Numerical comparison between relaxation and nonlinear equilibrium models. Application to chemical engineering

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Abstract

A model to take into account the finite exchange kinetic for the equilibrium between phases in the chromatography experiment is studied. The resulting hyperbolic system with a nonlinear relaxation term is then formally treated with a Chapman–Enskog type expansion. A first order correction to the classical quasilinear hyperbolic model is derived which consists of a nonlinear diffusion term. Numerical schemes for both models — relaxed and parabolic — are then tested and compared for different initial and boundary values. A range of validity for the first order approximation is obtained through numerical simulations where its computational performance indicates that it should be advantageously used.

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1. Introduction

We are interested in this paper in mathematical models for two separation processes widely used in chemical engineering: distillation and chromatography. Distillation is a well-known separation process, used in petroleum industry. Chromatography is a much more precise process, which can be used to analyse small amounts of mixtures (analytic chromatography), or to extract very purified compounds from mixtures, for instance in pharmaceutical...
or perfume industry (preparative chromatography). We shall be more concerned with the latter application. Before being more specific about models, let us recall briefly a few facts about these processes.

A common feature both to chromatography and distillation is that the separation follows from the interaction between two phases in motion with respect to each other. A distillation column is heated at the bottom, thus separating the mixture in a gaseous phase moving upwards, and a liquid one moving downwards by gravity. In standard chromatography, the mixture, in gaseous or liquid form, is injected in a column filled with some porous medium. The chemical components are partially retained by the pores, thus generating a stationary phase in the column. In other devices, the two phases move counter current (Simulated Moving Bed, SMB).

Therefore, in the modelling of such processes, two types of phenomena are to be considered. On the one hand, the propagation of the mobile phase(s) is ruled by the laws of fluid dynamics, e.g. gas dynamics, porous media. On the other hand, the repartition of matter between the two phases relies on thermodynamics, and the notion of diphasic equilibrium is involved here. The separation of mixtures follows actually from the competition between these two phenomena.

The aim of this work is to concentrate on thermodynamics, which will introduce a specific nonlinearity in the equations. Thus we are going to use a simplified model for the hydrodynamical part, being aware that more realistic frameworks are to be investigated in the future. First of all, the column is assumed to be 1D, which seems convenient in most of the cases. Next, we assume that the experiments are performed at constant temperature, or that the temperature is a given function of time, neglecting the heat transfers. Finally, we impose that the velocities of the phases are constant. This is a reasonable assumption only for liquid (incompressible) phases. The main advantage of these simplifications is of course that we are left only with the mass conservation equations. The last hypothesis here is that, in these equations, we neglect the axial diffusion of the species, which is usually modelled by a constant diffusion term. This is a sensible approximation for preparative chromatography and modifies only slightly the analysis that we shall perform. For a thorough discussion of these hypotheses, we refer to the book by Guiochon et al. [1], where a large bibliography can also be found.

Starting with this simplified form for the hydrodynamical model, we study more precisely how thermodynamics gets involved in the equations of motion. The key point here is that, given a certain amount of mixture, there exists a privileged repartition of the matter between the two phases: the so-called stable equilibrium state. This state can be characterized as the minimum of some energy of the system, so that under reasonable physical assumptions, existence and uniqueness are ensured. Depending upon the fact that the equilibrium state is reached in a short time with respect to the relative velocities of the phases or not, we obtain different regimes, characterized by the size of a parameter $\varepsilon$, which is proportional to the relaxation time to the equilibrium. More precisely, in the former case, known as instantaneous kinetic, we obtain by putting $\varepsilon = 0$ a quasilinear system of hyperbolic conservation laws: the process is always at equilibrium, or, in other words, it is a quasi-static process. In the latter case, of finite exchange kinetic, a semilinear system of transport equations with a stiff right-hand side arises, which will be referred to in the sequel as the relaxation model. In-between these models, we build a third one, through a Chapman–Enskog expansion of the semilinear model, which leads to a correction of order one of the above mentioned nonlinear hyperbolic system by a nonlinear diffusion term. A common feature in these models is the natural splitting in two physically significant operators: the transport operator on the one hand, the nonlinear diffusion or the stiff right-hand side on the other.

Our purpose is precisely to study numerically these three models, for the possible different thermodynamical regimes, in particular in order to quantify the domains where they actually provide comparable results. Since we are interested in both small and $O(1)$ values of the relaxation time to equilibrium, we have to design very carefully the numerical discretization of each operator involved in the splitting, as well as the numerical splitting itself. It turns out that second order accuracy is necessary to obtain reliable results, in particular to ensure that numerical dispersion is not mistaken for nonlinear diffusion. Higher order schemes may seem desirable, however we point out
the fact that the nonlinearity of the diffusion term, and boundary conditions, which are nonlinear and discontinuous, give rise to serious numerical difficulties, even for order 2 schemes.

Numerical results show that both models — parabolic and relaxation — enjoy a similar behaviour in two cases: near the equilibrium state, and for small initial and boundary data. More precisely, in this range of parameters where the solutions are close to each other, we can compare the performances of both algorithms. In particular, we show that, even though the diffusion model may lack a neat physical interpretation, it is interesting from a numerical point of view. First, for a given accuracy on the solution, it is much faster than the relaxation model. Moreover it does present the inherent drawback of the relaxation scheme which blows up for $\Delta t \approx \varepsilon$. Finally, experimental data are also considered, for which both models give a sensible approximation.

Therefore, the paper is organized as follows. In Section 2, we recall the modelling of thermodynamics, and precisely state the equations. Section 3 is devoted to the design of the numerical schemes. Finally, in Section 4, we give elements of comparison between the three models.

2. Presentation of the models

Let us first consider the thermodynamics of the problem. We do not intend to go into the precise mechanisms involved in adsorption or absorption of chemical species. For this, we refer again to [1]. The key point here is that we assume the existence (and uniqueness) of a stable equilibrium state for the thermodynamical system constituted by the two phases. Namely, for a mixture of $N$ components, if $c^1, c^2 \in \mathbb{R}^N$, $c^j_i \geq 0$ for $1 \leq i \leq N$ and $j = 1, 2$, denote the concentrations in phase 1 and 2, respectively, the equilibrium is modelled by a smooth function $h : \mathbb{R}^N \to \mathbb{R}^N$, such that $c^2 = h(c^1)$. Moreover, $h$ satisfies the constitutive properties

$$h(0) = 0, \quad h'(c^1) \text{ is diagonalisable with eigenvalues } \mu_i(c^1) > 0. \quad (1)$$

The function $h$ is classically called an isotherm since the equilibrium is supposed to be reached at constant temperature. There is a huge amount of literature about isotherms and their determination in chemical engineering, see [1] and the references therein. We merely notice here that Eq. (2) allows the variable change

$$w = c^1 + h(c^1), \quad c^1 = g(w), \quad (3)$$

where $w$ is, roughly speaking, the total amount of matter in the system. In all the numerical simulations shown here we use the well known Langmuir isotherm

$$h_i(c) = \frac{K_i c_i}{1 + \sum_{j=1}^N K_j c_j}, \quad (4)$$

where the $K_i$'s are the so-called Langmuir coefficients.

Since two different kinds of phenomena are involved here, we can consider that the process is endowed with two characteristic times: the first one, say $T$, corresponds to the hydrodynamics, and is related to the velocities and the size of the device; the second one, $\tau$, comes from the thermodynamics, and is the relaxation time to the equilibrium. The coupling between the two phenomena thus depends on the ratio $T/\tau$, and there are basically three different regimes. (1) $\tau \gg T$: the motion is too fast for the equilibrium to be reached. The two phases do not interact. (2) $\tau \sim T$: the equilibrium is never reached, but the biphasic interactions become important. This is known as finite exchange kinetic. (3) $\tau \ll T$: The relaxation time is negligible with respect to $T$. A good approximation is therefore to assume that the equilibrium holds at any time: this is the definition of a quasi-static process, and is also known as instantaneous exchange kinetic.
We emphasize the fact that, in this discussion, the relaxation time actually may depend for instance on each component of the mixture. However, we are going to make the simplifying assumption that there is only one relaxation time, denoted by $\tau$, which is somehow proportional to $\tau$. This means that all the species in the mixture have the same thermodynamical behaviour. Let us now concentrate on cases (2) and (3), and write specifically the equations. Recall that the two phases move countercurrent, with velocity $u > 0$ for phase 1, $v < 0$ for phase 2 ($v = 0$ is a model for chromatography, $v < 0$ for distillation or SMB). For a mixture of $N$ components, we denote by $\mathbf{c}^j \in \mathbb{R}^N$ the vector of concentrations in phase $j$ for $j = 1, 2$, referred to the overall (constant) volume of the column. Thus the mass balance equation is written as:

$$\partial_t (c_1^1 + c_2^1) + \partial_x (uc_1^1 + vc_2^1) = 0. \tag{5}$$

Notice that in the chemical engineering literature, this equation is usually written in terms of $\mathbf{c}^j$, concentrations in each phase. The bounds between $\mathbf{c}^j$ and $c^j$ involve the porosity or void fraction of the column, which is assumed to be constant. The key point is to give a closure equation relating $c_1^1$ to $c_2^1$. Depending on whether we are in case (2) or (3), the result is quite different.

Consider first the case of instantaneous kinetic. The closure equation consists in putting $c_2^1 = h c_1^1$ at any time and position in the column. Thus Eq. (5) is rewritten as:

$$\partial_t (c_1^1 + h(c_1^1)) + \partial_x (uc_1^1 + v h(c_1^1)) = 0, \tag{6}$$

or, if we perform the change of unknown function (3),

$$\partial_t \mathbf{w} + \partial_x \mathbf{f}(\mathbf{w}) = 0, \quad \mathbf{f}(\mathbf{w}) = u g(\mathbf{w}) + v h(g(\mathbf{w})). \tag{7}$$

The properties of $h$ ensure that Eq. (7) is a hyperbolic system of conservation laws. The Jacobian $A(\mathbf{w}) = \mathbf{f}'(\mathbf{w})$ has eigenvalues

$$\lambda_i(\mathbf{w}) = \frac{u + v \mu_i(g(\mathbf{w}))}{1 + \mu_i(g(\mathbf{w}))}, \tag{8}$$

which satisfy $v < \lambda_i(\mathbf{w}) < u$ since $\mu_i(g(\mathbf{w})) > 0$. Thus we model indeed a retention phenomenon: the actual velocities are slower than the imposed ones. Obviously, one could expect some kind of separation if the $\lambda_i$’s were distinct, corresponding to strict hyperbolicity. But this is not readily a consequence of general thermodynamics properties.

On the other hand, finite exchange kinetic can be modelled by the following system of equations:

$$\partial_t c_1^1 + \partial_x (uc_1^1) = \frac{1}{\varepsilon}(c_2^1 - h(c_1^1)), \quad \partial_t c_2^2 + \partial_x (vc_2^2) = -\frac{1}{\varepsilon}(c_2^1 - h(c_1^1)). \tag{9}$$

This system is very close to those obtained in the context of chemical reactions, although the physical phenomenon is of course different. The right-hand side is a pulling-back force, proportional to the deviation from equilibrium. The competition between hydrodynamics and thermodynamics is clearly evidenced, and is quantified by $\varepsilon$. Note that this form for the right-hand side may not be standard in the physical or chemical engineering literature (see, e.g. [1]). However, the qualitative behaviour and technical difficulties do not depend on it, so we choose to keep this one.

Note that this set of equations can be used at two levels. On the one hand, specific phenomena due to “slow” exchange kinetic are related to “large” values of $\varepsilon$. On the other hand, we formally recover Eq. (6) by putting $\varepsilon = 0$ in Eq. (9), which gives $c_2^1 = h(c_1^1)$, then summing the two equations. This asymptotic result can be justified in a few cases. Some results in the scalar case are obtained by Natalini [2]. For chromatography it is done by James [3] in the scalar case and in the vector case for the Langmuir isotherm. We refer to the bibliography in both papers for
more information. From another standpoint, the convergence when \( \varepsilon \to 0 \) can be exploited at a numerical level to build approximations schemes for Eq. (6) (see [4]).

We wish now to introduce a third model, which is a correction of order 1 in \( \varepsilon \) to the above mentioned asymptotic behaviour. This correction is obtained classically by a Chapman–Enskog expansion, following the ansatz used for the Boltzmann equation (in this context, see, e.g. [5], or [6]). We recall briefly the principle of the method, following the notations of Chen et al. [7], which are more adapted to our context. More detailed computations and results can be found in [7]. We set

\[
U = \left( \begin{array}{c} \mathbf{c}_1 \\ \mathbf{c}_2 \end{array} \right) \in \mathbb{R}^{2N}, \quad F(U) = \left( \begin{array}{c} \mathbf{u} \mathbf{c}_1 \\ \mathbf{v} \mathbf{c}_2 \end{array} \right), \quad R(U) = \left( \begin{array}{c} \mathbf{c}^2 - \mathbf{h} \mathbf{c}_1 \\ \mathbf{h} \mathbf{c}_1 - \mathbf{c}_2 \end{array} \right),
\]

and introduce the rank \( N \) linear operator \( Q \) defined by \( w = QU = \mathbf{c}_1 + \mathbf{c}_2 \), so that \( QF(U) = \mathbf{u} \mathbf{c}_1 + \mathbf{v} \mathbf{c}_2 \), and \( QR(U) = 0 \). The method consists in writing \( U \) as \( U = U^0 + \varepsilon U^1 + \cdots \), then plugging this ansatz in the system

\[
\frac{\partial_t U + \partial_x F(U)}{R(U)} = \frac{1}{\varepsilon} R(U),
\]

and finally applying \( Q \) to obtain a reduced system in \( w \). Next, we identify the coefficients in the expansion.

1. **Order \( \varepsilon^{-1} \)**: we get \( R(U^0) = 0 \), which means that the expansion holds in a neighborhood of the equilibrium manifold \( \{ U ; R(U) = 0 \} \), or with our notations \( \{ (\mathbf{c}_1, \mathbf{c}_2) ; \mathbf{c}_2 = \mathbf{h} \mathbf{c}_1 \} \). We write therefore, using the notations introduced in Eq. (3),

\[
U^0 = \mathcal{E}(w) \quad \text{with} \quad \mathcal{E}(w) = \left( \begin{array}{c} g(w) \\ h(g(w)) \end{array} \right).
\]

Notice that \( Q \mathcal{E}(w) = w \), and that \( QF(\mathcal{E}(w)) = f(w) \).

2. **Order \( \varepsilon^0 \)**: we have

\[
J_0 = \frac{\partial_t U^0 + \partial_x F(U^0)}{\partial_t R(U^0)} U^1,
\]

which leads on the one hand, using the above remarks and the relation \( Q \partial_t R(U) = 0 \), to the reduced hyperbolic system (7), on the other hand to the following equation for \( U^1 \):

\[
\frac{\partial_t R(U^0)}{U^1} = J_0.
\]

To solve Eq. (11) in \( \mathbb{R}^{2N} \), we notice that the rank of \( \partial_t R(U^0) \) is \( N \), and \( QJ_0 = 0 \), so we choose to complement Eq. (11) with

\[
QU^1 = 0,
\]

thus Eqs. (11) and (12) have a unique solution which we compute explicitly:

\[
U^1 = g'(w)^2 \left( \begin{array}{c} \mathbf{w} \\ u \mathbf{w} + \mathbf{w} \end{array} \right) \left( \begin{array}{c} 1 \\ -1 \end{array} \right).
\]

3. **Order \( \varepsilon^1 \)**: since \( Q \partial_t R(U^0) = Q \partial_t U^1 R(U^0) = 0 \), we have

\[
\frac{\partial_t w + \partial_x \left[ QF(U^0 + \varepsilon U^1) \right]}{\partial_t f(w)} = \frac{1}{\varepsilon} \partial_x [ QF(U^1) ],
\]

and \( F \) being linear, the order one correction to Eq. (7) can be written as

\[
\frac{\partial_t w + \partial_x f(w)}{\partial_t f(w)} = -\varepsilon \partial_x \left[ QF(U^1) \right].
\]
with $U^1$ given by Eq. (13). This expression holds for a general system; as a general rule, it turns out that the right-hand side of Eq. (7) can be written as $\epsilon \partial_t [\chi(w) \partial_x w]$, where $\chi(w)$ is positive definite (see [7]).

In our specific case, using Eq. (3), and therefore that $g'$ commutes with $h'$, a straightforward computation leads to

$$\chi(w) = (u - v)^2 g'(w)^2 h'(g(w)) g'(w).$$

Thus the intermediate model we propose is

$$\partial_t w + \partial_x f(w) = \epsilon \partial_t [\chi(w) \partial_x w], \quad \chi(w) = (u - v)^2 g'(w)^2 h'(g(w)) g'(w). \tag{15}$$

It easy to check that $g'(w)$ and $h'(w)$ are diagonalisable in the same basis of eigenvectors. The eigenvalues of $g'(w)$ are $1/(1 + \mu_i(w))$, therefore, the eigenvalues of the matrix $\chi(w)$ are given by

$$(u - v)^2 \frac{\mu_i(w)}{(1 + \mu_i(w))^3}.$$ 

In several models of isotherms, the eigenvalues $\mu_i$ of $h'$ tend to zero or $+\infty$ as the concentrations go to $+\infty$. In both cases, we notice that the eigenvalues of the diffusion matrix $\chi$ tend to zero. This indicates that the hyperbolic approximation could be justified for high concentrations. Thus, mathematical difficulties may arise, due to the degeneracy of the parabolic term at infinity, when there is no maximum principle for the system (15). There are several studies of the behaviour of the three models for large times (of order $\epsilon^{-1}$); see, e.g. [8] where the first-order correction is justified for the $p$-system, and [9] where several such behaviours are exhibited on different examples.

We have now to complement our systems with initial and boundary conditions. We consider a column of length $L$, which at $t = 0$ satisfies

− for Eqs. (7) and (15) $w(x, 0) = w^0(x)$, where $w^0$ is a given bounded function. In applications, it is often a constant initial state;
− for Eq. (9), $c^1(x, 0) = c^{1\circ}(x)$ and $c^2(x, 0) = h(c^{1\circ}(x))$. In other words, we assume that the initial state is at equilibrium.

Concerning boundary conditions, one has to be more careful. Let us begin with Eq. (9). A quite natural set of boundary conditions is the following, as far as chromatography and distillation are concerned:

$$c^1(0, t) = a(t), \quad \text{injection}, \tag{16}$$

$$uc^1(L, t) + uc^2(L, t) = b(t), \quad \text{reflux, if } v < 0. \tag{17}$$

If $v = 0$, the reflux boundary condition (17) simply disappears. It turns out that the system (9) together with Eqs. (16) and (17) is well-posed. However, a difficulty arises if one lets $\epsilon$ go to 0, because the boundary conditions are not at equilibrium for $\epsilon > 0$ (see [3]), so that boundary layers may appear.

Another problem occurs for the hyperbolic system (7). The natural “injection” condition would be $w(0, t) = (I + h)(a(t))$, but it is well known that this condition leads to theoretical and numerical difficulties if the eigenvalues of $f'(w)$ change sign at the boundary. Since we do not wish presently to investigate this kind of problems, we are going in the sequel of the paper to limit ourselves to the case $v = 0$, that is standard chromatography. From Eq. (8), it is clear that the eigenvalues of $f'(w)$ are positive for all $w$, so that the Dirichlet boundary condition is well-posed, both for Eq. (7) and for the diffusion system (15). For the same reason, no output boundary condition is needed at $x = L$ for (7). On the other hand, the second-order system has to be complemented at $x = L$ by the Neumann boundary condition $\partial_x w = 0$, which means nothing is imposed at the output of the column.
3. Description of the numerical methods

In this section we describe the numerical algorithms used to solve the relaxation model and its first order approximation by a nonlinear parabolic equation as described in the previous section. Our ultimate goal is not to devise the best high order algorithm but rather to compare qualitatively the solutions provided by the two models. More precisely we want to illustrate numerically that the parabolic approximation is valid for a certain range of the relaxation factor \( \varepsilon \) and moreover, useful from the point of view of computational costs. The precision requirement is therefore important in the sense that the effects of the relaxation term — or the diffusive one in the parabolic model — are not mistaken for numerical dispersion. For this reason we do not use the simplest available first order schemes. On the other hand, both models are non-standard — specially the parabolic one with its nonlinear diffusion term. Higher order schemes such as weighted ENO or discontinuous Galerkin methods are certainly desirable if one contemplates extensive computations in the context of parameters identification but their design in this specific context has been postponed to further work. One can reasonably assume that the comparison of computational performances between the two models would keep the same trend if higher order schemes were used for both of them. For the time being the selected schemes are theoretically of second order, but the numerical tests show that this performance is not reached, due to several causes such as the nonlinearity or the boundary conditions. Concerning the latter, little can be done since the experimental setup involves a time dependent Dirichlet condition at the head of the column, which in practice has often a steep pulse shape of only 1 time step width. This section is subdivided in paragraphs were we recall the algorithms used to solve both models and numerical tests where their actual order of accuracy is estimated.

3.1. The relaxation model

As far as numerical simulations are concerned we restrict ourselves temporarily to the case of chromatography, but the algorithm could very easily be adapted to the general case of a problem with two phases \( c \) and \( d \) moving in opposite directions with speeds \( u > 0 \) and \( v \leq 0 \),

\[
\partial_t c + u \partial_x c = \frac{1}{\varepsilon} (d - h(c)), \quad \partial_t d + v \partial_x d = - \frac{1}{\varepsilon} (d - h(c)).
\]

We use the second order Runge–Kutta method described in [10] to solve the general class of relaxation problems (10). In the specific case of chromatography, \( v = 0, U = (c, d)^T \) and \( F \) is linear diagonal \( F(U) = (uc, 0) \). Setting \( \lambda = \Delta t / \Delta x \), the final algorithm is

(i) \( c^* = c^n - \frac{\Delta t}{\varepsilon} (d^* - h(c^*)) \), \( d^* = d^n + \frac{\Delta t}{\varepsilon} (d^* - h(c^*)) \),

(ii) \( c^{(1)} = c^* + \lambda \left( F_{j+1/2}^* - F_{j-1/2}^* \right), \quad d^{(1)} = d^* \),

(iii) \( c^{**} = c^{(1)} + \frac{\Delta t}{\varepsilon} (d^* - h(c^*)) + \frac{2 \Delta t}{\varepsilon} (d^{**} - h(c^{**})) \), \( d^{**} = d^{(1)} - \frac{\Delta t}{\varepsilon} (d^* - h(c^*)) - \frac{2 \Delta t}{\varepsilon} (d^{**} - h(c^{**})) \),

(iv) \( c^{(2)} = c^{**} - \lambda \left( F_{j+1/2}^{**} - F_{j-1/2}^{**} \right), \quad d^{(2)} = d^{**} \),

(v) \( c^{n+1} = \frac{1}{2} (c^n + c^{(2)}), \quad d^{n+1} = \frac{1}{2} (d^n + d^{(2)}) \).
For each convection step (ii) and (iv) we use the linear version of the second order Van Leer scheme described in [11] (ch. IV, Section 3).

The source term steps (i) and (iii) are solved iteratively in the following way: \(d^*\) (respectively, \(d^{**}\)) is expressed in terms of \(c^*\) (respectively, \(c^{**}\)) using the second equation of the system, and replaced in this form in the first equation, providing a nonlinear equation in \(c^*\) (respectively, \(c^{**}\)) only, which is solved by using a standard Newton inversion. Introducing the ratio \(\frac{\Delta t}{\varepsilon}\), steps (i) and (iii) can be rewritten as follows:

\[
(i') \quad c^* - \frac{\theta}{1-\theta} h(c^*) = c^n - \frac{\theta}{1-\theta} d^n, \quad d^* = \frac{1}{1-\theta} (d^n + \theta h(c^*)),
\]

\[
(iii') \quad c^{**} + \frac{2\theta}{1+2\theta} h(c^{**}) = c^{(1)} + \frac{2\theta}{1+2\theta} d^{(1)} + \frac{\theta}{1+2\theta} (d^* - h(c^*)), \quad d^{**} = \frac{1}{1+2\theta} \left( d^{(1)} + 2\theta h(c^{**}) - \theta (d^* - h(c^*)) \right).
\]

There are three regimes to consider to solve step \((i')\), depending on the position of the coefficient \(\theta\) with respect to 1. Clearly, the algorithm is not adapted to cases where \(\varepsilon \approx \Delta t\), because then the coefficients of the equation blow up. Since the scheme is of order 2, this is not a major drawback: either \(\varepsilon\) is very small, and the convergence will be attained before reaching values of \(\Delta t\) for which the coefficients explode, or \(\varepsilon\) is relatively large, and in that case the range \(\theta < 1\) is reached for reasonable values of \(\Delta t\).

3.2. Parabolic approximation

We now describe how we solve numerically the nonlinear parabolic equation obtained by the Chapman–Enskog type development of the relaxation problem

\[
\partial_t w(x, t) + \partial_x f(w(x, t)) = \varepsilon u^2 \partial_x (\chi(w(x, t)) \partial_x w(x, t)),
\]

\[
w(0, t) = (I + h)(a(t)), \quad w(x, 0) = 0, \quad \partial_x w(L, t) = 0.
\]

In problem (18), \(f(w) = u g(w)\) where \(g\) is defined by Eq. (3). The nonlinear diffusion \(\chi\) depends also on the isotherm through the relation \(\chi(w) = g(w)^3 h'(g(w))\), since here \(g'\) and \(h'\) are scalar functions. Although the problem is one-dimensional, the numerical behaviour is not trivial due to the competition between the convection and the diffusion terms.

For small values of \(\varepsilon\), the equation behaves almost hyperbolically. Hence we are tempted to use a scheme designed only for the convection term, and to add the standard centered discretization of the diffusion term. Unfortunately, the generalization to nonlinear isotherms will preserve neither the stability nor the precision of the initial scheme. More precisely, we consider for the convection term a Van Leer type scheme which is second order in space and time and Total Variation Diminishing under a certain CFL condition [11]. Stability of numerical schemes for parabolic equations are not usually established through the Total Variation Diminishing property but rather either by computing the transfer coefficient in Fourier space or by energy inequalities. In the linear case it is easy to show that adding an explicit diffusion term makes the stability conditional. More precisely the stability condition on the CFL number \(u \Delta t / \Delta x\) is replaced by the following condition:

\[
\lambda \left( 1 + \frac{2 \varepsilon u}{\Delta x} \right) < 1, \quad \text{with} \quad \lambda = \frac{\Delta t}{\Delta x} \sup |F'(w)|.
\]

When \(\Delta x\) is small enough \(\Delta t\) should vary as \(\Delta x^2\) to preserve stability. To counteract this effect one can add the diffusion term implicitly. This of course makes the scheme unconditionally stable, but at a high cost in computing time increase and also the loss of the second order precision in time.
An alternative strategy is to switch to a parabolic scheme whenever $\varepsilon$ is large enough to make the hyperbolic scheme unstable — since in fact this situation corresponds to a predominance of the diffusion on the convection term. We could adopt in this case a Crank–Nicholson type scheme which is second order both in time and space. This scheme is unconditionally stable in the $L^2$ sense as well as in the Fourier space in the linear case. In the nonlinear case a global $L^2$ stability can be obtained, but since this is not equivalent to a TVD property, the solution exhibits local oscillations for small values of the diffusion. Therefore this scheme cannot be used in all cases.

In fact we choose an intermediate solution which consists in combining a second order TVD convection scheme — Van Leer — with a second order Runge–Kutta implicit scheme for the diffusion term. The latter is not unconditionally stable but well adapted to very stiff problems. Its performances are detailed in Appendix A. As far as the precision is concerned, mixing diffusive and convective discretized algorithms of order 2 does not ensure that the resulting scheme is of the same order of precision. More precisely, the study of the linear case shows that in the absence of commuting property between the operators, the second order is achieved using a Strang type method as described in [12] for alternate directions schemes. In our case, we denote by $C_k$ the — in general nonlinear — discrete operator for the convection term such that $w^{n+1} = C_k(w^n)$ is a second order approximation in time of

$$\partial_t w(t) = C(w) = -u_0\partial_x f(w(t)),$$

and similarly $D_k$ the discrete operator such that $w^{n+1} = D_k(w^n)$ is a second order approximation in time of

$$\partial_t w(t) = D(w) = \partial_x (\chi(w(t))) \partial_x w(t).$$

then the full equation

$$\partial_t w(t) = C(w) + D(w),$$

is discretized by

$$w^{n+1} = D_{k/2} \circ C_k \circ D_{k/2}(w^n).$$

In practice, since $D$ is a second order scheme $D_{k/2} \circ D_{k/2} u = D_k u + O(k^3)$ and consecutive $D_{k/2}$ coming from iterations of the Strang splitting can be reunited into single steps $D_k$. Only two half steps remain at the beginning and the end of the time span:

$$u_0 = \left( D_{k/2}(w^0) \right), \quad u^n = \left( C_k(u^n) \right) \text{ for } n = 0, \ldots, N - 2,$$

$$u^{n+1}_1 = \left( D_k(u^n_1) \right) \text{ for } n = 0, \ldots, N - 2, \quad u^{N-1}_2 = \left( C_k(u^{N-1}_1) \right), \quad w^N = \left( D_{k/2}(u^{N-1}_2) \right).$$

The discretization of the convection term can be improved using a slope limiter method which makes it of order 2 in space. Second order in time can be achieved by different means (see [11,13]). Among those we select the Van Leer method for which proofs of order of convergence and stability in the case of a nonlinear hyperbolic equation can be found in [11,14]. It is TVD and $L^\infty$ stable if the initial solution is BV and it is second order accurate in the domains of regularity of the solution and away from its sonic extrema (which do not occur here anyway).

The diffusive term

$$\partial_x (\chi(x)\partial_x w(x,t)),$$

is discretized in space with an order 2 scheme

$$\frac{1}{2\Delta x^2} \left( (\chi_{i+1} + \chi_i)(w_{i+1} - w_i) - (\chi_{i-1} + \chi_i)(w_i - w_{i-1}) \right).$$
We summarize this space discretization as \( N \) equations

\[
\partial_t w_i = r_i(w),
\]

with special forms for \( r_1 \) and \( r_N \) due to the discretization of the boundary conditions. We propose to solve Eq. (24) using a second order implicit Runge–Kutta scheme first introduced by Ianelli and Baker in [15].

\[
(I - a_1 \Delta t \nabla r)z_1 = r(w^n), \tag{25}
\]

\[
(I - a_2 \Delta t \nabla r)z_2 = r(w^n + \beta \Delta t z_1), \tag{26}
\]

\[
w^{n+1} = w^n + \Delta t (b_1 z_1 + b_2 z_2). \tag{27}
\]

where the coefficients \( a_1, a_2, \beta, b_1 \) and \( b_2 \) are chosen to ensure the second order precision and stiff stability as shown in Appendix A. In Eqs. (25) and (26) \( \nabla r \) is the \( N \times N \) matrix of components \( \partial r_i / \partial w_j \). For sake of completeness, we describe below the computation of \( \nabla r \) and the numerical scheme used to solve Eqs. (25) and (26). \( \partial r_i / \partial w_j \) is non-zero for three values of \( j \) only: \( i - 1 \leq j \leq i + 1 \)

\[
\frac{\partial r_i}{\partial w_{i-1}} = \frac{\varepsilon u_i^2}{2\Delta x^2} (\chi'_{i-1}(w_{i-1} - w_i) + \chi_i + \chi_{i-1}),
\]

\[
\frac{\partial r_i}{\partial w_i} = \frac{\varepsilon u_i^2}{2\Delta x^2} (\chi'_i(w_{i+1} - 2w_i + w_{i-1}) - (\chi_{i+1} + 2\chi_i + \chi_i - 1)),
\]

\[
\frac{\partial r_i}{\partial w_{i+1}} = \frac{\varepsilon u_i^2}{2\Delta x^2} (\chi'_{i+1}(w_{i+1} - w_i) + \chi_{i+1} + \chi_i).
\]

The matrices in the linear systems (25) and (26) are non-symmetric band matrices with three non-zero diagonals. The systems are solved by computing the LU decomposition.

An important obstacle to accuracy is the boundary condition. In the chromatography experiment it is not smooth at all. It consists in most cases of a sample injection — with the diffusion term ensuring the regularity of the solution at all positive times. The numerical tests in the next paragraph will show that this has a very negative effect on the actual order of accuracy of the schemes. Theoretically we assume of course that the boundary condition \( a \) is as smooth as necessary. In the hyperbolic operator it is taken into account by the method detailed by Shu [16]. The main result is that for an hyperbolic conservation law such as Eq. (18) with smooth boundary conditions \( w(0, t) = a(t) \), the \( r \)th order scheme for the initial value problem is also \( r \)th order if the necessary points \( w_{-1}, w_{-2} \ldots \), are computed using an order \( r \) extrapolation. This has been shown to preserve the stability in the case of explicit Van Leer type schemes. Here to get the second order scheme, we need to compute

\[
w_{-1} = 3w_0 - 3w_1 + w_2, \quad w_{-2} = 3w_{-1} - 3w_0 + w_1.
\]

In the discretization of the diffusion operator, both the Dirichlet boundary condition at the input of the column and the Neumann boundary condition at its output require a special treatment for the first and last equations. In the same spirit as for the hyperbolic scheme, the two points \( x_{-1} \) and \( x_{N+1} \) outside the column which appear formally in the space discretizations \( r_1 \) and \( r_N \) are computed by order 2 extrapolation. Using \( w_{-1} = 3w_0 - 3w_1 + w_2 + O(\Delta x^3) \) we obtain

\[
r_1(w) = \frac{\varepsilon u_1^2}{2\Delta x^2} ((\chi_2 + \chi_1)(w_2 - w_1) - (\chi_1 + \chi_0)(w_1 - w_0)),
\]

\[
\frac{\partial r_1}{\partial w_1} = \frac{\varepsilon u_1^2}{2\Delta x^2} (\chi'_1(w_2 - 2w_1 + w_0) - (\chi_2 + 2\chi_1 + \chi_0)),
\]

\[
\frac{\partial r_1}{\partial w_2} = \frac{\varepsilon u_1^2}{2\Delta x^2} (\chi'_2(w_2 - w_1) + \chi_2 + \chi_1).
\]
Similarly, using $w_{N+1} = w_{N-1} + O(\Delta x^3)$ in the computation of $r_N$ provides

$$r_N(w) = -\frac{e u^2}{2\Delta x^2} (\chi_{N-1} + \chi_N) (w_N - w_{N-1}),$$

$$\frac{\partial r_N}{\partial w_{N-1}} = -\frac{e u^2}{2\Delta x^2} (\chi_N' - 1 (w_N - w_{N-1}) - \chi_{N-1} - \chi_N).$$

Eventually, the computation of $r_1(w^n + \Delta t \beta z_1)$ needs the value $z_1$ at the boundary which will be once more computed by second order extrapolation $z_{10} = 3z_{11} - 3z_{12} + z_{13} + O(\Delta x^3)$.

The non-homogeneous boundary conditions must be extrapolated in both the hyperbolic scheme and parabolic schemes, but also interpolated at the right time point, in order to provide the good boundary value for the intermediate time steps in the Strang splitting. Following Abarbanel et al. [17] where it is done for the intermediate time steps of a Runge–Kutta scheme, we rewrite Eq. (22) as follows:

$$u_i^1 = (D_{\Delta t/2}(u^n))_i \quad \text{for } i = 1, \ldots, n \text{ and } u_0^1 = w_0 \left( t + \frac{\Delta t}{2} \right),$$

$$u_i^2 = (C_{\Delta t}(u^1))_i \quad \text{for } i = 1, \ldots, n \text{ and } u_0^2 = w_0 \left( t + \Delta t \right),$$

$$w_i^{n+1} = (D_{\Delta t/2}(u^2))_i \quad \text{for } i = 1, \ldots, n \text{ and } w_0^{n+1} = w_0 \left( t + \Delta t \right).$$

### 3.3. Validation of the algorithms and convergence study

As mentioned above step boundary conditions contain an order 1 error, which will be smoothened as time goes on, more so in cases with large diffusion factor. Nevertheless, it is important to check the accuracy of the algorithms without this additional difficulty. Hence the first simulations are done for smooth initial data

$$c^{1\epsilon}(x, 0) = \begin{cases} (x - x_c + \ell)^4(x - x_c - \ell)^4 & \text{for } x \in [x_c - \ell, x_c + \ell], \\ 0 & \text{elsewhere}, \end{cases}$$

with $x_c = 0.25 \text{ cm}$ and $\ell = 0.2 \text{ cm}$. The boundary conditions are homogeneous Dirichlet at the entrance of the column and homogeneous Neumann at the exit. The isotherm is of the Langmuir type (4) which in the scalar case boils down to

$$h(w) = N^* \frac{K w}{1 + K w},$$

with $N^* = 1, K = 1$. The speed $u$ for the convection operator is set equal to 1 cm/s. The length of the column is 1 cm. The dilute component is propagated until a given time, here $T = 0.2$. For a given CFL number, the computed concentration along the column at this time is a sequence $c(x_i, T; \Delta t)$. The discrete $L^1$ error is then computed as follows:

$$E_1(\Delta t; T, \Delta t^0) = \sum_i |c(x_i, T; \Delta t) - c(x_i, T; \Delta t^0)|,$$

where $c(x_i, T; \Delta t^0)$ is the numerical solution corresponding to the smallest available time sampling $\Delta t^0$, and is used as the reference solution. In all the figures, the errors are represented with logarithmic scales and as functions of the number of time samples $(T/\Delta t)$.

Fig. 1 shows these error curves for the two algorithms. The precision of the numerical scheme for the parabolic equation is of order 2 as expected in all cases $\epsilon = 10^{-2}$, $\epsilon = 10^{-3}$ and $10^{-4}$. For the relaxation problem however,
a numerical order of 1.5 is attained but the error curves point out the intrinsic drawback of the algorithm in the blow-up region $\Delta t \approx T$. In the cases $\varepsilon = 10^{-2}$ and $\varepsilon = 10^{-3}$ the range of discretization studied overlaps the region of instability and the error curves are of course very bad in this area. Two points are missing on the third graph corresponding to $\varepsilon = 10^{-2}$ because of actual blow-up of the numerical solution. Nevertheless for both values of $\varepsilon$ a satisfying precision can be achieved with realistic discretization steps. For $\varepsilon = 10^{-2}$ one has to pass the instability zone to reach satisfying accuracy; $\Delta t = 0.000625$ for instance, leads to $E_1 = 0.00528423$. For $\varepsilon = 10^{-3}$ a time step $\Delta t = 0.0025$ already suffices to obtain $E_1 = 0.00257995$.

The corresponding reference solutions, computed with the finest discretization, are represented in Fig. 2. For $\varepsilon = 10^{-3}$ they are almost indistinguishable, both very close to the hyperbolic model solution. In the case $\varepsilon = 10^{-2}$ they have roughly the same shape, although the parabolic approximation departs sensibly from the initial model. All this shows that we are in a range were the two models can be compared. It is clear that in the $\varepsilon = 10^{-3}$ case, it might be advantageous to use the parabolic approximation instead of the relaxation model which requires careful choice of the discretization step. This last point will be further developed in the next section.

The next batch of computations is more realistic in the sense that the initial condition is now 0 and the boundary condition is not smooth, as it would be in a chromatography experiment. The solute concentration is injected at the head of the column $x = 0$, at a fixed level during a finite time — here 0.04 s. Fig. 3 shows the error curves for both equations for several values of $\varepsilon = 10^{-4}$, $10^{-3}$ and $10^{-2}$. It shows again that for the relaxation model, the convergence is monotonous only in the stability zones $\Delta t \ll \varepsilon$ or $\Delta t \gg \varepsilon$. For the parabolic equation the convergence is monotonous for all values of $\varepsilon$. In almost all cases, neither scheme reaches the order 2 performance — the best fitting straight lines in logarithmic scale indicate an order 1.4 in the parabolic case, and 1.2 in the relaxation case.
For the smallest value of the parameter $\varepsilon = 10^{-4}$ the relaxation model is actually very close to the hyperbolic model. In that case only it achieves for small discretizations $\Delta t \ll \varepsilon$ the theoretical order 2.

### 4. Comparison of the relaxation model with its parabolic approximation

In this section, we compare the numerical solutions of the relaxation model and of its parabolic approximation for the same value of $\varepsilon$. Although we have not yet derived a theoretical justification by means of convergence of the Chapman–Enskog expansion, it is clear that the approximation will be valid only for small values of $\varepsilon$. Furthermore, its validity seems to depend also on the size of the solution: the differences between the solution of the relaxation model and the solution obtained using the parabolic approximation increase with the injected level as well as with $\varepsilon$. This is illustrated in Figs. 4–6 which represents both solutions, relaxation and parabolic, for three injected concentrations 1, 5 and 10 and three different values of $\varepsilon$: $10^{-2}$, $5 \times 10^{-2}$, and $10^{-3}$. For $\varepsilon = 10^{-2}$ the two models are comparable only for the smallest injection level. For the levels 5 and 10 the solutions have almost
nothing in common. For $\varepsilon = 5 \times 10^{-3}$ they are a little more alike even for high concentrations and for the very small value of $\varepsilon = 10^{-3}$ they are almost identical.

We take the intermediate case of $\varepsilon = 5 \times 10^{-3}$ and compare the two methods for an injected concentration of 1 for which the solutions are close. In Fig. 7 we see the $L^1$ error curves: the parabolic scheme is approximately of order 1.6 while the scheme for the relaxation model is at best 1.2. Also the absolute amplitude of the error for the parabolic scheme is much lower than for the relaxation — at all discretizations — by a ratio of 20 at least. To compare the two models from the numerical standpoint we choose for each scheme the discretization leading to a precision of about $10^{-4}$. For the parabolic scheme, this precision is achieved using $\Delta t = 6.25002 \times 10^{-4}$ and $\Delta x = 1.25 \times 10^{-3}$. Computing the solution up to $t = 0.1$ takes 0.56 s of CPU on an IBM RISC/6000. For the relaxation scheme, the same precision is achieved using $\Delta t = 5.5439 \times 10^{-5}$ and $\Delta x = 1.75781 \times 10^{-4}$ and it requires 39.10 s of CPU. Eventually, this same discretization for the parabolic scheme leads to a precision of $5 \times 10^{-6}$ and takes 77.66 s. In other words the parabolic scheme is more complicated and requires more — actually twice as much CPU time than the full relaxation model for the same discretization. This is because it involves the iterative solution of a tridiagonal nonlinear system of equations. On the other hand, because it is parabolic, the diffusive part makes it more regular and it does not require such a fine discretization as the relaxation scheme to achieve the same relative precision. A ratio of 70 between the discretizations needed for a precision of $10^{-4}$ leads to a similar ratio between the CPUs.

Eventually we show a numerical simulation performed with realistic parameters corresponding to a Tröger’s base enantiomer of micro crystalline cellulose triacetate, with ethanol as solvent, also studied in [18]. The isotherm is still Langmuir with $K = 0.157$ and $N^* = 10.16$. The velocity within the column is equal to $4.55$ cm/min. There are four graphs in Fig. 8 corresponding to four durations of injection all at the same level ($\approx 15$). The total injected
quantities and the corresponding durations are given in Table 1. On each of the four figures there are three curves corresponding to the experimental concentrations, and the relaxation and parabolic simulations. The measurements are made at the bottom of the column whose length is 25 cm for a diameter of 0.46 cm. The curves show the concentration at an abscissa $x = 25$ as a function of time. This would be a typical benchmark for our next goal which is the identification of the isotherm — along with the parameter $\varepsilon$. Here it just shows that both models provide realistic simulations of the concentration curves for this range of injection.

5. Conclusion

In conclusion we have shown that there exist ranges of concentrations and relaxation parameters for which the parabolic approximation can be used. In this case, it is very advantageous from the point of view of computing time and therefore very promising. We propose in the next future to implement it within the parameter identification method already developed in the hyperbolic context (see [19]). This seems the best way so far to take into account the diffusion effects which cannot be neglected in many experimental datasets. To be of practical interest, it requires first to be extended to the vector case, so that multi-component mixtures can be treated.
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Appendix A. Stiffly stable implicit Runge–Kutta scheme

We describe an implicit Runge–Kutta scheme which is used in [15] to solve a stiff system of ordinary differential equations:

$$\frac{dy}{dt} + f(y) = 0, \quad \text{(28)}$$

$$y^{n+1} - y^n = \Delta (b_1 f_1 + b_2 f_2), \quad (I + a_1 \Delta \nabla f^n) f_1 = -f(y^n), \quad (I + a_2 \Delta \nabla f^n) f_2 = -f(y^n + \beta \Delta f_1). \quad \text{(29)}$$

The coefficients $a_1$, $a_2$, $\beta$, $b_1$ and $b_2$ in the discretization given above are identified by imposing order 2 and stability. The order 2 condition is obtained by comparing the discretized scheme with the Taylor expansion of $y(t_{n+1})$ around $y(t_n)$. By replacing

$$f_1 = -f(y^n) + a_1 \Delta \nabla f^n f(y^n) + O(\Delta^2), \quad \text{(30)}$$

$$f_2 = -f(y^n) + (a_2 + \beta) \Delta \nabla f^n f(y^n) + O(\Delta^2), \quad \text{(31)}$$

in Eq. (29) one gets

$$y^{n+1} = y^n + \Delta (b_1 + b_2) f(y^n) + \Delta^2 [b_1 a_1 + b_2 (a_2 + \beta)] \nabla f(y^n) + O(\Delta^3), \quad \text{(32)}$$

to be compared with

$$y(t_n + \Delta) = y(t_n) - \Delta f(y(t_n)) - \frac{\Delta^2}{2} \nabla f(t_n) \cdot f(t_n) + O(\Delta^3)$$

which provides the first two equations

$$b_1 + b_2 = 1, \quad a_1 b_1 + (a_2 + \beta) b_2 = \frac{1}{2}. \quad \text{(32)}$$

To obtain other equations, linear stability is first imposed — in the case ($f(y) = Ay$):

$$f_1 = B_1 Ay^n, \quad f_2 = B_2 A(y^n + \beta \Delta f_1) = B_2 A(I + \beta \Delta B_1 A) y^n,$$

$$y^{n+1} = (I + b_1 \Delta B_1 A + b_2 \Delta B_2 A(I + \beta \Delta B_1 A)) y^n. \quad \text{(33)}$$

Since $A$ and $B_1$ commute this leads to

$$y^{n+1} = B_1 B_2 \left( I + \Delta (1 - a_1 - a_2) A + \Delta^2 (b_2 \beta - b_2 (a_1 + a_2) + a_1 a_2) A^2 \right) y^n. \quad \text{(34)}$$

The third equation is

$$b_2 \beta - b_2 (a_1 + a_2) + a_1 a_2 = 0,$$

which allows one to write

$$y^{n+1} = B_1 B_2 (I + \Delta (1 - a_1 - a_2) A) y^n.$$
or in another form

\[ y^{n+1} = \frac{a_1 + a_2 - 1}{a_1} B_2 \left( I - \frac{1 - a_2}{1 - a_1 - a_2} B_1 \right) y^n. \]

Matrices \( B_i \) are such that \( B_{ii} \) are such that

\[ \|B_i\|_\infty \leq 1, \]

TVD stability is therefore ensured if

\[ \frac{|a_1 + a_2 - 1| + |1 - a_2|}{|a_1|} \leq 1, \]

which happens if \( a_1 < 1 \) and \( a_1 + a_2 > 1 \). Another equation is obtained in a same way with a scalar function

\[ f(y) = ay^2 \]

\[ -8a_1^2a_2 + 4b_1a_1a_2 + 4b_2a_1^2 - 4\beta b_2a_1 + b_2\beta^2 = 0. \]

It is somewhat worrying that this method cannot be extended to a third order function to obtain a fifth equation because it would be incompatible with the first four equations. Third order accuracy cannot also be achieved because it amounts to two equations. The idea in the original paper [15] is to minimize one of the coefficients in front of the third order terms in the Taylor developpements. Minimization of

\[ b_1a_1^2 + b_2(\beta a_1 + a_2(\beta + a_2) - \frac{1}{6}, \]

with the four other equations acting as constraints provide the following coefficients:

\[ a_1 = a_2 = a = \frac{2 - \sqrt{2}}{2} = 0.292893129, \quad \beta = 0.485281374, \quad b_2 = 0.426776696, \quad b_1 = 0.573223304. \]

which are the coefficients that we also use in our simulations.

References