A dæmon for steady-state diffusion through membranes

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• Describing adsorption and diffusion phenomena are critical to design efficient separation methods
• Molecular simulation has become a very powerful tool to investigate such phenomena
• Focus on simulating steady-state membrane transport
• Crucial points: method to handle the dynamics of the system, method to ensure and maintain the driving force at microscopic level
Methods

- External field MD + PBC (external work on the system -> temperature coupling is essential) [1]
  - Self-adjusting plates technique (feed side reservoir problems) [2]
- Gradient relaxation MD (weakness: transient nature) [3,4]
- DCV-GCMD (coupling stochastic to deterministic) [5]
- NP+LEMC (diffusion constant is input parameter) [6]
- DMC+LEMC (MD like trajectory fragments) [7]
- Kinetic MC (rate coefficients required) [8]

Problems to solve

- Depletion/accumulation of particles in the bulk zones
  - we cannot simulate real size fluid reservoirs
    → reinjection/removal is a must

- Preservation of the steady-state flux of transporting particles
  - no sudden ’near membrane’ molecule appearance/annihilation
Pressure-tuned, boundary-driven MD

Features:

• Simplicity and connection to macroscopic physical picture of gas transport through membrane

• Pressure is the property that can be controlled relatively simply: partial pressure for each component on the input side and total pressure on the permeate side

• Similar to DCV-GCMD but insertion/deletion steps allowed in the boundary regions only (governing factor is pressure; not a real thermodynamic ensemble)

Pressure-tuned, boundary-driven MD

Arrangement of a PBD-MD simulation box

\[
\left| \left( \frac{N_{\text{control cell}} \pm 1}{N_{\text{control cell}}} \right) \cdot p_{\text{control cell}} \right| - p_{\text{target}} < |p_{\text{control cell}} - p_{\text{target}}| \]
• 5000 consecutive MD steps (time step: 2 fs)
  \( N_{\text{control cell}} \) and \( p_{\text{control cell}} \) collected as averages

• Insertion/deletion in regions far from the membrane
  check pressure (and avoid ’hard-core’ overlaps)

• Berendsen **thermostat**
  key point in these simulations,
  must preserve streaming velocities
Simple test cases

• Silicalite-1 membrane
  (rigid framework, built up from SiO$_4$ tetrahedrals,
  0.8 nm zig-zag and linear channels)

• Gases: CH$_4$, CO$_2$, H$_2$, and N$_2$
  (single component and equimolar mixtures)

• Adsorption & steady-state diffusion

• Molecular models:
  gases: single site shifted and cut LJ
  silicalite-1: O interactoin sites only [1]

Simple test cases

- quantifying the adsorption and diffusion

\[ S_E = \left( \frac{q_{CO_2}}{q_i} \right)_{i \neq CO_2} \]  
  equilibrium selectivity

\[ S_P = \left( \frac{J_{CO_2}}{J_i} \right)_{i \neq CO_2} \]  
  permeation selectivity  
  (dynamical selectivity)

\[ R_P \]  
  idealized permeation ratio

\[ P = J \cdot (\Delta p / \Delta x)^{-1} \]  
  permeance data
### Results

Steady-state concentration profiles

(a) pure CH$_4$ T=338 K $p=200$ kPa, vacuum on the permeate side

(b) CO$_2$-N$_2$ mixture at 408 K with $p = 140$ kPa (70 kPa for both components) on the feed side and vacuum on the permeate side,

(c) CO$_2$-H$_2$ mixture at 303 K with $p = 140$ kPa (70 kPa for both components) on the feed side and $p = 100$ kPa on the permeate side.

(For example, 0.1 mol dm$^{-3}$ means ~100 particles in our typical feed side reservoir with length of ~40 nm.)
Results

CO\textsubscript{2}-H\textsubscript{2}:

$\rho_{\text{permeate}} = 100$ kPa

$T / K$
ls1 branch

- Implementing the method in ls1
  
  Martin Horsch and coworkers (in progress)

- Molecular models from Jadran Vrabec and coworkers (available)

- Take advantage of the capabilities of ls1 and OCuLUS cluster (PC² Paderborn)
  
  • larger number of molecules
  • speed
  • parallelization
  • variability (other thermostats)
THANK YOU FOR YOUR ATTENTION!

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