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Highlights

- Numerical methods for solution of the equilibrium-dispersive model of liquid chromatography are compared.
- A stabilized spectral method is applied and benchmarked against state-of-the-art finite element methods.
- The spectral method is demonstrated to be suitable for simulation of convection-dominated liquid chromatographic processes.
- Arbitrary high-order methods are shown to outperform the traditionally applied second-order methods in terms of computational cost and discrete problem size.

A stabilized nodal spectral solver for liquid chromatography models

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Abstract

Numerical methods for simulation of linear and non-linear liquid chromatography processes are compared in terms of computational cost and quality of the solution using as few as possible degrees of freedom (discrete problem size). We apply, for the first time, the p-type (order enrichment) continuous Galerkin spectral method (p-CG) for spatial discretization with exponential decay of spatial errors (spectral convergence) for smooth problems. To stabilize the method for marginally resolved or very steep shock-waves typically encountered, we use a spectral filtering approach. This effectively removes aliasing driven instabilities while retaining the high-order accuracy of the numerical method. We benchmark the stabilized p-CG method against two state-of-the-art finite element methods, namely the second-order accurate h-type (element refinement) discontinuous Galerkin method using a total-variation-diminishing limiter (h-DG-TVD) and the arbitrary-order hp-type discontinuous Galerkin spectral element method (hp-DG). Not surprisingly, the three methods provide predictions of column elution profiles that converge to the same values. However, the computational costs differ considerably. Although second-order accurate shock-capturing methods are often adopted as the default implementation, the stable arbitrary high-order methods considered in this paper are found to significantly outperform these in terms of both computational cost and discrete problem size. The p-CG method performs as well as the hp-DG method in terms of computational cost, but it has superior convergence properties, even in the presence of strong shock-waves. Further, its implementation is much simpler.

Keywords: High-order; Nodal continuous Galerkin Spectral method; Nodal discontinuous Galerkin Spectral element method; Liquid chromatography; Linear and nonlinear isotherm; Equilibrium-dispersive model;

1. Introduction

Liquid chromatography is a central unit operation in the fine chemicals, pharmaceutical and biotechnological industries for downstream processing. The concept is successfully used in difficult separation processes, such as separation of enantiomers or isolation of active pharmaceuticals from fermentation broth.

In liquid batch chromatography, a mobile phase percolates through a bed packed with stationary and porous particles. It carries components from a feed mixture injected at the inlet of the column. The involved components interact differently with the stationary phase leading to characteristic retention behaviour. Conceptually, a complete separation is achieved for a sufficiently long column. The purified components are collected periodically at the column outlet.

A current trend in the fine chemicals, pharmaceutical and biotechnological industries is the digitalization of manufacturing processes to switch from a recipe-driven to a data-driven operational approach. This has great

scope, when considering rapid cost-effective process development for speed-to-market and facilitation of near-optimal operation using on-line monitoring strategies to control production costs. Digitalization of manufacturing processes has been successfully promoted over decades in other industries, such as the chemical and petrochemical industries. Provided that the necessary measurements are possible, the fine chemicals, pharmaceutical and biotechnological industries can reap similar benefits from digitalization.

The use of models of mechanistic nature for process prediction is key to successfully implement digital technology. A number of models have been successfully applied to model chromatographic process, such as the general rate model, various transport models, the equilibrium dispersive model and the ideal model (Guiochon et al. (2006)). These models include a description of both the fluid flow through the column and the column adsorption phenomena. The model complexity depends on how many band-broadening effects are

taken into account, ranging from the ideal model where no band-broadening effects are included to the general rate model where diffusion, pore diffusion and mass transfer resistances are accounted for. The resulting models are described by systems of partial-differential equations (PDEs) or partial-differential-algebraic equations (PDAEs), depending on the model assumptions applied. Closed-form solutions are available only in special cases. Therefore, we have to rely on numerical techniques to obtain approximate solutions. When using mechanistic models for method development, the use of computer optimization is essential. Optimization algorithms require a large number of simulations, often thousands. Therefore, efficient simulation software is key to the successful implementation of digital chromatographic manufacturing.

1.1. State-of-the-art simulation methods for liquid chromatography models

Currently, (low-order) shock-capturing methods are widely adopted as the default implementation to approximate chromatographic models, ranging from finite volume flux-limiting methods (Medi and Amanullah (2011); Javeed et al. (2011b)), weighted essentially non-oscillatory (WENO) methods (von Lieres and Andersson (2010); Brown et al. (2018); Donat et al. (2018)), particle transport methods (Shipilova et al. (2008)), conservation element/solution element methods (Lim et al. (2004)) and Runge-Kutta total variation diminishing (TVD) discontinuous Galerkin (DG) finite element methods (Javeed et al. (2011a)). These methods are designed with a fixed order of accuracy, often second order (low-order). However, they achieve stable and non-oscillatory solutions, even when discontinuities are present in the solution profile. In chromatographic theory, only the ideal model predicts discontinuities in the concentration profiles. Here, a numerical scheme with convergence rate higher than first order $O(h)$ will produce persistent and artificial oscillations, known as the Gibbs phenomenon (Gottlieb and Shu (1997); Gottlieb and Hesthaven (2001)). To resolve this, a reconstruction or limiting procedure is required (a shock-capturing scheme) to obtain more than first-order accuracy. A strictly non-oscillatory scheme achieves up to second order (low-order) accuracy $O(h^2)$ whereas an essentially non-oscillatory scheme can be designed with higher-order accuracy (Harten et al. (1987)). However, when using a real chromatography column, discontinuities cannot form in the concentration profile and instead very steep band fronts/rears (shock waves) are observed (Ma and Guiochon (1992)). Thus, realistic applications are described by models that include

one or more band-broadening effects. Furthermore, Danckwerts (1953) boundary conditions are considered valid (Guiochon et al. (2006)), such that discontinuous injection profiles (e.g. rectangular profiles) are dispersed immediately upon entering the column. Then, the Gibbs phenomenon is of less concern and arbitrary high-order methods can be used for cost-efficient simulations. Therefore, we (Meyer et al. (2018)) suggested to use a hp-type DG method, proposed by Hesthaven and Warburton (2002, 2008), to cost-efficiently predict realistic chromatographic systems. In short, the computational domain is partitioned into non-overlapping elements while the solution within an element is approximated by an p th order polynomial. The analytical fluxes on element boundaries are undefined as a result of non-overlapping elements and are instead replaced by numerical approximations. Convergence to a desired solution is obtained either by increasing the number of elements (h-type refinement) or by increasing the order of the polynomials (p-type refinement). For smooth solutions, p-type refinement is, in general, superior since it results in exponential decay of the error (spectral convergence). This enables the p-refinement strategy to reach the same level of accuracy with fewer degrees of freedom. A recent review of spectral element methods are given by e.g. Xu et al. (2018).

1.2. Paper objectives

The objective of this paper is to show that the classical p-type continuous Galerkin spectral method (p-CG) is robust and efficient for simulation of convection-dominated liquid chromatographic models. The p-CG method has traditionally in chemical engineering software been considered for fully diffusive problems. Here, the method is efficient, since it achieves spectral convergence for smooth problems, and stable, due to the presence of sufficient physical dissipation. However, when applied to convection-dominated processes, aliasing errors can lead to numerical instabilities for marginally resolved or very steep shock waves. These aliasing-driven instabilities are effectively removed using e.g. spectral filtering techniques (Hesthaven and Kirby (2008)) while retaining high-order accuracy of the method. Thus, we propose, for the first time, to simulate linear and non-linear liquid chromatographic processes using a stabilized p-CG method.

To assess the performance of the stabilized p-CG method, we benchmark it against the hp-DG method and the second-order (low-order) accurate discontinuous Galerkin method using a total variation diminishing limiter (h-DG-TVD). Zhou et al. (2001) demonstrated, that the discontinuous Galerkin method us-

ing a total-variation-bounded (TVB) limiter is usually more efficient compared to the finite volume method using WENO reconstruction. The TVD limiter will reduce the accuracy of the scheme to first order at smooth extremes, whereas the TVB limiter uses a tunable problem-dependent parameter to avoid this. In this work, we instead use the TVD limiter in combination with a shock-detector (a generalized TVD limiter) in order to avoid reducing the accuracy to first order at smooth extrema. Hence, we believe that our second-order h-DG-TVD method is at least as efficient as the second-order finite volume method with WENO reconstruction considered by other authors (von Lieres and Andersson (2010); Brown et al. (2018); Donat et al. (2018)).

We note that since we are applying a purely spectral method, we lose geometric flexibility. However, this is of less concern when considering the single domains used in the typical one-dimensional liquid chromatography models. In contrast to the hp-DG method, the p-CG can be applied without introducing any auxiliary variables, or rewriting the model problem into a larger system of equations saving computational cost. We are further motivated by the fact that the p-CG method is much simpler to implement and understand. In numerical experiments, we evaluate the performance of the three methods by their ability to translate a minimum amount of degrees-of-freedom (DoF) into a solution of sufficient quality (discrete problem size) and CPU time. We prefer to represent the solution on a coarse grid since a smaller state-vector needs to be stored and integrated. This is especially computationally beneficial when considering large-scale dynamic optimization used e.g. to obtain discretized multi-level elution trajectories for high productivity and high yield batch chromatographic processes (Holmqvist and Magnusson (2016); Sellberg et al. (2017)) or for global downstream optimization (Huuk et al. (2014); Baumann et al. (2015); Pirrung et al. (2017)). It is also computationally advantageous when considering closed loop non-linear model predictive control (MPC) applications including state-estimation.

1.3. Future solver capability considerations

The hp-DG method supports complex geometries, whereas the purely spectral p-CG method provides no such support. The typical liquid chromatography models considered in this paper predicts chromatographic behaviour for laboratory and industrial-scale applications with columns up to several litres of volume. These models are derived on simple one-dimensional grids

where support for complex geometries are unnecessary. However, when considering miniaturized columns on micro-scale or full-scale industrial applications with volumes of up to thousands of litres, the simple one-dimensional models cannot be used due to their simplifying assumptions. To simulate such processes, two-dimensional models are required for accurate predictions (Püttmann et al. (2014)). These two-dimensional models are solved on complex grids due to random packing of the stationary particles. Here, the hp-DG method can be naturally extended since it offers geometric flexibility, whereas the p-CG can not.

Furthermore, the hp-DG method supports parallel implementations, while p-CG does not. While it is possible to increase the efficiency of the hp-DG method by parallel implementations, such implementations are beyond the scope of this article.

1.4. Paper organization

This paper is organized as follows: In section two we summarize the equilibrium-dispersive model together with a linear and a multicomponent Langmuir isotherm. In section three we derive the numerical methods used in section four to perform a comparative study in numerical experiments. Finally, concluding remarks are collected in section five.

2. The equilibrium-dispersive model

The equilibrium-dispersive model is based on the following assumptions:

1. Permanent equilibrium between bound (solid) and unbound (liquid) states at all positions in the column.
2. Isothermal chromatographic column.
3. The column is homogeneously packed with porous spherical particles of uniform size.
4. Compressibility of the mobile phase is negligible leading to a flat velocity profile.
5. No interaction between the solvent (mobile) and the solid (stationary) phase.
6. Only axial dispersion causes band broadening.
7. No radial concentration gradients in the column.

With these assumptions, the equilibrium-dispersive model involving N_c components is given by (Guiochon et al. (2006))

$$\frac{\partial \mathbf{c}}{\partial t} + F \frac{\partial \mathbf{q}}{\partial t} + u \frac{\partial \mathbf{c}}{\partial x} - D_a \frac{\partial^2 \mathbf{c}}{\partial x^2} = 0 \quad (1)$$

where $\mathbf{c} = (c_1, \dots, c_{N_c})^T$ and $\mathbf{q} = (q_1, \dots, q_{N_c})^T$ are unbound (liquid) and bound (stationary) phase concentrations, respectively, $F = (1 - \epsilon_c)/\epsilon_c$ is the phase ratio, ϵ_c is the column porosity, u is the interstitial velocity, D_a is the apparent axial dispersion coefficient, t is time, and x is the space-coordinate.

In this paper we consider adsorption of multi-component mixtures in which the adsorption equilibria between unbound c_i and bound q_i states are described by the multicomponent Langmuir isotherm (Guiochon et al. (2006))

$$q_i = \frac{a_i c_i}{1 + \sum_{j=1}^{N_c} b_j c_j}, \quad i = 1, \dots, N_c \quad (2)$$

where a_i is a Henry's constant and b_j quantifies the non-linearity of the isotherm. For dilute systems, Eq. (2) simplifies to a linear isotherm, given for the i th component by

$$q_i = a_i c_i \quad (3)$$

It is assumed that the axial dispersion coefficient D_a is related to the column efficiency as (Guiochon et al. (2006))

$$D_a = \frac{Lu}{2N_a} \quad (4)$$

with N_a the number of apparent theoretical plates. The initial conditions for a pre-equilibrated column are given by

$$\mathbf{c}(0, x) = \mathbf{c}_{init}(x) \quad (5)$$

Finally, Danckwerts (1953) boundary conditions are applied. The inlet Robin condition is given by

$$u\mathbf{c}|_{x=0} - D_a \frac{d\mathbf{c}}{dx}\bigg|_{x=0} = u\mathbf{c}_{inj}(t) \quad (6)$$

such that the injection profile $u\mathbf{c}_{inj}(t)$ is dispersed immediately upon entering the column. In this work, we consider rectangular injection profiles, e.g.

$$u\mathbf{c}_{inj} = \begin{cases} u\mathbf{c}_f, & 0 \leq t \leq t_{inj} \\ 0, & t > t_{inj} \end{cases} \quad (7)$$

where $\mathbf{c}_f$ is the feed concentration. At the column outlet, a Neumann condition for finite column length L is used

$$\frac{\partial \mathbf{c}}{\partial x}\bigg|_{x=L} = 0 \quad (8)$$

3. Numerical methods

The equilibrium-dispersive model Eq. (1) is rewritten as follows

$$\frac{\partial \mathbf{w}(\mathbf{c})}{\partial t} + u \frac{\partial \mathbf{c}}{\partial x} - D_a \frac{\partial^2 \mathbf{c}}{\partial x^2} = 0 \quad (9)$$

where $\mathbf{w}(\mathbf{c}) := \mathbf{c} + F\mathbf{q}(\mathbf{c})$ represents the total mass in the column. However, since an explicit relationship is missing for the function $\mathbf{c}(\mathbf{w})$ in the multicomponent case ($N_c > 1$), the chain rule may be applied to obtain,

$$\left(1 + F \frac{\partial \mathbf{q}(\mathbf{c})}{\partial \mathbf{c}}\right) \frac{\partial \mathbf{c}}{\partial t} + u \frac{\partial \mathbf{c}}{\partial x} - D_a \frac{\partial^2 \mathbf{c}}{\partial x^2} = 0 \quad (10)$$

Although this approach is simple, the formulation is non-conservative, e.g. mass can disappear even when using a conservative numerical method. Thus, we use instead the following implicit function for $\mathbf{c}(\mathbf{w})$ which ensures a conservative formulation (Donat et al. (2018)),

$$c_i(\mathbf{w}) = \frac{w_i}{1 + F a_i \rho_0(\mathbf{w})} \quad (11)$$

where $\rho_0(\mathbf{w})$ is the only positive root of the following rational function,

$$R_w(y) = 1 - y + \sum_{i=1}^{N_c} \frac{y}{y + F a_i} b_i w_i \quad (12)$$

and $1 \leq \rho_0(\mathbf{w}) \leq 1 + \sum_j b_j w_j$. We approximate the only positive root of Eq. (12) using a non-linear solver based on Kelley's (2003) nsold algorithm, which is a Newton's method using Newton-Armijo iterations, adaptive Jacobian updates and parabolic line search via 3-point interpolation.

In the following subsections, we consider the approximation of Eq. (9) using a method-of-lines approach, e.g. the spatial and temporal discretizations are considered separately. The p-CG, hp-DG and the h-DG-TVD methods are applied for spatial discretization to obtain a semi-discrete set of ordinary differential equations (ODEs). The semi-discrete ODE system is integrated from appropriate initial conditions using a 5-stage, 4th-order low-storage explicit Runge Kutta (ERK) method (Carpenter and Kennedy (1994)). The solution to Eq. (9) contains the total mass $\mathbf{w}$ inside the column. Eq. (11) is applied to obtain concentrations in the mobile phase $\mathbf{c}$ based on the total mass $\mathbf{w}$.

3.1. The continuous Galerkin spectral method

3.1.1. General formulation

Following the p-CG discretization procedure (Kopriva (2009)), we multiply Eq. (9) by an arbitrary smooth test function v and integrate over the computational domain $\Omega \in [0, L]$, to obtain a weak form

$$\int_{\Omega} \frac{\partial \mathbf{w}(\mathbf{c})}{\partial t} v dx + \int_{\Omega} \frac{\partial \mathbf{f}(\mathbf{c}, \partial \mathbf{c} / \partial x)}{\partial x} v dx = 0 \quad (13)$$

where we have defined the flux $\mathbf{f}(\mathbf{c}, \partial \mathbf{c} / \partial x) := \mathbf{u} \mathbf{c} - D_a \partial \mathbf{c} / \partial x$. Applying spatial integration by parts on Eq. (13) gives

$$\int_{\Omega} \frac{\partial \mathbf{w}(\mathbf{c})}{\partial t} v dx - \int_{\Omega} \mathbf{f} \frac{\partial v}{\partial x} dx = \oint_{\partial \Omega} \hat{\mathbf{n}} v \mathbf{f} dx \quad (14)$$

where $\partial \Omega$ represent the domain boundaries, and $\hat{\mathbf{n}}$ is the unit outward normal vector to the boundary.

3.1.2. Nodal discretization

The exact solution $\mathbf{c}$, is approximated by a numerical solution $\mathbf{c}_h$, which we assume is a finite sum of the form

$$\begin{aligned} \mathbf{c}(t, x) &\approx \mathbf{c}_h(t, x) = \sum_{n=1}^{N_p} \hat{\mathbf{c}}_{h,n}(t) \phi_n(x) \\ &= \sum_{n=1}^{N_p} \mathbf{c}_h(t, x_n) l_n(x) = \sum_{n=1}^{N_p} \mathbf{c}_{h,n}(t) l_n(x) \end{aligned} \quad (15)$$

where $\hat{\mathbf{c}}_{h,n}$ and $\mathbf{c}_{h,n}$ are N_p unknown modal and nodal coefficients, respectively. ϕ_n are the chosen basis functions which we assume equal to our test functions (the Galerkin method) and l_n are the associated Langrange interpolating polynomials with the property $l_i(z_j) = \delta_{ij}$ (δ_{ij} is a Kronecker delta) at mesh nodes. The basis functions ϕ_n are chosen such that the numerical solution $\mathbf{c}_h$ belongs to the following approximation space,

$$\mathbb{V}_p^k = \{v : v \in \mathbb{P}^p(\Omega)\} \quad (16)$$

where $\mathbb{P}^p(\Omega)$ is a polynomial of degree at most $p = N_p - 1$ defined in Ω . The following orthonormal polynomial basis functions are chosen,

$$\phi_n(r) = \frac{P_{n-1}(r)}{\sqrt{\gamma_{n-1}}} = \tilde{P}_{n-1}(r), \quad r \in I = [-1, 1] \quad (17)$$

where $P_{n-1}(r)$ are the classical Legendre polynomials defined on the reference element I and $\gamma_n = 2/(2n+1)$ is the normalization. We define the vectors of nodal values on I as

$$\mathbf{c}_h^I = (\mathbf{c}_h(r_1), \dots, \mathbf{c}_h(r_{N_p}))^T \quad (18)$$

the vectors of modal values on I as

$$\hat{\mathbf{c}}_h^I = (\hat{\mathbf{c}}_h(r_1), \dots, \hat{\mathbf{c}}_h(r_{N_p}))^T \quad (19)$$

and the vectors of local Lagrange interpolating polynomials and basis functions on I by

$$\mathbf{l} = [l_1(r), \dots, l_{N_p}(r)]^T, \quad \tilde{\mathbf{P}} = [\tilde{P}_0(r), \dots, \tilde{P}_N(r)] \quad (20)$$

Further, we introduce the mass, stiffness and lifting matrices defined on I in Eqs. (21a)-(21c), respectively.

$$\mathcal{M}_{ij} = \int_{-1}^1 l_i(r) l_j(r) dr \quad (21a)$$

$$\mathcal{S}_{ij} = \int_{-1}^1 l_i(r) \frac{dl_j}{dr}(r) dr \quad (21b)$$

$$\mathcal{L} = \mathcal{M}^{-1} \mathcal{E} \quad (21c)$$

$$\mathcal{E}_{i1} = l_i(-1), \quad \mathcal{E}_{i2} = l_i(1) \quad (21d)$$

Finally, we define the Vandermonde matrix with entries

$$\mathcal{V}_{ij} = \tilde{P}_{j-1}(r_i) \quad (22)$$

Here, we choose to represent the nodal set $\mathbf{r} = (r_1, \dots, r_{N_p})^T$ inside the reference element I using the Legendre-Gauss-Lobatto quadrature points to ensure a well-conditioned Vandermonde matrix. This allows us to use operations requiring the inverse of the Vandermonde matrix $\mathcal{V}^{-1}$. The Vandermonde matrix is used to transform between modal and nodal forms and to relate the basis functions (Hesthaven and Warburton (2002)), e.g.

$$\mathbf{c}_h^I = \mathcal{V} \hat{\mathbf{c}}_h^I, \quad \hat{\mathbf{c}}_h^I = \mathcal{V}^{-1} \mathbf{c}_h^I, \quad \tilde{\mathbf{P}} = \mathcal{V}^T \mathbf{l} \quad (23)$$

Eq. (23) establishes the following relationships to compute the mass- and stiffness matrices for a standard element without using high-order Gaussian quadrature rules for the element integrals, leaving the implementation quadrature-free:

$$\mathcal{M} = (\mathcal{V} \mathcal{V}^T)^{-1}, \quad \mathcal{S} = \mathcal{M} \mathcal{D}_r \quad (24)$$

Here, we have defined the differentiation matrix with entries

$$\mathcal{D}_r = \left. \frac{dl_j}{dr} \right|_{r_i} \quad (25)$$

The differentiation matrix is used to transform point values to derivatives, e.g. $dc_h^I/dr = \mathcal{D}_r \mathbf{c}_h^I$. It is computed by

$$\mathcal{D}_r = \mathcal{V}_r \mathcal{V}^{-1} \quad (26)$$

where $\mathcal{V}_r$ is a matrix with entries given by the derivative of the basis,

$$\mathcal{V}_{r,(i,j)} = \left. \frac{d\tilde{P}_j}{dr} \right|_{r_i} \quad (27)$$

To rewrite Eq. (14) in compact form the continuous variables are replaced by the finite sum given by Eq. (15) and the above defined (constant) local element matrices are used. After rearrangement, we arrive at

$$\frac{d\mathbf{W}_h}{dt} = \frac{2}{L} \hat{\mathcal{M}}^{-1} \hat{\mathcal{S}}^T \mathbf{F}_h + \frac{2}{L} \hat{\mathcal{L}} \begin{bmatrix} -\mathbf{f}_h|_{x=0} \\ \mathbf{f}_h|_{x=L} \end{bmatrix} \quad (28)$$

where

$$\mathbf{W}_h = (\mathbf{w}_h(x_1), \dots, \mathbf{w}_h(x_{N_p}))^T \quad (29)$$

$$\mathbf{F}_h = (\mathbf{f}_h(x_1), \dots, \mathbf{f}_h(x_{N_p}))^T \quad (30)$$

are nodal values defined on the domain Ω and $\hat{\mathbf{M}} = \text{diag}(\mathbf{M})$, $\hat{\mathbf{S}} = \text{diag}(\mathbf{S})$ and $\hat{\mathbf{L}} = \text{diag}(\mathbf{L})$ are block diagonal matrices with N_c blocks. We note that since $\hat{\mathbf{M}}$ is block-diagonal, it is easily invertible such that the semi-discrete ODE system is explicit. The flux $\mathbf{f}_h$ is computed by

$$\mathbf{f}_h = u\mathbf{c}_h - D_a \frac{2}{L} \mathcal{D}_r \mathbf{c}_h \quad (31)$$

where we have used the differentiation matrix $\mathcal{D}_r$ to evaluate the nodal spatial derivatives of $\mathbf{c}_h$. In Eqs. (28) and (31) the factor $2/L$ is the inverse Jacobian of the affine transformation,

$$x(r) = \frac{(1+r)L}{2} \quad (32)$$

used to map the reference element I to the physical element Ω . Eq. (28) represents a semi-discrete system of N_p ODEs for N_p unknowns.

3.1.3. Stabilization

To stabilize the scheme, we apply a modal filter (Hesthaven and Kirby (2008); Hesthaven and Warburton (2008)) to the numerical approximation at regular intervals. We construct the filter matrix as

$$\mathcal{F} = \mathcal{V} \Lambda \mathcal{V}^{-1} \quad (33)$$

with the diagonal matrix Λ

$$\Lambda = \delta_{ij} \sigma(i-1), \quad i, j = 1, \dots, N_p \quad (34)$$

The modal filter coefficients $0 \leq \sigma_i \leq 1$ are given by

$$\sigma_i = \begin{cases} 1 & 0 \leq i \leq i_c \\ \exp(-\alpha((i - i_c)/(p - i_c))^s) & i_c \leq i \leq p \end{cases} \quad (35)$$

where α is a parameter that measures the modification of the maximum mode, i.e. $\sigma(p) = \exp(-\alpha)$. We define $\alpha = -\log(\epsilon_m)$ with ϵ_m the machine accuracy. The parameter s is the (even) order of the filter, and determines the strength of it (higher s means weaker filtering). i_c represents a cut-off index, below which the low modes are left untouched. The dissipation required for stabilization is then introduced by a cheap matrix-vector operation:

$$\bar{\mathbf{W}}_h = \mathcal{F} \mathbf{W}_h \quad (36)$$

3.1.4. Boundary conditions

Danckwerts (1953) boundary conditions Eqs. (6) and (8) are imposed by replacing the inlet flux with,

$$\mathbf{f}_h|_{x=0} = u\mathbf{c}_{inj}(t) \quad (37)$$

such that the combined convective and diffusive flux $\mathbf{f}_h$ just inside the column equals the inlet flux. The outlet Neumann condition is imposed by replacing the outlet flux as

$$\mathbf{f}_h|_{x=L} = u\mathbf{c}_h|_{x=L} \quad (38)$$

such that the diffusive part of the flux is zero on the outlet.

3.2. The hp discontinuous Galerkin method

3.2.1. General formulation

To apply the hp-DG method on second order differential operators, we follow the approach of Bassi and Rebay (1997) and rewrite Eq. (9) as a first order system,

$$\frac{\partial \mathbf{w}(\mathbf{c})}{\partial t} + \frac{\partial \mathbf{h}(\mathbf{c}, \mathbf{g})}{\partial x} = 0 \quad (39a)$$

$$\mathbf{g}(\mathbf{c}) - \sqrt{D_a} \frac{\partial \mathbf{c}}{\partial x} = 0 \quad (39b)$$

where we have defined the flux $\mathbf{h}(\mathbf{c}, \mathbf{g}) := u\mathbf{c} - \sqrt{D_a}\mathbf{g}$ and $\mathbf{g}$ are auxiliary gradient variables. Before applying the DG method to Eq. (39), we divide the computational domain Ω into K non-overlapping elements, such that $\Omega = \bigcup_{k=1}^K \Omega^k$ with $\Omega^k = x_R^k - x_L^k = \Delta x^k$.

Following the DG procedure, we multiply Eq. (39) by a smooth test function v and integrate over the element Ω^k . After applying spatial integration by parts, we obtain the local weak form

$$\int_{\Omega^k} \frac{\partial \mathbf{w}}{\partial t} v dx - \int_{\Omega^k} \mathbf{h} \frac{\partial v}{\partial x} dx = - \oint_{\partial \Omega^k} v \hat{\mathbf{h}}^* dx \quad (40a)$$

$$\int_{\Omega^k} \mathbf{g} v dx + \sqrt{D_a} \int_{\Omega^k} \mathbf{c} \frac{\partial v}{\partial x} dx = \sqrt{D_a} \oint_{\partial \Omega^k} v \hat{\mathbf{c}}^* dx \quad (40b)$$

Since we have an approximation space that is discontinuous across element interfaces $\partial \Omega^k$, we replace the non-defined analytical fluxes $\hat{\mathbf{h}}$ and $\hat{\mathbf{c}}$ by uniquely defined numerical fluxes $\hat{\mathbf{h}}^*$ and $\hat{\mathbf{c}}^*$, respectively. Suitable numerical fluxes are chosen in section 3.2.3.

3.2.2. Nodal discretization

On the k th element, we approximate the exact solution $\mathbf{Q} = [\mathbf{c}, \mathbf{g}]^T$ by a numerical solution $\mathbf{Q}_h^k = [\mathbf{c}_h^k, \mathbf{g}_h^k]^T$,

which we assume is a finite sum of equivalent form as in Eq. (15), e.g.

$$\begin{aligned} \mathcal{Q}(t, x) &\approx \mathcal{Q}_h^k(t, x) = \sum_{n=1}^{N_p} \hat{\mathcal{Q}}_{h,n}^k(t) \phi_n(x) \\ &= \sum_{n=1}^{N_p} \mathcal{Q}_h^k(t, x_n) l_n(x) = \sum_{n=1}^{N_p} \mathcal{Q}_{h,n}^k(t) l_n(x) \end{aligned} \quad (41)$$

where $\hat{\mathcal{Q}}_{h,n}^k$ and $\mathcal{Q}_{h,n}^k$ are unknown modal and nodal coefficients, respectively. The basis functions ϕ_n are chosen such that the solution $\mathcal{Q}_h^k$ belongs to the following approximation space,

$$\mathbb{V}_p^k = \{v : v^k \in \mathbb{P}^p(\Omega^k), \forall \Omega^k \in \Omega\} \quad (42)$$

where $\mathbb{P}^p(\Omega^k)$ are polynomials of degree at most $p = N_p - 1$ in each element Ω^k . To rewrite Eq. (40) in compact form the continuous variables are replaced by the finite sum given by Eq. (41) and the (constant) local element matrices defined in section 3.1.2 are used to give

$$\frac{d\mathbf{W}_h^k}{dt} = \frac{2}{\Delta x^k} \hat{\mathcal{M}}^{-1} \hat{\mathcal{S}}^T \mathbf{H}_h^k + \frac{2}{\Delta x^k} \hat{\mathcal{L}} \begin{bmatrix} -\mathbf{h}^*|_{x_L^k} \\ \mathbf{h}^*|_{x_R^k} \end{bmatrix} \quad (43a)$$

$$\begin{aligned} \mathbf{G}_h^k &= -\sqrt{D_a} \frac{2}{\Delta x^k} \hat{\mathcal{M}}^{-1} \hat{\mathcal{S}}^T \mathbf{C}_h^k \\ &\quad - \frac{2}{\Delta x^k} \sqrt{D_a} \hat{\mathcal{L}} \begin{bmatrix} -\mathbf{c}^*|_{x_L^k} \\ \mathbf{c}^*|_{x_R^k} \end{bmatrix} \end{aligned} \quad (43b)$$

where

$$\mathbf{H}_h^k = (\mathbf{h}_h^k(x_1), \dots, \mathbf{h}_h^k(x_{N_p}))^T \quad (44)$$

$$\mathbf{G}_h^k = (\mathbf{g}_h^k(x_1), \dots, \mathbf{g}_h^k(x_{N_p}))^T \quad (45)$$

$$\mathbf{C}_h^k = (\mathbf{c}_h^k(x_1), \dots, \mathbf{c}_h^k(x_{N_p}))^T \quad (46)$$

are nodal values defined on the domain Ω and the flux $\mathbf{h}_h^k$ is computed explicitly by

$$\mathbf{h}_h^k = u \mathbf{c}_h^k - \sqrt{D_a} \mathbf{g}_h^k \quad (47)$$

since we restrict the numerical flux $\mathbf{c}^*$ to depend on $\mathbf{c}_h^k$ only, e.g. the gradient variable $\mathbf{g}$ is a function of $\mathbf{c}$. In Eq. (43) the factor $2/\Delta x^k$ is the inverse Jacobian of the local affine transformation,

$$x^k(r) = x_L^k + 0.5(1+r)\Delta x^k \quad (48)$$

used to map the reference element I to the physical element Ω^k . Eq. (43) represents N_p ODEs for N_p unknowns in each local element. The global approximation is assembled as a direct sum of local contributions, e.g. $\mathcal{Q}_h = \bigoplus_{k=1}^K \mathcal{Q}_h^k$.

3.2.3. Numerical fluxes

To complete the scheme suitable numerical fluxes must be specified. We use the notation

$$\{\{\vartheta\}\} = 0.5(\vartheta^\ominus + \vartheta^\oplus), \quad [[\vartheta]] = 0.5(\hat{\mathbf{n}}^\ominus \vartheta^\ominus + \hat{\mathbf{n}}^\oplus \vartheta^\oplus) \quad (49)$$

for the average and jump at boundary interfaces $\partial\Omega^k$, respectively. In Eq. (49), the superscripts $\ominus$ and $\oplus$ denote the interior and exterior boundary values, respectively. The numerical flux h^* is written as a convective and a diffusive flux. It is reasonable to consider these contributions separately due to the convective-diffusive nature of the problem under consideration. Thus,

$$h^* = h_{\text{conv}}^* (c_h^{k,\ominus}, c_h^{k,\oplus}) + h_{\text{diff}}^* (g_h^{k,\ominus}, g_h^{k,\oplus}) \quad (50)$$

The convective flux is chosen as the Lax-Friedrichs flux given by

$$h_{i,\text{conv}}^* = u \{\{c_i^k\}\} + 0.5u [[c_i^k]] \quad (51)$$

For the diffusive flux we choose an internal penalty flux ((Douglas and Dupont (1976); Douglas et al. (2002))),

$$h_{i,\text{diff}}^* = \sqrt{D_a} (\{\{g_i^k\}\} - \tau [[c_i^k]]) \quad (52)$$

such that optimal convergence rates of order $p+1$ can be expected for all p . We note that choosing $\tau = 0$ will simplify the internal penalty flux to a central flux and for $\tau > 0$ the penalty term stabilizes the scheme by preventing large jumps in c_i^k . In our numerical experiments, we scale τ to the problem by

$$\tau = \frac{p^2}{\Delta x} \quad (53)$$

Finally, we specify the numerical flux $\sqrt{D_a} c_i^*$ as a central flux,

$$\sqrt{D_a} c_i^* = \sqrt{D_a} \{\{c_i^k\}\} \quad (54)$$

3.2.4. Boundary conditions

We impose boundary conditions weakly by exploiting a symmetry principle. The inlet Robin condition Eq. (6) is implemented by defining the combined convective and diffusive fluxes as

$$\begin{aligned} h_h^{1,\oplus}(x_L^1) &= -h_h^{1,\ominus}(x_L^1) + 2(uc_f) \\ &\Rightarrow \{\{h_h^1(x_L^1)\}\} = uc_f \end{aligned} \quad (55)$$

such that the inlet condition is satisfied on average. The outlet Neumann condition Eq. (8) is implemented by defining the convective flux as

$$\begin{aligned} h_{h,\text{conv}}^{K,\oplus}(x_R^K) &= h_{h,\text{conv}}^{K,\ominus}(x_R^K) \\ &\Rightarrow \{\{h_{h,\text{conv}}^K(x_R^K)\}\} = h_{h,\text{conv}}^{K,\ominus}(x_R^K) \end{aligned} \quad (56)$$

Table 1: Coefficients for the low-storage 5-stage 4th-order ERK method (Carpenter and Kennedy (1994))

i	a_i^{RK}	b_i^{RK}	c_i^{RK}
1	0	1432997174477/9575080441755	0
2	-567301805773/1357537059087	5161836677717/13612068292357	1432997174477/9575080441755
3	-2404267990393/2016746695238	1720146321549/2090206949498	2526269341429/6820363962896
4	-3550918686646/2091501179385	3134564353537/4481467310338	2006345519317/3224310063776
5	-1275806237668/842570457699	2277821191437/14882151754819	2802321613138/2924317926251

such that it is unmodified and the diffusive flux as

$$h_{h,\text{diff}}^{K,\oplus}(x_R^K) = -h_{h,\text{diff}}^{K,\ominus}(x_R^K) \Rightarrow \{h_{h,\text{diff}}^K(x_R^K)\} = 0 \quad (57)$$

such that it is zero on average.

3.3. The total variation diminishing discontinuous Galerkin method

The h-DG-TVD method is based on the hp-DG method using first-order polynomials in the approximation space. A post-processing procedure is applied after each stage of the ERK method (see section 3.4) to enforce the TVD property. In order to avoid destroying high-order accuracy in smooth regions of the solution, we apply a generalized slope limiter (Cockburn and Shu (2001)). We define the limited fluxes on the left and right element edge, respectively, as

$$\varrho_l^k = \bar{c}_h^k - m(\bar{c}_h^k - c_l^k, \bar{c}_h^k - \bar{c}_h^{k-1}, \bar{c}_h^{k+1} - \bar{c}_h^k) \quad (58a)$$

$$\varrho_r^k = \bar{c}_h^k - m(\bar{c}_h^k - c_r^k, \bar{c}_h^k - \bar{c}_h^{k-1}, \bar{c}_h^{k+1} - \bar{c}_h^k) \quad (58b)$$

where $\bar{c}_h^k$ is the element average and we have defined the minmod function,

$$m(y_1, y_2, y_3) = \begin{cases} s \min_{1 \leq n \leq 3} |y_n|, & \text{if } |s| = 1 \\ 0, & \text{otherwise} \end{cases} \quad (59)$$

with $s = 1/3 \sum_{i=1}^3 \text{sign}(y_i)$. The generalized slope limiter is then applied to each element after each stage of the Runge Kutta ERK method using the following procedure:

- Compute ϱ_l^k and ϱ_r^k using Eqs. (58a) and (58b)
- if $\varrho_l^k = c_h^k(x_l^k)$ and $\varrho_r^k = c_h^k(x_r^k)$, there is no need for limiting and the local solution is not altered.
- if not, then limiting is needed and we compute a limited version of $\bar{c}_h^k$ as $\Pi^1 \bar{c}_h^k$.

where $\bar{c}_h^k$ is the linear approximation to c_h^k ,

$$\bar{c}_h^k = \bar{c}_h^k + (x - x_0^k)(c_h^k)_x \quad (60)$$

with $(c_h^k)_x$ the linear slope of element k and x_0 represents the center coordinate of Ω^k . On elements where limiting is required, we apply the following limiter:

$$\Pi^1 \bar{c}_h^k = \bar{c}_h^k + (x - x_0^k)m\left((c_h^k)_x, \theta \frac{\bar{c}_h^{k+1} - \bar{c}_h^k}{\Delta x}, \theta \frac{\bar{c}_h^k - \bar{c}_h^{k-1}}{\Delta x}\right) \quad (61)$$

where the classical minmod limiter is obtained for $\theta = 1$ and the less restrictive, generalised minmod limiter for $\theta = 2$ (Cockburn and Shu (2001)).

3.4. The explicit Runge-Kutta method

The semi-discrete schemes obtained after spatial discretization are of the form,

$$\frac{dW}{dt} = F(t, W) \quad (62)$$

We advance Eq. (62) in time using a 5-stage 4th-order low-storage ERK method (Carpenter and Kennedy (1994)) which requires storage and overwriting of only two vectors $\mathbf{v}_j$ and $\boldsymbol{\mu}_j$. The ERK method is given by the following steps: Set $\boldsymbol{\mu}_0 = \mathbf{W}_h^n$, then for $j = 1, \dots, 5$ compute the intermediate functions:

$$\mathbf{v}_j = a_j^{RK} \mathbf{v}_{j-1} + \Delta t F(t_n + c_j^{RK} \Delta t, \boldsymbol{\mu}_{j-1}) \quad (63a)$$

$$\boldsymbol{\mu}_j = \boldsymbol{\mu}_{j-1} + b_j^{RK} \mathbf{v}_j \quad (63b)$$

The solution at the next time step is given by $\mathbf{W}_h^{n+1} = \boldsymbol{\mu}_5$. Here, $\mathbf{W}_h^n = \mathbf{W}_h(t_n)$, $\mathbf{W}_h^{n+1} = \mathbf{W}_h(t_{n+1})$ and the fixed coefficients a_{ij}^{RK} , b_j^{RK} and c_j^{RK} are given in Table 1. After obtaining the solution of the total mass at the next time step $\mathbf{W}_h^{n+1}$ we apply Eq. (11) to obtain the concentrations in the mobile phase $\mathbf{C}_h^{n+1} = (c_h^{n+1}(x_1), \dots, c_h^{n+1}(x_{N_p}))^T$.

In order to ensure linear stability of the ERK method, we constrain the time step as follows,

$$\Delta t \leq C_0 \frac{\min_i(\Delta x_i^k)}{u + 2D_a / \min_i(\Delta x_i^k)} \quad (64)$$

for some constant C_0 of order 1.

Figure 1: The error measured in the L^2 norm of the concentration band inside the column after advancing the problem in time from $T = 2$ until $T = 2.5$ as a function of degrees of freedom used in the spatial discretization. Shown in logarithmic scale.

4. Numerical test study

In this section, we perform numerical tests to evaluate the performance of the numerical methods presented in section 3 for both linear and non-linear chromatographic systems. The methods have been implemented in Matlab code and compiled on a Macbook Pro with a 2.7 GHz Intel Core i5 processor and 8 GB RAM.

Table 2: Simulation parameters used in the linear case study (section 4.1)

Parameters	Symbol	Values	Unit
Column length	L	1	cm
Porosity	ϵ	0.4	-
Interstitial velocity	u	0.46	cm min ⁻¹
Dispersion Coefficient	D_a	0.002	cm ² min ⁻¹
Henry's constant	a	1	-
Feed concentration	c_f	1	g l ⁻¹
Injection time	t_{inj}	1	min

4.1. Case 1: Linear chromatography with smooth initial conditions

The designed spatial convergence of the numerical methods are validated experimentally by convergence tests on a single-component problem with a linear isotherm Eq. (3). The analytical solution to this problem is given by Qamar et al. (2013) for $0 < t \leq t_{inj}$

as

$$c(t, z) = c_{init} + (c_{inj} - c_{init})H(t, z) \quad (65)$$

and by

$$c(t, z) = c_{init} + (c_{inj} - c_{init})H(t, z) - c_{inj}H(t - t_{inj}, z) \quad (66)$$

for $t > t_{inj}$ with

$$\begin{aligned}
 H(t, z) = & \frac{1}{2} \operatorname{erfc} \left[\frac{\alpha z - tPe_a}{2\sqrt{\alpha t}} \right] + \left(\frac{tPe_a^2}{\pi\alpha} \right)^{1/2} \\
 & \times \exp \left[-\frac{(\alpha z - tPe_a)^2}{4\alpha t} \right] - \frac{1}{2} \left(1 + zPe_a + \frac{tPe_a^2}{\alpha} \right) \\
 & \times \exp(zPe_a) \operatorname{erfc} \left[\frac{\alpha z + tPe_a}{2\sqrt{\alpha t}} \right] + \left(\frac{4tPe_a^2}{\pi\alpha} \right)^{1/2} \\
 & \times \left[1 + \frac{Pe_a}{4} \left(2 - z + \frac{tPe_a}{\alpha} \right) \right] \\
 & \times \exp \left[Pe_a - \frac{\alpha}{4t} \left(2 - z + \frac{tPe_a}{\alpha} \right)^2 \right] \\
 & - Pe_a \left[\left(2 - z + \frac{3tPe_a}{2\alpha} \right) + \frac{Pe_a}{4} \left(2 - z + \frac{tPe_a}{\alpha} \right)^2 \right] \\
 & \exp(Pe_a) \operatorname{erfc} \left[\frac{\alpha(2 - \alpha) + tPe_a}{2\sqrt{\alpha t}} \right] \quad (67)
 \end{aligned}$$

Here, $z := x/L$ is the normalized length, $Pe_a := Lu/D_a$ is the apparent Peclet number and $\alpha := (1 + aF)Pe_aL/u$ is a constant. We study a problem presented by Qamar et al. (2013) with detailed simulation parameters given in Table 2. Under these conditions, Qamar et al. (2013) used moment analysis to predict the elution of a normally distributed peak. After 2 min of simulation time, the problem is sufficiently smooth to expect experimental convergence rates equal to the theoretical values. We use the analytical solution to specify the column initial conditions after 2 min and advance the solution in time using our numerical methods from the exact initial conditions until the final time $t_f = 2.5$ min. We measure the L^1 , L^2 and L^∞ errors over the spatial domain, defined respectively by

$$L^1\text{-error} := \int_{\Omega} |E| d\Omega \quad (68a)$$

$$L^2\text{-error} := \sqrt{\int_{\Omega} E^2 d\Omega} \quad (68b)$$

$$L^\infty\text{-error} := \max_i |E_i| \quad (68c)$$

where $E = (e_1, \dots, e_{N_c})^T$ are errors evaluated at nodal points between the simulated and exact solution. We evaluate the integrals in Eqs. (68a) and (68b) using the nodal mass matrix given by Eq. (21a).

Table 3: L^1 , L^2 (g/cm²) and L^∞ (g/cm³) errors and convergence rates for the linear problem using the hp-DG and h-DG-TVD methods

Method	K	L^1 error	L^2 error	L^∞ error	L^1 order	L^2 order	L^∞ order	Theor.
hp-DG ($\mathbb{P}_1$)	32	1.49E-07	1.52E-07	7.99E-07	-	-	-	2
	64	3.66E-08	3.70E-08	1.95E-07	2.03	2.04	2.03	
	128	8.80E-09	8.88E-09	4.69E-08	2.06	2.06	2.06	
	256	2.03E-09	2.07E-09	1.10E-08	2.11	2.10	2.09	
hp-DG ($\mathbb{P}_2$)	32	5.16E-10	1.22E-09	1.03E-08	-	-	-	3
	64	5.73E-11	1.52E-10	1.14E-09	3.17	3.00	3.17	
	128	6.78E-12	1.93E-11	1.35E-10	3.08	2.98	3.08	
	256	8.26E-13	2.43E-12	1.65E-11	3.04	2.99	3.04	
hp-DG ($\mathbb{P}_3$)	32	2.80E-11	3.56E-11	2.86E-10	-	-	-	4
	64	1.73E-12	2.21E-12	1.90E-11	4.02	4.01	3.91	
	128	1.04E-13	1.34E-13	1.19E-12	4.05	4.04	3.99	
	256	6.18E-15	8.15E-15	7.48E-14	4.07	4.04	4.00	
hp-DG ($\mathbb{P}_4$)	16	2.28E-10	4.26E-10	4.42E-09	-	-	-	5
	32	5.58E-12	1.28E-11	1.34E-10	5.35	5.05	5.04	
	64	1.64E-13	4.19E-13	4.32E-12	5.09	4.94	4.95	
	128	5.31E-15	1.37E-14	1.47E-13	4.95	4.93	4.88	
h-DG-TVD ($\mathbb{P}_1$)	32	1.69E-07	2.14E-07	1.29E-06	-	-	-	2
	64	4.00E-08	4.65E-08	3.89E-07	2.08	2.20	1.73	
	128	9.60E-09	1.04E-08	5.56E-08	2.06	2.16	2.81	
	256	2.39E-09	2.50E-09	1.51E-08	2.01	2.06	1.88	

The computed solution is compared to the analytical solution. Results using the p-CG, hp-DG with $p \in [1, 4]$ and h-DG-TVD for different mesh resolutions are shown in Fig. 1 and Table 3. The time step size was in this case chosen sufficiently small not to affect the accuracy of the simulations. From Table 1, we conclude that the experimental convergence rate is $p+1$ for the hp-DG method while the h-DG-TVD method is second-order accurate. This gives confidence that our numerical methods are correctly implemented, and that both the temporal and spatial discretizations are working as expected. From Fig. 1 it is clear that the p-CG method has the superior convergence rate on this problem, achieving spectral (exponential) convergence. In Fig. 2 we show the numerical solution at the final time $t_f = 2.5$ obtained using (a) hp-DG ($\mathbb{P}_1$), (b) hp-DG ($\mathbb{P}_2$), (c) h-DG-TVD and (d) p-CG using 30 DoF in the spatial discretization together with the analytical solution. The results shows that the injected concentration profile has evolved into a normally distributed peak shape as expected. The solution obtained using p-CG is sufficiently

resolved, the solution by hp-DG ($\mathbb{P}_2$) is slightly unresolved while the solutions obtained using both hp-DG ($\mathbb{P}_1$) and h-DG-TVD are unresolved on this grid.

Table 4: Simulation parameters for the non-linear case study (section 4.2).

Parameters	Symbol	Values	Unit
Column length	L	1	cm
Porosity	ϵ	0.4	-
Interstitial velocity	u	1	cm min ⁻¹
Constants used in Eq. (2)	$\mathbf{a}$	(0.5, 1) ^T	-
Constants used in Eq. (2)	$\mathbf{b}$	(0.05, 0.01) ^T	1 g ⁻¹
Feed concentrations	$\mathbf{c}_f$	(10, 10) ^T	g l ⁻¹

4.2. Case 2: Two-component nonlinear chromatography

For non-linear models, no analytical solutions are available. Therefore, we rely on numerical techniques to obtain solutions. On the basis of the obtained accurate results in the previous linear case, we expect that

Figure 2: Simulation of the linear case. The solid black line is the exact solution and the blue squares are nodal values of the numerical approximations.

the proposed methods could produce accurate results for non-linear models as well. We consider a non-linear problem studied by Shipilova et al. (2008) where two components compete for available slots on the stationary phase according to the multicomponent Langmuir isotherm given by Eq. (2). The detailed simulation parameters are given in Table 4. A rectangular pulse of the two-component liquid mixture is injected at the column inlet for 1.2 min. In the following, we simulate the problem in a column of modest and high efficiency, respectively.

4.2.1. Column of modest efficiency

The problem is simulated using a low number of apparent theoretical plates of $N_a = 500$ to test the per-

formance of the numerical methods under typical liquid chromatography conditions. Fig. 3 shows the simulation results obtained using p-CG, hp-DG ($\mathbb{P}_3$) and h-DG-TVD using two different mesh resolutions. The numerical results obtained with p-CG included no stabilization. A highly resolved reference solution was obtained using a 9th-order hp-DG method with 100 elements (1000 DoF).

The simulation results are shown in Fig. 3 and are compared with the highly resolved reference solution (black line). Despite the low number of apparent theoretical plates, the reference solution includes rather steep concentration fronts. Since we are integrating the solution with high-precision in the spatial discretization due to the use of high-order methods the solution is fully

resolved leading to steep concentration fronts, even for low plate numbers. It might seem surprising that the elution profile of the first component 'shoots over' the injected concentration of 10 g/L. This phenomena is however well-known in non-linear liquid chromatographic processes and is a consequence of displacement effects. This provides evidence that our codes are working as expected.

In Fig. 3(b) we observe that the solution by the p-CG method has converged towards the reference solution using just 62 DoF in the spatial discretization (there is no visual difference between the simulated and reference solution). When using the p-CG method on an insufficiently resolved grid with 22 DoFs, the solution oscillates (see Fig. 3(a)). These oscillations do not indicate that the method is unstable, and they are removed simply by adding more resolution. In the following, we compare the convergence properties of the hp-DG and the h-DG-TVD methods with the p-CG method by visual inspection. Both methods are applied on the same problem using 62 DoF in the spatial discretization which resulted in a sufficiently resolved solution when the p-CG method was applied. The results of the simulations are shown in Fig. 3(d) and (f) using the hp-DG ($\mathbb{P}_3$) method and the h-DG-TVD method, respectively. By visual inspection, the hp-DG ($\mathbb{P}_3$) method provides an oscillatory solution while the solution by the h-DG-TVD method is artificially dispersed. Hence, in order to obtain accurate solutions, both methods must be applied with a larger amount of DoF in the spatial discretization compared to when the p-CG method was used. This indicates, that the p-CG method has the superior convergence properties on this problem (since it converges using the fewest DoFs). Fig. 3(c) and (d) shows, that the hp-DG method provides oscillatory solutions when applied with an insufficient resolution. Again, this does not indicate that the method is unstable, merely that an insufficient resolution was applied. The oscillations are removed simply by adding enough resolution. The only method that does not oscillate on an under-resolved grid is the h-DG-TVD method (see Fig. 3(e) and (f)). However, it comes at the high cost of reducing the accuracy to first order in some parts of the solution such that many DoFs are required to obtain fully resolved solutions. Since the hp-DG method is already stable for the simple linear fluxes used to model liquid chromatography applications without applying any stabilization, the use of a limiter to enforce additional (unnecessary) stabilization seems to only worsen the convergence properties of the hp-DG method. Therefore, we do not recommend solving non-linear liquid chromatography models under liquid chromatography conditions using shock-

Table 5: Computational cost for a fixed accuracy measured by the L^1 error (min g l^{-1}) for the non-linear case (Table 4) using $N_a = 500$ apparent theoretical plates.

Scheme	L_T^1 error	Δt (min)	DoFs	CPU (s)	CPU _{ratio}
p-CG ($\mathbb{P}_{61}$)	1.08E-02	1.6E-03	62	3.9	1
hp-DG ($\mathbb{P}_8$)	1.10E-02	1.6E-03	108	5.8	1.5
hp-DG ($\mathbb{P}_3$)	1.10E-02	1.6E-03	148	6.3	1.6
hp-DG ($\mathbb{P}_2$)	1.11E-02	1.6E-03	195	7.2	1.9
hp-DG ($\mathbb{P}_1$)	1.07E-02	1.6E-03	500	24.4	6.2
h-DG-TVD ($\mathbb{P}_1$)	1.12E-02	3.0E-04	1000	414.0	67.9

capturing methods. Instead, we suggest (based on the presented results) to consider arbitrary high-order methods.

Having investigated the convergence properties of the methods, we now study the the amount of work required to achieve a given level of accuracy. To this purpose, we compare the simulation results with the highly resolved reference solution and measure the L^1 errors over the temporal domain at the outlet of the column by

$$L_T^1\text{-error} = \int_T |\mathbf{E}| dt \quad (69)$$

where $T \in [0, t_f]$ is the temporal domain and $\mathbf{E} = (e_1, \dots, e_{N_c})^T$ are nodal errors between the simulated and the reference solution. The integral in Eq. (69) is evaluated using the trapezoidal method. We evaluate the performance of the three methods based on how much work is required in terms of CPU time to achieve an L_T^1 -error of at least $0.01 \text{ min} \times \text{g/l}$ (at this point we cannot tell the difference between the simulated and the reference solutions by visual inspection). In Table 5 we present the simulation results, showing that the p-CG method is the most efficient method for this problem in terms of both CPU time and discrete problem size. The hp-DG method becomes more efficient when using polynomials of higher order, although the effect seems to become less obvious after using more than third-order polynomials. The h-DG-TVD method is inefficient on this problem compared to the other methods. The limiter is activated whenever an oscillation is detected, reducing the accuracy to first-order in this element. Therefore, it requires two times more DoFs compared to the second-order accurate hp-DG ($\mathbb{P}_1$) method. Further, its stable time step size was more restrictive due to the use of many DoFs.

4.2.2. Column of high efficiency

We now study the simulation of the problem in a very efficient column with $N_a = 3000$ apparent theoretical plates to test the robustness of the numerical methods when dispersion is practically absent leading to strong

Figure 3: Simulation of the two component nonlinear case ($N_a = 500$). The solid black line is the fully resolved reference solution. The red and blue lines are numerical approximations for component one and two, respectively.

shock waves. In Fig. 4 we show the results of the simulations obtained using the p-CG, the hp-DG and the h-DG-TVD methods on two grids of different resolution. In this case, we applied a mild filter to stabilize the p-

CG method, e.g. we apply an 8th order ($s = 8$) filter to 10% of the highest modes in the basis. That is, if we use a 100th-order polynomial, then we apply the modal filter with $i_c = 90$. We applied the hp-DG method with no

Figure 4: Simulation of the two component nonlinear case ($N_a = 3000$). The solid black line is the fully resolved reference solution. The red and blue lines are numerical approximations for component one and two, respectively.

stabilization, since the numerical upwind fluxes already provide enough dissipation of high-frequency modes to prevent instabilities. A fully resolved reference solution was obtained using a 9th-order hp-DG method with 300

elements (3000 DoF) for comparison with our simulations. In Fig 4 the reference solution is depicted with a solid black line. We note that the problem is challenging to solve for a numerical method due to the presence

of strong shock-waves. In our simulations, we obtained shock-waves already after applying a column with just $N_a = 3000$ apparent plates. We therefore have no reason to increase it further. The steepness of the concentration fronts can be compared with those reported by Shipilova et al. (2008); Javeed et al. (2013) where $N_a = 5000$ apparent plates was used.

Comparing Fig. 4(b), (d) and (f), we see that it is again the p-CG method which has the superior convergence properties, even in the presence of strong shock waves. In Fig. 4(a), (c) and (d) we demonstrate that both the p-CG and the hp-DG methods are oscillating on under-resolved grids, although both methods are stable. The oscillations are localized near the shock-waves while in smooth regions the solution is accurate. In Fig. 4(e) and (f) we demonstrate that the h-DG-TVD method is capable of providing non-oscillatory solutions on under-resolved grids.

Albeit the convergence properties of the p-CG method is impressive, the decisive criterion for choosing between different numerical strategies is the cost required to obtain accurate solutions. We simulate the problem using the three methods until an L_T^1 error of 0.05 has been achieved (at this point the solution has converged by visual inspection). In Table 6 we show the simulation results, demonstrating that the p-CG method is faster compared to the hp-DG method using first and second order polynomials. When using the hp-DG method with third order polynomials the cost is similar. However, when using the hp-DG method with more than third-order polynomials, it becomes slightly faster. While the hp-DG method using $p > 3$ is faster, the p-CG method still has the superior convergence properties resulting in a smaller discrete problem size. A small discrete problem size is essential when considering e.g. dynamic optimization applications or state-estimation algorithms. Holmqvist and Magnusson (2016) found for the solution of open-loop optimal control problems that a finite volume scheme with a WENO limiter was computationally advantageous over other finite volume discretizations using TVD limiters, although the finite volume WENO scheme required several times more CPU time. However, the WENO scheme required less finite volume elements to spatially resolve smooth parts of the solution, which significantly reduced the size of the considered dynamic optimization problem. Thus, although the hp-DG method is faster, the p-CG method is to prefer for such applications. The p-CG method is about 10 times faster compared to the h-DG-TVD method, even for problems including strong shock-waves. Hence, we suggest to use arbitrary high-order methods for cost-efficient simula-

Table 6: Computational cost for a fixed accuracy measured by the L^1 error (min g l^{-1}) for the non-linear case (Table 4) using $N_a = 3000$ apparent theoretical plates.

Scheme	L^1 error	Δt (min)	DoFs	CPU (s)	CPU _{ratio}
p-CG ($\mathbb{P}_{210}$)	50.82E-03	1.0E-04	211	134.0	1.00
hp-DG ($\mathbb{P}_8$)	51.42E-03	1.0E-04	279	119.6	0.89
hp-DG ($\mathbb{P}_3$)	50.48E-03	1.0E-04	308	130.0	0.97
hp-DG ($\mathbb{P}_2$)	50.35E-03	1.0E-04	348	166.4	1.24
hp-DG ($\mathbb{P}_1$)	50.53E-03	1.0E-04	520	254.0	1.90
h-DG-TVD ($\mathbb{P}_1$)	50.74E-03	1.0E-04	1040	1297.0	9.7

tion of highly convection-dominated non-linear liquid chromatography processes instead of the second-order shock-capturing methods often used.

5. Conclusions

In this paper, we have compared several state-of-the-art methods for simulation of linear and non-linear liquid chromatographic processes using columns of both low and high efficiency. The computational efficiency of the methods is determined with reference to a fully converged simulation of high spatial resolution for non-linear processes. For linear processes, an analytical solution is available on which we analysed experimental convergence rates. We observed that a considerable saving in computational cost can be achieved by employing stable high-order methods compared to the second order (low-order) shock-capturing methods which are often used by default for simulation of liquid chromatography models. Furthermore, we have for the first time demonstrated, that the use of the continuous Galerkin spectral methods in combination with state-of-the-art spectral filtering techniques are highly suitable for efficient and accurate simulation of liquid chromatographic models.

The stable high-order methods presented here have been shown to oscillate on unresolved grids. While this is of less concern when considering Langmuir-type isotherms, it may become problematic for isotherms considering multipoint binding, e.g. the steric-mass-action isotherm (Brooks and Cramer (1992)) used to model ion-exchange chromatography. Here, numerical under/overshoots can lead to ill-posed solutions leading to a shut-down of the computer program. Therefore, the presented high-order methods should be used on sufficiently resolved grids to obtain non-oscillatory solutions when considering isotherms that support multipoint binding. On the other hand, the total variation diminishing discontinuous Galerkin method will suppress the numerical oscillations, even on unresolved grids, at the cost of producing an overly dispersed solution.

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