Crystal dissolution and precipitation in porous media: pore scale analysis

Citation for published version (APA):

Document status and date:
Published: 01/01/2003

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain.
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 29. Mar. 2019
CRYSTAL DISSOLUTION AND PRECIPITATION IN POROUS MEDIA: PORE SCALE ANALYSIS

C. J. VAN DUIJN AND I. S. POP

Abstract. In this paper we discuss a pore scale model for crystal dissolution and precipitation in porous media. We consider first general domains, for which existence of weak solutions is proven. For the particular case of strips we show that free boundaries occur in the form of dissolution/precipitation fronts. As the ratio between the thickness and the length of the strip vanishes we obtain the upscaled reactive solute transport model proposed in [12].

1. Introduction

This work is motivated by the crystal dissolution and precipitation model introduced in [12]. In that paper the authors present a macroscopic (core-scale) model, describing transport of ions by fluid flow in a porous medium while undergoing dissolution and precipitation reactions. The particularity of the model is in the description of the chemistry, which involves a multi-valued dissolution rate function. This leads to the occurrence of free boundaries (dissolution/precipitation fronts) that were discussed in [17] (equilibrium conditions) and in [3] (travelling waves).

If the dissolution rate were a linear term, the model proposed in [12] would fit in the class of porous media transport models with (non-)equilibrium adsorption. Such models received much attention during the past years: e.g. see [4], [1], [2], [6], [8], or [13].

All these papers are concerned with the upscaled formulation of the phenomena. A rigorous justification, starting from a well-posed microscopic (pore-scale) model and applying a suitable upscaling, has been given for important classes of problems. For instance, [9] deals with homogenization as a method for upscaling and contains an overview with particular emphasis on porous media flow including chemical reactions. In this respect we also mention [10], where the reaction rates and isotherms are linear (see also [18]), or [11], where nonlinear cases as well as multi-valued interface conditions are analyzed.

In this paper we study the pore-scale analogue of the model proposed in [12]. It builds on Stokes flow in the pores, transport of dissolved ions
by convection and diffusion, and dissolution/precipitation reactions on the surface of the porous skeleton (grains). The latter are described by an ordinary differential equation involving the multi-valued dissolution rate.

This paper is organized as follows. In the remainder of this section we present the model and recast it in a suitable dimensionless form. In Section 2 we use regularization techniques and a fixed point argument to obtain existence of a weak solution in general domains. The results of this section are a first step towards a rigorous justification of the macroscopic model in [12]. In a forthcoming paper we consider the second (homogenization) step, including various aspects of solute dispersion.

A particular geometry (a two-dimensional strip) is considered in Section 3. For certain initial and boundary data we show the occurrence of a dissolution front on the grain surface and we prove some qualitative properties. In case of over-saturation a precipitation front occurs with similar qualitative behavior. For a better understanding of the upscaled model we consider thin strips in Section 4. For vanishing width/length ratio, we end up with the model discussed in [12], [3] and [4] and thus provide existence of a suitable weak solution. For completeness we also show uniqueness.

Finally, in Section 5, a numerical example is presented. The results are in good agreement with the theory.

1.1. Model equations. We consider a porous medium at the pore scale, with $\Omega \subset \mathbb{R}^d$ ($d > 1$) denoting the void region. This region is occupied by a fluid in which cations ($M_1$) and anions ($M_2$) are dissolved. The boundary of $\Omega$ has an internal part ($\Gamma_G$), which is the surface between the fluid and the porous matrix (grains), and an external part, which is the outer boundary of the domain.
In a precipitation reaction, \( n \) particles of \( M_1 \), and \( m \) particles of \( M_2 \) can precipitate in the form of one particle of a crystalline solid \( M_{12} \), which is attached to the surface of the grains and thus is immobile. The reverse reaction of dissolution is also possible.

We assume that the flow geometry, as well as the fluid density and viscosity (\( \mu > 0 \), given) are not affected by the reactions and that the flow is described by the Stokes equations relating the fluid velocity \( \vec{q} \) and fluid pressure \( p \):

\[
\begin{align*}
\mu & \Delta \vec{q} = \nabla p, \\
\nabla \cdot \vec{q} & = 0,
\end{align*}
\]

in \( \Omega \).

Along the internal grain boundary we assume a no-slip condition, implying

\[
\vec{q} = \vec{0} \quad \text{along } \Gamma_G.
\]

Let \( c_i \) be the volumetric molar concentration of \( M_i \) in \( \Omega \) and \( c_{12} \) the surface molar concentration of \( M_{12} \) on \( \Gamma_G \). Assuming that both types of ions have the same diffusion coefficient \( D > 0 \) and since crystals are only present on the grains, mass conservation for \( M_i \) gives

\[
\partial_t c_i + \nabla \cdot (\vec{q} c_i - D \nabla c_i) = 0, \quad \text{in } \Omega.
\]

On the interior boundary \( \Gamma_G \) the flux of \( c_i \) is directly related to changes in crystalline concentration \( c_{12} \). Using (1.2) we have

\[
\partial_t c_{12} = -\frac{1}{n} D \vec{\nu} \cdot \nabla c_1 = -\frac{1}{m} D \vec{\nu} \cdot \nabla c_2 \quad \text{on } \Gamma_G,
\]

where \( \vec{\nu} \) denotes the normal unit vector pointing into the grains.

A second equation for \( c_{12} \) results from a description of the precipitation and dissolution processes. Following the detailed discussion in Knabner et al. [12] (see also [3] and [4]), we have

\[
\partial_t c_{12} = r_p - r_d \quad \text{on } \Gamma_G.
\]

Here \( r_p \) denotes the precipitation rate expressed by

\[
r_p = k_p r(c_1, c_2),
\]

where \( k_p \) is a positive rate constant and \( r \) a rate function depending on \( c_1 \) and \( c_2 \). A typical example is mass action kinetics leading to

\[
r(c_1, c_2) = c_1^n c_2^m.
\]

The dissolution rate \( r_d \) is constant (\( k_d > 0 \)) in the presence of crystal, i.e. for \( c_{12} > 0 \) somewhere on \( \Gamma_G \), and has to be such that in the absence of crystal the overall rate is zero (for a fluid that is not oversaturated,
i.e. $r(c_1, c_2) \leq k_d/k_p$). To achieve this we introduce the set-valued expression

$$r_d(c_{12}) \in k_dH(c_{12}),$$

where $H$ denotes the Heaviside graph,

$$H(u) = \begin{cases} 
0, & \text{if } u < 0, \\
[0, 1], & \text{if } u = 0, \\
1, & \text{if } u > 0.
\end{cases}$$

If $c_1$ and $c_2$ are such that

$$r(c_1, c_2) > \frac{k_d}{k_p} \text{ somewhere on } \Gamma_G,$$

we have oversaturation and precipitation ($\partial_t c_{12} > 0$) will occur at such points. If the concentrations $c_1$ and $c_2$ are below the solubility product, i.e.

$$r(c_1, c_2) < \frac{k_d}{k_p} \text{ somewhere on } \Gamma_G,$$

while crystal is present, we have $\partial_t c_{12} < 0$ at such points and dissolution occurs. If it also happen that $c_{12} = 0$, we set

$$r_d = \frac{k_p}{k_d}r(c_1, c_2) < 1,$$

implying $\partial_t c_{12} = 0$. Summarizing this discussion we have for the crystalline solid the equation

$$(1.6) \quad \partial_t c_{12} \in k_d\left(\frac{k_p}{k_d}r(c_1, c_2) - H(c_{12})\right) \text{ on } \Gamma_G.$$ 

1.2. Dimensionless form. The unknowns in the model are the fluid velocity $\vec{q}$ and fluid pressure $p$, which can be determined without a-priori knowledge of dissolution/precipitation, and the concentrations $c_1$, $c_2$ and $c_{12}$. We note that the total negative charge

$$(1.7) \quad c = mc_1 - nc_2,$$

is a conserved quantity with respect to the reactions. Indeed, (1.3) and (1.4) imply

$$\partial_t c + \nabla \cdot (\vec{q}c - D\nabla c) = 0 \quad \text{in } \Omega,$$

and

$$D\vec{p} \cdot \nabla c = 0 \quad \text{on } \Gamma_G.$$ 

Putting appropriate conditions on $c_1$ and $c_2$ along the outer boundary of $\Omega$, and thus on $c$, the total charge in (1.7) can be determined a-priori as well. With respect to the reactions, the essential variables therefore are $c_1$ (say) and $c_{12}$. The other concentration ($c_2$) follows directly from (1.7).
Let $\hat{c}_1$ and $\hat{c}_{12}$ be reference values for the concentrations of cation $c_1$ and precipitate $c_{12}$. Further, let $Q_R$, $P_R$ and $L_R$ be reference values for flow, pressure and distance. We scale length with $L_R$ and time with $L_R/Q_R$. To explicit the role of the length scale we distinguish between the original domain $\Omega^\text{real}$ and the original interior surface $\Gamma_G^\text{real}$, and their scaled counterparts $\Omega$ and $\Gamma_G$, respectively. They are related by

\begin{equation}
\Omega := \Omega^\text{real}/L_R^d \quad \text{and} \quad \Gamma_G := \Gamma_G^\text{real}/L_R^{d-1},
\end{equation}

where $d$ is the dimension of the flow domain. Setting

\begin{align*}
u := \frac{c_1}{\hat{c}_1}, & \quad v := \frac{c_{12}}{\hat{c}_{12}}, \quad c = \frac{c}{\hat{c}_1}, \\
\tilde{q} := \frac{\tilde{q}}{Q_R}, & \quad p := \frac{p}{P_R}, \quad \mu = \frac{\mu Q_R}{P_R L_R}, \\
D := \frac{D}{L_R Q_R}, & \quad k := \frac{k_d L_R}{Q_R \hat{c}_{12}}, \\
\varepsilon := \frac{\hat{c}_{12}}{L_R \hat{c}_1}, \quad \text{and} \quad r(u, c) := \frac{k_d}{k_d}(\hat{c}_1 u, \hat{c}_1 (mu - c)/n),
\end{align*}

gives in the scaled domain $\Omega$ the set of equations

\begin{equation}
\begin{cases}
\mu \Delta \tilde{q} = \nabla p, \\
\nabla \cdot \tilde{q} = 0, \\
\partial_t c + \nabla \cdot (\tilde{q} c - D \nabla c) = 0, \\
\partial_t u + \nabla \cdot (\tilde{q} u - D \nabla u) = 0.
\end{cases}
\end{equation}

On the scaled interior boundary $\Gamma_G$ we have

\begin{equation}
\begin{cases}
\tilde{q} = 0, \\
\nabla \cdot \tilde{q} = 0, \\
-D \tilde{q} \cdot \nabla u = \varepsilon n \partial_t v, \\
\partial_t v = k(r(u, c) - w), \\
w \in H(v).
\end{cases}
\end{equation}

Remark 1.1. The auxiliary function $w$ plays the role of the scaled dis-\mbox{s}olution rate $r_d/k_d$. At boundary points where $v > 0$, $w$ attains its maximal value ($w = 1$). At points where $v = 0$ and $\partial_t v = 0$ we have $w = r(u, c)$. \hfill \Box

Remark 1.2. It seems natural to choose the reference values $\hat{c}_1$ and $\hat{c}_{12}$ such that the system contains about the same number of moles for both
crystals and solutes. Mathematically this is expressed by
\[ \hat{c}_{12} \text{meas}(\Gamma_{G}^{\text{real}}) \approx \hat{c}_1 \text{meas}(\Omega^{\text{real}}). \]

Using the above definition of \( \varepsilon \) we find
(1.11a) \[ \varepsilon L_R \text{meas}(\Gamma_{G}^{\text{real}}) \approx \text{meas}(\Omega_{G}^{\text{real}}), \]
and after scaling (1.8)
(1.11b) \[ \varepsilon \text{meas}(\Gamma_G) \approx \text{meas}(\Omega), \]
implies in particular that \( \varepsilon \text{meas}(\Gamma_G) \) is uniformly bounded with re-
pect to \( \varepsilon \). Further we note that \( \varepsilon \) can be considered as the ratio of two
length scales: the characteristic pore scale \( \text{meas}(\Omega_{G}^{\text{real}})/\text{meas}(\Gamma_{G}^{\text{real}}) \)
and the problem related reference scale \( L_R \). The balance (1.11b) is
quite natural for a porous medium, where \( \text{meas}(\Gamma_G) \) denotes the total
(scaled) surface of the porous skeleton and \( \text{meas}(\Omega) \) the total (scaled)
void volume. For instance, if the medium is \( \varepsilon \)-periodic one has \( \text{meas}(\Omega) /
\text{meas}(\Gamma_G) = O(\varepsilon) \). This also holds in the case of thin strips, which
we consider in Section 4. When upscaling to a macroscopic model, the
total internal surface goes to infinity as \( \varepsilon \to 0 \). The appearance of \( \varepsilon \)
in the boundary flux in (1.10) allows us to control this growth. We
will need it when considering thin strips, and it will be needed when
homogenizing periodic structures (e.g. see [9]).

Remark 1.3. In the estimates that follow we pay special attention to
the role of \( \varepsilon \). In particular we indicate which of the constants are
\( \varepsilon \)-independent. This is useful for later purposes.

2. Analysis in general domains

Let \( \Omega \) be an open, connected and bounded domain in \( \mathbb{R}^d \). Its bound-
dary \( \partial \Omega \) is Lipschitz continuous and consists of three disjoint parts:
the internal (grain) boundary \( \Gamma_G \) and the external boundary where
Dirichlet (\( \Gamma_D \)) or Neumann (\( \Gamma_N \)) conditions are prescribed. Thus
\[ \partial \Omega = \Gamma_D \cup \Gamma_N \cup \Gamma_G \]
where both \( \Gamma_G \) and \( \Gamma_D \cup \Gamma_N \) have positive measure.

Further, \( \vec{v} \) denotes the outer normal to \( \partial \Omega \) and \( T > 0 \) a fixed but
arbitrarily chosen value of time. We consider stationary flow in the
domain \( \Omega \) and time dependent transport in the cylinder
\[ \Omega^T = (0, T] \times \Omega. \]
The various boundaries in time–space are denoted by \( \Gamma^T_X \), with \( X = G, 
D \) or \( N \). Their union is \( \partial \Omega^T \).

The model under consideration has four components:
Fluid flow:

\[
\begin{aligned}
\mu \Delta \vec{q} &= \nabla p, & \text{in } \Omega, \\
\nabla \cdot \vec{q} &= 0, & \text{in } \Omega, \\
\vec{q} &= \vec{q}_0, & \text{on } \Gamma_G, \\
\vec{q} &= \vec{q}_D, & \text{on } \Gamma_D, \\
\vec{v} \cdot \vec{q} &= 0, & \text{on } \Gamma_N;
\end{aligned}
\]

Total charge transport:

\[
\begin{aligned}
\partial_t c + \nabla \cdot (\vec{q} c - D \nabla c) &= 0, & \text{in } \Omega^T, \\
\vec{v} \cdot \nabla c &= 0, & \text{on } \Gamma_G^T, \\
c &= c_D, & \text{on } \Gamma_D^T, \\
\vec{v} \cdot \nabla c &= 0, & \text{on } \Gamma_N^T, \\
c &= c_I, & \text{in } \Omega, \text{ for } t = 0;
\end{aligned}
\]

Ion transport:

\[
\begin{aligned}
\partial_t u + \nabla \cdot (\vec{q} u - D \nabla u) &= 0, & \text{in } \Omega^T, \\
-D \vec{v} \cdot \nabla u &= \varepsilon n \partial_t v, & \text{on } \Gamma_G^T, \\
u &= u_D, & \text{on } \Gamma_D^T, \\
\vec{v} \cdot \nabla u &= 0, & \text{on } \Gamma_N^T, \\
u &= u_I, & \text{in } \Omega, \text{ for } t = 0,
\end{aligned}
\]

Precipitation/dissolution:

\[
\begin{aligned}
\partial_t v &= k(r(u,c) - w), & \text{on } \Gamma_T, \\
w &\in H(v), & \text{on } \Gamma_T, \\
v &= v_I, & \text{on } \Gamma_G, \text{ for } t = 0.
\end{aligned}
\]

With respect to the reaction rate function \( r(u,c) \) in (2.4) we assume:

\( (A_r) \)

(i) \( r : \mathbb{R}^2 \to [0, \infty) \) is locally Lipschitz in \( \mathbb{R}^2 \);

(ii) \( r(u,c) = 0 \) for all \( u \leq 0 \);

(iii) for each \( c \in \mathbb{R} \) there exists a unique \( u_* = u_*(c) \geq 0 \), with \( u_*(c) = 0 \) for \( c \leq 0 \) and \( u_* \) is strictly increasing for \( c > 0 \), such that

\[
r(u,c) = \begin{cases} 
0, & \text{for } u \leq u_*, \\
\text{strictly increasing for } u > u_* \text{ with } r(\infty,c) = \infty;
\end{cases}
\]

(iv) for each \( u > 0 \), \( r(u,c) \) strictly decreases with respect to \( c \) whenever \( r > 0 \).
Example. Assuming mass action kinetics (1.5), replacing \( c_i \) by its non-negative part \([c_i]_+\) and using (1.7), we obtain

\[
(2.5) \quad r(u, c) = K \left( [u]_+ \right)^m \left( \left[ \frac{mu - c}{n} \right]_+ \right)^n,
\]

for some \( K > 0 \). Here \( u_*(c) = \frac{|c|_+}{m} \). This example is sketched in Figure 2.

Concerning the data we assume:

\[(A_D) \quad \text{Boundary and initial data are bounded; for } u \text{ and } v \text{ these are also non-negative; all boundary data are constant in time and traces of } H^1 - \text{functions.}\]

Remark 2.1. Since \( u \) and \( v \) model concentrations, the sign assumptions and boundedness are not restrictive for applications. We consider here constant in time boundary data to avoid non essential technical details. \( \square \)

Remark 2.2. To express \( u = u_D \) on \( \Gamma_D \), for instance, we use below the well-known notation

\[
 u \in u_D + H^1_{0, \Gamma_D}(\Omega),
\]

where \( u_D \) is the \( H^1 \)-extension of the Dirichlet boundary condition. \( \square \)

2.1. Results concerning flow and total charge. Since chemistry does not affect flow, the Stokes system (2.1) can be treated independently from the ion transport. We follow [20] and obtain the existence
of a unique weak solution \( \bar{q} \in \bar{q}_D + \left( H^1_{0,\Gamma_D}(\Omega) \right)^d \) satisfying \( \nabla \cdot \bar{q} = 0 \) in \( \Omega \), \( \bar{q}|_{\Gamma_G} = \bar{0} \) and
\[
(2.6) \quad (\nabla \bar{q}, \nabla \bar{\Psi}) = 0,
\]
for all \( \bar{\Psi} \in \left( H^1_{0,\Gamma_D}(\Omega) \right)^d \) with \( \bar{\Psi}|_{\Gamma_G} = \bar{0} \) and \( \nabla \cdot \bar{\Psi} = 0 \) in \( \Omega \). Having \( \bar{q} \in (H^1(\Omega))^d \), the fluid pressure \( p \) is defined in \( L^2(\Omega) \) uniquely up to a constant.

Since the data \( \bar{q}_D \) is bounded on \( \Gamma_D \) we have:

**Lemma 2.3.** Let \( \|\bar{q}_D\|_{\infty,\Gamma_D} = M_q \). Then \( \|\bar{q}\|_{\infty,\Omega} = M_q \).

**Proof.** Testing with \( \bar{\Psi} = [\bar{q} \pm M_q]_+ \) in (2.6) yields the result. \( \square \)

With \( \bar{q} \) being defined in \( \Omega \) we consider the linear transport of the total charge \( c \). Let
\[
\mathcal{C} := \{ c \in c_D + L^2((0,T); H^1_{0,\Gamma_D}(\Omega)) : \partial_t c \in L^2((0,T); H^{-1}(\Omega)) \}.
\]
As in chapters 3.3 and 3.4 of [14], or chapter 23 of [22] we find a unique weak solution \( c \in \mathcal{C} \) of (2.2) satisfying \( c(0) = c_I \) in \( \Omega \) and
\[
(2.7) \quad (\partial_t c, \varphi)_{\Omega_T} + D(\nabla c, \nabla \varphi)_{\Omega_T} - (\bar{q}c, \nabla \varphi)_{\Omega_T} = 0,
\]
for all \( \varphi \in L^2((0,T); H^1_{0,\Gamma_D}(\Omega)) \).

Furthermore, the boundedness of the data extends to \( c \):

**Lemma 2.4.** Let \( M_c := \max\{ \|c_D\|_{\infty,\Gamma_D}, \|c_I\|_{\infty,\Omega} \} \). Then \( \|c\|_{\infty,\Omega_T} = M_c \).

**Remark 2.5.** Suppose \( \Gamma_D \) has measure 0. Then there are no prescribed values for the total charge on the boundary. With \( \chi_{(0,t)} \) denoting the characteristic function of the interval \( (0,t) \), \( \varphi \equiv \chi_{(0,t)} \) is an admissible test function in (2.7) for any \( t \leq T \). Thus we see that the total charge is a conserved quantity; i.e.
\[
\int_{\Omega} c(t,x) dx = \int_{\Omega} c_I(x) dx.
\]

\( \square \)

### 2.2. Analysis of crystal dissolution and precipitation

The chemical process is essentially modelled by (2.4) and the flux in (2.3). The main difficulty is the occurrence of the multi-valued function describing the dissolution. Let
\[
\mathcal{U} := \{ u \in u_D + L^2((0,T); H^1_{0,\Gamma_D}(\Omega)) : \partial_t u \in L^2((0,T); H^{-1}(\Omega)) \},
\]
\[
\mathcal{V} := \{ v \in H^1((0,T); L^2(\Gamma_G)) \},
\]
\[
\mathcal{W} := \{ w \in L^\infty(\Gamma_G^T), : 0 \leq w \leq 1 \}.
\]
Definition 2.1. A triple \((u, v, w) \in U \times V \times W\) is called a weak solution of (2.3) and (2.4) if \((u(0), v(0)) = (u_1, v_1)\) and if
\[
\begin{align*}
(\partial_t u, \varphi)_{\Omega^T} + D(\nabla u, \nabla \varphi)_{\Omega^T} - (\tilde{q} u, \nabla \varphi)_{\Omega^T} &= -\varepsilon n(\partial_t v, \varphi)_{\Gamma_G^T}, \\
(\partial_t v, \theta)_{\Gamma_G^T} &= k(r(u, c) - w, \theta)_{\Gamma_G^T}, \\
w &\in H(v) \quad \text{a.e. in } \Gamma_G^T,
\end{align*}
\]
for all \((\varphi, \theta) \in L^2(0, T); H^1_{0, \Gamma_D}(\Omega) \times L^2(\Gamma_G^T)\).

2.2.1. \(L^\infty\)-bounds. In view of (A.D) we expect \(u\) and \(v\) to be non-negative and bounded. These properties are shown in the following lemmas.

Lemma 2.6. The concentrations \(u\) and \(v\) are non-negative a.e. in \(\Omega^T\), respectively \(\Gamma_G^T\).

Proof. Since \(u(t) \in U_D + H^1_{0, \Gamma_D}(\Omega)\) for almost every \(0 < t < T\) and since \(u_D\) is positive, we have \([u]_- \in L^2(0, T); H^1_{0, \Gamma_D}(\Omega)\), where \([u]_-\) denotes the negative part of \(u\). For any \(0 < t < T\), we test (2.8) with \(\varphi := \chi_{(0,t)}[u]_-\) giving
\[
\frac{1}{2}||[u(t)]_-||^2_{\Omega^T} + D||\nabla [u]_-||^2_{\Omega^T} - (\tilde{q} u, \nabla [u]_-)_{\Omega^T} = \frac{1}{2}||[u]_-||^2_{\Omega^T} - \varepsilon n(\partial_t v, [u]_-)_{\Gamma_G^T}.
\]
The convection term in this expression vanishes. This follows from
\[
(\tilde{q} u, \nabla [u]_-)_{\Omega^T} = \frac{1}{2}(\tilde{q}, \nabla [u]_-)_{\Omega^T} = \frac{1}{2}(\tilde{q} \cdot \tilde{q}, [u]_-^2)_{\Gamma_G^T} + \frac{1}{2}(\tilde{q} \cdot \tilde{q}, [u]_-^2)_{\Gamma_G^T} - \frac{1}{2}(\tilde{q}^2, \nabla \cdot \tilde{q})_{\Omega^T}
\]
and the boundary conditions on \(\partial \Omega\), together with \(\nabla \cdot \tilde{q} = 0\) in \(\Omega\).

Moreover, since \(u_D \geq 0\) in \(\Omega\), the first term on the right vanishes as well. Finally, because \([u]_- \leq 0\) a.e. and belongs to \(L^2((0, T); H^1_{0, \Gamma_D}(\Omega))\), its trace \([u]_{\Gamma_G}^T\) is a non-positive \(L^2(\Gamma_G^T)\) function. Testing with \(\theta := \chi_{(0,t)}[u]_{\Gamma_G}^T\) in (2.9) gives
\[
(\partial_t v, [u]_-)_{\Gamma_G^T} = k(r(u, c) - w, [u]_-)_{\Gamma_G^T} = -k(w, [u]_-)_{\Gamma_G^T} \geq 0,
\]
where we have used (A1) and the positivity of \(w\).

Combining these observations leaves us with
\[
\frac{1}{2}||[u(t)]_-||^2_{\Omega^T} + D||\nabla [u]_-||^2_{\Omega^T} \leq 0,
\]
showing that \(u(t)\) is non-negative for all \(t \geq 0\).

Testing (2.9) with \(\theta := [v]_-\) gives the same result for \(v\).
Assumption (A_r) implies that for each \( c \in \mathbb{R} \) a unique \( u^*(c) > 0 \) exists such that
\[
r(u^*(c), c) = 1.
\]
The function \( u^* : \mathbb{R} \to \mathbb{R} \) is clearly continuous and non-decreasing. With \( M_c \) from Lemma 2.4 we define
\[
M_u := \max \{ \|u_I\|_{\infty, \Omega}, \|u_D\|_{\infty, \Gamma_D}, u^*(M_c) \}.
\]

**Lemma 2.7.** The concentration \( u \) satisfies \( u \leq M_u \) a.e. in \( \Omega^T \).

**Proof.** For any \( t \in (0, T] \) we test (2.8) with \( \varphi := \chi_{(0,t)}[u - M_u]_+ \in L^2((0, T); H^1_0(\Omega)) \) and obtain
\[
\frac{1}{2}\| [u(t) - M_u]_+ \|^2_\Omega + D\| \nabla [u - M_u]_+ \|^2_{\Gamma_D} - (\tilde{q}u, \nabla [u - M_u]_+)_{\Omega^t} + D \kappa (u - M_u)_+ - \varepsilon n(\partial_t v, [u - M_u]_+)_{\Gamma_G^t}.
\]

Arguing as in the proof of Lemma 2.6 we first observe that the convection term and the first term on the right vanish. To handle the reaction term we note that, if \( u \geq M_u \),
\[
r(u, c) \geq r(M_u, c) \geq r(M_u, M_c) \geq r(u^*(M_c), M_c) = 1.
\]
Together with the positivity of \( [u - M_u]_+ \) this implies
\[
(\partial_t v, [u - M_u]_+)_{\Gamma_G^t} = k(1 - w, [u - M_u]_+)_{\Gamma_G^t} \geq k(1 - w, [u - M_u]_+)_{\Gamma_G^t} \geq 0.
\]
Therefore we are left with
\[
\frac{1}{2}\| [u(t) - M_u]_+ \|^2_\Omega + D\| \nabla [u - M_u]_+ \|^2_{\Gamma_D} \leq 0,
\]
implying \( u \leq M_u \) a.e. in \( \Omega^T \).

As an immediate consequence we have for \( v \):

**Corollary 2.8.** Let \( M_v := \max \{ \|v_I\|_{\infty, \Omega}, 1 \} \). Then
\[
(2.10) \quad v(t, \cdot) \leq M_v e^{Ct} \quad \text{a.e. in } \Gamma_G^T
\]
for all \( 0 \leq t \leq T \). Here \( C := kr(M_u, -M_c)/M_v \).

**Remark 2.9.** On the compact set \( \{(u, c) : 0 \leq u \leq M_u, |c| \leq M_c\} \) the reaction rate function \( r(u, c) \) has the Lipschitz constant \( L_r \). Since \( r(u, c) = 0 \) for \( u \leq 0 \) we obtain the bounds
\[
0 \leq r(u, c) \leq L_r u \leq L_r M_u, \quad \text{a.e. in } \Gamma_G^T.
\]

If there are no prescribed boundary values for the ion concentration, we end up with the following mass balance:
Proposition 2.10. Let $\text{meas}(\Gamma_D) = 0$. Then
\[
\int_{\Omega} u(t, x)dx + \varepsilon n \int_{\Gamma_G} v(t, s)ds = \int_{\Omega} u_I(x)dx + \varepsilon n \int_{\Gamma_G} v_I(s)ds
\]
for all $0 \leq t \leq T$.

Proof. Testing (2.8) with $\varphi = \chi_{(0, t)} \in L^2((0, T); H^1(\Omega))$ yields directly the result.$\square$

2.2.2. Existence of a solution. To prove existence of a weak solution we replace the Heaviside graph by the Lipschitz approximation ($\delta$ being positive and small)

\[
H_\delta(v) := \begin{cases} 
0, & \text{if } v < 0, \\
n\delta, & \text{if } v \in (0, \delta), \\
1, & \text{if } v > \delta,
\end{cases}
\]
and consider the regularized problem:

Problem $P_\delta$: Find $(u, v) \in \mathcal{U} \times \mathcal{V}$, such that $(u(0), v(0)) = (u_I, v_I)$ and

\[
(\partial_t u, \varphi)_{\Omega^r} + D(\nabla u, \nabla \varphi)_{\Omega^r} - (\tilde{q} u, \nabla \varphi)_{\Omega^r} = -\varepsilon n(\partial_t v, \varphi)_{\Gamma_G^r},
\]

\[
(\partial_t v, \theta)_{\Gamma_G^r} = k(r(u, c) - H_\delta(v), \theta)_{\Gamma_G^r},
\]
for all $(\varphi, \theta) \in L^2((0, T); H^1_{0, \Gamma_D}(\Omega)) \times L^2(\Gamma_G^r)$.

We borrow some ideas of [1] to prove existence for $(P_\delta)$ with fixed $\delta > 0$. With $M_u$ and $M_v$ defined in Section 2.2.1, we consider the closed and convex sets

\[
\mathcal{K}_U := \{u \in u_D + L^2((0, T); H^1_{0, \Gamma_D}(\Omega)) : 0 \leq u \leq M_u \text{ a.e. in } \Omega^T\}, \\
\mathcal{K}_V := \{v \in \mathcal{V} : 0 \leq v \leq M_v e^{CT} \text{ a.e. in } \Gamma_G^T\}.
\]

For arbitrary $u \in \mathcal{K}_U$ we consider equation (2.12) subject to $v(0) = v_I$. Since $H_\delta$ is Lipschitz there exists a unique solution $v \in \mathcal{K}_V$. Further, given $v \in \mathcal{K}_V$, equation (2.11) with $u(0) = u_I$ has a unique solution $T u \in \mathcal{K}_U$ (see e.g. [14], chapter 5.7). In this way $u \in \mathcal{K}_U$ generates a unique $T u \in \mathcal{K}_U$, where the operator

\[
T : \mathcal{K}_U \rightarrow \mathcal{K}_U
\]
is defined by successively solving (2.12) and (2.11). Clearly, a fixed point of $T$ defines a solution of $(P_\delta)$.

We start with some a-priori estimates.
Lemma 2.11. There exists $C > 0$ such that
\[ \|T u(t)\|_{L^2(\Omega)}^2 + \|\nabla T u\|_{L^2(\Omega)}^2 + \|\partial_t T u\|_{L^2((0,t);H^{-1}(\Omega))}^2 \leq C \]
for all $0 \leq t \leq T$ and for all $u \in \mathcal{K}_U$. Here $C$ does not depend on $\delta$.

Proof. Fix an arbitrary $t \in (0, T]$ and test (2.11) with $\varphi := \chi_{(0,t)}(T u - u_D)$. Using (2.12) this gives
\[ \frac{1}{2} \int_0^t \partial_s \|T u(s) - u_D\|_{L^2(\Omega)}^2 ds + D \|\nabla T u\|_{L^2(\Omega)}^2 \]
\[ = D \int_0^t (\nabla T u(s), \nabla u_D)_{\Omega} ds + \int_0^t (\tilde{q} T u(s), \nabla (T u(s) - u_D))_{\Omega} ds \]
\[ + \varepsilon nk(\tilde{q} u, T u - u_D)_{\Gamma^c_T} - \varepsilon nk(r(u, c), T u - u_D)_{\Gamma^c_T}. \]
This expression contains six terms. Denoting them by $I_1, \ldots, I_6$ we estimate
\[ I_1 = \frac{1}{2} \left( \|T u(t) - u_D\|_{L^2(\Omega)}^2 - \|u_I - u_D\|_{L^2(\Omega)}^2 \right) \]
\[ \geq \frac{1}{4} \|T u(t)\|_{L^2(\Omega)}^2 - \frac{1}{2} \left( \|u_I\|_{L^2(\Omega)}^2 + \|u_D\|_{L^2(\Omega)}^2 \right) \]
\[ =: \frac{1}{4} \|T u(t)\|_{L^2(\Omega)}^2 - C_{I_1}. \]
The term $I_2$ needs no further estimate. For $I_3$ we have
\[ |I_3| \leq \frac{D}{4} \|\nabla T u\|_{L^2(\Omega)}^2 + D t \|\nabla u_D\|_{L^2(\Omega)}^2 \leq \frac{D}{4} \|\nabla T u\|_{L^2(\Omega)}^2 + C_{I_2}, \]
with $C_{I_2}$ chosen sufficiently large so that it is time independent.
To estimate $I_4$ we write
\[ |I_4| \leq \left| \int_0^t (\tilde{q} T u(s) - u_D, \nabla (T u(s) - u_D))_{\Omega} ds \right| + \int_0^t |(\tilde{q} u_D, \nabla T u(s))| ds + \int_0^t |(\tilde{q} u_D, \nabla u_D)| ds. \]
The first term on the right vanishes because $\nabla \cdot \tilde{q} = 0$ in $\Omega$ and $T u = u_D$ on $\Gamma_D$. The last two terms we estimate with Lemma 2.3 to obtain
\[ |I_4| \leq \frac{D}{4} \|\nabla T u\|_{L^2(\Omega)}^2 + \frac{t M_2}{2} \|u_D\|_{L^2(\Omega)}^2 + \frac{t M_2}{2} \|u_D\|_{H^1(\Omega)}^2 \]
\[ =: \frac{D}{4} \|\nabla T u\|_{L^2(\Omega)}^2 + C_{I_4}. \]
In $I_5$ the $L^\infty$–bounds of $u$ gives
\[ |I_5| \leq \varepsilon nk M_u \text{meas}(\Gamma_G) t + \varepsilon nk t \int_{\Gamma_G} |u_D| \leq C_{I_5}, \]
for $C_{I_5}$ sufficiently large. Finally, since both $T u$ and $r(u, c)$ are non–negative, Remark 2.9 implies
\[ |I_6| \leq \varepsilon nk L_v M_u t \int_{\Gamma_G} |u_D| \leq C_{I_6}, \]
again for $C_{I_6}$ large enough. Combining these estimates gives the first two inequalities of the Lemma.
To prove the last part of the lemma we notice that
\begin{equation}
|\langle \partial_t T u(t), \varphi \rangle_{\Omega}| \leq (D\|\nabla T u(t)\|_{\Omega} + M_q\|T u\|_{\Omega}) \|\nabla \varphi\|_{\Omega}
+ \varepsilon nk \left| \langle r(u(t), c) - H_\delta(v(t)), \varphi \rangle_{\Gamma_G} \right|
\end{equation}
for all \(\varphi \in H^1_0(\Omega)\) and almost all \(t > 0\). Using the \(L^\infty\)-bounds for \(u\), \(c\) and \(H_\delta\), and the trace inequality
\[\|\varphi\|_{\Gamma_G} \leq C(\Omega)\|\varphi\|_{H^1(\Omega)},\]
we obtain
\[
|\langle \partial_t T u(t), \varphi \rangle_{\Omega}| \leq \{D\|\nabla T u(t)\|_{\Omega} + M_q\|T u\|_{\Omega}
+ \varepsilon nk(1 + L_r M_u)C(\Omega)\} \|\varphi\|_{H^1(\Omega)}.
\]
Because \(\varphi \in H^1_0(\Omega)\) is arbitrary, it follows that
\[\|\partial_t T u(t)\|_{H^{-1}(\Omega)} \leq D\|\nabla T u(t)\|_{\Omega} + M_q\|T u\|_{\Omega} + \varepsilon nk(1 + L_r M_u)C(\Omega)\]
for almost every \(t > 0\). Using the first part of the lemma (proven before) gives the desired estimate.

\[\square\]

**Remark 2.12.** If (1.11b) holds, the constants in (2.14) and (2.15) can be chosen independently of \(\varepsilon\). Further, if the domain is \(\varepsilon\)-periodic we use Lemma 3 of [10], saying that there exists a constant \(C > 0\), independent of \(\varepsilon\), such that
\[\varepsilon \int_{\Gamma_G} \|\nabla \varphi\|^2_{\Gamma_G} \|\varphi\|^2_{\Gamma_G} \leq C \left( \|\varphi\|^2_{\Omega} + \varepsilon^2 \|\nabla \varphi\|^2_{\Omega} \right)^{1/2}\]
for all \(\varphi \in H^1(\Omega)\). Using this to estimate the boundary term in (2.16) yields a constant \(C\) in Lemma 2.11 which does not depend on \(\varepsilon\) as well.

\[\square\]

By similar arguments we obtain a-priori estimates for \(v\).

**Lemma 2.13.** Given \(u \in K_U\) let \(v\) denote the solution of (2.12) subject to \(v(0) = v_I\). Then there exists \(C > 0\) such that
\[\|v(t)\|_{\Gamma_G}^2 + \|\partial_t v\|_{\Gamma_G}^2 \leq C,
\]
for all \(t \in (0, T]\) and for all \(u \in K_U\). Here \(C > 0\) does not depend on \(\delta\).

**Proof.** The first part results from Corollary 2.8. The proof of the second part is similar to the last part of the proof of Lemma 2.11.

\[\square\]

**Remark 2.14.** Assuming again (1.11b), one directly deduces that the constant \(C\) in Lemma 2.13 is in fact \(\bar{C}/\varepsilon\), where \(\bar{C}\) does not depend on \(\varepsilon\).

\[\square\]
To show existence of a fixed point for $T$ we use a contraction argument. To this end we consider any $u_1, u_2 \in K_U$, with $v_1, v_2 \in K_V$ the corresponding solutions of (2.12). Further we introduce the notation

$$N(u, t) := \|u\|_{L^2((0, t); H^1(\Omega))}^2 = \|u\|_{\Gamma_t}^2 + \|\nabla u\|_{\Gamma_t}^2.$$  

By the trace inequality we have

$$\|u\|_{\Gamma_t}^2 \leq C(\Omega) N(u, t), \quad \text{for all } u \in L^2((0, T); H^1_{0, \Gamma_D}(\Omega)).$$  

The goal is to estimate $Tu := Tu_1 - Tu_2$ in terms of $u := u_1 - u_2$. We first consider the reaction equation.

**Lemma 2.15.** Let $v := v_1 - v_2$. For any $t \in (0, T]$ we have

$$\|v\|_{\Gamma_t}^2 \leq C_1 (e^t - 1) N(u, t),$$  

$$\|\partial_t v\|_{\Gamma_t}^2 \leq C_2 (t) N(u, t),$$

with $C_1 = C(\Omega) k^2 L^2$ and $C_2(t) = 2C_1 (1 + (k/\delta)^2 (e^t - 1))$. Here $L_r$ is the Lipschitz constant given in Remark 2.9 and $C(\Omega)$ is the constant from (2.17).

**Proof.** Writing (2.12) for the difference $v = v_1 - v_2$ and testing with $\theta = \chi_{(0, t)} v$ for arbitrary $0 < t \leq T$ gives

$$\frac{1}{2} \partial_t \|v\|_{\Gamma_t}^2 = k(r(u_1, c) - r(u_2, c) - (H_\delta(v_1) - H_\delta(v_2)), v)_{\Gamma_t}$$  

$$\leq k(r(u_1, c) - r(u_2, c), v)_{\Gamma_t}$$

by the monotonicity of $H_\delta$. Since $r$ is Lipschitz we have

$$\|v(t)\|_{\Gamma_t}^2 \leq 2kL_r (|u|, |v|)_{\Gamma_t} \leq k^2 L^2 \|u\|_{\Gamma_t}^2 + \|v\|_{\Gamma_t}^2$$

for all $0 \leq t \leq T$. In this expression we substitute (2.17). Direct integration gives the first estimate.

To obtain the second one we test with $\theta = \chi_{(0, t)} \partial_t v$. This gives for all $0 \leq t \leq T$

$$\|\partial_t v\|_{\Gamma_t}^2 = k(r(u_1, c) - r(u_2, c) - (H_\delta(v_1) - H_\delta(v_2)), \partial_t v)_{\Gamma_t}$$  

$$\leq kL_r (|u|, |\partial_t v|)_{\Gamma_t} + \frac{k}{2} (|v|, |\partial_t v|)_{\Gamma_t}$$  

$$\leq k^2 L^2 \|u\|_{\Gamma_t}^2 + \frac{k^2}{2} \|v\|_{\Gamma_t}^2 + \frac{1}{2} \|\partial_t v\|_{\Gamma_t}^2,$$

implying the desired estimate. \qed

Next we estimate $Tu = Tu_1 - Tu_2$. 
Lemma 2.16. For all \( t \in (0, T] \) and \( \mu > 0 \)
\[
\|Tu\|_{\Omega_t}^2 \leq \frac{\mu^3 A(t)}{\mu C_3 + C_4} \left( e^{\frac{t(\mu C_3 + C_4)}{\mu^2}} - 1 \right) N(u, t),
\]
\[
\|\nabla Tu\|_{\Omega_t}^2 \leq \frac{\mu A(t)}{D} e^{\frac{t(\mu C_3 + C_4)}{\mu^2}} N(u, t),
\]
where \( A(t) = \varepsilon^2 n^2 C_2(t)/2 \), with \( C_2(t) \) from Lemma 2.15, and where \( C_3 \) and \( C_4 \) are positive constants depending on \( \Omega \) and \( D \) but not on the regularization parameter \( \delta \).

Proof. Writing (2.11) for the difference \( Tu = Tu_1 - Tu_2 \) and testing with \( \theta = \chi_{(0, t)} Tu \) for arbitrary \( 0 < t \leq T \) gives
\[
\frac{1}{2} \|Tu(t)\|_{\Omega_t}^2 + D\|\nabla Tu\|_{\Omega_t}^2 = -\varepsilon n(\partial_t v, Tu)_{\Gamma_t \varepsilon}.
\]
Note that the convection term has disappeared. This is a consequence of (2.1) and the boundary conditions. Hence, for any \( \mu > 0 \)
\[
\frac{1}{2} \|Tu(t)\|_{\Omega_t}^2 + D\|\nabla Tu\|_{\Omega_t}^2 \leq \mu \frac{\varepsilon^2 n^2}{4} \|\partial_t v\|_{\Gamma_t \varepsilon}^2 + \frac{1}{\mu} \|Tu\|_{\Gamma_t \varepsilon}^2
\]
\[
\leq \mu \frac{\varepsilon^2 n^2}{4} C_2(t) N(u, t) + \frac{1}{\mu} \|Tu\|_{\Gamma_t \varepsilon}^2
\]
by Lemma 2.15.

Following the proof of the trace theorem, e.g. see [5], chapter 5.5 or [7], Theorem 1.5.1.10, there exists positive constants \( C_3 \) and \( C_4 \) such that
\[
\|\varphi\|_{\Gamma_t \varepsilon}^2 \leq C_3 \|\varphi\|_{\Omega}^2 + C_4 \|\varphi\|_{\Omega} \|\nabla \varphi\|_{\Omega}
\]
for all \( \varphi \in H^1_{0, \Gamma_t \varepsilon}(\Omega) \). Applying this inequality to \( \varphi = Tu \) yields
\[
\|Tu(t)\|_{\Omega_t}^2 + 2D\|\nabla Tu\|_{\Omega_t}^2 \leq \mu A(t) N(u, t) + \left( \frac{C_3}{\mu} + \frac{C_4}{\mu} \right) \|Tu\|_{\Omega_t}^2 + D\|\nabla Tu\|_{\Omega_t}^2,
\]
for an appropriately redefined \( C_4 \). Disregarding the gradient terms in this inequality, integrating the result with respect to \( t \) and using the monotonicity of \( A(\cdot) \) and \( N(u, \cdot) \), yields the first estimate of the lemma. Using it in (2.19) gives the gradient estimate.

A direct consequence of Lemma 2.16 is

Corollary 2.17. For all \( t \in (0, T] \) and \( \mu > 0 \), and for all \( u_1, u_2 \in K_U \)
\[
N(Tu_1 - Tu_2, t) \leq \mu A(t) \left[ \frac{\mu^2 e^{\frac{t(C_3 \mu + C_4)/\mu^2 - 1}}{C_3 \mu + C_4} + e^{\frac{t(C_3 \mu + C_4)/\mu^2}{D}}} \right] N(u_1 - u_2, t).
\]
The constants $C_1$, $C_3$ and $C_4$ in the estimates do not depend on the initial data. Further, taking $T$ as an upper bound for $t$, $C_2(t)$ and thus $A(t)$ can be bounded from above by a constant independent of $t$ and the initial data. Choosing now $t = \mu^2$, the estimate in Corollary (2.17) can be written as

\begin{equation}
N(T u_1 - T u_2, \mu^2) \leq \mu C N(u_1 - u_2, \mu^2),
\end{equation}

where the constant $C$ does not depend on the initial data and $\mu$. With $\mu$ small enough (but fixed) we thus have shown that $T$ is a contraction on the closed set $\{u \in u_D + L^2((0, \mu^2); H^1_0(\Omega)) : 0 \leq u \leq M_u\}$, and that it has a fixed point $u$ in this set. By Lemma 2.11, $u \in H^1((0, \mu^2); H^{-1}(\Omega))$ and satisfies its a-priori estimates. In particular $u \in C([0, \mu^2]; L^2(\Omega))$ with $0 \leq u(\mu^2) \leq M_u$. So $u(\mu^2)$ can be used as initial condition for extending the time interval of existence. Since $\mu$ does not depend on the initial data, we have obtained a fixed point of $T$ for the arbitrary time interval $(0, T)$:

**Lemma 2.18.** The fixed point $u$ of $T$ belongs to $\mathcal{K}_U \cap H^1((0, T); H^{-1}(\Omega))$, and satisfies

$$
\|u(t)\|^2_{\Omega} + \|\nabla u\|^2_{\Omega} + \|\partial_t u\|^2_{L^2((0,t);H^{-1}(\Omega))} \leq C,
$$

for all $t > 0$. Here $C > 0$ does not depend on $\delta$.

Starting with an arbitrary $u^0 \in \mathcal{K}_U$ a sequence $\{u^k\}_{k \geq 1} \subset \mathcal{K}_U \cap H^1((0, T); H^{-1}(\Omega))$ is constructed by the iterations $u^k = T u^{k-1}$, $k \geq 1$. This sequence converges strongly to the fixed point $u$ in $L^2((0, T); H^1_0(\Omega))$ and is uniformly bounded in $H^1((0, T); H^{-1}(\Omega))$. Hence it has a weakly convergent subsequence $\{u^{k_n}\}_{n \geq 0}$ with $u \in H^1((0, T); H^{-1}(\Omega))$ as the weak limit. By construction, all $u^{k_n}$ satisfy the initial and boundary data and

\begin{equation}
(\partial_t u^{k_n}, \varphi)_{\Omega_T} + D(\nabla u^{k_n}, \nabla \varphi)_{\Omega_T} - (\overline{q} u^{k_n}, \nabla \varphi)_{\Omega_T} = -\varepsilon n(\partial_t v^{k_n}, \varphi)_{\Gamma_0^G},
\end{equation}

for all $\varphi \in L^2((0, T); H^1_0(\Omega))$. Here $v^{k_n}$ solves

\begin{equation}
(\partial_t v^{k_n}, \theta)_{\Gamma_0^G} = k(r(u^{k_n-1}, c) - H_\delta(v^{k_n}), \theta)_{\Gamma_0^G},
\end{equation}

for all $\theta \in L^2(\Gamma_0^G)$, with $v_I$ as initial data. By Lemma 2.15, the sequence $\{v^{k_n}\}_{n \geq 0}$ converges strongly in $H^1((0, T); L^2(\Gamma_0^G))$ to a limit $v$. Since $r$ and $H_\delta$ are continuous we can pass to the limit in (2.21) and (2.22) and obtain that $(u, v)$ is a solution of the regularized problem $P_\delta$. We summarize:
Theorem 2.19. For each \( \delta > 0 \), Problem \( P_\delta \) has a solution \( (u_\delta, v_\delta) \in U \times V \) that satisfies

\[
0 \leq u_\delta \leq M_u, \quad 0 \leq v_\delta \leq M_v e^{CT} \quad \text{a.e. in } \Omega^T, \text{ respectively } \Gamma_G^T;
\]

and

\[
\|u_\delta(t)\|_{\Omega^t}^2 + \|\nabla u_\delta\|_{\Omega^t}^2 + \|\partial_t u_\delta\|_{L^2((0,t);H^{-1}(\Omega))}^2 + \varepsilon \|v_\delta(t)\|_{\Gamma_G}^2 + \varepsilon \|\partial_t v_\delta\|_{\Gamma_G^T}^2 \leq C,
\]

for all \( t > 0 \). Here \( C > 0 \) does not depend on \( \delta \). If in addition the conditions of Remark 2.12 hold, then \( C \) does not depend on \( \varepsilon \) as well.

Remark 2.20. Since both \( r \) and \( H_\delta \) are Lipschitz, Problem \( P_\delta \) has a unique solution. To see this we assume that both \( (u_1, v_1) \) and \( (u_2, v_2) \) solve \( P_\delta \). With \( u := u_1 - u_2 \) and \( v := v_1 - v_2 \), we follow the proof of Lemma 2.15 and find

\[
\|v\|_{\Gamma_G}^2 \leq k^2 L_r^2(e^t - 1) \|u\|_{\Gamma_G}^2
\]

for all \( 0 \leq t \leq T \). Since \( r \) is monotone, (2.11) and (2.12) imply

\[
\frac{1}{2} \|u(t)\|_{\Omega^t}^2 + D \|\nabla u\|_{\Omega^t}^2 \leq C \|u\|_{\Gamma_G}^2,
\]

where \( C = \frac{k^2 L_r^2}{\delta} \varepsilon \sqrt{e^t - 1} \). Using (2.18) we obtain

\[
\frac{1}{2} \|u(t)\|_{\Omega^t}^2 + D \|\nabla u\|_{\Omega^t}^2 \leq C \left( C_3 \|u\|_{\Omega^t}^2 + C_4 \|u\|\Omega^t \|\nabla u\|_{\Omega^t} \right)
\]

\[
\leq C \left[ \left( C_3 + \frac{C_4^3}{4\mu} \right) \|u\|_{\Omega^t}^2 + \mu \|\nabla u\|_{\Omega^t} \right].
\]

Taking \( \mu = D/C \) and using Gronwall’s lemma gives \( u = 0 \) and hence \( v = 0 \).

Finally we send \( \delta \searrow 0 \). Theorem 2.19 provides an approximate solution for each \( \delta > 0 \) and the necessary uniform estimates. Let \( w_\delta \in L^\infty(\Gamma_G^T) \) be defined by

\[
w_\delta(t,x) = H_\delta(v_\delta(t,x)) \quad \text{a.e. in } \Gamma_G^T.
\]

Compactness arguments give the existence of a triple \( (u, v, w) \in U \times V \times L^\infty(\Gamma_G^T) \) and a subsequence \( \delta \searrow 0 \), such that

a) \( u_\delta \rightharpoonup u \) weakly in \( L^2((0,T); H^1_{0,\Gamma_D}(\Omega)) \),

b) \( \partial_t u_\delta \rightharpoonup \partial_t u \) weakly in \( L^2((0,T); H^{-1}(\Omega)) \),

c) \( v_\delta \rightharpoonup v \) weakly in \( L^2((0,T); L^2(\Gamma_G)) \),

d) \( \partial_t v_\delta \rightharpoonup \partial_t v \) weakly in \( L^2(\Gamma_G^T) \),

e) \( w_\delta \rightharpoonup w \) weakly–star in \( L^\infty(\Gamma_G^T) \).

We now state the main result of this section.
Theorem 2.21. The triple \((u, v, w)\) is a weak solution of (2.3), (2.4) in the sense of Definition 2.1. It satisfies

\[
0 \leq u \leq M_u, \quad \text{a.e. in } \Omega^T
\]

\[
0 \leq v \leq M_v e^{CT}, \quad 0 \leq w \leq 1 \quad \text{a.e. in } \Gamma^T_G
\]

\[
\|u(t)\|_{\Omega}^2 + \|\nabla u\|_{\Omega}^2 + \|\partial_t u\|_{L^2((0,t);H^{-1}(\Omega))}^2 + \varepsilon \|v_\delta(t)\|_{G_G}^2 + \varepsilon \|\partial_t v_\delta\|_{G_G}^2 \leq C,
\]

for all \(0 \leq t \leq T\), where \(C\) is the constant from Theorem 2.19. Moreover,

\[
w = r(u, c) \quad \text{a.e. in } \{v = 0\} \cap \Gamma^T_G.
\]

Proof. By the weak convergence, all bounds are inherited from Theorem 2.19. Furthermore, it is immediate that \(u\) and \(v\) satisfy equation (2.8). Only the reaction equation needs additional attention. We first consider the behavior of \(u_\delta\) on \(\Gamma^T_G\). By the a–priori estimates and by Lemma 9 and Corollary 4 of [19], we have

\[
u(t, x) := \liminf_{\delta \searrow 0} v_\delta(t, x) \geq 0 \quad \text{a.e. in } \Gamma^T_G
\]

and pointwisely a.e. in \(\Gamma^T_G\). This observation and the weak-star convergence of \(w_\delta\) implies that \(u, v\) and \(w\) satisfy (2.9). It remains to show that (2.9) holds. This would be trivial in the case of pointwise \(v_\delta\) convergence. However we only have weak convergence. To resolve this we use the regularized reaction equation (2.12). First introduce

\[
\mathcal{v}(t, x) := \liminf_{\delta \searrow 0} v_\delta(t, x) \geq 0 \quad \text{a.e. in } \Gamma^T_G,
\]

and decompose \(\Gamma^T_G = S_1 \cup S_2\), where (in the almost everywhere sense)

\[
S_1 = \{\mathcal{v} > 0\} \quad \text{and} \quad S_2 = \{\mathcal{v} = 0\},
\]

We show that \(v > 0\) and \(w = 1\) in \(S_1\), while \(v = 0\) and \(w = r(u) \in [0, 1]\) in \(S_2\).
Figure 3. Rectangular domain, flow from left to right.

Since \( v \geq v \) we have \( v > 0 \) in \( S_1 \). Next let \((t, x) \in S_1\) be such that \( v(t, x) > 2\mu > 0 \) for \( \mu \) sufficiently small. Then \( v_\delta(t, x) > \mu \) and \( w_\delta(t, x) = 1 \) for all \( \delta \) small enough, implying \( w(t, x) = 1 \).

Next we rule out the possibility that \( v > 0 \) in \( S_2 \). Since \( \int_0^t w_\delta \to \int_0^t w \) weakly–star in \( L^\infty(\Gamma^T_G) \) we have \( \lim \inf_{\delta \to 0} \int_0^t w_\delta \leq \int_0^t w \) a.e. in \( \Gamma^T_G \).

Since both (2.9) and (2.12) hold a.e. in \( \Gamma^T_G \), integration in time gives

\[
\begin{align*}
v_\delta &= v_0 + k \int_0^t (r(u_\delta, c) - w_\delta) \\
&= v + k \int_0^t (r(u_\delta, c) - r(u, c)) - k \int_0^t (w_\delta - w) \quad \text{a.e. in } \Gamma^T_G.
\end{align*}
\]

Restricting ourselves to \( S_2 \), we take the \( \lim \inf_{\delta \to 0} \) of this expression. Since \( u_\delta \) converges pointwisely we find

\[
0 = v - k \lim \inf_{\delta \to 0} \int_0^t (w_\delta - w) \geq v \quad \text{a.e. in } S_2.
\]

Therefore \( v = 0 \) in \( S_2 \). Moreover, since \( \partial_t v \in L^2(\Gamma^T_G) \), it follows that \( \partial_t v = 0 \) a.e. in \( S_2 \), and therefore \( w = r(u, c) \) with \( 0 \leq w \leq 1 \).

3. DISSOLUTION FRONT

The specific form of the reaction equation, in particular the presence of the non-regular Heaviside graph, may cause the occurrence of precipitation and dissolution fronts. This strongly depends on the boundary and initial data. These fronts appear as free boundaries in the set \( \Gamma^T_G \), where they separate regions where crystals are present \( \{v > 0\} \) from regions where all crystals have been dissolved \( \{v = 0\} \).

For simplicity, and as a first step towards an understanding of porous media flow and transport, we consider here a dissolution front in a two-dimensional rectangular domain. In the original, unscaled setting it has
the form
\[ \Omega^{\text{real}} = (0, L^{\text{real}}) \times (-H^{\text{real}}, H^{\text{real}}). \]
With
\[ L := \frac{L^{\text{real}}}{L_R} \quad \text{and} \quad H := \frac{H^{\text{real}}}{L_R}, \]
and in view of the imposed symmetry, the relevant scaled flow domain is
\[ \Omega = (0, L) \times (0, H), \]
where \( L > 0 \) and \( H = 1 \) (without loss of generality). The various boundary types are defined in Figure 3. In Section 4 we consider thin domains with
\[ H = \frac{H^{\text{real}}}{L_R} = \varepsilon << 1. \]
Note that this is consistent with (1.11a), since
\[ \varepsilon L_R L^{\text{real}} = L^{\text{real}} H^{\text{real}}. \]

At the inlet \( \{x = 0\} \) and the outlet \( \{x = L\} \) we assume a parabolic velocity profile such that
\[ \bar{q} = \bar{q}(x, z) = (q(z), 0), \quad \text{with} \quad q(z) = C_q(1 - z^2), \]
and \( C_q := \frac{\Delta P}{(2 L \mu)}, \Delta P \) being the pressure drop in \( x \)-direction, solves the flow problem (2.1).

As in \cite{3} and \cite{12} we assume a constant charge distribution, \( c(t, x, z) = c_0 \) for all \( (x, z) \in \Omega \) and for all \( t > 0 \). With reference to Figure 2 we set
\[ u_* := u_*(c_0) \quad \text{and} \quad u^* = u^*(c_0) \quad (u^* > u_*). \]
and consider the initial/boundary data
\[ v_I(x) \equiv v_0 > 0, \quad u_I(x, z) = u_D(t, L, z) = u^*, \quad u_D(t, 0, z) = u_*, \]
for all \( x \in (0, L), z \in (0, 1), \) and \( t > 0 \). In this setting, all assumptions on the domain geometry and data are satisfied. Hence Theorem 2.21 applies and a bounded, weak solution of (2.3)–(2.4) exists. Since we have no uniqueness, we denote by \( (u, v, w) \) the particular solution obtained by the procedure of Section 2.

Note that the initial conditions for \( u \) and \( v \) are compatible in the sense that \( v = v_0 > 0 \) and \( u = u^* \) implies \( w = w_0 = 1 = r(u^*, c_0) \).
In this section the charge is assumed constant, so in what follows we simplify our notation by writing \( r = r(u) \).

Having initially crystals present everywhere on \( \Gamma_G \), and having \( u = u_* \) (implying \( r(u_*) = 0 \)) at the inlet, one expects a dissolution front travelling from left to right along the wall \( \Gamma_G \). More specifically, if \( s(t) \) denotes the distance between the dissolution front and the inlet \( \{x = 0\} \), one expects \( v(t, x) = 0 \) for \( 0 < x < s(t) \) and \( v(t, x) > 0 \)
for $x > s(t)$. An intuitive picture is sketched in Figure 4. Since $v \in H^1((0,T); L^2(\Gamma_G))$ is not necessarily continuous in both $x$ and $t$, we use the following definition:

**Definition 3.1.** The function $s: [0, T] \to [0, L]$, given by

$$s(t) = \sup \{ x \in [0, L] : \int_0^x v(t, y) dy = 0 \}$$

for all $0 \leq t \leq T$, is called the dissolution front for the data (3.2)–(3.4).

In this way it is well-defined. At points $t \in [0, T]$ where $s(t) > 0$ we have, since $v \geq 0$, $v(t, x) = 0$ for almost every $0 < x < s(t)$.

Before studying the behavior of $s(t)$, we first consider some qualitative properties of the concentrations $u$ and $v$ for the particular (rectangular) geometry and data (3.2), (3.4). As a preliminary observation we note that $u$ is smooth in $\Omega^T$. This is immediate since $u$ is a bounded, weak solution of the linear transport equation (2.3) (e.g. see [14], chapters 3.10 and 5.7).

**Lemma 3.1.** $\partial_t v \leq 0$ a.e. in $\Gamma_G^T$.

**Proof.** By the maximum principle,

$$u_* \leq u(t, x, z) \leq u^* \quad \text{in } \Omega^T$$

implying for the traces

$$u_* \leq u(t, x, z) \leq u^* \quad \text{a.e. in } \Gamma_G^T.$$

Since the reaction equation holds pointwisely, we have

$$\partial_t v = k(r(u) - w) \leq k(1 - w) \quad \text{a.e. in } \Gamma_G^T.$$
As before, let $\Gamma^T_G = S_1 \cup S_2$, where $S_1 = \{v = 0\}$ and $S_2 = \{v > 0\}$. Then $\partial_3 v = 0$ a.e. in $S_1$ and by (3.6), since $w = 1$ in $S_2$, $\partial_3 v \leq 0$ a.e. in $S_2$.

**Remark 3.2.** Lemma 3.1 is valid for general domains, provided the boundary and initial data for $u$ are not above $u^*$. In this situation precipitation is not possible.

**Lemma 3.3.** $\partial_t u < 0$ in $\Omega^T$.

**Proof.** To prove this result we introduce the time shift

$$u^h(t, x, z) := u(t + h, x, z) \quad \text{for } (t, x, z) \in \Omega^{T-h},$$

for sufficiently small $h > 0$. The weak equation for $u$ implies

$$\begin{aligned}
(\partial_t(u^h - u), \varphi)_{\Omega^{T-h}} + D(\nabla(u^h - u), \nabla \varphi)_{\Omega^{T-h}} \\
- (\overline{q}(u^h - u), \nabla \varphi)_{\Omega^{T-h}} + \varepsilon n(\partial_t(v^h - v), \varphi)_{\Gamma^{T-h}_G} = 0.
\end{aligned}$$

Clearly $\varphi = [u^h - u]_+ \in L^2((0, T-h); H^1_0, \Gamma_D(\Omega))$ is an admissible test function. It satisfies $\varphi|_{t=0} = 0$ since $u^h \leq u^*$ at $t = 0$. We need to estimate the boundary term, which reads

$$\varepsilon nk(r(u^h) - r(u), [u^h - u]_+)_{\Gamma^{T-h}_G} - \varepsilon nk(w^h - w, [u^h - u]_+)_{\Gamma^{T-h}_G}.$$

The first part is non-negative by the monotonicity of $r$. In the second part we use Lemma 3.1 and the monotonicity of $H$, giving $w^h - w \leq 0$ a.e. in $\Gamma^{T}_G$. Hence the boundary term in (3.7) is non-negative. Proceeding as in the proof of Lemma 2.6 gives $[u^h - u]_+ \equiv 0$ in $\Omega^{T-h}$. The interior smoothness of $u$ now implies $\partial_t u \leq 0$ in $\Omega^T$. Since $\partial_t u$ is a solution of equation (2.3$_1$), it cannot have an interior maximum and strict inequality results.

The concentrations are also monotone in the flow direction. The argument uses the auxiliary function $f : [0, T] \times [0, L] \rightarrow \mathbb{R}$ defined by

$$f(t, x) = u_* + \frac{(u^* - u_*)}{\sqrt{D\pi}} \left[ \frac{x}{L} \int_{-x}^{\xi} e^{-\xi^2/2\sigma} d\xi + \int_{-x}^{\xi} e^{-\xi^2/2\sigma} d\xi \right].$$

For this and later purposes we list some properties.
Property 3.4.

(i) \( f \in L^2((0, T); H^1(0, L)) \cap C([0, T] \times [0, L]/\{(0, 0)\}) \)

For all \( 0 < t < T \) and \( 0 < x < L \):

(ii) \( \partial_t f(t, x) < 0, \quad \partial_x f(t, x) > 0 \),

(iii) \( \lim_{x \downarrow 0} f(t, x) = u_\ast, \lim_{x \uparrow L} f(t, x) = u^\ast, \lim_{t \downarrow 0} f(t, x) = u^\ast \).

Proof. Since these statements follow by direct computation we omit the proof. \( \square \)

Lemma 3.5.

(i) \( \partial_x u > 0 \) in \( \Omega^T \);

(ii) \( v(t, x_1) \leq v(t, x_2) \) for a.e. \( (t, x_1), (t, x_2) \in \Gamma^T_0 \) such that \( x_1 < x_2 \).

Proof. We use the iteration scheme introduced in the proof of Theorem 2.19 and we use Remark 2.20 about the uniqueness for Problem \( P_\delta \). In particular we use the fact that the unique solution of \( P_\delta \) does not depend on the choice of the first element \( u^0 \), provided \( u^0 \in K_U \). Going from \( u^0 \) to the next \( u^1 \) means first solving (2.12) with \( u = u^0 \) to find \( v^0 \in K_V \) as solution, and next solving (2.11) with \( v = v^0 \) to find \( u^1 \in K_U \) as solution. Property 3.4 implies that \( f \in K_U \) and that \( \partial_x f > 0 \) in \( \Omega^T \). With \( u^0 = f \) we find \( v^0 \) satisfying \( v^0(t, x + h) \geq v^0(t, x) \) for sufficiently small \( h > 0 \) and for almost all \( (t, x) \in \Gamma^T_h \), where \( \Gamma^T_h = (0, T] \times (0, L - h) \). We now apply the same space shift to the solution of (2.11) in \( \Omega^T_h \) with \( \Omega_h = (0, L - h) \times (0, 1) \). As in the proof of Lemma 3.3 it can be shown that \( u^1(t, x + h, z) \geq u^1(t, x, z) \) in \( \Omega^T_h \). In other words, the \( x \)-monotonicity is preserved by the iterations and the unique solution \( (u_\delta, v_\delta) \) of \( P_\delta \) is \( x \)-monotone. Again, this monotonicity is preserved, now along the particular subsequence \( \delta \searrow 0 \) in the proof of Theorem 2.21. This proves (ii) and (i) with \( \partial_x u \geq 0 \) in \( \Omega^T \). Strict inequality results again from the fact that \( \partial_x u \) is a solution of (2.31). \( \square \)

The next lemma improves the upper bound for \( u \).

Lemma 3.6. The weak solution \( \overline{U} \in \mathcal{U} \) of

\[
\begin{align*}
\begin{array}{ll}
\partial_t \overline{U} + q(\overline{z}) \partial_x \overline{U} &= D \Delta \overline{U}, & \text{in } \Omega^T, \\
-D \partial_z \overline{U} &= \varepsilon n k(r(\overline{U}) - 1), & \text{on } \Gamma^T_G, \\
\overline{U} &= u_\ast, & \text{on } \Gamma^T_D \cap \{x = 0\}, \\
\overline{U} &= u^\ast, & \text{on } \Gamma^T_G \cap \{x = L\} \text{ and } \{t = 0\} \times \Omega, \\
\partial_z \overline{U} &= 0, & \text{on } \Gamma^T_N.
\end{array}
\end{align*}
\tag{3.9}
\]
Crystal dissolution and precipitation in porous media

satisfies

(i) \( u_* \leq u \leq \bar{U} \leq u^* \) in \( \Omega^T \);
(ii) \( \partial_t \bar{U} < 0 \) and \( \partial_x \bar{U} > 0 \) in \( \Omega^T \);
(iii) \( \bar{U} \in C(\bar{\Omega}^T / \{ t = 0, x = 0, 0 \leq z \leq 1 \}) \) and \( \bar{U}(t, x, 1) < u^* \) for any \( 0 \leq x < L \) and \( 0 < t \leq T \).

Proof. Following the proof of Theorem 2.19 and Remark 2.20 we obtain existence and uniqueness of a weak solution \( \bar{U} \in \mathcal{U} \). It satisfies the same interior smoothness as \( u \).

(i) We test the equation for the difference \( \bar{U} - u \) with \( \varphi = [\bar{U} - u]_- \). Since \( w \leq 1 \) and \( r \) is monotone, we find as before \( [\bar{U} - u]_- \equiv 0 \) in \( \Omega^T \), implying \( u \leq \bar{U} \). The other inequalities follow as in Lemmas 2.6 and 2.7.

(ii) As in the proofs of Lemmas 3.3 and 3.5 we apply time and space shifts to show the corresponding monotonicity.

(iii) Away from the corner \( \{ t = 0, x = 0, 0 < z < 1 \} \), where the initial and boundary data are incompatible, the solution is at least continuous up to the boundary of \( \Omega^T \). This is a consequence of chapters 3.10 and 5.7 of [14]. To show the inequality we argue by contradiction. Suppose there exists \( (t_0, x_0) \in \Gamma_G^T \) where \( \bar{U}(t_0, x_0, 1) = u^* \), the smoothness of \( \bar{U} \) up to the flat boundary \( \Gamma_G^T \) allows us to use the strong maximum principle, implying \( \partial_z \bar{U}(t_0, x_0, 1) > 0 \). This contradicts the boundary flux (3.92).

We are now in a position to study the qualitative behavior of the dissolution front from Definition 3.1. As a first observation, recalling \( r(u^*) = 1 \) and \( r(u_*) = 0 \), we have:

**Proposition 3.7.** Let

\[
(3.10) \quad t^* = \frac{v_0}{k(r(u^*) - r(u_*))} = \frac{v_0}{k}.
\]

Then \( v > 0 \) a.e. in \( \Gamma_G^T \) and \( u = \bar{U} \) in \( \Omega^* \).

Proof. We note that any weak solution satisfies (2.9) with \( u \geq u_* \) a.e. in \( \Gamma_G^T \). For any pair \( 0 \leq x_1 < x_2 \leq 1 \) we test (2.9) with \( \chi(x_1, x_2) \). This gives

\[
\int_{x_1}^{x_2} v(t, x) = v_0(x_2 - x_1) + k \int_0^t \int_{x_1}^{x_2} \{ r(u) - w \} dx dt
\geq v_0(x_2 - x_1) + k(r(u_*) - 1)t(x_2 - x_1)
\geq (v_0 - kt)(x_2 - x_1) > 0
\]
for all $0 < t < t^*$. This proves the positivity of $v$ in $\Gamma^r_G$. With $w = 1$ in $\Gamma^r_G$, the concentration $u$ satisfies (3.9) in $\Omega^r$. By uniqueness we have $u = \overline{U}$ in $\Omega^r$. 

The proposition implies

\begin{equation}
(3.11) \quad s(t) = 0 \quad \text{for all } 0 \leq t < t^*.
\end{equation}

Next we show that the dissolution front moves away from $x = 0$ for $t > t^*$. Therefore we call $t^*$ the waiting time of the dissolution front. This agrees with [4], where the same waiting time was established for the macroscopic model.

**Proposition 3.8.** $s(t) > 0$ for all $t^* < t < T$.

**Proof.** We first show that for each $t > t^*$, where $s(t) < L$, we have

\begin{equation}
(3.12) \quad v(t, x) > 0 \quad \text{for a.e. } x \in (s(t), L).
\end{equation}

Let

$$g(x) := \int_0^x v(t, y)dy \quad \text{for } 0 \leq x \leq L.$$ 

Then $g \in C([0, T])$ satisfying

$$g(x) \begin{cases}
= 0, & \text{for } 0 \leq x \leq s(t), \\
> 0, & \text{for } s(t) < x \leq L.
\end{cases}$$

In particular, by Definition 3.1, there exists a sequence $x_n \searrow s(t)$ such that $g(x_n) > 0$ and $g(x_n) \to 0$ as $n \to \infty$. Hence there exists a related sequence of intervals $I_n$, with each $I_n \subset (s(t), x_n)$, such that $v > 0$ in $I_n$. The $x$-monotonicity of $v$ now gives $v > 0$ to the right of each $I_n$. This establishes (3.12).

Now suppose a $\bar{t} \in (t^*, T]$ exists such that $s(\bar{t}) = 0$. By (3.12) and Lemma 3.1 we have $v > 0$ and $w = 1$ in $\Gamma^r_G$ and $u = \overline{U}$ in $\Omega^r$. As in the proof of Proposition 3.7 we have for each $x > 0$

$$\int_0^x v(\bar{t}, y)dy = v_0x + k \int_0^{\bar{t}} \int_0^x \{ r(\overline{U}(\tau, y, 1)) - 1 \} dyd\tau$$

$$+ k \int_0^{\bar{t}} \int_0^x \{ r(\overline{U}(\tau, y, 1)) - 1 \} dyd\tau$$

$$\leq k \int_0^{\bar{t}} \int_0^x r(\overline{U}(\tau, y, 1))dyd\tau$$

$$- k(\bar{t} - t^*) \int_0^x \{ 1 - r(\overline{U}(t^*, y, 1)) \} dy.$$
Crystal dissolution and precipitation in porous media

(a)

\[ x = s(t) \quad t < t^* \]

\[ x = \bar{s}(t) \quad x = \bar{s}(\bar{t}) \]

\[ x - \zeta \quad v = 0 \]

\[ t^* \]

\[ t \]

\[ \bar{t} \]

\[ 0 \quad \bar{x} = \bar{s}(t) \quad \bar{x} + \zeta \quad L \]

\[ x \]

\[ \bar{x} - \zeta \quad \bar{x} = \bar{s}(t) \quad \bar{x} + \zeta \quad L \]

(b)

\[ v = 0 \]

\[ \bar{x} \]

\[ v > 0 \]

\[ v > 0 \]

\[ v > 0 \]

\[ R \]

\[ 0 \]

\[ t \]

\[ t^* \]

\[ \bar{t} \]

\[ \bar{x} = \bar{s}(t) \quad \bar{x} + \zeta \quad L \]

\[ x \]

\[ \bar{x} - \zeta \]

\[ \bar{x} = \bar{s}(t) \quad \bar{x} + \zeta \quad L \]

Figure 5. Horizontal segments in dissolution front.

Here we used (3.10) and Lemma 3.6, (ii). The left-hand side is positive, while the right-hand side becomes negative if

\[ \bar{t} > t^* + \frac{\int_0^{t^*} \int_0^x r(U(\tau, y, 1)) dy d\tau}{\int_0^x \{1 - r(U(\tau, y, 1))\} dy} =: t^* + \zeta(x). \]

The function \( \zeta \) is well-defined, positive and continuous. Moreover, since \( r(U(\tau, y, 1)) \to 0 \) as \( y \to 0 \), we have \( \zeta(0+) = 0 \). This contradicts the existence of \( \bar{t} \) and completes the proof. \( \square \)

Further we have

**Proposition 3.9.** We have

(i) \( s \) is non-decreasing in \([0, T]\);

(ii) \( s \in C([0, T]) \).

**Proof.** The first assertion is a direct consequence of Lemma 3.1 and (3.12). Since \( s \) is monotone and bounded, continuity follows if we can rule out horizontal segments in the \( x-t \) plane. We argue by contradiction. Suppose there exists \( t^* \leq \bar{t} \leq T \) such that one of the situations displayed in Figure 5 occurs.

We first show that Figure 5a cannot occur. By (3.12) and Definition 3.1 we have \( v(\cdot, \bar{t}) > 0 \) and \( v(\cdot, t) = 0 \) for any \( t > \bar{t} \), a.e. in \((\bar{x}, \bar{x} + \zeta)\). This contradicts the \( v \)-regularity since \( v \in C([0, T]; L^2(\Gamma_G)) \). To rule out Figure 5b we argue as follows. In the rectangle \( R \) we have \( v > 0 \) and \( w = 1 \). Further \( v = 0 \) in the segment \( \{(t, x) : t = \bar{t}, \bar{x} - \zeta < x < \bar{x}\} \) and \( v = v_0 \) in \( \{(t, x) : t = 0, \bar{x} - \zeta < x < \bar{x}\} \). Testing (2.9) with
\[ \theta = \chi_{(0,t)} \varphi(x), \varphi \in L^2((\bar{x} - \zeta, \bar{x})), \] gives

\[ \int_{\bar{x} - \zeta}^{\bar{x}} (v(t, x) - v_0) \varphi(x) \, dx = k \int_{\mathbb{R}} (r(u(\tau, x, 1)) - 1) \varphi(x) \, dx \, d\tau, \]
or

\[ \int_{\bar{x} - \zeta}^{\bar{x}} \left\{ \int_{0}^{t} [1 - r(u(\tau, x, 1))] \, d\tau - \frac{v_0}{k} \right\} \varphi(x) \, dx = 0. \]

Since this holds for any \( \varphi \) we have, in fact,

\[ (3.14) \quad \int_{0}^{t} [1 - r(u(\tau, x, 1))] \, d\tau = \frac{v_0}{k} \quad \text{a.e. in } (\bar{x} - \zeta, \bar{x}). \]

Since \( u \) is strictly increasing with respect to \( x \) in the interior of \( \Omega^T \), its trace is non-decreasing in \( \Gamma^T_G \) and in particular in any segment \( \{ t = \tau, \bar{x} - \zeta < x < \bar{x} \} \) in \( \mathbb{R} \). Combined with equality (3.14) this implies \( u(\tau, \cdot, 1) \) is constant in \( (\bar{x} - \zeta, \bar{x}) \) for each \( 0 < \tau < \bar{t} \). But in \( \Omega^T \) we have \( u = \overline{U} \). Hence \( \overline{U}(\tau, \cdot, 1) \) is also constant in \( (\bar{x} - \zeta, \bar{x}) \) for each \( 0 < \tau < t^* \). This gives a contradiction because \( \overline{U}(t) \) is strictly increasing in \( \Gamma_G \) for any \( t > 0 \). To see this we consider the difference \( \overline{U}_h(t, x, z) := \overline{U}(t, x + h, z) - \overline{U}(t, x, z) \). It satisfies (3.9) in \( \Omega^T_h \) and, by Lemma 3.6, it is continuous up to the boundary for all \( t > 0 \). Further \( \overline{U}_h > 0 \) in \( \Omega^T_h \) and, for \( h < \zeta \), \( \overline{U}_h = 0 \) in the boundary set \( \Gamma^T_G \cap \{ \bar{x} - \zeta < x < \bar{x} - h \} \). By the strong maximum principle this means \( \partial_z \overline{U}_h < 0 \) in that set, while the boundary condition implies \( \partial_z \overline{U}_h = 0 \).

We now improve the monotonicity of the front by showing that for \( t > t^* \) no additional waiting times occur in \( \{0 < x < L\} \). In other words:

**Proposition 3.10.** \( s \) is strictly increasing when \( 0 < s < L \).

**Proof.** By Proposition 3.9 it suffices to rule out vertical segments in the \( x-t \) plane. We argue again by contradiction. Suppose, as in Figure 6, that there exists \( s_0 \in (0, L) \) and \( t_1 < t_2 \) such that \( s(t) = s_0 \) for \( t_1 \leq t \leq t_2 \). Here we take \( t_1 \) minimal in the sense that \( s(t) < s_0 \) for all \( t < t_1 \). We first estimate \( v \) in \( \{x > s_0\} \). By (3.12) and Lemma 3.1, we have \( v > 0 \) and \( w = 1 \) a.e. in \( \{(t, x) : t < t_2, x > s_0\} \). Hence, with \( \mu > 0 \) and fixed, we have for any \( t \leq t_1 \) and for almost all
Crystal dissolution and precipitation in porous media

Figure 6. Vertical segment in dissolution front.

\[ s_0 < x < s_0 + \mu \]

\[ v(t, x) = v(t_2, x) + k \int_t^{t_2} \{1 - r(u(\tau, x, 1))\} d\tau \]

\[ \geq k \int_t^{t_2} \{1 - r(\bar{U}(\tau, x, 1))\} d\tau \]

\[ \geq k(t_2 - t_1)\{1 - r(\bar{U}(\tau, x, 1))\} d\tau \]

\[ \geq k(t_2 - t_1)\{1 - r(\bar{U}(t_1, s_0 + \mu, 1))\} =: C > 0. \]

For \(0 < \delta < C/(4k)\) and sufficiently small, we consider the horizontal segment \(\{(t, x) : t = t_1 - \delta, s_0 - \zeta < x < s_0 + \mu\}\). For \(0 < \zeta < s_0 - s(t_1 - \delta)\), we have \(v > 0\) and \(w = 1\) in the rectangle \(R = \{(t, x) : 0 < t < t_1 - \delta, s_0 - \zeta < x < s_0 + \mu\}\). Next we consider (2.8) and (2.9) in the box \(B \subset \Omega^T\), defined by

\[ B = \{(t, x, z) : (t, x) \in R, 0 < z < 1\}, \]

with appropriate initial and boundary conditions and with \(w\) replaced by 1. This means that the \(u\)-equation is decoupled from the \(v\)-equation and in \(B\) \(u\) has the same smoothness as the supersolution \(\bar{U}\) from Lemma 3.6. In particular \(u(\cdot, \cdot, 1) \in C(R)\), implying that \(v \in C(R)\).

Finally let \(t = t_1 - 2\delta\). Then, since \(-k \leq \partial_t v \leq 0\) a.e. in \(\Gamma^T_0\) and \(v(t_1, x) = 0\) for \(x < s_0\), we have

\[ v(t_1 - 2\delta, x) < 2\delta k < \frac{C}{2} \quad \text{for all} \quad s_0 - \zeta < x < s_0, \]

while, by (3.15),

\[ v(t_1 - 2\delta, x) > C \quad \text{for all} \quad s_0 < x < s_0 + \mu, \]
We conclude the qualitative statements about $s$ with the estimate:

**Proposition 3.11.** There exists a constant $C > 0$, not depending on $L$ and $T$, such that

$$s(t) \leq Ct^2 \quad \text{for all } t > 0.$$  

**Proof.** Since $v = 0$ in $\{ (t, x) : t^* < t < T, \ 0 < x < s(t) \}$, $-k \leq \partial_t v \leq 0$ a.e. in $\Gamma^T_G$ and $s$ is strictly increasing, we deduce that $v(t, s(t)) = 0$ for almost all $t \in (t^*, T)$ where $s(t) < L$. We use this observation and $w = 1$ a.e. in $\{ (t, x) : 0 < t < T, \ s(t) < x < L \}$ to derive from (2.41) the free boundary equation

$$v_0 = \left\{ \begin{array}{ll} \frac{v_0}{k} = \int_0^t \{ 1 - r(u(t, s(t))) \} \, dt & \text{for } t \in (t^*, T) \ \\
 & \text{where } s(t) \leq L \end{array} \right.$$  


for those $t \in (t^*, T)$ where $s(t) < L$. With $L_r$ given in Remark 2.9 we have

$$1 - r(u) = r(u^*) - r(u) \leq L_r(u^* - u).$$

We estimate

$$u^* - u \leq (u^* - u_*) \xi \quad \text{in } \Omega_T,$$

where $\xi$ is the one-dimensional solution satisfying

$$\begin{cases}
\partial_t \xi + C_q \partial_x \xi = D \partial_{xx}^2 \xi & \text{in } \{(t, x) : t > 0, x > 0\}, \\
\xi(0, t) = 1 & \text{for } t > 0, , \\
\xi(x, 0) = 0 & \text{for } x > 0.
\end{cases}$$

Combining (3.16) and (3.17) gives

$$K := \frac{v_0}{kL_r(u^* - u_*)} \leq \int_0^t \xi(\tau, s(\tau)) \, d\tau \leq t \xi(\tau, s(\tau)),$$

where we used $\partial_t \xi > 0$. We note here that $K < t^*$. Since $\partial_x \xi < 0$ we also have

$$s(t)\xi(t, s(t)) \leq \int_0^{s(t)} \xi(t, y) \, dy = \int_0^{s(t)} \left( \int_0^t \partial_t \xi(\tau, y) \, d\tau \right) \, dy$$

$$= \int_0^t \left( \int_0^{s(t)} \partial_t \xi(\tau, y) \, dy \right) \, d\tau$$

$$\leq \int_0^t \left( -D \partial_x \xi(\tau, 0) - C_q \xi(\tau, s(\tau)) \right) \, d\tau + C_q t,$$

or

$$s(t)\xi(t, s(t)) + C_q \int_0^t \xi(\tau, s(t)) \, d\tau \leq -D \int_0^t \partial_x \xi(\tau, 0) + C_q t.$$  

We estimate the flux term on the right by the solution of (3.18) with $C_q = 0$. This is a subsolution for the complete (3.18). It is closely related to (3.8) with $L = \infty$. Using this subsolution and (3.19) in (3.20) gives

$$s(t)\xi(t, s(t)) \leq 2\sqrt{\frac{D}{\pi}t^{1/2}} + C_q(t - K).$$

Again using (3.19) yields

$$s(t) < \frac{C_q}{K}t(t - K) + \frac{2}{K}\sqrt{\frac{D}{\pi}t^{3/2}} \quad \text{for } t > t^*.$$

Remark 3.12. So far we discussed the dissolution front for the special initial/boundary data (3.4). Similar results can be obtained for more general data. For instance, if

$$v_I(x) \geq 0 \quad (\neq 0), \quad u_I(x, z) \leq u^*,$$

$$u^* \leq u_D(t, 0, z) < u_D(t, L, z) \leq u^*,$$

for all $x \in (0, L)$, $z \in (0, 1)$ and $t > 0$, and if $c = c_0$ in $\Omega^T$, precipitation is not possible. This follows from the maximum principle for $u$, giving $u \leq u^*$ and thus $\partial_t u \leq 0$ in $\Gamma_G^T$. Hence, for data satisfying (3.21), only dissolution occurs and this will strongly depend on the specific form of the functions in (3.21). As an example, let $v_I$ be hat-shaped with

$$v_I(x) = \begin{cases} v_0 > 0, & \text{if } x \in [x_1, x_2] \subset (0, L), \\ 0, & \text{otherwise}, \end{cases}$$

and let $u$ satisfy (3.4). Then we find two dissolution fronts: a left front starting at $x = x_1$ with waiting time $t^*_1$, and a right front starting at $x = x_2$ with waiting time $t^*_2$. The waiting times are determined by the free boundary equation (3.16) at $x_1$ and $x_2$, i.e.

$$\frac{v_0}{k} = \int_0^t \{1 - r(u(\tau, x_i, 1))\}d\tau \quad \text{for } i = 1, 2.$$ 

Here ions enter the fluid only when $x_1 < x < x_2$. Therefore the $x$-monotonicity of $u$ does not hold anymore and it is not clear which of the two waiting times is the biggest. After $t^*_1$, the left front moves to the right and after $t^*_2$, the right front moves to the left. They will meet at a finite $t^*$ when all crystals are dissolved. □
Remark 3.13. Precipitation or precipitation fronts occur if \( u_I \) and/or \( u_D \) are above \( u^* \). This is the only possibility for \( \partial_tv > 0 \) somewhere in \( \Gamma^T_G \). For instance, if

\[
v_I(x) = 0, \quad u_I(x, z) = u_D(t, L, z) = \underline{u} \leq u^*, \quad u_D(t, 0, z) = \bar{u} > u^*,
\]

for all \( x \in (0, L) \), \( z \in (0, 1) \) and \( t > 0 \), and if \( c = c_0 \) in \( \Omega^T \), we find a precipitation front moving from left to right on \( \Gamma_G \). If \( u = u^* \) then, by the maximum principle for \( u \), \( u > u^* \) in \( \Omega^T \) and instantaneous precipitation occurs everywhere in \( \Gamma_G \). The condition \( \bar{u} > u^* \) means that the injected fluid is oversaturated.

\[\square\]

4. Thin strips

In this section we maintain the framework of Section 3, but assume additionally that the strip is thin with \( H \) given by (3.1). Using the same value for the scaling factor in (1.11b), and thus assuming that for all \( \varepsilon > 0 \) the system contains about the same number of moles for both crystals and solutes, we study the limit as \( \varepsilon \to 0 \). As a result we recover the one-dimensional reactive solute transport model proposed in [12] and [3].

To stress the dependence on \( \varepsilon \) we use superscripts as, for instance, in

(4.1) \[ \Omega^\varepsilon = (0, L) \times (0, \varepsilon). \]

To ensure that the average flow in \( x \)-direction does not vanish and remains constant as \( \varepsilon \to 0 \) we impose

(4.2) \[ \bar{q}^\varepsilon(x, z) = (q^\varepsilon(z), 0), \quad \text{with} \quad q^\varepsilon(z) = \frac{3}{2}Q \left( 1 - z^2/\varepsilon^2 \right), \]

where \( Q = \frac{1}{\varepsilon} \int_0^\varepsilon q^\varepsilon(z)dz \) is a prescribed average flow.

Remark 4.1. The thin strip is a simplified model for the void space between two grains in a porous medium. If the pressure gradient is of order 1, a velocity profile as in (4.2) can only be achieved if the scaled fluid viscosity \( \mu = O(\varepsilon^2) \). This assumption is commonly encountered when homogenizing periodic structures – see for instance [9] and [16]. It prevents one from obtaining a trivial upscaled velocity corresponding to an immobile fluid as \( \varepsilon \to 0 \). \[\square\]

Imposing the same initial and boundary conditions as in Section 3, we obtain a bounded weak solution \((u^\varepsilon, v^\varepsilon, w^\varepsilon)\) and a corresponding dissolution front \( s^\varepsilon \) satisfying all properties discussed in that section.

The scaling \( \xi = z/\varepsilon \), with \( 0 < \xi < 1 \), transforms the domain \( \Omega^\varepsilon \) back to \( \Omega = (0, L) \times (0, 1) \). Further \( q^\varepsilon(z) = q(\xi) := \frac{3}{2}Q(1 - \xi^2) \). In terms of
Crystal dissolution and precipitation in porous media

\[ x, \xi \text{ and } t \text{ the solution } (u^\varepsilon, v^\varepsilon, w^\varepsilon) \text{ satisfies} \]

\[
\begin{align*}
& (\partial_t u^\varepsilon, \varphi)_{\Omega^T} + D(\partial_x u^\varepsilon, \partial_x \varphi)_{\Omega^T} + 2\varepsilon (\partial_x u^\varepsilon, \partial_x \varphi)_{\Omega^T} \\
& + (q \partial_x u^\varepsilon, \varphi)_{\Omega^T} + n(\partial_t v^\varepsilon, \varphi)_{\Gamma^T_0} = 0,
\end{align*}
\]

(4.3)

\[
(\partial_t v^\varepsilon, \theta)_{\Gamma^T_0} = k(r(u^\varepsilon) - w^\varepsilon, \theta)_{\Gamma^T_0}
\]

(4.4)

\[ w^\varepsilon \in H(v^\varepsilon), \text{ a.e. in } \Gamma^T_0, \]

for all \((\varphi, \theta) \in L^2((0, T); H^1_0(\Omega)) \times L^2(\Gamma^T_0). \]

Next we define the average

\[ U^\varepsilon(t, x) := \int_0^1 u^\varepsilon(t, x, \xi) \, d\xi. \]

(4.5)

The properties of \(u^\varepsilon\) imply that \(U^\varepsilon \in U_{av} := L^2((0, T); H^1(0, L)) \cap H^1((0, T); H^{-1}(0, L))\) and satisfies \(U^\varepsilon(t, 0) = u^*,\) and \(U^\varepsilon(t, L) = U^\varepsilon(0, x) = u^*\). Let \(\Omega_{av} := (0, L). \)

Writing for consistency of notation \(V^\varepsilon(t, x) := v^\varepsilon(t, x)\) and \(W^\varepsilon(t, x) := w^\varepsilon(t, x),\) and testing (4.3) with \(\xi\)-independent functions, gives

\[
\begin{align*}
& (\partial_t U^\varepsilon, \varphi)_{\Omega_{av}^T} + D(\partial_x U^\varepsilon, \partial_x \varphi)_{\Omega_{av}^T} + (\partial_x U^\varepsilon, \varphi)_{\Omega_{av}^T} \\
& + n(\partial_t V^\varepsilon, \varphi)_{\Omega_{av}^T} = \left(\int_0^1 (Q - q) \partial_x u^\varepsilon, \varphi\right)_{\Omega_{av}^T},
\end{align*}
\]

(4.6)

for all \(\varphi \in L^2((0, T); H^1_0(\Omega_{av})). \)

Further,

\[
\begin{align*}
& (\partial_t V^\varepsilon, \theta)_{\Omega_{av}^T} = k(r(U^\varepsilon) - W^\varepsilon, \theta)_{\Omega_{av}^T} \\
& + k(r(u^\varepsilon(\cdot, \cdot, 1)) - r(U^\varepsilon), \theta)_{\Omega_{av}^T}
\end{align*}
\]

(4.7)

\[ W^\varepsilon \in H(V^\varepsilon), \text{ a.e. in } \Omega_{av}^T, \]

for all \(\theta \in L^2(\Omega_{av}^T). \)

Below we make precise that as \(\varepsilon \searrow 0,\) the triple \((U^\varepsilon, V^\varepsilon, W^\varepsilon)\) converges towards \((U, V, W),\) being the weak solution of the reactive solute transport equations

\[
\begin{align*}
\partial_t (U + nV) + Q \partial_x U &= D \partial_{xx}^2 U, \\
\partial_t V &= k(r(U) - W), \\
W &\in H(V),
\end{align*}
\]

in \(\Omega_{av}^T. \)

These equations were proposed in [12] and [3] to describe crystal dissolution in a homogenized porous medium. The appropriate weak formulation is:
Problem $\text{P}_{\text{av}}$: Find $(U, V, W) \in U_{\text{av}} \times V \times W$ such that $U(t, 0) = u_*$, $U(t, L) = U(0, x) = u_*$, $V(0, x) = v_0$, and

$$
(\partial_t U, \varphi)_{\Omega_{\text{av}}} + D(\partial_x U, \partial_x \varphi)_{\Omega_{\text{av}}} \\
+ (Q \partial_x U, \varphi)_{\Omega_{\text{av}}} + n(\partial_t V, \varphi)_{\Omega_{\text{av}}} = 0,
$$

(4.8)

$$
(\partial_t V, \theta)_{\Omega_{\text{av}}} = k(r(U) - W, \theta)_{\Omega_{\text{av}}},
$$

(4.9)

for all $(\varphi, \theta) \in L^2((0, T); H^1(\Omega_{\text{av}})) \times L^2(\Omega_{\text{av}}^T)$.

We start with some a-priori estimates.

Lemma 4.2. For any $T > 0$, there exists a constant $C > 0$ such that

$$
\|u^\varepsilon(t)\|_0^2 + D\|\partial_x u^\varepsilon\|_0^2 + \frac{D}{\varepsilon^2} \|\partial_x u^\varepsilon\|_0^2 \leq C,
$$

for all $\varepsilon > 0$ and for all $0 \leq t \leq T$.

Proof. The proof is immediate after testing (4.3) with $\varphi = \chi_{(0, t)}(u^\varepsilon - u_* - (u^* - u_*)x/L)$.

The following proposition uses the idea of the trace theorem; see for instance [5], chapter 5.5.

Proposition 4.3. Let $f \in H^1(\Omega)$ and let $F : [0, L] \to \mathbb{R}$ be defined by $F(x) = \int_0^1 f(x, \xi) \, d\xi$. Then, in the sense of traces,

$$
\|f(\cdot, \xi_0) - F\|_{(0, L)} \leq \|\partial_\xi f\|_{\Omega}
$$

for each $\xi_0 \in [0, 1]$.

Proof. We demonstrate the inequality for $f \in C^1(\overline{\Omega})$. The extension to $f \in H^1(\Omega)$ in the sense of traces follows from the usual density argument. For arbitrary $\xi_0 \in [0, L]$ we have

$$
\|f(\cdot, 1) - F\|_{(0, L)}^2 = \int_0^L \left\{ f(x, \xi_0) - \int_0^1 f(x, \zeta) \, d\zeta \right\}^2 \, dx
$$

$$
= \int_0^L \left\{ f_0^1 (f(x, \xi_0) - f(x, \zeta)) \, d\zeta \right\}^2 \, dx
$$

$$
= \int_0^L \left\{ f_0^1 \left( \int_\zeta^{\xi_0} \partial_\zeta f(x, \xi) \, d\xi \right) \, d\zeta \right\}^2 \, dx \leq \|\partial_\xi f\|_{\Omega}^2
$$

Combining Lemma 4.2 and Proposition 4.3 gives
Lemma 4.4. For any $T > 0$ we have
\[ \|u^\varepsilon(\cdot, \cdot, \xi_0) - U^\varepsilon\|_{L^2_{av}(\Omega_{av})}^2 \leq \frac{\varepsilon^2}{D} C. \]
for all $\varepsilon > 0$ and for all $\xi_0 \in [0, 1]$. Here $C$ is the constant from Lemma 4.2.

Proof. For almost every $t \in (0, T)$ we apply Proposition 4.3 to $u^\varepsilon(t, \cdot, \cdot)$. The assertion now follows from the gradient estimate in Lemma 4.2. \hfill \square

The weak formulations for $U^\varepsilon$ (4.6) and $U$ (4.8) differ by the term
\[(4.10a) \quad T_1^\varepsilon(\varphi) := \left( \int_0^1 (Q - q) \partial_x u^\varepsilon, \varphi \right)_{\Omega_{av}^T}, \]
the ones for $(V^\varepsilon, W^\varepsilon)$ (4.7) and $(V, W)$ (4.9) by
\[(4.10b) \quad T_2^\varepsilon(\theta) := k(r(u^\varepsilon(\cdot, \cdot, 1)) - r(U^\varepsilon), \theta)_{\Omega_{av}^T}. \]
These terms are estimated in the lemma below.

Lemma 4.5. For any $T > 0$ we have
\[ |T_1^\varepsilon(\varphi)| \leq \varepsilon Q \sqrt{\frac{C}{5D}} \|\partial_x \varphi\|_{L^2(\Omega_{av}^T)}, \]
\[ |T_2^\varepsilon(\theta)| \leq \varepsilon k L_r \sqrt{\frac{C}{D}} \|	heta\|_{L^2(\Omega_{av}^T)}, \]
for all $\varphi \in L^2((0, T); H^1_0(\Omega_{av}))$, $\theta \in L^2(\Omega_{av}^T)$ and for all $\varepsilon > 0$. Here $C$ is the constant from Lemma 4.2 and $L_r$ the Lipschitz constant from Remark 2.9.

Proof. We integrate $T_1$ by parts and subtract $0 = (\int_0^1 (Q - q) U^\varepsilon, \partial_x \varphi)_{\Omega_{av}^T}$. Then Cauchy’s inequality and Lemma 4.4 provide the first estimate. The Lipschitz continuity of $r$ and again Lemma 4.4 give the second one. \hfill \square

We are now in a position to estimate the average $U^\varepsilon$ and $V^\varepsilon, W^\varepsilon$.

Lemma 4.6. For any $T > 0$ we have
\[ \text{i) } u_* \leq U^\varepsilon \leq u^*, \quad 0 \leq V^\varepsilon \leq v_0, \quad 0 \leq W^\varepsilon \leq 1 \text{ a.e. in } \Omega_{av}^T; \]
\[ \text{ii) } \text{there exists a constant } C > 0 \text{ such that} \]
\[ \|U^\varepsilon(t)\|_{L^2(\Omega_{av})}^2 + D \|\partial_x U^\varepsilon\|_{L^2(\Omega_{av})}^2 \leq C, \]
\[ \|\partial_t U^\varepsilon\|_{L^2((0, t); H^{-1}(\Omega_{av}))}^2 \leq C \left( 1 + \frac{\varepsilon^2}{T} \right), \]
\[ \|V^\varepsilon(t)\|_{L^2(\Omega_{av})}^2 + \|\partial_t V^\varepsilon\|_{L^2(\Omega_{av})}^2 \leq C, \]
for all $0 < t \leq T$ and for all $\varepsilon > 0$. \hfill \square
Proof. The $L^\infty$ bounds are straightforward. They directly imply the $L^2$-bounds for $U^\varepsilon(t)$ and $V^\varepsilon(t)$. The estimate on $\partial_x U^\varepsilon$ follows from Lemma 4.2 and the estimate on $\partial_t V^\varepsilon$ is obtained by testing (4.7) with $\theta = \chi_{(0,t)}\partial_t V^\varepsilon$. Finally, (4.6) yields
\[
|\langle \partial_t U^\varepsilon, \varphi \rangle_{\Omega_{av}}| \leq D \|\partial_x U^\varepsilon\|_{\Omega_{av}} \|\partial_x \varphi\|_{\Omega_{av}} + Q \|U^\varepsilon\|_{\Omega_{av}} \|\partial_x \varphi\|_{\Omega_{av}} + n \|\partial_t V^\varepsilon\|_{\Omega_{av}} \|\varphi\|_{\Omega_{av}} + |T^\varepsilon_1(\varphi)|
\]
for all $\varphi \in L^2((0,t); H^1_0(\Omega_{av}))$. Then the previous estimates and Lemma 4.5 give the $H^{-1}$ bound. \hfill \square

The estimates in Lemma 4.6 imply that $\{U^\varepsilon\}_{\varepsilon > 0}$ is uniformly bounded in $L^\infty(\Omega_{av}^T) \cap L^2((0,T); H^1(\Omega_{av})) \cap H^1((0,T); H^{-1}(\Omega_{av}))$;

$\{V^\varepsilon\}_{\varepsilon > 0}$ is uniformly bounded in $L^\infty(\Omega_{av}^T) \cap H^1((0,T); L^2(\Omega_{av}))$;

$\{W^\varepsilon\}_{\varepsilon > 0}$ is uniformly bounded in $L^\infty(\Omega_{av}^T)$.

Compactness arguments give the existence of a triple $(U, V, W) \in \mathcal{U}_{av} \times H^1((0,T); L^2(\Omega_{av})) \times L^\infty(\Omega_{av}^T)$ and a sequence $\varepsilon \searrow 0$ such that

a) $U^\varepsilon \rightharpoonup U$ weakly in $L^2((0,T); H^1(\Omega_{av}))$

b) $\partial_t U^\varepsilon \rightharpoonup \partial_t U$ weakly in $L^2((0,T); H^{-1}(\Omega_{av}))$

c) $V^\varepsilon \rightharpoonup V$ weakly in $L^2(\Omega_{av}^T)$

d) $\partial_t V^\varepsilon \rightharpoonup \partial_t V$ weakly in $L^2(\Omega_{av}^T)$

e) $W^\varepsilon \rightharpoonup W$ weakly-star in $L^\infty(\Omega_{av}^T)$

The following theorem shows that the limit $(U, V, W)$ thus obtained is the unique solution of Problem $P_{av}$.

**Theorem 4.7.** Problem $P_{av}$ has the triple $(U, V, W)$ as its unique weak solution.

Proof. We first demonstrate uniqueness. It implies that $\{(U^\varepsilon, V^\varepsilon, W^\varepsilon)\}_{\varepsilon > 0}$ converges towards $(U, V, W)$ along any sequence $\varepsilon \searrow 0$. Let $(U_1, V_1, W_1)$ and $(U_2, V_2, W_2)$ both solve Problem $P_{av}$. One easily verifies that $u_\ast \leq U_1, U_2 \leq u_\ast$ a.e. in $\Omega_{av}^T$. Set

\[ U := U_1 - U_2, \quad V := V_1 - V_2 \quad \text{in } \Omega_{av}^T \]

To simplify notation we write below $\langle \cdot, \cdot \rangle$ and $\| \cdot \|$ instead of $\langle \cdot, \cdot \rangle_{\Omega_{av}}$ and $\| \cdot \|_{\Omega_{av}}$, respectively. In the spirit of [1], we test (4.9) with $\theta(t,x) = \chi_{(0,t)} V$ for any $0 < t \leq T$. Using the monotonicity of $H$ and the
Lipschitz continuity of $r$, we obtain
\[ \|V(t)\|^2 \leq k^2 L_r^2 \int_0^t \|U(\tau)\|^2 d\tau + \int_0^t \|V(\tau)\|^2 d\tau, \]
for all $t \leq T$. Applying Gronwall’s lemma gives
\[ (4.11) \quad \|V(t)\|^2 \leq e^{t} k^2 L_r^2 \int_0^t \|U(\tau)\|^2 d\tau, \]
\[ \int_0^t \|V(\tau)\|^2 d\tau \leq (e^{t} - 1) k^2 L_r^2 \int_0^t \|U(\tau)\|^2 d\tau. \]

The difference $U$ satisfies
\[ (4.12) \quad (\partial_t U, \varphi) + D(\partial_x U, \partial_x \varphi) + Q(\partial_x U, \varphi) + n(\partial_t V, \varphi) = 0 \]
for all $\varphi \in L^2((0,T); H_0^1(\Omega_{av}))$. For fixed $s \leq T$, chosen arbitrarily, we test (4.12) with $\varphi(t, x) = \chi_{(0,s)} \int_0^s U(\tau, x) d\tau$ and evaluate each of the resulting terms. In a straightforward way we obtain
\[ \int_0^s \|U(t)\|^2 dt + D\|\partial_x \varphi(0)\|^2 \leq 2n^2 \int_0^s \|V(t)\|^2 dt + 2Q^2 \int_0^s \|\partial_x \varphi(t)\|^2 dt. \]
Using (4.11) and taking $s \leq \ln (1 + 1/(2nkL_r)^2)$ gives
\[ (4.13) \quad \frac{1}{2} \int_0^s \|U(t)\|^2 dt + D\|\partial_x \varphi(0)\|^2 \leq 2Q^2 \int_0^s \|\partial_x \varphi(t)\|^2 dt. \]
Estimating
\[ \int_0^s \|\partial_x \varphi(t)\|^2 dt = \int_0^s \int_0^L \left| \int_0^t \partial_x U(\tau, x) d\tau \right|^2 dx dt \]
\[ \quad \leq 2 \int_0^s \int_0^L \left| \int_0^t \partial_x U(\tau, x) d\tau \right|^2 dx dt + 2 \int_0^s \int_0^L \left| \int_0^t \partial_x U(\tau, x) d\tau \right|^2 dx dt \]
\[ \quad = 2s \int_0^L \left| \int_0^t \partial_x U(\tau, x) d\tau \right|^2 dx + 2 \int_0^s \int_0^L \left| \int_0^t \partial_x U(\tau, x) d\tau \right|^2 dx dt \]
in (4.13) and taking further $s \leq \frac{D}{8Q^2}$ we obtain
\[ (4.14) \quad \int_0^s \|U(t)\|^2 dt + D\zeta(s) \leq 8Q^2 \int_0^s \zeta(t) \, dt, \]
where $\zeta(t) = \int_0^L \left| \int_0^t \partial_x U(\tau, x) \, d\tau \right|^2 dx$. By Gronwall’s lemma we deduce
\[ \zeta(s) = 0, \]
and consequently
\[ \int_0^s \|U(t)\|^2 dt = 0, \]
for all $0 \leq s \leq \min \left\{ \frac{D}{8Q^2}, \ln \left( 1 + \frac{1}{(2nkL_r)^2} \right) \right\}$. This establishes uniqueness.
To obtain existence we consider (4.6)–(4.7). By Lemma 4.5 and the convergence properties of $U^\varepsilon$, $V^\varepsilon$ and $W^\varepsilon$ we directly obtain that $(U, V, W)$ satisfies (4.8)–(4.9). To establish (4.7) we argue as in the proof of Theorem 2.21. The essential difference is that here, from (4.7),

$$
\partial_t V^\varepsilon = k(r(U^\varepsilon) - W^\varepsilon) + k(r(u^\varepsilon(\cdot, \cdot, 1)) - r(U^\varepsilon))
$$

and thus

(4.15) \hspace{1cm} V^\varepsilon = v_0 + k \int_0^t (r(U^\varepsilon) - W^\varepsilon) + k \int_0^t (r(u^\varepsilon(\cdot, \cdot, 1)) - r(U^\varepsilon))

a.e. in $\Omega^T_{av}$. By Lemma 4.4, however, the last term on the right in (4.15) vanishes as $\varepsilon \searrow 0$. Therefore we can proceed exactly along the lines of the proof of Theorem 2.21. We omit the details. \hfill \Box

**Remark 4.8.** Theorem 4.7 gives existence and uniqueness for the one dimensional case of the model proposed in [12] and [3]. In the multi–dimensional case existence can be obtained by regularization arguments as used in Section 2. The uniqueness proof cannot be extended straightforwardly to the multi–dimensional case, since $v$ is defined on a lower dimensional manifold. In the estimates we then have to use trace results, involving also gradients of $U$, in inequalities like (4.11). \hfill \Box

**Remark 4.9.** As in Theorem 2.21, in addition to $W \in H(V)$ we have that $W = r(U)$ a.e. in $\{ V = 0 \} \cap \Omega^T_{av}$. \hfill \Box

As noted before there exists for each $\varepsilon > 0$ a dissolution front $S^\varepsilon$ that separates the region where all crystals are dissolved from the region where crystals are still present. In particular,

$$
S^\varepsilon(t) = \begin{cases} 
0, & \text{for } 0 \leq t \leq t^* = \frac{v_0}{k}, \\
\text{continuous and strictly increasing for } t > t^* 
\end{cases}
$$

and

$$
V^\varepsilon(t, x) = \begin{cases} 
0, & \text{if } 0 < x < S^\varepsilon(t) \text{ and } t > t^*, \\
> 0, & \text{if } x > S^\varepsilon(t) \text{ and } t > 0 
\end{cases}
$$

for all $\varepsilon > 0$. These properties carry over in the averaging process. Related to Problem $P_{av}$ we call $S : [0, T] \to [0, L]$, defined by

$$
S(t) := \sup \left\{ 0 \leq x \leq L : \int_0^x V(t, y)dy = 0 \right\}
$$

for $0 \leq t \leq T$, the dissolution front.

Then we have
Theorem 4.10.

(i) \( S(t) = \begin{cases} 
0, & 0 \leq t \leq t^*, \\
> 0, & t^* < t \leq T; 
\end{cases} \)

(ii) \( S \in C([0,T]) \) and strictly increasing when \( 0 < S < L; \)

(iii) \( V(t,x) = 0, W(t,x) = r(U(t,x)) \) for \( t > t^* \) and \( 0 < x < S(t); \)

(iv) \( V(t,x) > 0, W(t,x) = 1 \) for \( t > 0 \) and \( S(t) < x \leq L; \)

(v) along any sequence \( \varepsilon \searrow 0, S^\varepsilon \to S \) pointwisely in \([0,T].\)

Proof. Assertions (i)–(iv) are proven by the methods and ideas developed in Section 3. We omit the details. To show (v) we first note that \( S^\varepsilon(t) = S(t) = 0 \) for any \( \varepsilon > 0 \) and for all \( 0 \leq t \leq t^*. \) Thus it remains to consider \( t > t^*. \)

With \( t \in (t^*,T] \) chosen arbitrarily we show that \( \lim_{\varepsilon \searrow 0} S^\varepsilon(t) = S(t) \) along any sequence \( \varepsilon \searrow 0. \) To this aim we first observe that \( V(t,x) = 0 \) for almost every \( x \in [0,L] \) where \( \lim_{\varepsilon \searrow 0} V^\varepsilon(t,x) = 0. \) This follows from an argument similar to the one used in the proof of Theorem 2.21. Hence \( V(t,x) > 0 \) implies \( \lim_{\varepsilon \searrow 0} V^\varepsilon(t,x) > 0, \) so

\begin{equation}
S(t) \geq S^\varepsilon(t)
\end{equation}

if \( \varepsilon \) is small enough.

Next assume that there exists a \( \mu > 0 \) and a sequence \( \varepsilon \searrow 0 \) such that

\( S^\varepsilon(t) \leq S(t) - \mu. \)

Then by the monotonicity of \( S^\varepsilon \) and the continuity of \( S, \) there exists \( t_0 < t \) such that

\( S^\varepsilon(\tau) \leq S(t) - \mu < S(t) - \frac{\mu}{2} < S(\tau) \)

for all \( t_0 \leq \tau \leq t. \) Consequently, along this sequence \( \varepsilon \searrow 0, \)

\( V^\varepsilon > 0 \) and \( W^\varepsilon = 1 \) a.e. in \( R, \)

while

\( V = 0 \) and \( W = r(U) \) a.e. in \( R, \)

where \( R \) denotes the rectangle \( (t_0,t) \times (S(t) - \mu, S(t) - \frac{\mu}{2}). \)

Applying Lemma 3.6 to \( u^\varepsilon, \) since \( U^\varepsilon \) converges almost everywhere to \( U \) we directly obtain

\( U \leq \int_0^1 U(\cdot,\cdot, \xi) \, d\xi < u^* \) a.e. in \( Q_{av}. \)
and thus
\[ r(U) < 1 \quad \text{a.e. in } R. \]
This contradicts the weak–star convergence of \( W^\varepsilon \) towards \( W \) and, together with (4.16) completes the proof of assertion (v). \qed

**Remark 4.11.** In the previous analysis we assumed \( D = O(1) \). Different regimes would occur when considering \( D = O(\varepsilon^\gamma) \). Taking \( \gamma \in (0,2) \), formal upscaling would lead to a hyperbolic version of (4.8), in which the diffusive term has vanished. We expect the case \( \gamma \geq 2 \) to be more involved, and the corresponding upscaled equations more difficult to obtain. \qed

## 5. Numerical example

In this section we present some numerical results obtained for the particular geometry considered in Sections 3 and 4. Specifically, for \( L = 20.0 \) and a given \( \varepsilon > 0 \) we consider the thin strip \( \Omega^\varepsilon = (0,L) \times (0,\varepsilon) \), which is transformed back to \( \Omega = (0,L) \times (0,1) \) by the scaling proposed in Section 4. This leads to the model given in (4.3)–(4.4).

We have used the following parameters and rate function:
\[ D = Q = m = n = 1.0, \quad k = 0.9, \quad \text{and } r(u,c) = \frac{10}{9} [u]_+ [u - c]_+. \]
The total charge is kept constant, with \( c = 0.1 \). The fluid velocity \( q \) is given in (4.2). The initial and (external) boundary conditions are specified in (3.4), with
\[ u_* = 0.1, \quad u^* = 1.0, \quad \text{and } v_0 = 1.0. \]

Computations are performed for two values of \( \varepsilon \): \( \varepsilon = 1 \) and \( \varepsilon = 0.2 \). We computed up to \( T = 30 \). The choice \( L = 20 \) ensures that, within the specified time, the influence of the boundary condition at the outlet is minimal. Discretization in space is obtained by finite differences on a regular grid of size \( h = 0.05 \). For the transport term we have applied a standard first order upwinding. For the time discretization we have used the forward Euler scheme with a fixed time step \( \tau = 10^{-5} \). By this choice the CFL-condition is satisfied. As mentioned in the appendix of [3] (see also Theorem 2.21), we set \( w = r(u) \) whenever \( v = 0 \).

Figure 7 displays level curves of the cation concentration \( u \). In the first pair \( t = 10 \), with \( \varepsilon = 1 \) in Figure 7a and \( \varepsilon = 0.2 \) in Figure 7b. In the second pair \( t = 30 \), with \( \varepsilon = 1 \) in Figure 7c and \( \varepsilon = 0.2 \) in Figure 7d. The level curves are curved due to the parabolic velocity profile which attains its largest value at the centre of the strip, here denoted by \( \Gamma_N \). Along the wall \( \Gamma_G \), cations are being fed to the fluid by the chemical reactions. This causes an increase in longitudinal spreading.
In the rescaled setting $z \to \xi = z/\varepsilon$ the effective $\xi$-diffusivity becomes $D/\varepsilon^2$. This explains the rather straight level curves when $\varepsilon = 0.2$.

Figure 8 shows the crystal concentration $v$ for $\varepsilon = 1$ and $\varepsilon = 0.2$, at the times $t = 10$, $t = 20$ and $t = 30$. Note that the profiles for $\varepsilon = 0.2$ (dashed curves) are slightly steeper than the ones for $\varepsilon = 1$. Further note that the distance between the profiles within and between the pairs
Figure 8. Crystal concentration $v$ for $\varepsilon = 1$ (solid) and $\varepsilon = 0.2$ (dashed): (a) $t = 1$; (b) $t = 2$; (c) $t = 3$.

Figure 9. Evolution of the free boundary (dissolution front), $\varepsilon = 1$ (solid) and $\varepsilon = 0.2$ (dashed). (a), (b) and (c) is nearly constant in time. This can also be observed in Figure 9, displaying the evolution of the dissolution front. According to Proposition 3.7, the dissolution front moves to the right after the waiting time $t^* = 1/0.9 = 1.11 \ldots$. Computationally we find $t^* = 1.1581$ ($\varepsilon = 1$) and $t^* = 1.1245$ ($\varepsilon = 0.2$). From Figure 9 we also observe
that the free boundaries are nearly parallel and move with a constant speed $\dot{a} = 0.47$. This is in good agreement with the one-dimensional upscaled case, where a travelling wave solution exists, moving with speed $a = \frac{Q (u^* - u_0)}{u^* - u_0 + v_0} = 9/19 \approx 0.4737 \ldots$ (see Proposition 1.2 of [3]).

References


Department of Mathematics and Computing Science
Eindhoven University of Technology
P.O. Box 513, 5600 MB Eindhoven, The Netherlands
e-mail: {C.J.v.Duijn, I.Pop}@tue.nl