, i.e.

$$\varsigma(v-w,n) := b\left(\frac{v-w}{|v-w|}\cdot n\right) = b(\cos\theta),$$

where $b : [-1,1]\to\mathbb{R}^+$, and we assume $b\in L^1([-1,1])$ and $b\geq 0$. Therefore,

$$\Sigma(v-w) = 2\pi\|b\|_{L^1(-1,1)}, \tag{8.79}$$

and

$$\int_{\mathbb{S}^2} n\varsigma(v-w,n)\,\mathrm{d}n = 0. \tag{8.80}$$

The proofs of these results can be found for example in [33].

Proposition 8.10. *For a Maxwellian collision kernel, the expressions of operators Θ_F^ϵ and Θ_f^ϵ of Corollary 8.7 become*

$$\begin{cases} \Theta_F^\epsilon = 2\pi\|b\|_{L^1}\frac{\gamma\sqrt{\eta}}{1+\eta}\rho_f^\epsilon\rho_F^\epsilon(u_f^\epsilon - u_F^\epsilon), \\ \Theta_f^\epsilon = 2\pi\|b\|_{L^1}\frac{\gamma}{1+\eta}\rho_f^\epsilon\rho_F^\epsilon(u_F^\epsilon - u_f^\epsilon). \end{cases} \tag{8.81}$$

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Moreover, the operators Ξ_F^ϵ and Ξ_f^ϵ, expressed for a general collision kernel in Corollary 8.9, in the Maxwellian case can be written as

$$\Xi_F^\epsilon = \frac{2\pi\|b\|_{L^1}}{(1+\eta)^2}\rho_f^\epsilon\rho_F^\epsilon\Big[\eta\left(2T_p^\epsilon + 3\theta_f^\epsilon - 3\eta\theta_F^\epsilon\right) - 6\eta\theta_F^\epsilon \\ +\eta\gamma^2\left(|u_f^\epsilon|^2 - |u_F^\epsilon|^2\right) + 2\gamma^2\left(u_F^\epsilon\cdot u_f^\epsilon - |u_F^\epsilon|^2\right)\Big], \tag{8.82}$$

and

$$\Xi_f^\epsilon = \frac{2\pi\|b\|_{L^1}}{(1+\eta)^2}\rho_f^\epsilon\rho_F^\epsilon\Big[-6\eta\theta_f^\epsilon + 2T_p^\epsilon - 3\theta_f^\epsilon + 3\eta\theta_F^\epsilon \\ +2\eta\gamma^2\left(u_F^\epsilon\cdot u_f^\epsilon - |u_f^\epsilon|^2\right) + \gamma^2\left(|u_F^\epsilon|^2 - |u_f^\epsilon|^2\right)\Big]. \tag{8.83}$$

Proof. Expressions (8.81) are direct consequences of the applications of (8.79) and (8.80) to the general forms (8.69) and (8.70) of Θ_F^ϵ and Θ_f^ϵ. Whereas, (8.82) and (8.83) follow by using (8.79) and (8.80) in the general expressions (8.75) and (8.76) of Ξ_F^ϵ and Ξ_f^ϵ. □

Proposition 8.11. *For Maxwellian collision kernel, T_p^ϵ solves*

$$\gamma\delta\nu^2(1+\eta)\bar\tau\rho_F^\epsilon\left(\partial_t T_p^\epsilon + u_F^\epsilon\cdot\nabla_x T_p^\epsilon\right) = \rho_F^\epsilon\rho_f^\epsilon\left(3\eta\theta_F^\epsilon + 3\theta_f^\epsilon - 2T_p^\epsilon + \gamma^2|u_F^\epsilon - u_f^\epsilon|^2\right), \tag{8.84}$$

where $\bar\tau := \frac{\tau}{2\pi\|b\|_{L^1}}$.

Proof. Thanks to (8.79), $I_1(F^\epsilon, f^\epsilon)$ and $I_2(F^\epsilon, f^\epsilon)$ take the form

$$I_1(F^\epsilon, f^\epsilon) = 2\pi\|b\|_{L^1}\rho_F^\epsilon\rho_f^\epsilon, \qquad I_2(F^\epsilon, f^\epsilon) = 2\pi\|b\|_{L^1}\rho_F^\epsilon\rho_f^\epsilon\left(3\eta\theta_F^\epsilon + 3\theta_f^\epsilon + \gamma^2|u_F^\epsilon - u_f^\epsilon|^2\right),$$

hence we can conclude. □

8.5.4 Hard-Sphere collision kernel

In a model with hard sphere collision kernel, we consider that a particle moves in a straight line, until it bounces against another one. In this case:

$$\varsigma(v-w,n) := [(v-w)\cdot n]_+ = ((v-w)\cdot n)\,\mathbb{1}_{\{(v-w)\cdot n\geq 0\}},$$

Therefore, for $y\in\mathbb{R}^3$

$$\int_{\mathbb{S}^2}\varsigma(y,n)\,\mathrm{d}n = \pi|y|, \qquad \int_{\mathbb{S}^2} n\varsigma(y,n)\,\mathrm{d}n = \frac{2\pi}{3}y. \tag{8.85}$$

The proofs of these results can be found for example in [58].

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Proposition 8.12. *For a hard-sphere collision kernel, the expressions of operators Θ_F^ϵ and Θ_f^ϵ of Corollary 8.7 become*

$$\Theta_F^\epsilon = \frac{\sqrt{\eta}}{1+\eta}\pi\Bigg[\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}(w-\sqrt{\eta}v)\,F^\epsilon(v)f^\epsilon(w)|\sqrt{\eta}v-w|\mathrm{d}w\mathrm{d}v + \gamma\frac{\sqrt{\pi}}{3}\sqrt{T_p^\epsilon}\rho_F^\epsilon\rho_f^\epsilon(u_f^\epsilon-u_F^\epsilon)\Bigg], \tag{8.86}$$

and

$$\Theta_f^\epsilon = \frac{1}{1+\eta}\pi\Bigg[\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}(\sqrt{\eta}v-w)\,F^\epsilon(v)f^\epsilon(w)|\sqrt{\eta}v-w|\mathrm{d}w\mathrm{d}v + \gamma\frac{\sqrt{\pi}}{3}\sqrt{T_p^\epsilon}\rho_F^\epsilon\rho_f^\epsilon(u_F^\epsilon-u_f^\epsilon)\Bigg]. \tag{8.87}$$

Moreover, the operators Ξ_F^ϵ and Ξ_f^ϵ, expressed for a general collision kernel in Corollary 8.9, in the hard-sphere case can be written as

$$\begin{aligned}\Xi_F^\epsilon = \frac{\pi}{(1+\eta)^2}\Bigg[&\left(-2\eta-\eta^2\right)\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}|v|^2F^\epsilon(v)f^\epsilon(w)|\sqrt{\eta}v-w|\,\mathrm{d}w\mathrm{d}v\\ &+\eta\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}|w|^2F^\epsilon(v)f^\epsilon(w)|\sqrt{\eta}v-w|\,\mathrm{d}w\mathrm{d}v\\ &+2\eta T_p^\epsilon\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}F^\epsilon(v)f^\epsilon(w)|\sqrt{\eta}v-w|\,\mathrm{d}w\mathrm{d}v\\ &+2\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}v\cdot wF^\epsilon(v)f^\epsilon(w)|\sqrt{\eta}v-w|\,\mathrm{d}w\mathrm{d}v\\ &-\frac{2}{3}\frac{1}{\sqrt{\eta}}\sqrt{\pi T_p^\epsilon}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}(\sqrt{\eta}v+\eta w)\,F^\epsilon(v)f^\epsilon(w)\cdot(\sqrt{\eta}v-w)\,\mathrm{d}w\mathrm{d}v\Bigg],\end{aligned} \tag{8.88}$$

and

$$\begin{aligned}\Xi_f^\epsilon = \frac{\pi}{(1+\eta)^2}\Bigg[&(-1-2\eta)\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}|w|^2F^\epsilon(v)f^\epsilon(w)|\sqrt{\eta}v-w|\,\mathrm{d}w\mathrm{d}v\\ &+\eta\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}|v|^2F^\epsilon(v)f^\epsilon(w)|\sqrt{\eta}v-w|\,\mathrm{d}w\mathrm{d}v\\ &+2T_p^\epsilon\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}F^\epsilon(v)f^\epsilon(w)|\sqrt{\eta}v-w|\,\mathrm{d}w\mathrm{d}v\\ &+2\eta\sqrt{\eta}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}v\cdot wF^\epsilon(v)f^\epsilon(w)|\sqrt{\eta}v-w|\,\mathrm{d}w\mathrm{d}v\\ &+\frac{2}{3}\sqrt{\pi T_p^\epsilon}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}(\sqrt{\eta}v+\eta w)F^\epsilon(v)f^\epsilon(w)\cdot(\sqrt{\eta}v-w)\,\mathrm{d}w\mathrm{d}v\Bigg].\end{aligned} \tag{8.89}$$

Proof. It is the direct consequence of the application of (8.85) to the general expressions (8.69), (8.70), (8.75), and (8.76). □

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Proposition 8.13. *For hard-sphere collision kernel, the equation for T_p^ϵ becomes:*

$$\begin{aligned}&\rho_F^\epsilon \frac{\tau}{\pi}\gamma\delta\nu^2(1+\eta)\Big(\partial_t T_p^\epsilon + u_F^\epsilon\cdot\nabla_x T_p^\epsilon\Big) + 2T_p^\epsilon \iint F^\epsilon(v)f^\epsilon(w)|\sqrt{\eta}v-w|\mathrm{d}v\mathrm{d}w\\ &= \iint F^\epsilon(v)f^\epsilon(w)|\sqrt{\eta}v-w|^3\mathrm{d}v\mathrm{d}w.\end{aligned} \tag{8.90}$$

Proof. It is the direct application of (8.85) to $I_1(F^\epsilon, f^\epsilon)$ and $I_2(F^\epsilon, f^\epsilon)$. □

8.6 Macroscopic equations and formal asymptotic

At this point, we are able to perform a formal macroscopic limit when all the parameters tend to zero. We adopt the point of view of the particles. With $\eta \to 0$ we say that the particles perceive the molecules of the gas as much faster than themselves, but much lighter and smaller ($\nu \to 0$). In particular, we consider a fluid model in the limit, as the Knudsen number of the gas δ goes to zero. Moreover, the Strouhal number γ also vanishes as well in the diffusive asymptotic. We summarise all the limits by saying

$$\epsilon = (\gamma, \nu, \delta, \eta) \to 0.$$

Moreover, we assume that we have the following link between parameters.

Hypothesis 8.5. *We assume*

$$\delta\nu^2 \sim \gamma \qquad \text{and} \qquad \frac{\gamma^2}{\eta} \to 0 \quad \text{when } \epsilon \to 0. \tag{8.91}$$

Notice that, thanks to Remark 8.5 and Remark 8.6, also the Knudsen number and the Strouhal number of the dust vanish in the limit.

We assume that all the above assumptions have been verified, and we assume that the macroscopic quantities (8.57), (8.58), and (8.59) have a limit when $\epsilon \to 0$. We denote

$$\rho_F(t,x) := \lim_{\epsilon\to 0}\rho_F^\epsilon(t,x), \qquad \rho_f(t,x) := \lim_{\epsilon\to 0}\rho_f^\epsilon(t,x), \tag{8.92}$$

$$u_F(t,x) := \lim_{\epsilon\to 0}u_F^\epsilon(t,x), \qquad u_f(t,x) := \lim_{\epsilon\to 0}u_f^\epsilon(t,x), \tag{8.93}$$

$$\theta_F(t,x) := \lim_{\epsilon\to 0}\theta_F^\epsilon(t,x), \qquad \theta_f(t,x) := \lim_{\epsilon\to 0}\theta_f^\epsilon(t,x). \tag{8.94}$$

As a consequence $f^\epsilon(t,x)$ and $F^\epsilon(t,x)$ have a limit when $\epsilon \to 0$, that we denote $f(t,x)$ and $F(t,x)$ respectively. Moreover, if the previous limits exist also the limit of T_p^ϵ exists, thanks to the following proposition. We will denote it as $T_p(t,x)$.

Proposition 8.14. *Assume that $\partial_t T_p^\epsilon$ and $\nabla_x T_p^\epsilon$ are bounded when $\epsilon \to 0$. Then*

$$2I_1(F^\epsilon, f^\epsilon)T_p^\epsilon - I_2(F^\epsilon, f^\epsilon) = \mathcal{O}(\gamma^2), \tag{8.95}$$

and thus

$$T_p^\epsilon(t,x) \to T_p := \frac{I_2(F,f)}{2I_1(F,f)} \qquad \text{when } \epsilon \to 0. \tag{8.96}$$

Proof. This is a direct consequence of equation (8.77) and Hypothesis 8.91, i.e. $\delta\nu^2 \sim \gamma$. □

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8.6.1 General collision kernel

We start by expressing the equations that can be obtained for any kind of collision kernel.

Theorem 8.2. *Let (ρ_F, u_F, θ_F), (ρ_f, u_f, θ_f) and T_p defined by (8.92), (8.93), (8.94) and (8.96). For general collision kernel, the macroscopic variables satisfy the conservation of mass equations*

$$\begin{cases} \partial_t \rho_F + \nabla_x \cdot (\rho_F u_F) = 0, \\ \partial_t \rho_f + \nabla_x \cdot (\rho_f u_f) = 0, \end{cases} \tag{8.97}$$

the equation

$$\nabla_x (\rho_F \theta_F) + \nabla_x (\rho_f \theta_f) = 0, \tag{8.98}$$

and the conservation of the total energy

$$3\partial_t (\rho_F \theta_F + \rho_f \theta_f) + 5\nabla_x \cdot (u_F \theta_F \rho_F + u_f \theta_f \rho_f) + \rho_F \tau (\partial_t T_p + u_F \cdot \nabla_x T_p) = 0. \tag{8.99}$$

Remark 8.10. *We obtain 6 equations for 11 unknowns. We can then see the need to obtain other relations. Other relations will be obtained for particular choices of collision kernel.*

Proof. The system (8.97) is a direct consequence of (8.64). Equation (8.98) follows by summing up the equations of System (8.65) and then performing the formal limit, after having applied Hypothesis (8.91). To deduce Equation (8.99), we use (8.74) and (8.77):

$$\begin{aligned} \Xi_F^\epsilon + \Xi_f^\epsilon &= \frac{1}{1+\eta} \left(2I_1(F^\epsilon, f^\epsilon) T_p^\epsilon - I_2(F^\epsilon, f^\epsilon) \right) \\ &= -\delta \nu^2 \gamma \, \rho_F^\epsilon \tau \left(\partial_t T_p^\epsilon + u_F^\epsilon \cdot \nabla_x T_p^\epsilon \right). \end{aligned}$$

Then the addition of the two relation of (8.71) gives

$$\begin{aligned} &\partial_t (3\rho_F^\epsilon \theta_F^\epsilon) + \nabla_x \cdot (5 u_F^\epsilon \theta_F^\epsilon \rho_F^\epsilon) + \partial_t \left(3\rho_f^\epsilon \theta_f^\epsilon \right) + \nabla_x \cdot \left(5 u_f^\epsilon \theta_f^\epsilon \rho_f^\epsilon \right) \\ &+ \frac{\gamma^2}{\eta} \left[\partial_t \left(|u_f^\epsilon|^2 \rho_F^\epsilon \right) + \nabla_x \cdot \left(|u_F^\epsilon|^2 u_F^\epsilon \rho_F^\epsilon \right) \right] + \gamma^2 \left[\partial_t \left(|u_f^\epsilon|^2 \rho_f^\epsilon \right) + \nabla_x \cdot \left(|u_f^\epsilon|^2 u_f^\epsilon \rho_f^\epsilon \right) \right] \\ &= \frac{1}{\gamma \delta \nu^2} \left(\Xi_F^\epsilon + \Xi_f^\epsilon \right) \\ &= -\rho_F^\epsilon \tau \left(\partial_t T_p^\epsilon + u_F^\epsilon \cdot \nabla_x T_p^\epsilon \right). \end{aligned}$$

□

8.6.2 Maxwellian collision kernel

As anticipated earlier, the form of the bi-species collision kernel significantly influences the computations. In the case of a Maxwellian collision kernel, we can characterize the limits of the right-hand sides of the momentum equations (8.65) and of the energy equations (8.71).

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Additionally, we can deduce a relationship between the three temperatures in the limit, namely θ_f, θ_F, and T_p. These claims are made explicit in the following proposition.

Proposition 8.15. *In the Maxwellian collision kernel case, we have, under the assumptions* (8.91),

$$\begin{aligned}\lim_{\epsilon\to 0}\frac{1}{\delta\nu^2\sqrt{\eta}}\Theta_F^\epsilon &= 2\pi\|b\|_{L^1}\rho_f\rho_F(u_f-u_F) =: \Theta_F\\ \lim_{\epsilon\to 0}\frac{1}{\delta\nu^2}\Theta_f^\epsilon &= 2\pi\|b\|_{L^1}\rho_f\rho_F(u_F-u_f) =: \Theta_f\end{aligned} \tag{8.100}$$

and

$$\begin{aligned}\lim_{\epsilon\to 0}\frac{1}{\gamma\delta\nu^2}\Xi_F^\epsilon &=: \Xi_F\\ \lim_{\epsilon\to 0}\frac{1}{\gamma\delta\nu^2}\Xi_f^\epsilon &=: \Xi_f\end{aligned} \tag{8.101}$$

with

$$\begin{aligned}\Xi_F =& 2\pi||b||_{L^1}\rho_f\rho_F\left[K+2u_F\cdot u_f-|u_F|^2\right],\\ \Xi_f =& -2\pi||b||_{L^1}\rho_f\rho_F\left[2u_F\cdot u_f+2|u_F|^2+K\right]\\ &-\tau\rho_F\left(\partial_t T_p+u_F\cdot\nabla_x T_p\right),\end{aligned} \tag{8.102}$$

respectively, where $K := 6\lim_{\epsilon\to 0}\frac{\eta}{\gamma^2}\left(\theta_f^\epsilon-\theta_F^\epsilon\right)$. *Moreover, in the limit*

$$\theta_F=\theta_f=\frac{2}{3}T_p. \tag{8.103}$$

Proof. To show (8.100), we apply the Hypothesis 8.5 to the formulas (8.81).

For deducing (8.102), we start considering the expressions (8.82) and (8.83) of Ξ_F^ϵ and Ξ_f^ϵ for Maxwellian collision kernel. By re-arranging the terms, we can write:

$$\begin{aligned}\frac{1}{\gamma^2}\Xi_F^\epsilon = \frac{2\pi\|b\|_{L^1}}{(1+\eta)^2}\rho_f^\epsilon\rho_F^\epsilon\Bigg[&\frac{\eta}{\gamma^2}\left(2T_p^\epsilon-3\theta_f^\epsilon-3\eta\theta_F^\epsilon\right)+\eta\left(|u_f^\epsilon|^2-|u_F^\epsilon|^2\right)\\ &+6\frac{\eta}{\gamma^2}\left(\theta_f^\epsilon-\theta_F^\epsilon\right)+2\left(u_F^\epsilon\cdot u_f^\epsilon-|u_F^\epsilon|^2\right)\Bigg],\end{aligned}$$

where we added and subtracted $3\frac{\eta}{\gamma^2}\theta_f^\epsilon$ inside the squared brackets, and

$$\begin{aligned}\frac{1}{\gamma^2}\Xi_f^\epsilon = \frac{2\pi\|b\|_{L^1}}{(1+\eta)^2}\rho_f^\epsilon\rho_F^\epsilon\Bigg[&\frac{1}{\gamma^2}\left(2T_p^\epsilon-3\theta_f^\epsilon-3\eta\theta_F^\epsilon\right)+\left(|u_F^\epsilon|^2-|u_f^\epsilon|^2\right)\\ &-6\frac{\eta}{\gamma^2}\left(\theta_f^\epsilon-\theta_F^\epsilon\right)+2\eta\left(u_F^\epsilon\cdot u_f^\epsilon-|u_f^\epsilon|^2\right)\Bigg],\end{aligned}$$

where we added and subtracted $3\frac{\eta}{\gamma^2}\theta_F^\epsilon$ inside the squared brackets. Under the assumptions that quantities on the left hand side of equations of the system (8.71) are bounded, since

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$2T_p^\epsilon - 3\theta_f^\epsilon - 3\eta\theta_F^\epsilon = O(\gamma^2)$ (thanks to (8.95)), we get that there exists $K \in \mathbb{R}$ (possibly equal to zero) such that

$$\frac{\eta}{\gamma^2}\left(\theta_f^\epsilon - \theta_F^\epsilon\right) \to K$$

and since $\gamma^2/\eta \to 0$ (hypothesis (8.91)), it also implies $\theta_f = \theta_F$ in the limit. In particular, from (8.96), we also have that

$$T_p := \lim_{\epsilon\to 0} T_p^\epsilon = \lim_{\epsilon\to 0} \frac{I_2(F^\epsilon, f^\epsilon)}{2I_1(F^\epsilon, f^\epsilon)} = \frac{1}{2}\lim_{\epsilon\to 0}\left(3\eta\theta_F^\epsilon + 3\theta_f^\epsilon + \gamma^2|u_F^\epsilon - u_f^\epsilon|^2\right) = \frac{3}{2}\theta_f$$

from which we deduce (8.103). Furthermore, from (8.84) and (8.95), we deduce

$$\begin{aligned}&\lim_{\epsilon\to 0}\frac{2\pi\|b\|_{L^1}}{(1+\eta)^2}\rho_f^\epsilon\rho_F^\epsilon\left[\frac{1}{\gamma^2}\left(2T_p^\epsilon - 3\theta_f^\epsilon - 3\eta\theta_F^\epsilon\right)\right]\\ &= 2\pi||b||_{L^1}\rho_f\rho_F\left(|u_F - u_f|^2\right) - \tau\rho_F\left(\partial_t T_p + u_F\cdot\nabla_x T_p\right),\end{aligned}$$

and (8.102) follows.

□

8.6.3 Hard-Sphere collision kernel

For hard-sphere collision kernel, we can characterize the limits of the right-hand sides of the momentum equations (8.65). However, the result for the right-hand sides of the energy equations (8.71) is still a work in progress due to the difficult computations involved with a hard-sphere collision kernel. Nevertheless, we can deduce a relationship between the three temperatures in the limit, namely θ_f, θ_F, and T_p. The following proposition presents what has been only summarised here.

Proposition 8.16. *In the hard-sphere collision kernel case, the limits* (8.100) *take the form*

$$\begin{aligned}\Theta_F &= \tfrac{\pi}{3}\rho_F\rho_f\left(\sqrt{\pi}\sqrt{T_p} - 16\sqrt{\theta_f}\right)(u_f - u_F),\\ \Theta_f &= \tfrac{\pi}{3}\rho_F\rho_f\left(\sqrt{\pi}\sqrt{T_p} - 16\sqrt{\theta_f}\right)(u_F - u_f).\end{aligned} \tag{8.104}$$

Moreover, in the limit

$$\theta_f = \frac{1}{2}T_p. \tag{8.105}$$

Since we need to introduce technical tools to prove them, their proofs are postponed at the end of the Section. Indeed, the study of the limit for the hard-sphere collision kernel case requires dealing with more difficult integral computations than for the Maxwellian collision kernel one. For this reason, we introduce the following functions:

$$q(a) := \int_{\mathbb{R}^3}(a-y)|a-y|e^{-\frac{|y|^2}{2}}\frac{\mathrm{d}y}{(2\pi)^{3/2}}, \tag{8.106}$$

$$q_1(a) := \int_{\mathbb{R}^3}|a-y|e^{-\frac{|y|^2}{2}}\frac{\mathrm{d}y}{(2\pi)^{3/2}}, \tag{8.107}$$

$$q_3(a) := \int_{\mathbb{R}^3}|a-y|^3e^{-\frac{|y|^2}{2}}\frac{\mathrm{d}y}{(2\pi)^{3/2}}. \tag{8.108}$$

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The relations

$$q(a) = a\,\bar{q}(|a|), \tag{8.109}$$

and

$$q_1(a) = q_1(0) + |a|^2\bar{q}_1(|a|), \qquad q_3(a) = q_3(0) + |a|^2\bar{q}_3(|a|), \tag{8.110}$$

with

$$q_1(0) = 2\sqrt{\frac{2}{\pi}}, \qquad q_3(0) = 4q_1(0), \tag{8.111}$$

are valid. Hence, the following useful formulas hold:

$$\begin{aligned}\int_{\mathbb{R}^3} |z|^2 \exp -\frac{|z|^2}{2}\,|z-a|\,\frac{\mathrm{d}z}{(2\pi)^{\frac{3}{2}}} &= q_3(a) + |a|^2 q_1(a) - aq(a)\\ &= q_1(0)\left(4 + |a|^2\right) + |a|^2\left(\bar{q}_3(a) + \bar{q}_1(a) - \bar{q}(a)\right)\end{aligned} \tag{8.112}$$

and

$$\begin{aligned}\int_{\mathbb{R}^3} z \exp -\frac{|z|^2}{2}\,|z-a|\,\frac{\mathrm{d}z}{(2\pi)^{\frac{3}{2}}} &= aq_1(a) - q(a)\\ &= q_1(0)a + a\left(|a|^2\bar{q}_1(a) - \bar{q}(a)\right),\end{aligned} \tag{8.113}$$

Remark 8.11. *As shown in Lemma B.13, the functions $\bar{q}$, $\bar{q}_1$, and $\bar{q}_3$ possess all the necessary properties to prove the above results in the case of hard-sphere collision kernels. In fact, they are $C^2([0,+\infty))$ and, for every $\delta > 0$, they are bounded over $[0,\delta]$, as well as are their first and second derivatives.*

An additional assumption is required to perform the asymptotic analysis for hard-sphere collision kernel.

Hypothesis 8.6. *We take*

$$\frac{\eta^{3/2}}{\gamma} \to 0.$$

Remark 8.12. *Hypothesis 8.6, does not contradict Hypothesis 8.5. Indeed, if $\gamma \sim \eta^\alpha$, with $\alpha \in \left(\frac{1}{2}, \frac{3}{2}\right)$, then both the limit $\frac{\gamma^2}{\eta} \to 0$ and the limit $\frac{\eta^{3/2}}{\gamma} \to 0$ hold.*

We will now present the two important tools we will use to prove Proposition 8.16. The first lemma is used to compute the limits of the integral terms appearing in the expressions (8.86) and (8.87) of Θ_F^ϵ and Θ_f^ϵ for hard-sphere kernels.

Lemma 8.9. *For hard-sphere collision kernel it holds that*

$$\frac{1}{\gamma}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} (w - \sqrt{\eta}v)\,F^\epsilon(v) f^\epsilon(w)|w - \sqrt{\eta}v|\mathrm{d}w\mathrm{d}v \to -\rho_F\rho_f\bar{q}(0)\sqrt{\theta_f}(u_f - u_F). \tag{8.114}$$

as $\epsilon \to 0$, where $\bar{q}(0) = \frac{16}{3}$.

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Proof. By explicitly writing the ansatz F^ϵ and f^ϵ, we have

$$\begin{aligned}\frac{1}{\gamma}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}(w-\sqrt{\eta}v)\,F^\epsilon(v)f^\epsilon(w)|w-\sqrt{\eta}v|\mathrm{d}w\mathrm{d}v\\ =\frac{1}{\gamma}\rho_F^\epsilon\rho_f^\epsilon\left(\frac{1}{2\pi\theta_F^\epsilon}\right)^{\frac{3}{2}}\left(\frac{1}{2\pi\theta_f^\epsilon}\right)^{\frac{3}{2}}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}(w-\sqrt{\eta}v)\exp\left(-\frac{1}{2\theta_F^\epsilon(t,x)}\left|v-\frac{\gamma}{\sqrt{\eta}}u_F^\epsilon(t,x)\right|^2\right)\\ \times\exp\left(-\frac{1}{2\theta_f^\epsilon}\left|w-\gamma u_f^\epsilon\right|^2\right)|w-\sqrt{\eta}v|\mathrm{d}w\mathrm{d}v\end{aligned}$$

We can perform the change of variables

$$z:=\left(w-\gamma u_f^\epsilon\right)\sqrt{\frac{1}{\theta_f^\epsilon}},\qquad s:=\left(v-\frac{\gamma}{\sqrt{\eta}}u_F^\epsilon\right)\sqrt{\frac{1}{\theta_F^\epsilon}},\tag{8.115}$$

so that

$$\begin{aligned}\frac{1}{\gamma}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}(w-\sqrt{\eta}v)\,F^\epsilon(v)f^\epsilon(w)|w-\sqrt{\eta}v|\mathrm{d}w\mathrm{d}v\\ =\frac{1}{\gamma}\rho_F^\epsilon\rho_f^\epsilon\frac{1}{(2\pi)^{\frac{3}{2}}}\frac{1}{(2\pi)^{\frac{3}{2}}}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\left(\left(z\sqrt{\theta_f^\epsilon}-\sqrt{\eta}s\sqrt{\theta_F^\epsilon}\right)+\gamma(u_f^\epsilon-u_F^\epsilon)\right)\exp-\frac{|s|^2}{2}\\ \times\exp-\frac{|z|^2}{2}\left|\left(z\sqrt{\theta_f^\epsilon}-\sqrt{\eta}s\sqrt{\theta_F^\epsilon}\right)+\gamma(u_f^\epsilon-u_F^\epsilon)\right|\mathrm{d}z\mathrm{d}s\end{aligned}$$

If we define:

$$a^\epsilon=a^\epsilon(s):=\frac{\sqrt{\eta}s\sqrt{\theta_F^\epsilon}-\gamma(u_f^\epsilon-u_F^\epsilon)}{\sqrt{\theta_f^\epsilon}},$$

than

$$\begin{aligned}&\frac{1}{\gamma}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}(w-\sqrt{\eta}v)\,F^\epsilon(v)f^\epsilon(w)|w-\sqrt{\eta}v|\mathrm{d}w\mathrm{d}v\\ &\quad=\frac{1}{\gamma}\rho_F^\epsilon\rho_f^\epsilon\int_{\mathbb{R}^3}\exp-\frac{|s|^2}{2}\left(\int_{\mathbb{R}^3}\theta_f^\epsilon\,(z-a^\epsilon)\exp-\frac{|z|^2}{2}\,|z-a^\epsilon|\,\frac{\mathrm{d}z}{(2\pi)^{\frac{3}{2}}}\right)\frac{\mathrm{d}s}{(2\pi)^{\frac{3}{2}}}\\ &\quad=\frac{1}{\gamma}\rho_F^\epsilon\rho_f^\epsilon\theta_f^\epsilon\int_{\mathbb{R}^3}\exp-\frac{|s|^2}{2}q(a^\epsilon(s))\frac{\mathrm{d}s}{(2\pi)^{\frac{3}{2}}},\end{aligned}$$

where we used the Definition 8.106 of the function q. By using the property (8.109) and the definition of $a^\epsilon(s)$, we deduce that

$$\begin{aligned}&\frac{1}{\gamma}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}(w-\sqrt{\eta}v)F^\epsilon(v)f^\epsilon(w)|w-\sqrt{\eta}v|\mathrm{d}w\mathrm{d}v\\ &\qquad=\rho_F^\epsilon\rho_f^\epsilon\frac{\sqrt{\eta}}{\gamma}\sqrt{\theta_F^\epsilon}\sqrt{\theta_f^\epsilon}\int_{\mathbb{R}^3}\exp\left(-\frac{|s|^2}{2}\right)s\bar{q}(|a^\epsilon(s)|)\frac{\mathrm{d}s}{(2\pi)^{\frac{3}{2}}}\\ &\qquad-\rho_F^\epsilon\rho_f^\epsilon\sqrt{\theta_f^\epsilon}(u_f^\epsilon-u_F^\epsilon)\int_{\mathbb{R}^3}\exp\left(-\frac{|s|^2}{2}\right)\bar{q}(|a^\epsilon(s)|)\frac{\mathrm{d}s}{(2\pi)^{\frac{3}{2}}}.\end{aligned}$$

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Since for all $\delta > 0$, $\bar{q} \in C^2([0,\delta])$, as detailed in Lemma B.13, we can write $\bar{q}$ via the Taylor expansion around zero. Moreover, from Lemma B.13, we also have the boundedness of $\bar{q}'$ on $[0,\delta]$. So, by defining $M := \max_{x\in[0,\delta]} \bar{q}'(x)$, we deduce that

$$\int_{\mathbb{R}^3} \exp -\frac{|s|^2}{2} \left|\bar{q}(|a^\epsilon(s)|) - \bar{q}(0)\right| \mathrm{d}s \leq \frac{M\delta^2}{2} \int_{\mathbb{R}^3} \exp -\frac{|s|^2}{2} \mathrm{d}s,$$

thanks to the Taylor's Theorem. Hence

$$\int_{\mathbb{R}^3} \exp -\frac{|s|^2}{2} \bar{q}(|a^\epsilon(s)|)\mathrm{d}s \to \int_{\mathbb{R}^3} \exp -\frac{|s|^2}{2} \bar{q}(0)\mathrm{d}s = \bar{q}(0)(2\pi)^{\frac{3}{2}},$$

as $\delta \to 0$. Moreover, $\forall \epsilon \leq \bar{\epsilon}$:

$$\frac{\sqrt{\eta}}{\gamma} \left|\bar{q}(|a^\epsilon(s)|) - \bar{q}(0)\right| = \frac{\sqrt{\eta}}{\gamma} \left|R_1(|a^\epsilon(s)|)\right| \leq M \frac{\sqrt{\eta}}{\gamma} \frac{|a^\epsilon(s)|^2}{2} = \frac{M}{2\theta_f^\epsilon} \left| \frac{\eta^{3/4}}{\gamma^{1/2}} \sqrt{\theta_F^\epsilon} s - \eta^{1/4}\gamma^{1/2}(u_f^\epsilon - u_F^\epsilon) \right|^2,$$

which converges to zero almost everywhere when $\epsilon \to 0$, as a consequence of Hypothesis 8.6. Hence, thanks to the Dominated Convergence Theorem, we deduce

$$\frac{\sqrt{\eta}}{\gamma} \int_{\mathbb{R}^3} \exp -\frac{|s|^2}{2} s\bar{q}(|a^\epsilon(s)|)\mathrm{d}s \to 0,$$

since there exists $\tilde{\epsilon}$ such that the term $\frac{\sqrt{\eta}}{\gamma}\bar{q}(|a^\epsilon(s)|)$ is uniformly bounded on $[0,\delta]$ and also $\int_{\mathbb{R}^3} \exp -\frac{|s|^2}{2} s\mathrm{d}s = 0$. □

This second lemma establishes the limit of the terms $I_1(F^\epsilon, f^\epsilon)$ and $I_2(F^\epsilon, f^\epsilon)$ appearing in the surface's temperature equation (8.90). Then, from formula (8.96) a relation between the limit temperature can be deduced.

Lemma 8.10. *For hard-sphere collision kernel, the rescaled terms $I_1(F^\epsilon, f^\epsilon)$ and $I_2(F^\epsilon, f^\epsilon)$ in the limit $\epsilon \to 0$ behave like*

$$I_1(F^\epsilon, f^\epsilon) = \pi \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} F^\epsilon f^\epsilon |\sqrt{\eta}v - w| \mathrm{d}v\mathrm{d}w \;\to\; \pi q_1(0)\rho_f\rho_F\theta_f^{1/2},$$

and

$$I_2(F^\epsilon, f^\epsilon) = \pi \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} F^\epsilon f^\epsilon |\sqrt{\eta}v - w|^3 \mathrm{d}v\mathrm{d}w \;\to\; \pi q_3(0)\rho_f\rho_F\theta_f^{3/2},$$

for hard-sphere collision kernel, where $q_1(0) = 2\sqrt{\frac{2}{\pi}}$, and $q_3(0) = 8\sqrt{\frac{2}{\pi}}$.

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Proof. Let's consider the adimensionalised expressions (8.50) of I_1 and I_2 for a general collision kernel and general functions F and f. By plugging in the hard-sphere collision kernel and by explicitly writing the ansatz F^ϵ and f^ϵ, we get

$$\begin{aligned} I_1(F^\epsilon, f^\epsilon) &= \pi\rho_F^\epsilon\rho_f^\epsilon \int_{\mathbb{R}^3} \exp -\frac{|s|^2}{2} \left(\int_{\mathbb{R}^3} \sqrt{\theta_f^\epsilon} \exp -\frac{|z|^2}{2} |z - a^\epsilon| \frac{\mathrm{d}z}{(2\pi)^{\frac{3}{2}}} \right) \frac{\mathrm{d}s}{(2\pi)^{\frac{3}{2}}} \\ &= \pi\rho_F^\epsilon\rho_f^\epsilon \sqrt{\theta_f^\epsilon} \int_{\mathbb{R}^3} \exp -\frac{|s|^2}{2} q_1(a^\epsilon(s)) \frac{\mathrm{d}s}{(2\pi)^{\frac{3}{2}}} \\ &= \pi\rho_F^\epsilon\rho_f^\epsilon \sqrt{\theta_f^\epsilon} \int_{\mathbb{R}^3} \exp -\frac{|s|^2}{2} \left(q_1(0) + |a^\epsilon(s)|^2 \bar{q}_1(|a^\epsilon(s)|) \right) \frac{\mathrm{d}s}{(2\pi)^{\frac{3}{2}}} \\ &= \pi\rho_F^\epsilon\rho_f^\epsilon \sqrt{\theta_f^\epsilon} q_1(0) + \pi\rho_F^\epsilon\rho_f^\epsilon \sqrt{\theta_f^\epsilon} \int_{\mathbb{R}^3} \exp -\frac{|s|^2}{2} |a^\epsilon(s)|^2 \bar{q}_1(|a^\epsilon(s)|) \frac{\mathrm{d}s}{(2\pi)^{\frac{3}{2}}} \end{aligned}$$

whereas

$$\begin{aligned} I_2(F^\epsilon, f^\epsilon) &= \pi\rho_F^\epsilon\rho_f^\epsilon \int_{\mathbb{R}^3} \exp -\frac{|s|^2}{2} \left(\int_{\mathbb{R}^3} (\theta_f^\epsilon)^{\frac{3}{2}} \exp -\frac{|z|^2}{2} |z - a^\epsilon|^3 \frac{\mathrm{d}z}{(2\pi)^{\frac{3}{2}}} \right) \frac{\mathrm{d}s}{(2\pi)^{\frac{3}{2}}} \\ &= \pi\rho_F^\epsilon\rho_f^\epsilon (\theta_f^\epsilon)^{\frac{3}{2}} \int_{\mathbb{R}^3} \exp -\frac{|s|^2}{2} q_3(a^\epsilon(s)) \frac{\mathrm{d}s}{(2\pi)^{\frac{3}{2}}} \\ &= \pi\rho_F^\epsilon\rho_f^\epsilon (\theta_f^\epsilon)^{\frac{3}{2}} \int_{\mathbb{R}^3} \exp -\frac{|s|^2}{2} \left(q_3(0) + |a^\epsilon(s)|^2 \bar{q}_3(|a^\epsilon(s)|) \right) \frac{\mathrm{d}s}{(2\pi)^{\frac{3}{2}}} \\ &= \pi\rho_F^\epsilon\rho_f^\epsilon (\theta_f^\epsilon)^{\frac{3}{2}} q_3(0) + \pi\rho_F^\epsilon\rho_f^\epsilon (\theta_f^\epsilon)^{\frac{3}{2}} \int_{\mathbb{R}^3} \exp -\frac{|s|^2}{2} |a^\epsilon(s)|^2 \bar{q}_3(|a^\epsilon(s)|) \frac{\mathrm{d}s}{(2\pi)^{\frac{3}{2}}}, \end{aligned}$$

where we performed the same change of variables as in Lemma 8.9 and we used the same notation. Thanks to the continuity of the functions $\bar{q}_1$ and $\bar{q}_3$ (see Lemma B.13), as $\epsilon \to 0$,

$$|a^\epsilon(s)|^2 \bar{q}_1(|a^\epsilon(s)|) \to 0 \qquad \text{and} \qquad |a^\epsilon(s)|^2 \bar{q}_3(|a^\epsilon(s)|) \to 0,$$

almost everywhere. Moreover,

$$\bar{q}_1(x) = \bar{q}_1(0) + R_1(x), \qquad \bar{q}_3(x) = \bar{q}_3(0) + R_1(x).$$

Thanks to the properties of $\bar{q}_1$ and $\bar{q}_3$, we can proceed as in Lemma 8.9's proof and hence conclude via the dominated convergence theorem. □

With these tool results, we are ready to prove Proposition 8.16.

Proof of Proposition 8.16. For hard-sphere collision kernel, we know that

$$\begin{aligned} \Theta_F &= \lim_{\epsilon\to 0} \frac{1}{\gamma\sqrt{\eta}} \Theta_F^\epsilon \\ &= \lim_{\epsilon\to 0} \frac{\pi}{1+\eta} \left[\frac{1}{\gamma} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} (w - \sqrt{\eta} v) F(v) f(w) |\sqrt{\eta} v - w| \mathrm{d}w \mathrm{d}v + \frac{\sqrt{\pi}}{3} \sqrt{T_p} \rho_F^\epsilon \rho_f^\epsilon (u_f^\epsilon - u_F^\epsilon) \right], \end{aligned}$$

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and

$$\begin{aligned}\Theta_f &= \lim_{\epsilon\to 0}\frac{1}{\gamma}\Theta_f^\epsilon \\ &= \lim_{\epsilon\to 0}\frac{\pi}{1+\eta}\left[\frac{1}{\gamma}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}(\sqrt{\eta}v-w)\,F(v)f(w)|\sqrt{\eta}v-w|\mathrm{d}w\mathrm{d}v+\frac{\sqrt{\pi}}{3}\sqrt{T_p}\rho_F^\epsilon\rho_f^\epsilon(u_F^\epsilon-u_f^\epsilon)\right].\end{aligned}$$

Thanks to Lemma 8.9, we can hence deduce (8.104). Moreover, thanks to Lemma 8.10, we have that

$$2I_1(F^\epsilon,f^\epsilon)T_p^\epsilon - I_2(F^\epsilon,f^\epsilon) \;\to\; 2\pi q_1(0)\rho_f\rho_F\theta_f^{1/2}T_p - \pi q_3(0)\rho_f\rho_F\theta_f^{3/2} = 2\pi q_1(0)\rho_f\rho_F\sqrt{\theta_f}(T_p-2\theta_f).$$

From formula (8.95) we also know that

$$2I_1(F^\epsilon,f^\epsilon)T_p^\epsilon - I_2(F^\epsilon,f^\epsilon) \;\to\; 0,$$

and hence (8.105) follows. □

Appendix B

We detail below some of the calculations used in this paper.

Lemma B.11 (Computations for $h_n(z)$)**.** *Given a function*

$$h_n(t,x,z) = \frac{2c^4}{\pi}\,(n\cdot z)\,e^{-c^2|z|^2}\mathbb{1}_{\{z\cdot n\geq 0\}},$$

for $c = c(t,x)\in\mathbb{R}$ constant in n and z, it holds that

$$\int_{\mathbb{R}^3} h_n(z)\,\mathrm{d}z = 1. \tag{8.116}$$

Moreover,

$$\int_{\mathbb{R}^3} z h_n(z)\mathrm{d}z = \frac{1}{2}\sqrt{\frac{\pi}{c}}n, \tag{8.117}$$

and

$$\int_{\mathbb{R}^3} |z|^2 h_n(z)\mathrm{d}z = \frac{2}{c^2}. \tag{8.118}$$

The interested lector can find the proof of these results in [58, Annexe C.]

Lemma B.12 (Expression of $\bar{q}$, $\bar{q}_1$, and $\bar{q}_3$)**.** *For all $a\in R^3$,*

$$q(a) := \int_{\mathbb{R}^3}(a-y)|a-y|e^{-\frac{|y|^2}{2}}\frac{\mathrm{d}y}{(2\pi)^{3/2}} = a\,\bar{q}(|a|), \tag{8.119}$$

where

$$\bar{q}(|a|) = \frac{1}{\sqrt{2\pi}}\left\{2|a|I_2(|a|)+\frac{4}{3}|a|^{-1}I_4(|a|)-\frac{2}{15}|a|^{-3}I_6(|a|)+\frac{8}{15}|a|^2J_1(|a|)+\frac{8}{3}J_3(|a|)\right\} \tag{8.120}$$

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with, for $k \in \mathbb{N}, x \in \mathbb{R}_+$,

$$I_k(x) = \int_0^x t^k e^{-t^2/2}\,\mathrm{d}t, \qquad J_k(x) = \int_x^\infty t^k e^{-t^2/2}\,\mathrm{d}t.$$

Moreover,

$$\begin{aligned} q_1(a) &:= \int_{\mathbb{R}^3} |a-y| e^{-\frac{|y|^2}{2}} \frac{\mathrm{d}y}{(2\pi)^{3/2}} \\ &= \frac{1}{\sqrt{2\pi}} \left(2|a| I_2(|a|) + \frac{2}{3}|a|^{-1} I_4(|a|) + 2J_3(|a|) + \frac{2}{3}|a|^2 J_1(|a|) \right), \end{aligned}$$

$$\begin{aligned} q_3(a) &:= \int_{\mathbb{R}^3} |a-y|^3 e^{-\frac{|y|^2}{2}} \frac{\mathrm{d}y}{(2\pi)^{3/2}} \\ &= \frac{1}{\sqrt{2\pi}} \left(2|a|^3 I_2(|a|) + \frac{4}{3}|a| I_4(|a|) + \frac{6}{15}|a|^{-1} I_6(|a|) + \frac{6}{15}|a|^4 J_1(|a|) + \frac{10}{3}|a|^2 J_3(|a|) + 2J_5(|a|). \right) \end{aligned}$$

Proof. The equalities (8.119) and (8.120) are shown in [76, Lemma A.3] □

Lemma B.13 (Properties of $\bar{q}$, $\bar{q}_1$, and $\bar{q}_3$)**.** *The functions* $\bar{q}(\cdot)$, $\bar{q}_1(\cdot)$, *and* $\bar{q}_3(\cdot)$ *are* $C^2([0,+\infty))$. *Moreover, for all* $\delta > 0$, *they are bounded on* $[0,\delta]$, *as are their first and second derivatives.*

Proof. Via the expression (8.120), thanks to the fundamental theorem of calculus, we deduce the continuity of $\bar{q}$ on $(0,+\infty)$. Moreover, by applying a first order Taylor expansion of I_4 and I_6 around zero, we can show the continuity of $\bar{q}$ in zero. Indeed, $I_4(0) = I_6(0) = 0$ and, from the fundamental theorem of calculus, we also have that $I_4'(x) = x^4 e^{-x^2/2}$ and $I_6'(x) = x^6 e^{-x^2/2}$. Therefore:

$$\lim_{x\to 0^+} \sqrt{2\pi}\bar{q}(x) = \lim_{x\to 0^+} \left\{ \frac{4}{3} I_4'(x) - \frac{2}{45}\frac{I_6'(x)}{x^2} \right\} + \frac{8}{3} J_3(0) = \frac{8}{3} J_3(0) = \frac{16}{3},$$

and hence the conclusion. To prove the continuity of $\bar{q}'$ and $\bar{q}''$, as well as the one of $\bar{q}_1$, $\bar{q}_3$ and their first and second derivatives, the procedure is analogous.

Given $\delta > 0$, the boundedness of $\bar{q}$, $\bar{q}_1$, and $\bar{q}_3$, and their derivatives, over $[0,\delta]$ is a direct consequence of their continuity over $[0,\infty)$. □

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