Conservative numerical schemes for generalized models in chromatography

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Joint work with
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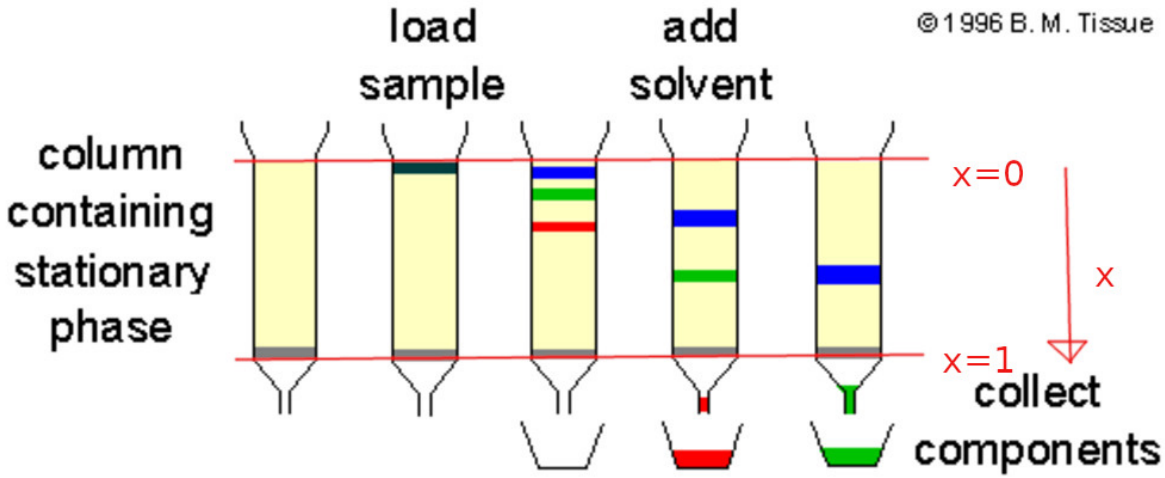
Contents

Outline

Liquid chromatography (from chemicool Chem. Dict.)

- Liquid chromatography uses a column holding a porous solid (**stationary phase**) to separate each substance in a solution by their different interactions with the stationary phase.
- The mixture to be separated is loaded onto the top of the column followed by more solvent (**displacer**).
- If things are done correctly (therefore the importance of simulations), each substance can be collected at the bottom of the column.



- $N \equiv$ number of substances in solution ($N = 3$ in this example)
- Follow notation in **[Guiochon, Shirazi, and Katti., 2006]**

Liquid chromatography I

- Concentrations $c_*(x,t)$ functions of position in column x and time t

$$c_i \equiv \text{concentration of substance } i \text{ in solvent}$$
$$c_{s,i} \equiv \text{concentration of substance } i \text{ in stationary phase.}$$

- $\varepsilon \equiv$ porosity (ratio of void space that can be filled by solution)

$$\Rightarrow \varepsilon c_i + (1-\varepsilon)c_{s,i} \equiv \text{ concentration of substance } i$$

- $u \equiv$ velocity of mobile phase (solution)

$$\Rightarrow u\varepsilon c_i \equiv \text{ convective flux substance } i$$

- Radial effects in the column are “swept” into a diffusion term, with coefficient D_a (**axial dispersion coefficient**)

$$\Rightarrow D_a \varepsilon \frac{\partial c_i}{\partial x} \equiv \text{ diffusive flux substance } i$$

Liquid chromatography II

- Continuity equations read, for $i = 1, \ldots, N$:

$$\frac{\partial(\varepsilon c_i + (1-\varepsilon)c_{s,i})}{\partial t} + \frac{\partial(u\varepsilon c_i)}{\partial x} = \frac{\partial^2(D_a \varepsilon c_i)}{\partial x^2}$$

$$\Leftrightarrow \frac{\partial c_i}{\partial t} + \frac{1-\varepsilon}{\varepsilon}\frac{c_{s,i}}{\partial t} + u\frac{\partial c_i}{\partial x} = D_a \frac{\partial^2 c_i}{\partial x^2}.$$

- In kinetic non-equilibrium models there are ODE

$$\frac{\partial c_{s,i}}{\partial t} = g_i(c_1, \ldots, c_N, c_{s,1}, \ldots, c_{s,N}), \quad i = 1, \ldots, N,$$

with stationary solutions given by $c_{s,i} = q_i(c_1, \ldots, c_N)$, where q_i are some (known) functions named **adsorption isotherms**.

Equilibrium Dispersive Model

- In **Equilibrium Dispersive Model (EDM)**, assume instant equilibrium, so that $c_{s,i} = q_i(c_1, \ldots, c_N)$ holds at any time $\Rightarrow$

$$\frac{\partial}{\partial t}\left(c_i + \frac{1-\varepsilon}{\varepsilon} q_i(c_1, \ldots, c_N)\right) + u\frac{\partial c_i}{\partial x} = D_a \frac{\partial^2 c_i}{\partial x^2} \qquad \textbf{EDM}$$

- There are initial conditions $c_i(x, 0)$ (usually $= 0$, corresponding to an empty column) and boundary conditions

$$(uc_i - D_a\frac{\partial c_i}{\partial x})(0,t) = uc_i^{inj}(t), \qquad \textbf{left (up) Dankwerts BC}$$

$$D_a\frac{\partial c_i}{\partial x}(1,t) = 0 \qquad \textbf{right (down) Neumann BC}$$

for given **injection functions** $c_i^{inj}(t)$.

Ideal chromatography

- In **ideal** chromatography, $D_a = 0$, so that EDM model

$$\frac{\partial}{\partial t}\left(c_i + \frac{1-\varepsilon}{\varepsilon} q_i(c_1, \ldots, c_N)\right) + u\frac{\partial c_i}{\partial x} = 0.$$
$$c_i(x,0) = c_i^0(x)$$
$$c_i(0,t) = c_i^{inj}(t)$$

  can be regarded as a system of conservation laws with conserved variables c_i if the roles of x and t are reversed, so that $c_i(0,t) = c_i^{inj}(t)$ is the "initial condition" and $c_i(x,0) = c_i^0(x)$ is the "boundary condition".
- This is the usual chromatography model in many textbooks

Non-ideal chromatography

- For $D_a \neq 0$, one should regard c_i as **primitive variables** and $w_i = c_i + \frac{1-\varepsilon}{\varepsilon} q_i(c_1, \ldots, c_N)$ as **conserved variables** and hope this mapping be a **change of variables**

$$\boldsymbol{W} \colon [0,\infty)^N \to [0,\infty)^N,$$
$$\boldsymbol{W}_i(\boldsymbol{c}) = \boldsymbol{W}(\boldsymbol{c})_i = c_i + \frac{1-\varepsilon}{\varepsilon} q_i(\boldsymbol{c}), \boldsymbol{c} = (c_1, \ldots, c_N)$$

- **Langmuir** isotherm

$$q_i(c_1, \ldots, c_N) = \frac{a_i c_i}{1 + \sum_{j=1}^{N} b_j c_j}$$

for $a_i, b_i > 0$ are the standard for multicomponent liquid chromatography.

- Can (and will) assume $b_1 = \cdots = b_N = 1$

Non-conservative formulation

- For the Langmuir isotherm in **[Javeed, Qamar, Seidel-Morgenstern, and Warnecke., 2011]** a non-conservative scheme was proposed for the EDM: provided $\boldsymbol{W}'(\boldsymbol{c})$ is invertible (as we will see is the case) for classical solutions we have the following equivalences

$$\frac{\partial \boldsymbol{W}(\boldsymbol{c})}{\partial t} + u\frac{\partial \boldsymbol{c}}{\partial x} = D_a \frac{\partial^2 \boldsymbol{c}}{\partial x^2} \Leftrightarrow$$

$$\boldsymbol{W}'(\boldsymbol{c})\frac{\partial \boldsymbol{c}}{\partial t} + u\frac{\partial \boldsymbol{c}}{\partial x} = D_a \frac{\partial^2 \boldsymbol{c}}{\partial x^2} \Leftrightarrow$$

$$\frac{\partial \boldsymbol{c}}{\partial t} + u\boldsymbol{W}'(\boldsymbol{c})^{-1}\frac{\partial \boldsymbol{c}}{\partial x} = D_a \boldsymbol{W}'(\boldsymbol{c})^{-1}\frac{\partial^2 \boldsymbol{c}}{\partial x^2}$$

- Numerical schemes applied to this **primitive variables** formulation might lead to lack of conservation and wrong shock speeds.

Conservative formulation

- For Langmuir isotherms, we prove in **[Donat, Guerrero, and Mulet, 2018]** that $\boldsymbol{W}$ is a change of variables with solution of EDM given by $\boldsymbol{c}(x,t) = \boldsymbol{C}(\boldsymbol{w}(x,t))$, $\boldsymbol{C} = \boldsymbol{W}^{-1}$, and $\boldsymbol{w}(x,t)$ solving

$$\frac{\partial \boldsymbol{w}}{\partial t} + u\frac{\partial \boldsymbol{C}(\boldsymbol{w})}{\partial x} = D_a \frac{\partial^2 \boldsymbol{C}(\boldsymbol{w})}{\partial x^2} = D_a \frac{\partial}{\partial x}\left(\boldsymbol{C}'(\boldsymbol{w})\frac{\partial \boldsymbol{w}}{\partial x}\right),$$

  where $\boldsymbol{C}'(\boldsymbol{w})$ has distinct eigenvalues $\geq \lambda_{\min} > 0$, so that linearizations of these equations are well-posed.
- Although there is no closed-form for C, Implicit-Explicit conservative schemes were proposed.

Objective

- Generalize results in **[Donat, Guerrero, and Mulet, 2018]** to isotherms

$$q_i(c_1, \ldots, c_N) = \frac{a_i c_i}{\varphi\left(\sum_{j=1}^{N} c_j\right)}, \quad a_i > 0$$

for functions φ satisfying:

1. $\varphi\colon [0, \infty) \to [1, \infty)$ continuous and increasing bijection
2. $\varphi'(c) > 0$ continuous in $(0, \infty)$
3. $\left(\frac{c}{\varphi(c)}\right)' > 0 \, \forall c \in (0, \infty)$

- $\varphi(c) = 1 + c$ for Langmuir isotherm satisfies these requirements.
- Tóth isotherms $\varphi(c) = (1 + c^\nu)^{\frac{1}{\nu}}$ for heterogeneity parameter $\nu \in (0, 1]$ also satisfy these requirements (Langmuir isotherm for $\nu = 1$).

Outline

Notation

Assume $0 < a_1 < \cdots < a_N$ and denote $\eta_i = \frac{(1-\varepsilon)a_i}{\varepsilon}$ so that

$$\boldsymbol{W} : [0,\infty)^N \to [0,\infty)^N,$$

$$W_i(c_1,\ldots,c_N) = c_i v_i(\boldsymbol{c}), \quad v_i(\boldsymbol{c}) = 1 + \frac{\eta_i}{\varphi(\sum_{j=1}^N c_j)}$$

$$1 < v_1(\boldsymbol{c}) < \cdots < v_N(\boldsymbol{c}) < 1 + \eta_N$$

- Aim to prove that $\boldsymbol{W}$ is a change of variables

Jacobians $\boldsymbol{W}'$ I

Theorem 2.1

For $c_i > 0, i = 1, \ldots, N$, $\boldsymbol{W}'(\boldsymbol{c})$ is diagonalizable with N distinct eigenvalues $\lambda_i(\boldsymbol{c}), i = 1, \ldots, N$, satisfying this **interlacing property**

$$1 < \lambda_1(\boldsymbol{c}) < v_1(\boldsymbol{c}) < \lambda_2(\boldsymbol{c}) < v_2(\boldsymbol{c}) < \cdots < \lambda_N(\boldsymbol{c}) < v_N(\boldsymbol{c}) < 1 + \eta_N$$

The (right) eigenvector $R^i(\boldsymbol{c})$ corresponding to $\lambda_i(\boldsymbol{c})$ is

$$R^i_j(\boldsymbol{c}) = \frac{c_j}{v_j(\boldsymbol{c}) - \lambda_i(\boldsymbol{c})}, \quad j = 1, \ldots, N.$$

Jacobians W' II

- $W_i(\boldsymbol{c}) = c_i\left(1+\frac{\eta_i}{\varphi(\sum_k c_k)}\right) \Rightarrow$

$$\boldsymbol{W}'(\boldsymbol{c})_{ij} = \frac{\partial W_i(\boldsymbol{c})}{\partial c_j} = \delta_{i,j}\overbrace{\left(1+\frac{\eta_i}{\varphi(\sum_k c_k)}\right)}^{v_i} - c_i\eta_j\overbrace{\frac{\varphi'(\sum_k c_k)}{\varphi(\sum_k c_k)^2}}^{\frac{\partial v_i}{\partial c_j}} \Rightarrow$$

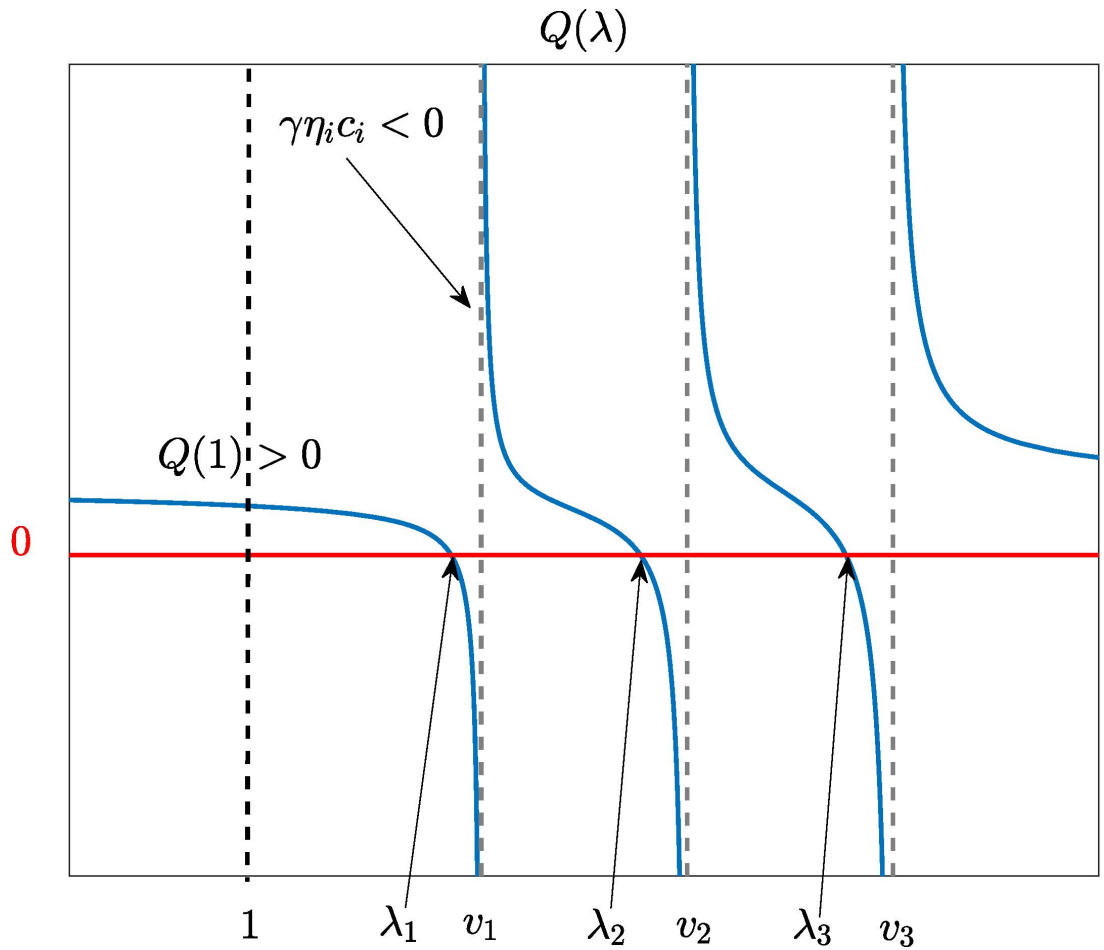
$$\boldsymbol{W}'(\boldsymbol{c}) = D + \gamma \boldsymbol{c}\boldsymbol{\eta}^T, \quad D = \mathsf{diag}(v_1,\ldots,v_N), \gamma = -\frac{\varphi'(\sum_k c_k)}{\varphi(\sum_k c_k)^2}$$

- **[Anderson, 1996, Donat and Mulet., 2010]** N eigenvalues λ of "diagonal" + "rank one matrix" given by N roots of **secular equation**

$$0 = Q(\lambda) = 1 + \sum_{i=1}^{N} \frac{\gamma\eta_i c_i}{v_i - \lambda}$$

($\lim_{\lambda\to v_i\pm} Q(\lambda) = \pm\infty$, coefficients $\gamma\eta_i c_i < 0$, $\lim_{\lambda\to\pm\infty} Q(\lambda) = 1$)

Jacobians W' III



- Since roots of Q are located in known intervals, Newton+bisection can be used for their efficient computation.

Invertibility of $\boldsymbol{W}$ I

Theorem 2.2

$\boldsymbol{W}\colon [0,\infty)^N \to [0,\infty)^N$ (or $\boldsymbol{W}\colon (0,\infty)^N \to (0,\infty)^N$),

$$W_i(c_1,\dots,c_N) = c_i v_i(\boldsymbol{c}), \quad v_i(\boldsymbol{c}) = 1 + \frac{\eta_i}{\varphi\left(\sum_{j=1}^N c_j\right)},$$

is a bijection with inverse given by

$$\boldsymbol{C}_i(\boldsymbol{w}) = \frac{w_i}{1 + \frac{\eta_i}{p(\boldsymbol{w})}},$$

where $p = p(\boldsymbol{w}) \geq 1$ is the unique solution of the (scalar) equation

$$0 = S(p) = \sum_{i=1}^N \frac{w_i}{p+\eta_i} - \frac{\varphi^{-1}(p)}{p}$$

Invertibility of $\boldsymbol{W}$ II

- For $\boldsymbol{w} = (w_1, \ldots, w_N), w_i \geq 0$, how solving for $\boldsymbol{c} = (c_1, \ldots, c_N), c_i \geq 0$

$$w_i = \boldsymbol{W}_i(\boldsymbol{c}) \Leftrightarrow w_i = c_i\left(1 + \frac{\eta_i}{\varphi(\sum_{j=1}^N c_j)}\right) \Leftrightarrow \frac{w_i}{1 + \frac{\eta_i}{\varphi(\sum_{j=1}^N c_j)}} = c_i \Rightarrow$$

$$\sum_{j=1}^N \frac{w_i}{1 + \frac{\eta_i}{\varphi(\sum_{j=1}^N c_j)}} = \sum_{j=1}^N c_i$$

- This leads to $p = \varphi(\sum_{j=1}^N c_j)$ satisfying

$$0 = \sum_{i=1}^N \frac{w_i}{p + \eta_i} - \frac{\varphi^{-1}(p)}{p} =: S(p).$$

- Conversely, it can be seen that

$$\boldsymbol{C}_i(\boldsymbol{w}) = \frac{w_i}{1 + \frac{\eta_i}{p}}, S(p) = 0 \Rightarrow \boldsymbol{C}(\boldsymbol{W}(\boldsymbol{c})) = \boldsymbol{c}, \boldsymbol{W}(\boldsymbol{C}(\boldsymbol{w})) = \boldsymbol{w}.$$

Invertibility of $\boldsymbol{W}$ III

- Can assume $\boldsymbol{w} \neq \mathbf{0}$ for the existence of a unique solution of

$$0 = \sum_{i=1}^{N} \frac{w_i}{p + \eta_i} - \frac{\varphi^{-1}(p)}{p} = S(p).$$

  - $S(p)$ strictly decreasing, since $\frac{w_i}{p+\eta_i}$ is so and

$$\frac{\varphi^{-1}(p)}{p} = \frac{\varphi^{-1}(p)}{\varphi(\varphi^{-1}(p))} = \left(\frac{c}{\varphi(c)} \circ \varphi^{-1}\right)(p)$$

    is increasing (crucial $\varphi^{-1}, c/\varphi(c)$ increasing)
  - S changes sign between 1 and $\overline{p}(\boldsymbol{w}) = \varphi(\sum_{j=1}^{N} w_j) > \varphi(0) = 1$,

$$\Rightarrow \exists! p \in (1, \overline{p}(\boldsymbol{w}))/S(p) = 0$$

    (p efficiently found with bisection+Newton).

Invertibility of $\boldsymbol{W}$ IV

Theorem 2.3

$\boldsymbol{C} = \boldsymbol{W}^{-1}\colon (0,\infty)^N \to (0,\infty)^N$ is continuously differentiable, $\boldsymbol{C}'(\boldsymbol{w})$ is diagonalizable with N distinct eigenvalues

$$\frac{1}{\lambda_i(\boldsymbol{C}(\boldsymbol{w}))} \in (\frac{1}{1+\eta_N}, 1), i = 1, \ldots, N$$

and same eigenvectors as $\boldsymbol{W}'(\boldsymbol{C}(\boldsymbol{w}))$.

- $\boldsymbol{W}\colon (0,\infty)^N \to (0,\infty)^N$ bijection, $\det \boldsymbol{W}'(\boldsymbol{c}) \neq 0 \; \forall \boldsymbol{c} \in (0,\infty)^N$
- By Inv. Fun. T., $\boldsymbol{C} = \boldsymbol{W}^{-1}$ is differentiable
- The chain rule yields $\boldsymbol{C}'(\boldsymbol{w}) = (\boldsymbol{W}'(\boldsymbol{C}(\boldsymbol{w}))^{-1}$, so that eigenvalues of $\boldsymbol{C}'(\boldsymbol{w})$ are $1/\lambda_i(\boldsymbol{C}(\boldsymbol{w}))$, $i = 1, \ldots, N$. □

Well-posedness I

- From Theorem 2.3 EDM can be written as system of N equations

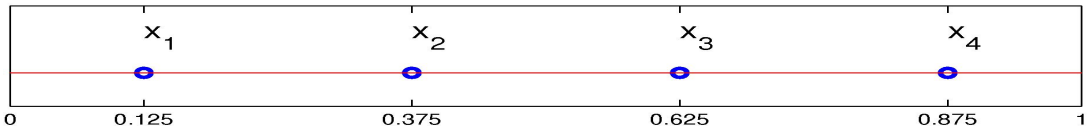
$$\frac{\partial \boldsymbol{w}}{\partial t} + \frac{\partial \boldsymbol{f}(\boldsymbol{w})}{\partial x} = D_a \frac{\partial}{\partial x}\left[\boldsymbol{C}'(\boldsymbol{w})\frac{\partial \boldsymbol{w}}{\partial x}\right], \quad \boldsymbol{f}(\boldsymbol{w}) = u\boldsymbol{C}(\boldsymbol{w}).$$

- For $D_a = 0$, it is a strictly hyperbolic system of conservation laws, since eigenvalues of $u\boldsymbol{C}'(\boldsymbol{w}), \boldsymbol{w} \in (0,\infty)^N$, are real and distinct.
- For $D_a \neq 0$ the system is parabolic, since the eigenvalues of $D_a\boldsymbol{C}'(\boldsymbol{w}), \boldsymbol{w} \in (0,\infty)^N$, are real and bounded below by positive numbers, so that linearized problems are well-posed.

Outline

Method Of Lines: $w_t + \gamma w_x = \delta w_{xx}$, $x \in (0,1)$, $\gamma, \delta > 0$

- For each $x_j = (j - \frac{1}{2})\Delta x$, $j = 1, \ldots, L$, $\Delta x = \frac{1}{L}$ of the grid



we consider Finite Difference approximations

$$w_x(x_j, t) \approx \frac{w(x_j, t) - w(x_{j-1}, t)}{\Delta x} \text{ (1st order, } \textbf{upwind}\text{)}$$

$$w_{xx}(x_j, t) \approx \frac{w(x_{j+1}, t) - 2w(x_j, t) + w(x_{j-1}, t)}{\Delta x^2} \quad \text{(2nd order)}$$

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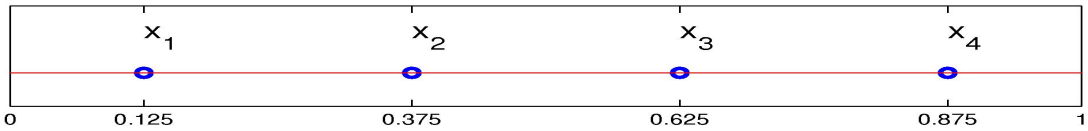

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- Substitute into $w_t(x_j,t) = (-\gamma w_x + \delta w_{xx})(x_j,t) \Rightarrow$

$$w_t(x_j,t) \approx -\gamma \frac{w(x_j,t) - w(x_{j-1},t)}{\Delta x} + \delta \frac{w(x_{j+1},t) - 2w(x_j,t) + w(x_{j-1},t)}{\Delta x^2}$$

Method Of Lines: $w_t + \gamma w_x = \delta w_{xx}$, $x \in (0,1)$, $\gamma, \delta > 0$

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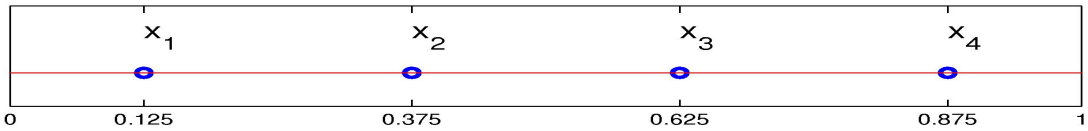

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- Get **spatial semidiscretization** for $w_j(t) \approx w(x_j,t), j = 1, \ldots, L$ (Periodic B.C. $\Rightarrow w_0 = w_L, w_{L+1} = w_1$)

$$w_j'(t) = -\gamma \frac{w_j(t) - w_{j-1}(t)}{\Delta x} + \delta \frac{w_{j+1}(t) - 2w_j(t) + w_{j-1}(t)}{\Delta x^2}$$

Method Of Lines: $w_t + \gamma w_x = \delta w_{xx},\ x \in (0,1)$

- Linear PDE and linear discretization $\Rightarrow$ linear ODE.
- In vector form:

$$\begin{bmatrix} w_1'(t) \\ \vdots \\ w_L'(t) \end{bmatrix} = \frac{\gamma}{\Delta x} \underbrace{\begin{bmatrix} -1 & 0 & \dots & 1 \\ 1 & -1 & \ddots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & \dots & 1 & -1 \end{bmatrix}}_{A_{\text{conv}}} \begin{bmatrix} w_1(t) \\ \vdots \\ w_L(t) \end{bmatrix}$$

$$+ \frac{\delta}{\Delta x^2} \underbrace{\begin{bmatrix} -2 & 1 & 0 & \dots & 1 \\ 1 & -2 & 1 & \ddots & 0 \\ \dots & \dots & \dots & \dots & \dots \\ 1 & \dots & 0 & 1 & -2 \end{bmatrix}}_{A_{\text{diff}}} \begin{bmatrix} w_1(t) \\ \vdots \\ w_L(t) \end{bmatrix}$$

$\Rightarrow$

$$w'(t) = Aw(t), \quad A = \frac{\gamma}{\Delta x} A_{\text{conv}} + \frac{\delta}{\Delta x^2} A_{\text{diff}} \in \mathbb{R}^{L\times L}, \quad w(t) \in \mathbb{R}^L$$

Stability I

- **Fully discrete numerical method** for $w_j^n \approx w_j(t_n) \approx w(x_j, t_n)$ by applying **Euler's method** to $w' = Aw$ ($\Delta t = t_{n+1} - t_n$ for sake of argument):

$$w^{n+1} = w^n + \Delta t\, Aw^n = (I + \Delta t\, A)w^n \Rightarrow$$
$$w^n = (I + \Delta t A)^n w^0, \quad w_j^0 = w(x_j, 0)$$

- Powers of $I + \Delta t A$, written in terms of spectral decomposition of A,

$$w^0 = \sum_{p=1}^{L} z^p, \quad Az^p = \lambda_p z^p \Rightarrow (I + \Delta t A)^n w^0 = \sum_{p=1}^{L} (1 + \Delta t \lambda_p)^n z^p$$

do not blow up (**solutions do not**) if $|1 + \Delta t \lambda_p| \leq 1$, $\forall p$ (**stability**)

Stability II

- **von Neumann analysis**: A **circulant matrix** $\Rightarrow$ eigenvectors $z^p, p = 1, \ldots, L$, given by discrete harmonics $z_j^p = e^{\theta_p j\, i}$, $\theta_p = \frac{2p\pi}{L}\Delta x$

$$(Az^p)_j = -\gamma \frac{z_j^p - z_{j-1}^p}{\Delta x} + \delta \frac{z_{j+1}^p - 2z_j^p + z_{j-1}^p}{\Delta x^2}$$

$$= \Big(\underbrace{-\gamma \frac{1 - e^{-\theta_p\, i}}{\Delta x} + \delta \frac{e^{\theta_p\, i} - 2 + e^{-\theta_p\, i}}{\Delta x^2}}_{\lambda_p} \Big) z_j^p$$

$$\lambda_p = \left(\frac{\gamma}{\Delta x} + \frac{2\delta}{\Delta x^2} \right) (\cos\theta_p - 1) - i \frac{\gamma}{\Delta x} \sin\theta_p \Rightarrow$$

$$|1 + \Delta t \lambda_p| \leq 1, \quad \forall p \Leftrightarrow \Delta t \left(\frac{\gamma}{\Delta x} + \frac{2\delta}{\Delta x^2} \right) \leq 1$$

- To attain fixed $T = M\Delta t > 0$ for $\Delta x \downarrow 0$, many ($M \to \infty$) tiny time steps Δt (**no need for accuracy**).

Stability III

- **Upwinding crucial for stability:** If $\delta = 0$ and we had chosen the 2nd order central approximation $w_x(x_j, t) \approx \frac{w(x_{j+1},t)-w(x_{j-1},t)}{2\Delta x}$ then Euler's method would yield

$$\lambda_p = -\gamma \frac{e^{\theta_p\, i} - e^{-\theta_p\, i}}{2\Delta x} = -\gamma \frac{\sin(\theta_p)}{\Delta x}\, i \Rightarrow |1 + \lambda_p \Delta t| > 1 \, \forall \Delta t > 0.$$

- On the other hand, no restriction on Δt for stability of **Implicit Euler's method** $w^{n+1} = w^n + \Delta t\, A w^{n+1}$

$$w^0 = \sum_{p=1}^{L} z^p, \quad A z^p = \lambda_p z^p \Rightarrow$$

$$w^n = \sum_{p=1}^{L} (1 - \Delta t \lambda_p)^{-n} z^p, |1 - \Delta t \lambda_p|^{-1} < 1 \, \forall \Delta t > 0$$

but anyway need $\Delta t \propto \Delta x$ for accuracy

General spatial semidiscretization

- **Spatial discretization** of

$$\frac{\partial \boldsymbol{w}}{\partial t} + \frac{\partial \boldsymbol{f}(\boldsymbol{w})}{\partial x} = D_a \frac{\partial^2}{\partial x^2} \boldsymbol{C}(\boldsymbol{w}) \quad + \text{B.C.}$$

denoted by (remember $x_{j+1} - x_j = \Delta x \, \forall j$)

$$\boldsymbol{w}' = \mathcal{L}(\boldsymbol{w}) + \mathcal{D}(\boldsymbol{w}), \quad \boldsymbol{w}_j(t) \approx \boldsymbol{w}(x_j, t) \in \mathbb{R}^N, j = 1, \ldots, L$$

$$\mathcal{D}(\boldsymbol{w})_j = D_a \frac{\boldsymbol{C}(\boldsymbol{w}_{j+1}) - 2\boldsymbol{C}(\boldsymbol{w}_j) + \boldsymbol{C}(\boldsymbol{w}_{j-1})}{\Delta x^2}$$

$$(\mathcal{L}(\boldsymbol{w}) = -\frac{\gamma}{\Delta x} A_{\text{conv}} \, \boldsymbol{w}, \mathcal{D}(\boldsymbol{w}) = \frac{\delta}{\Delta x^2} A_{\text{diff}} \, \boldsymbol{w} \text{ in example})$$

- For convergence to weak solutions, the convective term should be obtained by differences of **numerical fluxes** (**Lax-Wendroff Th.**),

$$\mathcal{L}(\boldsymbol{w})_j = -\frac{\widehat{\boldsymbol{f}}(\boldsymbol{w})_{j+\frac{1}{2}} - \widehat{\boldsymbol{f}}(\boldsymbol{w})_{j-\frac{1}{2}}}{\Delta x}, \widehat{\boldsymbol{f}}(\boldsymbol{w})_{j+\frac{1}{2}} = \widehat{\boldsymbol{f}}(\underbrace{\boldsymbol{w}_{j-r+1}, \ldots, \boldsymbol{w}_{j+r}}_{2r}), r \geq 1$$

Convective terms and upwinding I

- In a finite volume setting, numerical fluxes are usually obtained by solving **Riemann problems**.
- Although solving Riemann problems for chromatography for arbitrary N can be challenging, the numerical flux for Godunov's method is

$$\widehat{\boldsymbol{f}}(\boldsymbol{w}_j, \boldsymbol{w}_{j+1}) = \boldsymbol{f}(\boldsymbol{R}(0)),$$

where $\boldsymbol{w}(x,t) = \boldsymbol{R}(x/t)$ is the solution of the **Riemann problem**

$$\frac{\partial \boldsymbol{w}}{\partial t} + \frac{\partial \boldsymbol{f}(\boldsymbol{w})}{\partial x} = 0 \quad \boldsymbol{w}(x,0) = \begin{cases} \boldsymbol{w}_j & x > 0 \\ \boldsymbol{w}_{j+1} & x < 0 \end{cases}$$

- Since the wave speeds are dictated by the eigenvalues (> 0) of $\boldsymbol{f}'(\boldsymbol{w})$, it follows that all the waves move right, so

$$\boldsymbol{w}(0,t) = \boldsymbol{R}(0) = \boldsymbol{w}_j, \forall t > 0,$$

and Godunov's method is given by

$$\widehat{\boldsymbol{f}}(\boldsymbol{w}_j, \boldsymbol{w}_{j+1}) = \boldsymbol{f}(\boldsymbol{w}_j) \quad \textbf{(upwind)}$$

Convective terms and upwinding II

- Nice properties for Godunov's method, but only 1st order accurate.
- There are higher-order Godunov-type methods, as MUSCL schemes (**[van Leer, 1979]**)

$$\widehat{\boldsymbol{f}}^{\text{MUSCL}}(\boldsymbol{w}_{j-1},\boldsymbol{w}_j,\boldsymbol{w}_{j+1},\boldsymbol{w}_{j+2}) = \widehat{\boldsymbol{f}}^{\text{Godunov}}(\boldsymbol{w}^-_{j+\frac{1}{2}},\boldsymbol{w}^+_{j+\frac{1}{2}})$$

$$\boldsymbol{w}^-_{j+\frac{1}{2}} = \boldsymbol{w}_j + \frac{1}{2}\textbf{minmod}(\boldsymbol{w}_j - \boldsymbol{w}_{j-1}, \boldsymbol{w}_{j+1} - \boldsymbol{w}_j),$$

$$\boldsymbol{w}^+_{j+\frac{1}{2}} = \boldsymbol{w}_{j+1} - \frac{1}{2}\textbf{minmod}(\boldsymbol{w}_{j+1} - \boldsymbol{w}_j, \boldsymbol{w}_{j+2} - \boldsymbol{w}_{j+1})$$

$$\textbf{minmod}(\mathbf{a},\mathbf{b})_j = \frac{1}{2}(\text{sign}(a_j) + \text{sign}(b_j))\min(|a_j|,|b_j|)$$

- For scalar equations, they have the Total Variation Diminishing (**TVD**) property, which ensures stability, but are at most 2nd order accurate and 1st order accurate at smooth extrema.

Convective terms and upwinding III

- Instead of this, we aim at using finite difference schemes, following **[Shu and Osher, 1988]**
- Consider the example $w_t + \gamma w_x - \delta w_{xx} = 0$, $f(w) = \gamma w, \gamma > 0$ $w_j(t) = w(x_j, t) \Rightarrow$

$$\begin{cases} w_j' = w_t(x_j, t), \\ \mathcal{L}(v)_j = -\dfrac{\gamma w_j - \gamma w_{j-1}}{\Delta x} = -\gamma w_x(x_j, t) + \mathcal{O}(\Delta x) \\ \mathcal{D}(v)_j = \delta \dfrac{w_{j+1}(t) - 2w_j(t) + w_{j-1}(t)}{\Delta x^2} = \delta \dfrac{\partial^2}{\partial x^2} w(x_j, t) + \mathcal{O}(\Delta x)^2 \end{cases}$$

- The local truncation error of the semidiscrete scheme is

$$\boldsymbol{w}' - \mathcal{L}(\boldsymbol{w}) - \mathcal{D}(\boldsymbol{w}) = \mathcal{O}(\Delta x) + \mathcal{O}(\Delta x^2) = \mathcal{O}(\Delta x)$$

so that the scheme is 1st order (and will be so when getting fully discrete scheme with ODE solvers)

Convective terms and upwinding IV

- For a second order approximation of the convective term, need also **upwinding**, which does not necessarily imply that **all** the information should be taken from the left, for $\gamma > 0$.
- The challenge is getting an approximation of $\gamma w_x(x_j, t)$:
  - with accuracy of order ≥ 2.
  - involving more points to the left of x_j than to the right.
  - being a finite difference of two numerical fluxes.

$$\widehat{f}(w_{j-1}, w_j, w_{j+1}, w_{j+2}) = \gamma(-\frac{1}{6}w_{j-1} + \frac{5}{6}w_j + \frac{1}{3}w_{j+1}) \Rightarrow$$

$$w_j = w(x_j, t), w(\cdot, t) \in \mathcal{C}^4 \Rightarrow$$

$$\frac{\widehat{f}(w_{j-1}, w_j, w_{j+1}, w_{j+2}) - \widehat{f}(w_{j-2}, w_{j-1}, w_j, w_{j+1})}{\Delta x}$$

$$= \gamma \frac{\frac{1}{6}w_{j-2} - w_{j-1} + \frac{1}{2}w_j + \frac{1}{3}w_{j+1}}{\Delta x} = \gamma w_x(x_j, t) + \mathcal{O}(\Delta x^3)$$

Convective terms and upwinding V

- How do we get these formulae? If for a sufficiently smooth f

$$\frac{1}{\Delta x}\int_{x_l-\frac{\Delta x}{2}}^{x_l+\frac{\Delta x}{2}} p_+(x)dx = f(x_l) = f_l, l = k, \dots, k+n$$

$$\frac{1}{\Delta x}\int_{x_l-\frac{\Delta x}{2}}^{x_l+\frac{\Delta x}{2}} p_-(x)dx = f(x_l), l = k-1, \dots, k+n-1$$

where $p_\pm$ are polynomial **reconstructions** of degree $\leq n$, then

$$\frac{p_+(x+\frac{\Delta x}{2}) - p_-(x-\frac{\Delta x}{2})}{\Delta x} = f'(x) + \mathcal{O}(\Delta x^{n+1})$$

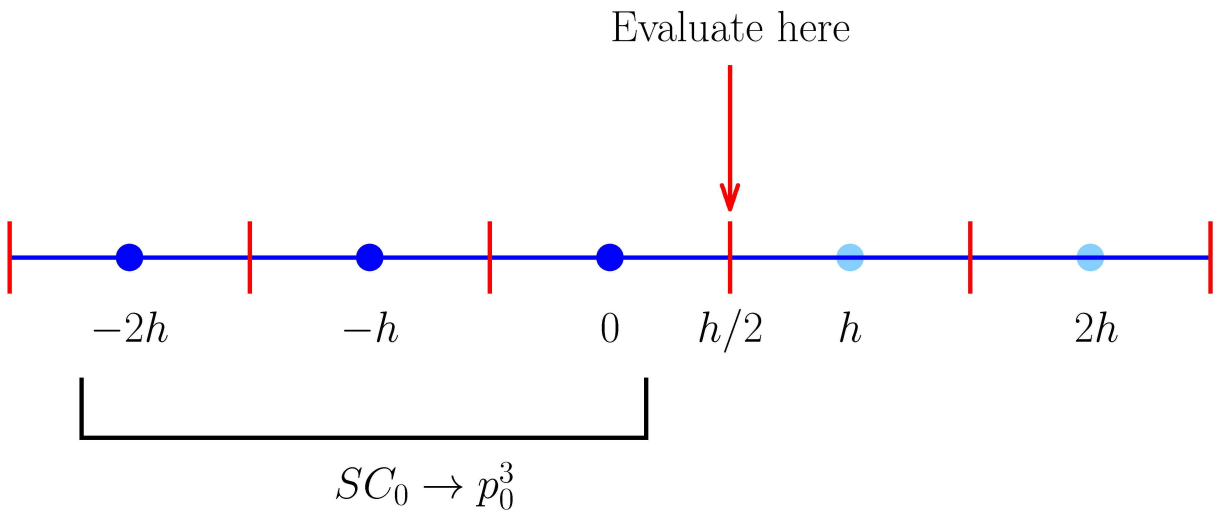
- The previous formula is obtained with $n = 2, k = j-1, f_l = \gamma w_l$

$$\widehat{f}(w_{j-1}, w_j, w_{j+1}, w_{j+2}) = p_+(x_j + \frac{\Delta x}{2}) = -\frac{1}{6}f_{j-1} + \frac{5}{6}f_j + \frac{1}{3}f_{j+1}$$

Essentially Non-Oscillatory Schemes

- Essentially Non-Oscillatory property

  [Harten, Engquist, Osher, and Chakravarthy, 1987]: let TV increase at the level of the order of the method to get beyond 2nd order.
- As example, consider the ENO3 reconstructions ($n = 2$, three points in **substencil** SC_*, $h = \Delta x, x_0 = 0, p_+ \equiv p_*^3$) which selects the substencil from the whole 5 points stencil for which the data is smoothest (based on divided differences) in order to avoid discontinuities $\Rightarrow$ 3rd order schemes with ENO property.



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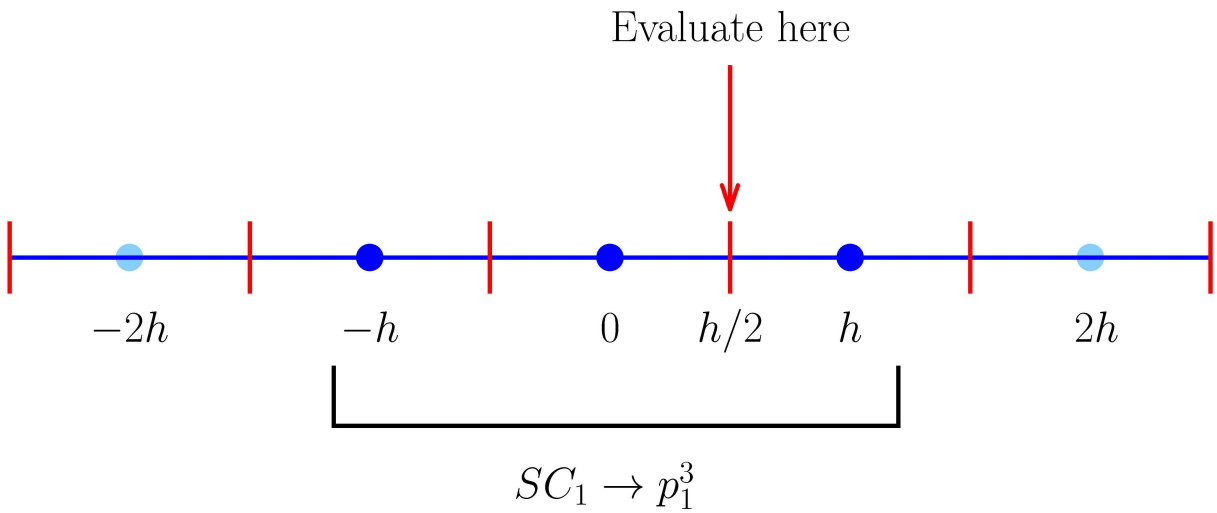

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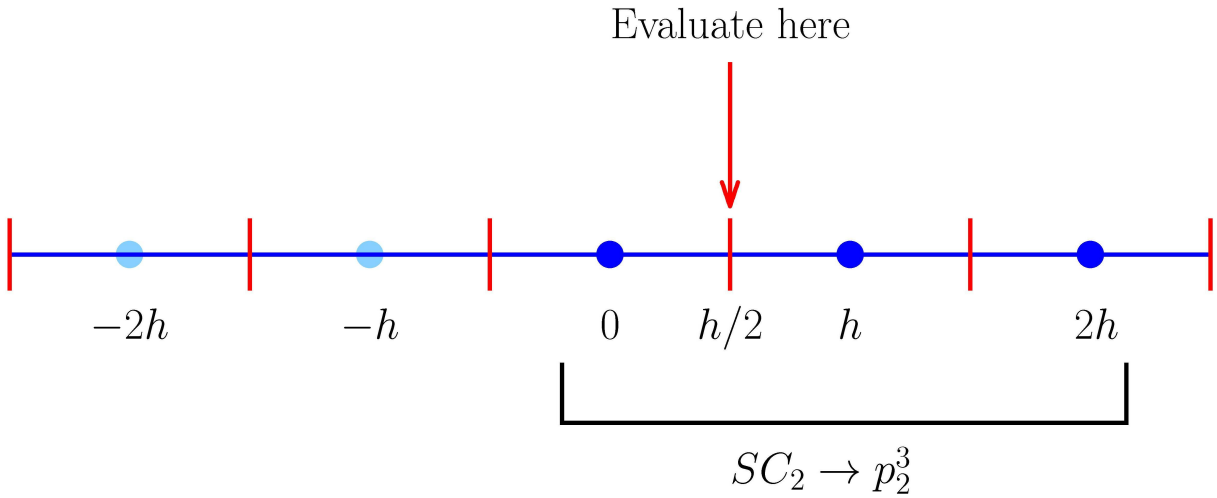

- Can get ENO if enough points can be fitted between discontinuities.

Weighted Essentially Non-Oscillatory Schemes

- If we had used the entire five-points stencil, then the scheme would be 5th order accurate, but it would not be ENO.
- In **[Liu, Osher, and Chan, 1994, Jiang and Shu, 1996]** **Weighted Essentially Non-Oscillatory** schemes are proposed to transition smoothly from the 5th order reconstruction in smooth zones to the 3rd order reconstruction in nonsmooth zones.
- This is achieved by **weighting** the reconstructions p_0^3, p_1^3, p_2^3

$$\widehat{f}_{j+\frac{1}{2}} = \omega_0 p_0^3(x_{j+\frac{1}{2}}) + \omega_1 p_1^3(x_{j+\frac{1}{2}}) + \omega_2 p_2^3(x_{j+\frac{1}{2}}) \textbf{ (WENO5)}$$

$$\omega_0 = \omega_0(f_{j-2}, f_{j-1}, f_j),\ \omega_1 = \omega_1(f_{j-1}, f_j, f_{j+1}),\ \omega_2 = \omega_2(f_j, f_{j+1}, f_{j+2})$$

$$\omega_* \geq 0, \omega_0 + \omega_1 + \omega_2 = 1$$

- ω_* computed through **smoothness indicators** (scaled Sobolev seminorms of p_j^3), so that $\omega_j \approx 0$ if SC_j crosses discontinuity.

Extension to systems

- ENO property when discontinuities are well separated: ENO OK when only 1 discontinuity, not OK for interacting discontinuities.
- **Example:** $\boldsymbol{w}_t + A\boldsymbol{w}_x = 0$, A 2×2, eigenvalues ± 1, right eigenvectors $\boldsymbol{R}_\pm$, left eigenvectors $\boldsymbol{L}_\pm \Rightarrow$ solutions of Cauchy problems with $\boldsymbol{w}(x,0) = \boldsymbol{w}^0(x)$ given by

$$\boldsymbol{w}(x,t) = \beta_-(x+t)\boldsymbol{R}_- + \beta_+(x-t)\boldsymbol{R}_+,$$
$$\boldsymbol{w}^0(x) = \beta_-(x)\boldsymbol{R}_- + \beta_+(x)\boldsymbol{R}_+ \Leftrightarrow \beta_\pm(x) = \boldsymbol{L}_\pm^T \boldsymbol{w}^0(x)$$

- If $\beta_\pm$ have isolated discontinuities at $x_\pm$, with $x_- > x_+$, then waves will collide at $t = \frac{x_- - x_+}{2} > 0$, so that reconstructions applied directly to the components of $\boldsymbol{w}$ might exhibit oscillations
- Reconstructions applied to the system of **characteristic variables** $\boldsymbol{L}_\pm^T \boldsymbol{w}$ will be ENO, since $\beta_\pm(x \mp t)$ have isolated discontinuities.
- Use reconstructions of **local characteristic fluxes** for nonlinear systems.

Nonlinear stability

- Non-practical rigorous nonlinear stability analysis of **[Verwer and Sanz-Serna, 1984]** $\Rightarrow$ **Poor man's analysis** based on linearization about $\bar{w}$ and linear stability analysis:

$$w_t + f(w)_x - (A(w)w_x)_x = 0, \quad w(x,t) \in \mathbb{R} \Rightarrow$$

(**linearization about** $\bar{w}$, $w(x) = \bar{w} + \widetilde{w}(x)$)

$$\widetilde{w}_t + \underbrace{f'(\bar{w})}_{\gamma}\widetilde{w}_x - \underbrace{A(\bar{w})}_{\delta}\widetilde{w}_{xx} = 0$$

- For **Explicit Euler's method**, practical bound

$$\Delta t \left(\frac{\gamma}{\Delta x} + \frac{2\delta}{\Delta x^2} \right) \leq 1$$

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(**linearization about** $\bar{w}$, $w(x) = \bar{w} + \widetilde{w}(x)$)

$$\widetilde{w}_t + \underbrace{f'(\bar{w})}_{\gamma}\widetilde{w}_x - \underbrace{A(\bar{w})}_{\delta}\widetilde{w}_{xx} = 0$$

- For **Explicit Euler's method**, practical bound, **semiempirical** K

$$\Delta t \left(\frac{\max_{\bar{w}} |f'(\bar{w})|}{\Delta x} + \frac{2 \max_{\bar{w}} A(\bar{w})}{\Delta x^2} \right) \leq K$$

- For systems

$$\Delta t \left(\frac{\max_{p,\bar{w}} |\lambda_p(f'(\bar{w}))|}{\Delta x} + \frac{2 \max_{p,\bar{w}} \lambda_p(A(\bar{w}))}{\Delta x^2} \right) \leq K$$

IMEX schemes I

- Fully discrete 2nd order schemes are obtained by using Runge-Kutta ODE solvers on MOL equations for approximations $\mathbb{R}^N \ni \boldsymbol{w}_j^n \approx \boldsymbol{w}_j(t_n), j = 1, \ldots, L$ ($\boldsymbol{w}^n$ is a $N \times L$ matrix).
- Typical stability restriction of explicit solvers:

$$\Delta t \left(\frac{u/\max_{\boldsymbol{w}} \lambda_1(\boldsymbol{C}(\boldsymbol{w}))}{\Delta x} + \frac{D_a/\max_{\boldsymbol{w}} \lambda_1(\boldsymbol{C}(\boldsymbol{w}))}{\Delta x^2} \right) \leq K$$

  (Remember eigenvalues of $\boldsymbol{C}'(\boldsymbol{w})$ are $1 > 1/\lambda_1(\boldsymbol{C}(\boldsymbol{w})) > \cdots > 1/\lambda_N(\boldsymbol{C}(\boldsymbol{w})) > 1/(1+\eta_N)$)
- $D_a \approx 0 \Rightarrow \Delta t \propto \Delta x \Rightarrow$ explicit solver ✓
- $D_a \gg 0 \Rightarrow \Delta t \propto \Delta x^2 \Rightarrow$ explicit solver ✗

IMEX schemes II

- Since Δx^2 comes from treating diffusion explicitly and do not want to treat convection implicitly, we consider the **Implicit-Explicit midpoint rule [Ascher, Ruuth, and Spiteri., 1997]**

$$\boldsymbol{w}^{n+1/2} = \boldsymbol{w}^n + \frac{\Delta t}{2}\left(\boldsymbol{\mathcal{L}}(\boldsymbol{w}^n, t_n) + \boldsymbol{\mathcal{D}}(\boldsymbol{w}^{n+1/2})\right)$$

$$\boldsymbol{w}^{n+1} = \boldsymbol{w}^n + \Delta t\left(\boldsymbol{\mathcal{L}}(\boldsymbol{w}^{n+\frac{1}{2}}, t_n + \frac{\Delta t}{2}) + \boldsymbol{\mathcal{D}}(\boldsymbol{w}^{n+1/2})\right).$$

- Need to solve nonlinear equation for $\boldsymbol{w}^{n+1/2}$, second step is explicit.
- It is 2nd order accurate and is stable under $\Delta t \propto \Delta x$

IMEX schemes III

- The lack of an explicit expression for $\boldsymbol{C}(\boldsymbol{w})$ in

$$\boldsymbol{\mathcal{D}}(\boldsymbol{w})_j = D_a \frac{\boldsymbol{C}(\boldsymbol{w}_{j+1}) - 2\boldsymbol{C}(\boldsymbol{w}_j) + \boldsymbol{C}(\boldsymbol{w}_{j-1})}{\Delta x^2}$$

  can be circumvented by a change of variables

$$c_{i,j} = \boldsymbol{C}_i(\boldsymbol{w}_j^{n+\frac{1}{2}}) \ (i \equiv \text{component}, \ j \equiv \text{location}),$$

  so that (i,j) equation becomes

$$\underbrace{c_{i,j}\left(1 + \frac{\eta_i}{\varphi\left(\sum_{k=1}^{N} c_{k,j}\right)}\right)}_{w_{i,j}^{n+\frac{1}{2}}} - \frac{\Delta t}{2}\frac{D_a}{\Delta x^2}\left(c_{i,j-1} - 2c_{i,j} + c_{i,j+1}\right) = \underbrace{\mathcal{G}_{i,j}^n}_{\text{known}}$$

- Change of variables shifts nonlinearity from the diffusion term, so that solution by Newton's method involves solving a block-tridiagonal system with small blocks of size $N \times N$ at each iteration step.

Outline

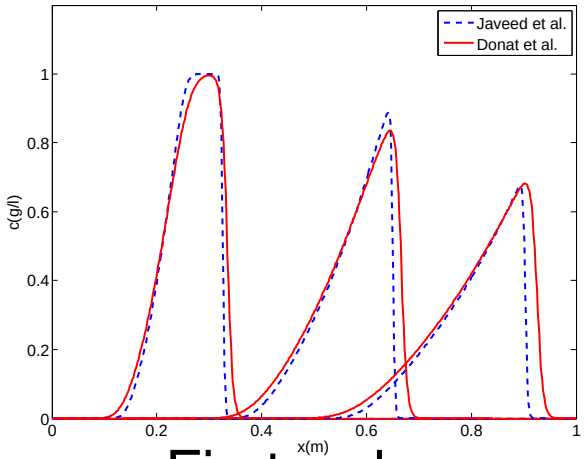
Loss of conservation of total mass, $N = 1, D_a = 0$

$\text{Loss}(T) = |\int_0^T u c_{\text{inj}}(t)dt - \Delta x \sum_{j=1}^{L} w_j^M|, M\Delta t = T$

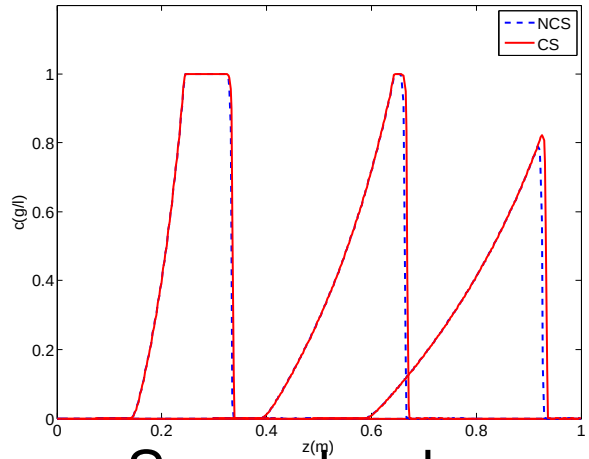
NCS: Non Conservative Scheme (**[Javeed et al., 2011]**)

CS: Conservative Scheme (**[Donat et al., 2018]**)

	First order		Second Order	
	NCS	CS	NCS	CS
$T = 0.5$	0.016	4.1e-14	0.004	3.7e-14
$T = 1.0$	0.029	6.7e-14	0.008	6.4e-14
$T = 1.4$	0.036	8.5e-14	0.01	7.8e-14



First order



Second order

Numerical setup

- Tóth isotherms $\varphi(c) = (1 + c^{\nu})^{\frac{1}{\nu}}$, heterogeneity parameter $\nu \in (0, 1]$.
- Use reference solution computed with $\Delta z = \frac{1}{25600}$ to compute approximate L^1-errors of different schemes.
- **CMP-UPW5**: Upwind WENO5 applied to components of physical flux
- **CHR-UPW5**: Compute local characteristic fluxes (using left eigenvectors), reconstruct them with WENO5 and then go back to physical fluxes (using right eigenvectors)
- Stability restriction is better for CHR-UPW5 (better estimate of characteristic velocities) $\Rightarrow$ larger Δt for stability:

$$u\frac{\Delta t}{\Delta z} < K, \quad \text{CMP-UPW5, no characteristic information}$$

$$u\rho^n\frac{\Delta t}{\Delta z} < K, \quad \rho^n = \max_{w^n} \lambda_N(\boldsymbol{C}'(w^n)) < 1, \quad \text{CHR-UPW5}$$

with (CFL) $K = 0.8$ sufficient to prevent instabilities in tests.

Three component displacement chromatography

- Mixture of two components and one displacer (solvent) proposed in **[Javeed, Qamar, Seidel-Morgenstern, and Warnecke., 2011]**, $N = 3$.
- Parameters: $a_1 = 4, a_2 = 5, a_3 = 6, b_1 = 4, b_2 = 5, b_3 = 1$, $\epsilon = 0.5, u = 0.2$.
- Injection function in left (top) Dankwerts BC:

$$(\boldsymbol{f}(\boldsymbol{w}) - D_a \frac{\partial \boldsymbol{C}(\boldsymbol{w})}{\partial x})(x = 0, t) = u\boldsymbol{c}_{inj}(t)$$

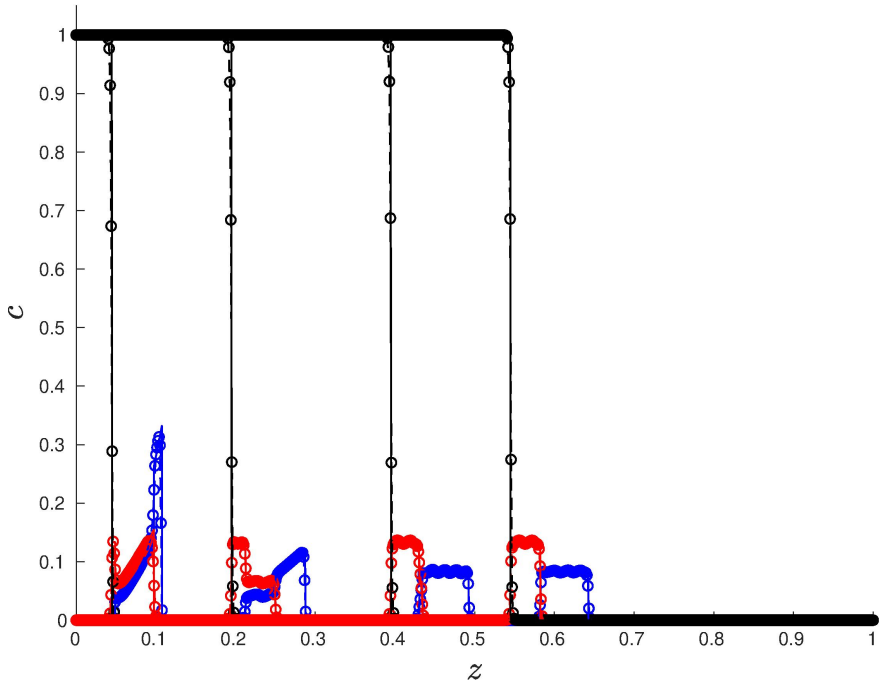
$$\boldsymbol{c}_{inj}(t) = \begin{cases} (1, 1, 0) & 0 \leq t < 0.1 \\ (0, 0, c^{\text{disp}}) & t \geq 0.1 \end{cases}$$

$u \equiv$ injection velocity
Components 1 and 2 are injected between $t = 0$ and $t = 0.1$ with $c_1 = c_2 = 1$ at $x = 0$.
Component 3 (displacer) is injected from $t = 0.1$ with $c_3 = c^{\text{disp}}$.

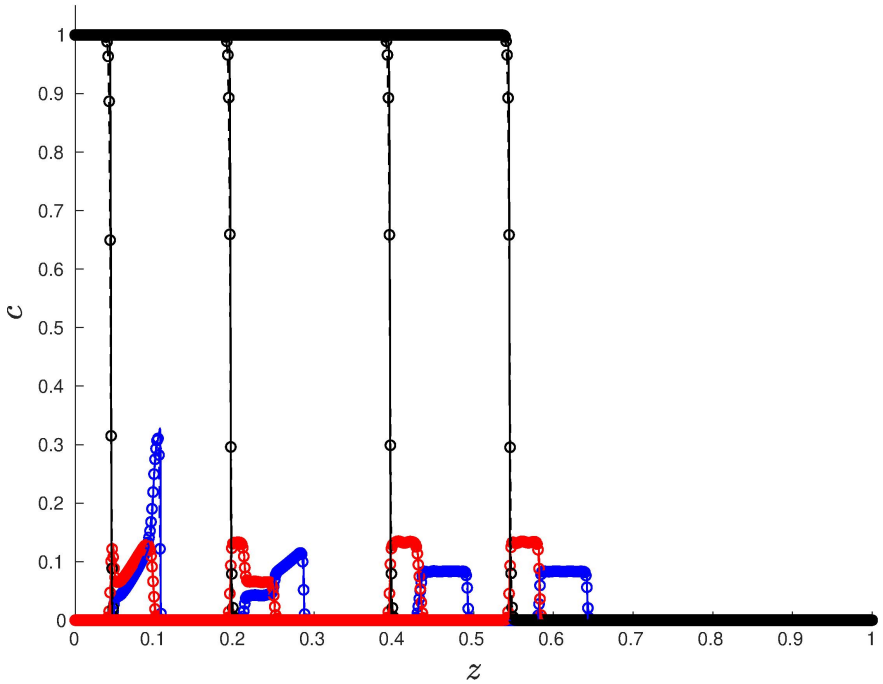
- Initial empty column: $c_i(x, 0) = 0 \, \forall x \in (0, 1), i = 1, 2, 3$.

Same $\nu = 1$, different D_a, $c^{\text{disp}} = 1$

Solution for $\Delta x = \frac{1}{800}, \nu = 1$ (Langmuir isotherm) at times $T = 1, 4, 8, 11$ (remember $x = 0 \equiv$ top of column)



$D_a = 0$



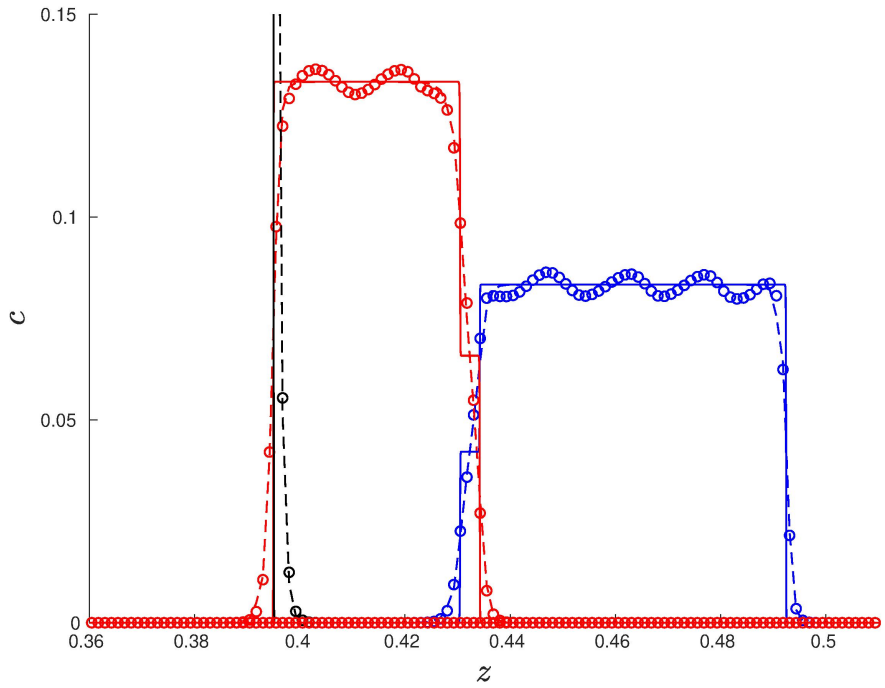
$D_a = 10^{-5}$

CMP-UPW5 ($\circ$) CHR-UPW5 ($--$) reference ($-$)

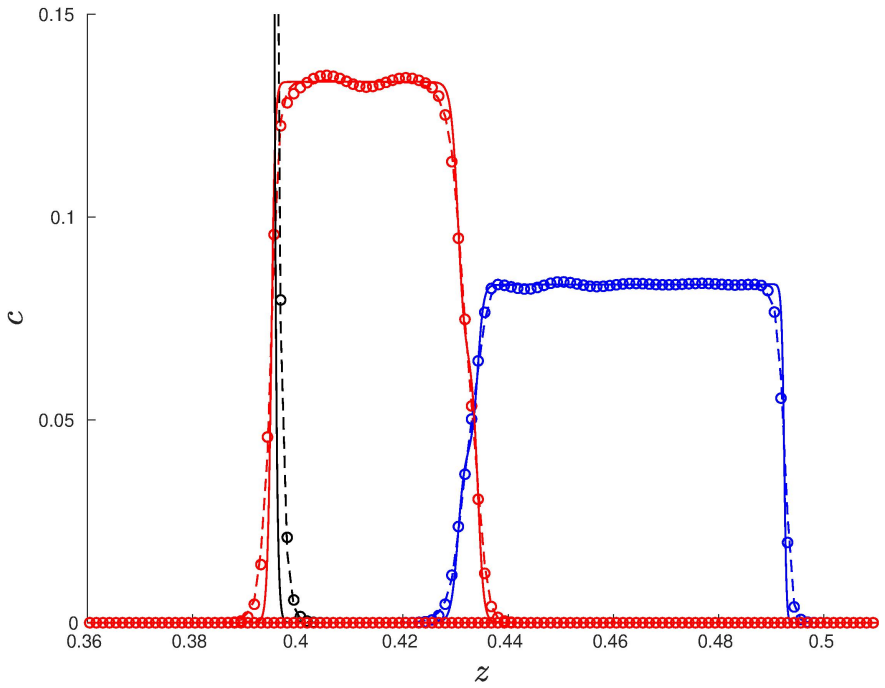
First component, second component, **third component (displacer)**

Same $\nu = 1$, different D_a, $c^{\text{disp}} = 1$

Zoom $T = 8$ (smoother for larger D_a): **isotachic train (square pulses)**



$D_a = 0$



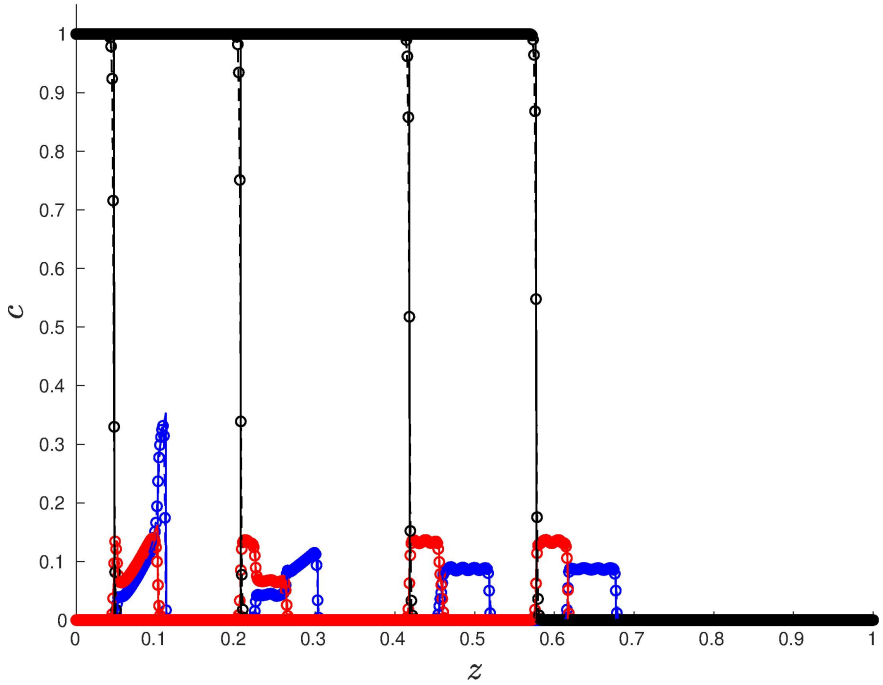
$D_a = 10^{-5}$

CMP-UPW5 ($\circ$) CHR-UPW5 ($--$) reference ($-$)

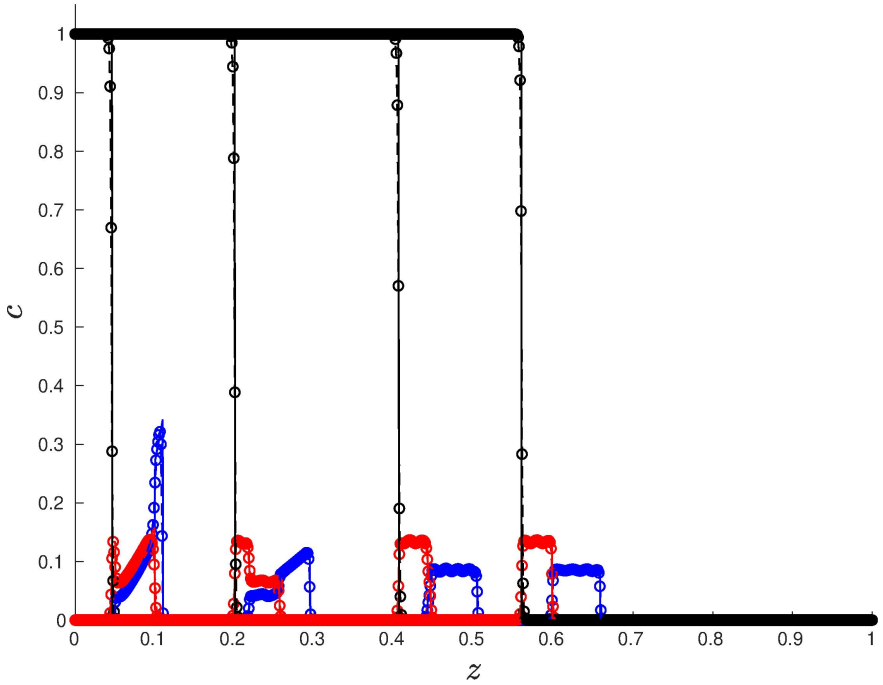
First component, second component, **third component (displacer)**

Same $D_a = 10^{-6}$, different ν, $c^{\text{disp}} = 1$

Solution for $\Delta x = \frac{1}{800}, D_a = 10^{-6}$ at times $T = 1, 4, 8, 11$



$\nu = 0.9$



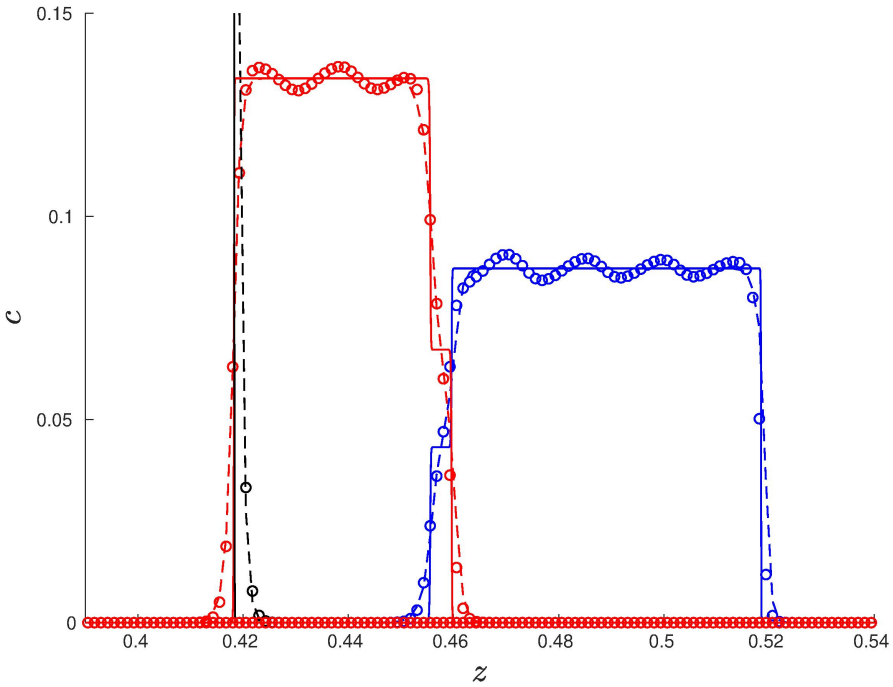
$\nu = 0.95$

CMP-UPW5 ($\circ$) CHR-UPW5 ($--$) reference ($-$)

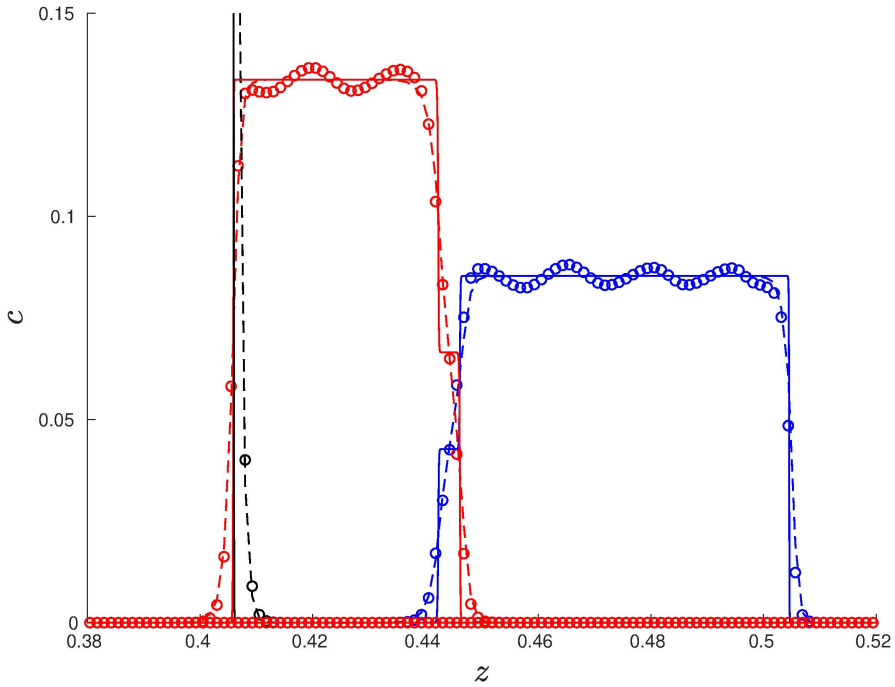
First component, second component, **third component (displacer)**

Same $D_a = 10^{-6}$, different ν, $c^{\text{disp}} = 1$

Zoom $T = 8$ (faster displacement for lower ν)



$\nu = 0.9$



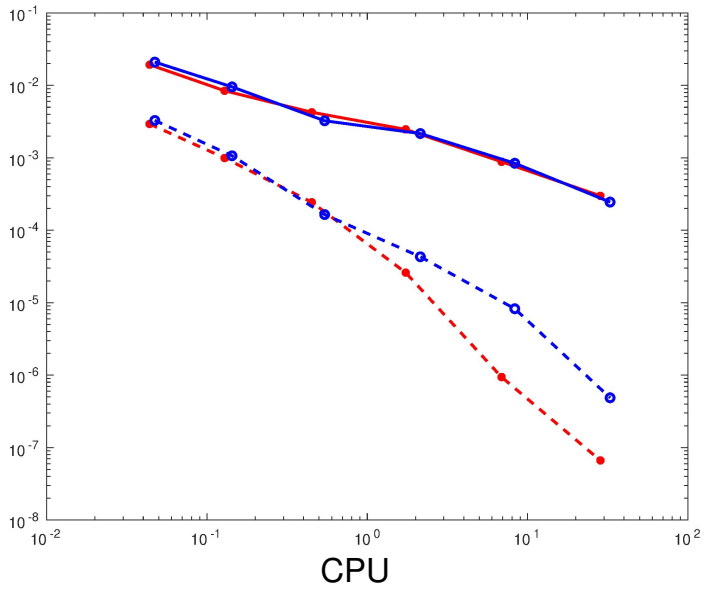
$\nu = 0.95$

CMP-UPW5 ($\circ$) CHR-UPW5 ($--$) reference ($-$)

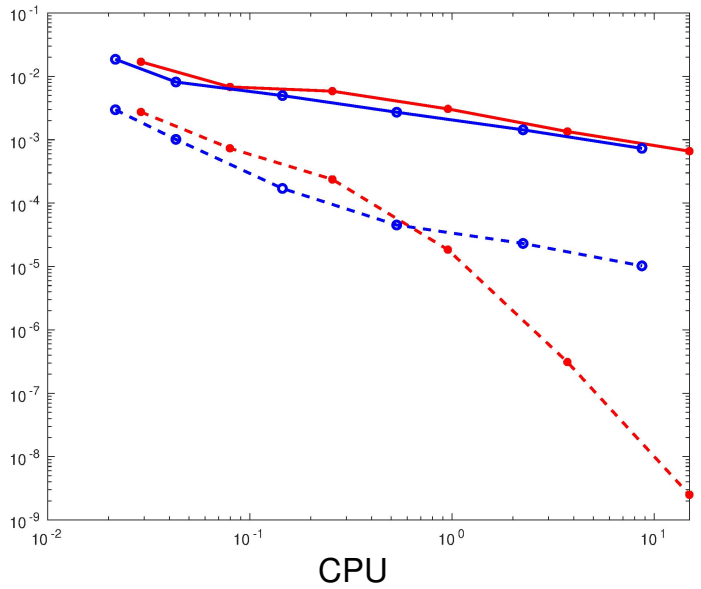
First component, second component, **third component (displacer)**

Efficiency

Efficiency comparison (approximate L^1 errors vs. CPU time) of CHR-UPW5 $(*-)$ and CMP-UPW5 $(\circ-)$ schemes for $T = 8$



$\nu = 0.9,\ D_a = 10^{-5}$

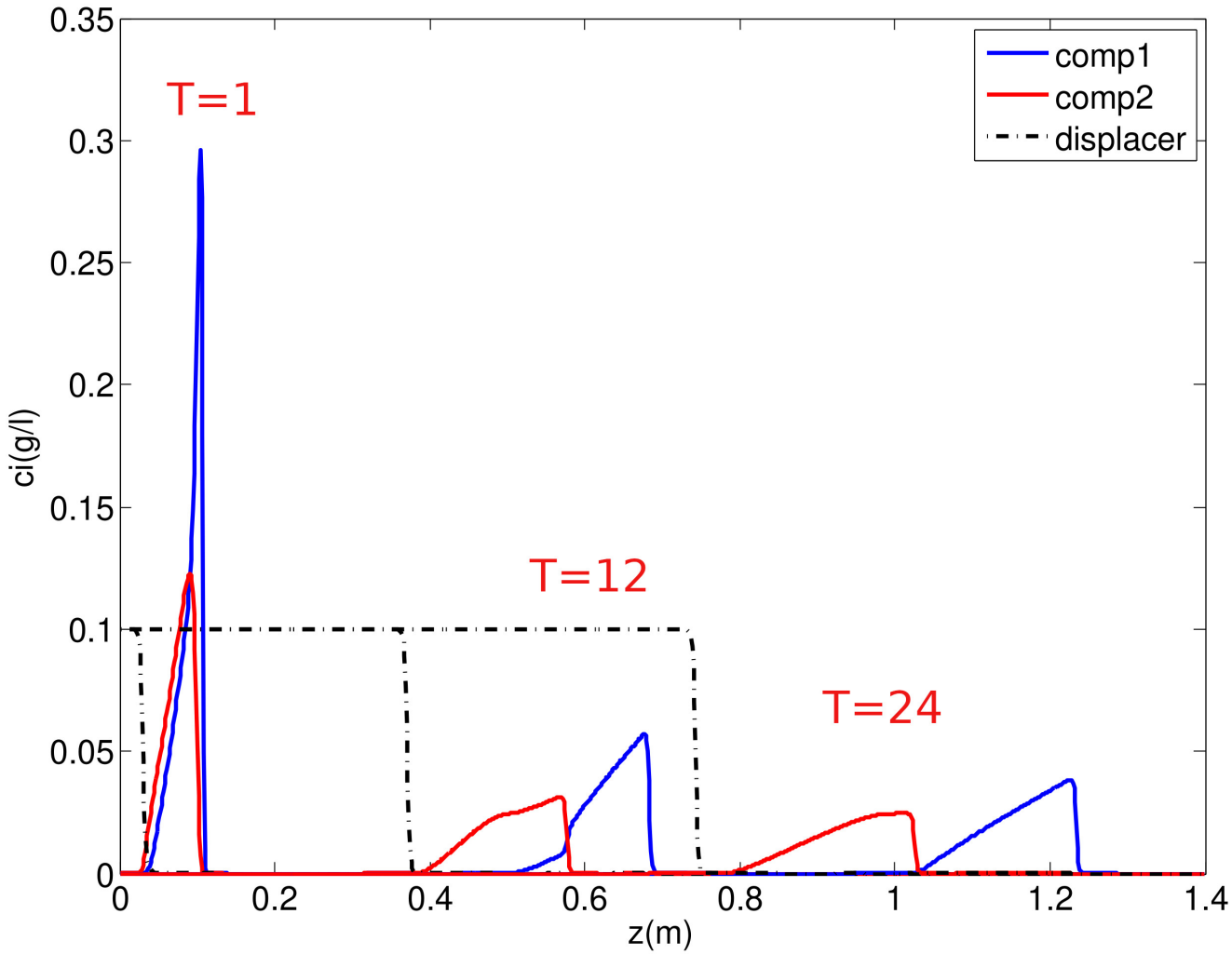


$\nu = 1,\ D_a = 0$

- Solid lines for approximate L^1 error.
- $\mathcal{O}(1)$ errors at shocks dominate: discard 2% largest errors as outliers and compute approximate L^1 error with the rest (dashed lines).

$\nu = 1, D_a = 10^{-5}, c^{\text{disp}} = 0.1$

Not enough displacer concentration $\Rightarrow$ no isotachic train (square pulses)



Outline

Conclusions

- Extended conservative formulation of EDM to generalized Langmuir-type adsorption isotherms.
- Used numerical fluxes with high-order reconstructions of local characteristic fluxes to improve smearing and oscillations near the high gradients formed in the solutions.
- Shown IMEX schemes with characteristic-based convective fluxes may be competitive with respect to component-wise alternatives.
- Need to perform more experiments.

Outline

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