Crystal dissolution and precipitation in porous media : L^1-contraction and uniqueness

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CRYSTAL DISSOLUTION AND PRECIPITATION IN POROUS MEDIA: L^1-CONTRACTION AND UNIQUENESS

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Abstract. In this note we continue the analysis of the pore-scale model for crystal dissolution and precipitation in porous media proposed in [C. J. van Duijn and I. S. Pop, *Crystal dissolution and precipitation in porous media: pore scale analysis*, J. Reine Angew. Math. 577 (2004), 171–211]. There the existence of weak solutions was shown. We prove an L^1-contraction property of the pore-scale model. As a direct consequence we obtain the uniqueness of (weak) solutions.

1. **Introduction.** Crystal dissolution and precipitation is an important process arising in different real life applications. In the pore-scale model introduced in [5], the flow of a fluid and the transport of a certain chemical substrate through a porous medium is coupled with dissolution/precipitation processes on the grain boundary. In [1, 5] an analytical and numerical study of this model is performed but the question of uniqueness of (weak) solution was left open. In this note we prove an L^1-contraction property of weak solution, which in particular implies uniqueness of the solution.

1.1. **The pore-scale model.** To describe the model introduced in [5] we consider a porous medium consisting of the *pore space* and the solid (impermeable) matrix. This matrix consists of solid grains, whose boundary we call *grain boundary.* Let the pore space be represented by an open, connected and bounded domain $\Omega \subset \mathbb{R}^d$, $d > 1$. The boundary $\partial\Omega$ is assumed to be Lipschitz continuous and consists of two disjoint parts: an internal part Γ_G describing the boundary of all grains, and an external boundary Γ_D - the outer boundary of the medium. Both boundary parts are assumed to have a non-zero measure. We denote by $\vec{\nu}$ the outer normal to $\partial\Omega$, fix an arbitrarily chosen value of time $T > 0$ and set

$$\Omega^T := (0,T] \times \Omega, \quad \Gamma_G^T := (0,T] \times \Gamma_G, \quad \text{and} \quad \Gamma_D^T := (0,T] \times \Gamma_D.$$

We consider a fluid flowing through the pores of a porous medium and transporting cations and anions of a certain chemical substrate. These ions can precipitate on the grain boundary and form a crystalline solid, the *precipitate.* The reverse reaction of dissolution is also possible. The flow, as well as the precipitation and

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dissolution process will be described by the following (dimensionless) quantities:

$$\begin{array}{ll} q : \Omega \to \mathbb{R}^d, & \text{the fluid velocity,} \\ u : \Omega^T \to \mathbb{R}, & \text{the solute concentration (cation),} \\ v : \Gamma_G^T \to \mathbb{R}, & \text{the precipitate concentration,} \\ w : \Gamma_G^T \to \mathbb{R}, & \text{the dissolution rate.} \end{array}$$

Notice that q and u are defined in the entire pore space Ω, whereas v and w are defined only on the grain boundary Γ_G^T.

Remark 1. In the above we have only considered one solute (the cation), whereas dissolution and precipitation involves another species, the anion. Following [8], this second species is eliminated in [5] by involving another quantity, the total electric charge in the fluid. This is a linear combination of the concentrations of the ions, and can be determined by solving a linear parabolic problem that depends only on the flow and not on the precipitation process. Therefore the problem is simplified by reducing the number of unknown quantities, since the electric charge can be decoupled from the chemistry and thus be determined separately. Moreover, for simplicity we assume here that the initial data are compatible in the sense of [4] and [8]. Essentially this means that initially the system is in equilibrium. Moreover, the boundary data are assumed such that the total charge remains constant in time and space, therefore in the model considered here we consider the charge being a given constant. However, the results presented here can be extended to the case of a known, non-constant electric charge.

In a dimensionless form the model considered in [5] is given by the following system:

$$\partial_t u + \nabla \cdot (\vec{q}u - D\nabla u) = 0 \qquad \text{in } \Omega^T, \tag{1}$$

together with

$$\left\{ \begin{array}{rcll} -D\vec{\nu} \cdot \nabla u &=& \varepsilon n \partial_t v, & \text{on } \Gamma_G^T, \\ \partial_t v &=& k(r(u) - w), & \text{on } \Gamma_G^T, \\ w &\in& H(v), & \text{on } \Gamma_G^T, \end{array} \right. \tag{2}$$

Here $\varepsilon > 0$ is a, typically small, parameter and $n \in \mathbb{N}$, $D > 0$ are given constants describing the valence of the anions and a diffusion coefficient, respectively. k is another constant related to the ratio of the characteristic precipitation/dissolution time scale and the characteristic transport time scale (the Damköhler number). Finally, $r : \mathbb{R} \to [0, +\infty)$ denotes the precipitation rate described in Section 1.3 below and H the set-valued Heaviside function,

$$H(v) = \left\{ \begin{array}{ll} \{0\}, & \text{if } v < 0, \\ [0,1], & \text{if } v = 0, \\ \{1\}, & \text{if } v > 0. \end{array} \right.$$

The system (1)-(2) is complemented by the following initial- and boundary conditions,

$$\left\{ \begin{array}{rcll} u(0,\cdot) &=& u_I & \text{in } \Omega, \\ v(0,\cdot) &=& v_I, & \text{on } \Gamma_G, \\ u &=& u_D, & \text{on } \Gamma_D^T. \end{array} \right. \tag{3}$$

For simplicity, in the present paper we only consider boundary data of Dirichlet type. The results can be extended straightforwardly to the case where also Neumann type boundary conditions are defined on the external part of the boundary.

We remark that (1)-(3) couples a parabolic problem defined in the domain Ω^T through the boundary conditions to a differential inclusion on the grain boundary Γ_G^T . The problem above is the pore-scale-counterpart of the macroscopic (core-scale) model introduced in [8].

One basic assumption in the pore-scale model is that the porous skeleton is not affected by the chemical processes. This situation occurs if the size of the crystals is small when compared to a grain, and therefore the changes in the void space are negligible. A one dimensional model involving variations in the fluid domain is analyzed in [10]. Further, it is also assumed that the fluid properties are not affected by the precipitation process: the flow is a decoupled part of the model and is obtained independently. We therefore consider $\vec{q}$ to be a given, divergence free velocity, having a zero trace along the internal grain boundary Γ_G:

$$\nabla \cdot \vec{q} = 0 \text{ in } \Omega, \qquad \vec{q} = \vec{0} \text{ on } \Gamma_G. \tag{4}$$

1.2. **Notations.** Using standard notations of functional analysis we denote by $H^1(\Omega)$ the space of functions defined on Ω and having L^2 generalized derivatives, and by $H^1_{0,\Gamma_D}(\Omega)$ those elements of $H^1(\Omega)$ vanishing on Γ_D. Moreover let $(\cdot,\cdot)_\Omega$ be the scalar product in $L^2(\Omega)$, or the duality pairing between $H^1_{0,\Gamma_D}(\Omega)$ and $H^{-1}(\Omega)$ - the dual of $H^1_{0,\Gamma_D}(\Omega)$. The notations $L^2(\Gamma_Y)$ (with $Y = G$ or D) have similar meanings. Moreover, with $X \in \{\Omega, \Gamma_G\}$, by $(\cdot,\cdot)_{X^T}$ we mean the time integral $\int_0^T (\cdot,\cdot)_X$. The corresponding norms are denoted by $\|\cdot\|_X$, $\|\cdot\|_{X^T}$.

1.3. **Assumptions on the precipitation rate.** The equations (2) are the challenging part in the pore-scale dissolution and precipitation model. Several model-specific functions are involved. For the precipitation rate r we assume here

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

(ii) there exists a unique $u_* \geq 0$, such that

$$r(u) = \begin{cases} 0, & \text{for} \quad u \leq u_*, \\ \text{strictly increasing for } u > u_* \text{ with } r(\infty) = \infty. \end{cases}$$

A typical example is suggested by the mass action kinetics:

$$r(u) = [u]_+^m [(mu - c)/n]_+^n, \tag{5}$$

with c the given electric charge (assumed constant here) and m the valence of the cation; $[\cdot]_+$ denotes the non-negative cut

$$[u]_+ = \begin{cases} 0, & \text{if } u < 0, \\ u, & \text{if } u > 0. \end{cases} \tag{6}$$

Remark 2. In the setting above, a unique $u^* > u_*$ exists for which $r(u^*) = 1$. This value can be interpreted as an equilibrium value: if $u = u^*$ for all t and x, then neither precipitation nor dissolution occurs. As we will see below, in this case the precipitation rate is balanced by the dissolution rate regardless of the presence or absence of crystals.

Remark 3. The particularity of the model is in the description of the dissolution by means of a multi-valued rate function. This implies that the dissolution rate w is constant (and scaled to 1) in the presence of crystals, i.e. for $v > 0$ somewhere on Γ_G. In the absence of crystals ($v = 0$), the dissolution rate takes values in $[0, 1]$. To be more precise, in this situation we have to distinguish between two possibilities. In the *oversaturated* case, i. e. for $u > u^*$ implying $r(u) > 1$, we prescribe that $w = 1$ and the overall precipitation/dissolution rate is strictly positive. Whenever $u \leq u^*$ - thus $r(u) \leq 1$, the fluid is not containing sufficient dissolved ions for an effective gain in precipitate (the *undersaturated* regime). Since $v = 0$ a.e. in the regions of Γ_G being in contact with the undersaturated fluid, it follows that $\partial_t v = 0$ there, implying that $w = r(u)$ so that the overall rate is 0. Following the detailed discussion in [3], this can be summarized in

$$w = \begin{cases} 0, & \text{if } v < 0, \\ \min\{r(u), 1\}, & \text{if } v = 0, \\ 1, & \text{if } v > 0. \end{cases} \tag{7}$$

This description of the dissolution process allows for dissolution and precipitation fronts. For the upscaled model, these fronts are investigated in [11] (assuming equilibrium conditions) and in [3] (as traveling waves). For the pore scale model, the dissolution fronts are investigated analytically in [5] and numerically in [1], where also the convergence of a numerical scheme is proven. For the analysis of similar models with particular emphasize on homogenization we mention [6] and [7]. The effect of having high Peclet and Damköhler numbers is investigated in [2, 9] for models of the same type, but involving a simplified chemistry on the grain boundary.

2. **Existence of weak solutions.** The main difficulty in the pore-scale model is associated with the multi-valued function describing the dissolution. In general we do not expect to find classical solutions. In [5] the existence of weak solution is proved, under the following assumption on the data and $\vec{q}$:

(A_D) The boundary and initial data are essentially bounded and non-negative; the boundary data are constant in time and traces of H^1 – functions. Further, $\vec{q} \in [H^1(\Omega)]^d$ is essentially bounded and satisfies (4).

The positivity and boundedness of the data are not restrictive, since u and v model concentrations. By considering here boundary data that are constant in time we avoid non essential technical details.

For defining a weak solution we consider the following function spaces

$$\begin{aligned} \mathcal{U} &:= \{u \in u_D + L^2(0,T; H^1_{0,\Gamma_D}(\Omega)) : \partial_t u \in L^2(0,T; H^{-1}(\Omega))\}, \\ \mathcal{V} &:= \{v \in H^1(0,T; L^2(\Gamma_G))\}, \\ \mathcal{W} &:= \{w \in L^\infty(\Gamma_G^T), : 0 \leq w \leq 1\}. \end{aligned}$$

Note that the definition of $\mathcal{U}$ takes care of the Dirichlet-boundary-condition.

Definition 1. A triple $(u, v, w) \in \mathcal{U} \times \mathcal{V} \times \mathcal{W}$ is called a weak solution of (1)-(3) if $(u(0, \cdot) = u_I$, $v(0, \cdot) = v_I$ and if

$$(\partial_t u, \varphi)_{\Omega^T} + D(\nabla u, \nabla \varphi)_{\Omega^T} - (\vec{q}u, \nabla \varphi)_{\Omega^T} = -\varepsilon n(\partial_t v, \varphi)_{\Gamma_G^T}, \tag{8}$$

$$\begin{aligned} (\partial_t v, \theta)_{\Gamma_G^T} &= k(r(u) - w, \theta)_{\Gamma_G^T}, \\ w &\in H(v) \quad \text{a.e. in } \Gamma_G^T, \end{aligned} \tag{9}$$

for all $(\varphi, \theta) \in L^2(0,T; H^1_{0,\Gamma_D}(\Omega)) \times L^2(\Gamma_G^T)$.

Moreover, following the discussion in Remark 3, (9_2) should be understood in the sense of (7).

We can now state the following existence result:

Theorem 1 ([5] Theorem 2.21)**.** *Assume (A_r) and (A_D), then there exists a weak solution of* (1)-(3)*. In addition, such a solution satisfies*

$$\begin{aligned}\|u\|^2_{L^\infty(0,T;L^2(\Omega))} + \|\nabla u\|^2_{L^2(\Omega^T)} + \|\partial_t u\|^2_{L^2(0,T;H^{-1}(\Omega))}&\\ +\varepsilon\|v\|^2_{L^\infty(0,T;L^2(\Gamma_G))} + \varepsilon\|\partial_t v\|^2_{L^2(\Gamma_G^T)} &\le C,\end{aligned} \tag{10}$$

where the constant $C > 0$ is independent of u, v, w and ε.

Furthermore, it is proven in [5, Lemmas 2.6-2.8] that a weak solutions also satisfies

$$0 \le u \le \max\{\|u_I\|_{\infty,\Omega}, u^*\} \quad \text{a.e. in } \Omega^T \tag{11}$$

$$0 \le v(t,\cdot) \le M_v e^{C_v t} \text{ for all } t \in [0,T] \text{ and a.e. on } \Gamma_G, \tag{12}$$

$$0 \le w \le 1 \text{ a.e. on } \Gamma_G^T, \tag{13}$$

where $M_v := \max\{\|v_I\|_{\infty,\Omega}, 1\}$, $C_v := \frac{r(M_u)}{M_v}$.

3. L^1-contraction and uniqueness.

In this section we analyze the solution of the pore scale model (1)-(3). We prove an L^1-contraction result and obtain as a corollary the uniqueness of weak solutions.

The basis of the contraction property is in a monotone structure of the overall precipitation-rate given by the right-hand side of (2_2).

Lemma 1. *Consider the precipitation rate r satisfying (A_r), let the dissolution rate $w(u,v)$ be defined by* (7) *and set*

$$f(u,v) := r(u) - w(v,u). \tag{14}$$

Then f is monotone with respect to both arguments:

$$u \mapsto f(u,v) \text{ is monotone increasing}, \tag{15}$$

$$v \mapsto f(u,v) \text{ is monotone decreasing}. \tag{16}$$

Proof. Whenever $v \neq 0$, the first claim follows directly from the monotonicity of r. In the case $v = 0$ we obtain $f(u,v) = r(u) - \min(1, r(u))$, which is monotone increasing in u. This proves (15).

The second claim follows from the definition of w in (7). □

We now prove the L^1-contraction principle.

Theorem 2. *Let the assumptions (A_r) and (A_D) be satisfied and consider two weak solutions $(u^{(i)}, v^{(i)}, w^{(i)}) \in \mathcal{U} \times \mathcal{V} \times \mathcal{W}$, $i = 1,2$ of* (1)-(3) *with initial values $(u_I^{(i)}, v_I^{(i)})$, $i = 1,2$ respectively. Then for any $t \in (0,T]$ we have*

$$\begin{aligned}&\textstyle\int_\Omega |u^{(1)}(t,x) - u^{(2)}(t,x)|dx + \varepsilon n \int_{\Gamma_G} |v^{(1)}(t,s) - v^{(2)}(t,s)|ds\\ &\qquad \le \textstyle\int_\Omega |u_I^{(1)}(x) - u_I^{(2)}(x)|dx + \varepsilon n \int_{\Gamma_G} |v_I^{(1)}(s) - v_I^{(2)}(s)|ds.\end{aligned} \tag{17}$$

Proof. We start by defining

$$\mathcal{T}_\delta(x) := \begin{cases} -x - \dfrac{\delta}{2}, & \text{if } x < -\delta, \\ \dfrac{x^2}{2\delta}, & \text{if } x \in [-\delta, \delta], \\ x - \dfrac{\delta}{2}, & \text{if } x > \delta, \end{cases}$$

where $\delta > 0$ is arbitrary small. Its derivative is the regularized sign function

$$\mathcal{T}_\delta'(x) = \mathcal{S}_\delta(x) := \begin{cases} -1, & \text{if } x < -\delta, \\ \dfrac{x}{\delta}, & \text{if } x \in [-\delta, \delta], \\ 1, & \text{if } x > \delta. \end{cases}$$

Subtracting (8) written for $u^{(2)}$ from the one fulfilled by $u^{(1)}$ and using (9) gives for $u := u^{(1)} - u^{(2)} \in L^2((0,T); H_0^1(\Omega))$:

$$\begin{aligned} &(\partial_t u, \varphi)_{\Omega^T} + D(\nabla u, \nabla\varphi)_{\Omega^T} - (\vec{q}u, \nabla\varphi)_{\Omega^T} \\ &\qquad + \varepsilon n k (r(u^{(1)}) - r(u^{(2)}) - (w^{(1)} - w^{(2)}), \varphi)_{\Gamma_G^T} = 0, \end{aligned} \tag{18}$$

for all $\varphi \in L^2((0,T); H^1_{0,\Gamma_D}(\Omega))$. Similarly, for $v := v^{(1)} - v^{(2)} \in L^2(\Gamma_G^T)$ we obtain

$$(\partial_t v, \theta)_{\Gamma_G^T} = k(r(u^{(1)}) - r(u^{(2)}) - (w^{(1)} - w^{(2)}), \theta)_{\Gamma_G^T} \tag{19}$$

for all $\theta \in L^2(\Gamma_G^T)$, where $w^{(i)} \in H(v^{(i)})$ a.e. in Γ_G^T.

With χ_I being the characteristic function of a time interval I, for any $t \in (0,T]$ we test (18) with $\varphi := \chi_{(0,t)}\mathcal{S}_\delta(u) \in L^2((0,T); H^1_{0,\Gamma_D}(\Omega))$ and (19) with $\theta := \varepsilon n \chi_{(0,t)}\mathcal{S}_\delta(v)$. Adding the resulting gives

$$\begin{aligned} &\textstyle\int_0^t (\partial_t u, \mathcal{S}_\delta(u))_\Omega dt + \varepsilon n \int_0^t (\partial_t v, S_\delta(v))_{\Gamma_G} dt \\ &\quad \textstyle + D\int_0^t (\nabla u, \nabla\mathcal{S}_\delta(u))_\Omega dt - \int_0^t (\vec{q}u, \nabla\mathcal{S}_\delta(u))_\Omega dt \\ &\qquad \textstyle + \varepsilon n k \int_0^t (r(u^{(1)}) - r(u^{(2)}) - (w^{(1)} - w^{(2)}), \mathcal{S}_\delta(u) - S_\delta(v))_{\Gamma_G} dt = 0. \end{aligned} \tag{20}$$

We proceed by estimating each of the terms in the equation above, denoted by I_δ^1, I_δ^2, …, I_δ^5. For I_δ^1 we obtain

$$I_\delta^1 = \int_0^t \int_\Omega \partial_\tau \mathcal{T}_\delta(u(\tau, x)) dx d\tau = \int_\Omega \mathcal{T}_\delta(u(t,x)) dx - \int_\Omega \mathcal{T}_\delta((u_I^{(1)} - u_I^{(2)})(x)) dx.$$

Recalling (A$_D$), since $|T_\delta(s)| \leq |s| + \delta/2$ and $u^{(1)}(t), u^{(2)}(t) \in L^2(\Omega)$, we obtain by the Dominated Convergence Theorem that

$$\lim_{\delta\to 0} I_\delta^1 = \int_\Omega |u^{(1)}(t,x) - u^{(2)}(t,x)| dx - \int_\Omega |u_I^{(1)}(x) - u_I^{(2)}(x)| dx. \tag{21}$$

In a similar manner,

$$\lim_{\delta\to 0} I_\delta^2 = \int_{\Gamma_G} |v^{(1)}(t,s) - v^{(2)}(t,s)| ds - \int_\Omega |v_I^{(1)}(s) - v_I^{(2)}(s)| ds. \tag{22}$$

For I_δ^3 we notice that $\mathcal{S}_\delta' \geq 0$ a.e. on $\mathbb{R}$. Therefore we have

$$I_\delta^3 = D\int_0^t \int_\Omega \mathcal{S}_\delta'(u) |\nabla u|^2 dx d\tau \geq 0 \tag{23}$$

uniformly in δ. Furthermore, I_δ^4 gives no contribution since

$$I_\delta^4 = \int_0^t \int_\Omega \nabla \cdot (\vec{q}\, \mathcal{T}_\delta(u)) dx d\tau = \int_0^t \int_{\partial\Omega} \vec{\nu} \cdot \vec{q}\, \mathcal{T}_\delta(u) ds d\tau = 0. \tag{24}$$

In the above we have used (4), as well as the vanishing trace of u on Γ_D.

Finally, we claim that

$$\lim_{\delta \searrow 0} I_\delta^5 \ \geq\ 0. \tag{25}$$

By (14) we can rewrite

$$I_\delta^5 \ = \int_0^t \int_\Omega \Big(f\big(u^{(1)}, v^{(1)}\big) - f\big(u^{(2)}, v^{(2)}\big)\Big) \Big(S_\delta\big(u\big) - S_\delta\big(v\big)\Big)\, dx\, d\tau. \tag{26}$$

The integrand of this expression converges pointwise as $\delta > 0$ and is uniformly dominated in $L^1(\Gamma_G^T)$. Therefore, to prove (25) it suffices to show that

$$\lim_{\delta \searrow 0} \Big(f\big(u^{(1)}, v^{(1)}\big) - f\big(u^{(2)}, v^{(2)}\big)\Big) \Big(S_\delta\big(u\big) - S_\delta\big(v\big)\Big) \ \geq\ 0 \tag{27}$$

almost everywhere in Γ_G^T. Next we notice that (27) is invariant under permuting $(u^{(1)}, v^{(1)})$ and $(u^{(2)}, v^{(2)})$. Without loss of generality we therefore can restrict ourselves to the case that $u = u^{(1)} - u^{(2)} \geq 0$. Moreover, since

$$\lim_{\delta \to 0} \big(S_\delta(u) - S_\delta(v)\big) \ \to\ 0$$

if u and v are both positive or both zero, it only remains to consider the two cases

1. $v \leq 0$,
2. $v > 0$, $u = 0$.

In the first case we obtain that $\lim_{\delta \to 0}(S_\delta(u) - S_\delta(v)) \geq 0$ and

$$\begin{aligned} & f(u^{(1)}, v^{(1)}) - f(u^{(2)}, v^{(2)}) \\ & \quad = \ f(u^{(1)}, v^{(1)}) - f(u^{(2)}, v^{(1)}) + f(u^{(2)}, v^{(1)}) - f(u^{(2)}, v^{(2)}) \ \geq\ 0 \end{aligned}$$

by Lemma 1. This proves (27) if $v \leq 0$. In the second case ($v > 0$ and $u = 0$) we obtain that $S_\delta(u) - S_\delta(v) < 0$ and

$$f(u^{(1)}, v^{(1)}) - f(u^{(2)}, v^{(2)}) = f(u^{(1)}, v^{(1)}) - f(u^{(1)}, v^{(2)}) \ \leq\ 0,$$

giving again (27). In this way we have proven (27), yielding (25).

The proof of the Theorem is concluded by letting $\delta \searrow 0$ in in (20) and using (21) - (25). ☐

A direct consequence of Theorem 2 is the following uniqueness result:

Corollary 1. *The system (1)-(3) has a unique solution in the sense of Definition 1.*

Remark 4. The weak solution of (1)-(3) is obtained by compactness arguments, as a limit of a sequence $\delta \searrow 0$ of solutions of the regularized problems obtained by replacing the Heaviside graph H by

$$H_\delta(v) := \begin{cases} 0, & \text{if } v < 0, \\ v/\delta, & \text{if } v \in (0, \delta), \\ 1, & \text{if } v > \delta, \end{cases}$$

By the uniqueness result, any regularizing sequence $\delta \searrow 0$ converges to the same weak solution. Further, the same holds for the numerical approximation constructed in Theorem 2.15 of [1].

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