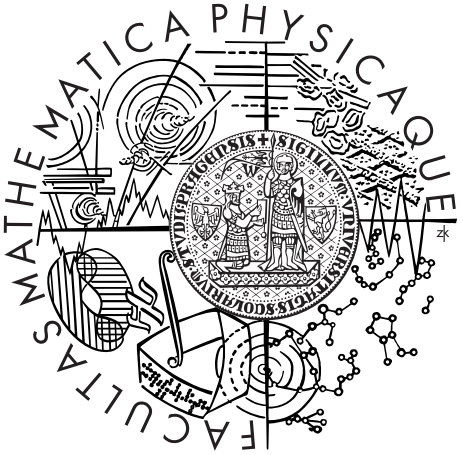
Charles University in Prague

Faculty of Mathematics and Physics

MASTER THESIS



Vít Orava

Modeling, Analysis and Computation of heterogeneous catalysis in microchannels

Mathematical Institute of Charles University

Supervisor of the master thesis:	prof. RNDr. Josef Málek CSc., DSc.
Co-advisor of the master thesis:	Prof. Dr. Dieter Bothe
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I declare that I carried out this master thesis independently, and only with the cited sources, literature and other professional sources.

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Název práce: Modelování, analýza a numerická simulace heterogenní katalýzy v mikroreaktorech Autor: Vít Orava
Katedra: Matematický Ústav UK (32-MUUK)
Vedoucí diplomové práce: prof. RNDr. Josef Málek CSc., DSc., MUUK
Konzultant diplomové práce: Prof. Dr. Dieter Bothe (TU Darmstadt)

Abstrakt: Tato práce se zabývá nelineárním systémem parciálních diferenciální rovnic, konkrétně kombinací reakce-difuze a konvekce-difuze systémů. Vycházíme z fyzikálního popisu heterogenní katalýzy, kdy je proudění objemových částic buzené daným stacionárním rychlostním polem. Absorpční mechanismy, mezi objemovou a povrchovou částí modelové oblasti, jsou popsány pomocí Langmuir-Hinschelwoodovy absorpční kinetiky a jednosměrné reakce na katalytickém povrchu splňují zákon akce hmoty (law of mass action). V první části práce se zaměřujeme na analýzu systému zkoumanou ze dvu perspektiv; v Kapitole 1 dokážeme existenci a jednoznačnost tzv. *mild* řešení pro vhodně zjednodušený problém s využitím teorie nelineárních semigrup; v Kapitole 2 zkoumáme daný problém z hlediska slabé formulace. Dokážeme existenci slabého řešení pro upravený systém, který za určitých podmínek přejde v systém původní. V druhé části diplomove práce (Kapitola 4) se zabýváme numerickou simulací evoluce proudění v modelu mikroreaktoru pro výrobu bio-dieselu. Pro výpočet numerického řešení použijeme několik metod, jejichž výsledky následně verifikujeme pomocí analytických a fyzikálních kritérií.

Klíčová slova: heterogenní katalýza, spárovaný reakce-difuze a konvekce-difuze systém, teorie nelineárních semigrup, slabé řešení, bio-diesel mikroreaktor

Title: Modeling, Analysis and Computation of heterogeneous catalysis in microchannels

Author: Vít Orava
Department: Mathematical Institute of Charles University
Supervisor: prof. RNDr. Josef Málek CSc., DSc., MUUK
Consultant: Prof. Dr. Dieter Bothe (TU Darmstadt)

Abstract: We investigate a nonlinear reaction-diffusion system coupled with convection-diffusion system. This combined system corresponds to physical description of heterogeneous catalysis when the flow of bulk-constituents is driven by a given stationary velocity field; diverse mechanisms between bulk- and surface-parts of the model-domain are described by Langmuir-Hinshelwood absorption kinetics; and the irreversible reactions on the catalytic walls meets the law of mass action with quadratic rate. The first part of the thesis is focused on analytical results; in Chapter 2 we prove existence and uniqueness of a mild solution for so-called near-by problem using nonlinear semigroup theory; in Chapter 3 we investigate the weak formulation of the problem. We prove an existence of a weak solution for little modified problem which, under an assumption, coincides with the original problem. In the second part of the thesis (Chapter 4) we numerically investigate the evolution of the bio-diesel microreactor. We compute numerical solutions using several methods and we test the results by analytical and physical conditions; with the aim to find the most efficient way to compute precise and physically correct solution.

Keywords: heterogeneous catalysis, coupled reaction-diffusion/convection-diffusion system, nonlinear semigroup theory, weak solution, bio-diesel microreactors

Contents

List of used symbols and abbreviations

Notation	Meaning
ACP	Abstract Cauchy Problem
$\mathcal{A}_i, A, B, C$	operators on X
c_i	molar concentration of i^{th} bulk constituent
c_i^{ref}	characteristic molar concentration for c_i
c_i^*	dimensionless quantity $c_i^* := c_i/c_i^{ref}$
$c_{i\|\Sigma}$	restriction of c_i of Σ in sense of trace
c_i^{in}	inflow boundary condition for c_i
c_i^0	initial boundary condition for c_i
d	characteristic width
$\frac{\mathrm{d}}{\mathrm{d}t}$	total time-derivative
div	three dimensional divergence operator
div_Σ	two dimensional surface divergence operator
D_i	coefficient of diffusive flux of i^{th} bulk constituent
D_i^Σ	coefficient of diffusive flux of i^{th} surface constituent
$D(\mathcal{A})$	domain of the operator $\mathcal{A}_i$
FEM	Finite Element Method
$gr(\mathcal{A})$	graph of the operator $\mathcal{A}$
$\mathbf{J}_i$	diffusive flux of i^{th} bulk constituent
$\mathbf{J}_i^\Sigma$	diffusive flux of i^{th} surface constituent
$\mathbf{J}_i^{tot}$	total flux of i^{th} bulk constituent
$\mathbf{J}\Sigma, tot_i$	total flux of i^{th} surface constituent
$\mathbf{J}_i^{so}$	sorption flux of i^{th} bulk constituent
L	characteristic length
L^p	Lebesgue space with $\|\cdot\|_{L^p}$-norm
M_i	molar mass of i^{th} bulk constituent
$\mathbf{n}$	outer normal vector
ODE	ordinary differential equation
PDE	partial differential equation
$(\mathrm{Pe})_i$	Pèclet number of i^{th} bulk constituent; $(\mathrm{Pe})_i = \frac{LU}{D_i}$, resp. $(\mathrm{Pe}) = \mathrm{Re}\cdot\mathrm{Sc}$
r_i	molar surface reaction rate of i^{th} surface constituent
r_i^{so}	molar sorption rate of i^{th} surface constituent
$rg(\mathcal{A})$	range of the operator $\mathcal{A}$
R_i	surface reaction rate of i^{th} surface constituent
R_i^{so}	sorption rate of i^{th} surface constituent
R_i^{tot}	total rate of change of i^{th} bulk constituent
$R_i^{\Sigma,tot}$	total rate of change of i^{th} surface constituent
$R_\lambda(\mathcal{A})$	λ-resolvent of the operator $\mathcal{A}$; $R_\lambda(\mathcal{A}) = (I+\lambda\mathcal{A})^{-1}$
Re	Reynolds number; $\mathrm{Re} = \frac{\mathrm{LU}}{\nu}$
Sc	Schmidt number; $\mathrm{Sc} = \frac{\nu}{\mathrm{D}}$

Notation	Meaning
t	time
t^*	characteristic time
tr	trace operator
T	characteristic hydrodynamic residence time
U	characteristic velocity
$\mathbf{v}$	three dimensional velocity field
$\mathbf{v}_{\|\Sigma}$	velocity on Σ
$\mathbf{v}_i$	partial velocity of i^{th} constituent
$\mathbf{v}^{in}$	inflow boundary condition for $\mathbf{v}$
$\mathbf{V}$	a set of appropriate velocity fields
$W^{k,p}$	Sobolev space containing a function with k^{th}-weak derivatives in L^p
x	element of a vector space
$\mathbf{x}$	position vector
X	a real Banach space
Δ	three dimensional Laplace operator, i.e. $\Delta = \operatorname{div} \nabla$
Δ_Σ	two dimensional Laplace-Beltrami operator, i.e. $\Delta_\Sigma = \operatorname{div}_\Sigma \nabla_\Sigma$
Γ_{in}	inflow part of $\partial\Omega$
Γ_{out}	outflow part of $\partial\Omega$
κ	surface reaction coefficient
κ_i	coefficient of Langmiur isotherm for sorption pair $[c_i, \theta_i]$
∂_t	partial time-derivative
∇	three dimensional gradient operator
∇_Σ	two dimensional surface gradient operator
ν	kinematic viscosity or direction-vector of surface reactions
ν_i	direction(sign) of surface reaction
$\partial\Sigma$	boundary of Σ
$\partial\Omega$	boundary of Ω
ρ	total bulk density
ρ_i	partial bulk density
ρ^Σ	surface density
ρ_i^Σ	partial surface density of i^{th} constituent
Σ	catalytic walls (part of $\partial\Omega$)
θ_i	molar concentration of i^{th} surface constituent, resp. fraction coverage
θ_i^0	initial boundary condition for θ_i
θ_i^{ref}	characteristic molar concentration for θ_i
θ_i^*	dimensionless quantity $\theta_i^* := \theta_i / \theta_i^{ref}$
Ω	domain of the channel

Preface

This thesis should represent a work in the area of mathematical modelling field including both mathematical and engineering aspects. This concept can be introduced as follows: choose a model based on real industrial applications; prove existence and uniqueness of a solution of the problem, resp. appropriate near-by problem; perform numerical computations using several methods; test the results under analytical and physical conditions; choose the most efficient methods to compute the correct solution.

A problem is very often examined just with respect to the one aspect. Mathematical analysis studies academical (mostly simplified) models; but on the other hand, most of the people in practice are focused on the numerical computations only, without sufficient analysis or physical insight into the problem. The reason for this separation is simple; real industrial problems have mostly such a complicated structure that they cannot be handled by mathematical analysis tools and, besides, the use of commercial computing software is mostly not so difficult. The problem of the correctness of the computed solution could arise very quickly, e.g. the investigated system is very sensitive to small data-changes or even unstable; the solution is not unique; a blow-up occurs, etc. Therefore, the deeper analytical and physical insight is needed.

Concept of the thesis

We split the thesis into four chapters, Conclusion and Appendix. Chapter 1 includes a motivation and physical description of the problem. The observed phenomena are by are expressed by physical laws and convenient constitutive theory. First of all, we derive the general system of balance equation without specifications of sorption- and reaction-terms. This system can also serve as a starting point for other models which undergo chemical mechanisms different from our case. For further consideration, we chose the Langmuir-Hinschelwood adsorption kinetics and elementary (surface) reactions as the most suitable mechanisms describing our model-setting. The employment of these two mechanism determines the basic equation-system of the model.

In Chapter 2 we prove existence and uniqueness of a mild solution for so called near-by problem. The near-by problem could generally mean a modification which is still, in some sense, connected to the original problem, i.e. special boundary or initial conditions; linearized problem; long-time (stationary) solution; modification of the geometry, etc. The last case, where we enclose the domain by reactive boundary in shape of compact manifold, is what we use for the purpose of analysis in this chapter. Some of the other near-by problems play the role in later numerical verification of the used methods.

In Chapter 3 we examine the problem from a weak sense. We prove an existence of a weak solution for the system which, under some assumptions, coincides with the original one. This result is especially useful for verification of the consequent numerical results whose realization is based on a weak formulation.

In Chapter 4 we perform numerical computations using several methods. This is done in program FreeFem++ 3.20, a freeware using language FreeFem++ as an idiom of C++. The

discretization of the domain is done by Finite Element Methods (FEM), and the solution is computed using standard linear solvers, therefore, an appropriate implementation of linearized algorithm is needed. The obtained numerical results are consequently verified by analytical and physical conditions, resp. by "other" near-by problems mentioned above.

In Appendix we recall definitions and theorems used in Chapter 2.

1. Physical description of the mixture-model

1.1 Motivation

Heterogeneous catalysis and reaction-type

Generally speaking, catalysis is the way how to increase speed of chemical reactions due to the participation of a substance called catalyst. In other words, catalyzed reactions have a lower activation energy compared to the corresponding un-catalyzed reaction, resulting in a higher reaction rate under the same physical conditions. Unlike other reagents entering chemical transformations, a catalyst is not consumed and it may participate in many ways.[1]

We distinguish two kinds of catalysis - homogeneous and heterogeneous; depending on whether the catalyst exists in the same phase as the substrate or not. Heterogeneous catalysis refers to the form of catalysis where the phase of the catalyst differs from that of the reactants. In real industrial applications, the great majority of heterogeneous-catalysts-phase are solids and the great majority of reactants are gases or liquids. The later combination is matched by our model-setting.

There are several sorption kinetics of the chemical transformation between surfaces and bulk, depending on how and where the sorption [2] takes place (e.g. Langmuir-Hinshelwood, Eley-Rideal, Mars-van Krevelen, etc.). Generally speaking, the reactants diffuse near the catalyst surface and adsorb onto it. There, the surface diffusion takes place (convection on the walls is usually not present) and, after a collision with other suitable constituents, the reaction occurs. Consequently, the products desorb from the surface and diffuse away. Let us mentioned that the bulk diffusion near the walls plays important role, since, there is a no-slip condition for velocity field, i.e. no convection near the walls. For a deeper insight into the heterogeneous catalysis and chemical phenomena we refer e.g. to [25] or [22].

The fabrication of a catalytic surface is usually done using catalytic-coating. The catalyst creates a thin film ($0.1 \sim 10\mu m$) on the walls, cf. [10]. Since the surface area of coated walls (boundary) plays usually the main role in catalysis-efficiency, the devices of sub-millimeter dimensions (flat- or string-shape) are taken into account.

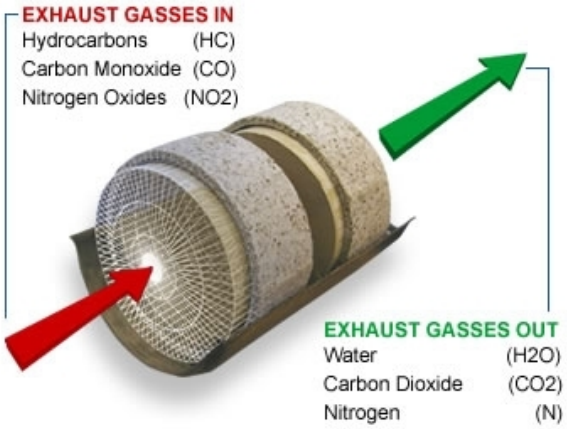
Despite the small sub-millimeter dimensions of our interest, diffusion is still slow; especially in liquids where Schmidt numbers are in the range of 1000. Therefore, a better

[1] Chemical transformations generally mean any chemical phenomena where a substrate converses to a product. In context of the thesis, we distinguish two of them, namely, sorption-processes and chemical reactions.

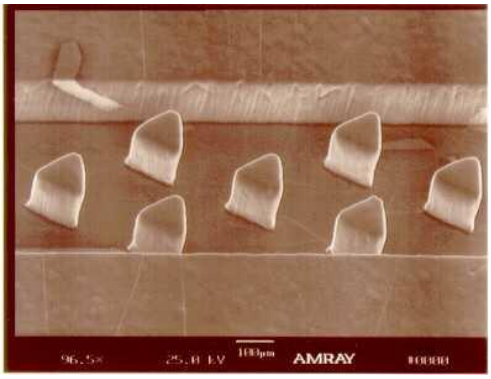
[2] The chemical mechanism "sorption" involves both absorption and adsorption processes; but treating with liquid/solid phases, where the liquid constituents adhere to the solid walls, involves adsorption only. The expression "sorption" was chosen to stress the fact that the adsorption takes place in both bulk $\rightarrow$ surface and surface $\rightarrow$ bulk directions. Despite of the definition, usually the couple adsorption/desorption is used to distinguish these adsorption-directions.

understanding of the strong interplay between transport processes (convection, diffusion); sorption as exchange mechanism between bulk and boundary; as well as chemical reactions, is strongly required. Such physical settings correspond to industrial devices called microchannels or microreactors.

Real applications of the microchannels are well spread through many fields of industry where the models mostly differ by geometry, number of reactants or types/rates of chemical transformations. In our case, we are interested in simple-geometry models of microchannels, e.g. microreactors producing biodiesel [3] , automobile catalytic converters, heterogeneous catalysis in a capillary, etc.



(a) Catalytic converter



(b) (SEM) of a $500\mu m \times 500mm \times 125\mu m$ biodiesel-microreactor - from [19]

Note to the notation: *In the text beneath we assume all variables dependent on space coordinates x, y, z and time t unless specified differently. From context it should be obvious, if we are treating with constants, scalar variables, vector variables (bold small letters), tensor variables (bold capital letters) or other objects as operators, elements of Banach spaces, etc.*

1.2 Balance equations

1.2.1 Mass-balance of mixture

The basic concept of the model is based on the mixture theory. This theory is well known and widely described for example by Truesdell in [29] or by Atkin and Craine in [2]. In our case, we will restrict this brief mixture-theory introduction on the basic governing equations which will be used in the sequel.

[3] More information about application and description of biodiesel microreactor model can be found in [19], [30], [6] .

Let us consider a channel $\Omega \subset \mathbb{R}^3$ - a stationary control volume; catalytic two-dimensional impermeable walls $\Sigma \subset \partial\Omega$; and $\Gamma_{in}, \Gamma_{out}$ which are inflow and outflow parts of the boundary $\partial\Omega$. Schematically $\partial\Omega = \Sigma \cup \Gamma_{in} \cup \Gamma_{out}$. [4] and a given velocity field $\mathbf{v}$ which is incompressible with no-slip condition on the walls, i.e. $\operatorname{div} \mathbf{v} = 0$ and $\mathbf{v}_{|\Sigma} = 0$. Moreover, let as assume a mixture of n bulk-constituents and n corresponding surface-constituents; that coexist in a homogenized sense in corresponding domains $\overline{\Omega}, \Sigma$ with the surface-constituents being capable of interacting with each other.

Denoting, in sequence, bulk/surface partial densities $(\rho_i)_{i=1,..,n}, (\rho_i^\Sigma)_{i=1,..,n}$ and partial velocities $(\mathbf{v}_i)_{i=1..,n}, (\mathbf{v}_i^\Sigma)_{i=1..,n}$; we define the total bulk/surface density of the mixture as

$$\rho := \sum_{i=1}^{n} \rho_i \ , \ \rho^\Sigma := \sum_{i=1}^{n} \rho_i^\Sigma$$

and barycentric bulk/surface velocity of the full mixture as

$$\rho\, \mathbf{v} := \sum_{i=1}^{n} \rho_i\, \mathbf{v}_i \ , \ \rho^\Sigma \mathbf{v}^\Sigma := \sum_{i=1}^{n} \rho_i^\Sigma \mathbf{v}_i^\Sigma.$$

To understand the nature of the chemical-transformation terms, we prefer to introduce an integral description of the investigated problem; firstly the balance equations for the bulk and surface constituents separately and then for the whole mixture.

As already mentioned, within the concept of heterogeneous catalysis, we are dealing deal with sorption and surface reactions. The sorption between bulk and catalytic walls can be understood in two ways. In case of bulk relation, we treat the sorption-effect as a flux through the boundary; on the other hand, the sorption-effect represents the source term for surface constituents (similar to reactions). This can be described, together with surface reactions, by the following balance equations in the integral form

$$\partial_t \int_V \rho_i \,\mathrm{d}V = -\int_{\partial V} \mathbf{J}_i^{tot} \cdot \mathbf{n} \,\mathrm{d}S \tag{1.1a}$$

$$\partial_t \int_\Sigma \rho_i^\Sigma \,\mathrm{d}S = -\int_{\partial\Sigma} \mathbf{J}_i^{\Sigma,tot} \cdot \mathbf{n}^\Sigma \,\mathrm{d}s + \int_\Sigma R_i^{so} + R_i \,\mathrm{d}S, \tag{1.1b}$$

where $\mathbf{n}$, resp. $\mathbf{n}^\Sigma$, are outer-normal vectors to Σ, resp. $\partial\Sigma$. [5] The law of mass action, resp. the mass conservation for chemical reactions, states no supply/loss for chemical reactions, namely

$$\sum_{i=1}^{n} R_i = 0.$$

[4] In concept of heterogeneous catalysis, we understand a surface constituent as a constituent situated on Σ only. There is no surface constituent on $\partial\Omega \setminus \Sigma$.

[5] Outer normal vectors $\mathbf{n}^\Sigma$ to $\partial\Sigma_0$ are not unique because $\partial\Sigma_0$ is one-dimensional object in three-dimensional space; therefore, we specify these outer-normal vectors in general geometry as tangential to Σ and perpendicular to Γ_{in}, resp. to Γ_{out}.

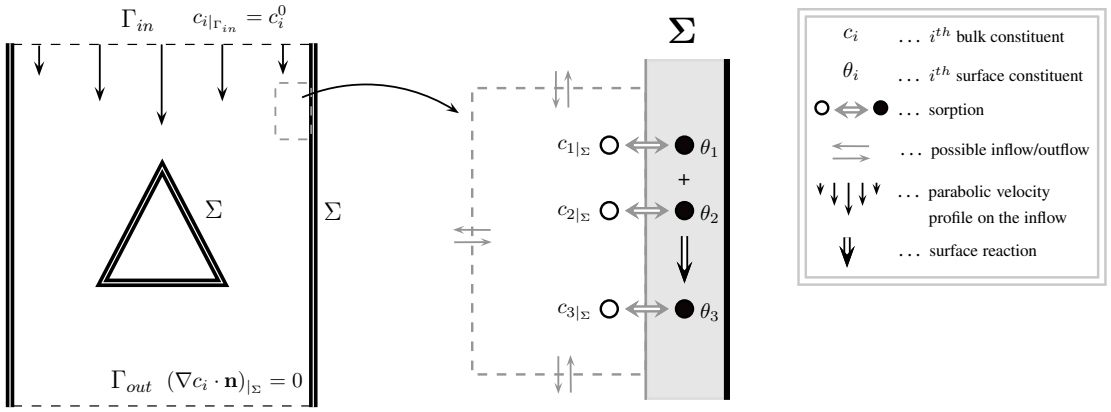


Figure 1.1: Flow in a channel with sorptions and surface reactions on the walls.

Denoting the bulk/surface diffusion fluxes as

$$\mathbf{J}_i := \rho_i(\mathbf{v}_i - \mathbf{v}) \ , \ \mathbf{J}_i^\Sigma = \rho_i^\Sigma(\mathbf{v}_i - \mathbf{v})$$

and recalling the impermeability of Σ, we can write the total bulk fluxes as

$$\mathbf{J}_i^{tot} \cdot \mathbf{n} = \begin{cases} (\rho_i \mathbf{v} + \mathbf{J}_i) \cdot \mathbf{n} & \text{on } \partial V \setminus \Sigma, \\ \mathbf{J}_i \cdot (-\mathbf{n}) & \text{on } \Sigma \end{cases},$$

where the fluxes caused by sorption are in the direction of the inner normal, hence the negative sign in the relation above. Note that the total surface fluxes, with no-slip velocity condition on Σ, possess only diffuse part, i.e. $\mathbf{J}_i^{\Sigma,tot} = \mathbf{J}_i^\Sigma$. Using these relations, we rewrite (1.1) as follows

$$\partial_t \int_V \rho_i \,\mathrm{d}V = -\int_{\partial V \setminus \Sigma} (\rho_i \mathbf{v} + \mathbf{J}_i) \cdot \mathbf{n} \,\mathrm{d}S + \int_\Sigma \mathbf{J}_i \cdot \mathbf{n} \,\mathrm{d}S \tag{1.2a}$$

$$\partial_t \int_\Sigma \rho_i^\Sigma \,\mathrm{d}S = -\int_{\partial\Sigma} \mathbf{J}_i^\Sigma \cdot \mathbf{n}^\Sigma \,\mathrm{d}s + \int_\Sigma R_i^{so} + R_i \,\mathrm{d}S. \tag{1.2b}$$

Secondly, consider the balance equation for whole mixture where the sorption terms in bulk and surface neglect each other. Then we end up with relation

$$\int_V \partial_t \rho_i \,\mathrm{d}V + \int_\Sigma \partial_t \rho_i^\Sigma \,\mathrm{d}S = -\int_{\partial V \setminus \Sigma} (\rho_i \mathbf{v} + \mathbf{J}_i) \cdot \mathbf{n} \,\mathrm{d}S - \int_{\partial\Sigma} \mathbf{J}_i^\Sigma \cdot \mathbf{n}^\Sigma \,\mathrm{d}s + \int_\Sigma R_i \,\mathrm{d}S \tag{1.3}$$

and, by subtracting of (1.2) from (1.3), we obtain the relation for sorption flux, namely

$$\int_\Sigma \mathbf{J}_i \cdot \mathbf{n} \,\mathrm{d}S = \int_\Sigma R_i^{so},$$

hence

$$\mathbf{J}_i \cdot \mathbf{n} = R_i^{so}.$$

Let M_i be the molar mass of i^{th} (bulk/surface) constituent, then we define the molar quantities as follows: the bulk concentration; the surface concentration; diffusive flux; surface diffusive flux; surface reaction rate and sorption rate, in sequence as

$$c_i = \frac{\rho_i}{M_i},\ \theta_i = \frac{\rho_i^\Sigma}{M_i},\ \mathbf{j}_i = \frac{\rho_i(\mathbf{v}_i - \mathbf{v})}{M_i},\ \mathbf{j}_i^\Sigma = \frac{\rho_i^\Sigma(\mathbf{v}_i - \mathbf{v})}{M_i},\ r_i = \frac{R_i}{M_i},\ r^{so} = \frac{R^{so}}{M_i}\ .$$

This gives us the balance-equation system for (molar)[6] bulk and surface concentrations

$$\partial_t c_i + \operatorname{div}(c_i\mathbf{v} + \mathbf{j}_i) = 0 \text{ on } \Omega \tag{1.4a}$$
$$\mathbf{j}_i \cdot \mathbf{n} = r_i^{so} \text{ on } \Sigma \tag{1.4b}$$
$$\partial_t \theta_i + \operatorname{div}_\Sigma \mathbf{j}_i^\Sigma = r_i^{so} + r_i \text{ on } \Sigma, \tag{1.4c}$$

for all $t > 0$ and $i = 1, .., n$.

1.3 Fick's law and boundary conditions

As a constitutive relation, we use Fick's law for the diffusive fluxes, namely

$$\mathbf{j}_i = -D_i \nabla c_i\ ,\ \mathbf{j}_i^\Sigma = -D_i^\Sigma \nabla_\Sigma c_{i|\Sigma},$$

where D_i, D_i^Σ are positive constant coefficients and the symbol "∇_Σ" the denotes surface gradient. Moreover, let us denote "Δ_Σ" $= \operatorname{div}_\Sigma(\nabla_\Sigma)$ the Laplace-Beltrami operator on Σ. These two operators are defined on tangential space for $x \in \partial\Omega$, cf. [7].

The specification of remaining boundary- and initial-conditions follows from the industrial application. Naturally, we consider a Dirichlet boundary conditions on the inflow as a representation of the fluid-mixture entering the microchannel-domain. As the outflow conditions, we consider so-called do-nothing conditions, i.e. homogeneous Neumann conditions. These conditions are also considered in case of surface constituent on whole $\partial\Sigma$ because the no-slip condition for velocity on Σ causes neither driven inflow nor outflow. The boundary conditions then follow as

$$\begin{aligned} -D_i(\nabla c_i \cdot \mathbf{n})_{|\Sigma} &= r_i^{so}(c_{i|\Sigma}, \theta_i) \text{ on } \Sigma \\ c_i = c_i^{in} &\geq 0 \text{ on } \Gamma_{in} \\ \nabla c_i \cdot \mathbf{n} &= 0 \text{ on } \Gamma_{out} \\ \nabla_\Sigma\, \theta \cdot \mathbf{n}^\Sigma &= 0 \text{ on } \partial\Sigma, \end{aligned}$$

for all $i = 1, .., n$.

[6] In sequel, if it is not written explicitly in other way, we always consider molar quantities.

Considering initial conditions c_i^0, θ_i^0, the complete balance system of PDEs reads as

$$\partial_t c_i + \mathbf{v} \cdot \nabla c_i - D_i \Delta c_i = 0 \text{ in } \Omega \tag{1.5a}$$

$$-D_i(\nabla c_i \cdot \mathbf{n})_{|\Sigma} = r_i^{so}(c_{i|\Sigma}, \theta_i),\ c_{i|\Gamma_{in}} = c_i^{in},\ (\nabla c_i \cdot \mathbf{n})_{|\Gamma_{out}} = 0 \tag{1.5b}$$

$$c_i(0, \cdot) = c_i^0 \tag{1.5c}$$

$$\partial_t \theta_i - D_i^{\Sigma} \Delta_{\Sigma} \theta_i = r_i^{so}(c_{i|\Sigma}, \theta_i) + r_i(\theta_1, .., \theta_n) \text{ on } \Sigma \tag{1.5d}$$

$$\nabla_{\Sigma} \theta \cdot \mathbf{n}^{\Sigma} = 0 \text{ on } \partial\Sigma \tag{1.5e}$$

$$\theta_i(0, \cdot) = \theta_i^0, \tag{1.5f}$$

for all $t > 0$ and $i = 1, .., n$; where $\mathbf{v}$ is a given stationary velocity field.

1.4 Dimensionless form

For further consideration, we introduced the dimensionless form of the system (1.5). Let us denote

$$c_i^* := c_i / c_i^{ref},\ \theta_i^* = \theta_i / \theta_i^{ref},\ t^* := t/T,\ \mathbf{x}^* := \mathbf{x}/L,\ \mathbf{v}^* := \mathbf{v}/U,$$

the dimensionless variables where we $c_i^{ref}, \theta_i^{ref}$ are the maximal (characteristic) concentrations of i^{th} species; and T, L, U are the characteristic (reference) time, length and velocity, see figure (1.2). For choosing the characteristic time-scale we have more possibilities but,

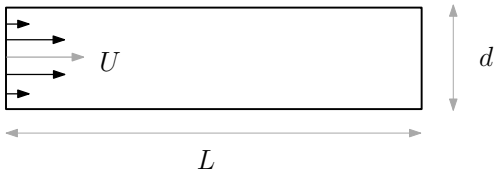


Figure 1.2: Characteristic quantities for the model.

from rational viewpoint, we should take advantage of such a relation which reasonably couples the dimensionless quantities T, L, U. Therefore we choose the characteristic time as the hydrodynamic residence time $T := \frac{L}{U}$. Consequently

$$\frac{\partial c_i}{\partial t} = \frac{\partial (c_i^{ref} c_i^*)}{\partial (T t^*)} = \frac{c_i^{ref}}{T} \partial_{t^*} c_i^*$$

and

$$\nabla c_i = \left(\frac{\partial c_i^{ref} c_i^{1*}}{\partial L x_1^*}, \frac{\partial c_i^{ref} c_i^{2*}}{\partial L x_2^*}, \frac{\partial c_i^{ref} c_i^{3*}}{\partial L x_3^*} \right) = \frac{c_i^{ref}}{L} \nabla^* c_i^*.$$

Denoting $c_i^{ref} r_i^{so} = r^{so}(c_i^*, \theta_i^*)$, we can write a dimensionless form of the balance equation-system (1.5) as

$$\frac{c_i^{ref}}{T} \partial_{t^*} c_i^* + \frac{1}{L} \operatorname{div}^* \left(c_i^{ref} U c_i^* \mathbf{v}^* - \frac{D_i c_i^{ref}}{L} \nabla^* c_i^* \right) = 0 \text{ in } \Omega$$

$$\frac{1}{T}\,\partial_{t^*}\theta_i^* - \frac{D_i^\Sigma}{L^2}\Delta_\Sigma^*\,\theta_i^* = r_i^{so}(c_i^*,\theta_i^*) + r_i(\theta_1^*,..,\theta_n^*) \text{ on } \Sigma$$

$$-\frac{D_i c_i^{ref}}{L}\,\nabla^* c_i^*\,\mathbf{n} = r_i^{so}(c_i^*,\theta_i^*) \text{ on } \Sigma.$$

Then, multiplying by hydrodynamic residence time $T := \frac{L}{U}$ gives

$$\partial_{t^*} c_i^* + \mathrm{div}^*(c_i^*\mathbf{v}^*) - \frac{D_i}{LU}\,\Delta^* c_i^* = 0 \text{ in } \Omega$$

$$\partial_{t^*}\theta_i^* - \frac{D_i^\Sigma}{LU}\,\Delta_\Sigma^*\,\theta_i^* = \frac{L}{U}\,(r_i^{so}(c_i^*,\theta_i^*) + r_i(\theta_1^*,..,\theta_n^*)) \text{ on } \Sigma$$

$$-\frac{D_i c_i^{ref}}{LU}\,\nabla^* c_i^* \cdot \mathbf{n} = \frac{1}{U}\,(r_i^{so}(c_i^*,\theta_i^*)) \text{ on } \Sigma.$$

Note 1.1. *Focusing on the coefficients in the equations above, the question, whether we can neglect some of them (without lose of generality), lies ahead. This causes the fact that*

$$\frac{D_i}{UL} = \frac{l/U}{L^2/D_i} = \frac{d^2}{L^2}\,\frac{L/U}{d^2/D_i} = \left(\frac{d}{L}\right)^2\,\frac{T_{tras}}{T_{diff}^{coax}} << 1,$$

where the transport time T_{trans} and the coaxial diffusion time T_{diff}^{coax} are similar, but the ratio $\left(\frac{d}{L}\right)^2$ is considered very small. Denoting $\frac{D_i}{UL} =: \frac{1}{(\mathrm{Pe})_\mathrm{i}}$ where $(\mathrm{Pe})_\mathrm{i}$ is Péclet number[7] of i^{th} constituent, the situation leads to the equation symbolically written as

$$\partial_t u + f(\nabla u) - \varepsilon\Delta u = g(u)\ ,\ \varepsilon_i << 1,$$

where $\varepsilon = \frac{1}{(\mathrm{Pe})} \sim 10^{-6} - 10^{-2}$. The neglecting of the coefficient ε leads to the change the order/type of PDEs from second order parabolic one to first order hyperbolic (eventually first order ODE for θ_i). This complicates the analysis and it could lead to incompatibility with boundary conditions. Moreover, the diffusion-effects are necessary for both bulk and surface processes. Therefore, we cannot neglect them and we handle a couple of two systems - namely convection/diffusion system for bulk concentrations c_i and reaction/diffusion system for surface concentrations θ_i.

The industrial applications, cf. [19], allow us to w.l.o.g. put $T = 1$ and $\frac{1}{U} = 1$. Furthermore, we suppress the "*" notation and we will denote the dimensionless quantities

[7]The Péclet number can be also defined by Reynolds (Re) and Schmidt (Sc) numbers as $\mathrm{Pe} = \mathrm{Re}\cdot\mathrm{Sc}$.

as c_i and θ_i. Then, the dimensionless system of $2n$ coupled equations yields

$$\partial_t c_i + \mathbf{v}\cdot\nabla c_i - \tfrac{1}{(\mathrm{Pe})_i}\Delta c_i = 0 \text{ in } \Omega \tag{1.6a}$$

$$-\tfrac{1}{(\mathrm{Pe})_i}\nabla c_{i|_{\Gamma_{in}}}\cdot\mathbf{n} = r_i^{so}(c_i,\theta_i),\ c_{i|_{\Gamma_{in}}} = c_i^{in},\ \nabla c_{i|_{\Gamma_{out}}}\cdot\mathbf{n} = 0 \tag{1.6b}$$

$$c_i(0,\cdot) = c_i^0 \text{ on } \Omega \tag{1.6c}$$

$$\partial_t\theta_i - \tfrac{1}{(\mathrm{Pe})_i^{\Sigma}}\Delta_{\Sigma}\theta_i = r_i^{so}(c_i,\theta_i) + r_i(\theta_1,..,\theta_n) \text{ on } \Sigma \tag{1.6d}$$

$$\nabla_{\Sigma}\theta_i\cdot\mathbf{n} = 0 \text{ on } \Sigma \tag{1.6e}$$

$$\theta_i(0,\cdot) = \theta_i^0 \text{ on } \Sigma \tag{1.6f}$$

for all $t>0$; $i=1,..n$; and given stationary vector-field $\mathbf{v}$. This general dimensionless system of balance-equations serves as a starting point for further constitutive relations which can differ with respect to occurring sorption- and reaction-kinetics.

Note 1.2. *The characteristic (reference) quantities could be chosen also differently. In our case, the second reasonable possibility would be choosing the characteristic length as d, the diameter of the channel; and the characteristic velocity as* $U = \frac{D^{ref}}{d}$ *where* D^{ref} *is the characteristic diffusive coefficient. This leads to the following set of the dimensionless quantities*

$$c_i^* := c_i/c_i^{ref},\ \theta_i^* = \theta_i/\theta_i^{ref},\ D_i^* := D_i/D^{ref},\ t^* := t/T,\ \mathbf{x}^* := \mathbf{x}/d,\ \mathbf{v}^* := \mathbf{v}/U,$$

where $T := \frac{d}{U} = \frac{d^2}{D^{ref}}$. *We obtain the equation-system*

$$\frac{c_i^{ref}}{T}\,\partial_{t^*}c_i^* + \frac{1}{d}\,\mathrm{div}\left(\frac{c_i^{ref}D^{ref}}{d}\,c_i^*\mathbf{v}^* - \frac{c_i^{ref}D^{ref}}{d}\,D_i^*\nabla^* c_i^*\right) = 0 \text{ in } \Omega$$

$$\frac{1}{T}\,\partial_{t^*}\theta_i^* - \frac{D^{\Sigma,ref}}{d^2}\,D_i^{\Sigma,*}\Delta_{\Sigma}^*\theta_i^* = r_i^{so}(c_i^*,\theta_i^*) + r_i(\theta_1^*,..,\theta_n^*) \text{ on } \Sigma$$

$$-\frac{c_i^{ref}D^{ref}}{d}\,D_i^*\nabla^* c_i^*\,\mathbf{n} = r_i^{so}(c_i^*,\theta_i^*) \text{ on } \Sigma$$

which can be rewritten as a

$$\partial_{t^*}c_i^* + \mathbf{v}^*\cdot\nabla c_i^* - D_i^*\,\Delta^* c_i^* = 0 \text{ in } \Omega$$

$$\partial_{t^*}\theta_i^* - \frac{D^{\Sigma,ref}}{D^{ref}}\,D^{\Sigma,*}\Delta_{\Sigma}^*\theta_i^* = T\,[r_i^{so}(c_i^*,\theta_i^*) + r_i(\theta_1^*,..,\theta_n^*)] \text{ on } \Sigma$$

$$-d\,c_i^{ref}\,D_i^*\,\nabla^* c_i^*\,\mathbf{n} = \frac{1}{T}\,r_i^{so}(c_i^*,\theta_i^*) \text{ on } \Sigma,$$

for all $t>0$ *and* $i=1,..,n$. *We see that this system is basically the same as for the previous set of characteristic quantities, therefore we w.l.o.g choose the first one.*

1.5 The systems

1.5.1 Sorptions and reactions

In the considered model we chose Langmuir-Hinshelwood adsorption mechanics (resp. Langmuir adsorption model) which corresponds to isothermal state for solid surface cata-

lyst and liquid or gas bulk-reactants, cf. [22]. The basic equation of the Langmuir isotherm, between the surface fractional coverage θ_i and corresponding bulk concentration c_i, reads as

$$\theta_i = \frac{\alpha_i\, c_i}{1 + \alpha_i\, c_i} \tag{1.7}$$

for α_i assumed to be positive constant coefficients and $i = 1, .., n$ where n is number of corresponding pairs.

Let us mentioned that the sorption takes place near the catalytic walls Σ only and the relation (1.7) is defined for physically correct ranges of the concentration $c_{i|_\Sigma}$ and fractional coverage θ_i. From physical point of view, the choice $\theta_i^{ref} = \sum_{i=1}^{3} \theta_i$ would lead to the condition $\theta_i \in [0, 1]$ and to the identification of the the fractional coverage with the surface concentration. However, this is not so simple from mathematical aspect where the non-negativity and boundedness of the functions c_i, θ_i are not a priori given. We will therefore introduce two kind of formulations.

Note 1.3. *Until now we have worked with general n bulk/surface pairs according to independence of each pair. This is still possible in case of the sorption-terms but not for surface reactions. Therefore for further consideration we will restrict ourselves to three pairs only.*

1.5.2 Untruncated system

Assuming physical behavior of system (1.6); i.e. the non-negativity and boundedness of $[c_i, \theta_i]$; we define the sorption term $r_i^{so} : \mathbb{R}_0^+ \times [0, 1] \to \mathbb{R}$ [8] as follows

$$c_{i|_\Sigma} \overset{r_i^{so}}{\Longleftrightarrow} \theta_i \ , \ r_i^{so} = r_i^{so}(c_{i|_\Sigma}, \theta_i) := c_{i|_\Sigma}(1 - \theta_i) - \kappa_i \theta_i,$$

where κ_i are constant non-negative coefficients.

The irreversible [9] elementary reactions [10] take place on the coated walls (catalytic surface), satisfying the law of mass action. Restricting to three bulk- (c_1, c_2, c_3) and three corresponding surface-constituents $(\theta_1, \theta_2, \theta_3)$, we consider surface reactions with stoichiometric coefficients equal to one, i.e. with forward quadratic rates, in the form

$$\theta_1 + \theta_2 \overset{r_i}{\to} \theta_3, \ r_i = r_i(\theta_1, \theta_2) = \kappa_i^{re}\, \theta_1 \theta_2, \ -\kappa_1^{re} = -\kappa_2^{re} = \kappa^{re} = \kappa_3^{re}.$$

This setting allow us to rewrite the equation (1.6) in the form of the basic equation-system

[8] Note that $c_i \in [0, \infty) \Rightarrow \theta_i \in [0, 1]$ which matches the physically correct ranges.

[9] Very often also a backward reactions take place but in the case of enough strong catalysis we can neglect this backward rate and consider just forward reactions i.e. irreversible reactions.

[10] Reaction with single mechanistic step, see [22].

used for later purpose, namely

$$\partial_t c_i + \mathbf{v}\cdot\nabla c_i - \tfrac{1}{(\mathrm{Pe})_i}\Delta c_i = 0 \text{ in } \Omega \tag{1.8a}$$

$$-\tfrac{1}{(\mathrm{Pe})_i}(\nabla c_i\cdot\mathbf{n})_{|\Sigma} = c_{i|\Sigma}(1-\theta_i) - \kappa_i\theta_i,\quad c_{i|\Gamma_{in}} = c_i^{in},\ \nabla c_{i|\Gamma_{out}}\cdot\mathbf{n} = 0 \tag{1.8b}$$

$$c_i(0,\cdot) = c_i^0 \text{ on } \Omega \tag{1.8c}$$

$$\partial_t\theta_i - \tfrac{1}{(\mathrm{Pe})_i^{\Sigma}}\Delta_{\Sigma}\theta_i = c_{i|\Sigma}(1-\theta_i) - \kappa_i\theta_i + \kappa_i^{re}\theta_1\theta_2 \text{ on } \Sigma \tag{1.8d}$$

$$\nabla_{\Sigma}\theta_i\cdot\mathbf{n} = 0 \text{ on } \Sigma \tag{1.8e}$$

$$\theta_i(0,\cdot) = \theta_i^0 \text{ on } \Sigma, \tag{1.8f}$$

for all $t>0$; $i=1,2,3$; and given velocity-field $\mathbf{v}$.

1.5.3 Truncated system

The physical range for $[c,\theta]$ is mathematically described by the maximum/minimum principle for evolution equations, i.e. the limits of the ranges are determined by the initial and boundary conditions. Since we treat autonomous problem with mixed boundary conditions, the values on the boundary are determined by initial conditions. As we will see later on, without additional assumptions we can not a priori guarantee the correct physical behavior for c_i and θ_i - the solutions of the nonlinear system (1.8). Therefore we need to introduce truncations to ensure the physically correct behavior of sorption- and reaction-terms. These truncations provide for physically correct initial data the physically correct solutions $[c_i(t;\mathbf{x}),\theta_i(t;\tilde{\mathbf{x}})]$ in the range of $[0,\infty)\times[0,1]$ for all $t>0, \mathbf{x}\in\Omega, \tilde{\mathbf{x}}\in\Sigma$.

We introduce the truncations as follows

$$r_i^{so}(c_{i|\Sigma},\theta_i) = c_{i|\Sigma}^{+}(1-[\theta_i]) - \kappa_i[\theta_i]\ ,\ r_i(\theta_1,\theta_2) = \kappa_i^{re}[\theta_1][\theta_2]$$
$$f^{+} := \max\{f,0\}\ ,\ [g] := \min\{g^{+},1\}.$$

and, consequently, the truncated system reads as

$$\partial_t c_i + \mathbf{v}\cdot\nabla c_i - \tfrac{1}{(\mathrm{Pe})_i}\Delta c_i = 0 \text{ in } \Omega \tag{1.9a}$$

$$-\tfrac{1}{(\mathrm{Pe})_i}(\nabla c_i\cdot\mathbf{n})_{|\Sigma} = c_{i|\Sigma}^{+}(1-[\theta_i]) - \kappa_i[\theta_i],\ c_{i|\Gamma_{in}} = c_i^{in},\ \nabla c_{i|\Gamma_{out}}\cdot\mathbf{n} = 0 \tag{1.9b}$$

$$c_i(0,\cdot) = c_i^0 \text{ on } \Omega \tag{1.9c}$$

$$\partial_t\theta_i - \tfrac{1}{(\mathrm{Pe})_i^{\Sigma}}\Delta_{\Sigma}\theta_i = c_{i|\Sigma}^{+}(1-[\theta_i]) - \kappa_i[\theta_i] + \kappa_i^{re}[\theta_1][\theta_2] \text{ on } \Sigma \tag{1.9d}$$

$$\nabla_{\Sigma}\theta_i\cdot\mathbf{n} = 0 \text{ on } \Sigma \tag{1.9e}$$

$$\theta_i(0,\cdot) = \theta_i^0 \text{ on } \Sigma, \tag{1.9f}$$

for all $t>0$; $i=1,2,3$; and given velocity field $\mathbf{v}$.

Note 1.4. *In following chapters we investigate the problem* (1.8)*, resp.* (1.9)*, from two viewpoints. Within Chapter 2 we examine so-called near-by problem* (2.1) *(truncated system with modified geometry) in sense of mild-solution.*

On the other hand, in Chapter 3 we choose concept of weak-solution. On the beginning of the chapter we investigate so-called semi-truncated system (3.1) *which is more convenient for analysis-purpose and from physical point of view it lies somewhere between truncated* (1.9) *and the original system* (1.8)*. As we will see later on, this system - under some assumptions - keeps all the solutions $c_i, \theta_i, i = 1, 2, 3$, in physically correct ranges which implies that truncations are in fact inactive and, therefore, the semi-truncated system coincides with the original system* (1.8)*.*

1.5.4 Other balances

As already mentioned, the whole process of heterogeneous catalysis is assumed to be isothermal, i.e. each constituent has the same temperature $T = const$ in the whole mixture. Furthermore, the flow of the is considered to be incompressible, i.e. $\rho = \sum_{i=1}^{n} \rho_i = const$, in Ω, resp. $\rho^{\Sigma} = \sum_{i=1}^{n} \rho_i^{\Sigma} = const$ on Σ; and, finally, we understand $\mathbf{v}$ as a given velocity field with no-slip condition on Σ.

Since we consider the internal energy $e = e(T, \rho)$ and entropy $\eta = \eta(e, \rho)$ there is no reason to provide any additional balance equations and the physical setting with the constitutive theory above completes the system. In other words, we obtain a system of 3 bulk-variables c_1, c_2, c_3 with 3 bulk equations (1.8a), and three surface-variables $\theta_1, \theta_2, \theta_3$ with three surface equation (1.8d).

1.5.5 Velocity field

We treat with a given velocity field $\mathbf{v}$ but, to be precise, we consider this field to be a solution of incompressible Navier-Stokes equation for Newtonian fluid with no-slip condition on Σ; Dirichlet inflow condition on Γ_{in}; and "do-nothing" Neumann condition on the outflow region Γ_{out}. The NS system follows as

$$-\nu\Delta\mathbf{v} + (\mathbf{v}\cdot\nabla)\mathbf{v} = \nabla p \text{ in } \Omega \tag{1.10a}$$

$$\operatorname{div}\mathbf{v} = 0 \text{ in } \Omega \tag{1.10b}$$

$$\mathbf{v}_{|\Gamma_{in}} = \mathbf{v}^{in},\ (\mathbf{v}\cdot\mathbf{n})_{|\Gamma_{out}},\ \mathbf{v}_{|\Sigma} = 0, \tag{1.10c}$$

where the $\mathbf{v}^{in}$ is a (given) positive continuous stationary parabolic profile; ν is the kinematic viscosity; and the channel-domain Ω possess Lipschitz-boundary, see schematic figure (1.1). Then the velocity field $\mathbf{v}$ satisfy the system (1.10) in classical sense having the regularity $\mathbf{v} \in C^2(\Omega) \cap C(\overline{\Omega})$, denote the set of these velocity fields as $\mathbf{V}$. Let us mention that for the analysis-purpose is important the embedding $C^2(\Omega) \cap C(\overline{\Omega}) \hookrightarrow W^{1,\infty}(\Omega)$.

2. Existence and uniqueness by nonlinear semigroup theory

For an introduction to the linear semigroup theory we refer e.g. to [11] and for the nonlinear case to classical work of Crandall and Liggett [9]. The extensive theory of nonlinear semigroups, used in our case, can be found in the habilitation of Bothe [3] and the book of Ito and Kappel [15]. Let us mention that we choose the concept of accretivity (6.7), based on classical work of Crandall and Liggett. This concept is equivalent to the dissipativity-concept used e.g. in [15]. For clarity, we recall definitions and theorems later on in the Appendix.

As we already mentioned, to prove the existence and uniqueness of a mild solution, we have to simplify the model-geometry which also involve the change of the boundary conditions. This modification consists in letting Σ become all $\partial\Omega$, i.e. enclosing the flow domain Ω with Σ - a smooth compact manifold. This concept is closely related to the periodical boundary conditions on Γ_{in} and Γ_{out}.

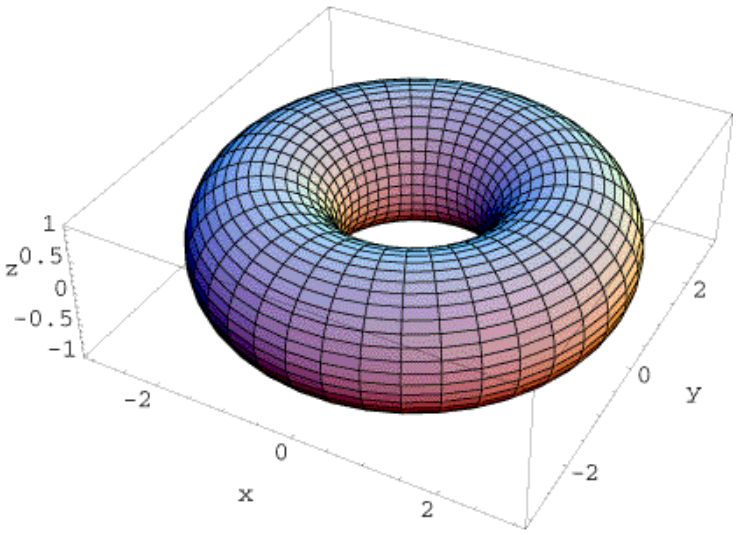


Figure 2.1: Illustration of the modified geometry.

Then the previous geometry-modification of the problem (1.9) leads to the enclosed truncated problem, which will serve as the basic problem for semigroup approach, in the following form:

Find $[c_1,\theta_1]\times[c_2,\theta_2]\times[c_3,\theta_3]\in X=(L^1(\Omega)\times L^1(\Sigma))^3$ such that

$$\partial_t c_i+\mathbf{v}\cdot\nabla c_i-\tfrac{1}{(\mathrm{Pe})_i}\Delta c_i=0 \text{ in } \Omega \tag{2.1a}$$

$$-\tfrac{1}{(\mathrm{Pe})_i}(\nabla c_i\cdot\mathbf{n})_{|\Sigma}=c^+_{i|\Sigma}(1-[\theta_i])-\kappa_i[\theta_i] \tag{2.1b}$$

$$c_i(0,\cdot)=c_i^0 \text{ on } \Omega \tag{2.1c}$$

$$\partial_t\theta_i-\tfrac{1}{(\mathrm{Pe})_i^\Sigma}\Delta_\Sigma\theta_i=c^+_{i|\Sigma}(1-[\theta_i])-\kappa_i[\theta_i]+\kappa_i^{re}[\theta_1][\theta_2] \text{ on } \Sigma \tag{2.1d}$$

$$\theta_i(0,\cdot)=\theta_i^0 \text{ on } \Sigma, \tag{2.1e}$$

for all $t>0$; $c_i^0\in L^1(\Omega),\theta_i^0\in L^1(\Sigma)$; $-\kappa_1^{re}=-\kappa_2^{re}=\kappa^{re}=\kappa_3^{re}$; $i=1,2,3$; and for the given velocity field $\mathbf{v}\in\mathbf{V}$.

The first step to apply the semigroup approach is rewriting the governing equation (2.1) as a system of three coupled non-homogeneous autonomous abstract Cauchy problems. Using a vector form it states: Find $\boldsymbol{u}\in C(J;X)$ such that

$$\begin{aligned}\dot{\boldsymbol{u}}(t)+\boldsymbol{A}\boldsymbol{u}(t)&=\boldsymbol{f}(\boldsymbol{u}(t)),\ t\in J\\ \boldsymbol{u}(0)&=\boldsymbol{u}^0\in\boldsymbol{X},\end{aligned} \tag{ACP-NH}$$

where [1]

$$\boldsymbol{u}=\begin{bmatrix}u_1\\u_2\\u_3\end{bmatrix},\ \boldsymbol{A}(\boldsymbol{u})=\begin{bmatrix}\mathcal{A}(u_1)\\\mathcal{A}(u_2)\\\mathcal{A}(u_3)\end{bmatrix},\ \boldsymbol{f}(\boldsymbol{u})=\begin{bmatrix}f(u_1,u_2)\\f(u_1,u_2)\\-f(u_1,u_2)\end{bmatrix}$$

$$u_i=\begin{bmatrix}c_i\\\theta_i\end{bmatrix},\ \mathcal{A}\begin{bmatrix}c_i\\\theta_i\end{bmatrix}=\begin{bmatrix}-\frac{1}{(\mathrm{Pe})_i}\Delta c_i+\nabla c_i\cdot\mathbf{v}\\-\frac{1}{(\mathrm{Pe})_i^\Sigma}\Delta_\Sigma\theta_i-c^+_{i|\Sigma}(1-[\theta_i])-\kappa_i[\theta_i]\end{bmatrix},\ f\left(\begin{bmatrix}c_1\\\theta_1\end{bmatrix},\begin{bmatrix}c_2\\\theta_2\end{bmatrix}\right)=\begin{bmatrix}0\\\kappa^{re}[\theta_1][\theta_2]\end{bmatrix}$$

$$\boldsymbol{X}=X^3=(L^1(\Omega)\times L^1(\Sigma))^3,\ \|\boldsymbol{u}\|_{\boldsymbol{X}}=\sum_{i=1}^3\|u_i\|_{L^1(\Omega)\times L^1(\Sigma)}=\sum_{i=1}^3\left(\|c_i\|_{L^1(\Omega)}+\|\theta_i\|_{L^1(\Sigma)}\right)$$

$$D(\boldsymbol{A})=(D(\mathcal{A}))^3, D(\mathcal{A})=\left\{\begin{bmatrix}c_i\\\theta_i\end{bmatrix}:\begin{bmatrix}\Delta c_i\\\Delta_\Sigma\theta_i\end{bmatrix}\in X,-\tfrac{1}{(\mathrm{Pe})_i}(\nabla c_i\cdot\mathbf{n})_{|\Sigma}=c^+_{i|\Sigma}(1-[\theta_i])-\kappa_i[\theta_i]\right\}$$ [2]

and $\mathbf{v}\in\mathbf{V}$.

Theorem 2.1. *Let $\Omega\subset\mathbb{R}^N$ be a bounded domain with a smooth boundary Σ and $J=[0,\alpha]\subset[0,\infty)$. Then for each $\boldsymbol{u}^0\in(L^\infty(\Omega)\times L^\infty(\Sigma))^3$ the autonomous system* (ACP-NH) *with operator $\boldsymbol{A}\subset\boldsymbol{X}\times\boldsymbol{X}$, domain $D(\boldsymbol{A})$ and autonomous perturbation $\boldsymbol{f}$ defined as above, posses a unique mild solution on J.*

[1] For clarity of writing, we sometimes switch between the notation $\begin{bmatrix}\cdot\\\cdot\end{bmatrix}$ and $[\cdot,\cdot]$, but the meaning is the same.

[2] For simplification, we do not write explicitly the conditions for velocity field $\mathbf{v}$ into the domain $D(\mathcal{A})$, but we consider them implicitly; resp. by expression "the regular" velocity field $\mathbf{v}\in\mathbf{V}$.

The main tool to prove Theorem 1. is Crandall-Liggett the generation theorem (see Theorem 6.3 in Appendix) [3] applied on m-accretive, densely defined operators. There are more possibilities how to handle the problem; we choose the way of treating the convective part as a perturbation bounded by diffusion part of the operator. The later addition of chemical reactions can be done as a continuous dissipative/bounded perturbation, resp. through invariance technique.

The concept of the proof can be introduced as follows:

(i) Associate the (ACP-NH) the homogeneous problem, i.e. with $\boldsymbol{f} = 0$; suppress the index, i.e. $\boldsymbol{A} \cong \mathcal{A}$; and split the operator $\mathcal{A}$ into a diffusive-sorption part A and a transport part B.

(ii) Prove accretivity of diffusive-sorption part A and, subsequently, m-accretivity by Schauder's fixed-point theorem.

(iii) Prove s-accretivity of the transport part B and its boundedness relative to operator A.

(iv) Apply Kato's perturbation theorem on the sum $A + B$ and receive the m-accretivity of the original operator $\mathcal{A}$.

(v) Add the reactions as continuous dissipative/bounded perturbations of the operator $\boldsymbol{A}$ and obtain a mild solution of the problem (ACP-NH).

Note 2.1. *The truncations can either be built into the operator-domain $D(\mathcal{A})$, or the sorption- and reaction-terms can be modified in such way that they form a reasonable extension to all $[c, \theta] \in \mathbb{R} \times \mathbb{R}$. In the first case, the operator will not be m-accretive, but only accretive plus satisfying the range-condition; this complicates the analysis. We take the later approach, where we have to check "by hand" that, with physically correct initial conditions, the solutions will stay in the physically correct range.*

Note 2.2. *The choice of the L^1-setting, instead of a more common L^2-, resp. L^p-settings, is not a priori given. It is chosen because of mass conservation and the fact that the L^1-norm, from a physical point of view, is the most natural norm in this case. Moreover, the comparison principle is expected from physical considerations and, since it will turn out, that only $L^1(\Omega) \times L^1(\Sigma)$-setting gives the accretivity of the operator $\mathcal{A}$. The later is directly related to the fact that the bilinear sorption term $r_i^{so}(c_i, \theta_i)$, according to Langmuir adsorption kinetics, is increasing in c_i and decreasing in θ_i. This leaves no other choice than $p = 1$.*

Note 2.3. *The L^1-setting and corresponding theory is not so spread as the theory of Hilbert spaces or reflexive L^p-spaces, but we can still find some classical results sufficient for our purpose. For L^1 regularity-results, see e.g. [14]; and for L^1-extension of the original Kato perturbation theorem to non-reflexive Banach spaces we refer to [18].*

[3] Which can be seen as an analogue to Lumer-Phillips generation theorem (6.2) in nonlinear case.

2.1 ACP-H

Let us consider $\boldsymbol{f} = 0, i = 1, 2, 3$ - alias homogeneous problem. Under this assumption, the system becomes decoupled for each pair $[c_i, \theta_i], i = 1, 2, 3$, i.e. we can restrict ourselves to a one-species problem, i.e. suppress the indexes. Moreover, as we are interested just in qualitative properties of the operator $\mathcal{A}$, we rescale nearly all the coefficients to one. This yields the no-reaction semigroup-system in the following form

$$\partial_t c + \mathbf{v} \cdot \nabla c - \Delta c = 0 \text{ in } \Omega \tag{2.2a}$$
$$-(\nabla c \cdot \mathbf{n})_{|\Sigma} = c^+_{|\Sigma}(1 - [\theta]) - \kappa[\theta] \tag{2.2b}$$
$$c(0, \cdot) = c^0 \text{ on } \Omega \tag{2.2c}$$

$$\partial_t \theta - \Delta_\Sigma \theta = c^+_{|\Sigma}(1 - [\theta]) - \kappa[\theta] \text{ on } \Sigma \tag{2.2d}$$
$$\theta(0, \cdot) = \theta^0 \text{ on } \Sigma, \tag{2.2e}$$

for all $t > 0$; $[c^0, \theta^0] \in X$; and $\mathbf{v} \in \mathbf{V}$.

Note 2.4. *Let us mention that the (uncoupled) system* (2.2) *corresponds to the no-reaction system with arbitrary n-pairs. The symmetry, because of the law of mass action, breaks by employment of the reaction terms.*

This leads to the homogeneous abstract Cauchy problem

$$\dot{x}(t) + \mathcal{A}x(t) = 0 \tag{ACP-H}$$
$$x(0) = x$$

$$x(t) = \begin{bmatrix} c(t) \\ \theta(t) \end{bmatrix}, \mathcal{A} \begin{bmatrix} c \\ \theta \end{bmatrix} = \begin{bmatrix} -\Delta c + \mathbf{v} \cdot \nabla c \\ -\Delta_\Sigma \theta - c^+_{|\Sigma}(1 - [\theta]) + \kappa[\theta] \end{bmatrix}$$

$$X = L^1(\Omega) \times L^1(\Sigma)$$

$$D(\mathcal{A}) = \left\{ \begin{bmatrix} c \\ \theta \end{bmatrix} : \begin{bmatrix} \Delta c \\ \Delta_\Sigma \theta \end{bmatrix} \in X, -(\nabla c \cdot \mathbf{n})_{|\Sigma} = c^+_{|\Sigma}(1 - [\theta]) - \kappa[\theta] \right\},^4$$

for all $t > 0$; $x \in X$; and $\mathbf{v} \in \mathbf{V}$.

Furthermore, similarly as in the linear case[5] also for the nonlinear case holds that the solution of the initial value problem (ACP-H) on $\overline{D(\mathcal{A})}$ is sufficient to solve the stationary resolvent equation

$$x + \lambda \mathcal{A}x = y, \ \forall y \in \overline{D(\mathcal{A})}, \tag{RE}$$

where $\lambda > 0$ is sufficiently small and $\mathcal{A}$ being accretive operator, see Crandall-Liggett theorem (6.3).

[4] All the inclusions are meant in the sense of distributions.

[5] Directly by combination of Hille-Yoshida theorem (6.1) and Lumer-Phillips theorem (6.2).

Because of our interest in the solution of (ACP-H) on the whole space X, we need to additionally require $D(\mathcal{A})$ to be a dense subset of X and the operator $\mathcal{A}$ to be m-accretive.[6] However, the specification of $D(A)$ is not so straightforward. Note that $X = L^1(\Omega)\times L^1(\Sigma)$ is a non-reflexive Banach space and the regularity of solutions to the equation

$$u - \Delta u = f,\ f \in L^1(\Omega), \Omega \in \mathbb{R}^N,$$

with sufficiently regular boundary conditions, is just $u \in W^{1,q}$ for $q \in \left[1, \frac{N}{}\right)$, cf. [4, §2]. Since N is arbitrary, we only prescribe $c \in W^{1,1}(\Omega), \theta \in W^{1,1}(\Sigma)$ and add the conditions $\Delta c \in L^1(\Omega), \Delta\theta \in L^1(\Sigma)$ into the operator-domain; this is sufficient to have the transport term $\mathbf{v}\cdot\nabla c$ and trace $c_{|\Sigma}$ in $L^1(\Omega)$.

In sequel, we will treat the operator $\mathcal{A}$ as the sum of two parts; the (nonlinear) reaction-diffusion part A and the (linear) transport part B as its perturbation, namely

$$A\begin{bmatrix}c\\ \theta\end{bmatrix} = \begin{bmatrix}-\Delta c\\ -\Delta_\Sigma\theta - c^+_{|\Sigma}(1-[\theta]) + \kappa[\theta]\end{bmatrix},\ D(A) = D(\mathcal{A})$$
$$B\begin{bmatrix}c\\ \theta\end{bmatrix} = \begin{bmatrix}\mathbf{v}\cdot\nabla c\\ 0\end{bmatrix},\ D(B) = \begin{bmatrix}W^{1,1}(\Omega)\\ L^1(\Sigma)\end{bmatrix} \supset D(A).$$

2.2 Accretivity of the operator A

Using the bracket notation for L^1-setting, see (6.10), an operator A is said to be accretive iff

$$[u-\tilde{u}, Au - A\tilde{u}]_X \geq 0,\ \forall u, \tilde{u} \in D(A), \tag{2.3}$$

where

$$[u,w]_X := \max\int_\Omega w_1(\mathbf{x})\mathrm{Sgn}[u_1(\mathbf{x})]\,dx + \max\int_\Sigma w_2(\mathbf{x})\mathrm{Sgn}[u_2(\mathbf{x})]\,ds \geq 0. \tag{2.4}$$

To check the previous relation, it is sufficient to substitute Sgn for a pointwise approximation s_ε, and investigate the limit case when $s_\varepsilon(x) \overset{\varepsilon\to 0_+}{\to} \mathrm{Sgn}(x)$. In our case, we chose the piecewise linear approximation s_ε with a.e. positive derivate, namely

$$s_\varepsilon(x) = \begin{cases}\mathrm{Sgn}(x) & \text{if } |x| \geq \varepsilon,\\ \frac{x}{\varepsilon} & \text{if } |x| \leq \varepsilon\end{cases}$$

and s^Σ_ε analogously. Note that here we distinguish the notation from $\mathbf{x} \in \overline{\Omega}$ and $x \in \mathbb{R}$. Denoting $Au = \begin{bmatrix}A_c(u)\\ A_\theta(u)\end{bmatrix}$ and writing sorption term in symbolical form r^{so}, the condition

[6] For $\mathcal{A}$ being an m-accretive operator, a solvability of (RE) for some $\lambda > 0$ is equivalent to a solvability for all $\lambda > 0$.

(2.3) reads as

$$[u-\tilde{u},Au-A\tilde{u}]_X = \begin{bmatrix} (c-\tilde{c}), A_c(u-\tilde{u}) \\ (\theta-\tilde{\theta}), A_\theta u - A_\theta \tilde{u} \end{bmatrix}_X$$
$$= \lim_{\varepsilon\to 0_+} \int_\Omega A_c(u-\tilde{u})\, s_\varepsilon(c-\tilde{c}) + \int_\Sigma (A_\theta u - A_\theta\tilde{u})\, s_\varepsilon^\Sigma(\theta-\tilde{\theta}) \geq 0, \qquad (*)$$

where we used the fact that

$$-\int_\Omega \Delta(c-\tilde{c})\, s_\varepsilon(c-\tilde{c}) - \int_\Sigma \Big(\Delta_\Sigma\theta + r^{so}(c,\theta) - \Delta_\Sigma\tilde{\theta} - r^{so}(\tilde{c},\tilde{\theta})\Big)\; s_\varepsilon^\Sigma(\theta-\tilde{\theta})$$
$$\overset{Green}{=} \int_\Omega |\nabla(c-\tilde{c})|^2\, s_\varepsilon'(c-\tilde{c}) - \int_\Sigma \nabla(c-\tilde{c})\cdot\mathbf{n}\, s_\varepsilon(c-\tilde{c}) +$$
$$\int_\Sigma |\nabla_\Sigma(\theta-\tilde{\theta})|^2\, s_\varepsilon'^\Sigma(\theta-\tilde{\theta}) - \int_\Sigma \Big(r^{so}(c,\theta) - r^{so}(\tilde{c},\tilde{\theta})\Big)\, s_\varepsilon^\Sigma(\theta-\tilde{\theta})$$
$$\overset{BC}{\geq} \int_\Sigma \Big(r^{so}(c,\theta) - r^{so}(\tilde{c},\tilde{\theta})\Big)\Big(s_\varepsilon(c-\tilde{c}) - s_\varepsilon^\Sigma(\theta-\tilde{\theta})\Big) \geq 0.$$

The last inequality holds for any physically correct choice[7] of r^{so} which include also the case of Langmuir adsorption model. This will be clear after the following observation:

(a) If $c-\tilde{c}$ and $\theta-\tilde{\theta}$ have the same sign, then $s_\varepsilon(c-\tilde{c}) - s_\varepsilon^\Sigma(\theta-\tilde{\theta}) \overset{\varepsilon\to 0}{\longrightarrow} 0$ and we are done. Especially when $c(\mathbf{x}) = \tilde{c}(\mathbf{x})$, resp. $\theta(\mathbf{x}) = \tilde{\theta}(\mathbf{x})$, then $s_\varepsilon(c(\mathbf{x}) - \tilde{c}(\mathbf{x})) = s_\varepsilon(0) = 0$ and $s_\varepsilon^\Sigma(\theta(\mathbf{x}) - \tilde{\theta}(\mathbf{x})) = s_\varepsilon^\Sigma(0) = 0$.

(b) If $c > \tilde{c}$ and $\theta < \tilde{\theta}$, then the fact that $r^{so}(c,\theta)$ is increasing in the first variable and decreasing in the second, implies the relation $r^{so}(c,\theta) \geq r^{so}(\tilde{c},\tilde{\theta})$.

(c) If $c < \tilde{c}$ and $\theta > \tilde{\theta}$, then we obtain $r^{so}(c,\theta) \leq r^{so}(\tilde{c},\tilde{\theta})$ using the same argumentation as above.

Let us mention that, as in many applications also in ours, the Banach space X is equipped with a natural partial ordering $\leq$. In such a situation it is important to know whether the given operator respects the ordering; this is closely related to the the concept of T-accretivity, cf. (6.9).

Let $(X, \|\cdot\|_X, \leq)$ be a Banach lattice. Then an operator which satisfies relation (2.4) but using the Heaviside function $H(x)$ instead of $\mathrm{Sgn}(x)$, is called T-accretive. Such operators, their resolvents and, hence, the generated semigroup are order preserving, i.e. $x_1 \leq x_2 \Rightarrow Ax_1 \leq Ax_2$, and single-valued.

The operator A under consideration has this property which follows from (*) and the subsequent observations.

[7]Here we require a natural behavior of the sorption term according to physical experiments. This can be mathematically expressed - requiring the term r^{so} to be increasing in the first variable and decreasing in second.

2.3 Resolvent equation by fixed-point approach

To solve (ACP-H) problem we need to prove m-accretivity of the operator $\mathcal{A} = A + B$. In this sense, we require the operator A to be closed, m-accretive operator and the operator B to be bounded relative to the operator A. The first requirement is associated with the range condition $rg(I + \lambda A) = X, \lambda > 0$ or, equivalently, with solvability of the resolvent equation

$$x + \lambda Ax = y, \quad \text{for } y \in D,$$

where D is a dense subset of $X = L^1(\Omega) \times L^1(\Sigma)$ and A is a closed operator.

Let us choose $D := L^p(\Omega) \times L^p(\Sigma), p > N - 1$. Then the resolvent equation leads to the nonlinear system R

$$(R) \begin{cases} c - \lambda \Delta c \ = f \text{ in } \Omega, f \in L^p(\Omega); \ -(\nabla c \cdot \mathbf{n})_{|\Sigma} = c^+_{|\Sigma}(1 - [\theta]) - \kappa[\theta] \text{ on } \Sigma, \\ \theta - \lambda \Delta_\Sigma \theta = g + \lambda \left(c^+(1 - [\theta]) - \kappa[\theta] \right) \text{ in } \Sigma, g \in L^p(\Sigma), \end{cases}$$

where $\lambda > 0$. This can be solved by the fixed point approach.

For this purpose we are going to define a continuous mapping F which maps any closed bounded set $K \subset D$ into a relatively compact subset of itself. Putting the nonlinearities, resp. the whole sorption term $r^{so}(c, \theta)$, to the right-hand side and treating them like time-independent inhomogeneity, we end up with the following fixed-point-mapping $F : [\hat{c}, \hat{\theta}] \to [c, \theta]$

$$(F) \begin{cases} c - \lambda \Delta c \ = f \text{ in } \Omega, f \in L^p(\Omega); \ -(\nabla c \cdot \mathbf{n})_{|\Sigma} = \hat{c}^+_{|\Sigma}(1 - [\hat{\theta}]) - \kappa[\hat{\theta}] \text{ on } \Sigma, \\ \theta - \lambda \Delta_\Sigma \theta = g + \lambda \left(\hat{c}^+_{|\Sigma}(1 - [\hat{\theta}]) - \kappa[\hat{\theta}] \right) \text{ in } \Sigma, g \in L^p(\Sigma). \end{cases}$$

Let us mention that this system is a special case of another system

$$(\tilde{F}) \begin{cases} c - \lambda \Delta c \ = f \text{ in } \Omega, f \in L^p(\Omega); \ -(\nabla c \cdot \mathbf{n})_{|\Sigma} = h, h \in L^p(\Sigma) \text{ on } \Sigma, \\ \theta - \lambda \Delta_\Sigma \theta = \tilde{g} \text{ in } \Sigma, \tilde{g} \in L^p(\Sigma), \end{cases}$$

where we used the fact that the truncation $[\cdot]$ maps the L^p-functions into L^∞-functions and therefore $r^{so}(\hat{c}_{|\Sigma}, \hat{\theta}) \in L^p(\Sigma)$.

The choice of the acting space for F is based on a priori regularity-estimates for elliptic problems in the form of $(\tilde{F})$ which are determined by regularity and nature of the boundary conditions. Since in case of the constituent c we handle the Neumann boundary condition, it gives us weaker regularity than in homogeneous Dirichlet-case. Concretely, for $f \in L^p(\Omega)$ we obtain $c \in W^{1+\frac{1}{p},p}(\Omega), p > 1$, see e.g. [14]. Here took an advantage of separating the transport part $B = \nabla c \cdot \mathbf{v}$. Without this separation one would not obtain even this regularity results.

Furthermore, θ "lives" on a smooth compact manifold without boundary which gives us similar results as in the Dirichlet case, i.e. $\theta \in W^{2,p}(\Sigma)$ for the data $g \in L^p(\Sigma), p > 1$. Together, we have a solution $[c, \theta] \in W^{1+\frac{1}{p},p}(\Omega) \times W^{2,p}(\Sigma)$ which is continuously embedded

(even with compactness) into continuous functions, namely in $\mathcal{C}(\overline{\Omega}) \times \mathcal{C}(\Sigma); \Sigma = \overline{\Sigma}$, and for arbitrary $p > N-1$. This gives us a well-defined trace $c_{|\Sigma}$ and allows us to choose the searching space as

$$Y = \mathcal{C}(\overline{\Omega}) \times \mathcal{C}(\Sigma).$$

Consequently with this choice, for all $[\hat{c}, \hat{\theta}] \in Y$ we obtain $F([\hat{c}, \hat{\theta}]) = [c, \theta] \in Y$ and the following regularity estimates holds

$$\begin{aligned} \|c\|_{W^{1+1/p,p}(\Omega)} &\leq K_1(\|h\|_{L^p(\Sigma)} + \|g\|_{L^p(\Omega)}) \\ \|\theta\|_{W^{2,p}(\Sigma)} &\leq K_2\|\tilde{g}\|_{L^p(\Sigma)}, \end{aligned}$$

for all $p > N-1$. This implies also the continuity of F.

The next step is to find an invariant set $K \subset Y$. For this purpose we use a method of sub- and supersolution, see e.g. [12, §9.3], and comparison principles for elliptic PDEs, see e.g. [27, §10].

Note 2.5. *The construction of the sub- and supersolutions has usually a clear physical meaning. Concretely in our case, we consider only the sink-terms in the bulk and outflow-terms through the boundary to obtain a subsolution; or the source-terms in the bulk and the inflow through the boundary only to receive a supersolution.*

For fixed functions $f \in L^p(\Omega), g \in L^p(\Sigma)$ and $[\hat{c}, \hat{\theta}] \in Y$, consider a solution $[c, \theta]$ of the problem (F). By comparison principle, denoting $|\cdot|$ the L^p-norm on Ω resp. Σ, we state the sub- and supersolution $\underline{c}, \bar{c}$ for c, in sequence, as the solutions of

$$\begin{aligned} \underline{c} - \lambda\Delta\underline{c} &= -|f|, \ -(\nabla\underline{c} \cdot \mathbf{n})_{|\Sigma} = \hat{c}^+_{|\Sigma} \\ \bar{c} - \lambda\Delta\bar{c} &= |f|, \ -(\nabla\bar{c} \cdot \mathbf{n})_{|\Sigma} = -\kappa. \end{aligned}$$

Note that $\bar{c}$ depends only on the fixed function f and the parameter κ. So, if it is chosen as the supersolution, then $\hat{c}^+ \in [0, |\bar{c}|], \forall \hat{c} \in K$. Hence $\underline{c}$ is above the solution $\underset{\sim}{c}$ of

$$\underset{\sim}{c} - \lambda\Delta\underset{\sim}{c} = -|f| \ , \ -(\nabla\underset{\sim}{c} \cdot \mathbf{n})_{|\Sigma} = |\bar{c}|,$$

which is independent of $[\hat{c}, \hat{\theta}]$. Analogously, we define the sub- and supersolution $\underline{\theta}, \bar{\theta}$ for θ, in sequence, as the solutions of

$$\begin{aligned} \underline{\theta} - \lambda\Delta_\Sigma\underline{\theta} &= -|g| - \kappa \\ \bar{\theta} - \lambda\Delta_\Sigma\bar{\theta} &= |g| + \hat{c}^+_{|\Sigma}. \end{aligned}$$

Here, $\overline{\theta}$ is below the solution $\tilde{\theta}$ of

$$\tilde{\theta} - \lambda\Delta_\Sigma\tilde{\theta} = |g| + |\bar{c}_{|\Sigma}|,$$

where $|\bar{c}_{|\Sigma}|$ is independent of $[\hat{c}, \hat{\theta}]$ and so is $\tilde{\theta}$. This allows us to choose the set K as

$$K = \left\{ \begin{bmatrix} \hat{c} \\ \hat{\theta} \end{bmatrix} \in Y : \min_{\overline{\Omega}} \underset{\sim}{c} \leq \hat{c} \leq \bar{c}, \underline{\theta} \leq \hat{\theta} \leq \max_{\Sigma} \tilde{\theta} \right\}$$

which is a closed, bounded and convex set.

Now we need to show that the set $F(K)$ is relatively compact in X. Let $[f_n, \tilde{g}_n] \subset K$ be a given (bounded) sequence. From the previous regularity results, we have a bounded sequence of solutions $[c_n, \theta_n] \in W^{1+\frac{1}{p},p}(\Sigma) \times W^{2,p}(\Sigma), p > 1$ of the problem $(\tilde{F})$. The reflexivity of the space D implies that we can choose a weakly convergent subsequence which - by compact embedding $W^{1+\frac{1}{p},p}(\Sigma) \times W^{2,p}(\Sigma) \overset{c}{\hookrightarrow} Y = C(\overline{\Omega}) \times C(\Sigma)$, for $p > N-1$ - is strongly convergent in $Y \subset X$ and, therefore, $F(K)$ is relative compact in X.

Finally, according to Schauder's fixed point theorem, see e.g. [14, Cor. 11.2], the mapping $F : K \to K$ has a fixed point $[c, \theta]$ which is the solution of resolvent problem (R). Moreover, the solution is unique due to accretivity of the operator $\mathcal{A}$.

2.4 Density of $D(A)$

Since the boundary conditions are included in the definition of $D(A)$, its density in X is not trivial and one needs to explicitly show this property. Note that $D(\mathcal{A}) \subset C(\overline{\Omega}) \times C(\Sigma)$ which is dense in X, therefore, it suffices to show the density of $D(\mathcal{A})$ in $C(\overline{\Omega}) \times C(\Sigma)$.

Let us have $c_\infty \in C(\overline{\Omega})$ and $\theta_\infty \in C(\Sigma)$. From the construction of the resolvent equation we know that there is a solution $[c, \theta] \in K$ of the problem

$$c - \lambda \Delta c = c_\infty \text{ in } \Omega \tag{2.5a}$$

$$-(\nabla c \cdot \mathbf{n})_{|\Sigma} = c^+_{|\Sigma}(1 - [\theta]) - \kappa[\theta] \text{ on } \Sigma, \tag{2.5b}$$

$$\theta - \lambda \Delta_\Sigma \theta = \theta_\infty + \lambda \left(c^+_{|\Sigma}(1 - [\theta]) - \kappa[\theta]\right) \text{ in } \Sigma. \tag{2.5c}$$

for any $c_\infty \in L^p(\Omega)$, $\theta_\infty \in L^p(\Sigma)$, $p > 1$ and the smooth manifold Σ. The thing, which remains to do, is to prove the following convergences

$$\|c - c_\infty\|_{L^p(\Omega)} = \|\lambda \Delta c\|_{L^p(\Omega)} \leq \lambda \, \|c\|_{W^{2,p}(\Omega)} \overset{?}{\longrightarrow} 0, \ \lambda \to 0_+ \tag{2.6a}$$

$$\begin{aligned} \|\theta - \theta_\infty\|_{L^p(\Omega)} &= \|\lambda \Delta_\Sigma \theta + \lambda \, c^+_{|\Sigma}(1 - [\theta]) - \kappa[\theta]\|_{L^p(\Omega)} \\ &\leq \lambda \|\theta\|_{W^{2,p}(\Sigma)} + \lambda \|c^+_{|\Sigma}(1 - [\theta]) - \kappa[\theta]\|_{L^p\Sigma} \overset{?}{\longrightarrow} 0, \ \lambda \to 0_+. \end{aligned} \tag{2.6b}$$

As one can see, we need to bound corresponding norms by data, since c_∞ are θ_∞ are bounded as continuous functions on the compacts. For this purpose, let us once more recall the regularity results obtained by the construction of the resolvent equation in previous section. For any $[c_\infty, \theta_\infty] \in C(\overline{\Omega}) \times C(\Sigma) \subset L^p(\Omega) \times L^p(\Sigma)$, there is a solution of the system (2.5) such that for $p > N - 1$ the following embeddings hold

$$c \in W^{1+1/p,p}(\Omega) \subset C(\overline{\Omega}), \ \theta \in W^{2,p}(\Sigma) \subset C(\Sigma), c^+_{|\Sigma}(1 - [\theta]) - \kappa[\theta] \in C(\Sigma) \subset L^p(\Sigma).$$

The regularity of elliptic PDE (2.5a) with Neumann boundary condition in $L^p(\Sigma)$ directly gives $c \in W^{1+1/p,p}(\Omega)$ and, since

$$\|c^+_{|\Sigma}(1 - [\theta]) - \kappa[\theta]\|_{L^p(\Sigma)} \leq \|c\|_{L^p(\Sigma)} + K \leq \tilde{K}\big(\|c\|_{W^{1+1/p,p}(\Omega)}\big), \tag{2.7}$$

we obtain

$$\|c\|_{W^{1+1/p,p}(\Omega)} \leq K_1\big(\|c_\infty\|_{\mathcal{C}(\overline{\Omega})}\big). \tag{2.8}$$

Using these two estimates, the regularity of elliptic PDEs on the smooth manifold yields

$$\|\theta\|_{W^{2,p}} \leq K\big(\|\theta_\infty\|_{L^p\Sigma}, \|c_\infty\|_{L^p\Sigma}\big) \leq K_2\big(\|\theta_\infty\|_{C(\Sigma)}, \|c_\infty\|_{\mathcal{C}(\overline{\Omega})}\big). \tag{2.9}$$

which is sufficient to obtain the second convergence (2.6b).

To satisfy the first one, we need to improve regularity of Neumann condition (2.5b). This can be done by trace theorem [8] which yields

$$\begin{aligned}\|c^+_{|\Sigma}(1-[\theta]) - \kappa[\theta]\|_{W^{1,p}(\Sigma)} &\leq \|c_{|\Sigma}\|_{W^{1+1/p,p}(\Omega)}\big(1+\|\nabla\theta\|_{L^p(\Sigma)}\big) + \kappa\|\theta\|_{W^{1,p}(\Sigma)} \\ &\leq K\big(\|c\|_{W^{1+1/p,p}(\Omega)}, \|\theta\|_{W^{1,p}(\Sigma)}\big) \\ &\leq K_3\big(\|\theta_\infty\|_{C(\Sigma)}, \|c_\infty\|_{\mathcal{C}(\overline{\Omega})}\big) \end{aligned} \tag{2.10}$$

Having this smoothness for boundary condition, we finally obtain the better regularity for c, namely

$$\|c\|_{W^{2,p}(\Omega)} \leq K_4(\|c_\infty\|_{\mathcal{C}(\overline{\Omega})}, \|\theta_\infty\|_{C(\Sigma)}).$$

Hence we have

$$\begin{aligned}\|c - c_\infty\|_{L^p(\Omega)} &\leq \lambda\, K(\|c_\infty\|_{\mathcal{C}(\overline{\Omega})}, \|\theta_\infty\|_{C(\Sigma)}) \overset{\lambda\to 0_+}{\longrightarrow} 0 \\ \|\theta - \theta_\infty\|_{L^p(\Omega)} &\leq \lambda\, K(\|c_\infty\|_{\mathcal{C}(\overline{\Omega})}, \|\theta_\infty\|_{C(\Sigma)}) \overset{\lambda\to 0_+}{\longrightarrow} 0.\end{aligned}$$

2.5 Closedness of the operator A

Note 2.6. *If it is not specified in anther way, all the convergences are meant in the real Banach space $X = L^1(\Omega) \times L^1(\Sigma)$ with the corresponding norm $\|\cdot\|_X$. Furthermore, we will recall some regularity results for L^1-spaces which vary from the previous L^p-regularity results.*

To show the closedness of the operator A in X, we need that for

$$u_n = \begin{bmatrix} c_n \\ \theta_n \end{bmatrix}, u = \begin{bmatrix} c \\ \theta \end{bmatrix}, Au_n = \begin{bmatrix} -\Delta c_n \\ -\Delta_\Sigma\theta_n - c^+_{n|\Sigma}(1-[\theta_n]) - \kappa[\theta_n] \end{bmatrix} = \begin{bmatrix} f_n \\ g_n \end{bmatrix}, v = \begin{bmatrix} f \\ g \end{bmatrix}$$
$$\wedge\ -(\nabla c_n \cdot \mathbf{n})_{|\Sigma} = c^+_{n|\Sigma}(1-[\theta_n]) - \kappa[\theta_n]$$

the following to hold:

$$\{u_n \to u \text{ and } Au_n \to v\} \ \Rightarrow Au = v. \tag{2.11}$$

[8] For domain Ω with smooth $\partial\Omega$ there is a continuous trace operator $\mathrm{tr} : \mathrm{W}^{\mathrm{k,p}}(\Omega) \to \mathrm{W}^{\mathrm{k}-\frac{1}{\mathrm{p}},\mathrm{p}}(\partial\Omega)$, cf. [1].

We know that the Laplace operator is closed linear operator and the truncation "$[\cdot]$" maps $L^1(\Sigma)$ functions into $L^\infty(\Sigma)$ functions, hence it is sufficient to show

$$\left\{ \begin{bmatrix} c_n \\ \theta_n \end{bmatrix} \to \begin{bmatrix} c \\ \theta \end{bmatrix} \text{ in } X \ \wedge \ c^+_{n|_\Sigma} \to \alpha \text{ in } L^1(\Sigma) \right\} \ \Rightarrow c^+_{|_\Sigma} = \alpha. \tag{2.12}$$

First of all, we need to show that $\{c^+_{n|_\Sigma}\}_{n=1}^\infty$ is bounded in $L^1(\Sigma)$. Note that the sequence has already the lower bound so it remains to find the upper bound only. For this purpose, we will again use the comparison principle where the sequence of supersolutions $\{\bar{c}_n\}_{i=1}^\infty$ satisfies the equations

$$\Delta \bar{c}_n = f_n, \ -(\nabla \bar{c} \cdot \mathbf{n})_{|_\Sigma} = -\kappa[\theta_n].$$

The regularity for elliptic PDEs in the L^1-setting with smooth boundary and Neumann boundary condition, see [4, thm 20.], yields

$$\bar{c}_n \in W^{1,q}(\Omega), \ \forall q \in [1, N/(N-1))$$

and, consequently from [4, lemma 23.], we obtain

$$\|\bar{c}_n\|_{W^{1,q}(\Omega)} \leq K(\|f\|_{L^1(\Omega)} + \kappa \|[\theta_n]\|_{L^1(\Sigma)}). \tag{2.13}$$

Hence, by trace the theorem [12, §5.5], the sequence $\{c_{n|_\Sigma}\}_{n=1}^\infty$ is bounded in $L^q(\Sigma)$; from comparison principle the estimate (2.13) holds also for $c^+_n \in [0, \bar{c}^+_n]$; and therefore, we have the boundedness of $\{c^+_{n|_\Sigma}\}_{n=1}^\infty$ in $L^q(\Sigma)$, i.e. also in $L^1(\Sigma)$. Moreover, the reflexivity of the space $W^{1,q}(\Omega)$, for $q > 1$, provides the fact that from any bounded sequence we can choose weakly convergent subsequence, namely [9]

$$c_n \overset{w}{\to} c \text{ in } W^{1,q}(\Omega), \tag{2.14}$$

which implies the strong convergence in $L^1(\Omega)$ because of the compact embeddings $W^{1,q}(\Omega) \overset{c}{\hookrightarrow} L^1(\Omega), 1 \leq q < N$, cf. Rellich-Kondrachov Compactness Theorem [12, §5.7].

The next step is to show that this limit coincidences with the limit on the boundary. According to the assumption is $c^+_{n|_\Sigma} \to \alpha$. The question is whether $\alpha = c^+_{|_\Sigma}$. Unfortunately, we can not ensure $c^+_{|_\Sigma}$ to be continuous on $\mathcal{C}(\overline{\Omega})$. The way out leads through Mazur's theorem, see [24]. It states: Whenever (2.14) holds, there exists a sequence defined by its convex combination, i.e. $\tilde{c}_n \in \mathrm{Conv}\{\mathrm{c_k} : \mathrm{k} \geq \mathrm{n}\}$, such that

$$\tilde{c}_n \to c \text{ in } W^{1,q}(\Omega). \tag{2.15}$$

Using the trace operator $\mathrm{tr} : W^{1,q}(\Omega) \to L^q(\Sigma)$, which is continuous and linear, together with the assumption (2.12), we obtain the desired result

$$\alpha = \lim_{n\to\infty} \tilde{c}^+_{n|_\Sigma} = \lim_{n\to\infty} \mathrm{tr}(\tilde{c}_n)^+ = \mathrm{tr}(\lim_{n\to\infty} \tilde{c}_n)^+ = (\mathrm{tr}(\lim_{n\to\infty} \tilde{c}_n))^+ = (\mathrm{tr}(c))^+ = c^+_{|_\Sigma}.$$

[9] For simplification, we denote the chosen subsequence again c_n.

Let us mention that

$$|c_n^+ - c^+| \leq |c_n - c| \ \wedge \ |[\theta_n] - [\theta]| \leq |\theta_n - \theta|$$

and consequently

$$\begin{aligned}\left|c^+_{n|_\Sigma}[\theta_n] - c^+_{|_\Sigma}[\theta]\right| &\leq \left|c^+_{n|_\Sigma}[\theta_n] - c^+_{|_\Sigma}[\theta_n] + c^+_{|_\Sigma}[\theta_n] - c^+_{|_\Sigma}[\theta]\right| \\ &\leq \left|c^+_{n|_\Sigma} - c^+_{|_\Sigma}\right| + \left|c^+_{n|_\Sigma}\right| \ \left|[\theta_n] - [\theta]\right|.\end{aligned}$$

The convergences then directly follow as

$$\begin{aligned}\int_\Omega \left|(\Delta c_n - \Delta c)\varphi\right| \leq \int_\Omega &\left|(\nabla c_n - \nabla c)\nabla\varphi\right| \\ &+ \int_\Sigma \left|\Big(c^+_{n|_\Sigma}(1 - [\theta_n]) - \kappa[\theta_n] - c^+_{|_\Sigma}(1 - [\theta]) - \kappa[\theta]\Big)\,\varphi\right| \\ &\overset{n\to\infty}{\longrightarrow} 0, \ \forall\varphi \in C^\infty(\overline{\Omega})\end{aligned}$$

and analogously

$$\int_\Sigma \left|\Big(\Delta_\Sigma\theta_n + c^+_{n|_\Sigma}(1 - [\theta_n]) - \kappa[\theta_n] - (\Delta_\Sigma\theta + c^+_{|_\Sigma}(1 - [\theta]) - \kappa[\theta])\Big)\psi\right| \overset{n\to\infty}{\longrightarrow} 0, \ \forall\psi \in C^\infty(\Sigma).$$

Since, we satisfy the problem (2.11) for dense function in $D(\mathcal{A})$, the operator A is closed.

2.6 m-accretivity

The last step is to prove m-accretivity of the operator A, i.e. the range condition $rg(I + \lambda A) = X$, for some (or, equivalently, for all) $\lambda > 0$. From previous density result follows: For a given $u = [c, \theta] \in X$ there is a sequence $\hat{u}_n = [\hat{c}_n, \hat{\theta}_n] \in Y$ such that $\hat{u}_n \to u$ in X. Moreover, for any $[\hat{c}_n, \hat{\theta}_n]$ there is unique solution $[c_n, \theta_n] \in D(A)$ of the resolvent equation R_n in the form

$$(R_n)\begin{cases} c_n - \Delta c_n = \hat{c}_n; -\nabla c \cdot \mathbf{n} = c^+_{n|_\Sigma}(1 - [\theta_n]) - \kappa[\theta_n] \\ \theta_n - \Delta_\Sigma\theta_n = \hat{\theta}_n + c^+_{n|_\Sigma}(1 - [\theta_n]) - \kappa[\theta_n]. \end{cases}$$

Furthermore, the accretivity of the operator A states

$$\|(\lambda + A)u - (\lambda + A)\tilde{u}\| = \|\lambda(u - \tilde{u}) + Au - A\tilde{u})\| \geq \lambda\|(u - \tilde{u})\|, \ \forall\lambda > 0$$

and the resolvent mapping $R_\lambda(A) = (I + \lambda A)^{-1}$ is a non-expansive mapping for $\lambda = 1$. Hence

$$v_n = [c_n, \theta_n] = (I + A)^{-1}[\hat{c}_n, \hat{\theta}_n]$$

is a Cauchy sequence in Banach space X and therefore convergent in X. Moreover, the closedness of A implies the closedness of $(I + A)^{-1}$ which together with the fact that

$$(I + A)^{-1}(\hat{u}_n) \to v \quad \wedge \quad \hat{u}_n \to u$$

gives the existence of $u \in X$ for all $v \in X$ such that $(I + A)^{-1}(u) = v$, i.e. $rg(I + A) = X$.

2.7 Properties of the operator B

First of all, we consider only the first component of the operator B in the Hilbert space $X_0 = L^2(\Omega)$. Let us denote this operator as B_0 with $D(B_0) = W^{1,2}(\Omega)$. Then the following holds

$$\langle c, B_0\, c\rangle = \int_\Omega c\,\mathbf{v}\cdot\nabla c = \int_\Omega \mathbf{v}\cdot\nabla\frac{c^2}{2} \overset{Green}{=} -\int_\Omega \frac{c^2}{2}\cdot \operatorname{div}\mathbf{v} = 0.$$

Tt means that the operator B_0 is conservative (simultaneously dissipative and accretive). Since X_0 is a Hilbert space, it is also s-accretive (see Appendix (6.8)) and the adjoint operator reads as $B_0^* = -B_0$.

The next step to show closedness of B_0 is to show

$$\left\{c_n \to c \text{ in } L^2(\Omega) \quad \wedge \quad \mathbf{v}\cdot\nabla c_n \to w \text{ in } L^2(\Omega)\right\} \Rightarrow w = \mathbf{v}\cdot c.$$

This can be equivalently written in distributional sense, where for all $\varphi \in \mathcal{C}^\infty(\Omega)$ the following holds

$$\int_\Omega \operatorname{div}\left(\mathbf{v}\,(c_n - c)\right)\varphi \overset{Green}{=} \int_\Omega \left|\mathbf{v}\,(c_n - c)\cdot\nabla\varphi\right| \le \|\mathbf{v}\|_{L^\infty(\Omega)}\|c_n - c\|_{L^2(\Omega)}\|\nabla\varphi\|_{L^2(\Omega)} \overset{n\to\infty}{\longrightarrow} 0$$

where we have used Lebesgue's domination theorem (cf. [26]) to exchange the limit and integral. Hence both B_0 and B_0^* are closed and, by [15, thm 2.27], we obtain B_0 as m-accretive operator and infinitesimal generator of a $\mathcal{C}_0$ - semigroup of contraction.

The extension of this result to the original space X can be done by Lumer-Phillips theorem (6.2), requiring $rg(I + \lambda B)$ to be dense in X for some $\lambda > 0$. W.l.o.g. put $\lambda = 1$. Then the property of m-accretivity of B_0 in $L^2(\Omega)$ yields a solution $c \in D(B_0)$ of the resolvent equation $c + B_0\, c = f$ for any $f \in L^2(\Omega)$.

Since $B_{|_{D(B_0)}} = B_0$ and $D(B_0) \subset D(B)$, we also have a solution for $c + (Bc)_1 = f$ in $L^2(\Omega)$ and, consequently, we have a solution $u \in D(B)$ of the resolvent equation $u + Bu = g$ for any $g \in L^2(\Omega) \times L^1(\Sigma)$ which is dense in $X = L^1(\Omega) \times L^1(\Sigma)$. Because of the second component of the operator B is zero the closedness meets the same argumentation as above and by Lumer-Phillips theorem (6.2) we obtain the operator B as the generator of a $\mathcal{C}_0$ - semigroup. Moreover, by [11, Prop. 3.23] B is also s-accretive.

2.8 Perturbation

In this section we will use an extended perturbation theory for general Banach spaces. A lead role will have Kobayasi perturbation theorem (6.5), the generalization of classical Kato's perturbation theorem which require a uniform convexity of the space, see [17].

In our case, the transport operator B, where $D(B) = W^{1,1}(\Omega) \times L^1(\Sigma) \supset D(A)$, is linear and acts just on the constituent c. Unlike in the situation in L^p spaces with $p > 1$,

[9] Let us recall that the velocity field $\mathbf{v}$ is incompressible with no-slip boundary condition, therefore, $\mathbf{v}\cdot c_n = \operatorname{div}(\mathbf{v}\, c_n)$ and the boundary term is zero.

in case of $p = 1$ we can not use standard approach, e.g. applying the mean-value theorem considered in [11, Ex. 2.2]. The positive answer for the relative boundedness of operator B provide Lunardi and Metafune in [21]. They state that

$$\|\nabla u\|_{L^p(\Omega)} \leq C(N,p)\,\|u\|^{1-\gamma}_{L^1(\Omega)}\|\Delta u\|^{\gamma}_{L^1(\Omega)}$$

which $\Omega \subset R^N, p < \frac{N}{}$ and $\gamma = \frac{N(1-1/p)+1}{2} < 1$. For $N = 3$ and $p = 1$ we obtain by application of Cauchy ε-inequality, see [12, Appendix B],

$$\|\nabla u\|_{L^1(\Omega)} \leq C\,\|u\|^{\frac{1}{2}}_{L^1(\Omega)}\|\Delta u\|^{\frac{1}{2}}_{L^1(\Omega)} \leq C\left(\varepsilon\|\Delta u\|_{L^1(\Omega)} + \frac{\|u\|_{L^1(\Omega)}}{4\varepsilon}\right),\ \forall \varepsilon > 0.$$

Therefore $B = \mathbf{v}\cdot\nabla c$ is locally A-bounded for any bound $L > 0$. This implies

$$\|B\|_{\mathrm{x}} \leq \|\mathbf{v}\|_{L^\infty(\Omega)}\|\nabla c\|_{L^1(\Omega)} \leq \|A\|_{\mathrm{x}} = \|\Delta c\|_{L^1(\Omega)} + \|\cdot\|_{L^1(\Sigma)},$$

what immediately meets local Lipchitz condition $(L.2)$ in theorem (6.5), see Appendix. Furthermore, as was shown before, the operator B is s-accretive and therefore dissipative in the sense of Browder, see [5]. All these conditions give by Kobayashi perturbation theorem (6.5) that $\mathcal{A} = A + B$ is an m-dissipative operator.

2.9 Irreversible chemical reaction

Let us recall the quasi-autonomous abstract Cauchy problem (ACP-NH)

$$\begin{aligned} \dot{\boldsymbol{u}}(t) + \boldsymbol{A}\boldsymbol{u}(t) &= \boldsymbol{f}(\boldsymbol{u}(t)),\ t \in J \\ \boldsymbol{u}(0) &= \boldsymbol{u}^0 \in \boldsymbol{X} \end{aligned} \qquad \text{(ACP-NH)}$$

$$\boldsymbol{u} = \begin{bmatrix} u_1 \\ u_2 \\ u_3 \end{bmatrix}, \boldsymbol{A}(\boldsymbol{u}) = \begin{bmatrix} \mathcal{A}(u_1) \\ \mathcal{A}(u_2) \\ \mathcal{A}(u_3) \end{bmatrix}, \boldsymbol{f}(\boldsymbol{u}) = \begin{bmatrix} f(u_1,u_2) \\ f(u_1,u_2) \\ -f(u_1,u_2), \end{bmatrix}$$

where

$$u_i = \begin{bmatrix} c_i \\ \theta_i \end{bmatrix}, \mathcal{A}\begin{bmatrix} c_i \\ \theta_i \end{bmatrix} = \begin{bmatrix} -\Delta c_i + \mathbf{v}\cdot\nabla c_i \\ -\Delta_\Sigma\theta_i - c^+_{i|_\Sigma}(1-[\theta_i]) - \kappa_i[\theta_i] \end{bmatrix}, f(u_1,u_2) = \begin{bmatrix} 0 \\ -\kappa^{re}[\theta_1][\theta_2] \end{bmatrix}.$$

Since $\mathcal{A}(u_i)$ are m-accretive operators on X (independent of each other), so is $\boldsymbol{A}(\boldsymbol{u})$ the m-accretive operator on $\boldsymbol{X}$. Now we need to use the invariance technique, described e.g. in [3, §4], to obtain viable solution, i.e. the solution stays in some positive invariant set, see below. As we can see, the right-hand-side function $\boldsymbol{f}(\boldsymbol{u})$ does not depend on the third component u_3 (resp. θ_3), therefore, we will treat separately the first two components $u_1 \times u_2$ and the third one u_3. Since the operator

$$\mathcal{A}_{12}\begin{bmatrix} c_1 \\ \theta_1 \\ c_2 \\ \theta_2 \end{bmatrix} = \mathcal{A}_1\begin{bmatrix} c_1 \\ \theta_1 \end{bmatrix} \times \mathcal{A}_2\begin{bmatrix} c_2 \\ \theta_2 \end{bmatrix}$$

is m-accretive as well, let us treat the function $f(u_1, u_2)$ as perturbation C. This leads to the system

$$\begin{aligned} \dot{\boldsymbol{u}}_{12}(t) + (\mathcal{A}_{12} + C)\boldsymbol{u}_{12}(t) &= 0 \\ \boldsymbol{u}_{12}(0) &= u_1^0 \times u_2^0 \in X \times X, \end{aligned} \tag{ACP$_{12}$}$$

where

$$u_{12} = \begin{bmatrix} c_1 \\ \theta_1 \\ c_2 \\ \theta_2 \end{bmatrix} \text{ and } Cu_{12} = \begin{bmatrix} 0 \\ \kappa^{re}\,[\theta_1][\theta_2] \\ 0 \\ \kappa^{re}\,[\theta_1][\theta_2] \end{bmatrix}$$

Is easy to see that C as a continuous and non-decreasing in both variables; moreover, the following holds

$$\begin{aligned} [u_{12} - \tilde{u}_{12}, Cu_{12} - C\tilde{u}_{12}] &= \kappa^{re} \begin{bmatrix} c_1 - \tilde{c}_1, & 0 \\ \theta_1 - \tilde{\theta}_1, & [\theta_1][\theta_2] - [\tilde{\theta}_1][\tilde{\theta}_2] \\ c_2 - \tilde{c}_2, & 0 \\ \theta_2 - \tilde{\theta}_2, & [\theta_1][\theta_2] - [\tilde{\theta}_1][\tilde{\theta}_2] \end{bmatrix} \\ &\overset{\varepsilon \to 0_+}{\sim} \kappa^{re} \int_\Sigma \Big([\theta_1][\theta_2] - [\tilde{\theta}_1][\tilde{\theta}_2] \Big) \Big(s_\varepsilon(\theta_1 - \tilde{\theta}_1) + s_\varepsilon(\theta_2 - \tilde{\theta}_2) \Big) \geq 0. \end{aligned}$$

The last inequality follows from the fact that if $(\theta_1 - \tilde{\theta}_1)$ and $(\theta_2 - \tilde{\theta}_2)$ have different signs, then their sum is 0. If they are positive, the term $([\theta_1][\theta_2] - [\tilde{\theta}_1][\tilde{\theta}_2])$ is non-negative; and, on the other hand, if the they are negative, the term is non-positive.

Therefore, the operator C with $D(C) = X \times X$ is accretive and by [15, Corollary 1.32], we receive an m-accretive operator $\mathcal{A}_{12} + C$. The application of Crandall-Liggett generation theorem (6.3) gives the operator $\mathcal{A}_{12} + C$ as a generator of a strongly continuous semigroup of contractions.

In case of the operator $\mathcal{A}_3$, we have to treat the problem as a quasi-autonomous problem

$$\begin{aligned} \dot{u_3}(t) &= \mathcal{A}_3(u_3(t)) + f_3(t),\ t \in [0, T], \\ u_3(0) &= u_3^0, u_3^0 \in X, \end{aligned} \tag{QA}$$

where operator A_3 is an m-accretive operator.

Moreover, we have the positive invariance set to the problem (ACP$_{12}$), namely

$$M = \{[c_1, \theta_1, c_2, \theta_2] : 0 \leq \theta_1 \leq 1, 0 \leq \theta_2 \leq 1\}.$$

This means that all the solutions with initial values in $gr(K_{A_{12}}), K_{A_{12}} = M \cap \overline{D(A_{12})}$, remain in this set; which is possible due to the fact that resolvent mapping $R_\lambda(\mathcal{A}_{12}) = (I + \lambda\mathcal{A}_{12})^{-1}$ is a non-expansive mapping for $\lambda < 1$; and $Cu \in T_M(u)$ where $T_M(u)$ is the set of subtangential vectors to the set M.

Then the truncation $[\cdot]$ for u_3 is not needed anymore and $\kappa\,[\theta_1][\theta_2] = \kappa\,\theta_1\theta_2$ is bounded, hence, $\theta_1\theta_2 \in L^\infty(\Sigma) \subset L^1(\Sigma)$ and, consequently, $f(t) \in L^1(J; X)$. Moreover, the function

$f : gr(K_A) \to X$ is bounded, locally Lipchitz continuous and by [3, Thm. 4.1] we obtain a unique mild solution of (QA) for any $[c_1^0, \theta_1^0, c_2^0, \theta_2^0] \in M$ and, consequently, a unique mild solution of (ACP-NH) □

Remark 2.2. *In particular, this solution is global-in-time for $u^0 \in K$ where K is a weakly positive invariant set for* (ACP-NH).

Proof. Here we refer to [3, Thm. 6.1] which states that whether there is a solution for all $\alpha \in [0, \infty)$, we can extend the result and receive the global mild solution of (QA), resp. the global mild solution of (ACP-NH). □

3. Weak solution

In this chapter we prove the existence of a weak solution to original (untruncated) problem (1.8). We first introduce an auxiliary system (called semi-truncated system (3.1)). [1] Then we prove the existence of a weak solution to relevant initial and boundary value problem by Galerkin approximations and the energy estimates method. Finally, assuming that the data c_i^0, θ_i^0 and c_i^{in} fulfills the condition $c_i^0 \geq 0$, $\theta_i^0 \in [0,1]$ and $c_i^{in} \geq 0$, which correspond to the physical meaning of the quantities, we show via weak maximum/minimum principles that c_i and θ_i meet these condition in interval of $[0,T] \times \Omega$, resp. $[0,T] \times \Sigma$, as well. These imply that the truncations are in fact inactive and thus the solution of the semi-truncated system (3.1) is either the solution of original problem (1.8).

3.1 The weak formulation

Let us introduce the semi-truncated system: Let $\Omega \subset \mathbb{R}^3$ be bounded domain with Lipschitz boundary $\partial\Omega$ and $T \in [0,\infty)$; we seek for $c_i : [0,T] \times \Omega \to \mathbb{R}$ and $\theta_i : [0,T] \times \Sigma \to \mathbb{R}$, $i = 1,2,3$, such that

$$\partial_t c_i + \mathbf{v} \cdot \nabla c_i - \tfrac{1}{(\mathrm{Pe})_i} \Delta c_i = 0 \text{ in } [0,T] \times \Omega \tag{3.1a}$$

$$-\tfrac{1}{(\mathrm{Pe})_i}(\nabla c_i \cdot \mathbf{n})_{|\Sigma} = c^+_{i|\Sigma}(1 - [\theta_i]) - \kappa_i[\theta_i],\ c_{i|\Gamma_{in}} = c^{in}_{i|\Gamma_{in}},\ (\nabla c_i \cdot \mathbf{n})_{|\Gamma_{out}} = 0 \text{ on } [0,T] \times \partial\Omega \tag{3.1b}$$

$$c_i(0,\cdot) = c_i^0 \text{ on } \Omega \tag{3.1c}$$

$$\partial_t \theta_i - \tfrac{1}{(\mathrm{Pe})^\Sigma_i} \Delta_\Sigma \theta_i + \kappa_i \theta_i = c^+_{i|\Sigma}(1 - [\theta_i]) + \kappa^{re}_i [\theta_1][\theta_2] \text{ on } [0,T] \times \Sigma \tag{3.1d}$$

$$\nabla_\Sigma \theta_i \cdot \mathbf{n}^\Sigma = 0 \text{ on } [0,T] \times \partial\Sigma \tag{3.1e}$$

$$\theta_i(0,\cdot) = \theta_i^0 \text{ on } \Sigma, \tag{3.1f}$$

where given (time-independent) data $\mathbf{v}, c_i^0, \theta_i^0, c_i^{in}$ meet the following conditions

$$\mathbf{v} \in \mathbf{V}, c_i^0 \in L^2(\Omega), \theta_i^0 \in L^2(\Sigma), c_i^{in} \in W^{1,2}(\Omega) \ \text{ and } \ c_i^{in} \geq 0, c_i^0 \geq 0 \tag{3.2}$$

and constant coefficients satisfy

$$-\kappa_1^{re} = -\kappa_2^{re} = \kappa^{re} = \kappa_3^{re}, \ \ (\mathrm{Pe})_i, (\mathrm{Pe})_i^\Sigma, \kappa_i, \kappa^{re} > 0, \ i = 1,2,3. \tag{3.3}$$

Note 3.1. *Let us mention that in case of weak solution and consequent numerical computations, we always consider (uncurved) flat geometry, see figure* (4.3a)*, where all considered parts of the boundary $\partial\Omega$, resp. Σ, are parts of lines. Therefore the operators $\Delta_\Sigma, \nabla_\Sigma$ become standard Laplace Δ_{2D} and gradient ∇_{2D} operators defined on two dimensional bounded set.*

[1] Note that this semi-truncated system is different from (1.9) in terms $\kappa_i\theta_i$ in the equation (3.1d).

Treating the system with mixed boundary conditions, we standardly implicitly built-in the Neumann conditions into weak formulation. On the other hand, the implementation of (stationary) Dirichlet conditions is done by decomposition of the functions $c_i, i = 1, 2, 3$, into time-dependent homogeneous and time-independent non-homogeneous (non-negative) part where the later one satisfies the boundary condition, namely

$$c_i(t;x) = c_i^h(t;x) + c_i^{in}(x),\ c^h_{i|_{\Gamma_{in}}} = 0,\ c^{in}_{i|_{\Gamma_{in}}} = c_{i|_{\Gamma_{in}}} \text{ and } c_i^{in} = c_i^{in+}. \tag{3.4}$$

Denoting $W^{1,2}_{\Gamma_{in}} := \{v \in W^{1,2}(\Omega) : v_{|_{\Gamma_{in}}} = 0\}$ [2] and the dual spaces $W^{-1,2}(\Omega)) = \left(W^{1,2}_{\Gamma_{in}}(\Omega))\right)^*$ and $W^{-1,2}(\Sigma)) = (W^{1,2}(\Sigma)))^*$, we introduce the searching spaces $\mathcal{V}$ and $\mathcal{W}$ as follows

$$\begin{aligned}
\mathcal{V} &= \left\{L^2([0,T]; W^{1,2}_{\Gamma_{in}}(\Omega)) \cap L^\infty([0,T]; L^2(\Omega)), \partial_t c \in L^2([0,T]; W^{-1,2}(\Omega))\right\} \\
\mathcal{W} &= \left\{L^2([0,T]; W^{1,2}(\Sigma)) \cap L^\infty([0,T]; L^2(\Sigma)), \partial_t \theta \in L^2([0,T]; W^{-1,2}(\Sigma))\right\}.
\end{aligned}$$

Note that we already have the embeddings into time-continuous functions, namely $\mathcal{V} \hookrightarrow C([0,T]; L^2(\Omega))$ and $\mathcal{W} \hookrightarrow C([0,T]; L^2(\Sigma))$.

Using the decomposition (3.4) we can rewrite system (3.1a) multiplied by a test function $v \in W^{1,2}_{\Gamma_{in}}(\Omega)$ as

$$\begin{aligned}
&\int_\Omega \partial_t c_i^h\, v - \tfrac{1}{(\mathrm{Pe})_i} \int_\Omega \Delta c_i^h\, v + \int_\Omega \mathbf{v} \cdot \nabla c_i^h\, v \\
&\quad \overset{Gr}{=} \int_\Omega \partial_t c_i^h\, v + \tfrac{1}{(\mathrm{Pe})_i} \int_\Omega \nabla c_i^h \cdot \nabla v - \tfrac{1}{(\mathrm{Pe})_i} \int_{\partial\Omega} (\nabla c_i^h \cdot \mathbf{n}) v + \int_\Omega (\mathbf{v} \cdot \nabla c_i^h) v \\
&\quad \overset{BC}{=} \int_\Omega \partial_t c_i^h\, v + \int_\Omega \tfrac{1}{(\mathrm{Pe})_i} \nabla c_i^h \cdot \nabla v + \mathbf{v} \cdot \nabla c_i^h\, v + \int_\Sigma \left(c^{h+}_{i|_\Sigma}(1 - [\theta_i]) - (\kappa_i + c^{in}_{i|_\Sigma})\,[\theta_i] \right) v = \\
&\quad = -\int_\Omega \tfrac{1}{(\mathrm{Pe})_i} \nabla c_i^{in} \cdot \nabla v + \mathbf{v} \cdot \nabla c_i^{in}\, v - \int_\Sigma c^{in}_{i|_\Sigma}\, v.
\end{aligned}$$

In case of the equation (3.1d) we proceed analogously.

Note 3.2. *Let us mention that we can not generally ensure the relation* $(c_i^h + c_i^{in})^+ = c_i^{h+} + c_i^{in+}$ *even for non-negative function* c_i^{in} *but, since we prove the non-negativity of* c_i^h *as a weak solution of* (3.7) *(see below Theorem* (3.5)*), we obtain even better result* $(c_i^h + c_i^{in})^+ = c_i^h + c_i^{in}$. *Note that together with boundedness of* θ_i *the system* (3.7) *coincides with the system* (1.8) *in a weak sense.*

As in the standard concept with non-homogeneous Dirichlet condition, we suppress the index $(\cdot)^h$ in following lines. The weak formulation of the system (3.1) consequently states:

[2] This definition is suitable for domains with Lipschitz boundary. In more general case we would prefer the definition $W^{1,2}_{\Gamma_{in}} := \overline{C^\infty_{\Gamma_{in}}(\Omega)}^{\|\cdot\|_{W^{k,p}(\Omega)}}$ where $C^\infty_{\Gamma_{in}}(\Omega) = \{v \in C^\infty(\overline{\Omega}) : v_{|_{\Gamma_{in}}} = 0\}$.

We search for $\{[c_1,\theta_1],[c_2,\theta_2],[c_3,\theta_3]\} \in [\mathcal{V}\times\mathcal{W}]^3$ such that for any $v \in W^{1,2}_{\Gamma_{in}}(\Omega)$, $w \in W^{1,2}(\Sigma)$ and a.e. $t \in [0,T]$ the following holds

$$\int_\Omega \partial_t c_i\, v + \int_\Omega \tfrac{1}{(\mathrm{Pe})_i}\nabla c_i\cdot\nabla v + \mathbf{v}\cdot\nabla c\, v + \int_\Sigma \Big(c^+_{i|_\Sigma}(1-[\theta_i]) - (c^{in}_{i|_\Sigma}+\kappa_i)[\theta_i]\Big)\, v \tag{3.6a}$$
$$= -\int_\Omega \tfrac{1}{(\mathrm{Pe})_i}\nabla c^{in}_i\cdot\nabla v + \mathbf{v}\cdot\nabla c^{in}_i\, v - \int_\Sigma c^{in}_{i|_\Sigma}\, v$$

$$\int_\Sigma \partial_t\theta_i w + \int_\Sigma \tfrac{1}{(\mathrm{Pe})^\Sigma_i}\nabla_\Sigma\theta_i\cdot\nabla_\Sigma w + (\kappa_i + c^{in}_{i|_\Sigma})\theta_i w - \int_\Sigma\Big(c^+_{i|_\Sigma}(1-[\theta_i]) + \kappa^{re}_i[\theta_1][\theta_2]\Big)w = \int_\Sigma c^{in}_{i|_\Sigma}\, w, \tag{3.6b}$$

where the given data $\mathbf{v}, c^0_i(\cdot) = c_i(0,\cdot), \theta^0_i(\cdot) = \theta_i(0,\cdot), c^{in}_i, i = 1,2,3$, meet the conditions (3.2).

This system can be equivalently written using symbolical formulation with the forms B_Ω, B_Σ as

$$\langle \partial_t c_i(t), v\rangle_\Omega + B_\Omega[c_i,\theta_i,v] = \langle f_{c_i}, v\rangle,\ \forall v \in W^{1,2}_{\Gamma_{in}}(\Omega), a.e.\ t\in[0,T], \tag{3.7a}$$
$$\langle \partial_t \theta_i(t), w\rangle_\Sigma + B_\Sigma[c_i,\theta_i,v,\theta_1,\theta_2] = \langle f_{\theta_i}, w\rangle,\ \forall w \in W^{1,2}(\Sigma), a.e.\ t\in[0,T], \tag{3.7b}$$

where $T \in [0,\infty)$ and

$$B_\Omega[c_i,\theta_i,v] = \overbrace{\int_\Omega \tfrac{1}{(\mathrm{Pe})_i}\nabla c_i\cdot\nabla v + \mathbf{v}\cdot\nabla c_i\, v}^{B^L_\Omega[c_i,v]} + \int_\Sigma \Big(c^+_{i|_\Sigma}(1-[\theta_i]) - (c^{in}_{i|_\Sigma}+\kappa_i)[\theta_i]\Big)\, v$$
$$B_\Sigma[c_i,\theta_i,w,\theta_1,\theta_2] = \overbrace{\int_\Sigma \tfrac{1}{(\mathrm{Pe})_i}\nabla\theta_i\cdot\nabla w + (c^{in}_{i|_\Sigma}+\kappa_i)\theta_i\, w}^{B^L_\Sigma[\theta_i,w]} - \Big(c^+_{i|_\Sigma}(1-[\theta_i]) + \kappa^{re}_i[\theta_1][\theta_2]\Big)\, w$$
$$\langle f_{c_i}, v\rangle = -\int_\Omega \tfrac{1}{(\mathrm{Pe})_i}\nabla c^{in}_i\cdot\nabla v + \mathbf{v}\cdot\nabla c^{in}_i\, v - \int_\Sigma c^{in}_{i|_\Sigma}\, v$$
$$\langle f_{\theta_i}, w\rangle = (f_{\theta_i}, w)_\Sigma = \int_\Sigma c^{in}_{i|_\Sigma}\, w$$

for $\kappa^{re}_1 = \kappa^{re}_2 = -\kappa^{re} = -\kappa^{re}_3$. Symbols $B^L_\Omega[c_i,v]$ and $B^L_\Sigma[\theta_i,w]$ denote the corresponding bi-linear parts of B_Ω and B_Σ; $(\cdot,\cdot)$ denotes the scalar product, namely $(f,g)_\Omega = \int_\Omega f\, g\, dx$, $(f,g)_\Sigma = \int_\Sigma f\, g\, ds$; and $f_{c_i} \in W^{-1,2}(\Omega)$.

Definition. *We say that functions $c_i \in \mathcal{V} \hookrightarrow C([0,T];L^2(\Omega))$, $\theta_i \in \mathcal{W} \hookrightarrow C([0,T];L^2(\Sigma))$, $i = 1,2,3$, are weak solutions of the parabolic initial-boundary problem (3.1) iff*

(i) the relations (3.7) hold for all $w \in W^{1,2}_{\Gamma_{in}}(\Omega)$ and $v \in W^{1,2}(\Sigma)$ and a.e. $t \in [0,T]$.

(ii) c_i, θ_i meet the initial conditions

$$c_i(0) = c^0_i$$
$$\theta_i(0) = \theta^0_i.$$

3.2 Galerkin approximation

For the purpose of finding a weak solution of (3.1), we use a Galerkin approximation method - see also [12, §7.1.2] for linear case. Recalling that $W^{1,2}_{\Gamma_{in}}(\Omega) \hookrightarrow L^2(\Omega)$, $W^{1,2}(\Sigma) \hookrightarrow L^2(\Sigma)$ are separable Hilbert spaces and referring to following eigenvalue problems

$$\begin{aligned} -\Delta v &= \lambda v \text{ in } \Omega \\ v &= 0 \text{ on } \Gamma_{in} \\ \frac{\partial v}{\partial \mathbf{n}} &= 0 \text{ on } \partial\Omega \setminus \Gamma_{in} \end{aligned} \qquad \text{and} \qquad \begin{aligned} -\Delta w + w &= \lambda w \text{ in } \Sigma \\ \frac{\partial w}{\partial \mathbf{n}^\Sigma} &= 0 \text{ on } \partial\Sigma, \end{aligned}$$

we can construct orthonormal bases $\{v^k\}_{k=1}^\infty$ and $\{w^k\}_{k=1}^\infty$ in $W^{1,2}_{\Gamma_{in}}(\Omega)$ and $W^{1,2}(\Sigma)$ that are, in addition, orthogonal in $L^2(\Omega)$ and $L^2(\Sigma)$. Let us denote the corresponding projector operators as $P^m_\Omega : W^{1,2}_{\Gamma_{in}}(\Omega) \to \{v^1, \dots, v^m\}$ and $P^m_\Sigma : W^{1,2}(\Sigma) \to \{w^1, \dots, w^m\}$. For more details we refer to [23].

The first step is to build the finite-dimensional approximation. We seek for the functions $c^m_i : [0,T] \to W^{1,2}_{\Gamma_{in}}(\Omega)$ and $\theta^m_i : [0,T] \to W^{1,2}(\Sigma), i = 1,2,3$, of the form

$$c^m_i(t;x) = \sum_{k=1}^m d^m_{c_i,k}(t) v^k(x), \ x \in \Omega \tag{3.8a}$$

$$\theta^m_i(t;x) = \sum_{k=1}^m d^m_{\theta_i,k}(t) w^k(x), \ x \in \Sigma \tag{3.8b}$$

solving the weak finite-dimensional problem

$$\left((c^m_i(t))', v^k\right)_\Omega + B_\Omega[c^m_i, \theta^m_i, v^k] = \langle f_{c_i}, v^k \rangle, \ \forall k = 1, \dots, m \tag{3.9a}$$

$$\left((\theta^m_i(t))', w^k\right)_\Sigma + B_\Sigma[c^m_i, \theta^m_i, w^k, \theta_1, \theta_2] = \langle f_{\theta_i}, w^k \rangle, \ \forall k = 1, \dots, m \tag{3.9b}$$

where the coefficients $d^m_{c_i,k}$ and $d_{\theta_i,k}$ satisfy the initial conditions

$$d^m_{c_i,k}(0) = (c^0_i, v^k)_\Omega \tag{3.10a}$$

$$d^m_{\theta_i,k}(0) = (\theta^0_i, w^k)_\Sigma. \tag{3.10b}$$

Theorem 3.1. *The finite-dimensional system* (3.9) *with operators* B_Ω, B_Σ *and functions* f_{c_i}, f_{θ_i} *defined as above has for each integer* $m = 1, 2, \dots$ *a set of solutions* $\{c^m_1, \theta^m_1, \dots, c^m_3, \theta^m_3\}$ *of the form* (3.8) *and satisfying the initial conditions* (3.10).

Proof. Note that

$$\left((c^m_i(t))', v^k\right)_\Omega = \left(d^m_{c_i,k}(t)\right)' \tag{3.11a}$$

$$\left((\theta^m_i(t))', w^k\right)_\Sigma = \left(d^m_{\theta_i,k}(t)\right)'. \tag{3.11b}$$

This system is a system of first order differential equations in the form $\boldsymbol{y}' = \boldsymbol{f}(\boldsymbol{y})$ with continuous function $\boldsymbol{f}$, where $\boldsymbol{y} = (\boldsymbol{d}^m_{c_1}, \boldsymbol{d}^m_{\theta_1}, .., \boldsymbol{d}^m_{c_3}, \boldsymbol{d}^m_{\theta_3})^T$ with $\boldsymbol{d}^m_{c_i} = (\boldsymbol{d}^m_{c_i,1}, .., \boldsymbol{d}^m_{c_i,m})^T$ and $\boldsymbol{d}^m_{\theta_i} = (\boldsymbol{d}^m_{\theta_i,1}, .., \boldsymbol{d}^m_{\theta_i,m})^T$. According to Peano existence theorem [28] the system (3.9) posses a solution. □

3.3 Energy estimates

In order to let m to infinity and take the limit from finite-dimensional problem (3.9) to original problem (3.7), we need the energy estimates, respectively the convenient bounds for the sequences $\{c_i^m\}, \{(c_i^m)'\}$ and $\{\theta_i^m\}, \{(\theta_i^m)'\}$ for $i = 1, 2, 3$ and all $m = 1, 2, \dots$.

Theorem 3.2. *There exists constants C_1, C_2 depending on Ω and Σ only such that*

$$\begin{aligned}\|c_i^m\|_{L^\infty([0,T];L^2(\Omega))} + \|c_i^m\|_{L^2([0,T];W^{1,2}_{\Gamma_{in}}(\Omega))} + \|(c_i^m)'\|_{L^2([0,T];W^{-1,2}(\Omega))} \\ \leq C_1 \left(\|f_{c_i}\|_{W^{-1,2}(\Omega)} + \|c_i^0\|_{L^2(\Omega)}\right) + C_2\end{aligned}$$

for $i = 1, 2, 3$ and all $m = 1, 2, \dots$.

Proof. 1. In this proof we more or less follow the standard concept for linear parabolic equations (cf. [12, §7.1.2]) but, in addition, we employ the nonlinearities. Multiplying the relations (3.9a) by $d^m_{c_i,k}$ and sum for $k = 1, \dots, m$, we obtain the relations

$$((c_i^m)', c_i^m)_\Omega + B_\Omega[c_i^m, \theta_i^m, c_i^m] = \langle f_{c_i}, c_i^m \rangle. \tag{3.12}$$

for $i = 1, 2, 3$. Using the incompressibility of the velocity field and Green theorem we have

$$\int_\Omega \mathbf{v} \cdot \nabla c_i^m \, c_i^m \, dx = \int_\Omega \mathbf{v} \cdot \nabla \left(\frac{|c_i^m|^2}{2} \right) dx = \int_\Omega \operatorname{div} \left(\mathbf{v} \, \frac{|c_i^m|^2}{2} \right) dx = \int_{\partial\Omega} (\mathbf{v} \cdot \mathbf{n}) \, \frac{|c_i^m|^2}{2} \, ds,$$

and, consequently, the relation (3.12) turns to

$$\frac{1}{2}\frac{d}{dt}\|c_i^m\|^2_{L^2(\Omega)} + \tfrac{1}{(\mathrm{Pe})_i}\|\nabla c_i^m\|^2_{L^2(\Omega)} + \int_{\partial\Omega} (\mathbf{v}\cdot\mathbf{n}) \frac{|c_i^m|^2}{2} \, ds - \int_{\partial\Omega} (\nabla c_i^m \cdot \mathbf{n}) \, c_i^m \, ds = \langle f_{c_i}, c_i^m \rangle. \tag{3.13}$$

Now we recall $\partial\Omega = \overline{\Sigma \cup \Gamma_{in} \cup \Gamma_{out}}$ and the boundary conditions

$$(\mathbf{v}\cdot\mathbf{n})_{|\partial\Omega} = \begin{cases} 0 & \text{on } \Sigma, \\ \geq 0 & \text{on } \Gamma_{out}, \end{cases} \quad -\tfrac{1}{(\mathrm{Pe})_i}((\nabla c_i \cdot \mathbf{n}) \, c)_{|\partial\Omega} = \begin{cases} \left(c^+_{i|_\Sigma}(1 - [\theta_i]) - \kappa_i[\theta_i] \right) c_{i|_\Sigma} & \text{on } \Sigma, \\ 0 & \text{on } \Gamma_{out}. \end{cases}$$

Note and the condition $c_{i|_{\Gamma_{in}}} = 0$ is already built in $W^{1,2}_{\Gamma_{in}}(\Omega)$. Using Schwarz's and Cauchy's ε-inequality [3] - cf. [12, §B.2] - we obtain

$$|(f_{c_i}, c_i^m)_\Omega| \leq \|f_{c_i} c_i^m\|_{L^1(\Omega)} \leq \|f_{c_i}\|_{W^{-1,2}(\Omega)} \|c_i^m\|_{L^2(\Omega)} \leq \frac{1}{4\varepsilon}\|f_{c_i}\|^2_{W^{-1,2}(\Omega)} + \varepsilon \|c_i^m\|^2_{L^2(\Omega)}$$

for any $\varepsilon > 0$. Together with (3.13) and the boundary conditions above we receive the following

$$\begin{aligned}\frac{1}{2}\frac{d}{dt}\|c_i^m\|^2_{L^2(\Omega)} + \tfrac{1}{(\mathrm{Pe})_i}\|\nabla c_i^m\|^2_{L^2(\Omega)} + \int_\Sigma \left(c_i^{m+}(1 - [\theta_i^m]) - (c^{in}_{i|_\Sigma} + \kappa_i)[\theta_i^m] \right) c_i^m \, ds \\ \leq C_1 \|c_i^m\|^2_{L^2(\Omega)} + C_2 \|f_{c_i}\|^2_{W^{-1,2}(\Omega)}\end{aligned} \tag{3.14}$$

[3] In most of the cases we can, equivalently, use Hölder's and Young's inequality.

for C_1, C_2 appropriate constants. [4]

Simultaneously, using the fact that $c_i^{m+}c_i^m = \left(c_i^{m+}\right)^2 \geq 0 \Rightarrow c_i^{m+}(1-[\theta_i^m])c_i^m \geq 0$, we can neglect this term as a positive term on the left side of inequality (3.14). Furthermore

$$\int_\Sigma |c_i^m| ds \leq K\|c_i^m\|_{L^2(\Sigma)} \leq \tilde{K}\|c_i^m\|_{W^{\frac{1}{2},2}(\Omega)} \leq C_1\|c_i^m\|^2_{L^2(\Omega)} + \tfrac{1}{2(\mathrm{Pe})_i}\|\nabla c_i^m\|^2_{L^2(\Omega)}, \tag{3.15}$$

where we have used the interpolation inequality (cf. [8]) and Chauchy ε-inequality [5] which allows us to obtain the coefficient $\frac{1}{2(\mathrm{Pe})_i}$. This is sufficient to obtain from (3.14) the estimates

$$\frac{d}{dt}\|c_i^m\|^2_{L^2(\Omega)} \leq \frac{d}{dt}\|c_i^m\|^2_{L^2(\Omega)} + C\|\nabla c_i^m\|^2_{L^2(\Omega)} \leq C_1\|c_i^m\|^2_{L^2(\Omega)} + C_2\|f_{c_i}\|^2_{W^{-1,2}(\Omega)} \tag{3.16}$$

for $i = 1, 2, 3$ and positive constants C, C_1, C_2.

2. Denoting

$$\eta_i(t) := \|c_i^m(t)\|^2_{L^2(U)}$$

the inequality (3.16) can be written as

$$\eta_i(t) \leq C_1\eta_i(t) + C_1\|f_{c_i}\|^2_{W^{-1,2}(\Omega)}.$$

Using the Gronwall's inequality [12, §B.2], we obtain the estimate

$$\eta_i(t) \leq e_i^{C_1 t}\left(\eta_i(0) + C_1 t\|f_{c_i}\|^2_{W^{-1,2}(\Omega)}\right)$$

and, with the fact that $\eta_i(0) = \|c_i^m(0)\|^2_{L^2(\Omega)} \overset{(3.10)}{\leq} \|c_i^0\|^2_{L^2(\Omega)}$, we receive the relation

$$\max_{t\in[0,T]}\|c_i^m\|_{L^2(\Omega)} \leq C\left(\|c_i^0\|^2_{L^2(\Omega)} + \|f_{c_i}\|^2_{W^{-1,2}(\Omega)}\right). \tag{3.17}$$

Recalling the inequality (3.16), integrate over the time and using the inequality above we end up with the estimate

$$\|c_i^m\|^2_{L^2([0,T];W^{1,2}_{\Gamma_{in}})} = \int_0^T \|c_i^m\|^2_{W^{1,2}_{\Gamma_{in}}}\, dt \leq C\left(\|c_i^0\|^2_{L^2(\Omega)} + \|f_{c_i}\|^2_{W^{-1,2}(\Omega)}\right). \tag{3.18}$$

[4] For simplicity of writing we sometimes use constants C, C_1, C_2, C_3, K which can eventually vary from relation to relation.

[5] Other possible way is using a Chauchy ε-inequality only which gives the result with additional constant.

3. In order to obtain the estimates on the time-derivative of c_i^m, we take any $u \in W^{1,2}_{\Gamma_{in}}$ with $\|u\|_{W^{1,2}_{\Gamma_{in}}} \leq 1$ and consider the projection P^m_Ω onto m-dimensional space $V_i^m = span\{v^l\}_{l=1}^m$. Note that $(c_i^m)'$ is either element of V_i^m. Then

$$\langle \partial_t c_i^m, u\rangle_\Omega = ((c_i^m)', u)_\Omega = ((c_i^m)', P^m_\Omega(u))_\Omega \overset{(3.9)}{=} \langle f_{c_i}, P^m_\Omega(u)\rangle - B_\Omega[c_i^m, \theta_i^m, P^m_\Omega(u)].$$

Using the fact that also $\|P^m_\Omega(u)\|_{W^{1,2}(\Omega)} \leq 1$, we have $|\langle f_{c_i}, P^m_\Omega(u)\rangle| \leq \|f_{c_i}\|_{W^{-1,2}(\Omega)}$ and

$$|B_\Omega[c_i^m, \theta_i^m, P^m_\Omega(u)]| \leq \|\mathbf{v}\|_{L^\infty(\Omega)}\|c_i\|_{W^{1,2}_{\Gamma_{in}}(\Omega)} + C_1\|c_i\|_{W^{1,2}_{\Gamma_{in}}(\Omega)} + C_2.$$

Furthermore

$$|\langle (c_i^m)', u\rangle_\Omega| \leq C_1\left(\|f_{c_i}\|_{W^{-1,2}(\Omega)} + \|c_i^m\|_{W^{1,2}_{\Gamma_{in}}(\Omega)}\right) + C_2$$

and, since u is arbitrary with $\|u\|_{W^{1,2}_{\Gamma_{in}}} \leq 1$, we finally obtain the estimate

$$\begin{aligned}\|(c_i^m)'\|_{L^2([0,T];W^{-1,2}(\Omega))} &\leq C_1\left(\|f_{c_i}\|^2_{W^{-1,2}(\Omega)} + \|c_i^m\|^2_{L^2([0,T];W^{1,2}_{\Gamma_{in}}(\Omega))}\right) + C_2\\ &\overset{(3.18)}{\leq} C_1\left(\|f_{c_i}\|^2_{W^{-1,2}(\Omega)} + \|c_i^0\|_{L^2(\Omega)}\right) + C_2\end{aligned}$$

for $i = 1, 2, 3$. □

Theorem 3.3. *There exists constants C_1, C_2 depending on Ω and Σ only, such that for $i = 1, 2, 3$ the following estimates hold*

$$\begin{aligned}\|\theta_i^m\|_{L^\infty([0,T];L^2(\Sigma))} + \|\theta_i^m\|_{L^2(W^{1,2}(\Sigma))} + \|(\theta_i^m)'\|_{L^2(W^{-1,2}(\Sigma))}&\\ \leq C_1\left(\|f_{c_i}\|_{W^{-1,2}(\Omega)} + \|f_{\theta_i}\|_{L^2(\Sigma)} + \|c_i^0\|_{L^2(\Omega)} + \|\theta_i^0\|_{L^2(\Omega)}\right) + C_2&\end{aligned}$$

for all $m = 1, 2, \ldots$

Proof. 1. Analogously to relation (3.12) in previous proof, we obtain

$$((\theta_i^m)', \theta_i^m)_\Sigma + B_\Sigma[c_i^m, \theta_i^m, \theta_i^m, \theta_1^m, \theta_2^m] = \langle f_{\theta_i}, w\rangle, \tag{3.19}$$

respectively

$$\begin{aligned}\frac{1}{2}\frac{d}{dt}\|\theta_i^m\|^2_{L^2(\Sigma)} + \tfrac{1}{(\mathrm{Pe})_i^\Sigma}\|\nabla\theta_i^m\|^2_{L^2(\Sigma)} + \left((c^{in}_{i|_\Sigma} + \kappa_i)\theta_i^m,\, \theta_i^m\right)_\Sigma&\\ = \int_\Sigma \left(c_i^{m+}(1 - [\theta_i^m]) + \kappa_i^{re}[\theta_1^m][\theta_2^m]\right)\, \theta_i^m\, ds + (f_{\theta_i}, \theta_i^m)_\Sigma&\end{aligned} \tag{3.20}$$

for $i = 1, 2, 3$. Note that

$$\left((c^{in}_{i|_\Sigma} + \kappa_i)\theta_i^m,\, \theta_i^m\right)_\Sigma \geq \kappa_i\|\theta_i^m\|^2_{L^2(\Sigma)}.$$

Here we distinguish between the situation for $\theta_i, i = 1, 2$ and θ_3.

2. Now use the fact that $[\theta_i]\theta_i \geq [\theta_i]^2 \geq 0$ and right-hand side of relation (3.20) for $i = 1, 2$ follows as

$$\begin{aligned}
&\int_\Sigma c_i^{m+}\theta_i^m - \underbrace{c_i^{m+}[\theta_i^m]\theta_i^m}_{\geq 0} - \underbrace{\kappa^{re}[\theta_1^m][\theta_2^m]\theta_i^m}_{\geq 0}\, ds \\
&\leq \int_\Sigma c_i^{m+}\theta_i^m\, ds \leq \int_\Sigma |c_i^m\theta_i^m|\, ds \leq \|c_i^m\|_{L^2(\Sigma)}\|\theta_i^m\|_{L^2(\Sigma)} \leq C\|c_i^m\|_{W^{1,2}_{\Gamma_{in}}(\Omega)}\|\theta_i^m\|_{L^2(\Sigma)} \\
&\leq C_1\|\theta_i^m\|^2_{L^2(\Sigma)} + C_2\|c_i^m\|^2_{W^{1,2}_{\Gamma_{in}}(\Omega)}. \qquad (3.21)
\end{aligned}$$

for appropriate C_1, C_2.

In the case of $i = 3$ is the reaction term with opposite sign and, therefore, we need to use Schwarz's and Cauchy's ε-inequality also there, namely

$$\int_\Sigma \kappa^{re}[\theta_1^m][\theta_2^m]\theta_3^m\, ds \leq \|\kappa^{re}\theta_3\|_{L^1(\Sigma)} \leq \|\kappa^{re}\|_{L^2(\Sigma)}\|\theta_3\|_{L^2(\Sigma)} \leq C_1 + \mathcal{C}_2\|\theta_3\|^2_{L^2(\Sigma)}$$

for appropriate C_1, C_2.

3. Considering all $i = 1, 2, 3$ we can write the obtained estimates in following way

$$\frac{d}{dt}\|\theta_i^m\|^2_{L^2(\Sigma)} \leq \frac{d}{dt}\|\theta_i^m\|^2_{L^2(\Sigma)} + \tfrac{1}{(\mathrm{Pe})_i^\Sigma}\|\theta_i^m\|^2_{W^{1,2}(\Sigma)} \leq C_1\|\theta_i^m\|^2_{L^2(\Sigma)} + C_2\|c_i^m\|^2_{W^{1,2}_{\Gamma_{in}}(\Omega)} + C_3. \quad (3.22)$$

From Theorem 3.2 we already have $c_i^m \in L^2([0,T]; W^{1,2}_{\Gamma_{in}}(\Omega)), i = 1.2.3$ and using the Gronwall's lemma we end up with the estimates

$$\max_{t\in[0,T]} \|\theta_i^m\|_{L^2(\Sigma)} \leq C_1\left(\|f_{\theta_i}\|_{L^2(\Sigma)} + \|\theta_i^0\|_{L^2(\Omega)} + \|c_i^m\|_{L^2([0,T];W^{1,2}_{\Gamma_{in}}(\Omega))}\right) + C_2.$$

Integrate relation (3.22) and (3.18) over the time and apply the inequality above. Then we receive the estimate

$$\begin{aligned}
\|\theta_i^m\|^2_{L^2([0,T];W^{1,2}(\Sigma))} &\leq C_1\left(\|f_{\theta_i}\|_{L^2(\Sigma)} + \|\theta_i^0\|^2_{L^2(\Omega)} + \|c_i^m\|^2_{L^2([0,T];W^{1,2}_{\Gamma_{in}}(\Omega))}\right) + C_2 \\
&\leq C_1\left(\|f_{\theta_i}\|_{L^2(\Sigma)} + \|f_{c_i}\|_{W^{-1,2}(\Omega)} + \|c_i^0\|_{L^2(\Omega)} + \|\theta_i^0\|^2_{L^2(\Omega)}\right) + C_2.
\end{aligned}$$

Further considerations again follow the technique in the proof of the Theorem 3.2 (§3.) and in the end we obtain the relation

$$\begin{aligned}
&\|\theta_i^m\|^2_{L^\infty([0,T];L^2(\Sigma))} + \|\theta_i^m\|^2_{L^2(W^{1,2}(\Sigma))} + \|(\theta_i^m)'\|^2_{L^2(W^{-1,2}(\Sigma))} \\
&\qquad \leq C_1\left(\|f_{\theta_i}\|_{L^2(\Sigma)} + \|f_{c_i}\|_{W^{-1,2}(\Omega)} + \|c_i^0\|_{L^2(\Omega)} + \|\theta_i^0\|_{L^2(\Omega)}\right) + C_2 \qquad (3.23)
\end{aligned}$$

for arbitrary $m \in \mathbb{N}$ and $i = 1, 2, 3$. □

3.4 Existence of a weak solution

Having the energy estimates from Theorem 3.2 and Theorem 3.3, we can pass to limits as $m \to \infty$ to obtain a weak solution of the problem (3.7).

Theorem 3.4. *There is a weak solution* $\{c_1, \theta_1, \dots, c_3, \theta_3\}$ *to the problem* (3.7).

Proof. 1. The previous theorems gives us the boundedness of the sequences c_i^m in $L^2([0,T]; W^{1,2}_{\Gamma_{in}}(\Omega))$ and θ_i^m in $L^2([0,T]; W^{1,2}(\Sigma)))$ and also $(c_i^m)'$ in $L^2([0,T]; W^{-1,2}(\Omega))$ and $(\theta_i^m)'$ in $L^2([0,T]; W^{-1,2}(\Sigma))$. All these spaces are reflexive and therefore we can choose a weakly-convergent subsequence, schematically

$$c_i^{m_k} \overset{w}{\to} c_i \text{ in } L^2([0,T]; W^{1,2}_{\Gamma_{in}}(\Omega)) \tag{3.24a}$$
$$(c_i^{m_k})' \overset{w}{\to} c_i' \text{ in } L^2([0,T]; W^{-1,2}(\Omega)) \tag{3.24b}$$
$$\theta_i^{m_k} \overset{w}{\to} \theta_i \text{ in } L^2([0,T]; W^{1,2}(\Sigma)) \tag{3.24c}$$
$$(\theta_i^{m_k})' \overset{w}{\to} \theta_i' \text{ in } L^2([0,T]; W^{-1,2}(\Sigma)). \tag{3.24d}$$

Recalling the searching spaces for c_i, θ_i in sequence as

$$\mathcal{V} = \left\{ L^2(W^{1,2}_{\Gamma_{in}}([0,T];\Omega)) \cap L^\infty([0,T]; L^2(\Omega)), \partial_t c \in L^2([0,T]; W^{-1,2}(\Sigma)) \right\}$$
$$\mathcal{W} = \left\{ L^2(W^{1,2}([0,T];\Sigma)) \cap L^\infty(L^2([0,T];\Sigma)), \partial_t \theta \in L^2([0,T]; W^{-1,2}(\Sigma)) \right\},$$

we obtain by Aubin-Lions theorem (cf. [20, §1.5]) and generalized trace theorem for Bochner spaces (cf. [16, lemma 1.12]) the following embeddings

$$\mathcal{V} \overset{c}{\hookrightarrow} L^2([0,T]; W^{\frac{1}{2},2}(\Omega)) \hookrightarrow L^2([0,T]; L^2(\Sigma)) \tag{3.25a}$$
$$\mathcal{W} \overset{c}{\hookrightarrow} L^2([0,T]; L^2(\Sigma)). \tag{3.25b}$$

Which mean that both sequences $\{c_i^m\}_{m=1}^\infty, \{\theta_i^m\}_{m=1}^\infty$ converge in $L^2([0,T]; L^2(\Sigma))$ even strongly.

2. The next step is to choose a convenient dense subset [6] of $L^2([0,T]; W^{1,2}_{\Gamma_{in}}(\Omega))$, respectively $L^2([0,T]; W^{1,2}(\Sigma))$. Fixing an integer N, we choose arbitrary functions $\varphi \in C^1([0,T]; W^{1,2}_{\Gamma_{in}}(\Omega))$, $\psi \in C^1([0,T]; W^{1,2}(\Sigma))$ having the form

$$\varphi(t;x) = \sum_{k=1}^{N} d_w^k(t) v^k(x) \tag{3.26a}$$
$$\psi(t;x) = \sum_{k=1}^{N} d_v^k(t) w^k(x), \tag{3.26b}$$

[6] Note that the density of the set already implies the validity for all $\varphi \in L^2([0,T]; W^{1,2}_{\Gamma_{in}}(\Omega))$, $\psi \in L^2([0,T]; W^{1,2}(\Sigma))$.

where $\{d_w^k\}_{k=1}^N, \{d_v^k\}_{k=1}^N$ are given $C^1([0,T])$ functions. Taking $m \geq N$ and making similar construction as in Theorem 3.1, i.e. we multiply (3.9) by d_w^k, d_v^k, sum for $k = 1, \ldots, N$ and integrate with respect to time, we obtain

$$\int_0^T \langle (c_i^m)', \varphi \rangle_\Omega + B_\Omega[c_i^m, \theta_i^m, \varphi]\, dt = \int_0^T \langle f_{c_i}, \varphi \rangle \tag{3.27a}$$

$$\int_0^T \langle (\theta_i^m)', \psi \rangle_\Sigma + B_\Sigma[c_i^m, \theta_i^m, \psi, \theta_1^m, \theta_2^m]\, dt = 0. \tag{3.27b}$$

Now set $m = m^l$ and the question remaining is whether we obtain desired relation, namely

$$\int_0^T \langle (c_i^m)', \varphi \rangle_\Omega + B_\Omega[c_i^m, \theta_i^m, \varphi]\, dt \stackrel{?}{=} \int_0^T \langle (c_i)', \varphi \rangle_\Omega + B_\Omega[c_i, \theta_i, \varphi]\, dt \tag{3.28a}$$

$$\int_0^T \langle (\theta_i^m)', \psi \rangle_\Sigma + B_\Sigma[c_i^m, \theta_i^m, \psi, \theta_1^m, \theta_2^m]\, dt \stackrel{?}{=} \int_0^T \langle (\theta_i)', \psi \rangle_\Sigma + B_\Sigma[c_i, \theta_i, \psi, \theta_1, \theta_2]. \tag{3.28b}$$

The bi-linear parts of relation (3.28) are clear because the weak convergences (3.24) are sufficient to satisfy bi-linear parts of (3.27). The only complications arise from nonlinear parts on Σ, concretely

$$(c_{i|_\Sigma}^m(1-\theta_i^m) - (c_{i|_\Sigma}^{in} + \kappa_i)[\theta_i] - c_{i|_\Sigma}(1-\theta_i) + (c_{i|_\Sigma}^{in} + \kappa_i)[\theta_i],\, \varphi)_{L^2([0,T];L^2(\Sigma))} \stackrel{?}{=} 0 \tag{3.29a}$$

$$(c_{i|_\Sigma}^m(1-\theta_i^m) + \kappa_i^{re}[\theta_1^m][\theta_2^m] - c_{i|_\Sigma}(1-\theta_i) - \kappa_i^{re}[\theta_1][\theta_2],\, \psi)_{L^2([0,T];L^2(\Sigma))} \stackrel{?}{=} 0. \tag{3.29b}$$

Note that from (3.25a) we have $|[\theta_i^m] - [\theta_i]| \leq |\theta_i^m - \theta_i|$ and $|c_i^{m+} - c_i^+| \leq |c_i^m - c_i|$. Consequently

$$\begin{aligned}
0 &\leq |c_{i|_\Sigma}^{m+}(1-[\theta_i^m]) - (c_{i|_\Sigma})^+(1-[\theta_i])| \\
&= |(c_{i|_\Sigma}^m))^+(1-[\theta_i^m]) - c_{i|_\Sigma}^{m+}(1-[\theta_i]) - c_{i|_\Sigma}^{m+}(1-[\theta_i]) - (c_{i|_\Sigma})^+(1-[\theta_i])| \\
&= |c_{i|_\Sigma}^{m+}([\theta_i]-[\theta_i^m]) - (c_{i|_\Sigma}^{m+} - (c_{i|_\Sigma})^+)(1-[\theta_i^m])| \\
&\leq |c_{i|_\Sigma}^{m+}([\theta_i]-[\theta_i^m])| + |(c_{i|_\Sigma}^{m+} - (c_{i|_\Sigma})^+)(1-[\theta_i^m])| \\
&\leq |c_{i|_\Sigma}^{m+}|\ |[\theta_i]-[\theta_i^m]| + |c_{i|_\Sigma}^{m+} - c_{i|_\Sigma}^+|\ |(1-[\theta_i^m])|
\end{aligned} \tag{3.30}$$

and by Schwarz's inequality $|(f,g)_{L^2([0,T];L^2(\Sigma))}| \leq \|f\|_{L^2([0,T];L^2(\Sigma))}\|g\|_{L^2([0,T];L^2(\Sigma))}$ we obtain from (3.29a) following convergence

$$\begin{aligned}
&|(c_{i|_\Sigma}^m(1-[\theta_i^m]) - c_{i|_\Sigma}(1-[\theta_i]),\, \varphi)_{L^2([0,T];L^2(\Sigma))}| \\
&\qquad \leq \|c_{i|_\Sigma}^{m+}\|_{L^2([0,T];L^2(\Sigma))}\|[\theta_i]-[\theta_i^m]\|_{L^2([0,T];L^2(\Sigma))}\|\varphi\|_{L^2([0,T];L^2(\Sigma))} \\
&\qquad\quad + \|c_{i|_\Sigma}^{m+} - c_{i|_\Sigma}^+\|_{L^2([0,T];L^2(\Sigma))}\|(1-[\theta_i^m])\|_{L^2([0T];L^2(\Sigma)}\|\varphi\|_{L^2([0,T];L^2(\Sigma))} \stackrel{m\to\infty}{\longrightarrow} 0,
\end{aligned}$$

where the last inequality follows from the fact that all the sequences: $\{c_{i|_\Sigma}^m\}_{m=1}^\infty$, $\{c_{i|_\Sigma}^{m+}\}_{m=1}^\infty$, $(1-[\theta_i^m])$ are convergent and function φ is bounded in $L^2(L^2(\Sigma))$.

Similarly we have the estimates

$$\begin{aligned}|((c^{in}_{i|_\Sigma}+\kappa_i)[\theta_i]-(c^{in}_{i|_\Sigma}+\kappa_i)[\theta^m_i],\varphi)_{L^2([0,T];L^2(\Sigma))}|\\ = K\|[\theta_i]-[\theta^m_i]\|_{L^2([0,T];L^2(\Sigma))}\|\varphi\|_{L^2([0,T];L^2(\Sigma))}\overset{m\to\infty}{\to}0\end{aligned}$$

and

$$\begin{aligned}0\le|\kappa^{re}_i[\theta_1][\theta_2]-\kappa^{re}_i[\theta^m_1][\theta^m_2]|\le\kappa^{re}_i|[\theta_1][\theta_2]-[\theta_1][\theta^m_2]+[\theta_1][\theta^m_2]-[\theta^m_1][\theta^m_2]|\\ \le\kappa^{re}_i|[\theta_1]([\theta_2]-[\theta^m_2])+([\theta_1]-[\theta^m_1])[\theta^m_2]|\le\kappa^{re}_i\left(|([\theta_2]-[\theta^m_2])|+|([\theta_1]-[\theta^m_1])|\right).\end{aligned}\tag{3.31}$$

Note that all these relations hold also for $\psi\in C^1([0,T];W^{1,2}(\Sigma))$. With the boundedness of $[\theta_i]$, resp $[\theta^m_i]$, we obtain the convergences

$$\begin{aligned}|(\kappa^{re}_i[\theta^m_1][\theta^m_2]-\kappa^{re}_i[\theta_1][\theta_2],\,\psi)_{L^2([0,T];L^2(\Sigma))}|\\ \le\kappa^{re}_i\left(\|([\theta_2]-[\theta^m_2])\|_{L^2([0,T];L^2(\Sigma))}\right)\|\psi\|_{L^2([0,T];L^2(\Sigma))}\\ +\kappa^{re}_i\left(\|([\theta_1]-[\theta^m_1])\|_{L^2([0,T];L^2(\Sigma))}\right)\|\psi\|_{L^2([0,T];L^2(\Sigma))}\overset{m\to\infty}{\longrightarrow}0\end{aligned}$$

and, finally, we obtain the desired result

$$\int_0^T\langle(c_i)',\varphi\rangle_\Omega+B_\Omega[c_i,\theta_i,\varphi]\,dt=\int_0^T\langle f_{c_i},\varphi\rangle\tag{3.32}$$

$$\int_0^T\langle(\theta_i)',\psi\rangle_\Sigma+B_\Sigma[c_i,\theta_i,\psi,\theta_1,\theta_2]\,dt=0.\tag{3.33}$$

This holds for all $\varphi\in L^2([0,T];W^{1,2}_{\Gamma_{in}}(\Omega))$ and $\psi\in L^2([0,T];W^{1,2}(\Sigma))$, since the functions in the form (3.26) are dense in $L^2([0,T];W^{1,2}_{\Gamma_{in}}(\Omega))$ and $L^2([0,T];W^{1,2}(\Sigma))$ respectively. Hence in particular we satisfied weak formulation (3.7), namely

$$\begin{aligned}\langle\partial_t c_i(t),v\rangle_\Omega+B_\Omega[c_i,\theta_i,v]=\langle f_{c_i},v\rangle,\ \forall v\in W^{1,2}_{\Gamma_{in}}(\Omega)\\ \langle\partial_t\theta_i(t),w\rangle_\Sigma+B_\Sigma[c_i,\theta_i,v,\theta_1,\theta_2]=0,\ \forall w\in W^{1,2}(\Sigma),\end{aligned}$$

for all $v\in W^{1,2}_{\Gamma_{in}}(\Omega), w\in W^{1,2}(\Sigma)$ and a.e. $t\in[0,T]$.

3. To satisfy the initial conditions, we firstly observe that from (3.7) by integration per-partes we obtain

$$\int_0^T-\langle\varphi',c_i\rangle_\Omega+B_\Omega[c_i,\theta_i,\varphi]\,dt=\int_0^T\langle f_{c_i},\varphi\rangle+(c_i(0),\varphi(0))_\Omega$$

$$\int_0^T-\langle\psi',\theta_i\rangle_\Sigma+B_\Sigma[c_i,\theta_i,\psi,\theta_1,\theta_2]\,dt=(\theta_i(0),\psi(0))_\Sigma.$$

Analogously from (3.27) we have

$$\int_0^T -\langle\varphi', c^m_{i|\Sigma}\rangle_\Omega + B_\Omega[c^m_{i|\Sigma}, \theta^m_i, \varphi]\,dt = \int_0^T \langle f_{c_i}, \varphi\rangle + (c^m_{i|\Sigma}(0), \varphi(0))_\Omega$$
$$\int_0^T -\langle\psi', \theta^m_i\rangle_\Sigma + B_\Sigma[c^m_{i|\Sigma}, \theta^m_i, \psi, \theta^m_1, \theta^m_2]\,dt = (\theta^m_i(0), \psi(0))_\Sigma.$$

and passing to weak limits (by same argumentation as above) we obtain

$$\int_0^T -\langle\varphi', c_i\rangle_\Omega + B_\Omega[c_i, \theta_i, \varphi]\,dt = \int_0^T \langle f_{c_i}, \varphi\rangle + (c^0_i, \varphi(0))_\Omega$$
$$\int_0^T -\langle\psi', \theta_i\rangle_\Sigma + B_\Sigma[c_i, \theta_i, \psi, \theta_1, \theta_2]\,dt = (\theta^0_i, \psi(0))_\Sigma.$$

Since $c^m_{i|\Sigma}(0) \overset{m\to\infty}{\longrightarrow} c^0_i$ in $L^2(\Omega)$ and $\theta^m_i(0) \overset{m\to\infty}{\longrightarrow} \theta^0_i$ in $L^2(\Sigma)$ and $\varphi(0), \psi(0)$ are arbitrary, we have $c_i(0) = c^0_i$ and $\theta_i(0) = \theta^0_i$. □

3.5 Non-negativity and boundedness

In this section we apply a weak Maximun/Minimun principle to obtain non-negativity (boundedness) of c_i and θ_i for non-negative (bounded) initial values c^0_i and θ^0_i.

Theorem 3.5. *Let $c_i, \theta_i, i = 1, 2, 3$, be weak solutions of the problem (3.7). Assume that $c^0_i \geq 0$ in Ω, $\theta^0_i \in [0, 1]$ and c^{in}_i are nonnegative constant functions. Moreover, we consider the additional condition $c^{in}_3 + \kappa_3 \geq \kappa^{re}$. Then $c_i(t; x) \geq 0$ for a.e. $(t; x) \in [0, T] \times \Omega$ and $\theta_i(t; x) \in [0, 1]$ for a.e. $(t; x) \in [0, T] \times \Sigma, i = 1, 2, 3$. Consequently, $\{c_1, \theta_1, \ldots, c_3, \theta_3\}$ is a weak solution to original problem (1.8).*

Proof. 1. Decompose θ_i in positive and negative part, i.e. $\theta_i = \theta^+_i + \theta^-_i$, where $\theta^+_i = \max\{0, \theta_i\}$ and $\theta^-_i = \min\{0, \theta_i\}$. We firstly prove the non-negativity of θ_i or, equivalently, $\theta^-_i = 0$. Similarly as in previous section, we use the special choice of the test functions in the relation (3.7b), namely θ^-_i. Note that $\theta^-_i \leq 0 \Rightarrow \theta^+_i = 0$ and $[\theta_i]\theta^-_i = 0$. These turn (3.7b) into

$$(\theta'_i, \theta^-_i)_\Sigma + (\nabla_\Sigma\theta_i, \nabla_\Sigma\theta^-_i)_\Sigma + ((c^{in}_{i|\Sigma} + \kappa_i)\theta_i, \theta^-_i)_\Sigma = \left(c^+_i(1 - [\theta_i]),\ \theta^-_i\right)_\Sigma + \kappa^{re}_i \left([\theta_1][\theta_2],\ \theta^-_i\right)_\Sigma.$$

for $-\kappa^{re}_1 = -\kappa^{re}_2 = \kappa^{re} = \kappa^{re}_3, i = 1, 2, 3$. Furthermore, note that

$$\left.\begin{array}{r} c^+_i(1 - [\theta_i])\,\theta^-_i \leq 0,\ i = 1, 2, 3 \\ -\kappa^{re}[\theta_1][\theta_2]\,\theta^-_i = 0,\ i = 1, 2 \\ \kappa^{re}[\theta_1][\theta_2]\,\theta^-_3 \leq 0 \end{array}\right\} \Rightarrow \frac{d}{dt}\|\theta^-_i\|^2_{L^2(\Sigma)} + K\|\theta^-_i\|^2_{L^2(\Sigma)} \leq 0$$

for $i = 1, 2, 3$ and a constant K. Substituting

$$y(t) = \|\theta^-_i(t)\|^2_{L^2(\Sigma)} \geq 0 \tag{3.34}$$

we construct the ODE for a supersolution $\bar{y}$, namely

$$\bar{y}'(t) = -K\bar{y},$$

which has solution $\bar{y}(t) = ce^{-Kt}, c \geq 0$. The initial condition $\theta_i^0 \in [0,1] \Rightarrow \theta_i^{0-} = 0$ allows the only solution $\bar{y}(0) \equiv 0 \Rightarrow y \leq 0$ and by the substitution (3.34) we obtain $y \equiv 0$, hence $\theta_i^-(t) \equiv 0$ for a.e. $t \in [0,T]$.

2. Analogue approach can be done using $(\theta_i - 1)^+$ as a test function, namely

$$\begin{aligned}\left(\partial_t\theta_i, (\theta_i-1)^+\right)_\Sigma + \left(\nabla_\Sigma\theta_i, \nabla_\Sigma(\theta_i-1)^+\right)_\Sigma + \left((c_{i|_\Sigma}^{in} + \kappa_i)\,\theta_i, (\theta_i-1)^+\right)_\Sigma \\ = \left(c_i^+(1-[\theta_i]), (\theta_i-1)^+\right)_\Sigma + \kappa_i^{re}\left([\theta_1][\theta_2], (\theta_i-1)^+\right)_\Sigma.\end{aligned}$$

Since we have already proved the non-negativity of $\theta_i, i = 1,2,3$, we can w.l.o.g consider $\theta_i = \theta_i^+$. Recalling the assumption $c_{i|_{\Gamma_{in}}}^{in} = c_{i|_{\Gamma_{in}}}^{in+}$ we obtain the following

$$\begin{aligned}(c_{i|_\Sigma}^{in} + \kappa_i)\,\theta_i\,(\theta_i-1)^+ = (c_{i|_\Sigma}^{in} + \kappa_i)^+\theta_i^+(\theta_i-1)^+ \geq 0,\ i = 1,2,3 \\ c_i^+(1-[\theta_i])(\theta_i-1)^+ = 0,\ i = 1,2,3 \\ -\kappa^{re}[\theta_1][\theta_2](\theta_i-1)^+ = 0,\ i = 1,2.\end{aligned}$$

Together with the observations: $\partial_t\theta_i = \partial_t(\theta_i-1)^+,\ \nabla_\Sigma\theta_i = \nabla_\Sigma(\theta_i-1)^+$ we directly receive for $i = 1,2$ the inequality

$$\frac{1}{2}\frac{d}{dt}\|(\theta_i-1)^+\|_{L^2(\Sigma)}^2 \leq \frac{1}{2}\frac{d}{dt}\|(\theta_i-1)^+\|_{L^2(\Sigma)}^2 + \|\nabla(\theta_i-1)^+\|_{L^2(\Sigma)}^2 \leq 0.$$

Again by substitution $y(t) = \|(1-\theta_i)^-(t)\|_{L^2(\Sigma)}^2 \geq 0$ we obtain ODE

$$y'(t) \leq 0.$$

It means that y is non-increasing and, since the initial condition reads as $y(0) = 0$, we have only solution $y \equiv 0$, i.e. $\theta_i \leq 1$ for any $\theta_i^0 \in [0,1]$ and $i = 1,2$.

3. The situation for $i = 3$ needs to use a contribution of the term $(c_{i|_\Sigma}^{in} + \kappa_i)\theta_i$, namely

$$\begin{aligned}\frac{1}{2}\frac{d}{dt}\|(\theta_3-1)^+\|_{L^2(\Sigma)}^2 &\leq \left(-(c_{i|_\Sigma}^{in} + \kappa_3)\theta_3 + \kappa^{re}[\theta_1][\theta_2],\ (\theta_3-1)^+\right)_\Sigma \\ &\leq \left(-(c_{i|_\Sigma}^{in} + \kappa_3)(\theta_3-1) - (c_{i|_\Sigma}^{in} + \kappa_3) + \kappa^{re},\ (\theta_3-1)^+\right)_\Sigma \\ &\leq -\left(c_{i|_\Sigma}^{in} + \kappa_3 - \kappa^{re},\ (\theta_3-1)^+\right)_\Sigma \leq 0,\end{aligned}$$

where we have used in last inequality the assumption $(c_{i|_\Sigma}^{in} + \kappa_3) \geq \kappa^{re}$. Moreover, by substitution $y(t) = \|(1-\theta_3)^-(t)\|_{L^2(\Sigma)}^2$ we obtain the same inequality as before. Following the same technique as in §1 of this proof, we obtain the result $\theta_3 \leq 1$ for any $\theta_3^0 \in [0,1]$.

4. The situation for c_i is similar as in case of θ_i. Using c_i^- as a test function and the fact that velocity field as incompressibility, we obtain from the relation (3.7a) the following

$$\int_\Omega \tfrac{1}{(\mathrm{Pe})_i}\nabla c_i\cdot\nabla v + \mathbf{v}\cdot\nabla c_i\, v + \int_\Sigma \Big(c^+_{i|_\Sigma}(1-[\theta_i]) - (c^{in}_{i|_\Sigma}+\kappa_i)[\theta_i]\Big)\, v$$

$$(\partial_t c_i, c_i^-)_\Omega + (\nabla c_i, \nabla_\Sigma c_i^-)_\Omega + \int_\Omega (\mathbf{v}\cdot\nabla c_i)\, c_i^- + \int_\Sigma \Big(c^+_{i|_\Sigma}(1-[\theta_i]) - (c^{in}_{i|_\Sigma}+\kappa_i)[\theta_i]\Big)\, c^-_{i|_\Sigma} \tag{3.35}$$
$$= -\int_\Omega \tfrac{1}{(\mathrm{Pe})_i}\nabla c_i^{in}\cdot\nabla c_i^- + \mathbf{v}\cdot\nabla c_i^{in}\, c_i^- + \int_\Sigma c^{in}_{i|_\Sigma} c^-_{i|_\Sigma}.$$

Note that

$$\int_\Omega (\mathbf{v}\cdot\nabla c_i)\, c_i^- \le \|\mathbf{v}\|_{L^\infty(\Omega)}\Big(C_1\|\nabla c_i\|^2_{L^2(\Omega)} + C_2\|c_i\|^2_{L^2(\Omega)}\Big)$$

and

$$\int_\Sigma c^-_{i|_\Sigma} \le \|c_i\|^2_{L^2(\Sigma)} \le \|c_i\|^2_{W^{1,2}(\Omega)} \le C_1\|\nabla c_i\|^2_{L^2(\Omega)} + C_2\|c_i\|^2_{L^2(\Omega)}.$$

Using interpolation- and Cauchy's ε-inequality, we have

$$|\langle f_{c_i}, c_i^-\rangle| \le C\|c_i^-\|_{L^2(\Sigma)} \le C\|c_i^-\|_{W^{\frac12,2}(\Omega)} \le C_1\|\nabla c_i^-\|^2_{L^2(\Omega)} + C_2\|\nabla c_i^-\|^2_{L^2(\Omega)}$$

for appropriate constants C_1, C_2. Finally, we obtain the estimates

$$\frac12\frac{d}{dt}\|c_i^-\|^2_{L^2(\Omega)} + C_1\|\nabla c_i^-\|^2_{L^2(\Omega)} \le C_2\|c_i^-\|^2_{L^2(\Omega)} \tag{3.36}$$

for $i=1,2,3$, and constants $C_1>0$ and appropriate $C_2 = C_2(\|\mathbf{v}\|_{L^\infty(\Omega)})$. Further steps follow analogously to §1 and we obtain $c_i^-\equiv 0$ which shows that c_i is non-negative. □

Remark 3.1. *Let us mention that within industrial applications we very often meet the condition $c^{in}_{i|_\Sigma} + \kappa_3 \ge \kappa^{re}$. The systems where this condition is not satisfied are so-called very fast or instantaneous reactions systems.*

Remark 3.2. *Although we have proved the existence for any $\mathbf{v}\in L^\infty(\Omega)$, one can expect from relation* (3.36) *a numerical sensitivity on the magnitude of the velocity field $\mathbf{v}$, resp. its norm $\|\mathbf{v}\|_{L^\infty(\Omega)}$. Within numerical computation this fact provides expectations on smaller accuracy for $\|\mathbf{v}\|_{L^\infty(\Omega)} >> 1$.*

4. Numerical approach

In this section we present methods to compute the problem of our interest, i.e. the system (1.8) with similar geometry as microchannel, see picture (1.1b), resp. (4.1). The verification of used methods is based on physical criteria and also numerically on two near-by models: firstly, the domain with a boundary in shape of a smooth compact manifold where we have proven the existence and uniqueness of a mild solution, cf. Chapter 2; secondly, on the microchannel-geometry but with zero velocity field and changed boundary conditions.

For numerical computation we use a non-commercial open-source program FreeFem++ version 3.20. As usual for programs based on finite element method (FEM), we treat the problem through its weak formulation. The implementation to FreeFem++ can be done with an explicit incorporation of the following numerical algorithms

- Implicit Euler method for a time-discretization of an evolution problem.
- Algorithms treating non-linearities, i.e. projection methods or Newton algorithm.
- Up-wind methods for treating the transport term $\mathbf{v} \cdot \nabla c$ for high Peclet number.

Note 4.1. *The expression "projection methods" can generally have two meanings. Firstly, it can be decoupling of equations for the bulk constituent c_i and the surface constituent θ_i. This is very similar to the original projection method used for a decoupling of a velocity $\mathbf{v}$ and the pressure p in case of incompressible Navier-Stokes equations.*

Secondly, it can mean a numerical method treating non-linearities which is based on the idea of fixed point iterations. In our case, because of the coupled non-linearities "$c_i\theta_i$" in the sorption term, both methods lead to the same and we call them together the "projection methods".

4.1 Implementation of the problem in FreeFem++

In this section we present the numerical weak formulation which we used for the program-implementation. Program FreeFem++ 3.20 uses standard linear solvers (CG, GMRES, LU, Cholesky, etc.) and non-linear problems has to be explicitly implemented by the projection-methods or Newton algorithm. Furthermore, for high Peclet number the bulk equations have nearly hyperbolic behavior and an up-wind scheme - for discretization of transport term - has to be used. Finally, the time-discretization in evolution problem is done by implicit Euler scheme. In the sequel we briefly introduce these techniques.

Implicit Euler method or sometimes called backward Euler method, is one of the most used implementation of a time discretization for evolution problems. This method can be described as follows: For an evolution problem in the form $\frac{\partial u}{\partial t} = f(u,t)$ we discretize the time derivative as

$$\frac{u_k - u_{k-1}}{\Delta t} = f(u_k, t_k),$$

where u_k denotes the solution in k^{th} iteration and u_0 is given initial condition. This method is first order and unconditionally stable.

Up-wind scheme is a numerical discretization method for solving hyperbolic partial differential equations. The scheme discretizes the equation (resp. hyperbolic part) in the direction determined by characteristic speed. Denoting

$$a^+ = max(a, 0),\ a^- = min(a, 0)$$

and

$$u_x^- = \frac{u_i^n - u_{i-1}^n}{\Delta x},\ u_x^+ = \frac{u_{i+1}^n - u_i^n}{\Delta x},$$

the one-dimensional hyperbolic equation

$$\frac{\partial u}{\partial t} + a\frac{\partial u}{\partial x} = 0$$

is discretized by the first-order up-wind scheme as follows

$$\frac{u_i^{n+1} - u_i^n}{\Delta x} = -(a^+ u_x^- + a^- u_x^+).$$

The extension to 2D/3D in FreeFem++-3.20 is done by the built-in function $convect(\mathbf{v}, -dt, \cdot)$ which solve the evolution hyperbolic PDE with the help of the Characteristic-Galerkin Method, i.e. it discretizes

$$\frac{\partial u}{\partial t} + \mathbf{v} \cdot \nabla u = 0 \ \text{ as } \ \frac{u^t - \boldsymbol{X}(u^{t-1}, \mathbf{v})}{\Delta t} = 0,$$

where $\boldsymbol{X}$ is the convect field defined by

$$\boldsymbol{X}(x, \mathbf{v}) = y(dt), x \in \Omega,$$

for y being a solution of the following ODE:

$$\dot{y} = \mathbf{v}(y), y(0) = x.$$

For more information about the implementation of the up-wind scheme in FreeFem++ see [13].

Newton algorithm has many different applications but, in our case, we use the iterative Newton algorithm to treat the non-linearities of the problem, i.e. transform the non-linear problem into an iterative linear problem with the second order approximation. For a non-linear problem, generally written as $F(u) = 0$, denote $DF(u)$ the differential of F at point u; then the algorithm can be described as follows

1. choose (guess) an initial value u_0

2. for $i = 0$ until a sufficient approximation, i.e. $\|F(u_i)\| < \varepsilon$,[1] repeat the following

   (a) solve $DF(u_i)w_i = F(u_i)$

   (b) $u_{i+1} = u_i - w_i$

The convergence of Newton algorithm depends on a nature of non-linearities and chosen initial values. Generally speaking, by the expansion to Taylor series, i.e

$$F(u + du) = F(u) + DF(u)du + \mathcal{O}(\|du\|^2),$$

the algorithm converges with the quadratic speed.

The program implementation is done through two embedded cycles, i.e. in each step of the time-cycle (the first cycle) we apply the iterative Newton algorithm (the second cycle). This we can write in the compact vector form as follows.

Let us denote vectors $\boldsymbol{c} = (c_1, c_2, c_3), \boldsymbol{dc} = (dc_1, dc_2, dc_3), \boldsymbol{\theta} = (\theta_1, \theta_2, \theta_3), \boldsymbol{d\theta} = (\theta_1, \theta_2, \theta_3), \boldsymbol{\kappa} = (\kappa_1, \kappa_2, \kappa_3)$ and $\boldsymbol{v} = (v_1, v_2, v_3), \boldsymbol{w} = (w_1, w_2, w_3)$. Moreover, we understand the symbols "::" and ":" as products by components, i.e. $\boldsymbol{c} : \boldsymbol{v} = (c_1v_1, c_2v_2, c_3v_3)$ and "::" analogously for matrices. The symbol "$\cdot$" denotes dot (scalar) product and a operator $\boldsymbol{X}(\cdot, \mathbf{v})$ is the operator of the up-wind scheme, see above. Then the implementation, in the compact vector form, states: We search for $\boldsymbol{dc} \in \mathcal{V}^3, \boldsymbol{d\theta} \in \mathcal{W}^3$ such that

$$\begin{aligned}
&\int_\Omega \frac{\boldsymbol{dc}^t \cdot \boldsymbol{v}}{\Delta t} + \tfrac{\mathbf{1}}{\mathbf{(Pe)}} \cdot (\nabla \boldsymbol{dc}^t :: \nabla \boldsymbol{v}) + \int_\Sigma \boldsymbol{dc}^t_{|_\Sigma} \cdot \boldsymbol{v} - (\boldsymbol{d\theta}^t : \boldsymbol{c}^t_{|_\Sigma}) \cdot \boldsymbol{v} - (\boldsymbol{\theta}^t : \boldsymbol{dc}^t_{|_\Sigma}) \cdot \boldsymbol{v} - (\boldsymbol{\kappa} : \boldsymbol{d\theta}^t) \cdot \boldsymbol{v} \\
&+ \int_\Sigma \frac{\boldsymbol{d\theta}^t \cdot \boldsymbol{w}}{\Delta t} + \tfrac{\mathbf{1}}{\mathbf{(Pe)^\Sigma}} \cdot (\nabla \boldsymbol{d\theta}^t :: \nabla \boldsymbol{w}) - \boldsymbol{dc}^t_{|_\Sigma} \cdot \boldsymbol{w} + (\boldsymbol{dc}^t_{|_\Sigma} : \boldsymbol{\theta}^t) \cdot \boldsymbol{w} + (\boldsymbol{c}^t_{|_\Sigma} : \boldsymbol{d\theta}^t) \cdot \boldsymbol{w} + (\boldsymbol{\kappa} : \boldsymbol{d\theta}^t) \cdot \boldsymbol{w} \\
&\qquad + \int_\Sigma \kappa^{re} (\theta_1^t d\theta_2^t + \theta_1^t d\theta_2^t)\,(1, 1, 0) \cdot \boldsymbol{w}
\end{aligned} \tag{FF++}$$

$$\begin{aligned}
&- \int_\Omega \frac{\boldsymbol{c}^t - \boldsymbol{X}(\boldsymbol{c}^{t-1}, \mathbf{v})}{\Delta t} \cdot \boldsymbol{v} + \tfrac{\mathbf{1}}{\mathbf{(Pe)}} \cdot (\nabla \boldsymbol{c}^t :: \nabla \boldsymbol{v}) + \int_\Sigma [\boldsymbol{c}^t_{|_\Sigma} : (\mathbf{1} - \boldsymbol{\theta}^t)] \cdot \boldsymbol{v} + (\boldsymbol{\kappa} : \boldsymbol{\theta}^t) \cdot \boldsymbol{v} \\
&\quad - \int_\Sigma \frac{\boldsymbol{\theta}^t - \boldsymbol{\theta}^{t-1}}{\Delta t} \cdot \boldsymbol{w} + \tfrac{\mathbf{1}}{\mathbf{(Pe)^\Sigma}} \cdot (\nabla \boldsymbol{\theta}^t :: \nabla \boldsymbol{w}) - [\boldsymbol{c}^t_{|_\Sigma} : (\mathbf{1} - \boldsymbol{\theta}^t)] \cdot \boldsymbol{w} (\boldsymbol{\kappa} : \boldsymbol{\theta}^t) \cdot \boldsymbol{w} \\
&\qquad - \int_\Sigma \kappa^{re} (\theta_1^t \theta_2^t)(1, 1, -1) \cdot \boldsymbol{w}.
\end{aligned}$$

holds for all $\boldsymbol{v} \in \mathcal{V}^3, \boldsymbol{w} \in \mathcal{W}^3$ and given functions $\mathbf{v} \in \mathbf{V}; c_i^0(\cdot) = c_i(0, \cdot), \theta_i^0(\cdot) = \theta_i(0, \cdot)$. The Dirichlet inflow-condition $c_{i|_{\Gamma_{in}}} = c_i^{in}$ is employed by choosing in each time step the initial value for the Newton algorithm $c_i^t = c_{i|_{\Gamma_{in}}}$ and, consequently, by the boundary condition $dc_{i|_{\Gamma_{in}}} = c^{t,n}_{i|_{\Gamma_{in}}} - c^{t,n-1}_{i|_{\Gamma_{in}}} = 0$ in each n^{th} cycle of the Newton algorithm.

[1] In particular we also check the alternative condition $\|u_{i+1} - u_i\| \leq \varepsilon$.

4.2 The test of the used methods

If we somehow modify the inflow boundary condition and neglect the velocity field, we obtain a convenient tool to test the used numerical methods. This is caused by the fact that a convenient modification would us allow to choose the test-function as $v_i \equiv const$, resp. $w_i \equiv const$. Consequently, we receive the following relation to hold

$$\partial_t \int_\Omega c_i + \int_\Sigma c_i(1-\theta_i) + \kappa_i \theta_i = 0 \tag{4.1a}$$

$$\partial_t \int_\Sigma \theta_i - \int_\Sigma c_i(1-\theta_i) + \kappa_i \theta_i = \nu_i \int_\Sigma \kappa^{re} \theta_1 \theta_2, \tag{4.1b}$$

for $i = 1, 2, 3$ and $\nu_1 = \nu_2 = -1 = -\nu_3$.

The only possibility permitting $v_i \neq 0$ is a change the searching space $\mathcal{V}$. We use the change of the inflow boundary condition from the Dirichlet to a Neumann one. [2] Considering

$$(\nabla c_i \cdot \mathbf{n})_{\Gamma_{in}} = 0 \ , \ \mathbf{v} = 0 \text{ in } \Omega$$

and the searching space for c_i in the form

$$\tilde{\mathcal{V}} = \left\{ L^2(0,T; W^{1,2}(\Omega)) \cup L^\infty(0,T; L^2(\Omega)), \partial_t c \in L^2(0,T; W^{-1,2}(\Omega)) \right\},$$

we define the *test-model* as follows

$$\partial_t \int_\Omega c_i \, v_i + \int_\Omega \tfrac{1}{(\mathrm{Pe})_i} \nabla c_i \cdot \nabla v_i + \int_\Sigma \left[c_{i|\Sigma}(1-\theta_i) - \kappa_i \theta_i \right] v_i = 0 \tag{TEST}$$

$$\partial_t \int_\Sigma \theta_i w_i + \tfrac{1}{(\mathrm{Pe})_i^\Sigma} \int_\Sigma \nabla_\Sigma \theta_i \cdot \nabla_\Sigma w_i - \left[c_{i|\Sigma}(1-\theta_i) - \kappa_i \theta_i + \kappa_i^{re} \theta_1 \theta_2 \right] w_i = 0$$

for all $v_i \in \tilde{\mathcal{V}}, w_i \in \mathcal{W}$ and a.e. $t \in (0,T), i = 1,2,3$, considering $-\kappa_1^{re} = -\kappa_2^{re} = \kappa^{re} = \kappa_3^{re}$ and $c_i^0 \in L^2(\Omega), \theta_i^0 \in L^2(\Sigma)$.

Using this *test-model* with the constant functions as the test-functions, see (4.1), together with a suitable summations, the following come out: If no chemical reaction occurs, then each summation of c_i and corresponding θ_i equation is mass-conservative in time, namely

$$\partial_t \left[\int_\Omega c_i + \int_\Sigma \theta_i \right] = 0, \ i = 1,2,3$$

If we do not neglect the reaction but multiply the equations for c_3 and θ_3 by two and sum with the rest, we receive the mass-conservation in time for whole mixture

$$\partial_t \left[\int_\Omega (c_1 + c_2 + 2c_3) + \int_\Sigma (\theta_1 + \theta_2 + 2\theta_3) \right] = 0.$$

[2] Note that here we do not decompose c_i into the homogeneous and the boundary-part like in Chapter 3.

Finally, by the maximal principle for evolution equations, see e.g. [12], we obtain for initial values $c_i^0 \in L^2(\Omega), \theta_i^0 \in L^2(\Sigma)$ and a.e $t \in (0,T)$ the following relation

$$\int_\Omega (c_1+c_2+2c_3)(t)+\int_\Sigma (\theta_1+\theta_2+2\theta_3)(t) = \int_\Omega (c_{0,1}+c_{0,2}+2c_{0,3})+\int_\Sigma (\theta_{0,1}+\theta_{0,2}+2\theta_{0,3}),. \quad (4.3)$$

This is required to hold as the *verification-condition* for the numerical methods.

4.3 Numerical computation

4.3.1 FreeFem++

I chose the freeware FreeFem++-3.20 as a suitable tool to solve the problem. Precisely spoken, FreeFem++ is a high level integrated development environment (IDE) for finding a numerical solution of partial differential equations (PDE) in the dimension 2 and 3 using finite element method (FEM). FreeFem++ is written in C++ and developed and maintained by Université Pierre et Marie Curie and Laboratoire Jacques-Louis Lions. It runs on GNU/Linux, Solaris, OS X and MS Windows systems. FreeFem++ is free software (GPL). It is useful to mention that the program is compatible with standard inputs/outputs files, i.e. it allows to load meshes generated by other softwares and to visualize the results by visualize-data-application e.g. Gnuplot, ParaView, e.t.c.

As the big advantages of this program seem to me the a user-friendly interface and a possibility to control many settings. Moreover, it has very good documentation and, already mentioned, the possibility cooperating with other softwares. On the other hand, between disadvantages one can engage a necessity of linearization of the equations, i.e. Newton algorithm is not implemented in the program but has to be implemented by user. Parallelization is possible but it is not automatic and require some programming efforts. Also 1D elements has to be solved by "trick" of reduced 2D elements. Like other suitable possibilities seem to me for example the freeware "Fenics" or "oomph.lib".

4.3.2 Physical and numerical characterization of the model

The first step in a program-realization is to obtain an incompressible velocity field. [3] Here is important to mention, that the Reynolds number Re is in the range $10^{-1} - 10^{-6}$ and we treat with a laminar creepy flow which radically reduce an influence of the non-linear (velocity) convective term in NS-equations. This allows us to use FEM method without big loss of a conservative-property. The computation is done by the standard Taylor-Hood P2/P1 elements for a velocity-pressure field. The constrain, which can arise for discretization by FEM of hyperbolic systems for structured mesh (which is built by gluing more meshes together), is a disappearing of the flow on a connected boundaries. Therefore, to control this effect, we generate a general unstructured mesh.

[3] Let us mention that this can be done also by other programs e.g. OpenFoam, which is based on FVM method.

Note to the notation. *In the sequel we use the following convention: c_i denotes i^{th} the bulk constituent, θ_i denotes i^{th} the surface constituent, $c_i\theta_i$ denotes i^{th} the bulk/surface non-linearities and $\theta_1\theta_2$ denotes surface/surface non-linearity. Furthermore, if the Peclet number* (Pe) *is not so high, i.e.* (Pe) $\sim 10^2$ *or lower, the bulk equation is "enough" away from hyperbolic equation, i.e. the diffusion effect is enough strong for numerical stabilization, and we can use standard implementation instead of Up-wind scheme.*

The own computation of the reaction-system (1.8) is done by P1-3D elements for both the bulk and the surface constituents. We used the following numerical methods

(i) Projection/Up-wind method (shortly P/U) used for the both bulk/surface and surface/surface non-linearities which decompose the system to $2n$ independent equations.

(ii) Newton/Up-wind method (shortly N/U) of the fully coupled system (FF++), where we treat all non-linearities by Newton method.

Let us mention that also a fixed-point method was used for better understanding of the differences between the results of P/U and N/U methods but whenever this method convergences, it ends up with the same results as N/U method .

4.4 Numerical results

In this section we would like to present results of our computations. This will be done for two kinds of problems. Firstly we compare used methods for *test-model*, i.e. $\mathbf{v} = 0$ and the homogeneous Neumann conditions on the both inflow/outflow parts of the boundary (Γ_{in} and Γ_{out}). We validate the results according to two viewpoints. The condition (4.3) has to be satisfied and, consequently, we require a convergence of both methods to a "fine" solution. i.e. we assume the existence of a precise solution where a refining of a mesh and a decreasing of a time-step tends to this solution. According to numerical efforts we compute just a part of a microchannel. The whole microchannel would require implementation of a parallel computing on clusters.

The system corresponding to a whole microchannel posses the coefficients in the following magnitude

$$(\mathrm{Pe})_i \doteq (\mathrm{Pe})_i^{\Sigma} \sim 10^2 - 10^6, \kappa_i \sim 10^{-4} - 10^0, \kappa^{re} \sim 10^{-4} - 10^2, \mathbf{v}^{ref} \sim 10^{-3} - 10^{-1}.$$

and we choose Reynolds number Re in the range $10^{-4} - 10^{-1}$. In the case of a part of a microchannel we consider the characteristic length $L \sim 10^{-3}$ and the square cross-section $[x, z] \in [0, 1]^2$ with the length (hight) coordinates in the range $y \in [0, 5]$, i.e. $\Omega = \{[x, y, z] : x \in [0, 1], y \in [0, 5], z \in [0, 1]\} \setminus \{\text{obstacles}\}$. [4]

To obtain a simulation similar the to real problem, where the length (z-coordinate) is approximately 1000× bigger that the size of the cross-section, we rearranged some of the considering coefficients in the following way.

$$(\mathrm{Pe})_i \sim (\mathrm{Pe})_i^{\Sigma} \sim 10^1 - 10^4, \kappa_i \sim 10^{-2} - 10^2, \kappa^{re} \sim 10^{-2} - 10^3, \mathbf{v}^{ref} \sim 10^{-1} - 10^2.$$

[4] See the illustration figure (4.1).

From numerical nature of convection/diffusion, resp. reaction/diffusion, systems with nonlinearities we distinguish two positive and negative effects according to influence of the numerical error. The negative effect occurs when

$$\frac{1}{(\mathrm{Pe})_i}, \frac{1}{(\mathrm{Pe})_i^{\Sigma}} \to 0_+, \ \mathbf{v}^{ref} \to \infty, \ \text{resp. } \kappa^{re} \to \infty.$$

These settings usually cause big gradient of c_i or θ_i near (on) the walls or increase the influence of nonlinearities which harm especially Projection/Up-wind method. On the other hand a strong diffusion, weak velocity field or increased desorption effect

$$\frac{1}{(\mathrm{Pe})_i}, \frac{1}{(\mathrm{Pe})_i^{\Sigma}} \sim 1, \ \mathbf{v}^{ref} \sim 0, \ \kappa_i \sim 1$$

have the opposite effect and we expect more precise results for his kind of data. Let us mention that within numerical computations we usually chose the same settings for c_1 and c_2 since its sufficient demonstrate the behavior of the system.

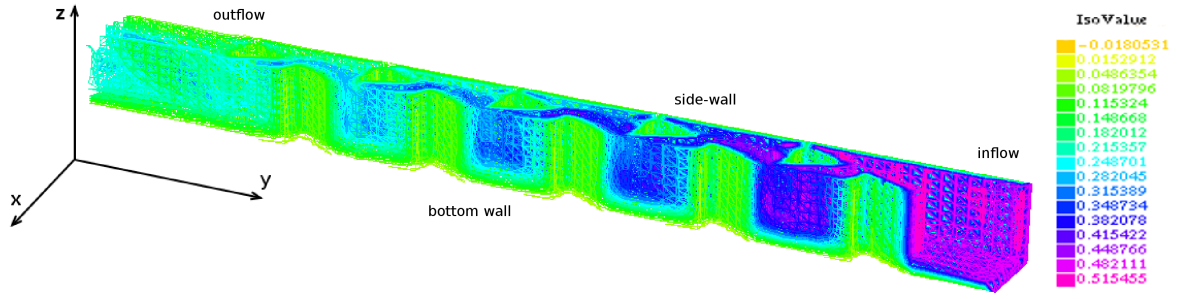


Figure 4.1: Illustration of the computed concentration c_1 on the quartile of bio-diesel microchannel.

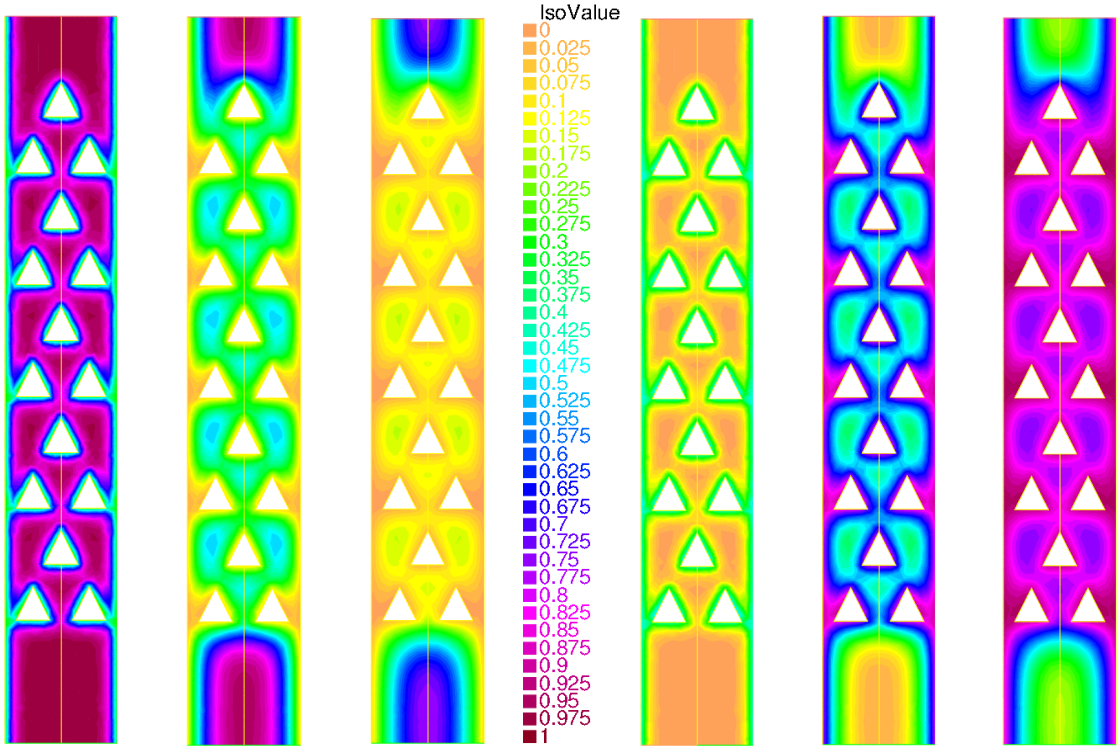
4.4.1 Test of the methods

In this section we we test the used methods by the condition (4.3).For a test of the used numerical methods on the *test-model* we consider the following settings

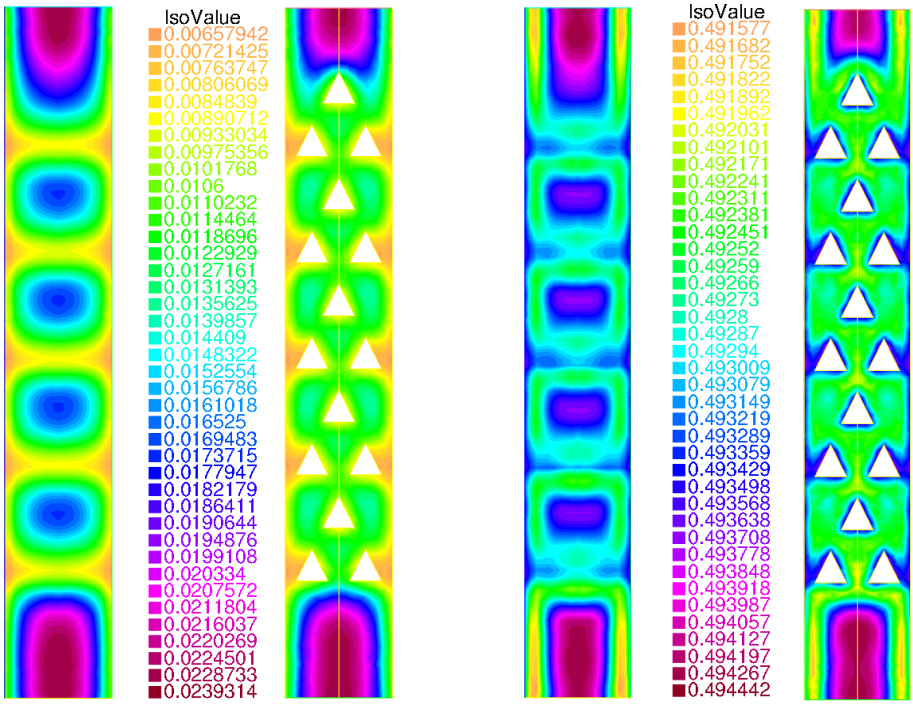
test-model	$(\mathrm{Pe})_i$	$(\mathrm{Pe})_i^{\Sigma}$	κ_i	κ^{re}	c_1^0	c_3^0	θ_1^0	θ_3^0
values	50	50	0.5	100	0.5	0.5	0.5	0.5

These settings of the initial values is situated in the initial chemical equilibrium, i.e. the equation of the Langmuir isotherm is fulfilled. The computations were performed on several meshes with a different accuracy-coefficient k (see the table below) and various time step Δt.

accuracy-coefficient:	k = 4	k = 6	k = 8	k = 9
Number of elements	2724	8280	21624	27864
Degrees of freedom	4842	13559	33388	42655



(a) $t = 0.2$ profile-cut c_1 (b) $t = 1$ profile-cut c_1 (c) $t = 2$ profile-cut c_1 (d) $t = 0.2$ profile-cut c_3 (e) $t = 1$ profile-cut c_3 (f) $t = 2$ profile-cut c_3



(g) $t = 2$ side-cut θ_1 (h) $t = 2$ bottom-cut θ_1 (i) $t = 2$ side-cut θ_3 (j) $t = 2$ bottom-cut θ_3

Figure 4.2: Evolution of c_1, c_3 (above) and θ_1, θ_3 (down) for ***test-model***; $\Delta t = 0.1, k = 9$.

Note 4.2. *We would like to mention that for* $\mathbf{v} = 0$ *both methods behave very well and we can prescribe even "fast" reactions (*$\kappa^{re} >> 0$*) without big harm to the numerical results. Relatively small Peclet numbers, i.e. bigger diffusion, were chosen for better visualization of the results because no convection is present. Without this modification, the thin layer of reaction-products would take a place near the reactive walls and the interior between the walls would be without significant changes.*

Note 4.3. *All computations are performed in 3D where we take advantage of a symmetry of the geometry according to plane* $[x, y, z] = [x, y, 0.5]$*, resp.* $[x, 0.5, z]$*. Therefore it is sufficient to compute one quadrant of* Ω *only. For clarity of the visualization we sometimes display the cut of* Ω *called the "profile-cut" for* $y = 0.5$*, resp. the parts of* Σ*, where "side-wall" correspond to* $\{[x, y, z] : x = 0, y \in [0, 5], z \in [0, 1]\}$ *and "bottom-wall" to* $\{[x, y, z] : x \in [0, 1], y \in [0, 5], z = 0\}$*.*

The results can be summarized in the following table

***test-model*:** $k = 9, \Delta t = 0.1$	t = 0.1	t = 0.5	t = 1.0	t = 2.0	t = 3.0
Projection/Up-wind	5.39 %	26.43%	42.03 %	61.06%	72.93 %
Newton/Up-wind	5.46 %	25.67%	41.65 %	60.91%	72.85 %

In the last case ($k = 9$), the condition (4.3) is satisfied with relative error $\sim 10^{-4}$ for P/U method and 10^{-12} for N/U method in each time step. The relative error of c_1 in $\|\cdot\|_{L^\infty(\Omega)}$ norm is 0.074%, resp. 0.28% for θ_1 in $\|\cdot\|_{L^\infty(\Sigma)}$-norm. These results were obtained using P1-elements and GMRES solver with accuracy $\varepsilon = 10^{-6}$.

As we would expect, the profiles of c_1 and c_3 have an opposite tendency, i.e. the mass-conservation carries out also locally. Both used methods have very similar concentration profiles of c_i and θ_i whose differences vanish with increasing time and by a mesh-refinement.

4.4.2 Results

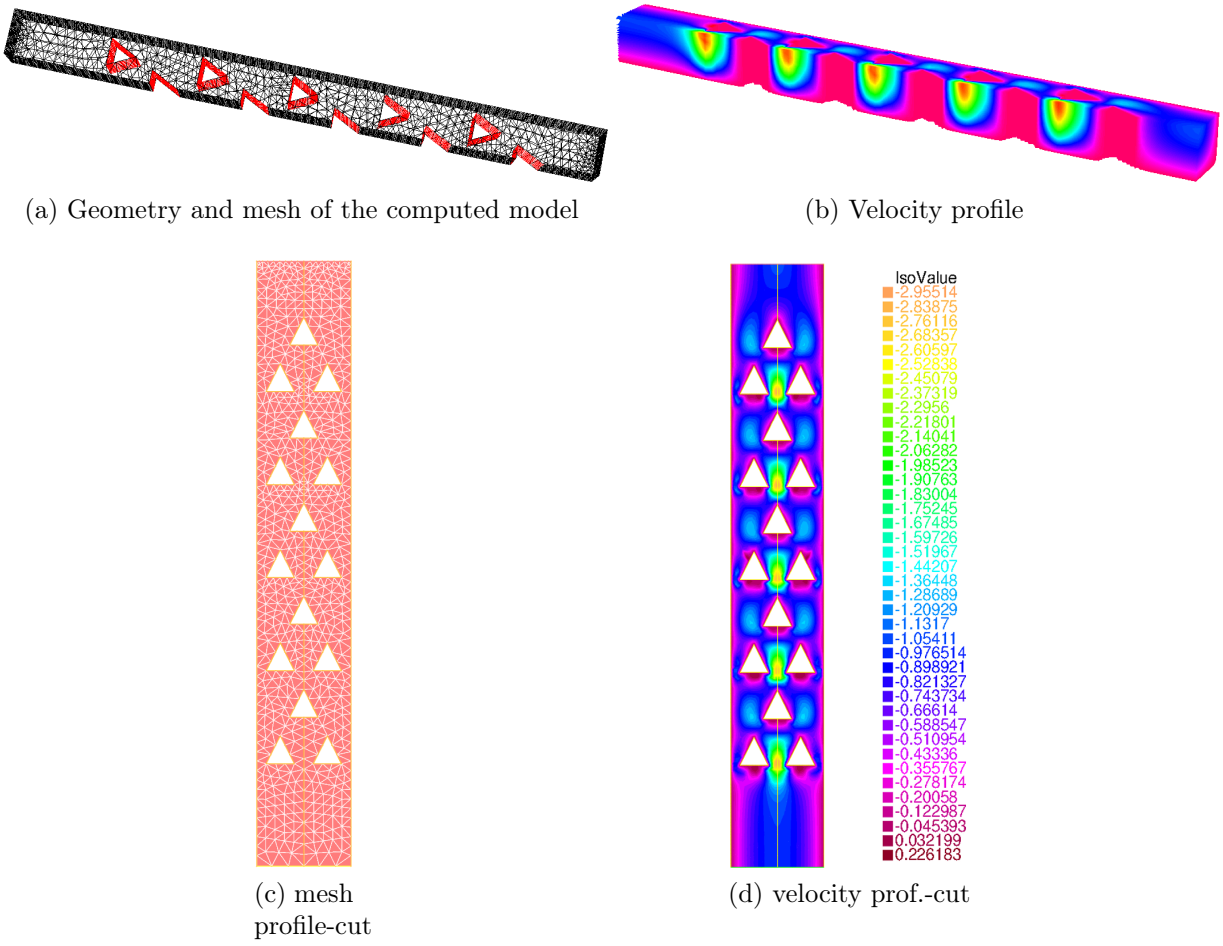
The computation of the velocity profile: Consider the boundary conditions for the velocity field as $\mathbf{v}_{\Gamma_{in}} = \mathbf{v}_{in}$ and $\nabla\mathbf{v} \cdot \mathbf{n} = 0$ on Γ_{out}. The inflow profile for $\mathbf{v}_{\Gamma_{in}}$ was computed as the outflow profile for an auxiliary model. In this auxiliary model we consider the inflow condition as the parabolic profile with characteristic velocity $\mathbf{v}^{ref}$. The channel is firstly considered without obstacles (eventually prolonged) to obtain the profile is close to fully developed stationary velocity field. Then with this inflow condition we computed the original velocity profile $\mathbf{v}$ on original geometry with obstacles.

Now we return to the original problem (1.8) on the same geometry. For the next computations we have used the following settings

settings 1	Re	$(\mathrm{Pe})_i$	$(\mathrm{Pe})_i^\Sigma$	κ_i	κ^{re}	c_1^0	c_3^0	θ_1^0	θ_3^0	$\mathbf{v}^{ref}$	dt
values	0.01	100	100	0.5	1	0.5	0.5	0.5	0.5	1	0.1

settings 2	Re	$(\mathrm{Pe})_i$	$(\mathrm{Pe})_i^\Sigma$	κ_i	κ^{re}	c_1^0	c_3^0	θ_1^0	θ_3^0	$\mathbf{v}^{ref}$	dt
values	0.01	100	100	1	100	1.0	1.0	0.5	0.5	5	0.1

and the geometry with mesh and velocity profile can be graphically introduced as follows:



(a) Geometry and mesh of the computed model

(b) Velocity profile

(c) mesh profile-cut

(d) velocity prof.-cut

Figure 4.3: Mesh and velocity profile of the model.

The settings 1 represents a class of the settings with relatively slow chemical reactions and slow velocity field. These settings also satisfy the conditions for existence of a weak solution - see Theorem (3.4) - and therefore we can rely on the obtained results since we sufficiently refine the mesh and lower the time step. We called these kind of settings as the "slow" settings. Here we obtain very good numerical results satisfying physical criteria with very small difference between both methods.

The setting 2 belongs to the second class of the settings. With increased rate of chemical reactions and magnitude of velocity field we generally do not satisfy the condition of existence theorem (3.4). Therefore we rely the evaluation of the numerical-consistency on the physical criteria. We called these class of the settings as the "fast" settings. In this case a numerical diffusion and other numerical effects, e.g. fake source/sink, take a place. The results of the methods generally vary from each other.

The results for settings 1 read as

setting 1, k = 8	t = 0.1	t = 1	t = 5	t = 10	t = 20	t = 30
P/U	0.24 %	5.49 %	53.75 %	82.17 %	92.65 %	95.116 %
N/U	0.23 %	5.49 %	53.39 %	81.85 %	92.49 %	95.098 %

The steady solution for this setting gives the outflow concentration of c_3 as 95.26% (on the mesh with accuracy $k = 8$). As we can see, in case of "slow" setting 1, both methods give very similar and realistic results. A negative influence of non-linearities in case of Projection/Up-wind method is very reduced.

On the other hand, considering the "fast" setting 2 the behavior of both methods is not the same any more, namely

P/U, setting 2	t = 0.1	t = 0.5	t = 1.0	t = 2.0	t = 3.0
k=4	6.74 %	25.92 %	67.39 %	95.73 %	98.21 %
k=6	5.97 %	22.78 %	58.17 %	91.42 %	96.19 %
k=8	5.67 %	22.09 %	52.72 %	87.67 %	94.36 %
k=9	5.67 %	22.31 %	52.71 %	87.96 %	94.01 %
N/U, setting 2	t = 0.1	t = 0.5	t = 1.0	t = 2.0	t = 3.0
k=4	6.06 %	25.28 %	66.76 %	95.27 %	97.40 %
k=6	5.36 %	22.19 %	57.53 %	90.25 %	93.97 %
k=8	5.09 %	21.53 %	52.09 %	85.94 %	90.93 %
k=9	5.11 %	21.73 %	52.01 %	85.32 %	90.36 %

In this case, the gradient of c_i is very high especially near the reactive boundary Σ. This in combination with big change-in-time causes the "fake-source-effect" in case of Projection/Method. The explanation for this negative numerical phenomenon evidently lies in the non-linearities. In P/U method we handle them using the "old" values of the quantities - symbolically written as $u_t^2 \sim u_t\, u_{t-1}$. Other numerical phenomena arising for "fast" settings are described in sequel.

Numerical phenomena inconsistent with physical behavior

(i) The effect of "lossing" a mass, i.e. we meet the condition (4.3) (for $\mathbf{v} \neq 0$ the inequality) with the opposite sign that the one corresponding to physically consistent behavior.

(ii) The steady concentration on the outflow (on mesh accuracy $k = 8$) reads as 91.21% which is far exceed.

(iii) The values of $c_i, \theta_i, i = 1, 2, 3$ are expected to be determined by initial values. In this sense, we require for the setting 2 the values $c_i \in [0, 1]$ and $\theta_i \in [0, 0.5]$ for $i = 1, 2, 3$.

(iv) Divergence of the method for the values $\theta_i^0 \sim 1$.

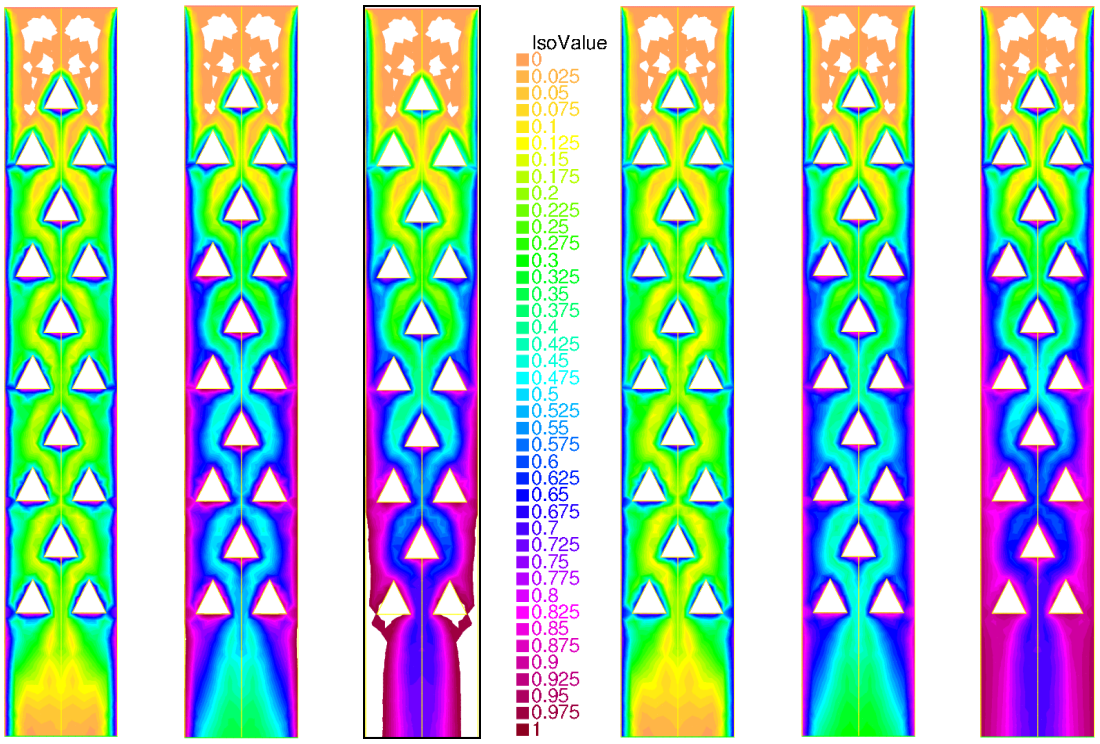
Some of the corrections of the methods are dependent on the accuracy of the discretization, namely fineness of the mesh and size of the time step. Let us mention that in case of the

reaction-diffusion systems in form $\partial_t u - \Delta u = \kappa^{re} u^2$ is the magnitude of the coefficient κ^{re} critical and many numerical methods require for $\kappa^{re} >> 1$ the time-step $\Delta t << \frac{1}{\kappa^{re}}$ which can lead to incapacity of numerical computations. The overview of the observed behavior and effects for P/U and N/U method can be found in the following table

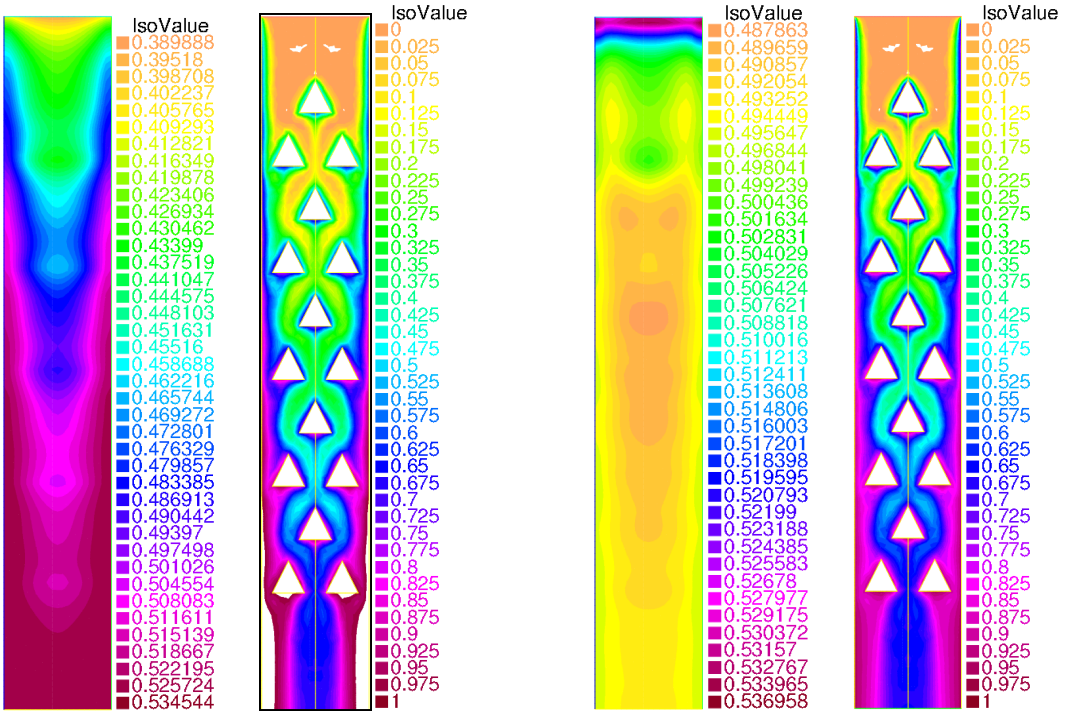
Overview for "fast" settings	Projection/Upwind	Newton/Upwind
Condition (4.3)	–	+
Behavior for $t \to \infty$	–	+
Consistency for $\theta \sim 1$	–	+
Physically correct ranges	–	(+)
Response on a refinement	(+)	+
CPU requirements	+	–

where the physically correct ranges can be obtained by a mesh-refinement in case of N/U method and P/U method responses positively on a mesh (resp. time) refinement but much less efficiently that N/U method.

Note to figure (4.4)**.** *On the picture below, we present the numerical results for "fast" setting 2. Since we expect* $c_i \in [0, 1]$*, the other values are not displayed - hence the white color spots. The spots near the top inflow (under* 0*) can be reduced by refining the mesh. This holds for both methods. On the other hand, for P/U method we have an overflow (above* 1*) of the values near the outflow (bottom). Although the refinement shows an improvement in both considered domains, the error neat the bottom is still relatively big.*



(a) $t = 0.5$ profile-cut c_1 (b) $t = 1$ profile-cut c_1 (c) $t = 3$ profile-cut c_1 **k = 8** (d) $t = 0.5$ profile-cut c_3 (e) $t = 1$ profile-cut c_3 (f) $t = 3$ profile-cut c_3



(g) $t = 3$ side-cut θ_3 (g) $t = 3$ profile-cut c_3 **k = 9** (i) $t = 3$ side-cut θ_3 (j) $t = 3$ profile-cut c_3

Figure 4.4: The results for P/U method (left) and N/U method (right) for setting 2.

4.4.3 Discussion

As we can see the employment of strong velocity field, resp. fast reactions, harm the accuracy of both method but it has much bigger impact on Projection/Up-wind method. This is to expected from analytical conditions needed for the existence of a weak solution - see Theorem (3.4) - were we consider bound for κ^{re}. The results of both method can be make more closer if we use more refined mesh or smaller time step. Especially in case of very fast reactions the smaller time-step on the beginning of evolution is strongly recommended. The difference of the method occurs especially in the first time-step where the Projection/Up-wind method take disadvantage of "using old values" for treating the nonlinearities. This cannot be treated by mesh-refining but need to be done by use a smaller time-step.

Let us mention, that in real industrial models [5] is much bigger ratio between a surface and volume of the microchannel and therefore the catalysis has much more efficiency that in our case and $\kappa^{re} < 1$.

Nevertheless, even with this disadvantage of Projection/Up-wind method, in real applications both method correctly demonstrate the evolution of occurring physical phenomena and in addition, both satisfy range condition for the setting 1, i.e. for used settings both methods keep all the values c_i, θ_i in range $[0, \alpha]$ where alpha is the constant depending on initial and inflow conditions. For the setting 2 the accuracy of P/U method is limited and we recommend to use N/U method. In real applications of these methods one has to keep on his mind that more accurate and sophisticated N/U method requires $3 - 10$ times more CPU-time that the linear P/U method.

Remark 4.4. *The txt documents with the full program-implementation written in FreeFem++ including both discussed methods are contained in attached DVD.*

[5] Where the ratio between width and length of the microchannel is usually between 1 : 100 and 1 : 1000.

5. Conclusion

We have build a physical model for heterogeneous catalysis consisted of solid-state catalyst and liquid mixture reactants whose flow is driven by a stationary velocity field. We considered an isothermal state where sorption effects meet the Langmuir-Hinshelwood kinetics; elementary surface reactions satisfies the law of mass action; and diffusion fluxes are in accordance with the Fick's law. This model is especially convenient to model a flow in small-size devices as are microchannels.

In Chapter 2 we analytically investigated the simplified model of toroid-like shapes of the microchannels; we proved existence and uniqueness of a mild solution using nonlinear semigroup theory in the L^1-settings.

In Chapter 3 we proved existence of a weak solution for semi-truncated system (3.1). Under the assumption $c^{in}_{i|_\Sigma} + \kappa^{re} \leq \kappa_3$ and $c^{in}_i = const. \geq 0$, $i = 1, 2, 3$ we proved the coincidence of the system with the original system (1.8). This analytical result gives solid roots to expectation on the convergence of the numerical solution of the system (1.8) based on FEM-discretization to a precise solution.

In Chapter 4 we performed numerical computations of the problem (1.8) on a similar geometry as in the case of bio-diesel microchannels. Using several numerical methods and FreeFem++ as an integrated development environment to solve the PDE-system based on Finite Element Method, we compute the simulation of the evolution of heterogeneous catalysis in microchannels. We tried several numerical methods which were tested from analytical and physical point of view and, finally, the Newton/Up-wind method was chosen as the best candidate.

All these analytical and numerical results manifest that the Newton/Up-wind method is suitable tool to simulate an evolution of a heterogeneous catalysis in microchannels.

6. Appendix

Definitions and basic theorems

Definition 6.1. *Let X_0 be a subset of $X, \omega \in \mathbb{R}$ and $T(t), t \geq 0$, be a family of operators $X_0 \to X_0$. The family $(T(t))_{t\geq 0}$, is called a* ***strongly continuous semigroup*** *of type ω on X_0 iff the following is true:*

(i) $T(t+s)x = T(t)T(s)x$, $\forall t, s \geq 0$ *and* $x \in X_0$.

(ii) $T(0)x = x$, $\forall x \in X_0$.

(iii) The function $S(t) : [0, \infty) \to X_0$ is continuous for any $x \in X_0$,.

(iv) $\forall x, y \in X_0$ *and* $t \geq 0$ *we have*

$$|T(t)x - T(t)y| \leq e^{\omega t}|x - y|.$$

If $\omega = 0$, we call $(T(t))_{t\geq 0}$, a ***strongly continuous semigroup of contractions*** *on X_0.*

Definition 6.2. *Let X be a real Banach space and $\emptyset \neq D \subset X$. A family $(T(t))_{t\geq 0}$ of operators $T(t) : D \to D$ is called a* ***semigroup of contraction*** *on D iff*

(i) $T(t+s)x = T(t)T(s)x$, $\forall t, s \geq 0$ *and* $x \in D$.

(ii) $T(0)x = x$, $\forall x \in D$.

(iii) $\lim\limits_{t\to 0_+} T(t)x = x$, $\forall x \in D$

(iv) $|T(t)x - T(t)\tilde{x}| \leq |x - \tilde{x}|$, $\forall x, \tilde{x} \in D$ *and* $t \geq 0$

Definition 6.3. *Moreover, if A is an accretive operator in a real Banach space and satisfies the range condition $rg(I+\lambda A) \supset \overline{D(A)}$ for all $\lambda \in [0, \lambda_0], \lambda_0 > 0$ [1], then there is a particular semigroup $(S(t))_{t\geq 0}$ on $\overline{D(A)}$ associated with A, which is given by*

$$S(t)x = \lim_{n\to\infty} \left(I + \frac{t}{n}A\right)^{-n} x,$$

where the convergence is uniform for t in bounded subsets of $[0, \infty)$. In this situation $(S(t))_{t\geq 0}$ is called the semigroup generated by $-A$, resp. $-A$ is ***generator of strongly continuous semigroup****, and the function $u(t) = S(t)u_0$ with $u_0 \in \overline{D(A)}$ is the* ***mild solution of the homogeneous Abstract Cauchy Problem*** (ACP).

Moreover, we define ***domain****,* ***range*** *and* ***graph*** *in sequence as*

$$D(A) = \{x \in X : Ax \neq \emptyset\}, rg(A) = \bigcup_{x\in D(A)} Ax, gr(A) = \{(x, Ax) : x \in D(A)\}$$

Note 6.1. *For equivalent definition of the generator of strongly continuous semigroup we refer to [15, §5.3].*

Let us mentioned that for m-accretive operator the condition $rg(I+\lambda_0 A) = X$ *for some* $\lambda_0 > 0$ *is equivalent with condition* $rg(I + \lambda A) = X$ *for all* $\lambda > 0$*, see [15, Thm. 1.12]. Moreover, we often choose w.l.o.g.* $\lambda = 1$ *to obtain, by dissipativity of the operator* A*, the resolvent mapping* $R_{\lambda=1}(A) = (I + A)^{-1}$ *as a contraction.*

Definition 6.4. *Let* X *be Banach space and* A *be a generator of strongly continuous semigroup* $T(t), t \geq 0$ *on* X*. Then the map* $x(t) := T(t)x \in X$ *is the* ***unique solution*** *of* X*-valued initial value problem (or* ***homogeneous Abstract Cauchy Problem****)*

$$\begin{aligned} \dot{x}(t) &= Ax(t),\ t \geq 0, \\ x(0) &= x. \end{aligned} \tag{ACP}$$

This solution is sometimes called the ***generalized solution*** *because its regularity is not apriori given and it depends on the operator* A *and the space* X*.*

Definition 6.5. *A continuous function* $u : J \to \overline{D(A)}$*, with* $u(0) = x$*;* $f \in L^1(J; X)$*; where* $J = [t_0, T] \subset [0, T_{max})$*, is said to be a* ***mild solution of quasi-autonomous problem***

$$\begin{aligned} \dot{u}(t) &= Au(t) + f(t),\ t \in J, \\ u(t_0) &= x,\ x \in X \end{aligned} \tag{QA}$$

if u *is uniform limit of* ε*-DS-approximate solutions* u^ε *as* $\varepsilon \to 0_+$*.*

Note 6.2. *By* ε*-DS-approximate solution* u^ε *of* (QA) *we understand a step function* u^ε *with* $u^\varepsilon(t) = u_k$ *on* $(t_{k-1}, t_k], k = 1, .., m$*;* $u^\varepsilon(t_0) = u_0 = x$*, where* u_k *is a solution of the implicit difference scheme*

$$\frac{u_k - u_{k-1}}{t_k - t_{k-1}} + Au_k = z_k,\ k = 1, .., m,$$

where $\{t_k\}_{k=0}^m$ *is a partition of the interval* $[t_0, T]$ *with a norm of the partition* $\leq \varepsilon$*; and* $z_k \in X$ *such that* $\sum\limits_{k=1}^{m} \int\limits_{t_{k-1}}^{t_k} |z_k - f(t)|dt \leq \varepsilon$*.*

Note 6.3. *The mild solution is said to be* ***global*** *if there is a mild solution of on* $J = [0, \alpha]$ *for any choice of* $\alpha > 0$*.*

Definition 6.6. *Furthermore, we introduce an* ***integral solution*** *of* (QA) *as a function* $u \in \mathcal{C}(J; X), u(0) = x$ *if all the following inequalities hold:*

$$|u(t) - x| \leq |u(s) - x| + \int_s^t [u(\tau) - x, f(\tau) - Ax]d\tau,\ \forall\ t_0 \leq s \leq t \leq T.$$

Moreover, when A *is m-accretive, the concept of mild solution of* (QA) *coincides with integral solution.*

[1] This condition is trivially satisfied when A is an m-accretive operator.

Note 6.4. *Let us mentioned that in case of A being linear, m-accretive, densely defined operator, and $(T(t))_{t\in J}$ a $\mathcal{C}_0$-semiproup generated by $-A$; we define for $f \in L^1(J;X)$ the mild solution of* (QA) *as a continuous function $u : J \to X$ such that*

$$u(t) = T(t)x + \int_{t_0}^{t} T(t-\tau)f(\tau), t \in J.$$

Definition 6.7. *A single-valued operator A in a real Banach space X is said to be* ***accretive*** *iff*

$$\|x - \tilde{x} + \lambda(Ax - A\tilde{x})\|_X \geq \|x - \tilde{x}\|_X, \forall \lambda \geq 0,\ x, \tilde{x} \subset D(A)$$

while A is said to be ***m-accretive*** *iff $rg(I + \lambda A) = X$ for all (or, equivalently, for some) $\lambda > 0$. Furthermore, an operator A is* ***dissipative*** *iff $-A$ is accretive.*

Note 6.5. *Let us mentioned that the common definition of a dissipative operator, i.e.*

$$\|\lambda(x - \tilde{x}) - (Ax - A\tilde{x})\|_X \geq \lambda\|x - \tilde{x}\|_X, \forall \lambda \geq 0,\ x, \tilde{x} \subset D(A).$$

is equivalent with the definition above. Moreover, the operator simultaneously dissipative and accretive is said to be ***conservative****.*

Definition 6.8. *For X being a real Banach space and X' its dual, let us denote*

$$J(x) := \left\{x' \in X' : \|x'\|_{X'}^2 = \|x\|_X^2 = \langle x', x\rangle\right\}.$$

Then, a single-valued operator A is said to be ***accretive*** *iff $\forall x, \tilde{x} \in D(A)$ there exists a $x', \tilde{x}' \in J(x)$ such that*

$$\langle x - \tilde{x}, Ax' - A\tilde{x}'\rangle \geq 0. \qquad (*)$$

Let us mentioned that for X being Hilbert space with scalar product $(\cdot,\cdot)$, the set $J(x)$ consists one element only, and we can reformulate previous condition (*) *as follows*

$$(x - \tilde{x}, Ax - A\tilde{x}) \geq 0, \forall x, \tilde{x} \in D(A). \qquad (**)$$

Moreover, if (*) *holds for all $x' \in J(x)$, resp.* (**) *in case of Hilbert space, then A is said to be* ***s-accretive****.*

Definition 6.9. *Let $(X, \|\cdot\|_X, \leq)$ is a Banach lattice. Denoting $x^+ = \sup\{x, 0\}$, the operator A is said to be* ***T-accretive*** *iff*

$$\|(x - \tilde{x} + \lambda(Ax - A\tilde{x}))^+\|_X \geq \|(x - \tilde{x})^+\|_X,\ \forall \lambda > 0, x, \tilde{x} \in D(A).$$

Definition 6.10. ***Bracket-notation****, which represents in some sense a generalization of a scalar product for a general Banach space X, is defined by*

$$[x, y]_X := \lim_{h \to 0_+} \frac{\|x + hy\|_X - \|x\|_X}{h}.$$

Moreover, a single-valued operator A is said to be accretive iff $[u - \tilde{u}, Au - A\tilde{u}]_X \geq 0$, $\forall u, \tilde{u} \in D(A)$ which corresponds to the relation (*) *in previous definition.*

Note 6.6. *It's easy to see, that for X being Hilbert spaces is $[\cdot,\cdot]$ a scalar product. In case of $\mathcal{L}^1$ space is the situation rather simple and we can identify bracket condition for $[x,y] \geq 0$ with the condition that there exist $U^+(0,\delta)$, the right neighborhood of 0, where $\|x - hy\|_1 - \|x\|_1 \geq 0, \forall h \in U^+(0,\delta)$ which implies in limit case $h \to 0_+$ condition $\|y \cdot \mathrm{Sgn}(x)\|_1 \geq 0$. In other words, for the operator considered in our case, where $u = \begin{bmatrix} u_1 \\ u_2 \end{bmatrix}$ and $w = \begin{bmatrix} w_1 \\ w_2 \end{bmatrix}$, we receive*

$$[u,w]_X = \max \int_\Omega w_1(x)\mathrm{Sgn}[u_1(x)] + \max \int_\Sigma w_2(x)\mathrm{Sgn}[u_2(x)] \geq 0.$$

The function Sgn *represents the generalization of signum function in more dimensional space. It is defined by*

$$\mathrm{Sgn} : \mathbb{R} \to \mathbb{R} \text{ with } \mathrm{Sgn}(x) := \begin{cases} 1 & \text{if } x > 0, \\ [-1,1] & \text{if } x = 0, \\ -1 & \text{if } x < 0. \end{cases}$$

Note 6.7. *The similar analogue can be done in case of T-accretivity using Heaviside function instead of* Sgn *function. For real Banach spaces $L^1(\Omega), L^1(\Sigma)$ both equipped with natural ordering $\leq$ we call A a T-accretive operator iff $[x - \tilde{x}, Ax - A\tilde{x}]_+ \geq 0, \forall x, \tilde{x} \in X$ where $x^+ = \sup\{x, 0\}$ and*

$$[u,w]_+ = \left[\begin{bmatrix} c \\ \theta \end{bmatrix}, \begin{bmatrix} \tilde{c} \\ \tilde{\theta} \end{bmatrix} \right]_+ = \int\limits_{\{c=0\}\cap\Omega} \tilde{c}^+ \,\mathrm{d}\omega + \int\limits_{\{c>0\}\cap\Omega} \tilde{c}\,\mathrm{d}\omega + \int\limits_{\{\theta=0\}\cap\Sigma} \tilde{\theta}^+ \,\mathrm{d}\sigma + \int\limits_{\{\theta>0\}\cap\Sigma} \tilde{\theta}\,\mathrm{d}\sigma.$$

Definition 6.11. *Let A, B are single-valued operator in a real Banach space X, both generally non-linear. We say that B is* ***locally A-bounded with L-bound*** < 1 *if $D(A) \subset D(B)$ and for each $x \in \overline{D(A)}$ there are a neighborhood U of x and constants $K \geq 0, L \geq 0$ with $L < 1$ s.t.*

$$\|Bu\|_X \leq K + L\|Au\|_X, \ \forall u \in D(A) \cap U$$

Definition 6.12. *Let A, B are single-valued operators in Banach space X. We say that operator B satisfies the local Lipschitz conditions (L.1), resp. (L.2), iff*

(L.1) $D(A) \subset D(B)$, and for each $x \in D_a(A)$ and each $M > 0$ there are a neighborhood U of x and a constant $K \geq 0$ such that

$$\|Bu - Bv\| \leq K\|u - v\|$$

whenever $u, v \in D(A) \cap U, \|Au\| \geq M$ and $\|Av\| \leq M$.

(L.2) $D(A) \subset D(B)$, and for each $x \in D_a(A)$ and are a neighborhood U of x and a constant $K \geq 0$ and $L > 0$ such that

$$\|Bu - Bv\| \leq K\|u - v\| + L\|Au - Av\| \ \forall u, v \in D(A) \cap U.$$

In following part we will recall some standard theorems of linear and non-linear semigroups. There are a lot of different but more or less equivalent versions. I chose that ones which I consider the most suitable for our situation.

Theorem: Hille, Yoshida 6.1. *Let A be a linear operator on X and $M \geq 0, \omega \in \mathbb{R}$ be constants. Then the following two statements are equivalent:*

(a) A is the infinitesimal generator of a $\mathcal{C}_0$ - semigroup

(b) A is closed, densely defined operator with $(\omega, \infty) \subset \rho(A)$ and

$$\|(\lambda I - A)^{-n}\|_X \leq \frac{M}{(\lambda - \omega)^n}, \text{ for } \lambda > \omega,\ n \in \mathbb{N}$$

For $M = 1$ we speak about A as a generator of $\mathcal{C}_0$ - semigroup of contractions.

If we use concept of accretivity we require these to hold for an operator $-A$.

Theorem: Lumer, Phillips 6.2. *For dense defined, dissipative operator $(A, D(A))$ on Banach space A the following statements are equivalent.*

(a) The closure $\overline{A}$ of A generates a contraction semigroup

(b) $rg(\lambda - A)$ is dense in X for some (hence all) $\lambda > 0$.

Note 6.8. *If we use instead of dissipativity the concept of accretivity, we require A accretive instead of dissipative and we replace (b) by (b'):*

(b') $rg(I + \lambda A)$ is dense in X for some (hence all) $\lambda > 0$

.

Theorem: Crandall, Liggett 6.3. *Assume that A is accretive operator on X, which satisfies the range condition*

$$\overline{D(A)} \subset rg(I + \lambda A) \text{ for sufficient small } \lambda > 0.$$

Then there exists a strongly continuous semigroup $T(t), t \geq 0$, of contractions on $\overline{D(A)}$. Moreover, for $x \in \overline{D(A)}$ we have the exponential formula

$$T(t)x = \lim_{\lambda \to 0_+} (I + \lambda A)^{\frac{t}{\lambda}} x \text{ uniformly on bounded } t\text{- intervals}, \qquad (*)$$

and for $x \in D(A)$, the estimate

$$|T(t)x - T(s)x| \leq |t - s| \cdot \|Ax\|,\ \forall t, s \geq 0.$$

Note 6.9. *The original Crandall-Liggett formulation of the assertion (*) read as*

$$\lim_{n \to \infty} (I + \frac{t}{n} A)^{-n} x \qquad (**)$$

exists for $x \in \overline{D(A)}$, $t \geq 0$. Moreover, if $T(t)x$ is defined as the limit in (**) , then $T(t), t \geq 0$, is strongly continuous semigroup of contractions.

Adjoint corollary 6.4. *Let $(A, D(A))$ be a densely defined operator on Banach space X. If both A and its adjoint A^* are dissipative, then the closure $\overline{A}$ of A generates a contraction semigroup on X.* [2]

Kobayasi perturbation theorem 6.5. *Assume that (generally multivalued) A is m-dissipative and that B is dissipative, locally A-bounded with A-bound < 1 and satisfies local Lipschitz condition (L.1) or (L.2). If at least one of A or B is dissipative in the sense of Browder, then $A + B$ in m-dissipative and $D_a(A + B) = D_a(A)$.*

Very often will be our aim to show that an operator A considered in A is m-accretive. To do that we have basically two possibilities which both will be used in sequel. The first takes advance by corollary (6.4).

The second one is direct consequence of the combination of Hille-Yoshida and Lumer-Phillips theorem In other words for linear, closed, densely defined operators holds, that the m-accretivity, where we require the condition $\mathrm{rg}(\lambda + \mathrm{A}) = \mathrm{X}$, is equivalent to satisfying the resolvent equation on a dense subset of X.

[2] For proof see e.g. [11, 3.17].

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