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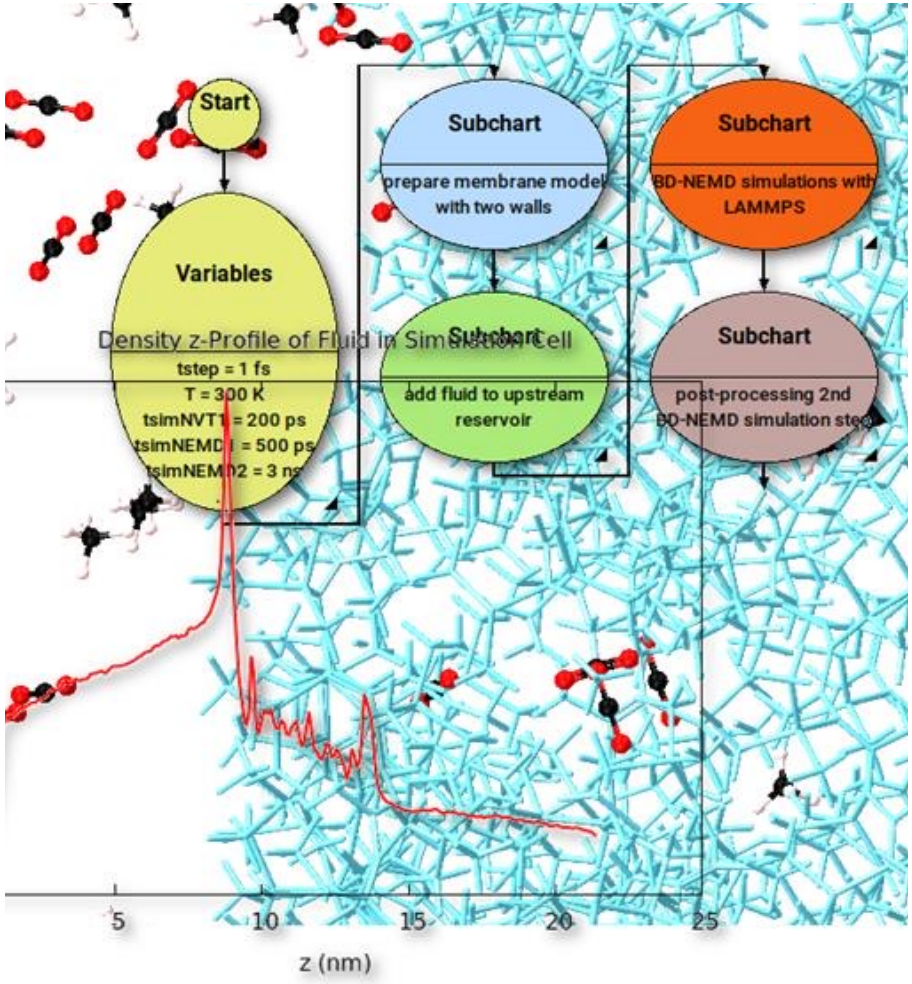
Materials Design 2022 UGM Training Series

Simulations of Gas Separation Through Nanofiltration

René Windiks

Materials Design

October 06, 2022



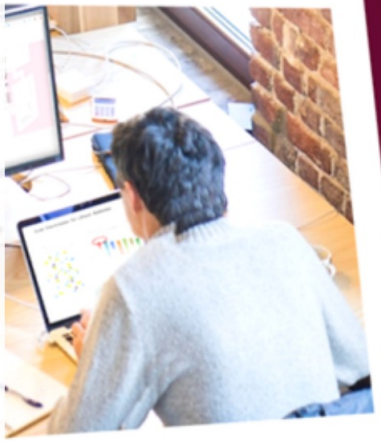
Materials Design UGM

UGM 2022

The Materials Design annual user event will be online for 2022.

Plenary Speakers include:

Prof. Jeffrey Grossman
Prof. Georg Kresse
Dr. Carla Verdi
Prof. Jörg Behler
Dr. Jozef Bicerano



https://ugm.materialsdesign.com/

Training & Support Team

René Windiks	***David Reith***	***Xiaoli Liu***	***Thomas Nilson***	***Shubham Pandey***
presenter	*moderator*			

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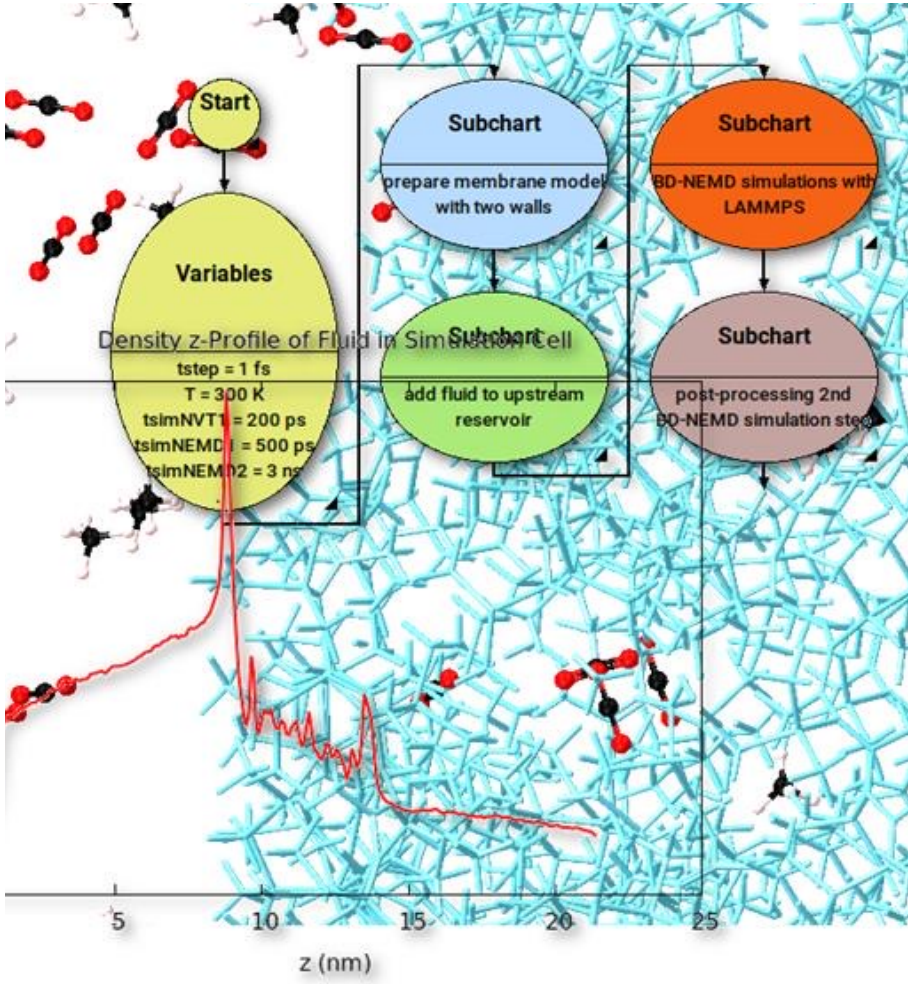

Materials Design UGM Training Series

- Share the plenary sessions with your colleagues!
  - Registration details

    https://www.ugm.materialsdesign.com
- We will be recording this session
  - Upcoming sessions are posted on the UGM site
  - Watch any of our earlier webinars anytime www.materialsdesign.com/webinars
- Brief survey
  - Take a 2 minutes brief survey at the end of the webinar
- Audio issues
  - Log out and log back in again
  - Check your audio output
  - Google Chrome (most recent 2 versions) Mozilla Firefox (most recent 2 versions) Apple Safari (most recent 2 versions) Microsoft Edge (most recent 2 versions)

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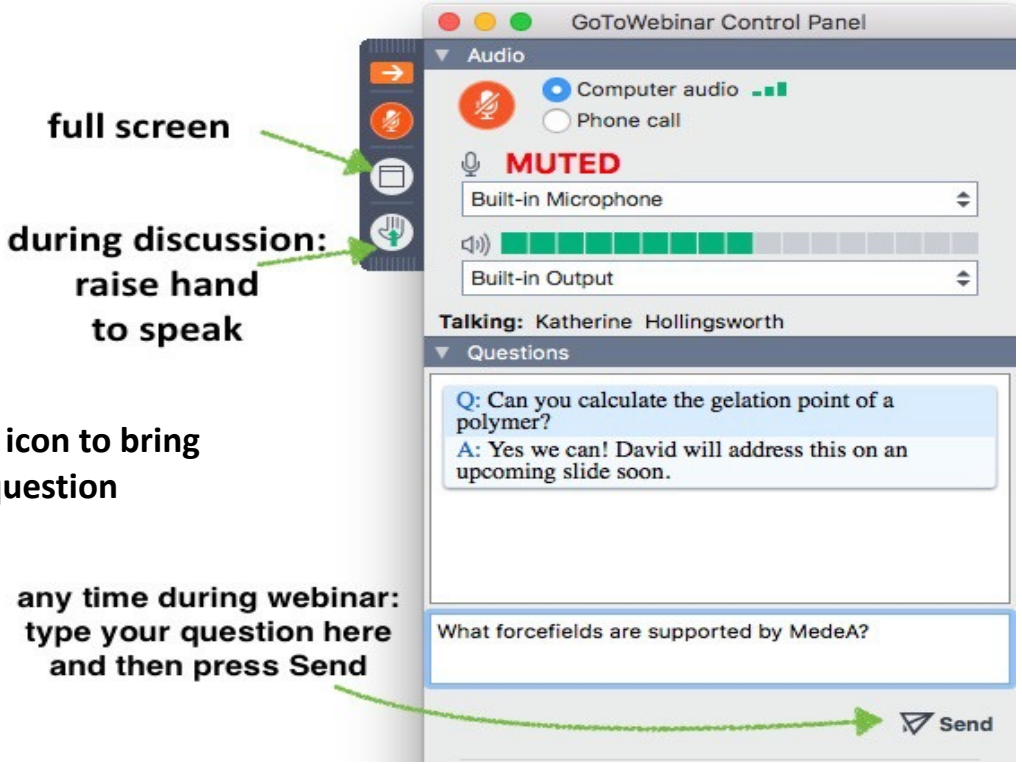
Please Ask Questions!



Use the raise hand icon to bring attention to your question

any time during webinar: type your question here and then press Send

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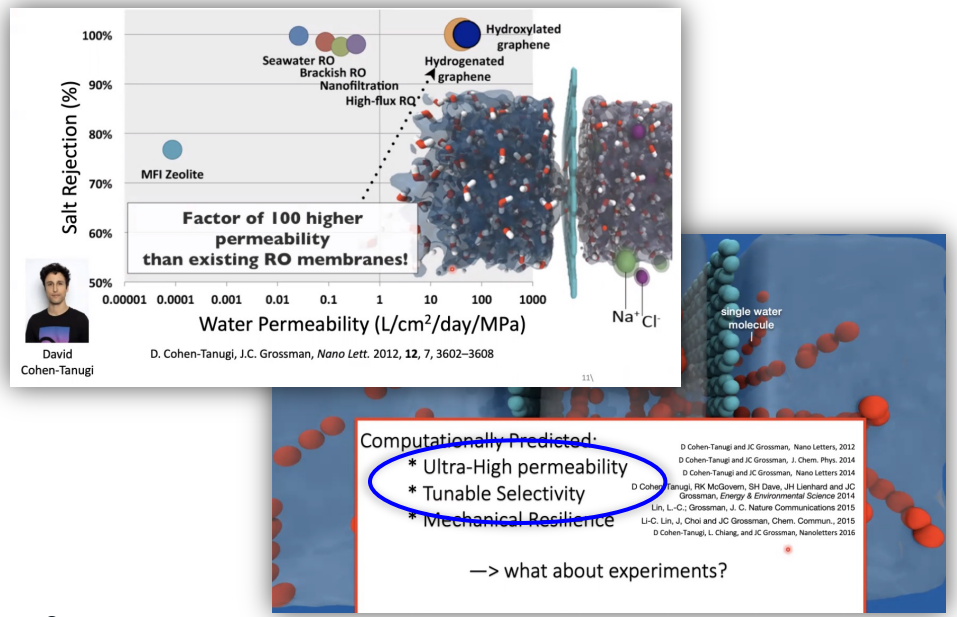
Outline

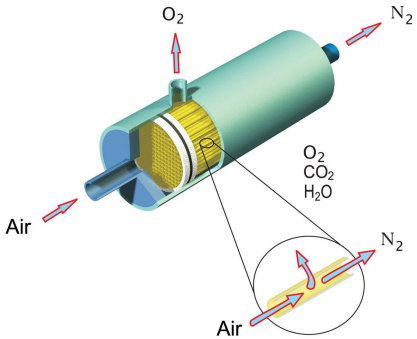
- Motivation
- Permeation & Permeability
- Simulation Approaches
  - At thermodynamic equilibrium
  - Non-equilibrium simulation technique
- Example in detail: **B**oundary-**D**riven **N**on-**E**quilibrium **M**olecular **D**ynamics simulation of nanofiltration of a N_2/CO_2 gas mixture
- Summary

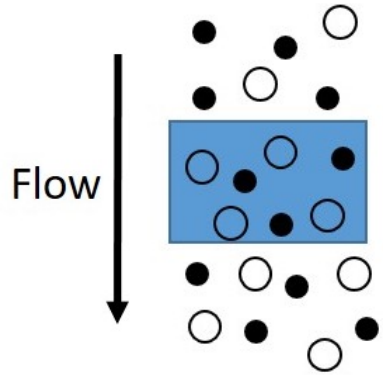
Motivation

- Purification of fluids by mechanical separation
  - Simulation of desalination of water, as discussed in Jeff Grossman's plenary talk



- Separation of gas mixtures with high pressure filtration through polymer membranes





https://en.wikipedia.org/wiki/Membrane_gas_separation

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Permeation and Permeability

Permeation is usually described experimentally by a **permeability coefficient**, P, defined by[1]:

$$P = \frac{(quantity\ of\ permeant) \times (membrane\ thickness)}{(area) \times (time) \times (pressure\ drop\ across\ membrane)}$$

which is equivalent to the following:

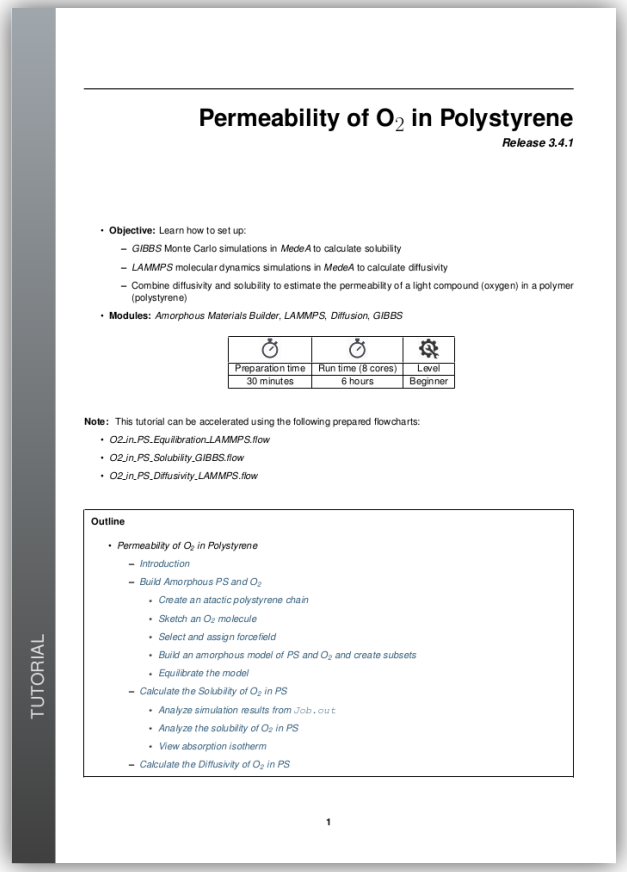
$$P = D \times S$$

where D denotes the diffusivity, and S the solubility.

In atomistic simulations of gas penetrant systems, D can often be obtained directly using molecular dynamics simulation, while S can be obtained by Monte Carlo methods.

1. see, for example, Polymer Handbook, J. Brandrup & E.H. Immergut (eds)

Tutorial: Simulation of Permeability of O_2 in Polystyrene



- Calculations of properties at thermodynamic equilibrium
  - **Diffusivity** based Brownian motion (mean-square displacements) using molecular dynamics (MD) simulations with *MedeA LAMMPS Diffusion*
  - **Solubility** based on adsorption using grand-canonical Monte Carlo simulations with *MedeA GIBBS*
  - Interatomic interactions are described with *PCFF+*: **p**olymer **c**onsistent **f**orce**f**ield, continuously extended & developed by Materials Design

- Tutorial available at http://my.materialsdesign.com/tutorials

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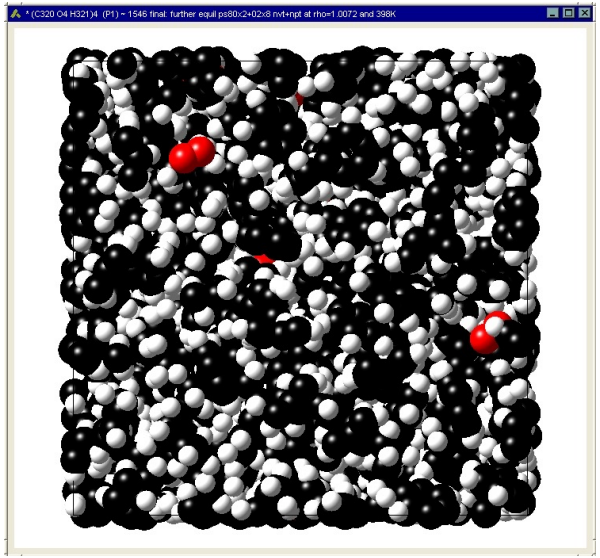
Example: Diffusivity of O_2 in Polystyrene

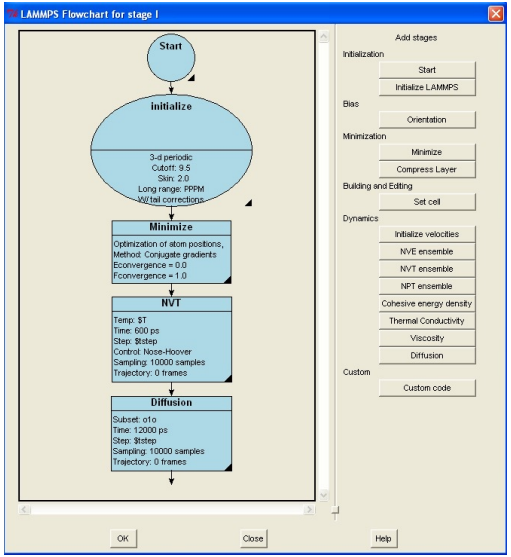
MD Simulations at thermodynamic equilibrium

Model system containing 2 atactic PS molecules with DP=80, with 8 added oxygen molecules (2580 atoms total), with *LAMMPS Diffusion* Flowchart

Amorphous Materials Builder



MedeA flowchart



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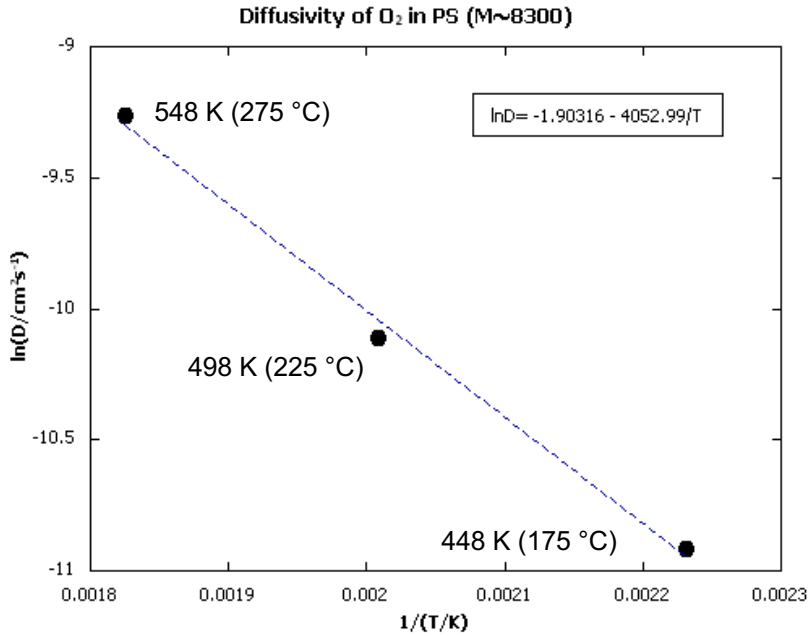
Diffusivity of O_2 in Polystyrene at Thermodynamic Equilibrium

Arrhenius plot for O_2 in atactic PS (448-548K)

- Predicts D ~ **1.87 x 10^{-7} cm^2s^{-1} at 298K (25 °C)**



Compute engine: *MedeA LAMMPS*
Property module: *MedeA Diffusion*
Interatomic potential: *MedeA PCFF+*

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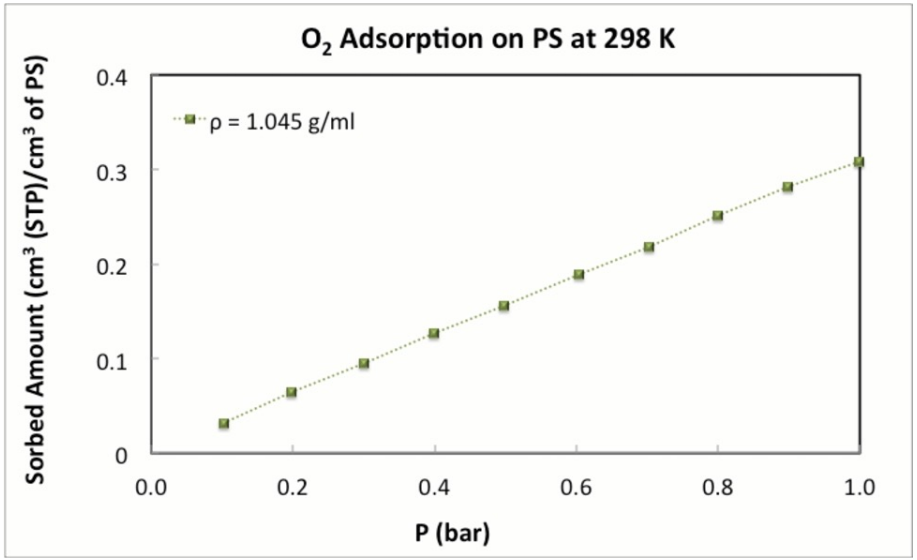
Solubility of O_2 in Polystyrene

Pressure dependence of solubility of O_2 in atactic PS at 298K

- Note: 0.3 cm^3(STP)/cm^3 of PS corresponds to ~0.21 molecules per simulation cell
- Experimental density: Zoller & Walsh (1995), p133



Compute engine: *MedeA GIBBS*
Interatomic potential: *MedeA PCFF+*

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Permeation and Permeability: Calc. vs Exp.

Comparison of calculated and experimental permeability data for O_2 in atactic PS at 298K

	D ($x10^7$) cm^2/s	S ($x10^6$) $cm^3(STP)/(cm^3.Pa)$	P ($x10^{13}$) $cm^3(STP).cm/(cm^2.s.Pa)$
Calculated	1.87[a)]	3.1-3.2	5.8-6.0
Burmeister et al	-	-	1.35-1.85
Wang & Ogilby	2.0±0.2	-	-
Rharbi et al	1.9±0.05	-	1.71-1.89

[a)] Determined by linear extrapolation in the Arrhenius plot

References:
Burmeister et al, Polym. Prepr. ACS Div Polym. Chem. **27**, 414 (1986)
Wang & Ogilby, Can. J. Chem. **73**, 1831 (1995)
Rharbi et al., Anal. Chem. **71**, 5045 (1999)

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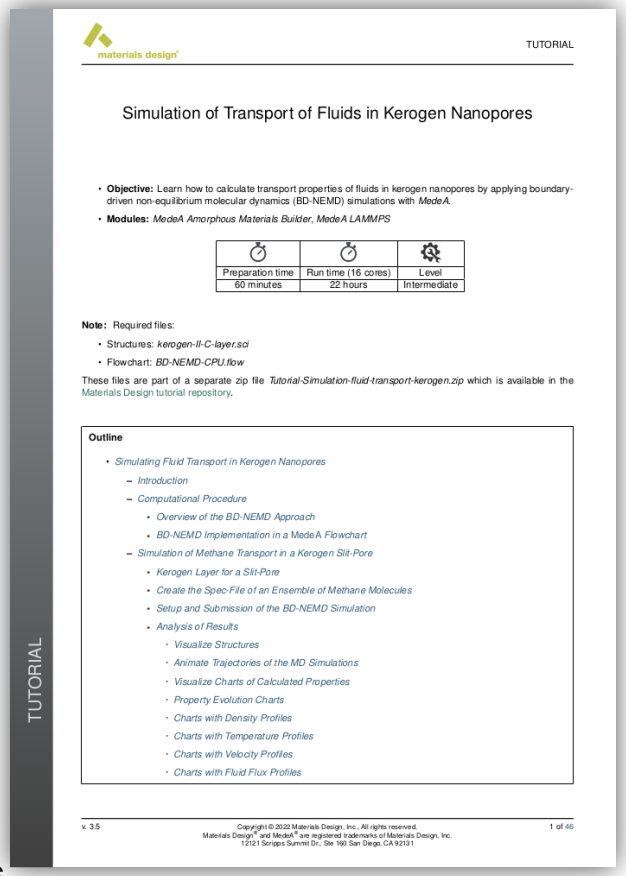
Tutorial: Simulation of Gas Transport Through Membranes



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TUTORIAL

Simulation of Transport of Fluids in Kerogen Nanopores

- **Objective:** Learn how to calculate transport properties of fluids in kerogen nanopores by applying boundary-driven non-equilibrium molecular dynamics (BD-NEMD) simulations with *MedeA*.
- **Modules:** *MedeA Amorphous Materials Builder, MedeA LAMMPS*

Preparation time	Run time (16 cores)	Level
60 minutes	22 hours	Intermediate

Note: Required files:

- Structures: *kerogen-II-C-layer.sci*
- Flowchart: *BD-NEMD-CPU.flow*

These files are part of a separate zip file *Tutorial-Simulation-fluid-transport-kerogen.zip* which is available in the Materials Design tutorial repository.

Outline

- *Simulating Fluid Transport in Kerogen Nanopores*
  - *Introduction*
  - *Computational Procedure*
    - *Overview of the BD-NEMD Approach*
    - *BD-NEMD Implementation in a MedeA Flowchart*
  - *Simulation of Methane Transport in a Kerogen Slit-Pore*
    - *Kerogen Layer for a Slit-Pore*
    - *Create the Spec-File of an Ensemble of Methane Molecules*
    - *Setup and Submission of the BD-NEMD Simulation*
    - *Analysis of Results*
      - *Visualize Structures*
      - *Animate Trajectories of the MD Simulations*
      - *Visualize Charts of Calculated Properties*
      - *Property Evolution Charts*
      - *Charts with Density Profiles*
      - *Charts with Temperature Profiles*
      - *Charts with Velocity Profiles*
      - *Charts with Fluid Flux Profiles*

v. 3.5

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TUTORIAL

- Calculation of Fickian diffusion which occurs in systems not in thermodynamic equilibrium due to due to, e.g. pressure gradients
- gas flux along one direction *i*: $J_i = K_P \, \Delta P/\Delta d_i$
  - ΔP: pressure difference between two regions separated by a distance Δd_i *(i = x,y,z)*
  - K_P: permeability of the membrane
- Simulation approach: **b**oundary-**d**riven **n**on-**e**quilibrium **m**olecular **d**ynamics (BD-NEMD) simulations introduced by Frentrup et al.
  (In Silico Determination of Gas Permeabilities by Non-Equilibrium Molecular Dynamics: CO_2 and He through PIM-1, Membranes 5, 99 (2015).
- Tutorial available at http://my.materialsdesign.com/tutorials

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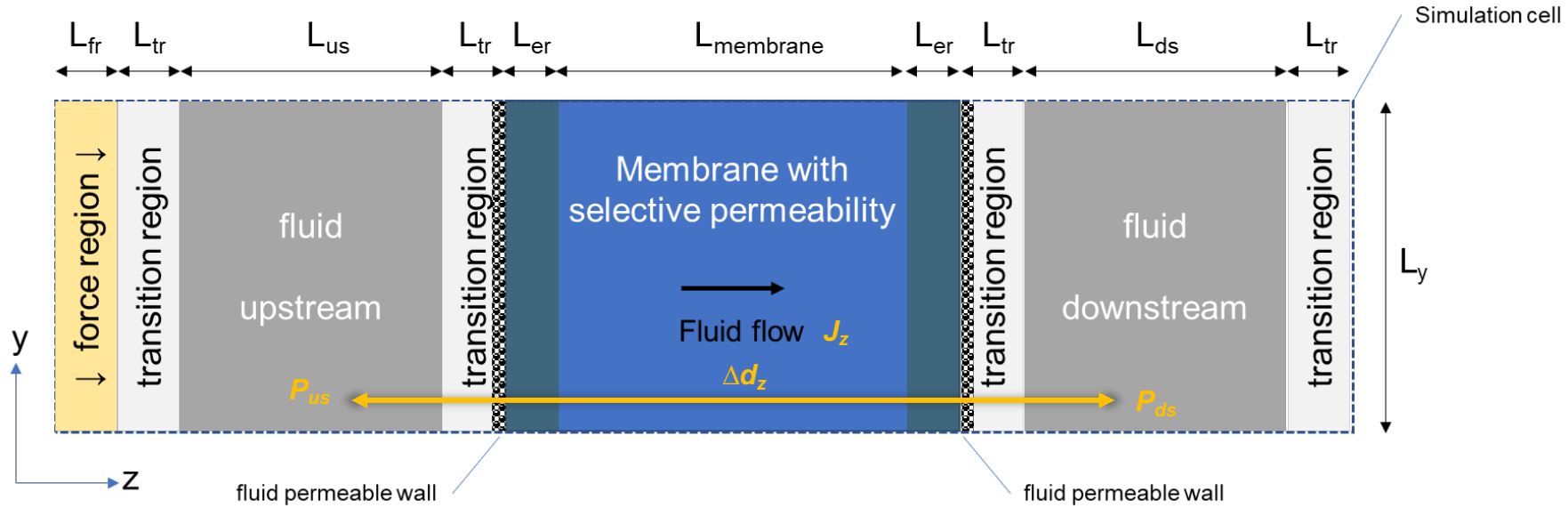
BD-NEMD Simulation Setup



- Flow/flux: $J_z = v_z\rho = K_P \Delta P/\Delta d_z$
  - v_z: average velocity of fluid in the membrane along the z-direction
  - ρ: average density of fluid in the membrane
- All lengths L_i are explained in the tutorial

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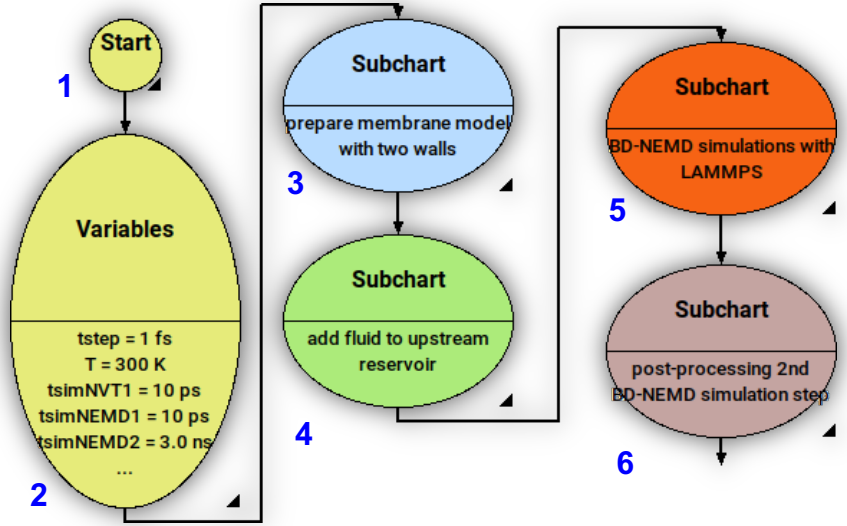
BD-NEMD Implementation in a *MedeA Flowchart*

Flowchart consists of six stages

1. Brief explanation about how to use the flowchart
2. defines running parameters
3. prepares the simulation cell with the membrane, two fluid-permeable walls, and the two empty fluid reservoirs
4. adds the fluid to the upstream reservoir of the simulation cell
5. performs BD-NEMD simulation with *MedeA LAMMPS*
6. post-processes the results of the BD-NEMD simulation



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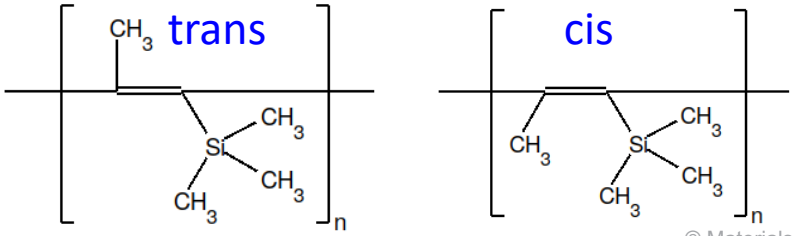
Selected Membrane for BD-NEMD Simulation: PTMSP

- **P**oly(1-**t**ri**m**ethyl**s**ilyl-1-**p**ropyne)
- typical high free volume, highly permeable glassy polymer
- Density (25°C): 0.75 g/cm^3
- Glass transition temp. > 200 °C

Fractional free volume (FFV): 33%, depends on ratio cis- / trans- isomers and the sequence in main chain

- Used to separate mixtures of
  - **CO_2/N_2**
  - CH_4/CO_2
  - n-C_4H_{10}/CH_4
- Predominant separation mechanism: competing solubility of gas constituents in PTMSP



1. Hofmannt al., Free Volume Distributions in Ultrahigh and Lower Free Volume Polymers: Comparison between Molecular Modeling and Positron Lifetime Studies, Macromolecules 35, 2129 (2002).
2. Ricci et al., Modelling Sorption and Transport of Gases in Polymeric Membranes across Different Scales: A Review, Membranes 12, 9 (2022).

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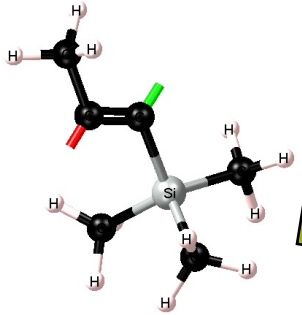
Steps to Perform BD-NEMD Simulation

1. Build polymer chain with trans- and cis-isomers of the TMSP polymer repeat units
2. Create initial structure of PTMSP membrane model
3. Condition PTMSP membrane model
4. Calculate density of 1:1 mixture of CO_2 and N_2 at 50 bar (5 MPa)
5. Create fluid mixture for BD-NEMD simulation based on the results of the previous step
6. Setup the BD-NEMD simulation
7. Analyse the results of the BD-NEMD simulation

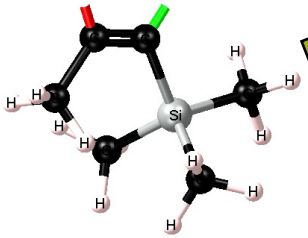
Build a PTMSP Chain

$(TMSP)_{50}$ with random order of the two repeat units

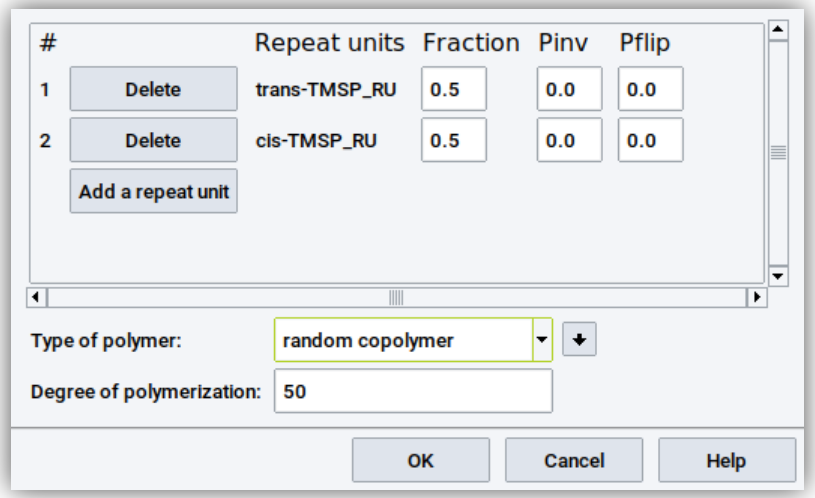
Trans-TMSP

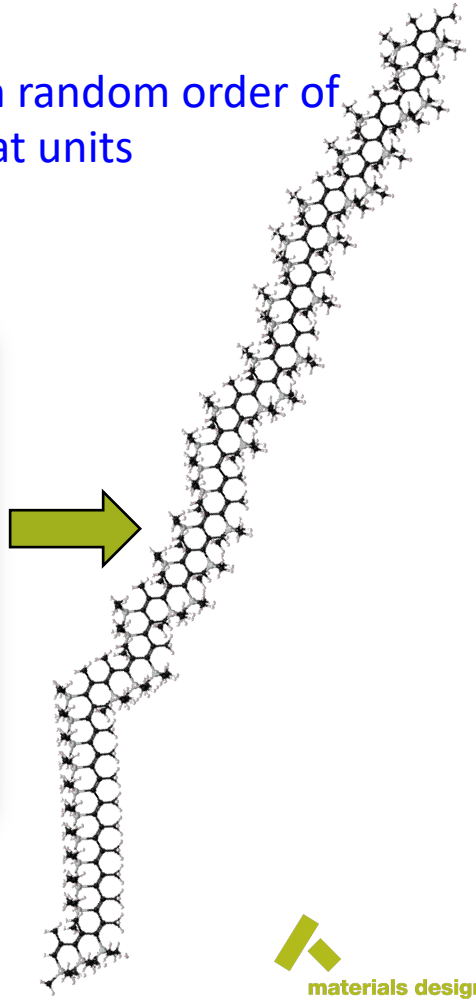


Cis-TMSP



Polymer Builder





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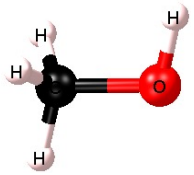
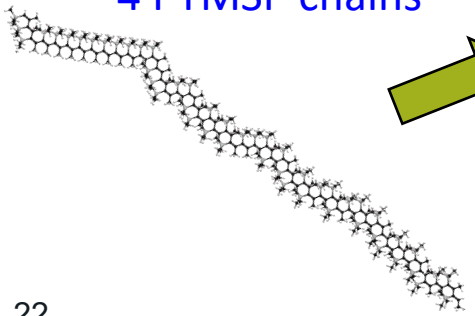
Building the Initial PTMSP Membrane Model



100 methanol molecules
As pore building agent

4 PTMSP chains



Amorphous Materials Builder

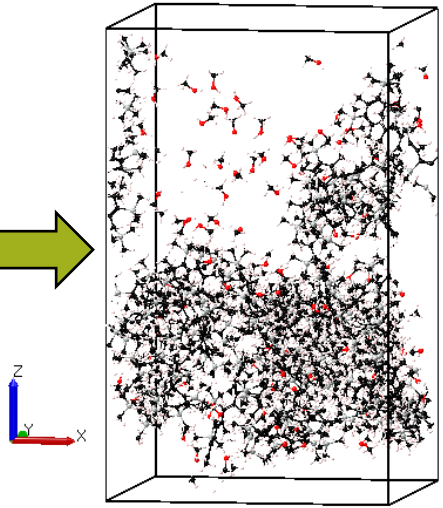
#	Component	Type	Nmols	Relax
Delete	1 Opened structure: poly(trans-TMSP_RU-...	Automatic	4	✓
Delete	2 Opened structure: MeOH	Automatic	100	✓

Add a component

System geometry:	layer
Specify cell:	density,a,b
Density (g/ml):	0.6
Cell length a (Ang):	35.0
Cell length b (Ang):	35.0
Cell details:	Refresh
Density: 0.6000 a: 35.0000 b: 35.0000 c: 57.9771	
Temperature (K):	298.2
Coordinate bias:	none
Orientation bias:	none
Action:	Build cell
Number of configurations:	5

OK Cancel Help

Initial membrane model



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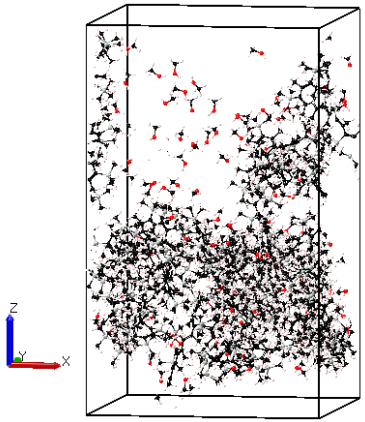
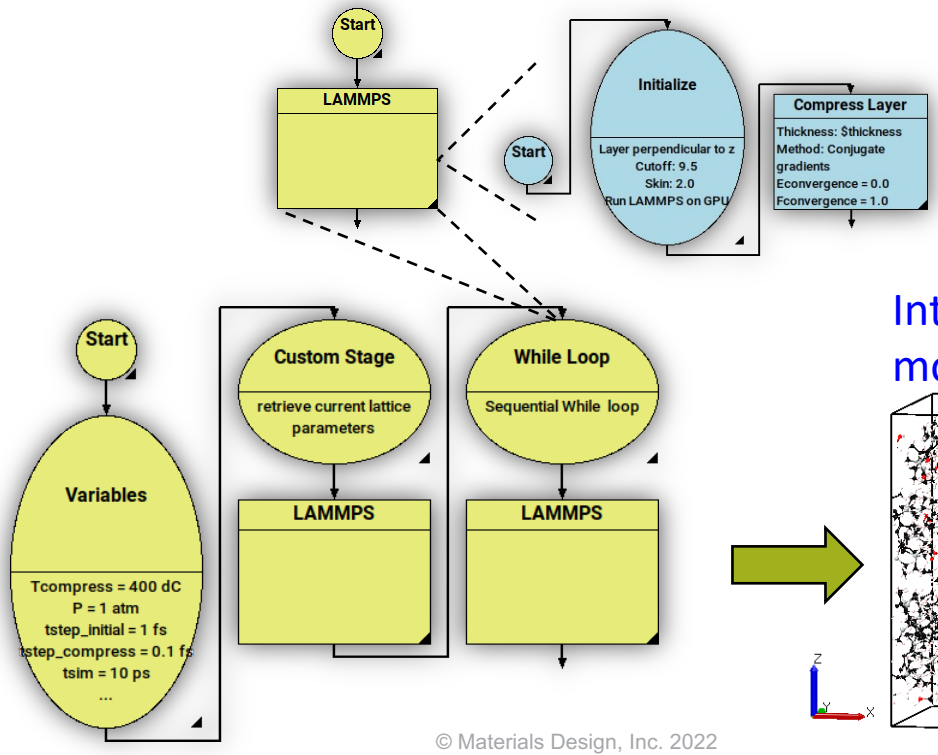
Building the Final PTMSP Membrane Model

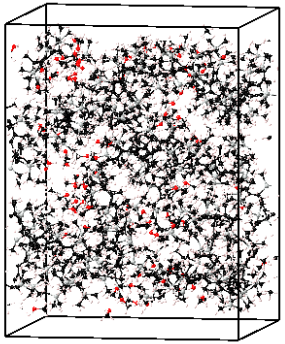
Initial model



MedeA Flowchart to create membrane layer with *LAMMPS*

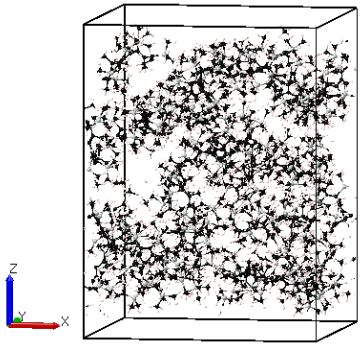


Intermediate model



Remove CH_3OH molecules

final



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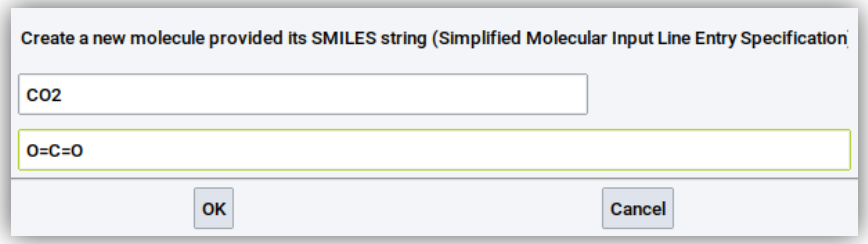
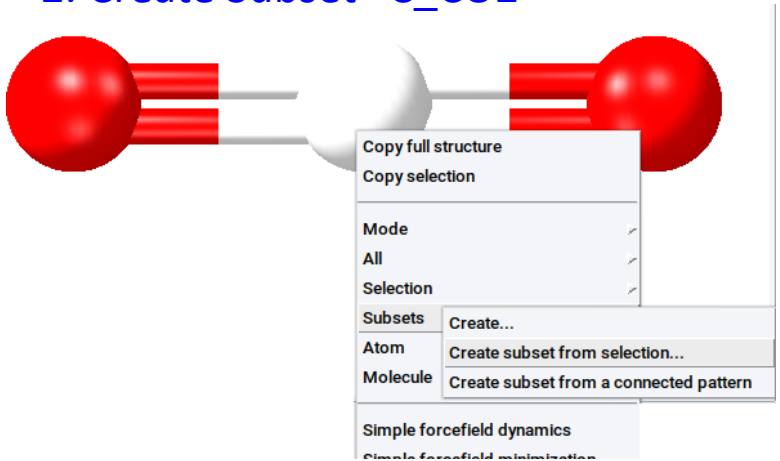
Prepare CO_2 for the Gas Mixture

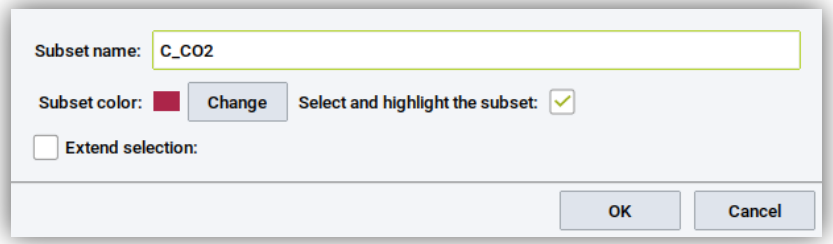
1. Create CO_2 molecule with SMILES



2. Create Subset "C_CO2"



Subset is essential to monitor presence of CO_2 molecules in the various regions of the simulation cell



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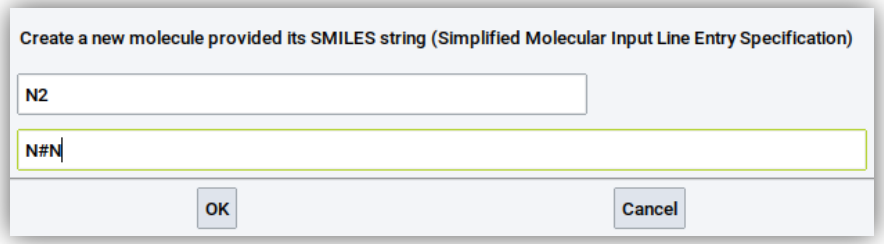
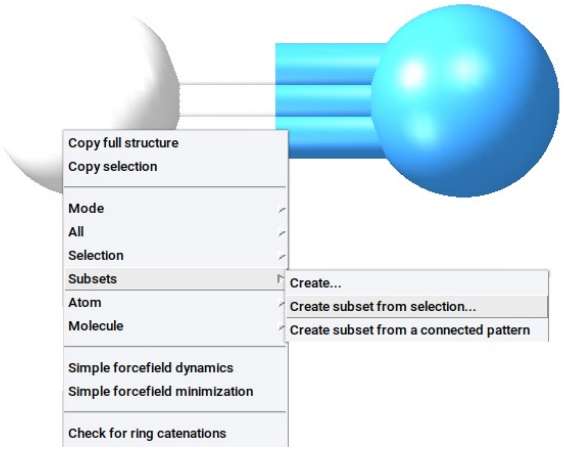
Prepare N_2 for the Gas Mixture

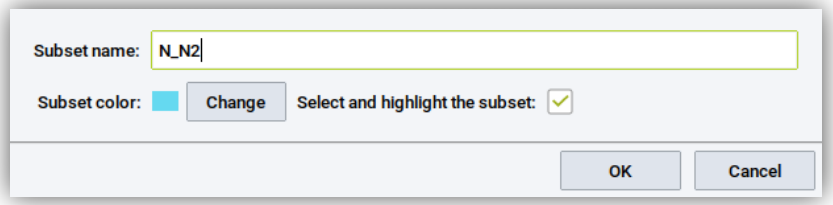
1. Create CO_2 molecule with SMILES



2. Create Subset "N_N2"



Subset is essential to monitor presence of CO_2 molecules in the various regions of the simulation cell



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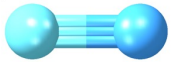
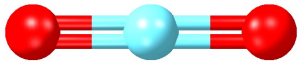
Calculate Density of Gas Mixture: Initial Structure

N_2



CO_2



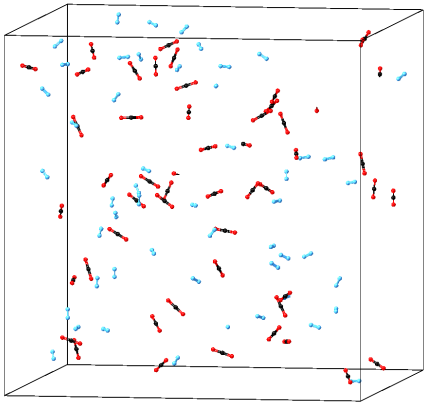
Amorphous Materials Builder

	#	Component	Type	Nmols	Relax
Delete	1	Opened structure: N2	Automatic	50	✓
Delete	2	Opened structure: CO2	Automatic	50	✓
Add a component					

System geometry:	bulk cell
Specify cell:	density
Density (g/ml):	0.05
Cell details:	Refresh
Density: 0.0500 a: 49.2694 b: 49.2694 c: 49.2694	
Temperature (K):	298.2
Coordinate bias:	none
Orientation bias:	none
Action:	Build cell
Number of configurations:	1

OK Cancel Help

Initial structure of gas mixture



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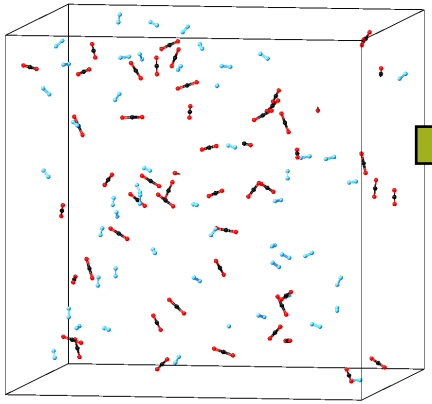
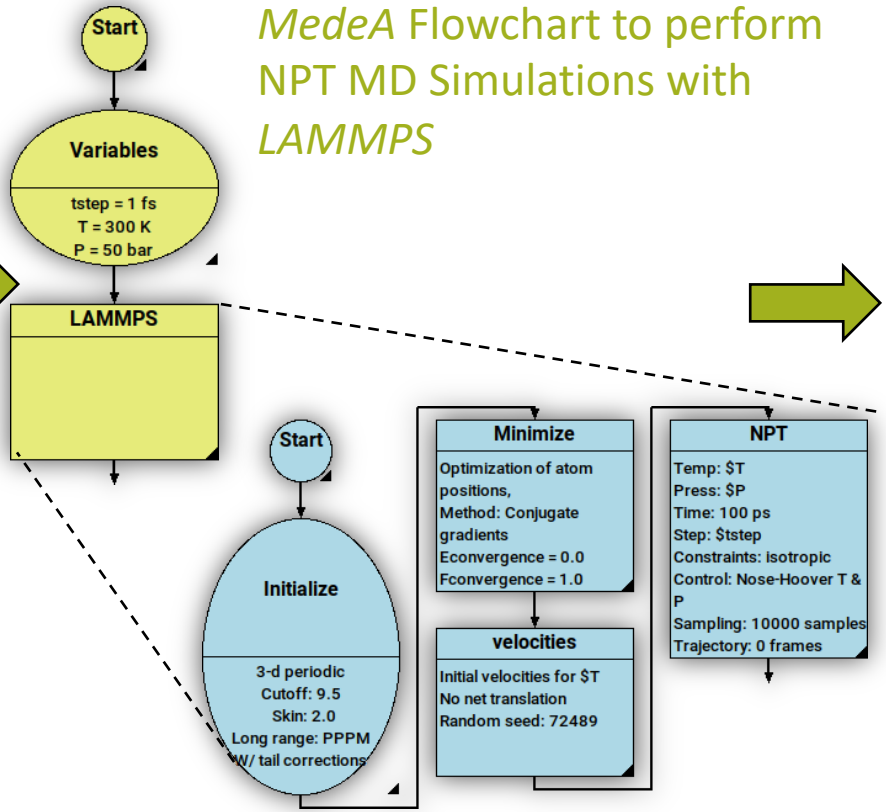
Calculate Density of Gas Mixture: MD Simulation

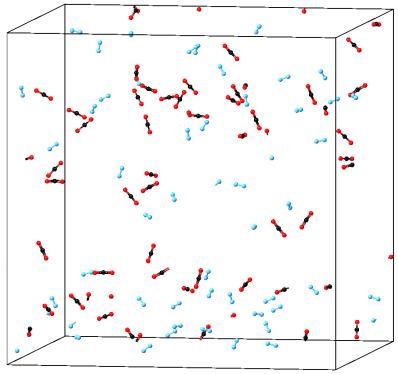
Initial structure of gas mixture



MedeA Flowchart to perform NPT MD Simulations with *LAMMPS*



Final structure of gas mixture



ρ_{calc} = 0.072 g/cm^3

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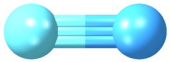
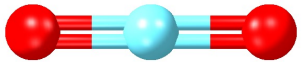
Fluid Layer for BD-NEMD Simulation

N_2



CO_2



Amorphous Materials Builder (AMB)

#	Component	Type	Nmols	Relax
Delete	1 Opened structure: N2	Automatic	50	✓
Delete	2 Opened structure: CO2	Automatic	50	✓
Add a component				

System geometry:	layer
Specify cell:	density,a,b
Density (g/ml):	0.07
Cell length a (Ang):	35.0
Cell length b (Ang):	35.0
Cell details:	Refresh
Density: 0.0700 a: 35.0000 b: 35.0000 c: 69.7378	
Temperature (K):	298.2
Coordinate bias:	none
Orientation bias:	none
Action:	Save system definition only
Number of configurations:	1

OK Cancel Help

Directory: /data/windiks/MedeA/AmorphousSpec

50-CH4+50-CO2-3.5nmx3.5nmx5.8nm.spec
50-CH4+50-CO2-3nmx3nmx6nm.spec
50-N2+50-CO2-3.5nmx3.5nmx7nm.spec
100-CH4+100-CO2-3nmx3nmx5.6nm.spec
100-CH4-
150-CH4-
200-CH4-
300-CH4-

File name: 50-CH4+50-CO2-3nmx3nmx6nm.spec Save

Files of type: Composition Files (*.spec) Cancel

Save *ABM* specifications for usage in BD-NEMD flowchart

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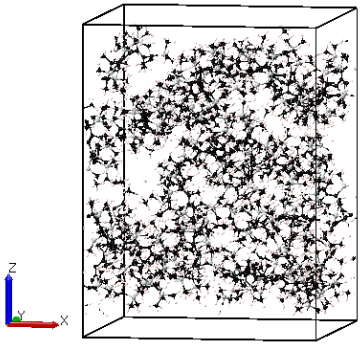
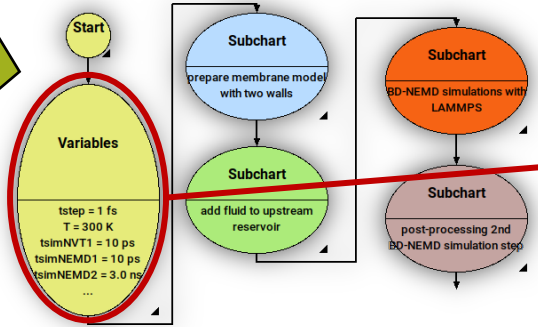
Set Up BD-NEMD Simulation

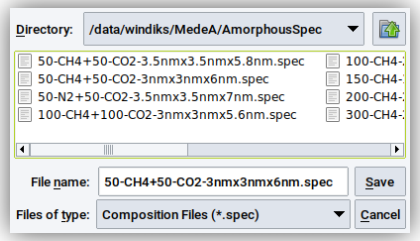
PTMSP
membrane model



BD-NEMD flowchart



AMB specification of gas mixture



Define running parameters in Variables Stage

Edit stage: Variables

Variable	Value	Units	
tstep	1	fs	Delete
T	300	K	Delete
tsimNVT1	10	ps	Delete
tsimNEMD1	10	ps	Delete
tsimNEMD2	3.0	ns	Delete
Lforce	4	nm	Delete
Ltransition	1	nm	Delete
LupReservoir	7.0	nm	Delete
LdownReservoir	7.0	nm	Delete
LmembraneEntry	0.8	nm	Delete
force	0.7	kcal/mol/Ang	Delete
NTrajectoryFrames	100		Delete
updateTempNevery	100		Delete
Nxbins	25		Delete
Nybins	50		Delete
Nzbins	250		Delete
dSlitPore	0.0	nm	Delete
			Add

Apply Reset

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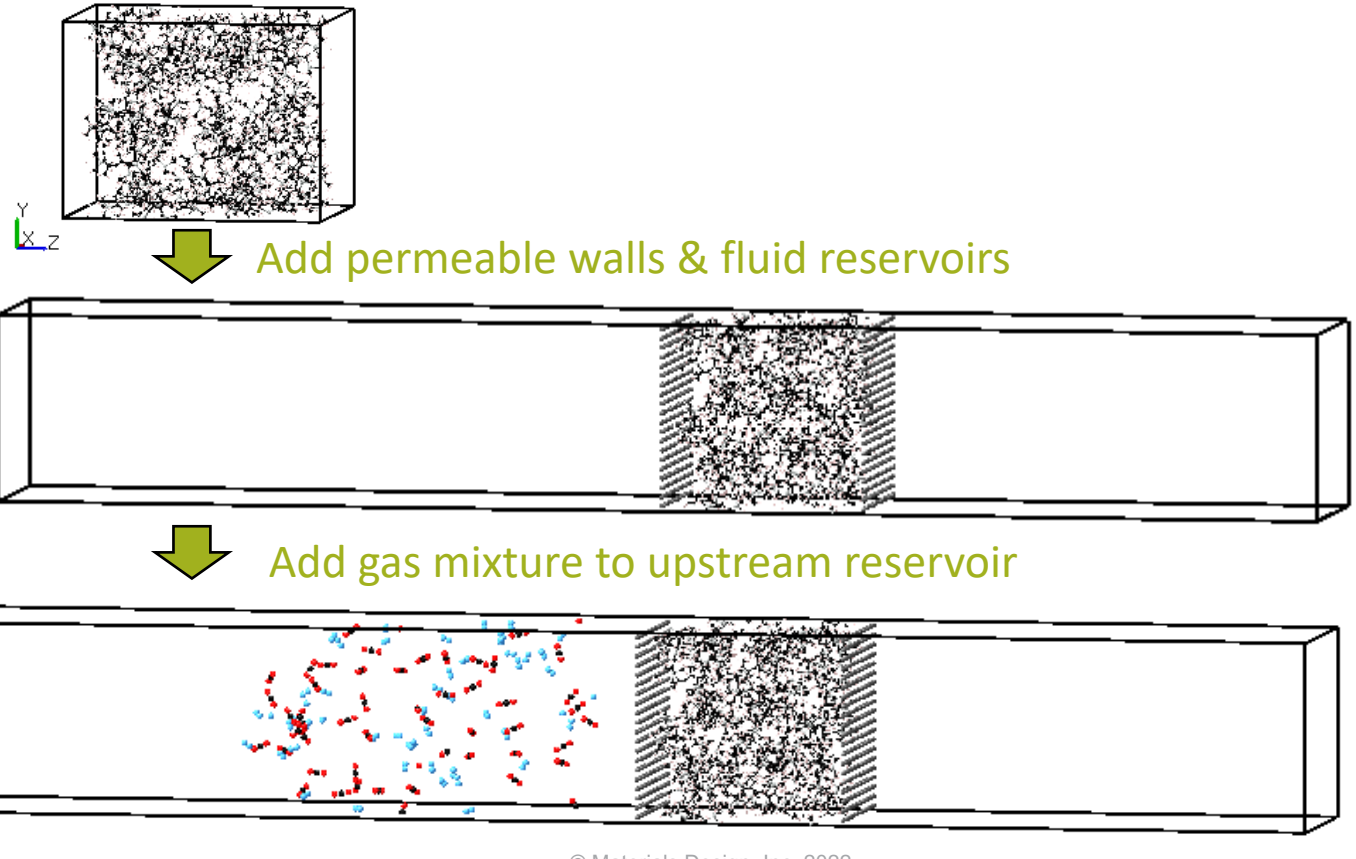
Building of Simulation Cell Within BD-NEMD Flowchart



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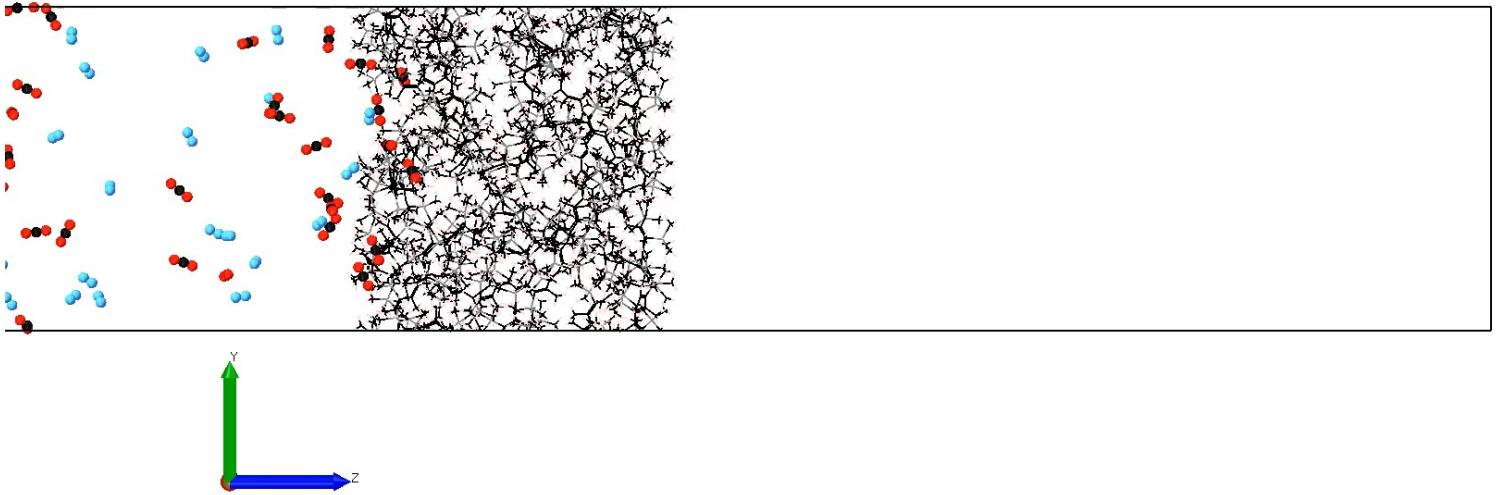
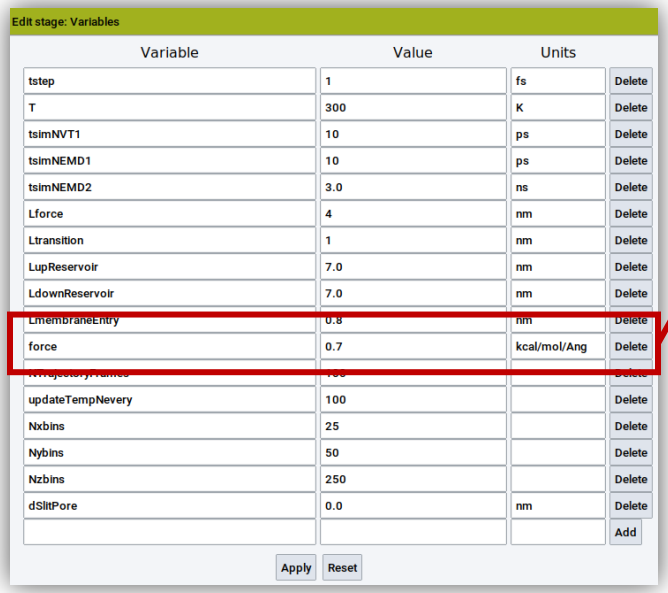
Results of BD-NMD Simulation (1)

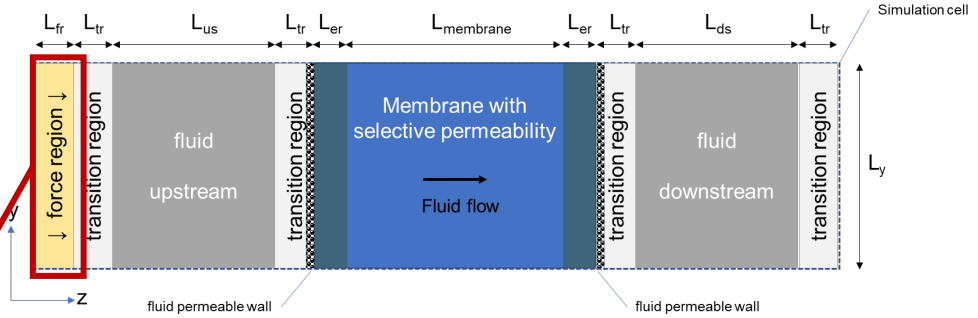
Recording of the animation of the trajectory



BD-NMD Simulations for Different Pressure Differences

Pressure difference ΔP can be tuned via the applied force on molecules in the force region





	T = 25 °C	# molecules in downstream reservoir		
Force (kcal/mol/Å)	**ΔP (bar)**	**CO_2**	**N_2**	**#CO_2 / #N_2**
0.5	30	0.151	0.003	50
0.7	40	0.137	0.007	20
1.5	60	0.426	0.251	2

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Summary

- BD-NEMD simulations are useful to calculate transport of gases through nano-porous membrane models
- Simulated transport is based on Fickian diffusion due to imposed pressure difference
- Key results of example calculation: separation of CO_2/N_2 gas mixture with PTMSP membrane depends on applied pressure difference
  - Best separation is achieved for pressure differences of 30-40 bar

- Nex steps: Test BD-NEMD approach for other transport phenomena of gases and liquids
  - Desalination of salt water
  - Transport of charge carriers in liquid electrolytes
  - …

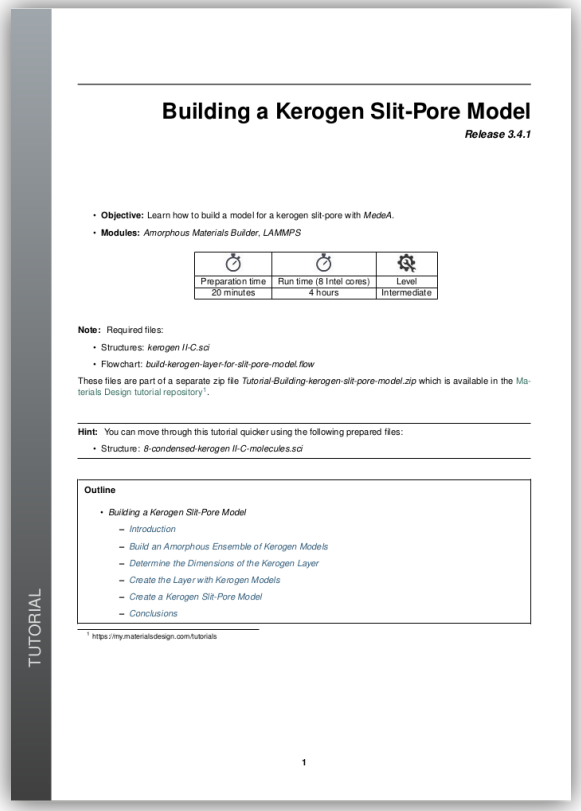
MedeA Modules Used in the Training

- *MedeA* Environment, incl. *MedeA LAMMPS*, *Polymer Builder*
- Amorphous Materials Builder (AMB)
- *MedeA HT Launchpad* for structure handling in flowcharts

- *MedeA GIBBS*
- *MedeA LAMMPS Diffusion*

Further Useful Tutorials

http://my.materialsdesign.com/tutorials



TUTORIAL

Building a Kerogen Slit-Pore Model

Release 3.4.1

- **Objective:** Learn how to build a model for a kerogen slit-pore with *MedeA*.
- **Modules:** *Amorphous Materials Builder, LAMMPS*

Preparation time	Run time (8 Intel cores)	Level
20 minutes	4 hours	Intermediate

Note: Required files:

- Structures: *kerogen II-C.sci*
- Flowchart: *build-kerogen-layer-for-slit-pore-model.flow*

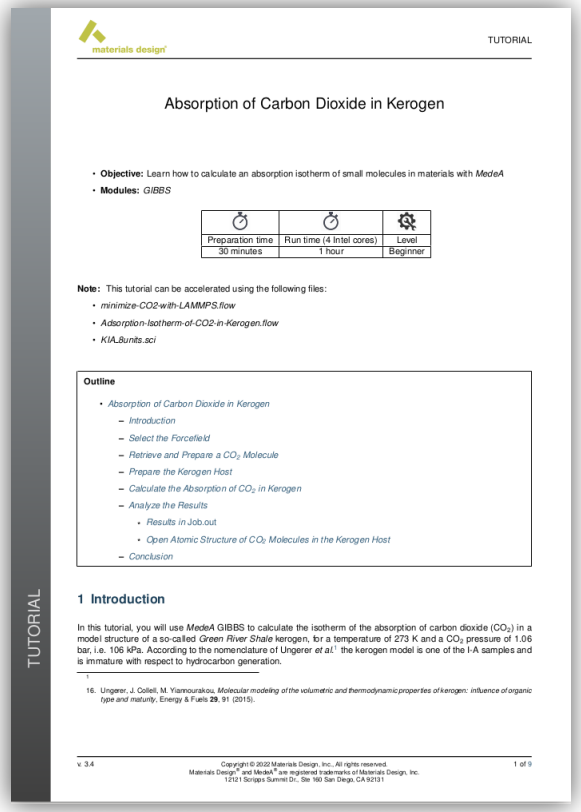
These files are part of a separate zip file *Tutorial-Building-kerogen-slit-pore-model.zip* which is available in the Materials Design tutorial repository[1].

Hint: You can move through this tutorial quicker using the following prepared files:

- Structure: *8-condensed-kerogen II-C-molecules.sci*

Outline

[1] https://my.materialsdesign.com/tutorials



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TUTORIAL

TUTORIAL

Absorption of Carbon Dioxide in Kerogen

- **Objective:** Learn how to calculate an absorption isotherm of small molecules in materials with *MedeA*
- **Modules:** *GIBBS*

Preparation time	Run time (4 Intel cores)	Level
30 minutes	1 hour	Beginner

Note: This tutorial can be accelerated using the following files:

- *minimize-CO2-with-LAMMPS.flow*
- *Adsorption-Isotherm-of-CO2-in-Kerogen.flow*
- *KIA_8units.sci*

Outline

1 Introduction

In this tutorial, you will use *MedeA* GIBBS to calculate the isotherm of the absorption of carbon dioxide (CO_2) in a model structure of a so-called *Green River Shale* kerogen, for a temperature of 273 K and a CO_2 pressure of 1.06 bar, i.e. 106 kPa. According to the nomenclature of Ungerer *et al.*[1] the kerogen model is one of the I-A samples and is immature with respect to hydrocarbon generation.

[1] 16. Ungerer, J. Collell, M. Yiannourakou, *Molecular modeling of the volumetric and thermodynamic properties of kerogen: influence of organic type and maturity*, Energy & Fuels **29**, 91 (2015).

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Question and Answer Session

Dr. René Windiks

Materials Design

Dr. David Reith

Materials Design

Announcements

ugm.materialsdesign.com

Next Week's Plenary Session

*****Wednesday, October 12th***

Professor Jörg Behler

University of Göttingen

MedeA Training

Thursday, October 13th

Dr. David Reith

Materials Design

Questions about Materials Design UGM

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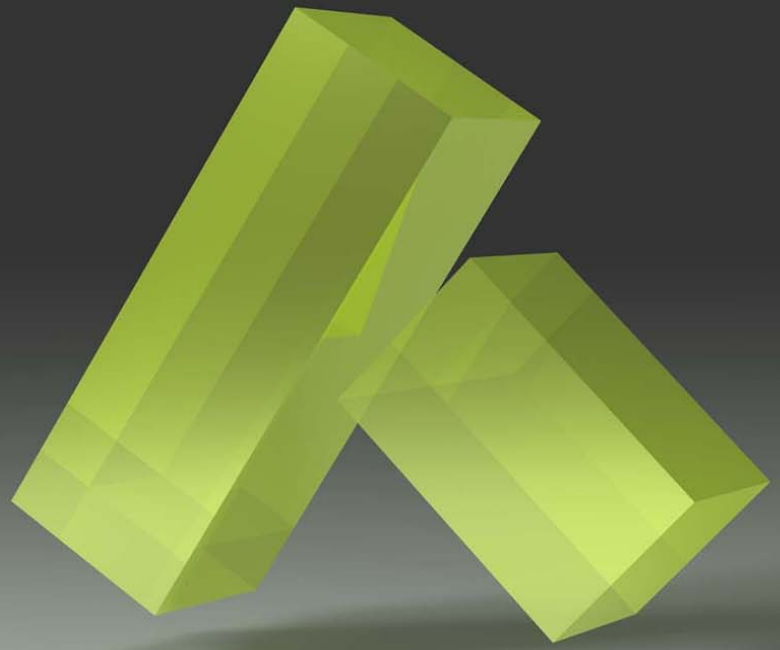

MedeA

Innovation by Simulation