Travelling wave behaviour of crystal dissolution in porous media flow

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In this paper we present a model for crystal dissolution in porous media and analyse travelling wave solutions of the ensuing equations for a one-dimensional flow situation. We demonstrate the structure of the waves and we prove existence and uniqueness. The travelling wave description is characterized by a rate parameter k and a diffusion/dispersion parameter D. We investigate the limit processes as $k \to \infty$ and $D \to 0$ and we obtain expressions for the rate of convergence. We also present some numerical results.

1 Introduction and travelling wave formulation

In this paper we study travelling wave solutions of the following system of differential equations:

$$\partial_t(\theta c_1) + n\rho\partial_t c_{12} - \nabla\cdot(\theta D\nabla c_1 - q^* c_1) = 0, \tag{1.1}$$

$$\partial_t(\theta c_2) + m\rho\partial_t c_{12} - \nabla\cdot(\theta D\nabla c_2 - q^* c_2) = 0, \tag{1.2}$$

$$\rho\partial_t c_{12} \in \theta(k_a r(c_1, c_2) - k_d H(c_{12})). \tag{1.3}$$

Here c_1, c_2, c_{12} denote the unknown functions; all the other quantities are assumed to be known. More specifically n, m, k_a, k_d are positive numbers, and the parameter functions θ, ρ, D, q^* are assumed to be positive constants to allow for the possibility of travelling wave solutions. The two non-linearities appearing in equation (1.3) are a smooth function r with properties described below and the set-valued Heaviside function, i.e.

$$H(u) = \begin{cases} \{1\} & \text{for } u > 0 \\ [0,1] & \text{for } u = 0. \\ \{0\} & \text{for } u < 0 \end{cases} \tag{1.4}$$

Equation (1.1)–(1.3) may be viewed as a model for the convective-dispersive transport of solutes in a porous medium undergoing a precipitation/dissolution reaction: assume, for example, a cation M_1 and an anion M_2 to be present in solution, where c_1 and c_2 denote the corresponding molar concentrations in solution relative to the water volume. The underlying geology and water flow regime are described by the water content θ, the bulk density ρ, the diffusion/dispersion coefficient D and the specific discharge q^*. In the reaction to be described, n particles of M_1 and m particles of M_2 can precipitate in the form of one particle of a (crystalline) solid $\bar{M}_3$, which is attached to the surface of the porous skeleton and thus immobile. The reverse reaction of dissolution is also possible. If c_{12} denotes the molar concentration of $\bar{M}_3$ relative to the mass of the porous skeleton, then

(1.1) and (1.2) describe the conservation of the total masses of M_1 and M_2. Equation (1.3) is the kinetic equation describing the overall reaction rate. The precipitation rate is given by $k_a r(c_1, c_2)$, where a typical example is given by mass action kinetics leading to

$$r(c_1, c_2) = c_1^n c_2^m \quad \text{for} \quad c_1, c_2 \geqslant 0. \tag{1.5}$$

The function r is assumed to be continuously differentiable on $\mathbb{R} \times \mathbb{R}$ and

$$r(c_1, c_2) = 0, \quad \text{if} \quad c_1 = 0 \quad \text{or} \quad c_2 = 0. \tag{1.6a}$$

Guided by (1.5), we assume

$$r(\cdot\,, c_2) \quad \text{is strictly monotone increasing for} \quad c_2 \geqslant 0, \tag{1.6b}$$

$$r(c_1, \cdot) \quad \text{is monotone non-decreasing for} \quad c_1 \geqslant 0. \tag{1.6c}$$

The dissolution rate is constant in the presence of crystal, i.e. for $c_{12} > 0$, and has to be such that in the absence of the crystal the overall rate is zero (for a not oversaturated fluid, i.e. if $r(c_1, c_2) \leqslant k_d/k_a$). The set-valued formulation of the dissolution rate is to account for this situation.

It will turn out that for our specific formulation, the set-valued Heaviside function cannot be substituted by a discontinuous Heaviside function. There is, however, an equivalent formulation (see the Appendix) for which the travelling wave solutions lead only to the values 0 and 1 in the Heaviside function. Nevertheless, allowing for general (multidimensional) situations, one should start with a formulation involving a set-valued Heaviside function.

A more detailed discussion of the model can be found in Knabner *et al.* [1]. We refer to Rubin [2] for a general account on flow and chemical reactions in porous media such as soils and aquifers, i.e. from the viewpoint of subsurface hydrology, and corresponding mathematical models.

Our model derivation [1] is rigorous except for one point: in principal, the precipitation/dissolution process affects the pore geometry, and thus Θ. We ignore this effect, as for the specific applications from subsurface hydrology we have in mind (cf. [2]) the possible crystal layer at the surfaces of the grains is very thin. In this sense, our scope of application is different from, for example, acid flow through porous rock in certain technological applications (cf. [3]), where the stress is more on such a coupling of dissolution and fluid flow and less on the description of the dissolution process. The description of the dissolution process used there (cf. [4]) corresponds to the linearized version of the equivalent form (i.e. (A 10) with $r(c_1, c_2) = c_1$), excluding oversaturation *a priori* and substituting $H(c_1)$ by $c_1^{2/3}$. For this model the existence of travelling wave solutions has been shown [4].

For a simplification of equations (1.1)–(1.3) later on we will use a conserved quantity, which is here given by

$$c := mc_1 - nc_2 \tag{1.7}$$

satisfying

$$\partial_t(\theta) - \nabla \cdot (\theta D \nabla c - q^* c) = 0. \tag{1.8}$$

Later on we will consider the equivalent problem given by (1.8), (1.1) and

$$\rho \partial_t c_{12} \in \theta(k_a g(c_1, c) - k_d H(c_{12})), \tag{1.9}$$

where g is defined by

$$g(c_1, c) := r\left(c_1, \frac{1}{n}(mc_1 - c)\right). \tag{1.10}$$

Due to (1.6) $g(\cdot, c)$ is strictly monotone increasing. Actually, only this property will be needed, and not the sufficient condition (1.6).

There are two important singular limits to be investigated. If the rate parameters k_a, k_d are very large compared to the parameters of the transport process, it is reasonable to substitute the non-equilibrium description (1.3) of the reaction by a quasistationary equilibrium description. Formally, this is obtained by letting $k_a \to \infty$, keeping $K := k_d/k_a$ constant. This leads to

$$r(c_1, c_1) \in K H(c_{12}) \tag{1.11}$$

which together with the natural sign condition $c_{12} \geqslant 0$ is equivalent to the *solubility product inequalities*

$$\begin{aligned} 0 \leqslant r(c_1, c_2) \leqslant K, \quad c_{12} \geqslant 0, \\ (K - r(c_1, c_2))\, c_{12} = 0. \end{aligned} \tag{1.12}$$

For one space dimension and for a specific initial and boundary condition, a free boundary problem formulation is possible (see Rubin [2]), which has been considered by Pawell and Krannich [5]. If the dispersive transport in negligible compared to the convective transport, it is reasonable to consider $D \searrow 0$, changing equations (1.1), (1.2) to hyperbolic equations in the limit.

We will investigate these limits in §§4 and 5 for the special case of travelling wave solutions. More specifically, we consider a one-dimensional stationary flow directed from $x = -\infty$ (upstream) to $x = +\infty$ (downstream), i.e. one space dimension and constant, positive parameters θ, ρ, D, q^*. Then we look for solutions of (1.1)–(1.3) only depending on $\eta = x - at$ with a wave speed a to be determined. After introducing the notion of solution and equivalent formulations in the following, in §2 we will investigate the qualitative properties of solutions; the most important is a front for the concentration c_{12}. The existence and the uniqueness proof of §3 are based on §2. In §4, properties of the limit problem and convergence to the limit problems are considered, whereas in §5 more specific convergence rates are established. Travelling wave solutions for a related general class of transport and adsorption problems have been investigated by van Duijn and Knabner [6] and further exemplified in [7, 8]. The main distinction is that these papers deal with continuous (but possibly not Lipschitz continuous) rate functions. Thus equations (1.3) may be viewed as a model, which itself is the singular limit of models with continuous rate functions (fitting into the framework of [6]). This approach is possible, for example, to show existence of a solution. To avoid unnecessary technical complications we prefer the direct approach of §§2 and 3 instead of the regularization approach. On the other hand, for the analysis and numerical approximation of a general multidimensional boundary value problem based on (1.1)–(1.3), the regularization is a decisive tool. Special solutions such as travelling waves will only have a 'physical' significance for the general problems if they are stable under small perturbations. This stability seems to hold in numerical experiments and accords with the wave's observability in simple experimental situations such as breakthrough column experiments with a continuous feed. Nevertheless, the analysis of this problem is beyond the scope of this paper. Despite the vast amount of literature concerning the stability of travelling waves for more standard semilinear reaction–diffusion problems (e.g. from biology), the stability problem for the class of models addressed above has hardly been studied. Only for the equilibrium adsorption model (i.e. a special case of [7]), (nonlinear) L^1-stability of travelling waves has been shown in [9]. The few approaches aiming at linearized stability including rate of convergence estimates require specific, smooth nonlinearities.

For given non-negative boundary condition $c_i^*, c_{i*}, i = 1, 2, c_{12}^*, c_{12*}$ we look for non-negative travelling wave solutions of (1.1)–(1.3), i.e. $c_i = c_i(\eta) \geqslant 0$, $c_{12} = c_{12}(\eta) \geqslant 0$ with $\eta = x - at$, satisfying

$$\left.\begin{aligned} &-a(\theta c_1 + n\rho c_{12})' - \theta D c_1'' + q^* c_1' = 0, \\ &-a(\theta c_2 + m\rho c_{12})' - \theta D c_2'' + q^* c_2' = 0, \\ &-a\rho c_{12}' \in \theta(k_a r(c_1, c_2) - k_d H(c_{12})), \end{aligned}\right\} \text{in } \mathbb{R} \tag{1.13}$$

and the boundary condition

$$\left.\begin{aligned} &c_i(-\infty) = c_i^*, \quad c_i(+\infty) = c_{i*}, \quad i = 1, 2, \\ &c_{12}(-\infty) = c_{12}^*, \quad c_{12}(+\infty) = c_{12*}. \end{aligned}\right\} \tag{1.14}$$

Because, by (1.8) and (1.14) $c = c(\eta)$ satisfies a linear equation and boundary conditions at $-\infty$ and $+\infty$, a solution of (1.13), (1.14) can only exist if c is constant or equivalently

$$mc_1^* - nc_2^* = mc_{1*} - nc_{2*}. \tag{1.15}$$

We will assume (1.15) to hold from now on. It may be interpreted as the requirement of a constant total electric charge everywhere in the fluid (see [1]). Then c is given by

$$c := mc_1^* - nc_2^*. \tag{1.16}$$

As indicated above, we can reduce the problem to one involving two variables. Define

$$\left.\begin{aligned} &u := c_1, \qquad v := n\rho/\theta\, c_{12}, \\ &q := q^*/\theta, \quad k := nk_a; \end{aligned}\right\} \tag{1.17}$$

then the solutions of (1.13), (1.14) (in a sense of be specified) are equivalent to solutions of the following equations, setting

$$c_2 := \frac{1}{n}(mu - c): \tag{1.18}$$

$$u = u(\eta), \quad u \geqslant \left(\frac{c}{m}\right)_+, \quad v = v(\eta), \quad v \geqslant 0, \tag{1.19}$$

$$\left.\begin{aligned} &-a(u' + v') - Du'' + qu' = 0, \\ &-av' \in k[g(u, c) - KH(v)], \end{aligned}\right\} \text{in } \mathbb{R} \tag{1.20}$$

and the boundary conditions

$$\left.\begin{aligned} &u(-\infty) = u^*, \quad u(+\infty) = u_* \\ &v(-\infty) = v^*, \quad v(+\infty) = v_* \end{aligned}\right\} (BC)$$

with $u^* := c_1^*, v^* := n\rho/\theta c_{12}^*$, etc. The condition $u \geqslant (c/m)_+$ is equivalent to $c_1 \geqslant 0$ and $c_2 \geqslant 0$.

To define the notion of solutions of (1.20) and (BC) we introduce

$$w := \left(\frac{a}{k}v' + g(u, c)\right)/K \in H(v)$$

as a new variable. The expected limited regularity is taken into account by proper regrouping in the equations:

Definition 1.1 The quadruple $\{u, v, w, a\}$ with u, v, w being functions defined on $\mathbb{R}$ and a a real number is called a *travelling wave* for the boundary condition (BC) if

$$(TW)\begin{cases} \text{(i)} & u\in C^1(\mathbb{R}), v\in C^1_{pw}(\mathbb{R}), w\in C_{pw}(\mathbb{R}),\\ \text{(ii)} & u\geqslant (c/m)_+, v, w\geqslant 0 \quad \text{on} \quad \mathbb{R},\\ \text{(iii)} & Du'+av\in C^1(\mathbb{R}),\\ \text{(iv)} & -av'+kKw\in C(\mathbb{R}),\\ \text{(v)} & 0\leqslant w\leqslant 1, w=1 \quad \text{on} \quad \{v>0\},\\ \text{(vi)} & \left.\begin{array}{l}(Du'+av)'=(q-a)u'\\ -av'+kKw=kg(u,c)\end{array}\right\} \quad \text{in} \quad \mathbb{R},\\ \text{(vii)} & u, v \quad \text{satisfy the boundary conditions} \quad (BC).\end{cases}$$

Here the constant c is given by (1.16). We use $C_{pw}(\mathbb{R})$ to denote the piecewise continuous functions on $\mathbb{R}$ (with finitely many points of discontinuity), which are continuous from the right, and $C^1_{pw}(\mathbb{R})$ to denote those $u\in C(\mathbb{R})$, for which $f\in C_{pw}(\mathbb{R})$ exists such that $u'=f$ except at the points of discontinuity of f. It is clear that under the assumption (1.15), Definition 1.1 is equivalent to an analogous notion of a non-negative solution of (1.13), (1.14). We obtain immediately

Proposition 1.2 *Let $\{u, v, w, a\}$ be a travelling wave for (BC), then:*

(i) *$u'(\pm\infty)$ exists and $u'(\pm\infty)=0$,*
(ii) *if $\Delta u+\Delta v \neq 0$, then*

$$a=\frac{\Delta u}{\Delta u+\Delta v}q, \tag{1.21}$$

where $\Delta u := u^* - u_*$, $\Delta v := v^* - v_*$.

Proof Integration of the first equation in (TW) (vi) leads to

$$Du' = -av+(q-a)u+A \quad \text{in} \quad \mathbb{R} \tag{1.22}$$

for some $A\in\mathbb{R}$. Thus (i) holds because of (BC) (compare Proposition 1.3 in [6]). For $\eta\to\pm\infty$ equation (1.22) leads to a set of equations for a and A yielding (ii) and

$$A=\frac{v_* u^* - u_* v^*}{\Delta u+\Delta v}q. \quad \square \tag{1.23}$$

Note that for $a \neq 0$

$$\frac{q-a}{a}=\frac{\Delta v}{\Delta u}. \tag{1.24}$$

From (1.21)–(1.23) an equivalent formulation as a first order system follows directly:

Corollary 1.3 *Assume $\Delta u+\Delta v \neq 0$, then $\{u, v, w, a\}$ is a travelling wave for (BC), iff*

(i) $u \in C^1(\mathbb{R})$, $v \in C^1_{pw}(\mathbb{R})$, $w \in C_{pw}(\mathbb{R})$,

(ii) $u \geqslant (c/m)_+, v, w \geqslant 0$ *on* $\mathbb{R}$,

(iii) $0 \leqslant w \leqslant 1$ *in* $\mathbb{R}$, $w = 1$ *on* $\{v > 0\}$,

(iv) $$u' = \frac{q-a}{D}(u-u^*) - \frac{a}{D}(v-v^*), \tag{1.25}$$

$$-av' + kKw = kg(u,c) \quad in \quad \mathbb{R} \tag{1.26}$$

where a is defined by (1.21),

(v) *u, v satisfy the boundary conditions* (*BC*). □

2 Properties of solutions

For a travelling wave to exist we need is to that the boundary conditions on u and v are equilibrium points for the differential equations. Considering the u-equation, this is guaranteed by the expression for the wave speed. For the v-equation it requires the additional conditions

$$0 \in g(u^*, c) - K H(v^*), \tag{2.1 a}$$

$$0 \in g(u_*, c) - K H(v_*). \tag{2.1 b}$$

We will assume from now on that

$$g(\cdot, c) \quad \text{is strictly increasing to} \quad u \geqslant \left(\frac{c}{m}\right)_+ .$$

Sufficient conditions are given by (1.6b, c). Therefore, we obtain a unique solution u of (2.1 a) or (2.1 b) for fixed $w \in H(v)$, $v = v_*$ or $v = v^*$, and $(c/m)_+ \leqslant u \leqslant u_s$, where $u_s > 0$ is the unique solution of

$$g(u, c) = K. \tag{2.2}$$

We first investigate the possible combinations of boundary conditions for which travelling waves in the sense of Corollary 1.3 can exist. Suppose $v^*, v_* > 0$ and $v^* \neq v_*$. Then we have to solve for both $u = u^*$ and $u = u_*$ equation (2.2). Hence $u^* = u_* = u_s$. Consequently, $a = 0$ and (1.25) implies $u = u_s$ on $\mathbb{R}$. Using this in (1.26) we obtain $w = 1$ on $\mathbb{R}$, but no information on v is available. So this choice of boundary conditions leads to trivial solutions. They describe the situation of a stationary, but arbitrary crystal distribution v in the presence of saturated fluid (characterized by $u = u_s$ and $w = 1$).

If both $v^* = v_*$ and $u^* \neq u_*$, then $a = q$ and equation (1.25) reduces to

$$u' = -\frac{q}{D} v \quad \text{on} \quad \mathbb{R}. \tag{2.3}$$

For the function v we now distinguish:

(i) $v = 0$ on $\mathbb{R}$. This would imply

$$u = \text{constant} \quad (= u^* = u_*) \quad \text{on} \quad \mathbb{R},$$

i.e. a contradiction.

(ii) $v(\eta_0) > 0$ and $v'(\eta_0) = 0$ for some $\eta_0 \in \mathbb{R}$. Using (1.26) and (2.3) we obtain $u(\eta_0) = u_s$ and $u(\eta) > u_s$ for $\eta < \eta_0$, respectively. In particular, $u^* > u_s$ which contradicts (2.1 a).

Thus, to obtain non-trivial solutions we need it so that precisely one of the boundary conditions on v is zero. In fact, we are left with the following classes, as the case $u^* = u_* = u_s$ has already been discussed above:

$$\text{I}\begin{cases} v_* \quad \text{arbitrary positive}, & v^* = 0 \\ u_* = u_s, & u^* \in \left[\left(\dfrac{c}{m}\right)_+, u_s\right], \end{cases}$$

$$\text{II}\begin{cases} v^* \quad \text{arbitrary positive}, & v_* = 0 \\ u^* = u_s, & u_* \in \left[\left(\dfrac{c}{m}\right)_+, u_s\right). \end{cases}$$

We have not considered the cases

$$v^* = v_* > 0, \quad u^* = u_* = u_s,$$

$$v^* = v_* = 0, \quad u^* = u_* \in \left[\left(\frac{c}{m}\right)_+, u_s\right],$$

where the wave speed a is not uniquely determined. For arbitrary a there are the trivial constant solutions. We doubt that non-trivial solutions exist, but cannot exclude this case at the moment.

Before we turn to the existence and uniqueness in §3, we consider here a number of qualitative, structural properties of travelling waves. Below $\{u, v, w, a\}$ denotes an arbitrary travelling wave in the sense of Corollary 1.3 with (BC) taken from the classes I or II. Note that in both cases $0 < a < q$.

Proposition 2.1

(i) *$u < u_s$ on $\mathbb{R}$,*

(ii) *v is continuously differentiable and $v' > 0$ in $\{v > 0\}$.*

Proof We first show that $u \leqslant u_s$ on $\mathbb{R}$. If this is not true, then the boundary conditions imply the existence of a point $\eta_0 \in \mathbb{R}$ where $u'(\eta_0) = 0$ and $u(\eta_0) > u_s$. Writing (1.25) as

$$u' = \frac{q-a}{D}(u-u^*) - \frac{a}{D}(v-v^*) = \frac{q-a}{D}(u-u_*) - \frac{a}{D}(v-v_*) \tag{2.4}$$

we obtain that $v(\eta_0) > v^* > 0 = v_*$ if (BC) is taken from class II and $v(\eta_0) > v_* > 0 = v^*$ if (BC) is taken from class I. Using this in (1.26) gives $w(\eta_0) = 1$ and $v'(\eta_0) < 0$. Since $v(-\infty) = v^*$, there must exist a point $\eta_1 < \eta_0$ such that $v(\eta) > v(\eta_0)$, $v'(\eta) < 0$ for all $\eta \in (\eta_1, \eta_0)$ and $v'(\eta_1) = 0$. Hence $w = 1$ and $u > u_s$ (from (1.26)) on (η_1, η_0) with $u(\eta_1) = u_s$. Substituting these observations into equation (2.4) leads to $u'(\eta_1) < 0$, which gives a contradiction.

Next suppose that $u(\eta_0) = u_s$ for some $\eta_0 \in \mathbb{R}$. Then clearly $u'(\eta_0) = 0$ (because $u \leqslant u_s$) and from (2.4) $v(\eta_0) = \tilde{v}$, where $\tilde{v} = v_*$ if (BC) satisfies I or $\tilde{v} = v^*$ if (BC) satisfies II. In either case, $v > 0$ and $w = 1$ in some neighbourhood of η_0. This means that (1.25) and (1.26) have $u = u_s$ and $v = \tilde{v}$ as unique solutions in this neighbourhood. A continuation argument now contradicts (BC). The second assertion of the proposition is an immediate consequence of (1.26). □

The second statement in Proposition 2.1 gives:

Corollary 2.2 *No travelling waves exist with (BC) from class* II. □

Next we show

Proposition 2.3

(i) *There exists an* $L \in \mathbb{R}$ *such that*

$$v(\eta) = \begin{cases} 0 & \text{for} \quad -\infty < \eta \leqslant L, \\ > 0 & \text{for} \quad \eta > L, \end{cases} \tag{2.5}$$

(ii) $u' > 0$ *on* $\mathbb{R}$,

(iii) $v'' < 0$ *on* (L, ∞), *i.e. in particular* $v'(L+)$ *exists and* $v'(L+) > 0$.

(iv) *The following jump relations hold at* $\eta = L$*:*

$$a[v'] = -D[u''] = k\,K[w] > 0,$$

where $[f] := f(L+) - f(L-)$.

Proof

(i) The boundary condition $v(\infty) > 0$ rules out $v = 0$ on $\mathbb{R}$. If we can also exclude $v > 0$ on $\mathbb{R}$, then (2.5) is guaranteed by Proposition 2.1 (ii). To reach a contradiction let us suppose $v > 0$, and consequently $w = 1$ on $\mathbb{R}$. Letting $\eta \to -\infty$ in (1.26), then $v'(-\infty)$ exists and

$$v'(-\infty) = \frac{k}{a}\{K - g(u^*, c)\} > 0,$$

contradicting $v(-\infty) = 0$.

(ii) First we consider the interval $(-\infty, L]$, in which u satisfies

$$u' = \frac{q-a}{D}(u - u^*)$$

with $u(-\infty) = u^*$. This implies either $u > u^*$, and consequently $u' > 0$ on $(-\infty, L]$ or $u = u^*$ on $(-\infty, L]$. Suppose the second possibility holds. Then $u(L) = u^*$. In the interval (L, ∞) we have for u

$$u' = \frac{q-a}{D}(u - u^*) - \frac{a}{D}v$$

and consequently

$$\left(\exp\left(-\frac{q-a}{D}\eta\right)(u - u^*)\right)' = -\frac{a}{D}v\exp\left(-\frac{q-a}{D}\eta\right) < 0,$$

which implies

$$u(\eta) < u^* \quad \text{for all} \quad \eta > L.$$

This contradicts $u(\infty) = u_S$. Hence $u' > 0$ in $(-\infty, L)$. To show that this also holds in (L, ∞), it is sufficient to rule out possible zeros of u' in (L, ∞). Suppose $u'(\eta_0) = 0$ with $\eta_0 > L$. Then $v'(\eta_0) > 0$ and from equation (1.25) $u''(\eta_0) < 0$. This gives a contradiction with the boundary values $u(L) < u(\infty) = u_S$.

(iii) On $\{\eta > L\}$ the v-equation becomes

$$v' = \frac{k}{a}\{K - g(u, c)\}.$$

Since g is a C^1-function, strictly increasing on $((c/m)_+, \infty)$, the result is obtained by direct differentiation.

(iv) Is an immediate consequence of (iii) showing $[v'] > 0$ and the notion of solution (TW) (iii) and (iv). □

On the set $\{\eta < L\}$ the v-equation reduces to

$$w = g(u, c).$$

Hence, the strict monotonicity of u and g imply

$$0 \leqslant g(u^*, c) < w(\eta) < g(u(L), c) < K \quad \text{on} \quad (-\infty, L). \tag{2.6}$$

It is also easy to verify that

$$u \text{ is } C^{\infty} \text{ on } (-\infty, L) \text{ and } u \text{ is } C^3 \text{ on } (L, \infty). \tag{2.7}$$

Furthermore, we have

Proposition 2.4 *$u'' > 0$ on $(-\infty, L)$ and $u'' < 0$ on (L, ∞).*

Proof The first inequality is a direct consequence of the strict monotonicity of u. To prove the second one, we differentiate the u-equation twice and use the concavity of v. This gives

$$u''' > \frac{q-a}{D} u'' \quad \text{on} \quad (L, \infty). \tag{2.8}$$

Now suppose there exists a point $\tilde{L} > L$ where $u''(\tilde{L}) = 0$. Inequality (2.8) then implies that $u'' > 0$ on $(\tilde{L}, \infty)$, which contradicts the boundary condition at $\eta = \infty$. Hence, such a point $\tilde{L}$ cannot exist, and $u'' < 0$ remains as the only possibility. □

The last result is about the asymptotic behaviour of $u(\eta), v(\eta)$ as $\eta \to \infty$.

Proposition 2.5 *Suppose that for some $\tilde{\alpha} > \alpha > 0$*

$$\alpha(u_S - u) \leqslant K - g(u, c) \leqslant \tilde{\alpha}(u_S - u) \quad \textit{for} \quad u^* \leqslant u \leqslant u_S. \tag{2.9}$$

Then there exist constants $C, \lambda > 0$ such that for all $\eta \geqslant L$

$$u(\eta) > u_S(1 - e^{-\lambda(\eta - L)})$$

and

$$v(\eta) > v_* - C e^{-\lambda(\eta - L)}.$$

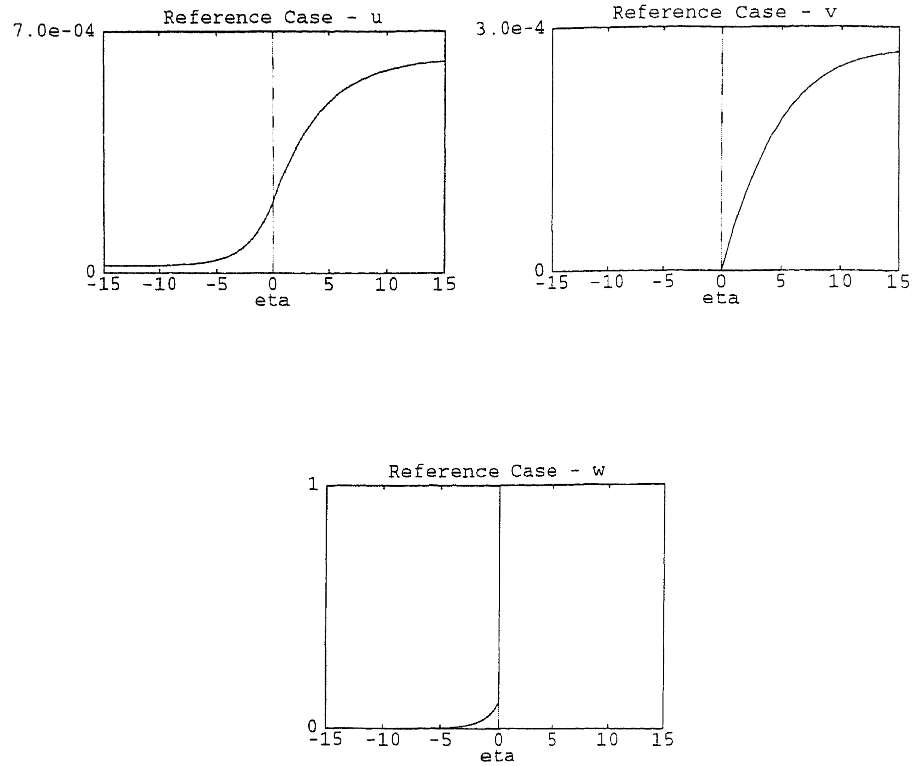

FIGURE 1. Numerical approximation of the functions u, v and w for moderate values of the parameters. For information about the data set as well as the numerical approximation, see [1].

Proof For $\eta > L$ the equations for u and v can be combined into the second-order equation

$$u'' = \frac{q-a}{D}u' + \frac{k}{D}\{g(u,c) - K\}. \tag{2.10}$$

Because of the first inequality of (2.9), straightforward comparison with the linear problem

$$z'' = \frac{q-a}{D}z' - \frac{\alpha k}{D}(u_s - z) \quad \text{for} \quad \eta > L,$$

$$z(L) = 0, z(\infty) = u_s$$

results in

$$u(\eta) > u_s\left\{1 - \exp\left(\frac{q-a}{2D}\left(1 - \sqrt{1 + \frac{4\alpha kD}{(q-a)^2}}\right)(\eta - L)\right)\right\}, \tag{2.11}$$

for all $\eta \geqslant L$.

Substituting the second inequality of (2.9) into the v-equation (1.26) for $\eta > L$, leads directly to the desired inequality. □

Note that a sufficient condition for (2.9) is given by

$$\partial g/\partial u(u_s, c) > 0. \tag{2.12}$$

The properties derived in this section are shown in Figure 1.

3 Existence and uniqueness

In the previous section we showed that the v-component of any travelling wave must vanish identically for large negative values of $\eta(\eta \leqslant L, L \in \mathbb{R})$. We shall use this observation in the proofs of the existence and uniqueness theorems. Note that in deriving this property we only used the continuity of the function $g(\cdot, c)$ and the monotonicity requirement for g, as stated after (2.1). Compared to the other sections, we can here slightly relax the requirements on $g(\cdot, c)$. Therefore, we will state explicitly in the following assertions what is needed:

Theorem 3.1 *Let* $g(\cdot, c) \in C^{0,1}([(c/m)_+, u_s])$ *and* $0 \leqslant g(u, c) \leqslant K$ *for* $u^* \leqslant u \leqslant u_s$. *Then for any set of boundary conditions from class* I, *there exists a travelling wave.*

Proof As in Corollary 1.3, the wave speed a is given by (1.21). Further, set $L = 0$ by translation, i.e. the solution to be constructed has to satisfy

$$v(\eta) > 0 \quad \text{for} \quad \eta > 0,$$
$$v(\eta) = 0 \quad \text{for} \quad \eta \leqslant 0$$

and

$$w(\eta) = 1 \quad \text{for} \quad \eta > 0.$$

The travelling wave functions u, v and w are found by matching the solutions of the following initial value problems:

$$(P^+)\begin{cases} u' = \dfrac{q-a}{D}(u-u^*) - \dfrac{a}{D}(v-v^*) =: f_1(u,v) & \text{for} \quad \eta > 0, \\ v' = \dfrac{k}{a}\{K - g(u,c)\} := f_2(u,v) & \text{for} \quad \eta > 0, \\ u(0) = u_0 \in (u^*, u_*) \quad \text{and} \quad v(0) = 0. \end{cases} \tag{3.1}$$

$$(P^-)\begin{cases} u' = \dfrac{q-a}{D}(u-u^*) & \text{for} \quad \eta < 0, \\ u(0) = u_0, \\ w(\eta) = g(u(\eta), c)/K & \text{for} \quad \eta < 0. \end{cases} \tag{3.2}$$

Using a shooting argument in the u, v phase we solve Problem (P^+) such that

$$(u(\eta), v(\eta)) \to (u_*, v_*) \text{ as } \eta \to \infty.$$

This leads to a value for $u_0 \in (u^*, u_*)$, which in turn is used in Problem (P^-).

We first investigate the sign of the functions f_1 and f_2. We have for $u \in [u^*, u_*]$, $v \in [v^*, v_*]$:

$$f_1(u,v) > 0 (\text{resp.} < 0) \quad \text{iff} \quad f(u) := \frac{q-a}{a}(u-u^*) + v^* < v (\text{resp.} > v),$$

$$f_2(u,v) > 0 \quad \text{iff} \quad u < u_s.$$

This leads to the phase plane shown in Figure 2.

For the set $S := \{(u,v) \mid u^* < u < u_*, v^* < v < f(u)\}$ we consider the following parts of its boundary:

$$\partial S_1 := \{(u,v) \mid u^* < u < u_*, v = f(u)\},$$
$$\partial S_2 := \{(u,v) \mid u = u_*, v^* < v < v_*\}.$$

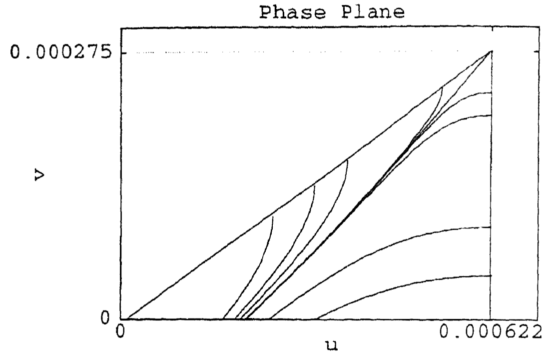

FIGURE 2. Computed orbits in the phase plane. Details concerning the data and numerical method are given in [1].

In the interval (u^*, u_*) we distinguish the subsets A and B according to the following criteria. We say that $\alpha \in A$ if the positive half-orbit corresponding to the solution of Problem (P^+) with $u(0) = \alpha, v(0) = 0$ leaves the set S through the boundary ∂S_1. Similarly, $\beta \in B$ if the positive half-orbit starting from $u(0) = \beta, v(0) = 0$ leaves the set S through the boundary ∂S_2. Proceeding as in [6], one shows that the sets A and B are non-empty, open and ordered $(\alpha \in A,\ \beta \in B \Rightarrow \alpha < \beta)$. Hence

$$\sup A = \bar{\alpha} \leqslant \bar{\beta} = \inf B,$$

where $\bar{\alpha} \notin A$ and $\bar{\beta} \notin B$.

This means that for any $u_0 \in [\bar{\alpha}, \bar{\beta}]$ the half orbit corresponding to Problem (P^+) ends up in the point (u_*, v_*) as $\eta \to \infty$. This gives the required solution in terms of $u = u(\eta)$, $v = v(\eta)$ for $\eta > 0$, as in particular $v(\eta) > 0$ for $\eta > 0$. The solution for $\eta < 0$ is obtained by explicitly solving (P^-):

$$u(\eta) = (u_0 - u^*)\exp\left(\frac{q-a}{D}\eta\right) + u^* \quad \text{for} \quad \eta \leqslant 0. \tag{3.3}$$

The boundary conditions (BC) and (iii) of Corollary 1.3 are satisfied by construction, the regularity conditions of Corollary 1.3(i) can be concluded from (P^-) and (P^+), and thus equations (1.25), (1.26). Finally, the sign conditions (ii) hold due to monotonicity of u. □

Theorem 3.2 *Let $g(\cdot, c) \in C[(c/m)_+, u_S]$ be nondecreasing and satisfy* (2.9). *Suppose there exist two travelling waves, characterized by (u_1, v_1, w_1) and (u_2, v_2, w_2), for the same boundary conditions from class* I. *Then there exists $\eta_0 \in \mathbb{R}$ such that*

$$(u_1(\cdot), v_1(\cdot), w_1(\cdot)) = (u_2(\cdot + \eta_0), v_2(\cdot + \eta_0), w_2(\cdot + \eta_0)) \quad \textit{in} \quad \mathbb{R}.$$

Proof Given both travelling waves, we apply to each a shift such that

$$v_1(\eta), v_2(\eta) > 0 \quad \text{for} \quad \eta > 0,$$

$$v_1(\eta) = v_2(\eta) = 0 \quad \text{for} \quad \eta \leqslant 0.$$

Then

$$w_1(\eta) = w_2(\eta) = 1 \quad \text{for} \quad \eta > 0.$$

Setting

$$u := u_1 - u_2, \quad v := v_1 - v_2 \quad \text{and} \quad w := w_1 - w_2$$

we obtain for u, v and w the equations

$$u' = \frac{q-a}{D}u - \frac{a}{D}v \quad \text{for} \quad -\infty < \eta < \infty,$$

$$v' = -\frac{k}{a}\{g(u_1, c) - g(u_2, c)\} \quad \text{for} \quad \eta > 0,$$

$$w = \{g(u_1, c) - g(u_2, c)\}/K \quad \text{for} \quad \eta < 0.$$

We first consider the equations for $\eta > 0$. Multiplying the v-equation by u and integrating the result with respect to η from $\eta = 0$ to $\eta = \infty$, yields

$$\int_0^\infty uv'\,d\eta = -\frac{k}{a}\int_0^\infty \{g(u_1, c) - g(u_2, c)\}\,u\,d\eta.$$

Note that this expression is well-defined, because, by Proposition 2.5, u and v decay exponentially fast to zero as $\eta \to \infty$. Integrating by parts and using $v(0) = v(\infty) = 0$, gives

$$\int_0^\infty u'v\,d\eta = \frac{k}{a}\int_0^\infty \{g(u_1, c) - g(u_2, c)\}\,u\,d\eta. \tag{3.4}$$

Next we multiply the u-equation by u' and again integrate the result. Using (3.4) leads to the identity

$$\int_0^\infty \{u'\}^2\,d\eta + \frac{k}{D}\int_0^\infty \{g(u_1, c) - g(u_2, c)\}\,u\,d\eta + \frac{q-a}{2D}\{u(0)\}^2 = 0. \tag{3.5}$$

The monotonicity of $g(\cdot, c)$ implies that the middle term is non-negative. Hence

(i) $u(0) = 0$, which implies $u_1 = u_2$ and $w_1 = w_2$ on $(-\infty, 0)$.
(ii) $u_1 = u_2$ on $(0, \infty)$, which implies $v_1 = v_2$ on $(0, \infty)$, from the v-equation. □

4 Limit cases

Here we discuss the behaviour of the travelling waves for the limit cases introduced in §1, namely $k_a\,\infty$, $K > 0$ fixed; then the chemical reaction is in equilibrium. Motivated by (1.12) and (1.13)–(1.20), we define

Definition 4.1 The triple $\{u, v, a\}$ with u, v being functions defined on $\mathbb{R}$ and a a real number is called a *travelling wave for* $k = \infty$ and the boundary condition (BC) if

$$(TWE)\begin{cases} \text{(i)} \ u \in C^1_{pw}(\mathbb{R}), v \in C_{pw}(\mathbb{R}), \\ \text{(ii)} \ u \geqslant (c/m)_+, v \geqslant 0 \quad \text{on} \quad \mathbb{R}, \\ \left.\begin{array}{l}\text{(iii)} \ Du' - av \in C^1_{pw}(\mathbb{R}), \quad (Du' + av)' = (q-a)\,u', \\ \text{(iv)} \ g(u, c) \leqslant K \quad (K - g(u, c))\,v = 0,\end{array}\right\} \quad \text{in} \quad \mathbb{R}, \\ \text{(v)} \ u, v \text{ satisfy the boundary conditions } (BC). \end{cases}$$

Remarks 4.2

1. The complementarity condition in (iv) can be equivalently stated as the existence of $w \in C(\mathbb{R})$ such that
$$0 \leqslant w \leqslant 1, \quad w = 1 \quad \text{on} \quad \{v > 0\}, \quad g(u,c) = Kw. \tag{4.1}$$
2. The regularity of u and v is less compared to Definition 1.1, and will be made more precise later on; on the other hand, w is continuous, contrary to the case of finite k (Proposition 2.3 (iv)).
3. Exactly as in the case of finite k Proposition 1.2 holds true such that a is given by (1.21) (up to some cases), and there is an equivalent formulation analogous to Corollary 1.3 with (iii) cancelled and (iv) substituted by
$$u' = \frac{q-a}{D}(u-u^*) - \frac{a}{D}(v-v^*), \tag{4.2}$$
$$g(u,c) \leqslant K, \quad (K - g(u,c))v = 0. \tag{4.3}$$

We do not repeat the discussion of §2, but restrict ourselves directly to class I, i.e. $v^* = 0$ and $u_* = u_s$. Then it turns out that problem (TWE) can be solved explicitly:

Proposition 4.3 *Let $\{u, v, a\}$ be a solution of (TWE). Then these exists on $L \in \mathbb{R}$ such that*
$$v(\eta) = \begin{cases} 0 & \text{for} \quad \eta < L \\ v_* & \text{for} \quad \eta \geqslant L \end{cases} \tag{4.4}$$
and
$$u(\eta) = \begin{cases} (u_* - u^*)\exp\left(\dfrac{q-a}{D}(\eta - L)\right) + u^* & \text{for} \quad \eta < L \\ u_* & \text{for} \quad \eta \geqslant L. \end{cases} \tag{4.5}$$
In particular, the following jump relations at $\eta = L$ hold:
$$av_* = a[v] = -D[u'] = -\frac{D}{q-a}[(Du' + av)']. \tag{4.6}$$

Proof By extracting the possible points of discontinuity of v and u', the real line is subdivided in finitely many open subintervals. We consider one of these and call it I. In an open (maximal) subinterval A, where $v > 0$, we have by (4.3) or (4.1) and the strict monotonicity of g for $u \geqslant (c/m)_+ : u = u_*$ in A. An equivalent form of (4.2) due to (1.21) is
$$u' = \frac{q-a}{D}(u-u_*) - \frac{a}{D}(v-v_*) \tag{4.7}$$
and thus $v = v_*$ in A. We see that the interval I is subdivided in open subintervals, where $v = v_*$ and closed subintervals, where $v = 0$. Assume there are subsequent intervals A, B, C, given by $\eta_1 < \eta_2 < \eta_3 < \eta_4$ such that $v = v_*$ in A and C and $v = 0$ in B. Then $u(\eta_2) = u(\eta_3) = u_*$ from the first assertion, but $u(\eta_3) > u_*$ from the second assertion and (4.5). The only combination still possible is given by (4.4).

The representation (4.5) follows immediately from (4.4), (4.3) and (4.2). Equation (4.6) follows from (4.2) and (TWE) (iv). □

Remark 4.4 Due to (1.21) we can also write (4.6) as

$$\frac{1}{\dfrac{1}{\Delta u}+\dfrac{1}{\Delta v}}q = D[u']. \tag{4.8}$$

In the following a general convergence result of solutions of (TW) to the solutions (TWE) is shown. Adding condition (2.9) to the function g leads to an explicit rate of convergence. This will be discussed in the next section.

Theorem 4.5 *Let $\{k_n\}_{n=1}^{\infty}$ be a sequence of positive numbers such that $k_n \to \infty$. For each $n \in \mathbb{N}$, $\{u_n, v_n, w_n, a\}$ denote travelling waves according to (TW), corresponding to $k = k_n$ and the same boundary conditions (BC), which have been translated such that*

$$v_n(\eta) = 0 \quad for \quad \eta \leqslant 0, \quad v_n(\eta) > 0 \quad for \quad \eta > 0.$$

Then $\{u_n, v_n, w_n, a\}$ converge from below to the solution $\{u, v, a\}$ of (TWE), for which $L = 0$, is the following sense: For $\Omega \subset\subset \mathbb{R}$ and $1 \leqslant p < \infty$:

$$\left.\begin{aligned} &u_n \to u \text{ pointwise in } \mathbb{R} \text{ and in } C(\Omega),\\ &v_n \to v \text{ a.e. in } \mathbb{R} \text{ and in } L^p(\Omega),\\ &w_n \to w := g(u,c)/K \text{ a.e. in } \mathbb{R} \text{ and in } L^p(\Omega). \end{aligned}\right\} \tag{4.9}$$

Proof Since $u^* \leqslant u_n \leqslant u_*$, $0 \leqslant v_n \leqslant v_*$ and $v_n' \geqslant 0$.

$$\|u_n\|_{\infty,\mathbb{R}}, \quad \|u_n'\|_{\infty,\mathbb{R}}, \quad \|v_n\|_{\infty,\mathbb{R}}, \quad \|v_n'\|_{1,\mathbb{R}}$$

are uniformly bounded with respect to n. Due to the Arzela–Ascoli Theorem and $W^{1,1}(\Omega) \subset\subset L^p(\Omega)$ for $\Omega \subset\subset \mathbb{R}$, there exist functions $u \in C(\mathbb{R}) \cap W^{1,\infty}(\mathbb{R})$ and $v \in L^\infty(\mathbb{R})$ such that

$$u^* \leqslant u \leqslant u_*, \quad 0 \leqslant v \leqslant v_* \quad \text{a.e. in} \quad \mathbb{R},$$

and for a subsequence (not distinguished in notation) we have

$$\begin{aligned} &u_n \to u \quad \text{in} \quad C(\Omega),\\ &v_n \to v \quad \text{in} \quad L^p(\Omega) \quad \text{and a.e. in} \quad \mathbb{R}. \end{aligned}$$

Thus (4.2) holds true because of (1.25), and from (1.26) we conclude

$$w_n \to w := \frac{1}{K} g(u,c) \quad \text{in} \quad L^p(\Omega).$$

We have $v(\eta) = 0$ for $\eta < 0$ and $w(\eta) = 1$ for $\eta \geqslant 0$, and thus $u(\eta) = u_*$ for $\eta \geqslant 0$. Inserting this into equation (4.2) shows $v(\eta) = v_*$ for $\eta \geqslant 0$. Due to (4.2) and $u(0) = u_*$, u is positive for $\eta < 0$, and thus strictly monotone increasing. Therefore, $u'(-\infty) = 0$ and $u(-\infty) = u^*$. This also shows that (4.7) is satisfied. The inequalities

$$v_n(\eta) < v(\eta), \quad u_n(\eta) < u(\eta) \quad \text{for} \quad \eta \geqslant 0 \tag{4.10a}$$

are obvious, and thus also due to (4.2), (1.25)

$$u_n(\eta) < u(\eta) \quad \text{for} \quad \eta < 0. \tag{4.10b}$$

As the limit is unique, the whole sequence converges. □

We now consider the limit $D \searrow 0$; then the influence of molecular diffusion and mechanical dispersion vanishes.

Definition 4.6 The quadruple $\{u, v, w, a\}$ with u, v, w being functions defined on $\mathbb{R}$ and a a real number is called a *travelling wave for* $D = 0$ and the boundary condition (BC), if

$$(TWH)\begin{cases} \text{(i)}\ u \in C^1_{pw}(\mathbb{R}), v \in C^1_{pw}(\mathbb{R}), w \in C_{pw}(\mathbb{R}), \\ \text{(ii)}\ u \geqslant (c/m)_+, v, w \geqslant 0 \quad \text{on} \quad \mathbb{R}, \\ \text{(iii)}\ 0 \leqslant w \leqslant 1, w = 1 \quad \text{on} \quad \{v > 0\}, \\ \text{(iv)}\ \left.\begin{aligned} -av' + (q-a)u' &= 0 \\ -av' + kKw &= kg(u, c) \end{aligned}\right\} \quad \text{in} \quad \mathbb{R}, \\ \text{(v)}\ u, v \text{ satisfy the boundary conditions } (BC). \end{cases}$$

Again, the regularity of u is reduced compared to Definition 1.1, and also here Proposition 1.2 is valid such that a is given by (1.21) (up to some cases) and then the equations (iv) can be expressed as:

$$(q-a)(u-u^*) = a(v-v^*), \tag{4.11}$$

$$v' = \frac{k}{a}(Kw - g(u, c)). \tag{4.12}$$

Again, we restrict ourselves to boundary conditions of class I. The structure of a solution is as follows:

Proposition 4.7 *Let $\{u, v, w, a\}$ be a solution of (TWH). Then there exists an $L \in \mathbb{R}$ such that*

$$v(\eta) = \begin{cases} 0 & \text{for} \quad \eta < L \\ \in (0, v_*) & \text{for} \quad \eta > L, \end{cases} \tag{4.13}$$

$$u = u^*, \quad w = g(u^*, c)/K \quad \text{for} \quad \eta < L,$$

$$u(\eta) < u_*, \quad u'(\eta), v'(\eta) > 0 \quad \text{for} \quad \eta \geqslant L,$$

$$u''(\eta), v''(\eta) < 0 \quad \text{for} \quad \eta \geqslant L, \quad \text{if} \quad \frac{\partial}{\partial u} g(u, c) > 0 \quad \text{for} \quad u \geqslant \left(\frac{c}{m}\right)_+.$$

The following jump relations at $\eta =$ hold:

$$[u'] = \left(\frac{\Delta u}{\Delta v} + 1\right)\frac{k}{q}(K - g(u^*, c)) = \frac{\Delta u}{\Delta v}[v']. \tag{4.14}$$

A solution of (TWH) is unique up to translation.

Proof First note that $u(\eta) < u_* = u_s$ for $\eta \in \mathbb{R}$.

If $u(\bar{\eta}) = u_*$ for some $\bar{\eta} \in \mathbb{R}$, then by (4.11) $v > 0$, i.e. $w = 1$ in a vicinity of $\bar{\eta}$, and thus u locally solves the following initial value problem:

$$u' = \frac{k}{q-a}(K - g(u, c)), \quad u(\bar{\eta}) = u_*,$$

which has the unique solution $u \equiv u_*$. By continuation $u = u_*$ on $\mathbb{R}$, i.e. a contradiction. As in Proposition 2.1 (ii), we now have

$$v' > 0 \quad \text{in} \quad \{v > 0\}$$

and can repeat the proof of Proposition 2.3 (i) to conclude the assertion (4.13). The further assertions are a direct consequence of (4.11), (4.12). For the jump relations, also note (1.21). Thus, if we fix L, a solution of (TWH) is given by

$$\left.\begin{aligned} &u = u^*, \quad v = v^*, \quad w = g(u^*, c)/K \quad \text{for} \quad \eta < L, \\ &u' = \frac{k}{q-a}(K - g(u, c)), \quad u(L) = u^* \quad \text{for} \quad \eta > L, \\ &v = \frac{q-a}{a}(u - u^*), \quad w = 1 \quad \text{for} \quad \eta > L, \end{aligned}\right\} \tag{4.15}$$

which has a unique solution. □

Again, we can show convergence of the solutions of (TW) to the solution of (TWH), analogous to Theorem 4.5. In §5 more precise order of convergence results for u will be established.

5 Rate estimates

Continuing the discussion about the limiting behaviour of the travelling waves as $k \to \infty$ or as $D \searrow 0$, we present in this section some explicit estimates for the corresponding rate of convergence. In deriving the estimates for $k \to \infty$, the lower bounds from Proposition 2.5 play a crucial role. Therefore, we assume in the first part of this section that g satisfies inequality (2.9). Further, we again take (BC) from class I.

First we consider the equilibrium limit case. For each $k > 0$ we denote by $\{u_k, v_k, w_k, a\}$ a travelling wave in the sense of Corollary 1.3, in which all other parameters are kept fixed. The waves have been translated such that

$$v_k(\eta) = 0 \quad \text{for} \quad \eta \leqslant 0 \quad \text{and} \quad v_k(\eta) > 0 \quad \text{for} \quad \eta > 0.$$

We observe from the lower bound (2.11) and Proposition 2.1 that, given any $k_0 > 1$, for all $k \geqslant k_0$ and $\eta > 0$

$$0 < u_s - u_k(\eta) < u_s e^{-\lambda_1 \sqrt{k}\eta} \tag{5.1}$$

with
$$\lambda_1 = \lambda_1(k_0) := \frac{q-a}{2D}\left\{\left(\frac{1}{k_0} + \frac{4\alpha D}{(q-a)^2}\right)^{1/2} - \frac{1}{k_0^{1/2}}\right\}.$$

This implies exponential decay for fixed $\eta > 0$ as $k \to \infty$ of $u_k(\eta)$ towards $u(\eta)$, where the limit u is defined by (4.5) with $L = 0$.

From equation (1.25) and Proposition 2.3, we obtain the bound

$$0 < u_k'(0) = \frac{q-a}{D}\{u_k(0)-u^*\} < \frac{q-a}{D}(u_S-u^*), \tag{5.2}$$

for all $k > 0$.

Next let $\delta > 0$. The strict concavity of u_k on $(0, \infty)$ due to Proposition 2.4 implies that for any $0 \leqslant \eta \leqslant \delta$

$$u_k(\eta) > u_k(\delta)-(\delta-\eta)\,u_k'(\eta) > u_k(\delta)-\delta u_k'(0). \tag{5.3}$$

Combining (5.1)–(5.3) results in

$$\begin{aligned} u(\eta)-u_k(\eta) &= u_S-u_k(\eta) < u_S-u_k(\delta)+\delta u_k'(0) \\ &< u_S\,\mathrm{e}^{-\lambda_1\sqrt{k}\delta}+\delta\frac{q-a}{D}(u_S-u^*) \end{aligned} \tag{5.4}$$

uniformly in $[0,\delta]$. Recalling that for $\eta < 0$

$$u_k(\eta) = (u_k(0)-u^*)\,\mathrm{e}^{\frac{q-a}{D}\eta}+u^*,$$

we obtain, using (4.5),

$$u(\eta)-u_k(\eta) = (u_S-u_k(0))\,\mathrm{e}^{\frac{q-a}{D}\eta} \quad \text{for all} \quad \eta \leqslant 0. \tag{5.5}$$

The above estimates allow us to prove

Theorem 5.1 *Let g satisfy inequality* (2.9) *and let u by given by* (4.5) *with $L = 0$. Then given any $k_0 > 1$, there exists a positive constant $C(k_0)$ such that for all $k \geqslant k_0$:*

$$0 \leqslant \frac{k^{1/2}}{C(k_0)\log k}\{u(\eta)-u_k(\eta)\} \leqslant \begin{cases} \mathrm{e}^{-\lambda_1\sqrt{k}(\eta-\delta(k))} & \text{for} \quad \eta > \delta(k), \\ 1 & \text{for} \quad 0 \leqslant \eta \leqslant \delta(k), \\ \mathrm{e}^{(q-a)/D\,\eta} & \text{for} \quad \eta < 0. \end{cases}$$

Here $\delta(k) := \log k/(2\lambda_1 k^{1/2})$.

Proof Substituting $\delta = \delta(k)$ in (5.4), we obtain for $0 \leqslant \eta \leqslant \delta(k)$ and $k \geqslant k_0$

$$\begin{aligned} 0 < \frac{1}{\delta(k)}\{u(\eta)-u_k(\eta)\} &< \frac{u_S}{\delta(k)}\mathrm{e}^{-\lambda_1\sqrt{k}\delta(k)}+\frac{q-a}{D}(u_S-u^*) \\ &\leqslant \frac{2\lambda_1 u_S}{\log k_0}+\frac{q-a}{D}(u_S-u^*). \end{aligned}$$

This implies the desired estimates for

$$C(k_0) = \frac{u_S}{\log k_0}+\frac{q-a}{2\lambda_1 D}(u_S-u^*).$$

□

Corollary 5.2 *For all $\eta > 0$ and $k > 0$ we have*

$$0 < v(\eta)-v_k(\eta) = v_*-v_k(\eta) < \frac{\tilde{a}u_S}{a\lambda_1}\sqrt{k}\,\mathrm{e}^{-\lambda_1\sqrt{k}\eta}.$$

Here the constant $\tilde{\alpha}$ has to satisfy (2.9).

Proof Equation (1.26) and inequality (2.9) give

$$av_k' \leqslant \tilde{\alpha}\, k(u_S - u_k),$$

which together with (5.1) results in

$$av_k'(\eta) < \alpha k u_S \, \mathrm{e}^{-\lambda_1 \sqrt{k}\, \eta} \quad \text{for all} \quad \eta > 0.$$

The estimate now follows upon integration. □

Next we turn to the hyperbolic limit case. For any given $D > 0$ we now denote a travelling wave by $\{u_D, v_D, w_D, a\}$. Again, they are shifted such that $v_D(\eta) = 0$ for $\eta \leqslant 0$ and $v_D(\eta) > 0$ for $\eta < 0$.

We first combine equations (1.25) and (1.26) into a second-order equation for u only. The result is

$$Du_D'' = (q-a)\, u_D' + kH(\eta)\{g(D, c) - K\}, \tag{5.6}$$

where H denotes the Heaviside function.

Using the strict concavity of u_D on $(0, \infty)$, the strict monotonicity of $g(\cdot, c)$ and $u_D(\eta) > u^*$ yields the inequalities

$$0 < u_D'(\eta) \leqslant u_D'(0) < \frac{k(K - g(u^*, c))}{q-a} \quad \text{for} \quad \eta \geqslant 0 \tag{5.7}$$

and for all $D > 0$.

Again using equation (1.25), now at $\eta = 0$, gives

$$u_D(0) - u^* = \frac{D}{q-a} u_D'(0). \tag{5.8}$$

Putting this expression and (5.7) together leads to

$$u_D(0) - u^* < \frac{kD(K - g(u^*, c))}{(q-a)^2} \tag{5.9}$$

and consequently to

$$u_D(\eta) - u(\eta) < \frac{kD(K - g(u^*, c))}{(q-a)^2} \mathrm{e}^{\frac{q-a}{D}\eta} \tag{5.10}$$

for all $\eta \leqslant 0$ and all $D > 0$, where u now denotes the hyperbolic limit function satisfying (4.11), (4.12) and Proposition 4.7.

Subtracting the combination of equations (4.11), (4.12) from equation (5.6) gives

$$Du_D'' = (q-a)(u_D - u)' + k\{g(u_D, c) - g(u, c)\} \tag{5.11}$$

for $\eta > 0$.

Integrating this expression and using (5.8) yields

$$Du_D'(\eta) = (q-a)(u_D-u)(\eta)+k\int_0^\eta \{g(u_D,c)-g(u,c)\}\,ds.$$

The concavity and boundedness of u_D imply $u_D'(\infty) = 0$ (see also Proposition 1.2). Hence

$$\int_0^\infty \{g(u_D,c)-g(u,c)\}\,d\eta = 0 \quad \text{for all} \quad D>0. \tag{5.12}$$

Expression (5.11) also implies that if $u_D(\tilde{\eta}) = u(\tilde{\eta})$ for some $\tilde{\eta} > 0$, then

$$(u_D-u)'(\tilde{\eta}) = \frac{D}{q-a}u_D''(\tilde{\eta}) < 0.$$

Consequently, $u_D > u$ in a left neighbourhood of any intersection point. This observation combined with (5.12) gives

Proposition 5.3 *The functions u_D and u have precisely one intersection point $\eta_D > 0$ with $u_D > u$ on $(-\infty, \eta_D)$.* □

Using equation (5.11) again, and also the monotonicity of g, we find

$$(u_D-u)'(\eta) < 0 \quad \text{on} \quad (0,\eta_D).$$

Hence
$$(u_D-u)(\eta) < (u_D-u)(0) < \frac{kD(K-g(u^*,c))}{(q-a)^2}, \tag{5.13}$$

for all $0 < \eta < \eta_D$ and for all $D > 0$.

To get an estimate in the interval (η_D, ∞) we first integrate (5.11) over the interval (η, ∞) with $\eta \geqslant \eta_D$. This yields

$$Du_D'(\eta) = (q-a)(u_D-u)(\eta)-k\int_\eta^\infty \{g(u_D,c)-g(u,c)\}\,ds. \tag{5.14}$$

As a consequence,

$$Du_D'(\eta_D) = k\int_{\eta_D}^\infty \{g(u,c)-g(u_D,c)\}\,ds. \tag{5.15}$$

From (5.14) we further obtain, with $\eta \geqslant \eta_D$,

$$\begin{aligned} 0 < (q-a)(u-u_D)(\eta) &= -Du_D'(\eta)+k\int_\eta^\infty \{g(u,c)-g(u_D,c)\}\,ds \\ &< k\int_{\eta_D}^\infty \{g(u,c)-g(u_D,c)\}\,ds \\ &= Du_D'(\eta_0) \quad \text{(with} \quad (5.15) \\ &< Du_D'(0) \end{aligned}$$

as u_D is strictly concave for $\eta \geqslant 0$.

Table 1. *Limit behaviour for numerical example*

k	error1(k)	error2(k)	D	error(D)
10	$0.841560*10^{-4}$	$1.937765*10^{-4}$	$6.25*10^{-4}$	0.2998
10^2	$0.431551*10^{-4}$	$1.987367*10^{-4}$	$6.25*10^{-5}$	0.4400
10^3	$0.289970*10^{-4}$	$2.003042*10^{-4}$	$6.25*10^{-6}$	0.4456
10^4	$0.218011*10^{-4}$	$2.007956*10^{-4}$	$6.25*10^{-7}$	0.4460
10^5	$0.174537*10^{-4}$	$2.009433*10^{-4}$		

Using (5.7) in this estimate and combining the results we have the following conclusion:

Theorem 5.4 *Let u be the hyperbolic limit as given in Definition* 5.1. *Then for all $D>0$ and for all $\eta\in\mathbb{R}$*

$$|u_D(\eta)-u(\eta)|\leqslant\frac{k(K-g(u^*,c))}{(q-a)^2}e^{\frac{q-a}{D}(\eta)_-}D.$$

Here $(x)_-:=-\max(-x,0)$. □

Remark 5.5 The estimate in Theorem 5.1 is nearly asymptotically optimal and the estimate in Theorem 5.4 is optimal because of the following observation: If we consider the linearized model, i.e.

$$g(u,c)=u \quad\text{and}\quad K=u_s,$$

then we can compute the solution of (TW) explicitly (compare [7]) and verify that

$$\sqrt{k}(u_s-u_k(0))\to\frac{(q-a)(u_s-u^*)}{\sqrt{D}}\quad\text{for}\quad k\to\infty, \tag{5.16}$$

$$\frac{u_D(0)-u^*}{D}\to\frac{k(u_s-u^*)}{(q-a)^2}\quad\text{for}\quad D\to 0. \tag{5.17}$$

Furthermore, numerical approximations of the problem depicted in Figures 1 and 2, but now for varying k or D (Figures 1 and 2 are for $k=0.1$, $D=6.25*10^{-4}$) show the behaviour reported in Table 1. Here

$$\text{error1}(k):=\frac{\sqrt{k}}{\ln(k)}(u_s-u_k(0)),$$

$$\text{error2}(k):=\sqrt{k}(u_s-u_k(0)).$$

Table 1 leads to the conjecture that, in line with Remark 5.5, the logarithmic term in the estimate of Theorem 5.1 seems to be too pessimistic, but it cannot be dispensed with totally in the general case. The limiting behaviour for $D\to 0$, with

$$\text{error}(D):=\frac{u_D(0)-u^*}{D}$$

is found even with the correct constant.

6 Conclusions

In this paper we have analysed travelling solutions for a model describing crystal dissolution in a porous medium. The model consists of two diffusion–convection equations for the anion and cation concentrations, respectively, and of an ordinary differential equation describing the ongoing dissolution/precipitation reactions. The model involves two important parameters. One is the rate parameter k for the reactions, the other is the diffusion/dispersion coefficient D in the transport equations for the dissolved species. The main complication is the occurrence of a Heaviside-graph in the reaction equation. In §2 we investigated the differential equations describing dissolution fronts (i.e. dissolution travelling waves) and explained the structure of the solutions. In particular, we have shown the existence of a free boundary which separates the region where the concentration of the crystalline solid is positive from the region where no crystalline solid is present, see also Figure 1. Existence and uniqueness of solutions has been proved in §3.

In §§4 and 5 we have investigated the equilibrium limit in which $k \to \infty$ and the hyperbolic limit in which $D \searrow 0$. For $k = \infty$, all the concentrations are constant whenever crystalline solid is present. Furthermore, the crystalline concentration is discontinuous across the free boundary, jumping from zero to the positive constant value, and the anion and cation concentrations are positive everywhere. For $D = 0$, anion and cation concentrations are constant in the region where the crystalline solid is absent. This is due to the missing diffusive transport term. Now all concentrations are continuous, growing from the free boundary to infinity.

For both cases, in §5 we constructed explicit bounds for the corresponding rates. We have also compared these rate estimates and numerically obtained convergence results. This leads us to the conclusion that the analytical results are close to optimal.

Appendix: An equivalent formulation

We consider general solutions of (1.1)–(1.3) in $Q_T := \Omega \times (0, T]$, where $\Omega \subset \mathbb{R}^N$ is a bounded domain and $T > 0$, supplemented by appropriate initial and boundary conditions. The solution is understood in a weak sense such that the derivatives, appearing in the following, exist with the indicated regularity. As for the travelling wave solutions, we introduce functions $w\colon Q_T \to \mathbb{R}$ such that

$$0 \leqslant w(x, t) \leqslant 1, \quad w(x, t) = 1 \quad \text{for} \quad c_{12}(x, t) = 1, \tag{A 1}$$

$$\rho \partial_t c_{12} = \theta(k_a r(c_1, c_2) - k_d w). \tag{A 2}$$

We analyse the properties of the function w. We subdivide Q_T into three disjoint sets,

$$Q_T = A \cup B \cup C, \tag{A 3}$$

where

$$\left.\begin{aligned} A &= \{(x, t) \in Q_T \mid c_{12}(x, t) > 0\},\\ B &= \operatorname{int}\{(x, t) \in Q_T \mid c_{12}(x, t) = 0\},\\ C &= \operatorname{bdry}\{(x, t) \in Q_T \mid c_{12}(x, t) = 0\} \setminus A. \end{aligned}\right\} \tag{A 4}$$

Here int and bdry denote the topological interior and boundary of the corresponding set. Note that in the definition of C we have to exclude points where $c_{12} > 0$ (e.g. points in A)

from the boundary of the set where $c_{12} = 0$, because c_{12} may be *a priori* discontinuous. We have by (A 1)

$$w(x, t) = 1 \quad \text{for} \quad (x, t) \in A, \tag{A 5}$$

and as $\partial/\partial t\, c_{12}(x, t) = 0$ for $(x, t) \in B$:

$$w(x, t) = r(c_1(x, t), c_2(x, t))/K \quad \text{for} \quad (x, t) \in B. \tag{A 6}$$

The topological structure of the set C is not clear *a priori*, as here we want to take into account all kinds of scenarios caused by various initial and boundary conditions. In particular, we do not know the regularity of the solutions *a priori*, i.e. we cannot expect that $\partial/\partial t\, c_{12}$ is continuous, etc. (compare the travelling wave solutions). For the travelling wave solutions, the set C will turn out to be a straight line, and thus of Lebesgue-measure zero in Q_T. In general, we expect that C is a collection of surfaces in the space-time domain, i.e. a free boundary in the problem. If the situation is more complex in the sense that the set C has positive measure, then due to a result in [10] (Lemma A 4, p. 53) we have $\partial/\partial_t\, c_{12}(x, t) = 0$ for almost every $(x, t) \in C$. Therefore,

$$w(x, t) = r(c_1(x, t), c_2(x, t))/K \quad \text{for almost every} \quad (x, t) \in C. \tag{A 7}$$

The function w is determined by c_1, c_2 as given by (A 5)–(A 7) up to a set of measure zero, which in general may be expected to be surfaces in the space-time domain, where the transition $c_{12} > 0$ to $c_{12} = 0$ takes place. The function w may be discontinuous there, as it will be the case for the solutions travelling wave.

An alternative rate description

Next we propose an alternative formulation for the reaction rate: Another equivalent form of the equilibrium conditions is given by

$$0 \in H(\max(c_{12}, r(c_1, c_2) - K))\,(k_p\, r(c_1, c_2) - k_d). \tag{A 8}$$

This suggests as an alternative to (A 2) the following rate description:

$$\rho \frac{\partial}{\partial t} c_{12} \in \theta k^*\, H(\max(c_{12}, r(c_1, c_2) - K))(k_p\, r(c_1, c_2) - k_d) \tag{A 9}$$

or equivalently

$$\left.\begin{aligned} &\rho \frac{\partial}{\partial t} c_{12} = \theta k^* w(k_p\, r(c_1, c_2) - k_d), \\ &\text{where} \quad w \in H(\max(c_{12}, r(c_1, c_2) - K)), \\ &\text{or equivalently} \\ &0 \leqslant w \leqslant 1, \quad \text{and} \\ &w = 1 \quad \text{for} \quad c_{12} > 0 \quad \text{or} \quad r(c_1, c_2) > K. \end{aligned}\right\} \tag{A 10}$$

This means that the precipitation rate $k_p\, r(c_1, c_2)$ and the dissolution rate k_d are kept, if crystalline solid is present or the fluid is oversaturated. Otherwise, an overall non-positive rate (i.e. dissolution rate) is possible.

The equivalence of the different formulations

To investigate the relation between this and the model (A 2), we consider the function w in (A 10). At points where the fluid is saturated, i.e. $r(c_1, c_2) = K$, w cannot be determined from equation (A 10). Thus, we do not change the solution if we select w in accordance with (A 10).

Repeating the above discussion leads to

$$\left.\begin{aligned} w(x,t) &= 1 \quad \text{for} \quad (x,t) \in A, \\ w(x,t) &= 0 \quad \text{for} \quad (x,t) \in B, \\ w(x,t) &= 0 \quad \text{for almost every} \quad (x,t) \in C. \end{aligned}\right\} \tag{A 11}$$

With this correspondence of the functions w, we see that the models (A 2) and (A 9) in fact are equivalent, if we compare weak solutions, where equations (1.1), (1.2), (A 2) or (A 9) are only considered almost everywhere in Q_T.

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