Research Summary

Modeling Hydrocarbon Filtration in Nanoporous Media

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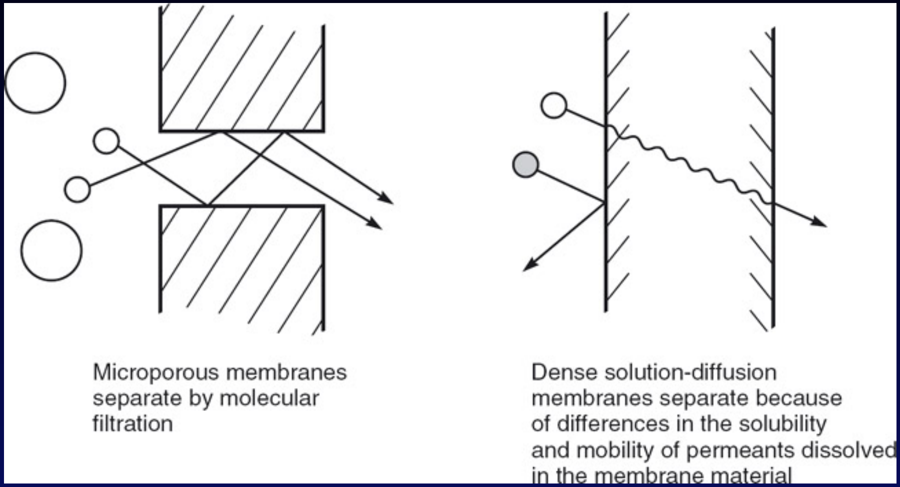
Background - Membrane Transport Theory

Molecular transport through membranes:
- by a flow through permanent pores
- by the solution-diffusion mechanism

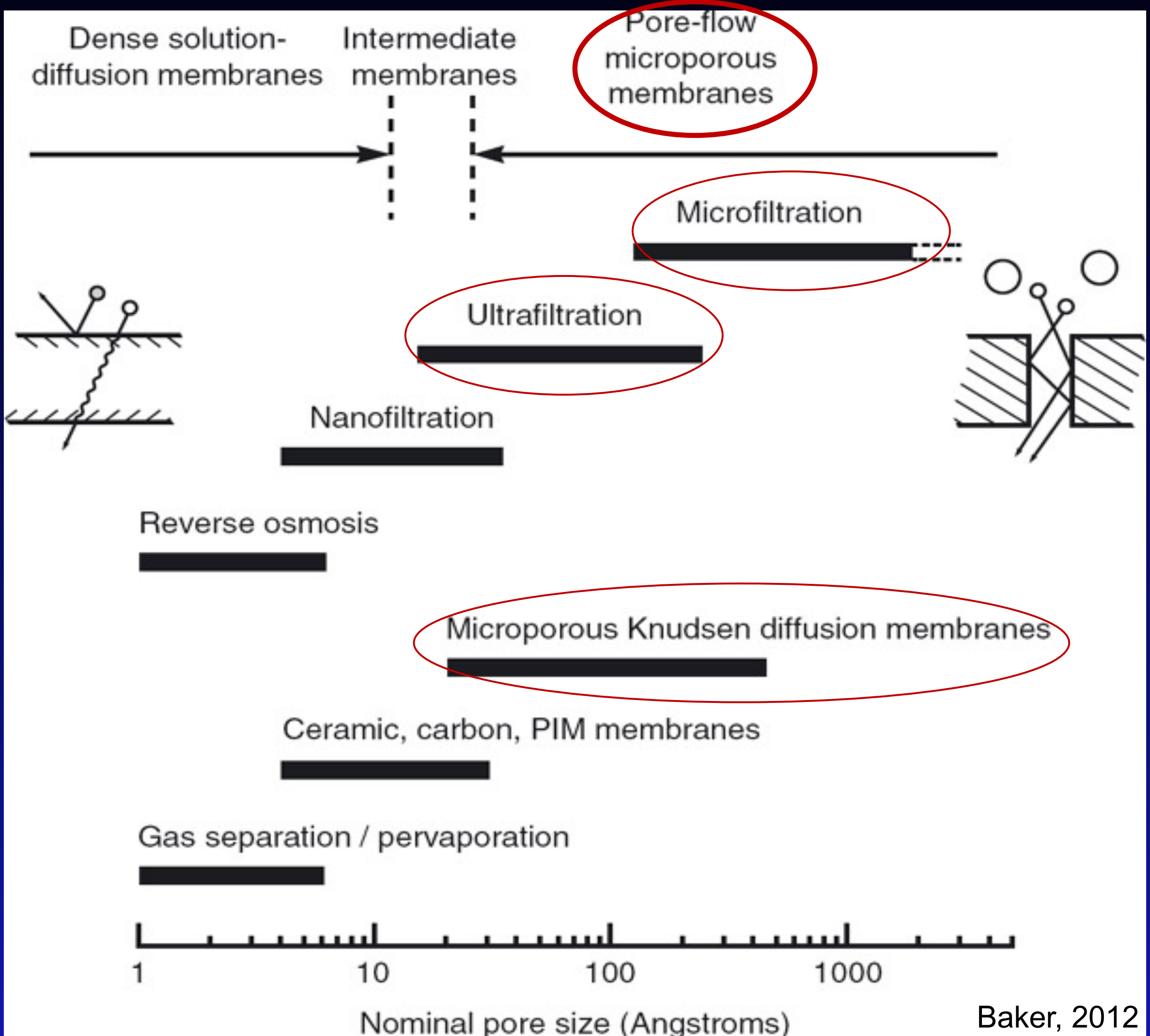


Pore-flow model: Transported by pressure-driven convective flow though nanoporous media.

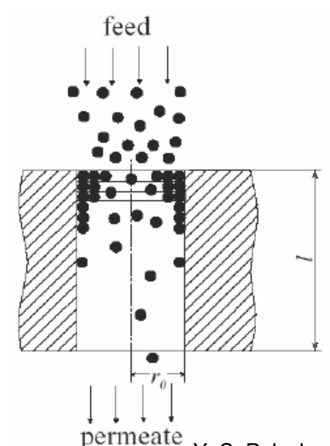
Solution-diffusion model: Dissolve in the membrane material & diffuse though the membrane down a concentration gradient.

Baker, 2012

Background - Membrane Transport Theory (cont`d)



Baker, 2012



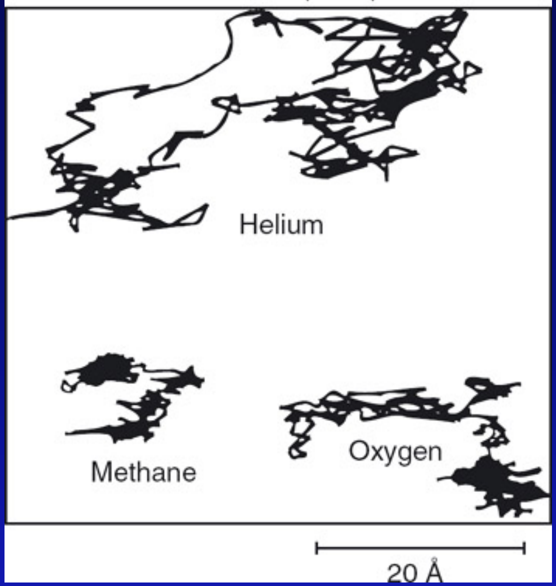
Y. S. Polyakov

Solution-Diffusion Model

- Applies to reverse osmosis, pervaporation, and gas permeation in polymer films
- Provides equations – correctly link concentration driving forces, pressure with flux, and selectivity
- Composition, pressure, and temperature of the fluids: determine the concentration of the diffusing species

The movements of 3 molecules by computational techniques:

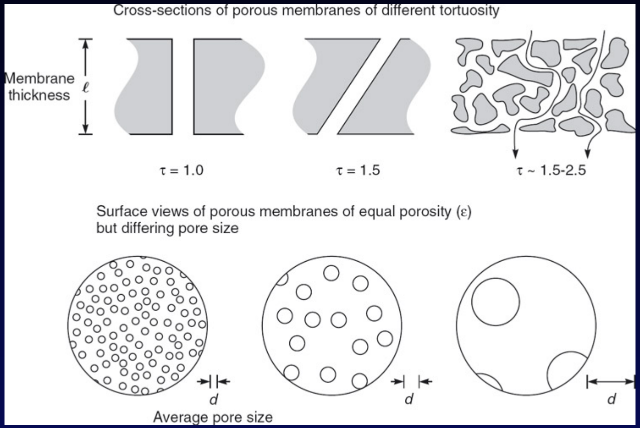
From Charati and Stern (1998)



Helium molecule:
- Smaller
- moves more frequently
- makes larger jumps

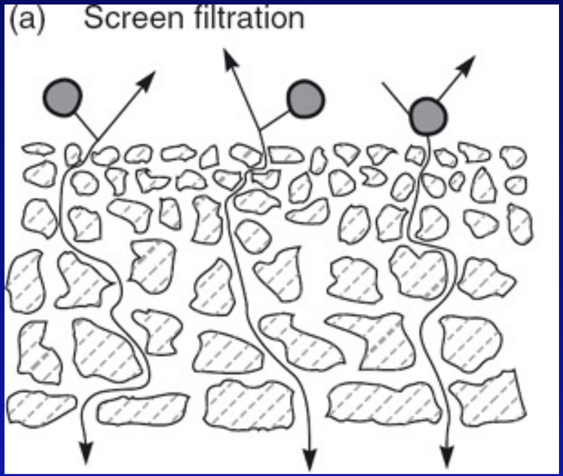
Pore-Flow Model

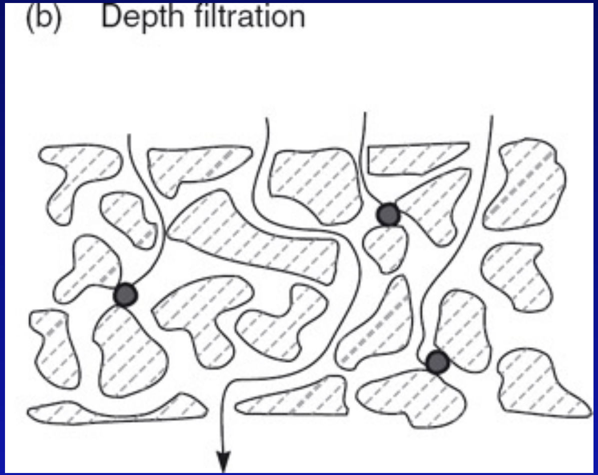
- Characterizing the complexity of microporous membranes – imperfect
- Mostly used parameters: tortuosity (τ), membrane porosity (ε) & average pore diameter (d)
- The most important: pore diameter



Separation of particulates:

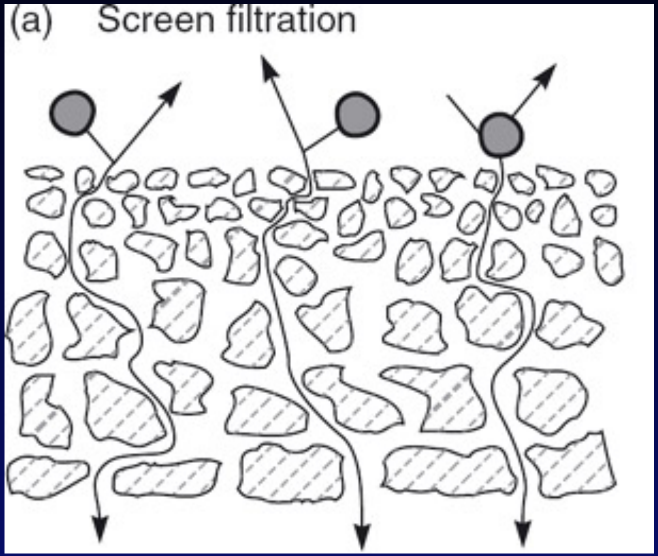
- at the membrane surface – **screen filtration mechanism**
- in the interior of the membrane – **depth filtration mechanism**





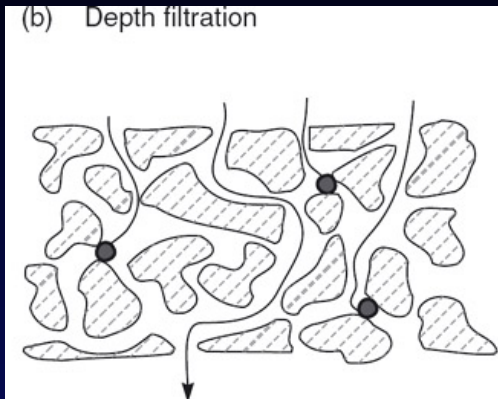
Baker, 2012

Pore-Flow Model – Screen filtration



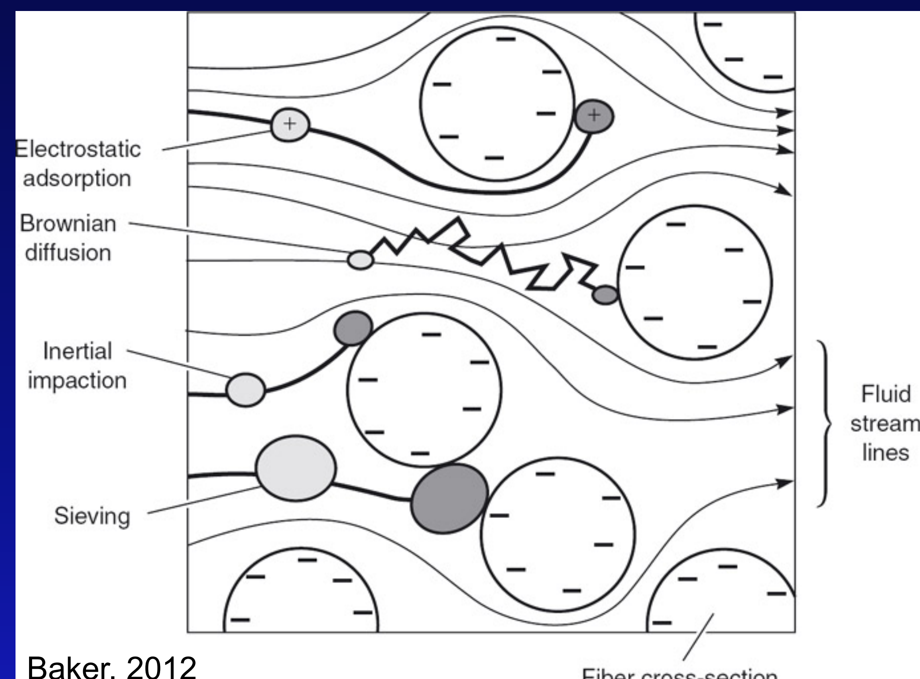
- The mechanism is relatively easily described.
- Surface pores are smaller than the particles to be removed.
- Small particles pass through the surface pores & not captured in the interior of the membrane.
- Ultrafiltration membranes

Pore-Flow Model – Depth filtration



- The mechanism is more complex
- Captures the particles to be removed in the interior of the membrane
- Microfiltration membranes
- 4 mechanisms contribute to capture particle

<u>*Sieving*</u>:
✓ captures particles at constrictions
<u>*Inertial impaction*</u>:
✓ capture particles by adsorption
✓ most efficient for larger particles
<u>*Brownian diffusion*</u>:
✓ capture particles by surface adsorption
✓ most efficient for smaller particles
<u>*Electrostatic adsorption*</u>:
✓ capture of charged particles



Baker, 2012

Pore-Flow Model - Motivation

- Transport modeling through microporous membranes in ultrafiltration & microfiltration is less developed
- Permeation

  affected by several effects – hard to compute

  function of membrane structure and composition
- Current theories cannot fully model the permeation properties of the membranes

Transport in Nanoporous Media

Empirical Darcy or Fick`s Law relate diffusive flux to the gradient of a process variable (pressure, concentration, temperature, etc.)

Thermodynamically, diffusion occurs so as to minimize the free energy.

Therefore, a more general expression for diffusive flux is given in terms of the chemical potential gradient.

$$J_i = -L_i \frac{\partial \mu_i}{\partial x}$$

If the driving forces are concentration and pressure

$$d\mu_i = RTd\ln(\gamma_i n_i) + v_i\left(p - p_i^0\right)$$

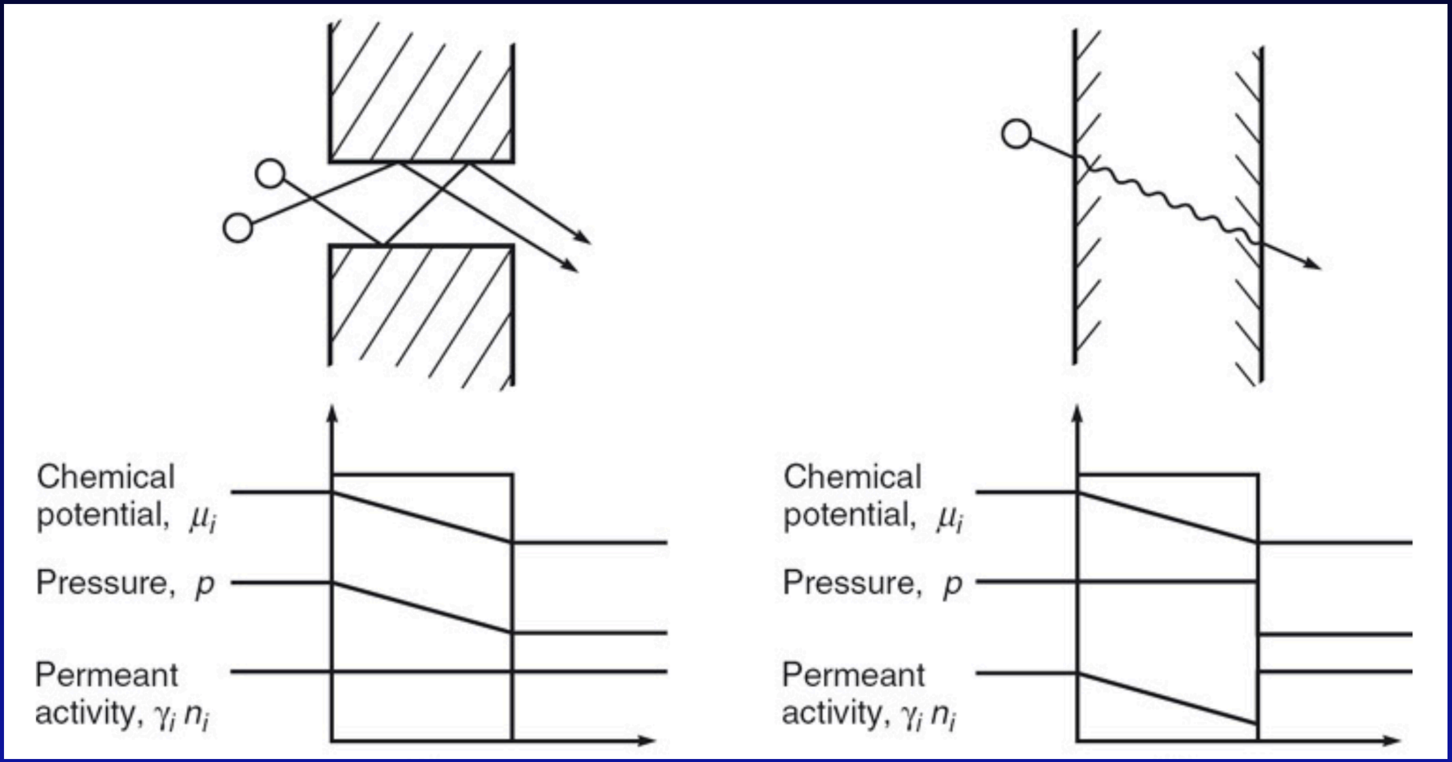
$$\mu_i = \mu_i^0 RTd\ln(\gamma_i n_i) + v_i\left(p - p_{i_{sat}}\right)$$

Transport in Nanoporous Media

Assumptions involved in filtration modeling

Pore-Flow Model

Solution-Diffusion Model



$$\mu_i = \mu_i^0 RTd \ln(\gamma_i n_i) + v_i(p - p_{i_{sat}})$$

Literature Review

Ruthven et al., 1973:
- Reported experimental results of sorption and diffusion of light HCs
- Diffusion activation energy proves a good correlation with critical diameter

Shelekhin et al., 1995:
- Proposed a mathematical model to define diffusion, permeation and separation of gases in microporous molecular-sieve membranes
- Showed that the diffusion activation energy increases with increasing kinetic diameter of the diffusant

Polyakov et al., 2002:
- Studied a mathematical model of a depth filter
- Used the solution to analyze the depth filter performance as a function of the size of filtration velocity, colloidal particles, specific filter surface, and filter depth

Smit, B., 2007:
- Demonstrated how molecular simulation can be useful in order to understand behavior of molecules inside the pores of zeolites
- Showed used rare event simulation techniques with practical use and importance

Literature Review

Polyakov, Y. S., 2008:

- Developed a macroscopic depth filtration theory for the standard blocking of the pores of 'Ultrafiltration'/'Microfiltration' membranes
- The theory guesses the membrane permeation rate and selectivity & shows the profile of the number of deposited particles
- The proposed formulations were confirmed with the experimental data

Sampath et al., 2014:

- Studied practicability of using different proposed models for filtration of a satisfying product at constant pressure
- Observed: smaller pore filters experience fouling through complete pore blocking
  larger pore filters experience fouling through intermediate pore blocking
- Recommended: "The proposed approach can be used for more accurate sizing of microfilters and depth filters"

Kuhn et al., 2017:

- Introduced a new model-based method to improve depth filters design
- Confirmed the numerical optimal control algorithm using a newly developed analytical solution of local filtration performance

Questions?

Thank you