Modeling species transport inside mesopores of catalytic washcoated monoliths for emission control

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Spatially-resolved modeling enables optimal design of catalytic monolith reactors for emission control!

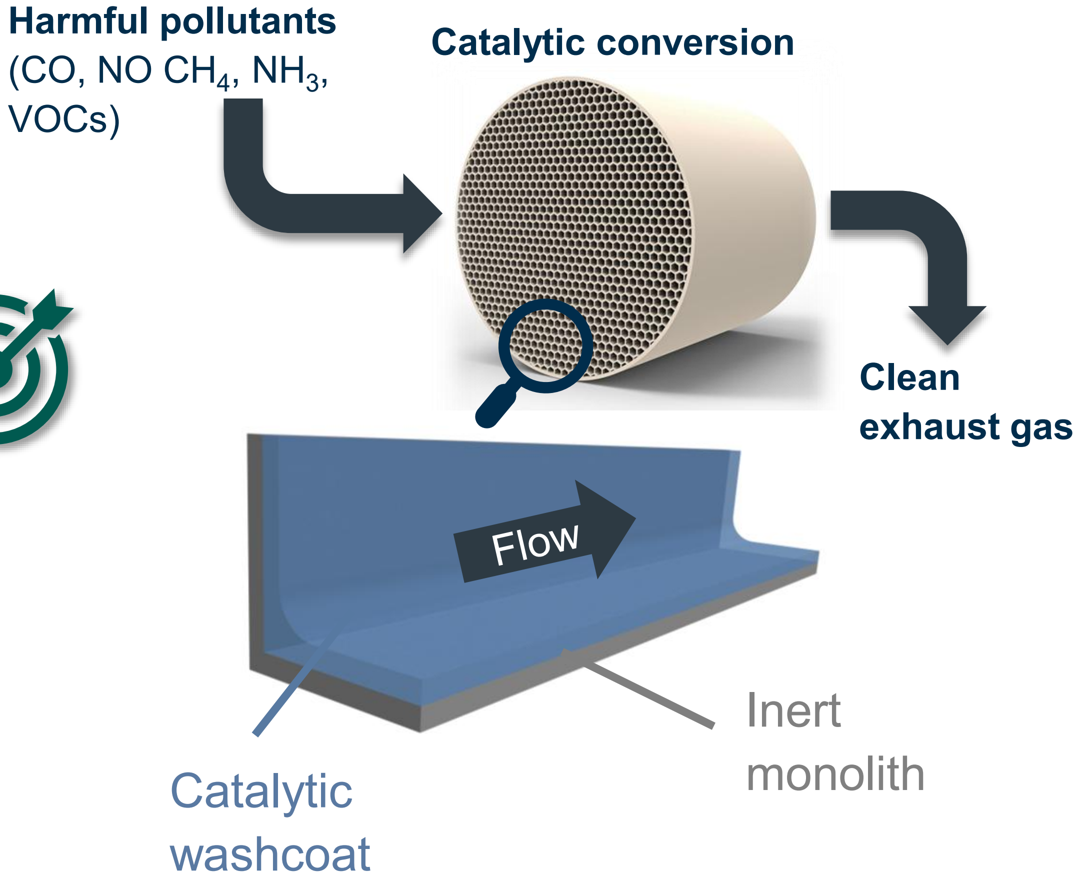
Motivation:

- Improved emission control (EC) systems essential for the transformation to a greener industry
- Reduced performance of catalytic monolith reactors due to heat and mass transport limitations

Goal:

- Better understanding of the interplay of chemical reaction and transport phenomena to improve monolith and washcoat design
- Tracking the way from the bulk to the active site
- Developing a spatially resolved, hierarchical multiscale model
- Model based optimization of monolith and washcoat design

Catalytic monolith reactors for EC :



Harmful pollutants
(CO, NO CH_4, NH_3, VOCs)

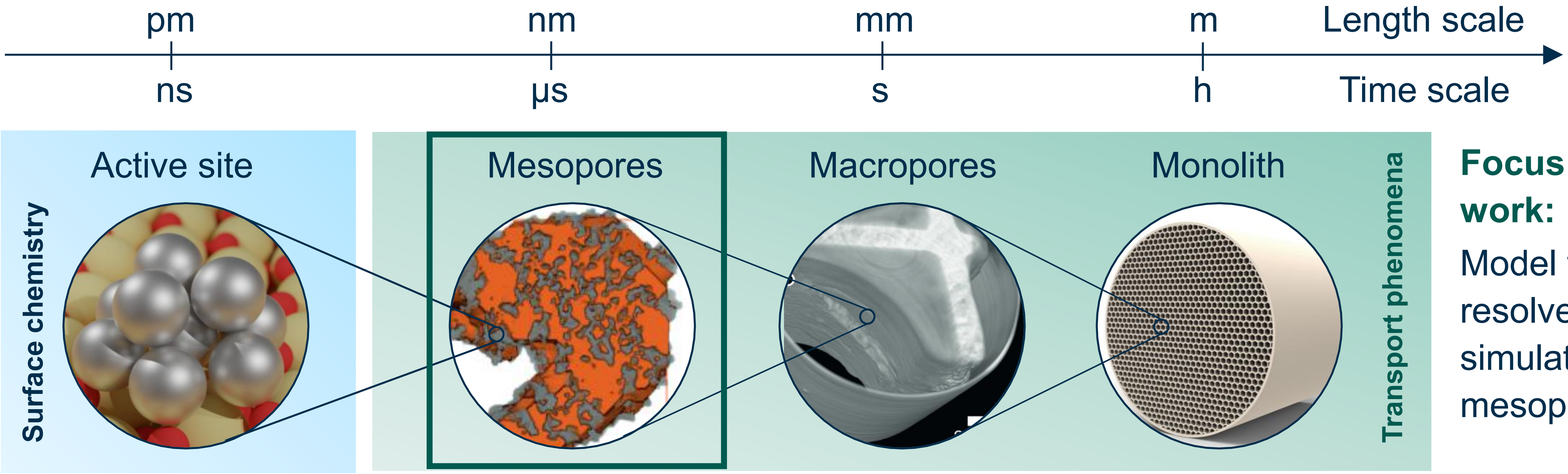
Catalytic conversion

Clean exhaust gas

Inert monolith

Catalytic washcoat

Catalytic monoliths are hierarchically structured and contain multiple scales!



Focus of this work:

Model for spatially resolved simulations at the mesopore scale!

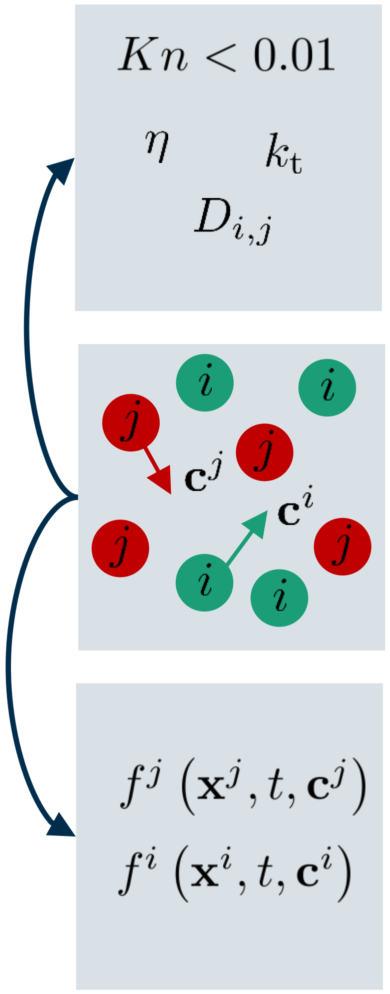
Predominant transport mechanism:

- Knudsen Diffusion
- Molecular Diffusion
- Forced convection

Model equation:

- **Kinetic Boltzmann equation**
- **Navier-Stokes-Fourier equations**

Continuum assumption breaks down in pore-resolved simulations of mesoporous systems!



Continuum models (Navier-Stokes-Fourier equations)

Describing transport in terms of transport coefficients

mean free path

$$Kn_i = \frac{\lambda_i}{L}$$

characteristic length

Kinetic Boltzmann equation

Describing evolution of the distribution function f in space and time for every molecule

Transport mechanism in mesoporous washcoat:

$0.01 < Kn_i < 2.00$ $\quad 10\,\mathrm{nm} < (L = d_\mathrm{p}) < 200\,\mathrm{nm}$

- Multicomponent diffusion (no forced convection)
- Diffusion is affected by molecule-molecule and molecule-wall collisions
- Transition regime between Knudsen and molecular diffusion (since characteristic length is small)

Continuum assumption breaks down and Navier-Stokes-Fourier equations cannot describe transport within the porous catalyst

Model needs to be based on kinetic Boltzmann equation

Recent advances in catalyst synthesis and characterization allows catalyst design at mesopore scale!

Recent advances in experimental methods enables to measure and modify the pore structure:

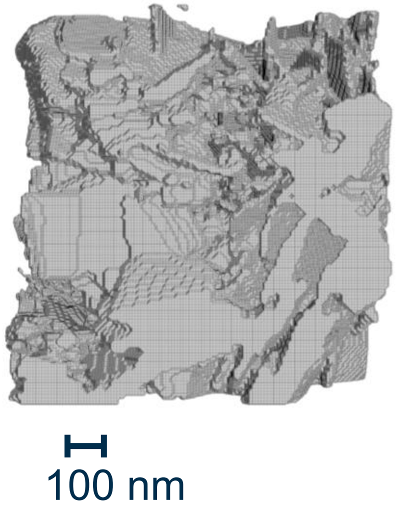
Spatial information by high resolution X-ray [1]:

- Morphology (3D geometry of the porous catalyst)
- Location of active sites (chemical imaging)

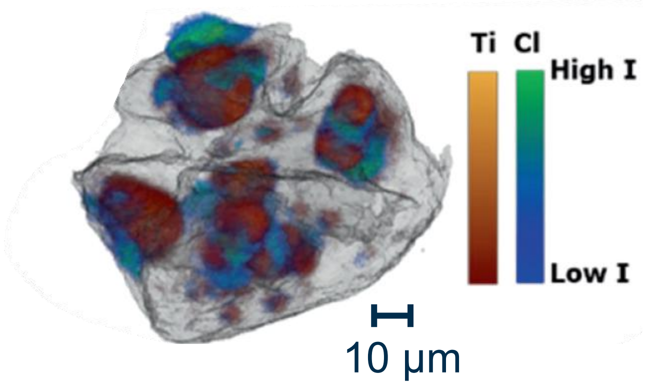
Pulsed field gradient NMR [3]:

- Measuring self diffusion in meso-porous media

Nanotomogram of a VPO catalyst for selective oxidation [2]



Chemical imaging of a Ziegler-Natta catalyst particle [1]



[1] Das et al. (2022) *Chem. Ing. Tech.*, 94, 11, 1591-1610.
[2] Gao et al. (2021*) Sci. Adv*., 7, 24, eabf6971.
[3] Kärger et al. (2021), *Adsorption*, 27, 3, 453-484.

Simulating **transport in a multicomponent mixture** coupled with **surface reaction** in **spatially resolved mesopores** based on **kinetic Boltzmann equation**.

The kinetic Boltzmann equation

Boltzmann equation from the total derivative of the distribution function with respect to time:

$$\mathbb{C}\left(f\right) = \frac{df}{dt}$$

$$\mathbb{C}\left(f\right) = \left(\frac{\partial f}{\partial t}\right)\frac{dt}{dt} + \left(\frac{\partial f}{\partial x_\alpha}\right)\frac{dx_\alpha}{dt} + \left(\frac{\partial f}{\partial c_\alpha}\right)\frac{dc_\alpha}{dt}$$

$$\frac{\partial f}{\partial t} + c_\alpha \frac{\partial f}{\partial x_\alpha} + \cancel{g_\alpha \frac{\partial f}{\partial c_\alpha}} = \mathbb{C}\left(f\right)$$

Neglecting external forces

Evolution in time

Movement in physical space

$$\frac{\partial f}{\partial t} + c_\alpha \frac{\partial f}{\partial x_\alpha} = \mathbb{C}\left(f\right)$$

Collision operator: Change due to molecule interactions

…or shorter:

$$\partial_t f + c_\alpha \partial_{x_\alpha} f = \mathbb{C}\left(f\right)$$

Multicomponent case: For gas mixtures the equation needs to be defined for each component *i*

$$\frac{\partial f^i}{\partial t} + c^i_\alpha \frac{\partial f^i}{\partial x_\alpha} = \mathbb{C}\left(f^i \dots f^n\right)$$

What’s there? Methods for solving the Boltzmann equation

Direct **S**imulation **M**onte **C**arlo (DSMC)

- \- Computationally intensive especially for dense gases as used in catalysis

Chapman-**E**nskog expansion (CE):

- \+ Results in Euler equation (0 order expansion) and Navier-Stokes-Fourier equation (1st order expansion) in continuum limit
- \- Results in Burnett/ super-Burnett equation beyond continuum limits, which are hard to solve [4]

Moment methods:

Quadrature **B**ased **M**oment **M**ethod (QBMM):

- \+ Computationally efficient calculation using FV mesh to solve moment transport equations

Available code:

No open-source or commercial QBMM code available for solving kinetic Boltzmann equation of multicomponent mixtures

Developing a **1D** and **2D** model to test if **QBMM** can describe **multicomponent diffusive transport** in the **continuum limit** and **transmission regime**

[4] Struchtrup, Macroscopic transport equations for rarefied gases, Springer, 2005.

Moments of the distribution function and the 1D moment transport equations

Definition of moments

General: 3D

Moments:

$$M_0 = m \int f d\mathbf{c},\ M_{1,\alpha} = m \int c_\alpha f d\mathbf{c}$$

$$M_{2,\alpha,\beta} = m \int c_\alpha c_\beta f d\mathbf{c},\ M_{3,\alpha,\beta,\gamma} = m \int c_\alpha c_\beta c_\gamma f d\mathbf{c}$$

to be continued…

with m as the molecule mass

Central moments:

Replacing the particle velocity with the relative velocity $\bar{c}$ and dividing with M_0 results in the central moments C

$$\bar{c}_\alpha = c_\alpha - v_\alpha$$

with the mean velocity v_α

Per definition: $C_0 = 1, \quad C_{1,\alpha} = 0$

Simplified: 1D

Moments up to order k:

$$M_k = m \int f c^k dc$$

Central moments up to order k:

$$C_k = \frac{m}{M_0} \int f\,(c - v)^k\, dc$$

Relation between central moments and moments

$$k \geq 2 : C_k = \sum_{i=0}^{k} \binom{k}{i} \left(\frac{M_1}{M_0}\right)^{k-i} \frac{M_i}{M_0}.$$

Some moments can be related to macroscopic properties!

Macroscopic properties of component *i*:

Density:

$$\rho_i = M_0^i$$

Momentum density:

$$\rho_i v_{i,\alpha} = M_{1,\alpha}^i$$

Velocity:

$$v_{i,\alpha} = \frac{M_{1,\alpha}^i}{M_0^i}$$

Partial pressure:

3D: $p_i = \frac{1}{3} m \int \bar{c}_{i,\alpha}^2 f d\mathbf{c}$

1D: $p_i = M_0^i C_2^i$

Total energy density:

3D: $\rho_i e_i = \frac{1}{2} m_i \int c_{i,\alpha}^2 f d\mathbf{c}$

1D: $\rho_i e_i = \frac{1}{2} M_2^i$

Internal Energy density:

3D: $\rho_i u_i = \frac{1}{2} m_i \int \bar{c}_{i,\alpha}^2 f d\mathbf{c}$

1D: $\rho_i u_i = \frac{1}{2} M_0^i C_2^i$

Kinetic Energy density:

$$\rho_i \upsilon_i = \frac{M_0^i}{2} \left(\frac{M_{1,\alpha}^i}{M_0^i} \right)^2 = \frac{\rho_i}{2} \left(v_{i,\alpha} \right)^2$$

Macroscopic properties of the mixture:

Density:

$$\rho = \sum_i \rho_i$$

Velocity:

$$v_\alpha = \sum_i \left(\rho_i v_{i\alpha} \right) \rho^{-1}$$

Pressure:

$$p = \sum_i p_i$$

Total Energy density:

$$\rho e = \sum_i \rho_i e_i$$

Kinetic Energy density:

$$\rho \upsilon = \frac{\rho}{2} \left(v_\alpha \right)^2$$

Internal energy density:

$$\rho u = \rho e - \rho \upsilon$$

Temperature:

$$T = \frac{2u\overline{m}}{dk} \qquad \overline{m} = \frac{\sum_i \rho_i}{\sum_i \frac{\rho_i}{m_i}}$$

with d as dimension (1,2,3)

Deriving 1D moment transport equations from Boltzmann equation

Multiplying the 1D Boltzmann equation with the molecule mass and the particle velocity and subsequently integration results in the moment transport equations of component i:

$$\left.\begin{aligned}\partial_t M_0^i + \partial_x M_1^i &= \Omega^0,\\ \partial_t M_1^i + \partial_x M_2^i &= \Omega^1,\\ &\vdots\\ \partial_t M_{2n}^i + \partial_x M_{2n+1}^i &= \Omega^{2n}\end{aligned}\right\}$$

In vector form:

$$\partial_t \mathbf{M}_{2n}^i + \partial_x \mathbf{F}(\mathbf{M}_{2n}^i) = \mathbf{\Omega_{2n}^i}$$

with:

$$\mathbf{M}_{2n}^i = \left(M_0^i, M_1^i \ldots . M_{2n}^i\right)^T$$

$$\mathbf{F}\left(\mathbf{M}_{2n}^i\right) = \left(M_1^i, M_0^i \ldots . M_{2n+1}^i\right)^T$$

Unclosed moment flux vector describing advection of the moment

$$\mathbf{\Omega_{2n}^i} = \left(\Omega_0^i, \Omega_1^i \ldots . \Omega_{2n}^i\right)^T$$

Moments of the collision operator

Moment transport equations should form a **hyperbolic system** of 1st order PDEs!

Tasks:

- Closure of the unclosed flux vector (Quadrature!)
- Modeling the collision operator and calculate its moments
- Numerical solution which guarantees **realizability** of the moments

Kinetic model for the collision operator and its moments

Kinetic models: A simplification of the collision operator

Best known and widely used kinetic model: **B**hatnagar-**G**ross-**K**rook model (BGK)

Concept of the BGK:

Collision relaxes moments towards equilibrium

One component:

$$\mathbb{C} = \frac{1}{\tau}\left(f^{\mathrm{eq}} - f\right)$$

Binary mixture:

$$\mathbb{C}^0 = \frac{1}{\tau_{0,0}}\left(f^{\mathrm{eq},0,0} - f^0\right) + \frac{1}{\tau_{0,1}}\left(f^{\mathrm{eq},0,1} - f^0\right)$$

Multicomponent mixture with N species:

$$\mathbb{C}^i = \sum_j^N \frac{1}{\tau_{i,j}}\left(f^{\mathrm{eq},i,j} - f^i\right)$$

with the collision time τ and the equilibrium distribution $f^{\mathrm{eq},i,j}$

Limits [4,5]:

- Reflects moments of the hard spere model only up to 2nd order
- Poor approximation if distribution function is far away from equilibrium

Moments of the collision operator:

k^{th}order moment of the collision operator results from the moments of f and $f^{eq,i,j}$:

$$\Omega_k^i = \sum_j^N \frac{1}{\tau_{i,j}}\left(M_k^{\mathrm{eq},i,j} - M_k^i\right)$$

[4] Struchtrup, Macroscopic transport equations for rarefied gases, Springer, 2005.
[5] Marchisio, Fox, Computational Models for Polydisperse and Multiphase Systems, Cambridge, 2013.

Compute equilibrium distribution and its moments from the moment of the distribution function!

In the 1D case equilibrium distribution is defined as an univariant Gaussian:

$$f^{\mathrm{eq},i,j}\left(c_i\right) = \frac{\rho_i}{\sqrt{2\pi\sigma_{i,j}}} \exp\left(-\frac{\left(c_i - v_{i,j}\right)^2}{2\sigma_{i,j}}\right)$$

Calculation of ρ_i, $v_{i,j}$ and $\sigma_{i,j}$ as well as the collision time τ from moments of f and the particle mass m and diameter d according to Marchisio and Fox [5]:

- Only the moments of f from 0th to 2nd order and 2nd order central moment are required
- For $i = j$ moments of f^i and d_i are needed
- For $i \neq j$ moments of f^i, f^j and d_i, d_j, m_i, m_j are needed

Moments of $f^{eq,i,j}$:

Using ρ_i, $v_{i,j}$ and $\sigma_{i,j}$ moments of the Gaussian equilibrium distribution can be calculated analytical (e.g., via standardized moments of a Gaussian, moment generating function)

➡ $\mathbf{\Omega^{i}_{2n}} = \mathrm{func}\left(\mathbf{M}^{i}_{2n}\ldots\mathbf{M}^{N}_{2n}\right)$

➡ No additional unclosed moments

[5] Marchisio, Fox, Computational Models for Polydisperse and Multiphase Systems, Cambridge, 2013.

Numerical implementation of BGK model: Evolution of moments due to collision

Neglecting moment advection results in 0D moment transport equation:

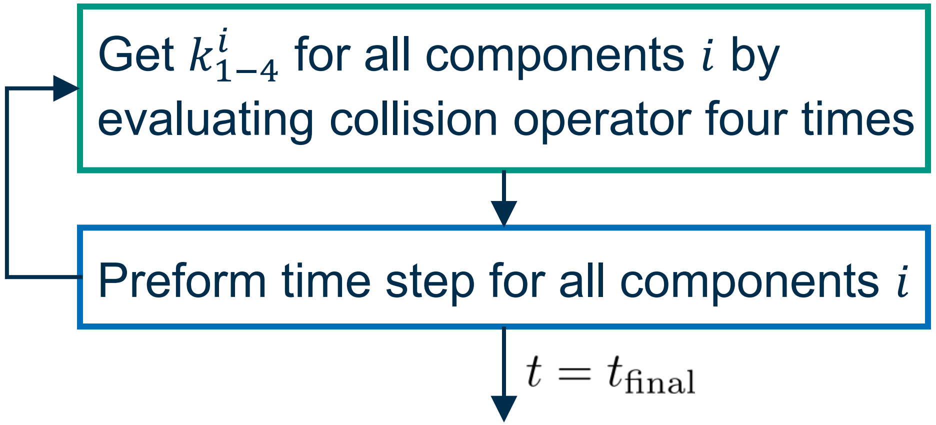
$$\partial_t \mathbf{M}_{2n}^{i} = \sum_{j}^{N} \frac{1}{\tau_{i,j}} \left(\mathbf{M}_{2n}^{\mathrm{eq},i,j} - \mathbf{M}_{2n}^{i} \right)$$

For $N = 1$ analytical solution is straightforward:

$$\mathbf{M}_{2n,t+\Delta t} = \mathbf{M}_{2n,t} \exp\left(\frac{-\Delta t}{\tau}\right) + \left(1 - \exp\left(\frac{-\Delta t}{\tau}\right)\right) \mathbf{M}_{2n,t}^{\mathrm{eq}}$$

For $N > 1$ analytical solution or higher order moments becomes complicated

➡ Numerical solution using an explicit 4th order Runge Kutta (**RK4**) method



Get k_{1-4}^{i} for all components i by evaluating collision operator four times

Preform time step for all components i

$t = t_{\mathrm{final}}$

$$\mathbf{M}_{2n,t+\Delta t}^{i} = \mathbf{M}_{2n,t}^{i} + \frac{\Delta t}{6} + \left(\mathbf{k}_1^{i} + 2\mathbf{k}_2^{i} + 2\mathbf{k}_3^{i} + \mathbf{k}_4^{i} + \right)$$

$$\mathbf{k}_1^{i} = \boldsymbol{\Omega}_{\mathbf{2n}}^{\mathbf{i}} \left(\mathbf{M}_{2n,t}^{i\,\mathrm{to}\,N}\right)$$

$$\mathbf{k}_2^{i} = \boldsymbol{\Omega}_{\mathbf{2n}}^{\mathbf{i}} \left(\mathbf{M}_{2n,t}^{i\,\mathrm{to}\,N} + \frac{\Delta t}{2}\mathbf{k}_1^{i}\right)$$

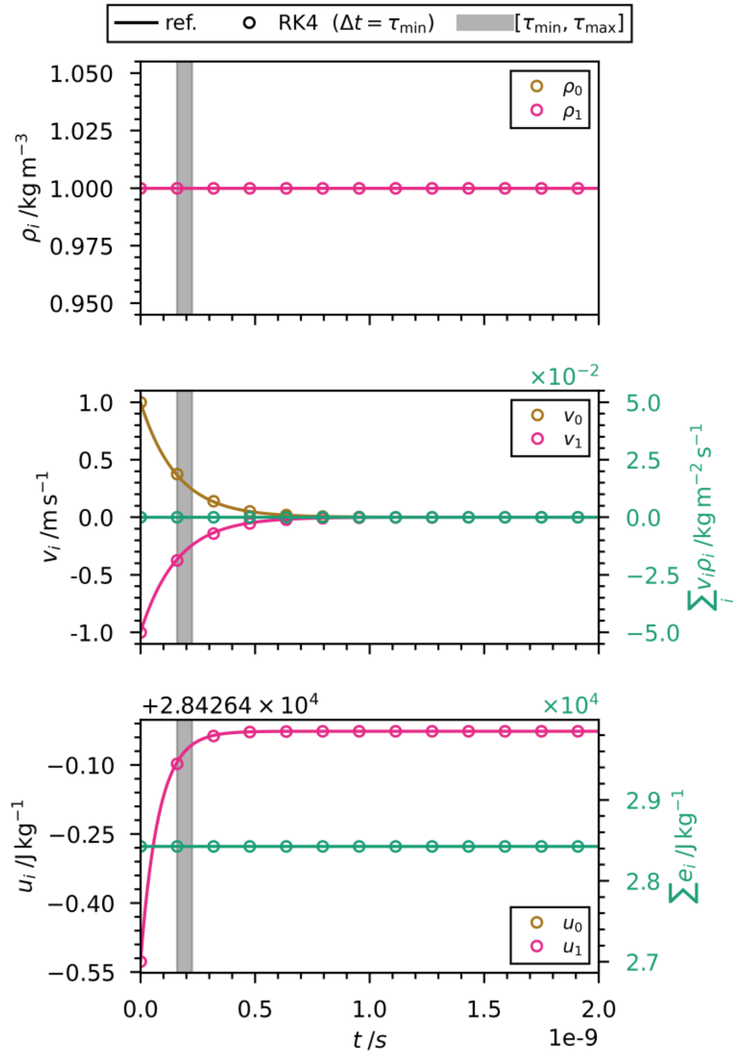
$$\mathbf{k}_3^{i} = \boldsymbol{\Omega}_{\mathbf{2n}}^{\mathbf{i}} \left(\mathbf{M}_{2n,t}^{i\,\mathrm{to}\,N} + \frac{\Delta t}{2}\mathbf{k}_2^{i}\right)$$

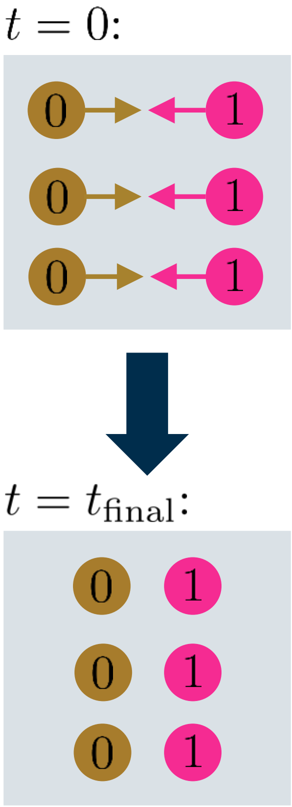
$$\mathbf{k}_4^{i} = \boldsymbol{\Omega}_{\mathbf{2n}}^{\mathbf{i}} \left(\mathbf{M}_{2n,t}^{i\,\mathrm{to}\,N} + \Delta t\, \mathbf{k}_3^{i}\right)$$

$$\boxed{\Delta t = \min\left(\tau_{i,j}\right)}$$

BGK collision model is conservative!

$\rho_0 = \rho_1,\ v_0 \neq v_1$:

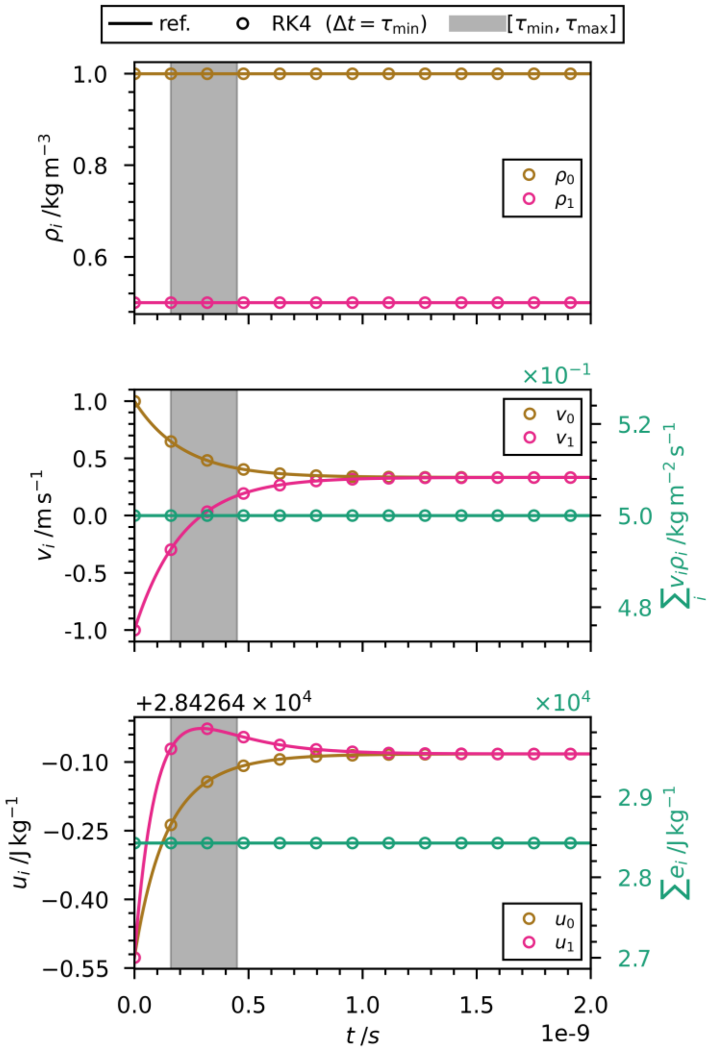


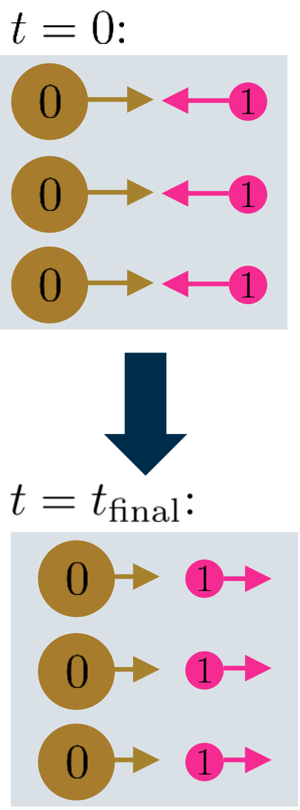


$t = 0$:

$t = t_{\text{final}}$:

$\rho_0 \neq \rho_1,\ v_0 \neq v_1$:





$t = 0$:

$t = t_{\text{final}}$:

Closure of the moment flux vector and moment advection

Quadrature to close the flux vector

Goal:

Calculating the unknown moment M^i_{2n+1} from the known moments $\boldsymbol{M}^i_{2n}$

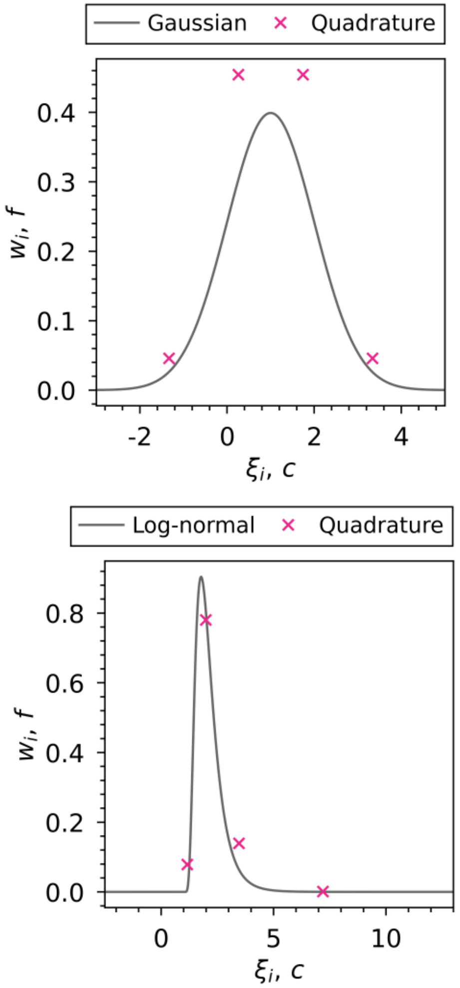
Concept:

- Approximation of the moments by quadrature:

$$M_k = \sum_i^N \omega_i \xi_i^k$$

- Calculating weights ω_i and abscissas ξ_i from the known moments (non-linear systems of equation) and calculate the unknown moment using the quadrature approximation

Four nodes quadrature:



Computation of the closure:

Relating the recurrence coefficient a_n and b_n of orthogonal polynomials to the moments enables fast closure calculation [5]

$$P_{n+1}(\xi) = (\xi - a_n)P_n(\xi) - b_n P_{n-1}(\xi) \quad n = 0, 1, 2...$$

[5] Marchisio, Fox, Computational Models for Polydisperse and Multiphase Systems, Cambridge, 2013.

Chebyshev algorithm enables direct calculation of the unclosed moment from recurrence coefficients [6]

Given moment set: $\mathbf{M}_{2n}^{i} = \left(M_0^i, M_1^i \ldots . M_{2n}^i\right)$

Calculating recurrence coefficients a_0 to a_{n-1} and b_0 to b_n from $\boldsymbol{M}_{2n}^{i}$ using **Chebyshev algorithm**

Using closure condition to calculate a_n: $a_n = \frac{1}{n} \sum_{k=0}^{n-1} a_k$

closure condition assuming Gaussian distribution **!**

Perform backward recurrence and calculate M_{2n+1}^i from a_0 to a_n and b_0 to b_n

reversed Chebyshev algorithm

Closed flux vector: $\mathbf{F}\left(\mathbf{M}_{2n}^{i}\right) = \left(M_1^i, M_2^i \ldots . M_{2n+1}^i\right)$

[6] Fox, Lauren (2022) *SIAM J. APPL. MATH.*, *82*, 2, 750-771.

Using Finite Volume Method to numerically solve moment advection

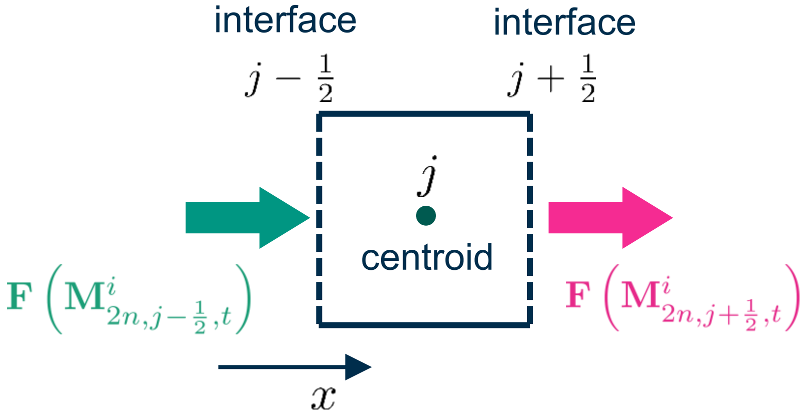
Neglecting collision results in the collisionless moment transport equation:

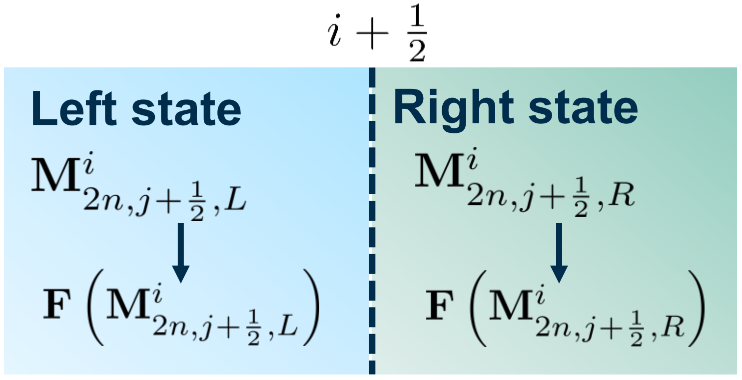
$$\partial_t \mathbf{M}_{2n}^i + \partial_x \mathbf{F}^i(\mathbf{M}_{2n}) = 0$$

Numerical implementation of the equation in Finite Volume Method (FVM):

$$\mathbf{M}_{2n,j,t+\Delta t}^i = \mathbf{M}_{2n,j,t}^i - \frac{\Delta t}{\Delta x}\left(\mathbf{F}\left(\mathbf{M}_{2n,j+\frac{1}{2},t}^i\right) - \mathbf{F}\left(\mathbf{M}_{2n,j-\frac{1}{2},t}^i\right)\right)$$

- Using Harten, Lax, van Leer (HLL) Riemann to calculate flux at the interface based on the left and right state of the interface
- Reconstruction of the left and right state at the interface from the centroids using a 2nd order **M**odified **U**pwind **S**cheme for **C**onservative **L**aw (MUSCL) with **minmod** slop limiter to prevent unrealizable moments





HLL: $\mathbf{F}\left(\mathbf{M}_{2n,j+\frac{1}{2}}^i\right)$

Reconstructed: $\mathbf{M}_{2n,j+\frac{1}{2},L}^i$, $\mathbf{M}_{2n,j+\frac{1}{2},R}^i$

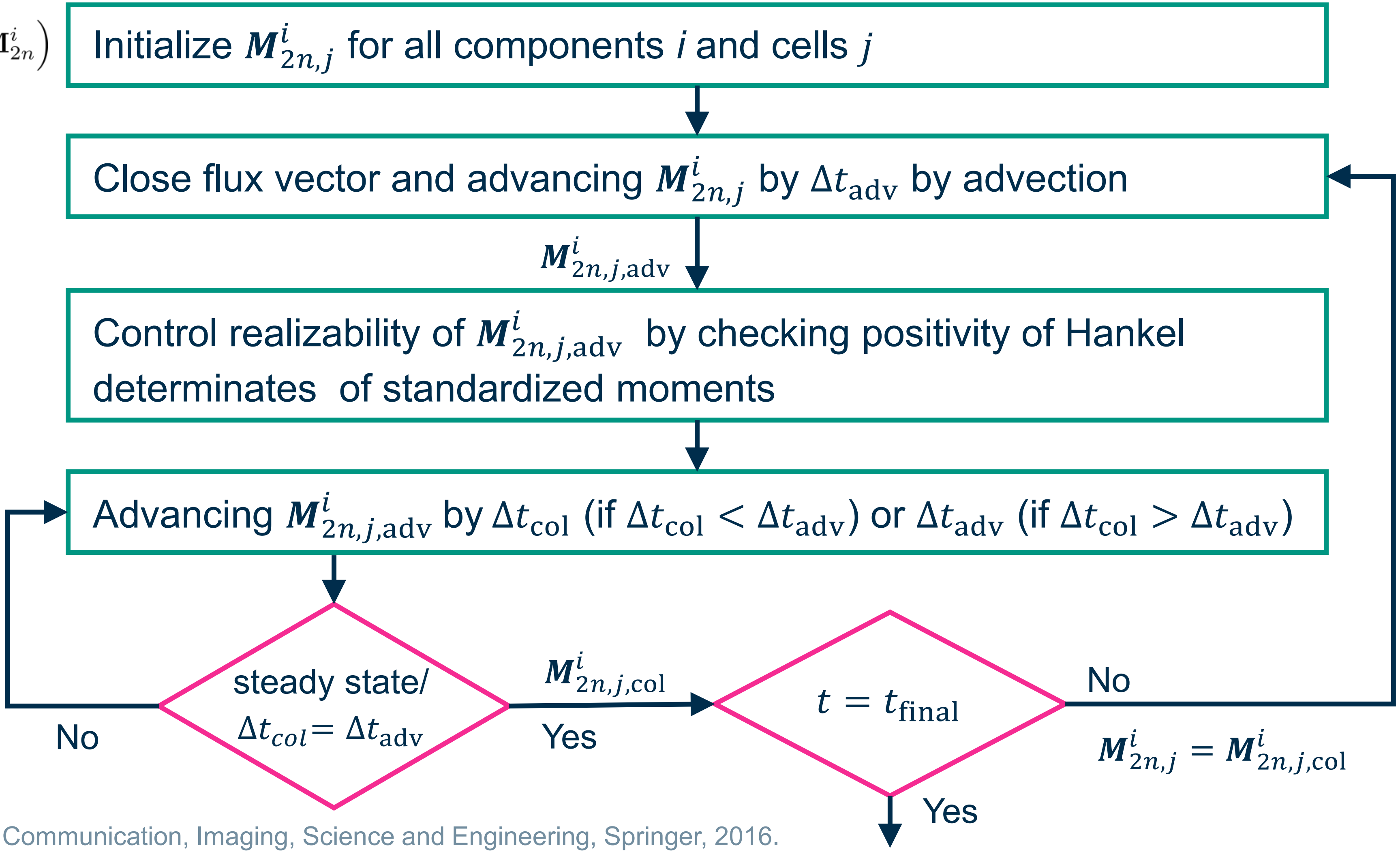
Put all together using operator splitting!

Operator splitting technique allows to evaluate moment advection and collision separately [9]!

$$\partial_t \mathbf{M}_{2n}^i + \partial_x \mathbf{F}^i(\mathbf{M}_{2n}) = \sum_j^N \frac{1}{\tau_{i,j}} \left(\mathbf{M}_{2n}^{\mathrm{eq},i,j} - \mathbf{M}_{2n}^i \right)$$

$$\partial_t \mathbf{M}_{2n}^i + \partial_x \mathbf{F}^i(\mathbf{M}_{2n}) = 0$$

$$\partial_t \mathbf{M}_{2n}^i = \sum_j^N \frac{1}{\tau_{i,j}} \left(\mathbf{M}_{2n}^{\mathrm{eq},i,j} - \mathbf{M}_{2n}^i \right)$$



Initialize $\boldsymbol{M}_{2n,j}^i$ for all components *i* and cells *j*

Close flux vector and advancing $\boldsymbol{M}_{2n,j}^i$ by Δt_{adv} by advection

Control realizability of $\boldsymbol{M}_{2n,j,\mathrm{adv}}^i$ by checking positivity of Hankel determinates of standardized moments

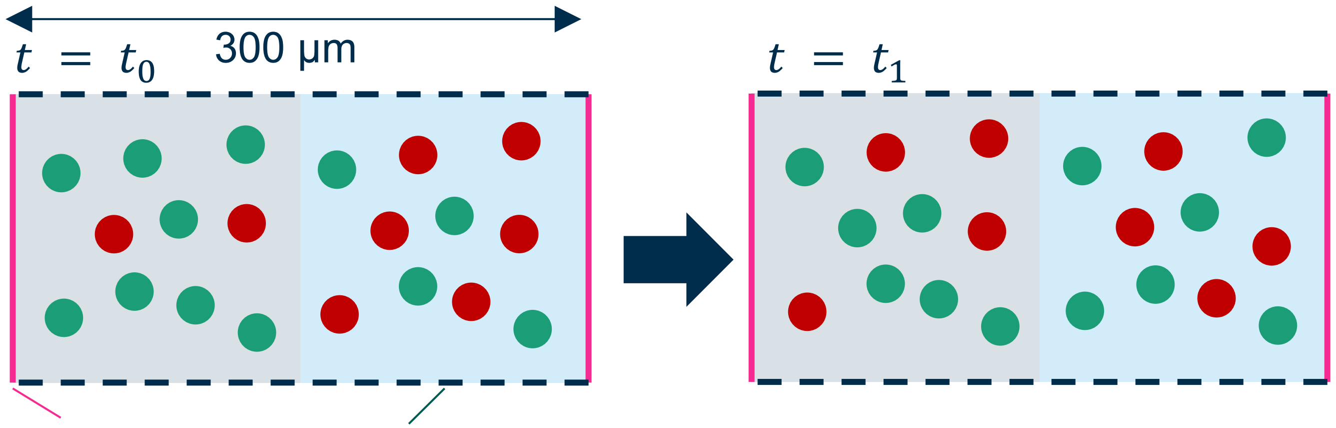
Advancing $\boldsymbol{M}_{2n,j,\mathrm{adv}}^i$ by Δt_{col} (if $\Delta t_{\mathrm{col}} < \Delta t_{\mathrm{adv}}$) or Δt_{adv} (if $\Delta t_{\mathrm{col}} > \Delta t_{\mathrm{adv}}$)

[9] Glowinski, Osher, Yin, Splitting Methods in Communication, Imaging, Science and Engineering, Springer, 2016.

Testing model and validation with continuum-model

Test case Diffusion in an infinitesimal slab

Setup:



Ideal gas, molecule diameters from Bird [10]

Moment initialization:

- $\boldsymbol{w}_{i,\mathrm{left}}$, $\boldsymbol{w}_{i,\mathrm{right}}$
- $T_{\mathrm{left}} = T_{\mathrm{right}}$, $p_{\mathrm{left}} = p_{\mathrm{right}}$ (constant overall number density)
- $\boldsymbol{v}_i = 0$

Using macroscopic properties to initialize moments assuming Gaussian distribution

Continuum model:

$$\delta_t \left(c\, \mathbf{y}_{n-1} \right) = \delta_x \dot{\mathbf{n}}_{n-1}$$

Solved by FVM

BC: $\delta_x \mathbf{y}_{n-1,x=0} = \delta_x \mathbf{y}_{n-1,x=L} = 0$

IC: Reflecting macroscopic initial condition of kinetic equation

Molar fluxes $\dot{\boldsymbol{n}}_{n-i}$ calculated using **Maxwell-Stefan model**

Binary diffusion coefficients $D_{i,j}$ from **1st order CE approximation** [10]:

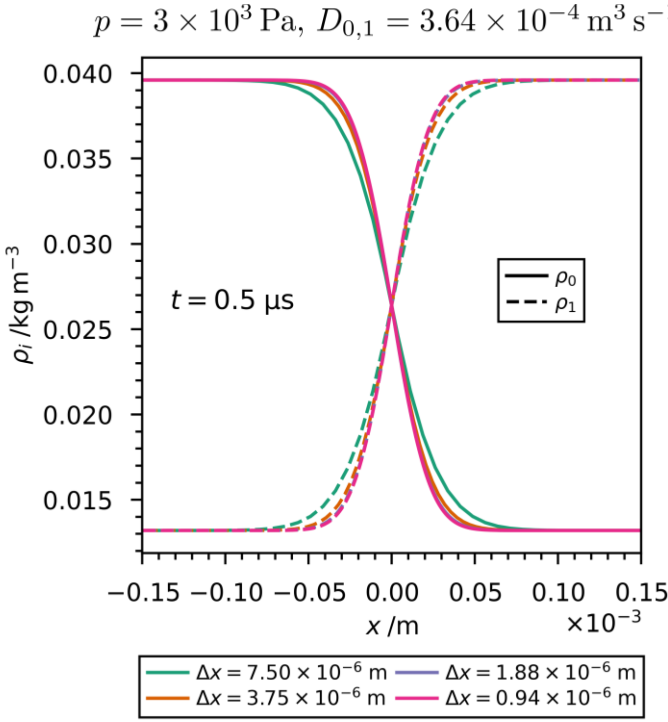
$$D_{i,j} = \frac{3\left(2\pi kT/m_{\mathrm{r}}\right)^{0.5}}{16\, n\, 0.5\left(d_i + d_j\right)}.$$

$$m_{\mathrm{r}} = \frac{m_i m_j}{m_i + m_j} \qquad n = \frac{p}{kT}$$

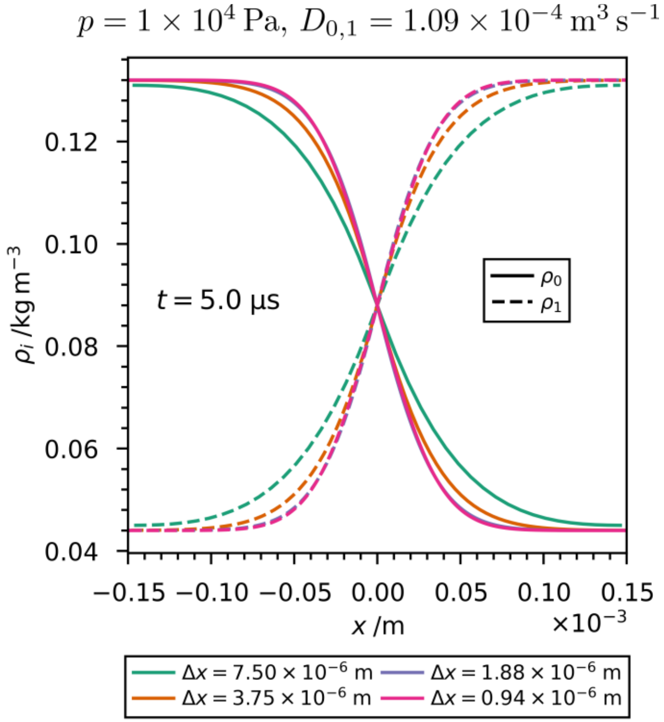
[10] Bird, Molecular gas dynamic and the direct simulation of gas flow, Oxford, 1994.

Second order MUSCL reconstruction enables mesh convergence at industrial relevant conditions!

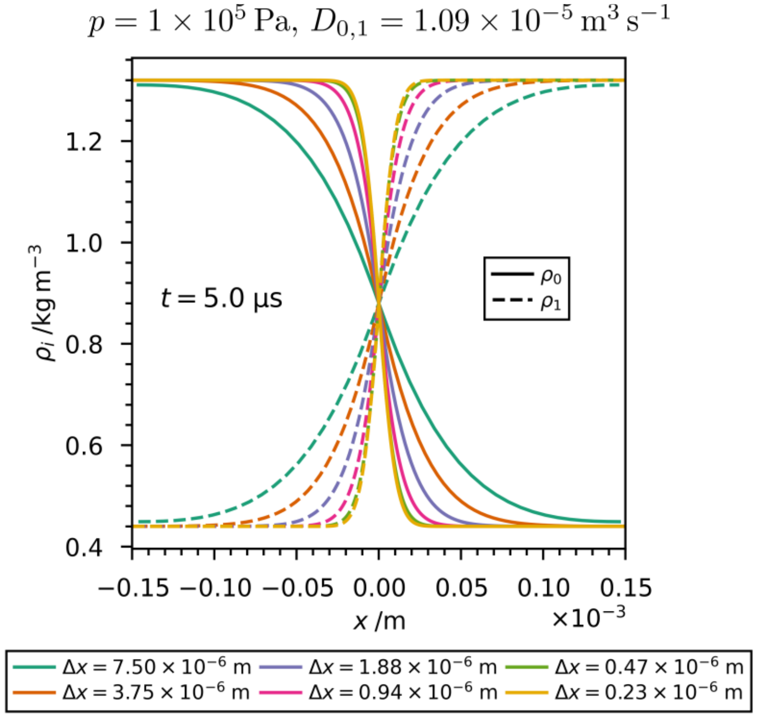
Self-diffusion of Argon at a temperature of 273 K and various pressures:



Convergence reached at $\Delta x = 3.75 \times 10^{-6}\ \mathrm{m}$



Convergence reached at $\Delta x = 1.88 \times 10^{-6}\ \mathrm{m}$



Convergence reached at $\Delta x = 0.47 \times 10^{-6}$

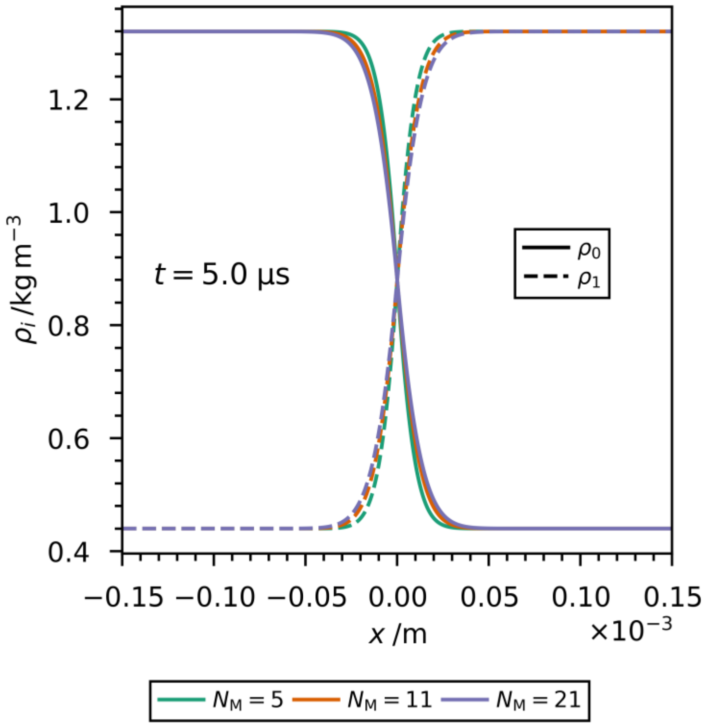
required resolution for mesh convergence

diffusion speed

Within continuum limit, the solution is less dependent on number of moments!

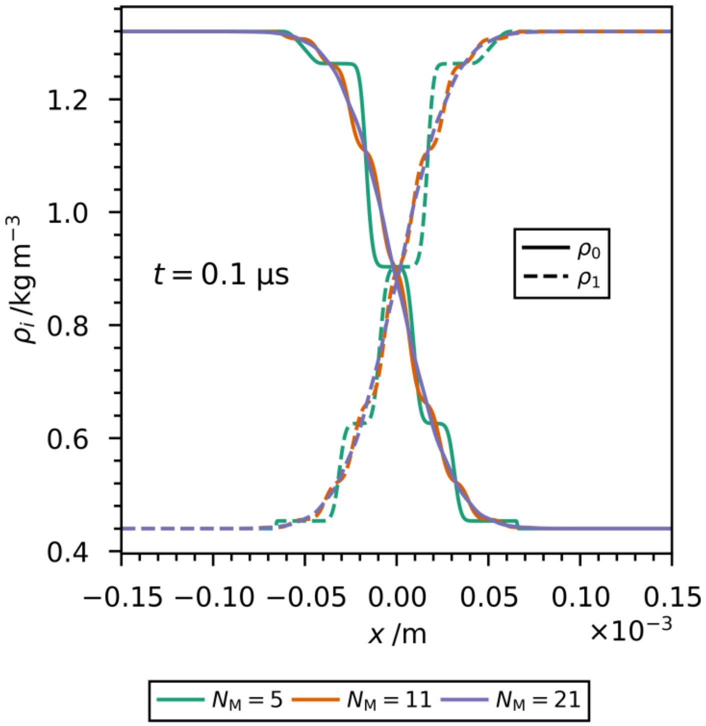
Self-diffusion of Argon at a temperature of 273 K and pressure of 10^5 Pa:

BGK collision operator



➡ Only small influence of the moment number

Collisionless ($\boldsymbol{\Omega}^i_{2n} = 0$), $\lambda \to \infty$, $\mathrm{Kn} \to \infty$

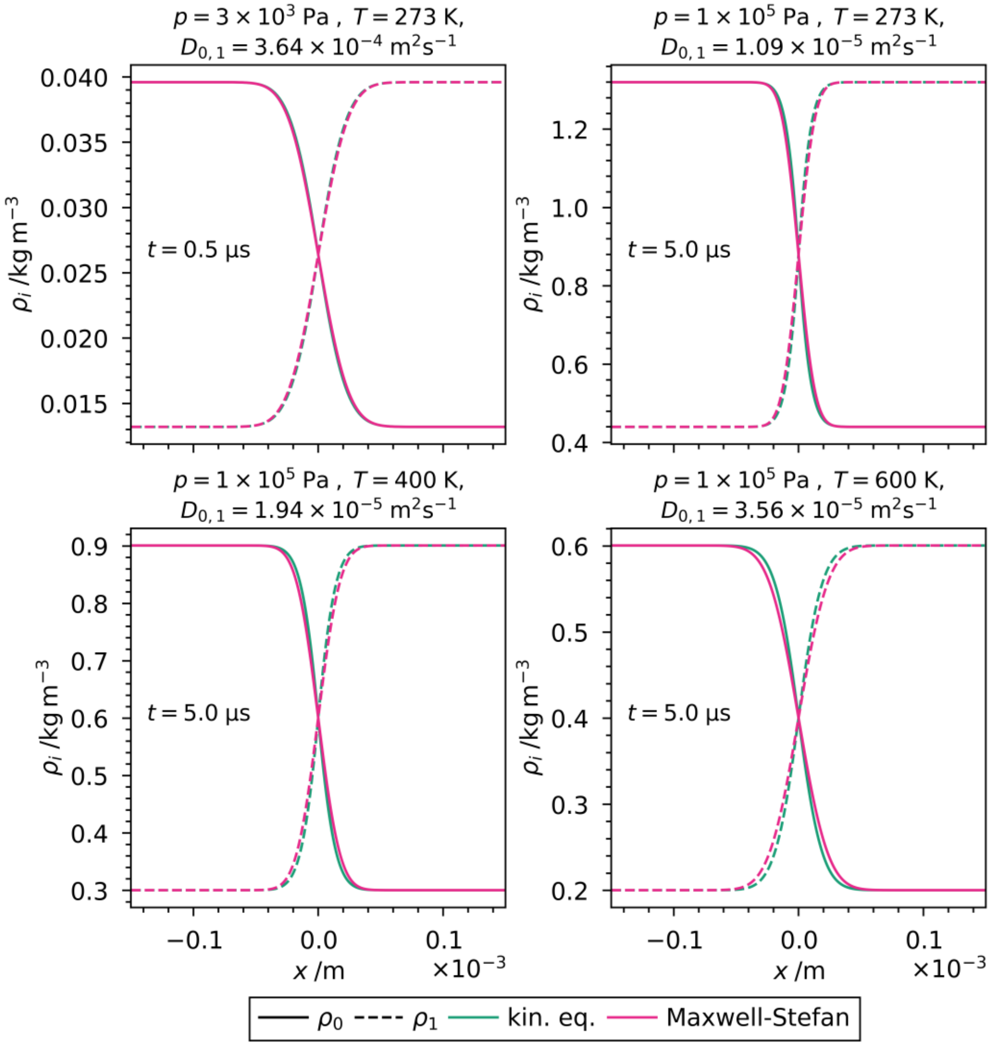


➡ Number of moments change partial density profiles

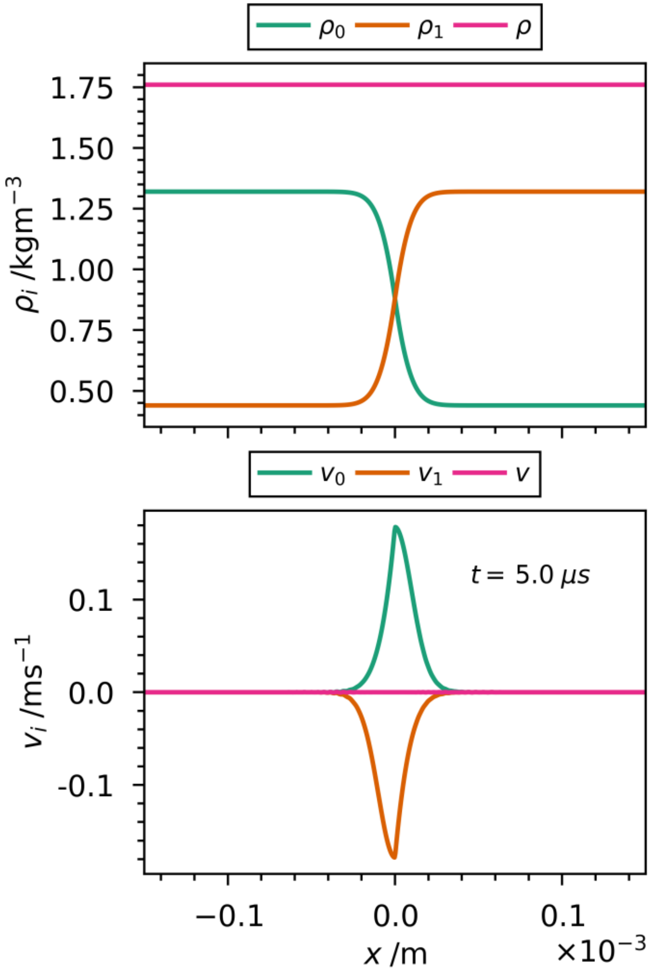
The **higher the Knudsen number** (the farther the distribution is away from a Gaussian), **the more moments are necessary** for a converged solution [4]

[4] Struchtrup, Macroscopic transport equations for rarefied gases, Springer, 2005.

Self diffusion Argon: Good agreement between kinetic equation and continuum model

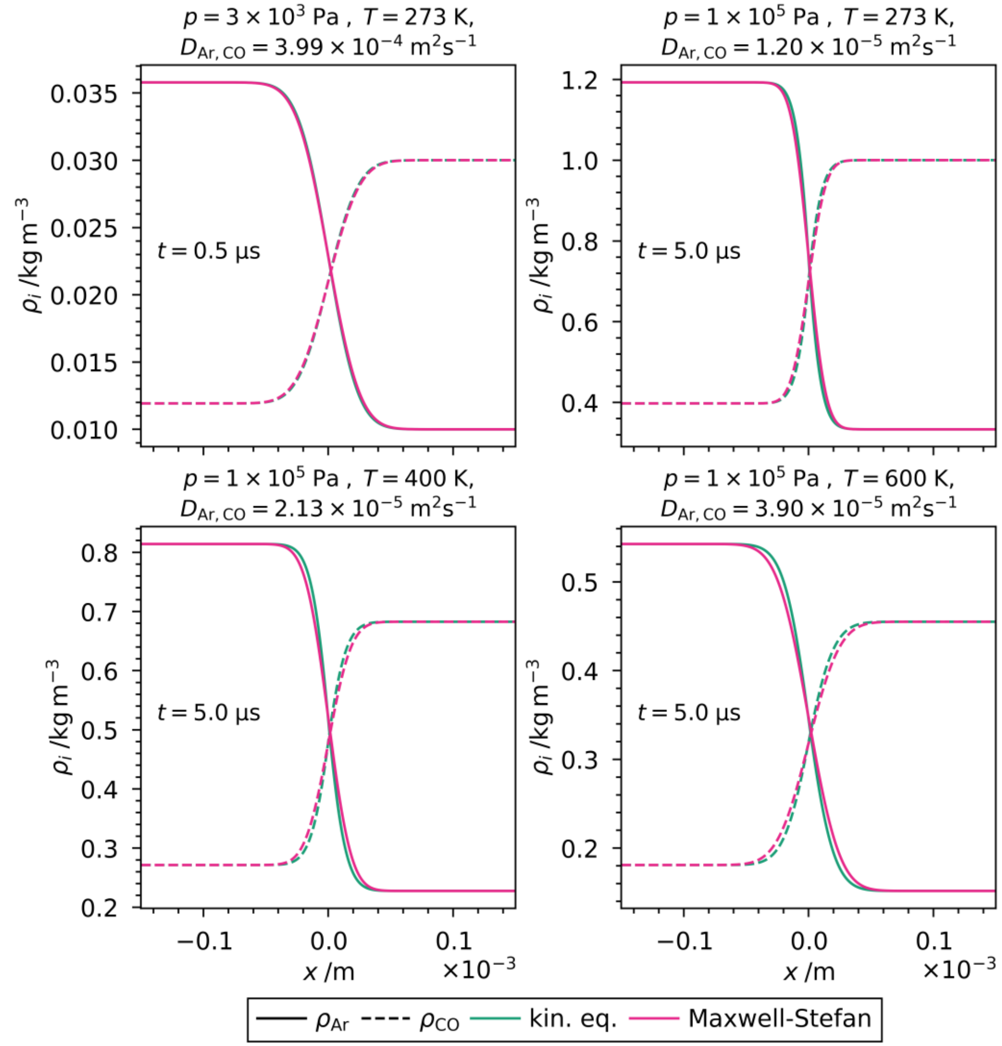


$p = 1 \times 10^5\,\mathrm{Pa},\ T = 273\,\mathrm{K}$:

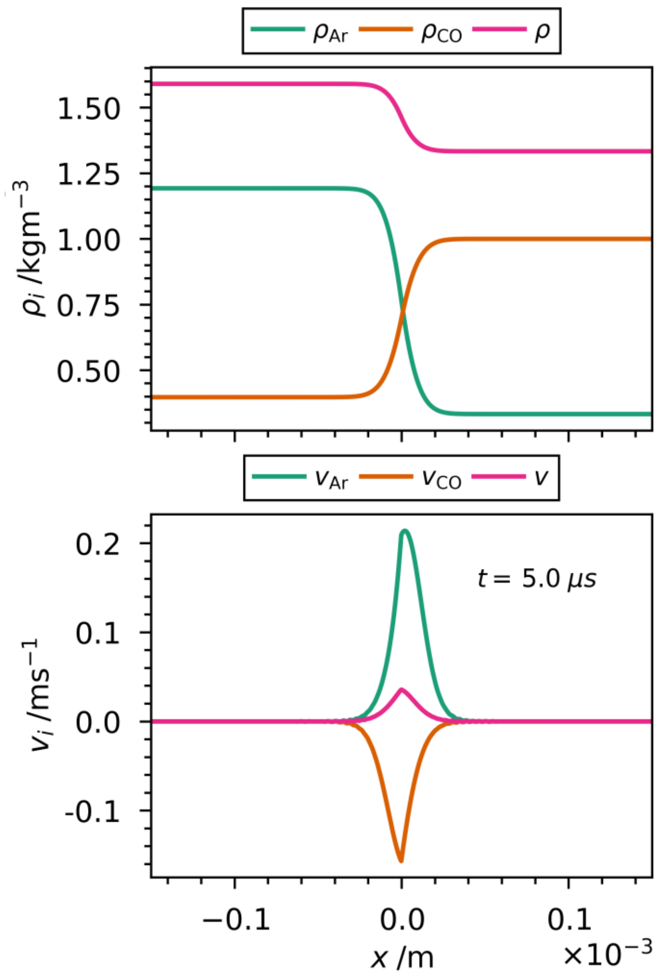


- Good agreement of kinetic equation and Maxwell-Stefan model for self diffusion of Argon
- Kinetic equation can describe the impact of temperature and pressure on diffusion over a wide range correctly

Good agreement between kinetic equation and continuum model for diffusion in a binary mixture!

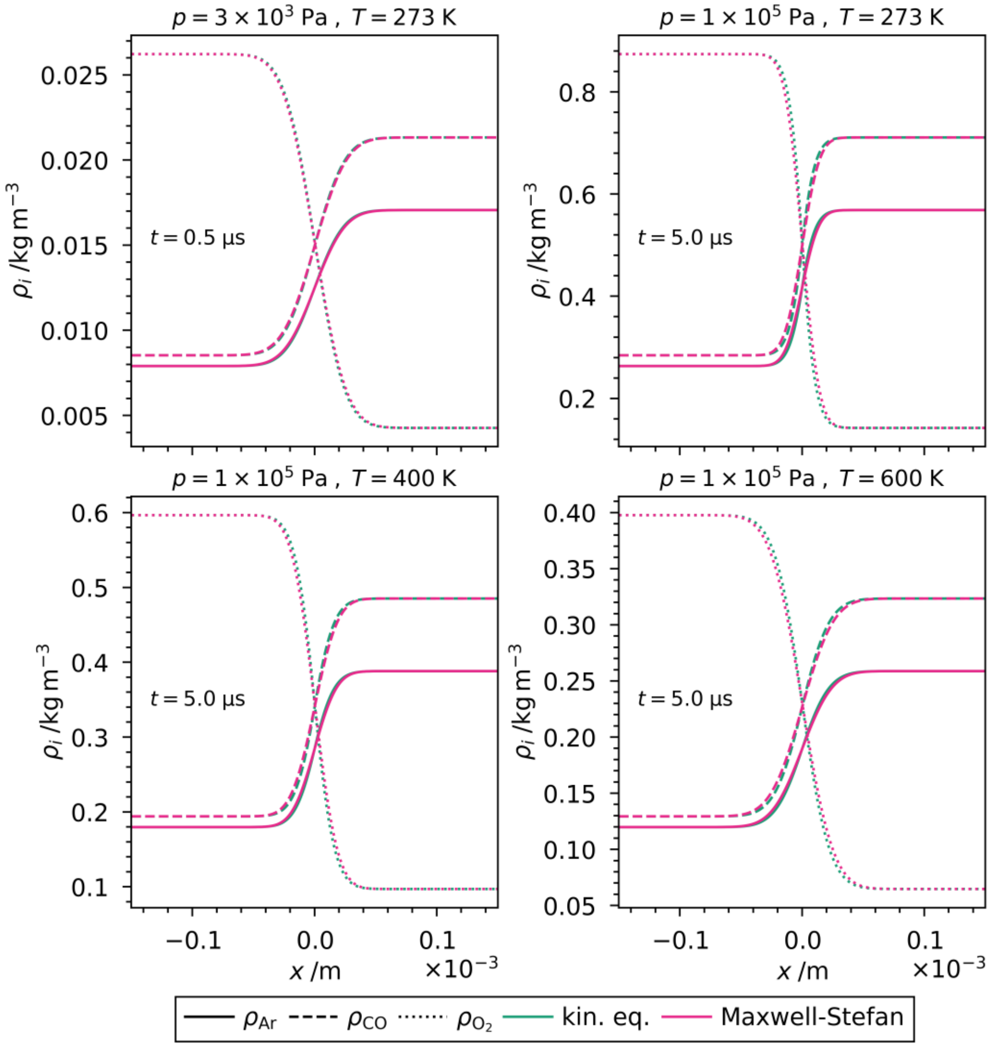


$p = 1 \times 10^5\,\mathrm{Pa},\ T = 273\,\mathrm{K}$:

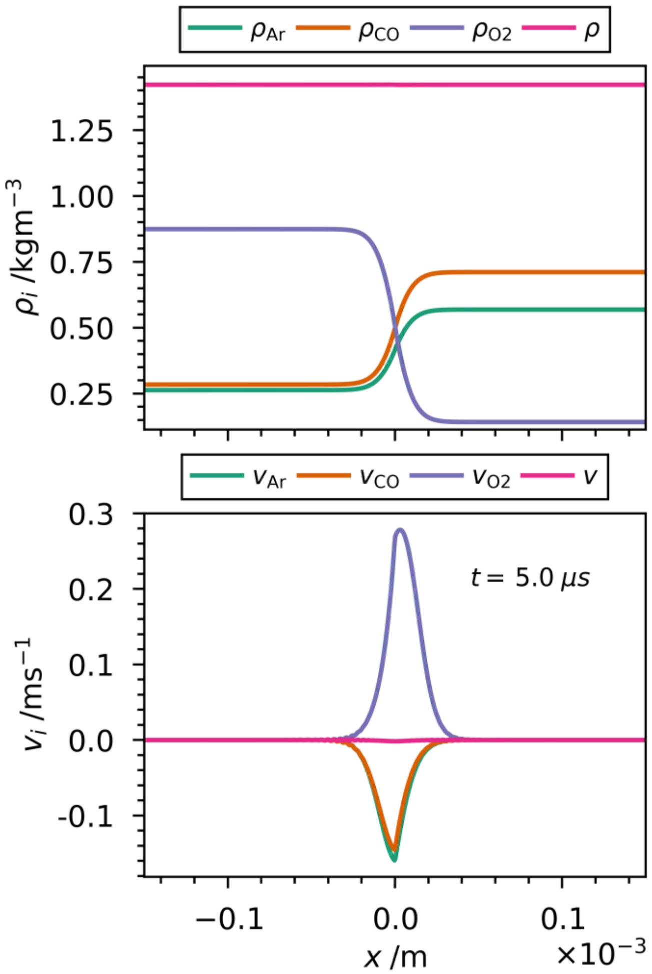


- Good agreement with Maxwell-Stefan diffusion model ✓
- Small numerical oscillation in 1st, 3rd order moment and 2nd order central moment at small times
- $v \neq 0$ due to different total densities at the left and right side

Kinetic equation is capable for simulation of multicomponent diffusion in the continuum limit!



$p = 1 \times 10^5\,\mathrm{Pa},\ T = 273\,\mathrm{K}$:



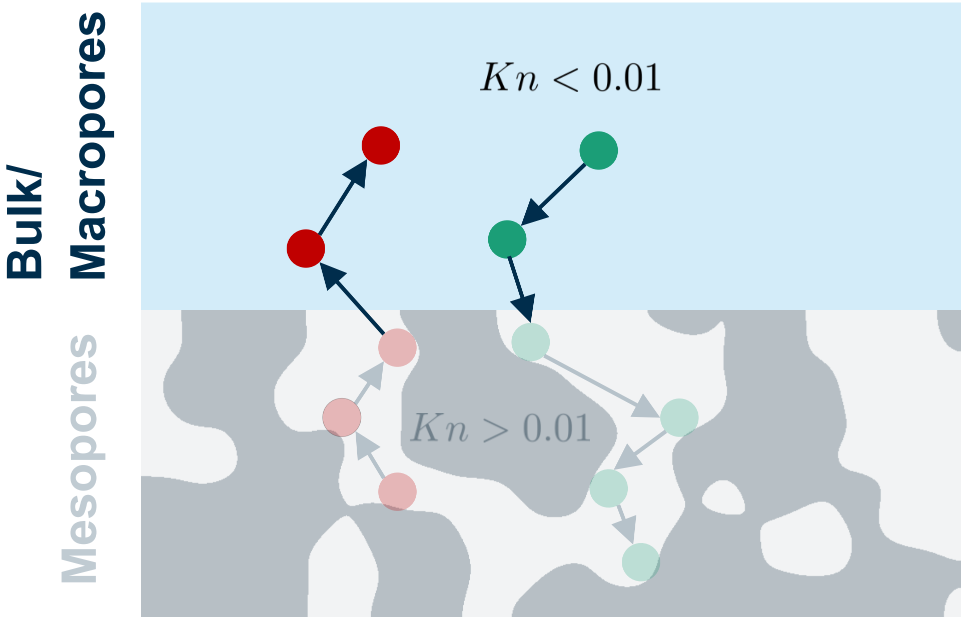
- Good agreement with Maxwell-Stefan diffusion model ✓
- Implemented model enables computation of diffusion in multicomponent mixture

Solving kinetic Boltzmann equation with QBMM can describe diffusive species transport in multicomponent mixtures

Summary

For the first time we showed: 1D kinetic equation with BGK collision model solved by **QBMM** using a **Chebyshev algorithm for closure** of the moment flux vector can describe **diffusive species transport in multicomponent mixtures** within the continuum limit (Maxwell-Stefan diffusion model) ✓

- Description of diffusion under industrial relevant conditions possible!
- In the **continuum limit a small number of moments** (5) results in an accurate solution
- Transport depends only on **molecule diameter** and **molecule mass**! No transport coefficients are required.

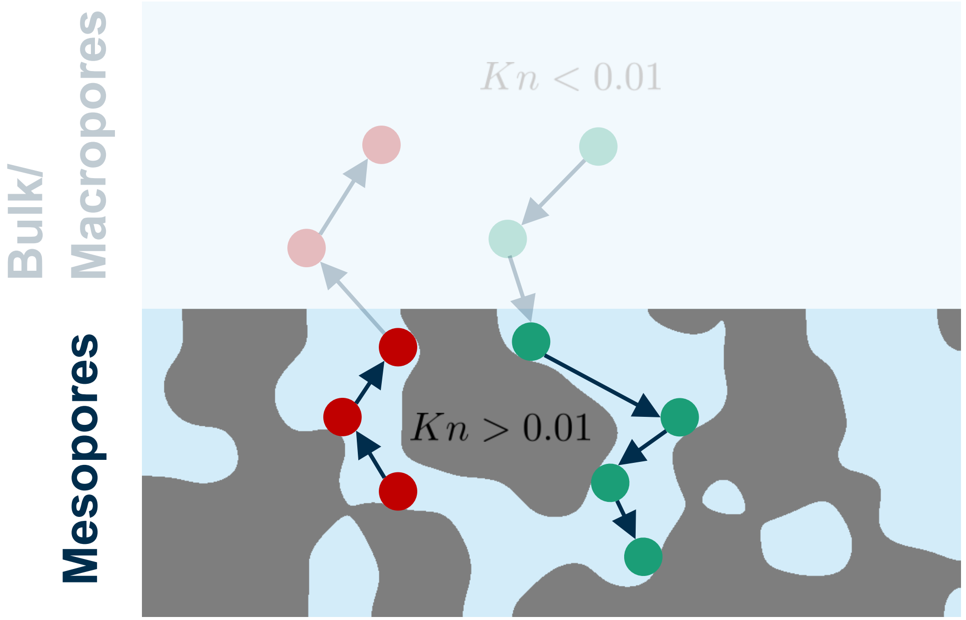


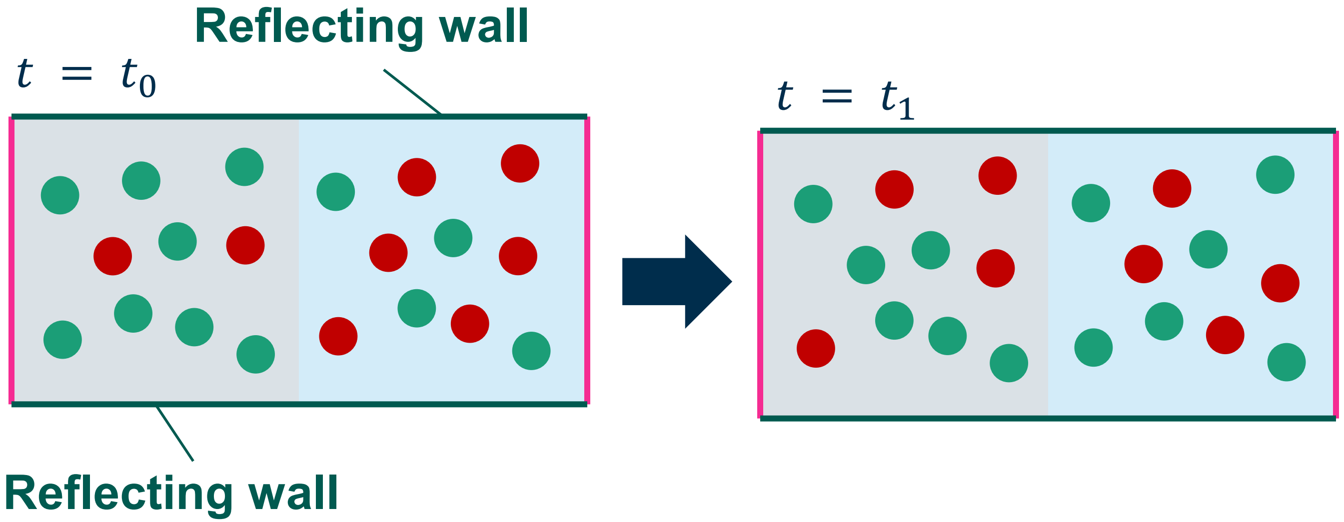
Kinetic Boltzmann equation solved with QBMM can describe multicomponent transport in the macropore and bulk regime !

Future steps

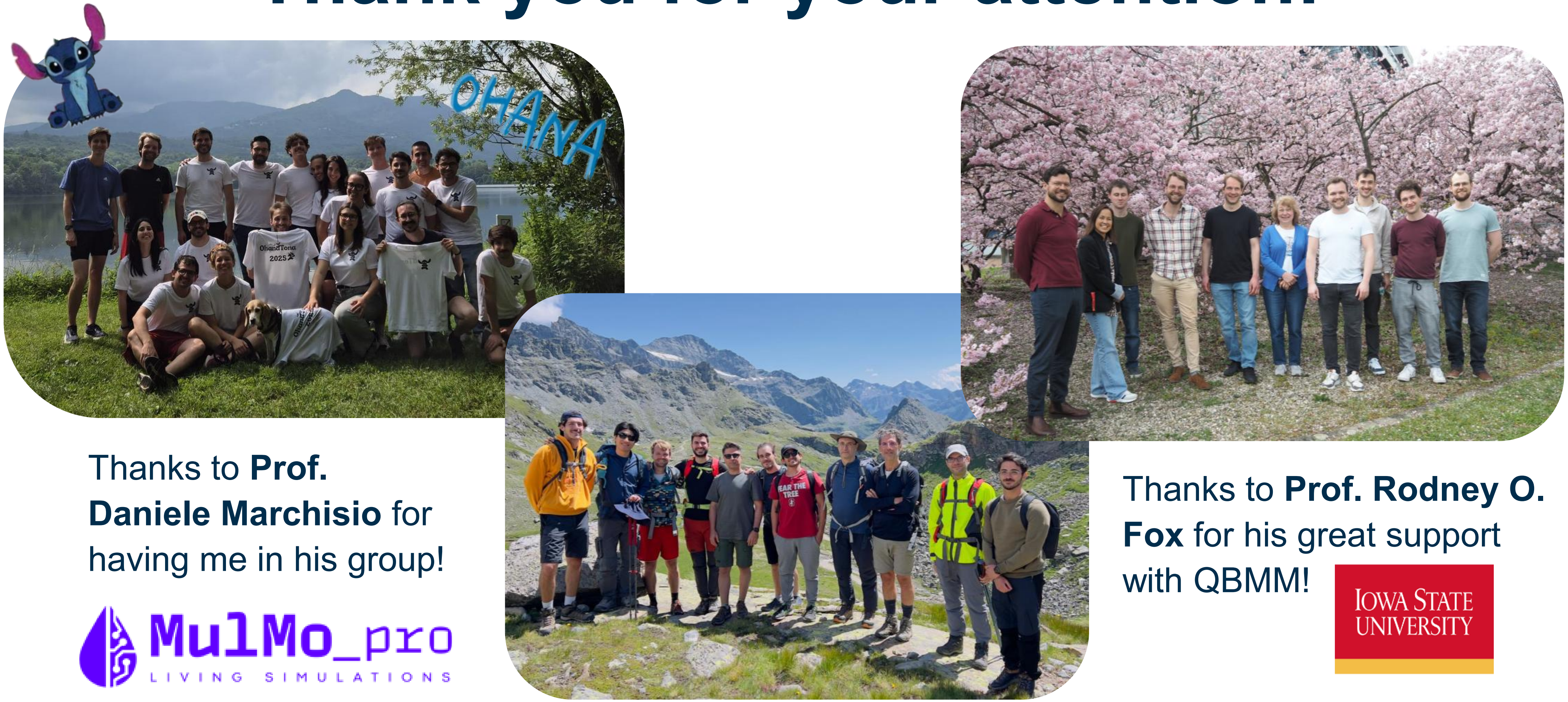
Next steps:

- Extending the presented concept to a 2D model to study, if the kinetic Boltzmann equation solved with QBMM can reflect diffusion in the transition regime between molecular and Knudsen diffusion
- Reflecting wall boundary condition for molecular-wall collisions
- Implementing of Boltzmann collision operator with hard sphere potential





Thank you for your attention!



Thanks to **Prof. Daniele Marchisio** for having me in his group!

MulMo_pro
LIVING SIMULATIONS

Thanks to **Prof. Rodney O. Fox** for his great support with QBMM!

IOWA STATE UNIVERSITY

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DFG Deutsche Forschungsgemeinschaft

KHYS
Karlsruhe House of Young Scientists

Backup

Calculation of properties of the equilibrium distribution

Equilibrium (univariant Gaussian): $f^{\mathrm{eq},i,j}\left(c_i\right)=\frac{\rho_i}{\sqrt{2\pi\sigma_{i,j}}}\exp\left(-\frac{\left(c_i-v_{i,j}\right)^2}{2\sigma_{i,j}}\right)$

Calculation of ρ_i, $v_{i,j}$ and $\sigma_{i,j}$ as well as the collision time τ from moments of f and the particle mass m_i and diameter d_i according to Marchisio and Fox [5]:

$$\rho_i=M_0^i$$

$$i=j:\ v_{i,j}=\frac{M_1^i}{M_0^i}$$

$$i\neq j: v_{i,j}=\mathrm{func}\left(m_i,m_j,M_1^i,M_0^i,M_1^j,M_0^j\right)$$

$$i=j:\ \sigma_{i,j}=\mathrm{func}\left(C_2^i\right)$$

$$i\neq j: \sigma_{i,j}=\mathrm{func}\left(C_2^i,C_2^j,M_1^i,M_0^i,M_1^j,M_0^j\right)$$

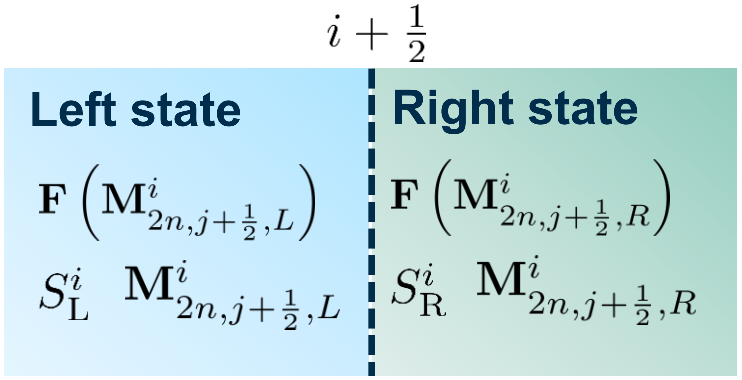
$$i=j:\ \tau_{i,j}=\mathrm{func}\left(d_i,C_2^i\right)$$

$$i\neq j: \tau_{i,j}=\mathrm{func}\left(d_i,d_j,C_2^i,C_2^j,M_1^i,M_0^i,M_1^j,M_0^j\right)$$

[5] Marchisio, Fox, Computational Models for Polydisperse and Multiphase Systems, Cambridge, 2013.

Calculation of moment fluxes using Harten, Lax and van Leer Riemann solver

Harten, Lax, van Leer (HLL) Riemann solver calculates fluxes by approximating the solution of a Riemann problem at the interface [7]:

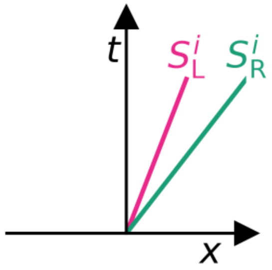


$i+\frac{1}{2}$

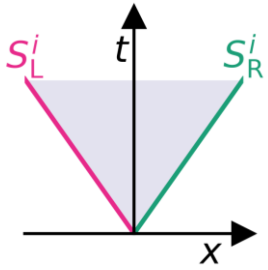
Left state	**Right state**
$\mathbf{F}\left(\mathbf{M}^i_{2n,j+\frac{1}{2},L}\right)$	$\mathbf{F}\left(\mathbf{M}^i_{2n,j+\frac{1}{2},R}\right)$
S^i_{L} $\mathbf{M}^i_{2n,j+\frac{1}{2},L}$	S^i_{R} $\mathbf{M}^i_{2n,j+\frac{1}{2},R}$

$S^i_{L/R}$ are the maximal speeds of molecules of component i going to the left/ right

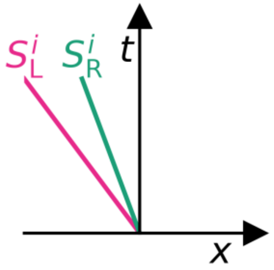
$$\text{if } S^i_{\mathrm{L}} > 0: \ \mathbf{F}\left(\mathbf{M}^i_{2n,j+\frac{1}{2}}\right) = \mathbf{F}\left(\mathbf{M}^i_{2n,j+\frac{1}{2},L}\right)$$



$$\text{if } S^i_{\mathrm{L}} \leq 0 \geq S^i_{\mathrm{R}}: \ \mathbf{F}\left(\mathbf{M}^i_{2n,j+\frac{1}{2}}\right) = \frac{S^i_{\mathrm{R}}\mathbf{F}\left(\mathbf{M}^i_{2n,j+\frac{1}{2},L}\right) - S^i_{\mathrm{L}}\mathbf{F}\left(\mathbf{M}^i_{2n,j+\frac{1}{2},R}\right) + S^i_{\mathrm{R}}S^i_{\mathrm{L}}\left(\mathbf{M}^i_{2n,j+\frac{1}{2},R} - \mathbf{M}^i_{2n,j+\frac{1}{2},L}\right)}{S^i_{\mathrm{R}} - S^i_{\mathrm{L}}}$$



$$\text{if } S^i_{\mathrm{R}} < 0: \ \mathbf{F}\left(\mathbf{M}^i_{2n,j+\frac{1}{2}}\right) = \mathbf{F}\left(\mathbf{M}^i_{2n,j+\frac{1}{2},R}\right)$$



[7] Toro, Riemann Solvers and Numerical Methods for Fluid Dynamic, Springer, 2009.

Calculation of maximal speeds by using eigenvalues of the Jacobian

Quasilinear form of the moment transport equations: $\partial_t \mathbf{M}^i_{2n} + \frac{D\mathbf{F}(\mathbf{M}^i_{2n})}{D\mathbf{M}^i_{2n}} \partial_x \mathbf{M}^i_{2n} = 0$

With the Jacobian $\frac{D\mathbf{F}(\mathbf{M}^i_{2n})}{D\mathbf{M}^i_{2n}}$

The maximal speeds can be calculated from the **maximum $\lambda^i_{\max}$ and minimum $\lambda^i_{\min}$ eigenvalues of the Jacobians** at both sides of the interface:

$$S^i_{\mathrm{L}} = \min\left(\lambda^i_{\mathrm{min,L}}, \lambda^i_{\mathrm{min,R}}\right)$$

$$S^i_{\mathrm{R}} = \max\left(\lambda^i_{\mathrm{max,L}}, \lambda^i_{\mathrm{max,R}}\right)$$

Stability of the solver is guaranteed by specifying the advection time based on the maximal absolute speed of all components $S_{\max}$:

$$\Delta t = \frac{\Delta x \, CFL}{S_{\max}} \qquad \text{with: } 0.5 \leq CFL \leq 0.9$$

[6] Fox, Lauren (2022) *SIAM J. APPL. MATH., 82*, 2, 750-771.

Maximal and minimal eigenvalue of the Jacobian are equal to the maximal and minimal eigenvalues of the recurrence coefficient matrix $\boldsymbol{K}_{n+1}$ [6]

$$\mathbf{K}_{n+1} = \begin{pmatrix} a_0 & \sqrt{b_1} & & & \\ \sqrt{b_1} & a_1 & \sqrt{b_2} & & \\ & \ddots & \ddots & \ddots & \\ & & \sqrt{b_{n-1}} & a_{n-1} & \sqrt{b_n} \\ & & & \beta_n & a_n \end{pmatrix}.$$

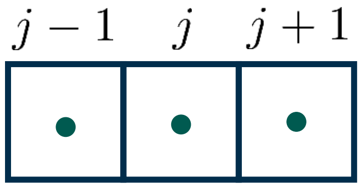
with: $\beta_n = \frac{2n+1}{n} b_n$

➡ Maximal speeds can be calculated from $\boldsymbol{M}^i_{2n}$

Interface Reconstruction of the moment vector

The states at left and right side of the interface are not a-priori given:

- States needs to be reconstructed from centroid values
- Only the moment vectors needs to be reconstructed (all states are function of $\boldsymbol{M}^i_{2n}$)



1st order:

$$\mathbf{M}^i_{2n,j+\frac{1}{2},\mathrm{L}} = \mathbf{M}^i_{2n,j} \qquad \mathbf{M}^i_{2n,j-\frac{1}{2},\mathrm{R}} = \mathbf{M}^i_{2n,j}$$

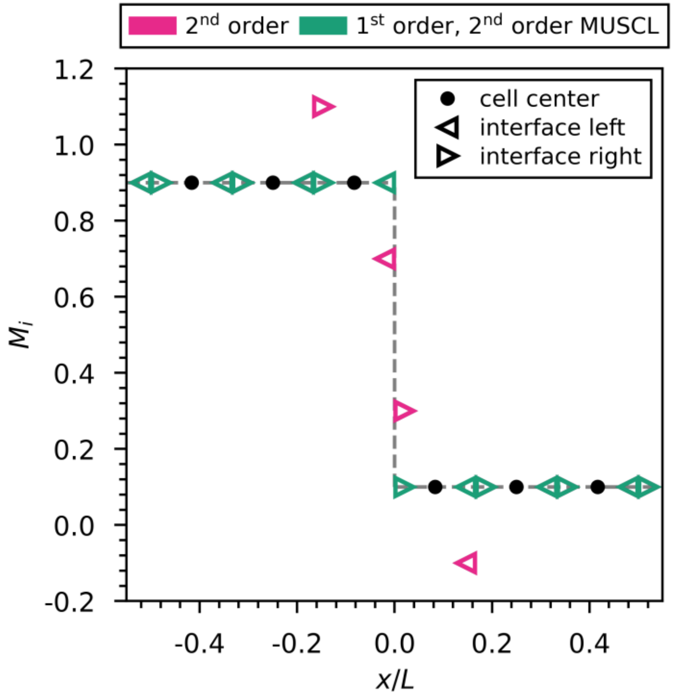
2nd order Modified **U**pwind **S**cheme for **C**onservative **L**aw (**MUSCL**) [8]:

$$\mathbf{M}^i_{2n,j+\frac{1}{2},\mathrm{L}} = \mathbf{M}^i_{2n,j} + \frac{1}{2}\widehat{\Delta M^i}_j \qquad \mathbf{M}^i_{2n,j-\frac{1}{2},\mathrm{R}} = \mathbf{M}^i_{2n,j} - \frac{1}{2}\widehat{\Delta M^i}_j$$

Unlimited slopes: $\Delta\mathbf{M}^i_{j+\frac{1}{2}} = \mathbf{M}^i_{2n,j+1} - \mathbf{M}^i_{2n,j} \qquad \Delta\mathbf{M}^i_{j-\frac{1}{2}} = \mathbf{M}^i_{2n,j} - \mathbf{M}^i_{2n,j-1}$

Limited slope: $\widehat{\Delta\mathbf{M}^i}_j = \mathrm{minmod}\left(\Delta\mathbf{M}^i_{j+\frac{1}{2}}, \Delta\mathbf{M}^i_{j-\frac{1}{2}}\right)$

Limiter function: $\mathrm{minmod}\,(x,y) = \mathrm{sign}\,(x)\left(\dfrac{1+\mathrm{sign}\,(xy)}{2}\right)\min\,(|x|,|y|)$

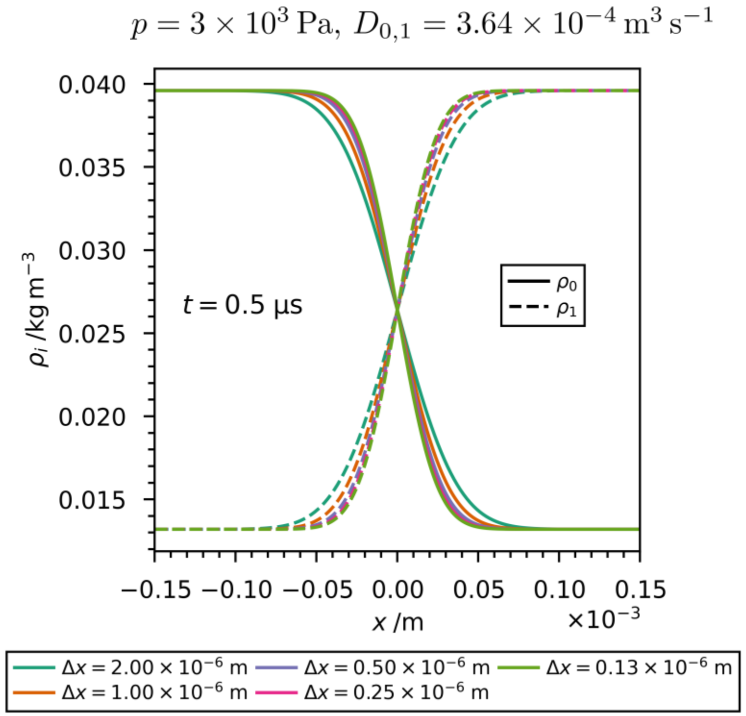


Standard higher order schemes adding **new extrema**, and may lead to **unrealizable moments**

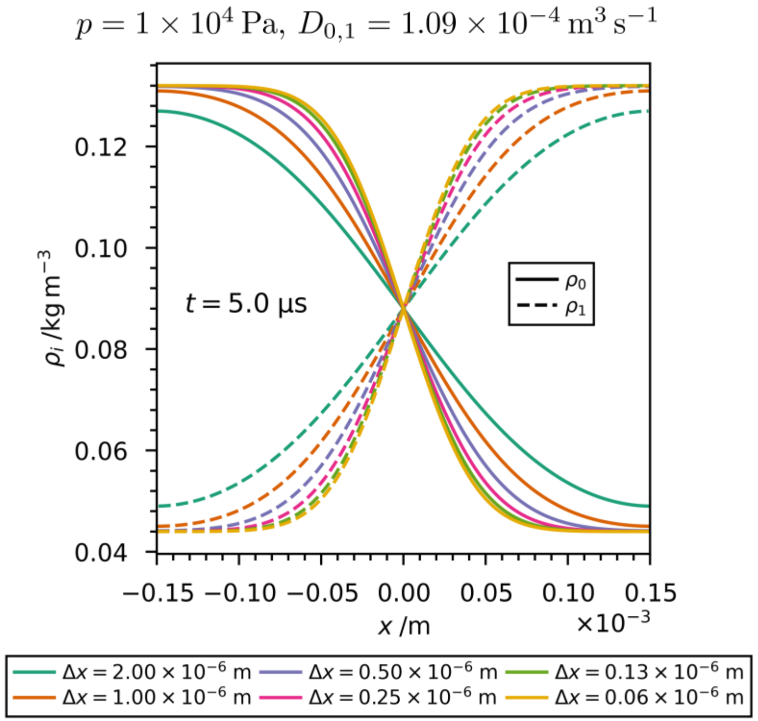
[8] Knight, Elements of Numerical Methods for Compressible Flows, Cambridge, 2006.

First order interface reconstruction results in non-acceptable numerical diffusion!

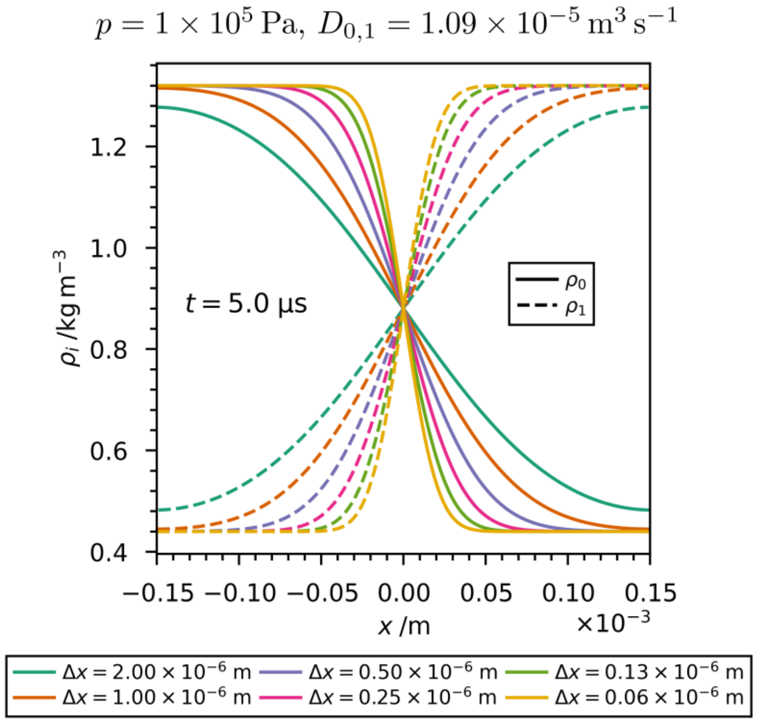
Self-diffusion of Argon at a temperature of 273 K and various pressures:



Convergence reached at $\Delta x = 0.5\ \times 10^{-6}\ \mathrm{m}$



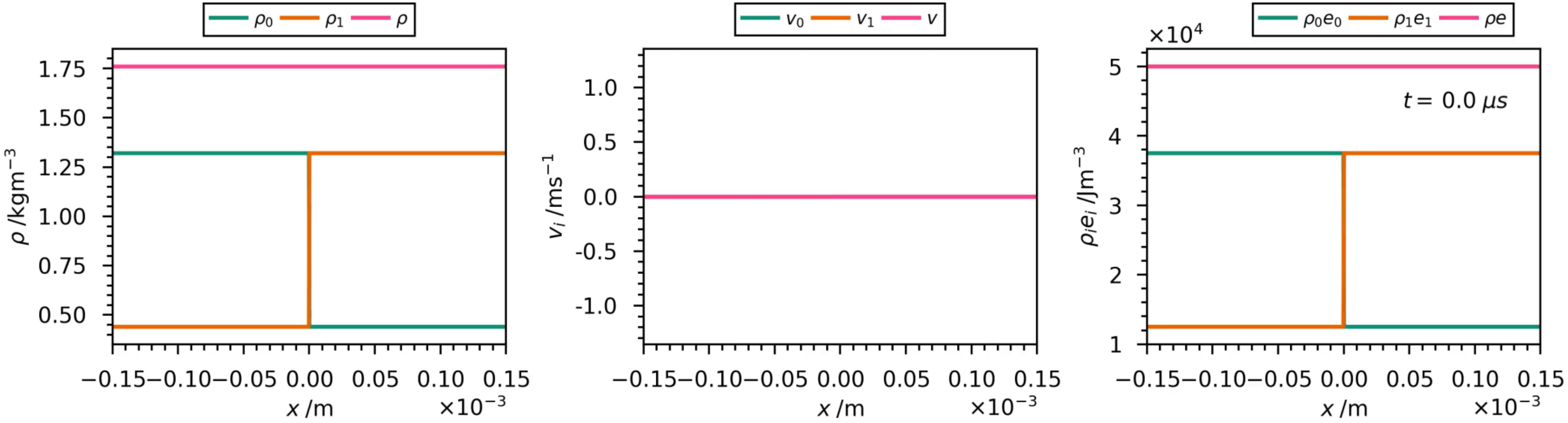
Convergence reached at $\Delta x = 0.125\ \times 10^{-6}\ \mathrm{m}$



Convergence reached at $\Delta x < 0.0625 \times 10^{-6}$

➡ Resolution required for mesh convergence is 8 to 20 times higher for the first order reconstruction than for the second order MUSCL reconstruction !

Moment transport equations fulfill conservation laws



➡ Total ,species mass, momentum and total energy are conserved!

The Maxwell-Stefan diffusion model for multicomponent mixtures

Species conservation of mixture with n components: $\delta_t \left(c\,\mathbf{y}_{n-1} \right) = \delta_x \dot{\mathbf{n}}_{n-1}$

BC: $\delta_x \mathbf{y}_{n-1,x=0} = \delta_x \mathbf{y}_{n-1,x=L} = 0$

IC: Reflecting macroscopic initial condition of kinetic equation

➡ System of **parabolic** PDEs!

Total molar concentration: $c = \dfrac{p}{k N_{\mathrm{A}} T}$

Concentration vector: $\mathbf{y}_{n-1} = \left(y_0, y_1, \ldots, y_{n-1} \right)^T$

Flux vector: $\dot{\mathbf{n}}_{n-1} = \left(\dot{n}_0, \dot{n}_1, \ldots, \dot{n}_{n-1} \right)^T$

Closure using unity condition: $y_n = 1 - \sum_{i=0}^{n-1} y_i$

Solution is independent on the choice of the n^{th} component !

Flux vector calculated using **Maxwell-Stefan approach** [11]:

$$\dot{\mathbf{n}}_{n-1} = -c\,\mathbf{B}_{n-1,n-1}^{-1} \delta_x \mathbf{y}_{n-1}$$

With the transport matrix $\boldsymbol{B}_{n-1,n-1} \in \mathbb{R}^{(n-1)\times(n-1)}$:

Diagonal: $B_{i,i} = \dfrac{y_i}{D_{i,n}} + \sum_{k=0,k\neq i}^{n-1} y_i D_{i,j}^{-1}$

Off-diagonal: $B_{i,j(i\neq j)} = -y_i \left(D_{i,j}^{-1} - D_{i,n}^{-1} \right)$

[11] Krishna, Wesselingh (1997) *Chem. Eng. Sci.*, *6*, 2, 861-911.