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- The solution of the equilibrium-dispersive model of chromatography is studied.
- The high-order nodal discontinuous Galerkin (DG) method is applied.
- Arbitrary high-order accuracy in space is demonstrated.
- The potential for accuracy and speedup gains are shown.

Accepted Manuscript

1 High-Order Approximation of Chromatographic Models 2 using a Nodal Discontinuous Galerkin Approach

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Abstract

3 A nodal high-order discontinuous Galerkin finite element (DG-FE) method
4 is presented to solve the equilibrium-dispersive model of chromatography
5 with arbitrary high-order accuracy in space. The method can be considered
6 a high-order extension to the total variation diminishing (TVD) framework
7 used by Javeed et al. [J. Chromatogr. A 1218 (40) (2011) 7137; Chem.
8 Eng. Sci. 90 (2013) 17] with an efficient quadrature-free implementation.
9 The framework is used to simulate linear and non-linear multicomponent
10 chromatographic systems. The results confirm arbitrary high-order accu-
11 racy and demonstrate the potential for accuracy and speed-up gains ob-
12 tainable by switching from low-order methods to high-order methods. The
13 results reproduce an analytical solution and are in excellent agreement with
14 numerical reference solutions already published in the literature.

Keywords: High-order; Discontinuous Galerkin finite element method;
Liquid chromatography; Equilibrium-Dispersive Model; Linear and
nonlinear isotherm

15 1. Introduction

16 Column liquid chromatography is among the most widely applied unit
 17 operations for downstream processing in the biopharmaceutical industry [1]
 18 with a global market predicted to be at \$167 billion by 2015 [2]. Manu-
 19 facturing costs of biopharmaceuticals remain high and it is estimated that
 20 50-80 % of them are due to downstream processing [3]. The potential that
 21 mathematical modelling can have on this industry is enormous. It has the
 22 potential to facilitate rapid, cost-effective process development for speed-
 23 to-market and near-optimal operation using on-line monitoring strategies in
 24 combination with process analytical technology (PAT) to control production
 25 costs.

26 Mathematical modelling is a well established tool for prediction of chro-
 27 matographic operation [4]. Traditional numerical methods used to discretize
 28 the spatial domain of chromatographic models include finite differences (FD)
 29 or orthogonal collocation on finite elements (OCFE) schemes [5]. Special fi-
 30 nite difference methods such as the Rouchon FD scheme [6] and the Martin-
 31 Synge method [7] have been developed to solve the equilibrium-dispersive
 32 model of chromatography [4]. Here axial dispersion is neglected and in-
 33 stead approximated by fixing the grid such that the numerical dispersion
 34 approaches the physical dispersion in the column. The Rouchon FD scheme
 35 does not work for all operating conditions and correctness can therefore not
 36 be guaranteed [8] while the Martin-Synge method has been shown to be
 37 robust. The OCFE scheme was introduced into chromatographic literature
 38 by Ma et al. [9] and later refined versions were presented by Kaczmarzski
 39 et al. [10, 11]. In chromatographic literature the OCFE scheme has been
 40 considered one of the most accurate and robust methods for solution of

41 chromatographic models for a long time [12]. However, for certain cases
 42 the OCFE method fails because it is non-conservative [7], and is in general
 43 expensive since the solution of a large linear system is required.

44 High order methods that aim to obtain a desired resolution using the
 45 smallest number of degrees of freedom (DOFs) possible have been developed
 46 during the last decades. The introduction of such methods in the field of
 47 chromatography is important since they have the potential to significantly
 48 reduce the required computational effort when solving large-scale [13, 14],
 49 dynamic [15] or large parameter estimation [16, 17] optimization problems
 50 which are gaining increasing practical importance due to the allowance of
 51 fast and cheap process development.

52 Recently, the efficiency of several high-order methods within the total
 53 variation diminishing (TVD) framework have been investigated for approx-
 54 imation of chromatographic systems. These methods achieve high-order ac-
 55 curacy in smooth regions while maintaining stable and non-oscillatory solu-
 56 tions near discontinuities. Javeed et al. [18] (and Medi et al. [19]) compared
 57 high-order accurate finite volume (FV) schemes using different Sweby-type
 58 flux limiters [20] available in the literature and concluded that a scheme de-
 59 veloped by Koren [21] was superior. von Lieres et al. [22] implemented the
 60 high-order accurate weighted essentially non-oscillatory (WENO) [23, 24]
 61 FV scheme (based on the essentially non-oscillatory (ENO) [25, 26] scheme)
 62 for approximation of the general rate model of chromatography [4] and
 63 solved a challenging multicomponent problem in just a few seconds. A
 64 discontinuous Galerkin finite element (DG-FE) scheme popular in compu-
 65 tational fluid dynamics (see review in [27]) was introduced into chromato-
 66 graphic literature by Javeed et al. [28, 29]. Here, the classical TVD frame-
 67 work of Cockburn et al. [30] was considered in which modal expansion

coefficients are used as DOFs and a finite grid is introduced by approximating these using high-order Gaussian quadrature rules. The scheme was compared to the Koren [21] FV scheme and the DG-FE scheme was concluded to be superior in both linear and non-linear chromatography. Other shock-capturing frameworks used for simulation of chromatographic systems include a particle transport method (PTM) by Shipilova et al. [31] and a space-time conservation element and solution element (CE/SE) method by Lim et al. [32].

For problems including discontinuities, high-order methods produce persistent and artificial oscillations known as the Gibbs phenomenon [33, 34] near the discontinuities. In order to resolve this phenomenon, the TVD property can be enforced to obtain high-order accuracy. The simplest model offered by chromatographic theory is the ideal model [4] which predicts the formation of a concentration shock, e.g. a discontinuity, on either side of an elution band, depending on the curvature of the isotherm considered. However, when using a real column, true concentration shocks cannot form and very steep band fronts/rears occur instead [35], known as shock layers. Hence, for real-world applications, the use of arbitrary high-order methods can be used for cost-efficient simulations instead of the above mentioned shock-capturing frameworks designed with a specific order of accuracy, often second (low) order. Therefore, we explore, for the first time, potential benefits of using a nodal high-order DG-FE framework proposed by Hesthaven and Warburton [36, 37] for solution of the parabolic and convection-dominated multicomponent equilibrium-dispersive model of chromatography. This framework is related to the classical one but is a more general formulation where the classical DG-FE method is a special case. Here, solution values at quadrature points are used directly as DOFs instead of expansion coefficients by

95 expressing the solution in terms of the Lagrange interpolating polynomials.
 96 The duality between the nodal and modal forms are exploited to obtain an
 97 implementation free of quadrature approximations and boundary conditions
 98 are enforced weakly through numerical fluxes. The framework offers geomet-
 99 ric flexibility and naturally extends to simulation of 2D and 3D problems
 100 with complex geometries. In chromatography, that is an important feature
 101 when modelling miniaturized chromatography columns where non-ideal flow
 102 behaviour is encountered [38]. A detailed implementation procedure is given
 103 that allows the introduction of arbitrary high order nodal basis functions in
 104 the approximation space leading to high-order accurate schemes. Therefore,
 105 the presented framework may be considered as a high-order extension of the
 106 method proposed by Javeed et al. [28, 29] with an improved implementation
 107 procedure. Although this implementation is efficient, it comes at the cost
 108 of potentially introducing aliasing errors since polynomial interpolations are
 109 considered instead of aliasing-free projections. For some problems, this may
 110 require de-aliasing techniques for stabilization. It is well known that the use
 111 of high-order methods may give large efficiency gains for time-dependent
 112 wave problems [39], although it may reduce the robustness of explicit time
 113 stepping methods due to a restrictive stable time step. To overcome this
 114 issue, mapping techniques have been developed [40]. Furthermore, the high-
 115 order framework automatically controls spurious solutions through selective
 116 dissipation of non-physical solutions, see e.g. [41]. The high-order accu-
 117 rate framework is validated and its performance is evaluated in numerical
 118 experiments. Here, we show how h - and p -type refinement strategies, e.g.
 119 increasing the number of elements at a fixed order or increasing the order
 120 at a fixed number of elements, respectively, can be used for cost-efficient
 121 simulation of problems with finite dispersion, e.g. smooth problems. In this

paper we are mainly concerned with the spatial discretization and use a non-linearly stable explicit strong stability preserving Runge-Kutta method to discretize the temporal domain.

What remains of the paper is organized as follows. In section two, the equilibrium-dispersive model of chromatography is summarized together with a linear isotherm and a competitive Langmuir isotherm. In section three the nodal DG-FE scheme is derived. In section four the scheme is verified for cases of linear and non-linear chromatography. Finally, concluding remarks are collected in section five.

2. Equilibrium-Dispersive Model of Chromatography

In the formulation of the Equilibrium-Dispersive model of chromatography [4], it is assumed that; (i) the stationary and mobile phases are at all positions in equilibrium, (ii) the column is one-dimensional, i.e. no radial concentration gradients, (iii) only axial dispersion causes band broadening, (iv) the chromatographic separation is isothermal and adiabatic, and (v) the compressibility of the mobile phase is negligible leading to a flat velocity profile. In this work, the axial dispersion coefficient is assumed equal for all components. Under these assumptions, the mass balance in the bulk mobile phase of the i 'th component is, complemented with Danckwerts boundary conditions [42], described by

$$\frac{\partial c_i}{\partial t} + v \frac{\partial c_i}{\partial z} + F \frac{\partial q_i}{\partial t} = D \frac{\partial^2 c_i}{\partial z^2} \quad \text{in } \Omega \times T, \quad (1a)$$

$$c_i = c_{i,0} \quad \text{on } \Omega \times 0, \quad (1b)$$

$$vc_i - D \frac{\partial c_i}{\partial z} = vc_{i,\text{in}} \quad \text{on } 0 \times T, \quad (1c)$$

$$\frac{\partial c_i}{\partial z} = 0 \quad \text{on } L \times T, \quad (1d)$$

for all $i = 1, \dots, N_c$ with N_c the number of components injected at the inlet of the column. Here, c_i and q_i are the mobile and stationary phase concentrations of each component, respectively, $c_{i,0}$ is the initial concentration in the column, $c_{i,\text{in}}$ is the inlet concentration, v is the interstitial velocity of the fluid, D is the axial dispersion coefficient, $F = (1 - \epsilon_c)/\epsilon_c$ is the phase ratio, ϵ_c is the column porosity, $\Omega \in [0, L]$ is the spatial domain, L is the length of the column, $T \in [0, T_f]$ is the temporal domain and T_f is the final simulation time. In this work, rectangular injection profiles are considered, i.e.,

$$c_{i,\text{in}}(t) = \begin{cases} c_{i,f}, & 0 \leq t \leq t_{\text{inj}} \\ 0, & t > t_{\text{inj}} \end{cases} \quad (2)$$

where $c_{i,f}$ is the inlet feed concentration and t_{inj} is the injection time. For efficient columns, Guiochon et al. [4] relates the dispersion coefficient to the number of theoretical plates N_t by

$$D = \frac{Lv}{2N_t} \quad (3)$$

The column adsorption equilibria between bound q_i and unbound c_i states are described by a competitive nonlinear Langmuir isotherm. The model is derived by Guiochon et al. [4] and is for the i 'th component given by

$$q_i = \frac{a_i c_i}{1 + \sum_{s=1}^{N_c} b_s c_s} \quad \forall i = 1, \dots, N_c \quad (4)$$

where b_s is the ratio of the rate constants of adsorption and desorption and the ratio a_i/b_i is the column saturation capacity. For dilute systems Eq. (4) simplifies to a linear isotherm:

$$q_i = a_i c_i \quad \forall i = 1, \dots, N_c \quad (5)$$

160 3. Numerical Methods

161 In this section a method-of-lines approach is considered in which the
 162 spatial and temporal discretizations are considered separately. The DG-FE
 163 method is used for the spatial discretization, and the resulting semi-discrete
 164 equation system is advanced in time from appropriate initial conditions using
 165 a non-linearly stable third order strong stability preserving explicit Runge
 166 Kutta method.

167 In the following we suppress the component index i for simplicity. Fol-
 168 lowing the approach of Bassi and Rebay [43] Eq. (1a) is rewritten as a first
 169 order system by

$$\frac{\partial}{\partial t} (c + Fq(c)) = -\frac{\partial}{\partial z} (vc - \sqrt{D}g(c)) \quad (6a)$$

$$g(c) = \sqrt{D} \frac{\partial c}{\partial z} \quad (6b)$$

170 We define the functions

$$h(c, g(c)) := vc - \sqrt{D}g(c) \quad \text{and} \quad w(c) := c + Fq(c) \quad (6c)$$

171 and introduce these into Eq. (6a) to give

$$\frac{\partial w(c)}{\partial t} = -\frac{\partial h(c, g(c))}{\partial z} \quad (6d)$$

172 The method-of-lines approach is performed on Eq. (6b) and (6d) in the
 173 following.

174 3.1. General formulation of the Discontinuous Galerkin method

175 The spatial domain Ω is discretized by N_e non-overlapping elements,
 176 $0 = z_{\frac{1}{2}} < z_{\frac{3}{2}} < \dots < z_{N_e - \frac{1}{2}} < z_{N_e + \frac{1}{2}} = L$ where the k 'th element is

177 $\Omega_k = (z_{k-\frac{1}{2}}, z_{k+\frac{1}{2}})$ with center $z_k = \frac{1}{2}(z_{k-\frac{1}{2}} + z_{k+\frac{1}{2}})$, $\forall k = 1, \dots, N_e$. We
 178 consider a uniform element size $\Delta z = z_{k+\frac{1}{2}} - z_{k-\frac{1}{2}}$ for simplicity.

179 On the k 'th element, the exact solution $\mathbf{Q} = [w, g]^T$ is approximated by
 180 a numerical solution $\mathbf{Q}^k = [w^k, g^k]^T$ which we assume is a finite-dimensional
 181 interpolation of the form

$$\mathbf{Q}^k(t, z) = \sum_{n=1}^{N_p} \hat{\mathbf{Q}}_n^k(t) \phi_n(z) = \sum_{n=1}^{N_p} \mathbf{Q}^k(t, z_n) l_n(z) = \sum_{n=1}^{N_p} \mathbf{Q}_n^k(t) l_n(z) \quad (7)$$

182 where we have N_p DOFs inside each element in terms of unknown modal
 183 expansion coefficients $\hat{\mathbf{Q}}_n^k = [\hat{w}_n^k, \hat{g}_n^k]^T$ or nodal coefficients $\mathbf{Q}_n^k = [w_n^k, g_n^k]^T$
 184 since we restrict g^k to be local. The Lagrange interpolating polynomials
 185 l_i has the property $l_i(z_j) = \delta_{ij}$ (δ_{ij} is a Kronecker delta) at mesh nodes
 186 and are defined on the set of nodes used in combination with the chosen
 187 orthogonal basis. The basis functions $\phi_n(z)$, $n = 1, \dots, N_p$ are chosen such
 188 that for each time $t \in [0, T]$, both c^k and g^k belongs to the finite dimensional
 189 approximation space

$$\mathbb{V}^N = \{v : v_k \in \mathbb{P}^N(\Omega_k), \forall \Omega_k \in \Omega\} \quad (8)$$

190 where $\mathbb{P}^N(\Omega_k)$ are polynomials of degree at most $N = N_p - 1$ in each element.

191 Following the DG-FE procedure, Eq. (6d) and (6b) is for each element
 192 multiplied by a test function, which is assumed to be the same as the ba-
 193 sis functions (the Galerkin method), and integrated over each element Ω_k .
 194 Two integrations by parts are carried out for the right-hand side terms of
 195 Eq. (6d) and (6b). Since each element is disconnected from the remain-
 196 ing elements, $\mathbf{Q}^k$ is discontinuous in each of its components. Therefore, we
 197 must in the intermediate step of these partial integrations replace the func-
 198 tions c^k and $h(c^k, g^k)$ by continuous numerical flux functions $c^*(c^-, c^+)$ and

199 $h^*(c^-, c^+, g^-, g^+)$, respectively, to connect adjacent elements. Here, nega-
 200 tive and positive superscripts refer to interior and exterior information at
 201 element boundaries, respectively. The numerical flux c^* has been restricted
 202 to depend on c^+ and c^- only, to allow for a local resolution of g^k . Suitable
 203 consistent numerical flux functions are chosen later. This leads to the fol-
 204 lowing strong DG-FE formulation of Eq. (6d) and (6b) for the k 'th element:

$$\int_{\Omega_k} \frac{\partial w^k}{\partial t} l_j^k dz = - \int_{\Omega_k} \frac{\partial h^k}{\partial z} l_j^k dz + \oint_{\partial\Omega_k} \hat{\mathbf{n}} (h^k - h^*) l_j^k dz \quad (9a)$$

$$\int_{\Omega_k} g^k l_j^k dz = \sqrt{D} \int_{\Omega_k} \frac{\partial c^k}{\partial z} l_j^k dz - \sqrt{D} \oint_{\partial\Omega_k} \hat{\mathbf{n}} (c^k - c^*) l_j^k dz \quad (9b)$$

205 for all the test functions $l_j^k \in \mathbb{V}_k^N$. Here, $\hat{\mathbf{n}}$ is the outward pointing unit
 206 normal and $\partial\Omega_k$ are the edges of the element. Note that the classical DG-
 207 FE method [30] is recovered from the strong form by a simple integration
 208 by parts.

209 3.2. Discontinuous Galerkin Operators

210 The following orthonormal polynomial basis functions are chosen,

$$\phi_n(r) = P_{n-1}(r)/\sqrt{2/(2n+1)} = \tilde{P}_{n-1}(r), \quad r \in I = [-1, 1] \quad (10)$$

211 where $P_{n-1}(r)$ are the classical Legendre polynomials defined on the refer-
 212 ence element I . We define the vectors of nodal values on I as

$$\mathbf{w}^k = [w^k(r_1), \dots, w^k(r_{N_p})]^T, \quad \mathbf{g}^k = [g^k(r_1), \dots, g^k(r_{N_p})]^T \quad (11)$$

213 the vectors of modal values on I as

$$\hat{\mathbf{w}}^k = [\hat{w}_1^k, \dots, \hat{w}_{N_p}^k]^T, \quad \hat{\mathbf{g}}^k = [\hat{g}_1^k, \dots, \hat{g}_{N_p}^k]^T \quad (12)$$

214 and the vectors of local Lagrange interpolating polynomials and basis func-
 215 tions on I by

$$\mathbf{l} = [l_1(r), \dots, l_{N_p}(r)]^T, \quad \tilde{\mathbf{P}} = [\tilde{P}_0(r), \dots, \tilde{P}_N(r)]^T \quad (13)$$

216 The generalized Vandermonde matrix is defined on I as

$$\mathcal{V}_{nj} = \tilde{P}_{j-1}(r_n) \quad (14)$$

217 Hesthaven and Warburton [36] showed, that by uniqueness of polynomial in-
218 terpolation, the following relationships between modal and nodal coefficients
219 and basis functions exists,

$$\mathbf{w}^k = \mathcal{V}\hat{\mathbf{w}}^k, \quad \mathbf{g}^k = \mathcal{V}\hat{\mathbf{g}}^k, \quad \tilde{\mathbf{P}} = \mathcal{V}^T \mathbf{l} \quad (15a)$$

220 where the nodes r_n are chosen as the Legendre-Gauss-Lobatto quadrature
221 points to ensure a well-conditioned Vandermonde matrix. We introduce the
222 mass, stiffness, differentiation and lifting matrices defined on I in Eq. (16a),
223 (16b), (16c) and (16d), respectively.

$$\mathcal{M}_{nj} = \int_{-1}^1 l_n(r) l_j(r) dr \quad (16a)$$

$$\mathcal{S}_{nj} = \int_{-1}^1 l_n(r) \frac{dl_j}{dr}(r) dr \quad (16b)$$

$$\mathcal{D} = \mathcal{M}^{-1} \mathcal{S} \quad (16c)$$

$$\mathcal{L} = \mathcal{M}^{-1} \mathcal{E} \quad (16d)$$

$$\mathcal{E}_{n1} = l_n(-1), \quad \mathcal{E}_{n2} = l_n(1) \quad (16e)$$

224 The lifting matrix is an operator that combines the effect of applying the
225 inverse mass matrix at both the left and right edge of the element. It 'lifts'
226 facial contributions to volume contributions, therefore it is called the lifting
227 matrix. Equation (15) establishes the following relationships to determine
228 both the mass and stiffness matrices exactly for a standard element without
229 using high-order Gaussian quadrature rules for the element integrals leaving
230 the implementation quadrature-free,

$$\mathcal{M} = (\mathcal{V}\mathcal{V}^T)^{-1}, \quad \mathcal{S} = \mathcal{M}\mathcal{D} \quad (17)$$

231 The differentiation matrix $\mathcal{D}$ is computed by

$$\mathcal{D}_r = \mathcal{V}_r \mathcal{V}^{-1} \quad (18)$$

232 where $\mathcal{V}_{r,(i,j)} = d\tilde{P}_j/dr|_{r_i}$.

233 To rewrite Eq. (9) in compact form the continuous variables are replaced
234 by the finite polynomial approximations given by Eq. (7) and the above
235 defined (constant) local element matrices are used to give

$$\frac{\partial \mathbf{w}^k}{\partial t} = -\frac{2}{\Delta z} \mathcal{D} \mathbf{h}^k + \frac{2}{\Delta z} \mathcal{L} \left(\hat{\mathbf{n}} \begin{bmatrix} (h^k - h^*)|_{z_{k-\frac{1}{2}}} \\ (h^k - h^*)|_{z_{k+\frac{1}{2}}} \end{bmatrix} \right) \quad (19a)$$

$$\mathbf{g}^k = \frac{2}{\Delta z} \sqrt{D} \mathcal{D} \mathbf{c}^k - \frac{2}{\Delta z} \sqrt{D} \mathcal{L} \left(\hat{\mathbf{n}} \begin{bmatrix} (c^k - c^*)|_{z_{k-\frac{1}{2}}} \\ (c^k - c^*)|_{z_{k+\frac{1}{2}}} \end{bmatrix} \right) \quad (19b)$$

236 where $\mathbf{w}^k$, $\mathbf{h}^k$, $\mathbf{c}^k$ and $\mathbf{g}^k$ are vectors containing N_p nodal coefficients defined
237 on Ω_k . The factor $2/\Delta z$ is the inverse Jacobian of the affine transformation
238 $z = r_{k+1/2} + 0.5(1+r)\Delta z$ used to map the reference element to the physical
239 element. Equation (19) gives the derivative of $\mathbf{w}$ with respect to time for
240 each component. The individual component contributions are arranged in
241 a vector $\partial \mathbf{w}_i^k / \partial t = [\partial \mathbf{w}_1^k / \partial t, \dots, \partial \mathbf{w}_{N_c}^k / \partial t]$. To get the derivative of $\mathbf{c}$ with
242 respect to time, chain rule algebra is used on the second definition in Eq.
243 (6c) to get

$$\frac{\partial \mathbf{c}_i^k}{\partial t} = \left(\mathcal{I} + F \frac{\partial \mathbf{q}_i^k}{\partial \mathbf{c}_i^k} \right)^{-1} \frac{\partial \mathbf{w}_i^k}{\partial t} \quad (20)$$

244 where $\mathbf{c}_i^k = [\mathbf{c}_1^k, \dots, \mathbf{c}_{N_c}^k]^T$ is a vector of nodal coefficients for each com-
245 ponent, $\mathcal{I}$ is the identity matrix and $\partial \mathbf{q}_i^k / \partial \mathbf{c}_i^k$ is a non-singular Jacobian
246 matrix.

247 3.3. Numerical Fluxes

248 To complete the scheme suitable consistent numerical fluxes, i.e. $h^*(c, c) =$
 249 $h(c, g(c))$, must be specified. On the boundary at $z_{\frac{1}{2}} = 0$ a central flux is
 250 specified to ease implementation of the inlet Robin condition Eq. (1c), that
 251 is

$$h^*(c^-, c^+) = 0.5 (h(c^-) + h(c^+)) \quad (21)$$

252 With this choice, the surface term in Eq. (19a) becomes,

$$\mathbf{n} (h^k - h^*) \big|_{z_{\frac{1}{2}}} = 0.5 \mathbf{n} (h(c^-) - h(c^+)) \quad (22)$$

253 On the remaining element boundaries $z_{\frac{3}{2}}, \dots, z_{N_e + \frac{1}{2}}$ the numerical flux
 254 h^* is written as a sum of a convective and a diffusive flux. It is reasonable
 255 to consider these contributions separately due to the convective-diffusive
 256 nature of the problem under consideration. Thus,

$$h^* = h_{\text{conv}}^*(c^-, c^+) + h_{\text{diff}}^*(g^-, g^+) \quad (23)$$

257 The convective flux is chosen to reflect upwinding, which is reasonable con-
 258 sidering the flat velocity profile in the column, although any consistent nu-
 259 merical flux could be used, see e.g. [44] for an extended list. That is,

$$h_{\text{conv}}^*(c^-, c^+) = 0.5v (c^- + c^+ + \hat{\mathbf{n}}c^- + \hat{\mathbf{n}}c^+) \quad (24)$$

260 The diffusive flux h_{diff}^* is defined as central flux,

$$h_{\text{diff}}^*(c^-, c^+) = 0.5\sqrt{D} (g^- + g^+) \quad (25)$$

261 which is reasonable due its diffusive nature. Then the surface term in Eq.
 262 (19a) becomes,

$$\begin{aligned} \hat{\mathbf{n}} (h^k - h^*) \big|_{z_{\frac{3}{2}}, \dots, z_{N_e + \frac{1}{2}}} &= \hat{\mathbf{n}} (0.5v (c^- - c^+) - 0.5\sqrt{D} (g^- - g^+)) \\ &\quad + 0.5v (c^- - c^+) \end{aligned} \quad (26)$$

263 It remains to specify the numerical flux c^* . It is defined on all element
264 boundaries as a central flux,

$$c^*(c^-, c^+) = 0.5 (c^- + c^+) \quad (27)$$

265 leading to the following surface term of Eq. (19b):

$$\hat{n} (c^k - c^*) = \hat{n} (c^- - c^+) \quad (28)$$

266 3.4. Boundary Strategy

267 The boundary conditions are imposed weakly through the numerical
268 fluxes h^* and c^* by defining exterior ghost states (c^+, g^+) such that the
269 average of the numerical flux correspond to the value we seek to impose.
270 The Robin condition Eq. (1c) is implemented by defining the following
271 exterior ghost states at the inlet:

$$c^+|_{z_{\frac{1}{2}}^+} = c^-|_{z_{\frac{1}{2}}^-} \quad (29)$$

$$h^+|_{z_{\frac{1}{2}}^+} = -h^-|_{z_{\frac{1}{2}}^-} + 2vc_{\text{in}} \quad (30)$$

272 and the Homogeneous Neumann condition Eq. (1d) is implemented by defin-
273 ing

$$c^+|_{z_{N_e+\frac{1}{2}}^+} = c^-|_{z_{N_e+\frac{1}{2}}^-} \quad (31)$$

$$g^+|_{z_{N_e+\frac{1}{2}}^+} = -g^-|_{z_{N_e+\frac{1}{2}}^-} \quad (32)$$

274 at the outlet.

275 3.5. Temporal Discretization

276 The semidiscrete scheme Eq. (20) is discretized in the temporal domain
277 using a nonlinearly stable third order strong stability preserving explicit

278 Runge Kutta method [26] given by

$$\mathbf{v}^{(1)} = \mathbf{c}^m + \Delta t \mathcal{H}(\mathbf{c}^m) \quad (33)$$

$$\mathbf{v}^{(2)} = \mathbf{c}^m + \Delta t \left(\frac{1}{4} \mathcal{H}(\mathbf{c}^m) + \frac{1}{4} \mathcal{H}(\mathbf{v}^{(1)}) \right) \quad (34)$$

$$\mathbf{c}^{m+1} = \mathbf{c}^m + \Delta t \left(\frac{1}{6} \mathcal{H}(\mathbf{c}^m) + \frac{2}{3} \mathcal{H}(\mathbf{v}^{(2)}) + \frac{1}{6} \mathcal{H}(\mathbf{v}^{(1)}) \right) \quad (35)$$

279 where $\mathcal{H}(\cdot)$ represents the right hand side of the semi-discrete scheme Eq.
280 (20) and $\mathbf{c}^m \in \mathbb{R}^{N_c N_p \times N_e}$ is the state vector given at time step m .

281 3.6. Limiting

282 To obtain a scheme that is guaranteed to be uniformly bounded in the
283 cell averages $\bar{c}^k$ a limiting procedure is required. Consider the minmod
284 function given by

$$m(\omega_1, \omega_2, \omega_3) = \begin{cases} s \cdot \min_{1 \leq i \leq 3} |\omega_i|, & |s| = 1 \\ 0, & \text{otherwise} \end{cases} \quad (36)$$

285 where $s = 1/m \sum_{i=1}^m \text{sign}(\omega_i)$. Define the linear approximation $\tilde{c}^k$ to c^k as
286 the tangent

$$\tilde{c}^k = \bar{c}^k + (z|_{\Omega_k} - z_k) \frac{dc^k}{dz} \quad (37)$$

287 Then the slope limited solution using a MUSCL limiter [45, 46] is given by

$$\Pi^1 \tilde{c}^k = \bar{c}^k + (z|_{\Omega_k} - z_k) m \left(\frac{dc^k}{dz}, \frac{\bar{c}^{k+1} - \bar{c}^k}{\Delta z}, \frac{\bar{c}^k - \bar{c}^{k-1}}{\Delta z} \right) \quad (38)$$

288 and replaces c^k in all elements after each stage of the explicit time stepping.
289 Using the presented scheme with linear basis functions, e.g. $N_P = 2$, to-
290 gether with the MUSCL limiter is mathematically equivalent to the scheme
291 proposed by Javeed et al. [28, 29] except we may introduce additional alias-
292 ing errors due to polynomial interpolations. We use this scheme as a bench-
293 mark against the use of high-order basis functions for problems with a finite
294 dispersion coefficient.

295 3.7. Implementation

296 The method described has been implemented in Matlab code and was
 297 compiled on a Macbook Pro with a 2.7 GHz Intel Core i5 processor and 8
 298 GB RAM. The overall structure of the code is outlined in Algorithm 1. Since
 299 the element operators in Eq. (19) are constant both $\mathbf{g}$ and $\mathcal{H}(\mathbf{w})$ can be
 300 computed for all elements using dense matrix-matrix multiplications. The
 301 operations are additive and the computations decomposes naturally into
 302 different tasks giving rise to high parallel efficiency [47] useful for large-scale
 303 simulations. For the non-linear multicomponent Langmuir isotherm Eq. (4),
 304 the Jacobian $\partial \mathbf{q}_i / \partial \mathbf{c}_i$ is special for each element. Therefore, we loop over
 305 each element to compute $\mathcal{H}(\mathbf{c}^k)$ by a dense matrix-vector multiplication and
 306 append the elemental contributions afterwards to a complete state vector.
 307 For a linear isotherm Eq. (5) the Jacobian is constant, and the computation
 308 simplifies to a single dense matrix-matrix multiplication.

309 3.8. Generality

310 3.8.1. Isotherms

311 The code is easily modified to solve for any explicit isotherm, for exam-
 312 ple the Bi-Langmuir isotherm [4] or the Toth isotherm [4] for heterogeneous
 313 surfaces to mention a few, by changing the Jacobian matrix $\partial \mathbf{q}_i^k / \partial \mathbf{c}_i^k$ accord-
 314 ingly. It is also straight forward to use any kinetic isotherm, for example the
 315 kinetic Langmuir mobile phase modulator (MPM) isotherm [48], the kinetic
 316 steric mass action (SMA) isotherm [49] or kinetic variations of the isotherms
 317 given in Mollerup's thermodynamic framework [50]. Here, the use of chain
 318 rule algebra performed in Eq. (20) is avoided and instead the state vector
 319 is doubled since an expression for $\partial \mathbf{q}^k / \partial t$ is available on which the DG-FE

method is performed as well. To solve for implicit isotherms, a differential algebraic equation (DAE) solver is needed. Implicit isotherms include the equilibrium form of the SMA isotherm [49] and the isotherms given in Mollerup's thermodynamic framework [50]. Often the kinetic form of these isotherms is used instead of the equilibrium form, not to model a specific kinetic mechanism, but to simplify the numerical solution and as a result speed up the computations since the solution of a large non-linear system is avoided.

3.8.2. Numerical flux functions

In subsection 3.3 we describe the numerical flux functions used in this work. Here, we have exploited that the column velocity profile is flat and hence use an upwinding flux for the convective part of the numerical flux function h^* . In case the velocity profile is not flat, other numerical flux functions may be more suitable to mimic the physics of the system. Currently, the code supports the following numerical flux functions [44]:

(i) The Lax-Friedrichs flux

$$h^{*,LF}(\alpha, \beta) = \frac{f(\alpha) + f(\beta)}{2} + \frac{C}{2} \hat{n}(\alpha - \beta) \quad (39a)$$

$$C = \max_{\inf c(z) \leq \gamma \leq \sup c(z)} |df(\gamma)/du| \quad (39b)$$

(ii) The local Lax-Friedrichs flux,

$$h^{*,LLF}(\alpha, b) = \frac{f(\alpha) + f(\beta)}{2} + \frac{C}{2} \hat{n}(\alpha - \beta) \quad (40a)$$

$$C = \max_{\min(\alpha, \beta) \leq \gamma \leq \max(\alpha, \beta)} |df(\gamma)/du| \quad (40b)$$

337 (iii) The Roe flux with entropy fix,

$$h^{*,R}(\alpha, \beta) = \begin{cases} f(\alpha) & \text{if } df/dc \geq 0 \quad c \in [\min(\alpha, \beta), \max(\alpha, \beta)] \\ f(\beta) & \text{if } df/dc \leq 0 \quad c \in [\min(\alpha, \beta), \max(\alpha, \beta)] \\ h^{*,LLF}(\alpha, \beta) & \text{otherwise} \end{cases} \quad (41)$$

338 where $f(c)$ is the flux and df/dc is the flux jacobian. In this work, all of the
 339 numerical fluxes gave equivalent results compared to the upwinding flux for
 340 the investigated model. This is in agreement with the results of Javeed et
 341 al. [28].

Algorithm 1 The nodal discontinuous Galerkin method

Require: The local operators $\mathcal{D}$ and $\mathcal{L}$ based on the chosen 1D finite element grid and the initial state vector $\mathbf{c}^m \in \mathbb{R}^{N_c N_p \times N_e}$.

Ensure: $\mathbf{c}^m, \forall m$.

```

1: for all time steps do
2:   for each component do
3:     Compute  $\mathbf{g}^m \in \mathbb{R}^{N_p \times N_e}$  using Eq. (19b).
4:     Compute  $\mathcal{H}(\mathbf{w}^m) \in \mathbb{R}^{N_p \times N_e}$  using Eq. (19a).
5:   end for
6:   Assemble  $\mathcal{H}(\mathbf{w}_i^m) \in \mathbb{R}^{N_c N_p \times N_e}$ .
7:   for each element do
8:     Compute the Jacobian  $\partial \mathbf{q}_i^k / \partial \mathbf{c}_i^k \in \mathbb{R}^{N_c N_p \times N_c N_p}$ .
9:     Compute  $\mathcal{H}(\mathbf{c}_i^{k,m}) \in \mathbb{R}^{N_c N_p}$  using Eq. (20).
10:  end for
11:  Assemble the complete state matrix  $\mathcal{H}(\mathbf{c}^m) \in \mathbb{R}^{N_c N_p \times N_e}$ .
12:  Advance the solution in time to get  $\mathbf{c}^{m+1}$ .
13: end for
```

342 4. Numerical Test Study

343 In this section the nodal DG-FE scheme is validated and its performance
 344 is tested in two case studies. First, a linear case is presented to validate the
 345 scheme with an analytical solution. Here, the performance is evaluated using
 346 the L^1 -norm in space, and is computed exactly by

$$\int_{\Omega} e_a dz = \sum_{k=1}^{N_e} \int_{\Omega_k} e_a^k dz = \sum_{k=1}^{N_e} \sqrt{(\mathbf{e}_a^k)^T \frac{\Delta z}{2} \mathcal{M} \mathbf{e}_a^k} \quad (42)$$

347 where $e_a = (c_a - c)$ is the error with respect to the analytical solution c_a .
 348 Next, the method is validated for a multicomponent non-linear case adopted
 349 from the literature where the performance is evaluated using the L^1 -norm
 350 in time at the column outlet, approximated by

$$\int e_r dt \approx \sum_{i=1}^{N_c} \sum_m^{N_t} |e_r^m| \Delta t \quad (43)$$

351 where $e_r = c_r - c$ is the error with respect to a numerical reference solution
 352 c_r , Δt is the time step size and N_t is the total number of time steps. In
 353 all simulations a time step small enough for spatial errors to dominate was
 354 used.

355 4.1. Case Study 1: One Component Linear Chromatography

356 The purpose of this case study is to verify the DG-FE scheme by com-
 357 parison with an analytical solution. The analytical solution to the single-
 358 component model problem given by Eq. (1) with a linear isotherm Eq. (5)
 359 is derived among others by Qamar et al. [51]. Their simulation parameters
 360 (table 1) are adopted in the following. A rectangular pulse is injected at
 361 the inlet of the column with an injection time of 1 minute. The simulation
 362 is stopped after 2 minutes, where the injected concentration band remains

Figure 1: Analytical solution of a one component system with a linear isotherm.

Figure 2: Convergence test by h - and p -type refinement strategies of a one component system with a linear isotherm.

Table 1: Simulation parameters for the linear case study (section 4.1)

Parameters	Symbol	Values	Unit
Column length	L	1	cm
Porosity	ϵ	0.4	-
Interstitial velocity	v	1	cm/min
Theoretical plates	N_t	250	-
Henry's constant	a	1	-
Initial concentration	c_0	0	g/L
Feed concentration	c_f	1	g/L

inside the column, allowing us to evaluate the error using an exact L^1 -norm in the spatial domain. Figure 1 presents the analytical solution to this problem while figure 2 presents results of h- and p-type refinement strategies and highlights an important advantage of the presented framework. For smooth problems the use of high-order basis functions leads to improvements in cost-efficiency by using fewer DOFs to achieve a similar level of accuracy as compared to lower order methods. Until now, previous work by Javeed et al. [28, 29] and Qamar et al. [51] has focused on the use of linear basis functions with a MUSCL limiter to enforce the TVD property resulting in a second-order accurate DG scheme. However, for smooth problems, it is undesirable to apply a TVD limiter, since it limits the accuracy at an increased cost due to data post processing, as clearly demonstrated in figure 2.

To further elaborate on the advantage of using high-order basis functions we evaluate the amount of work required to achieve a given level of accuracy. As a proof-of-concept, we require the L^1 -error in space to be less than 10^{-6} .

379 For engineering solutions, such level of accuracy is unnecessary, but serves
 380 here to challenge low order methods. In the next case study we demonstrate
 381 how these gains scale for a more challenging problem. Table 2 presents the
 382 results and shows that there is a speed-up of approximately 12610 and 74
 383 times by switching from a first order with and without a MUSCL limiter,
 384 respectively, to an 8'th order scheme. Note that the MUSCL limiter ren-
 385 ders the scheme highly cost-ineffective. Furthermore, a speed-up of $\times 3$ is
 386 obtained by switching from a second order scheme to an 8-th order scheme.

Table 2: Speed-up gains possible by switching from low-order methods to high-order methods for a one component system with a linear isotherm.

Order	L^1 -Error ($\times 10^{-6}$)	DOFs	CPU (s)	x-times slower
1 (MUSCL)	2.9	16000	8827	12610
1	1.0	4000	52	74
2	1.0	540	2.2	3
8	0.6	90	0.7	1

Table 3: Simulation parameters for the non-linear case study (section 4.2).

Parameters	Symbol	Values	Unit
Column length	L	1	m
Porosity	ϵ	0.4	-
Interstitial velocity	v	0.1	m/s
Henry's constant	a_1, a_2	0.5, 1	-
Constants used in Eq. (4)	b_1, b_2	0.05, 0.1	L/mol
Initial concentration	$c_{0,1}, c_{0,2}$	0, 0	mol/L
Feed concentration	$c_{f,1}, c_{f,2}$	10, 10	mol/L

387 4.2. Case Study 2: Two-component Nonlinear Chromatography

388 For non-linear models, no analytical solutions are available and we must
 389 rely on numerical techniques to obtain solutions. On the basis of the ob-
 390 tained accurate results in the previous linear case study, we conclude that
 391 the high-order DG scheme could produce accurate results for non-linear
 392 models as well. We consider a problem first studied by Shipilova et al. [31]
 393 and later by Javeed et al. [29] which includes two components competing
 394 for available sites in the stationary phase, modelled using the competitive
 395 Langmuir isotherm Eq. (4). The detailed model parameters are given in
 396 table 3. A rectangular pulse is injected for $t_{inj} = 12$ seconds. The problem
 397 is simulated in two columns of different efficiencies in the following sub-
 398 sections. The purpose is to show that high-order methods are beneficial
 399 not only for chromatography columns of modest efficiency but also for very
 400 efficient columns.

401 4.2.1. Liquid Chromatography Conditions

402 In this subsection the problem is simulated under liquid chromatura-
 403 phy conditions with $N_t = 500$ theoretical plates. The numerical reference
 404 solution is obtained using a 15th order nodal DG-FE scheme with 200 el-
 405 ements and is presented in figure 3. The simulation illustrates that strong
 406 non-linearities produce overshoots in the concentration profile, a well-known
 407 phenomenon in chromatography. It is also well-known, that for finite dis-
 408 persion coefficients, the shock layer at the band front has a thickness greater
 409 than zero [35]. Therefore it does not represent a true discontinuity, allowing
 410 the use of high-order basis functions.

411 Figure 4 demonstrates that convergence is obtained for both h - and p -
 412 type refinement strategies. As in the linear case, the p -type convergence

strategy is superior since it uses fewer DOFs to achieve a similar level of accuracy as compared to low-order methods. As for the linear case study, we elaborate on the advantage of using high-order basis functions in non-linear chromatography by requiring a specific level of accuracy. Here, we choose a modest level of accuracy of 0.01 in the L^1 -norm in time to elucidate that high gains are still achievable, even for modest requirements by switching from low-order to high-order methods. Table 4 presents the results and shows that a speedup of 930 and 11 times can be obtained by switching from a first order scheme with and without a MUSCL limiter respectively, to an 8-th order scheme. The amount of DOFs required by the first order method with a MUSCL limiter is in good agreement with the results obtained by Javeed et al. [29] (1300 elements). Furthermore, a speedup of approximately 2.5 times can be obtained by switching from a second-order scheme to an 8-th order scheme.

Table 4: Speed-up gains possible by switching from low-order methods to high-order methods for a two component system with a non-linear competitive Langmuir isotherm under liquid chromatography conditions ($N_t = 500$).

Order	L^1 -Error	DOFs (per comp.)	CPU (s)	x-times slower
1 (MUSCL)	0.01	2600	4281	930
1	0.01	500	51.5	11
2	0.01	195	11.4	2.5
8	0.009	117	4.6	1

A requirement for a numerical scheme to approximate chromatographic systems is that it preserves positivity of the solution, e.g. that concentrations are positive on all solution nodes. Javeed et al. [28] claims that the MUSCL

Figure 3: Numerical reference solution (15th order DG-FE scheme with 200 elements) of a two component system with a non-linear competitive Langmuir isotherm under liquid chromatography conditions ($N_t = 500$).

430 limiter described in section 3.6 guarantees positivity of the scheme, although
 431 it only guarantees positivity of the element averages. In order to guaran-
 432 tee positivity of the solution on all solution nodes, a maximum-principle-
 433 satisfying limiter must be applied [52]. Alternatively, for smooth solutions,
 434 h - and p -type refinement strategies can be used to cost-efficiently produce
 435 solutions with arbitrary small negative values on solution nodes. Table 5
 436 presents simulation results using an eight-order DG-FE scheme (DG(P8))
 437 and a first-order DG-FE scheme with a MUSCL limiter (DG(P1,MUSCL)).
 438 Both schemes are simulated on a domain discretized by 36 and 450 DOFs.
 439 On the coarse grid, the L_1 -error of the DG(P8) scheme is lower compared
 440 to the DG(P1,MUSCL) scheme, but it produces large negative values since
 441 the solution oscillates on this grid. In comparison, the DG(P1,MUSCL)

Figure 4: Convergence test by h - and p -type refinement strategies of a two component system with a non-linear competitive Langmuir isotherm under liquid chromatography conditions ($N_t = 500$).

442 scheme is uniformly bounded in the element averages, and therefore pro-
 443 duces very small, acceptable, negative values. Since the DG(P8) scheme pro-
 444 duces negative values and the DG(P1,MUSCL) scheme is highly dissipated,
 445 both solutions are unacceptable. Refining the grid with 450 DOFs results
 446 in a highly-resolved, essentially non-oscillatory solution using the DG(P8)
 447 scheme where very small but acceptable negative values are present. Using
 448 the same amount of DOFs, the DG(P1,MUSCL) scheme gives a uniformly
 449 bounded solution but it is still dissipative and does not capture sharp fronts
 450 accurately. It would require an impractical amount of computational work
 451 for the DG(P1,MUSCL) scheme to obtain a similar accuracy as the DG(P8)
 452 scheme using our Matlab implementation.

Table 5: Simulation results of a two component system with a non-linear competitive Langmuir isotherm under liquid chromatography conditions ($N_t = 500$).

Scheme	DOFs	L_1 -error (time)	$c_{\min}^k, \forall k$	CPU (s)
DG (P8)	36	0.5154	-1.5	0.66
	450	4.2×10^{-5}	-4.6×10^{-10}	281
DG (P1,MUSCL)	36	3.92	-2.4×10^{-14}	0.55
	450	0.24	-8.4×10^{-12}	188

4.2.2. High Performance Liquid Chromatography Conditions

In this subsection the problem is simulated under high performance liquid chromatograph conditions with $N_t = 5000$. Note that it is possible to simulate systems with even larger numbers of theoretical plates. However, as the number of theoretical plates increases the problem becomes increasingly large since a finer discretization is required to catch sharp fronts accurately. Currently our Matlab implementation is not prepared for simulation of such large-scale applications (e.g. more than 20000 states). Other low-level computer languages should be considered for such applications instead. This is however less of an issue for us, when simulating systems under liquid chromatography conditions. Figure 5 shows the numerical reference solution obtained using a 15th order nodal DG-FE scheme with 350 elements. The simulation shows that very steep concentrations fronts (practically vertical) are present as a result of high column efficiency. Despite very steep concentration fronts, both h- and p-type refinement strategies converges, as shown in figure 6. As in the previous cases, the p-type convergence strategy is superior since a higher accuracy is obtained using the same amount of DOFs

as used by low order methods.

Figure 5: Numerical reference solution (15th order DG-FE scheme with 350 elements) of a two component system with a non-linear competitive Langmuir isotherm under high-performance conditions ($N_t = 5000$).

470

471 5. Conclusions

472 A high-order nodal DG-FE framework has been presented to solve the
 473 equilibrium-dispersive model of chromatography in both linear and non-
 474 linear case studies. It has been shown that the use of arbitrary high-order
 475 basis functions produce accurate, fast and reliable results for simulation
 476 of convection dominated chromatographic processes with a finite physical
 477 dispersion, in both linear and non-linear chromatography. The use of p-
 478 type refinement strategies has been demonstrated to be superior over h-
 479 type refinement strategies, since high-order methods require fewer DOFs to
 480 obtain a similar level of accuracy as lower-order methods.

Figure 6: Convergence test by h - and p -type refinement strategies of a two component system with a non-linear competitive Langmuir isotherm under high-performance conditions ($N_t = 5000$).

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