Research Summary

Hindered Transport in Nanoporous Media

Erdal Ozkan
Colorado School of Mines

Why Hindered Transport?

Unconventional reservoirs predominantly produce light hydrocarbons

Source rocks are known to have heavier hydrocarbons also

Hydrocarbons are stored in the tight matrix of unconventional reservoirs

Nanoporous (shale) media are known to have membrane properties

Membranes can filter hydrocarbon mixtures through molecular sieving

Filtration process can be modeled as hindered transport

Understanding hindered transport may help us enhance recovery

Essential Understanding

Membrane properties of unconventional reservoirs

- Theoretical
- Experimental

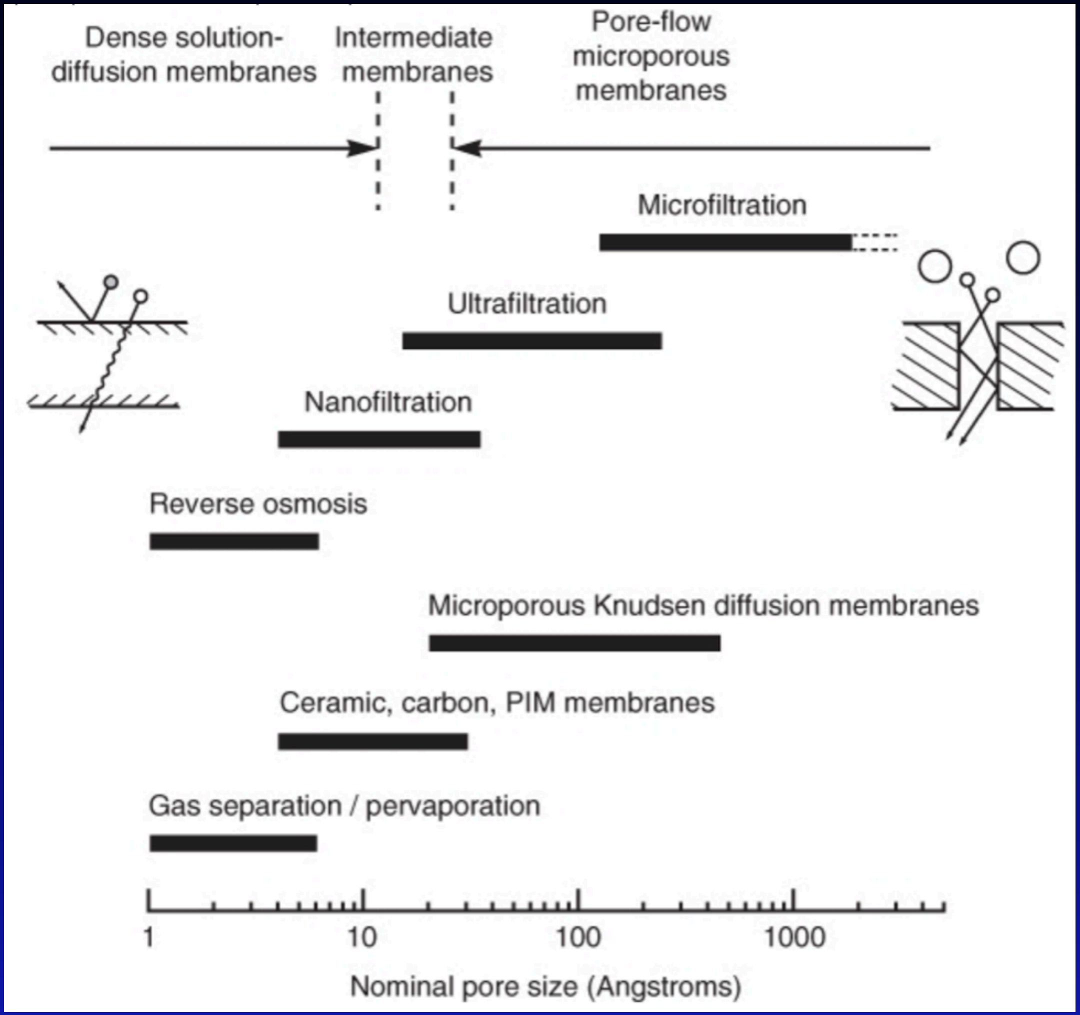
Fundamentals of hydrocarbon filtration

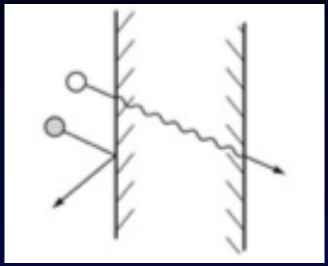
- Most filtration theory is on solid particle filtration
- Molecular sieving is inherently more complex
- Multiple filtration mechanisms prevail in porous material
- Experimentally difficult to identify, measure, and characterize

Constructing transport models

- Different filtration mechanisms lead to different types of flux
- Transport is a result of coupled fluxes
- Coupled flow models
- Facilitated transport(?)

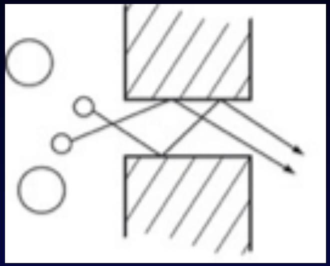
Membrane Types





Dense Nanoporous Membranes

Dense solution-diffusion membranes separate because of difference in solubility and mobility of permeants dissolved in the membrane material

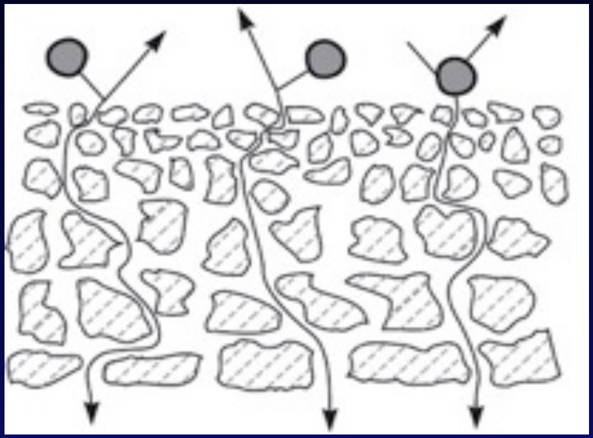


Pore-Flow Membranes

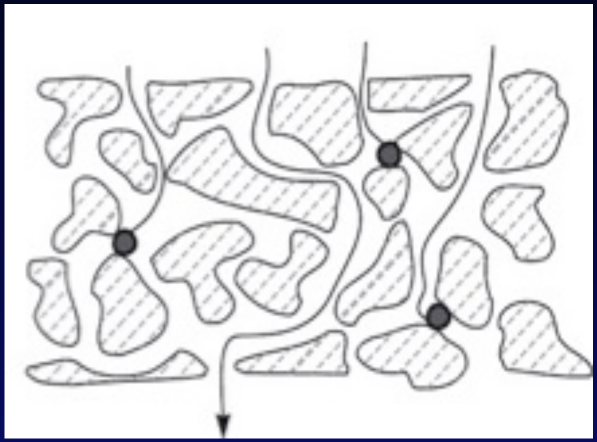
Microporous membranes separate by molecular filtration

(Baker 2012)

Pore-Flow Membranes vs. Nanoporous Media

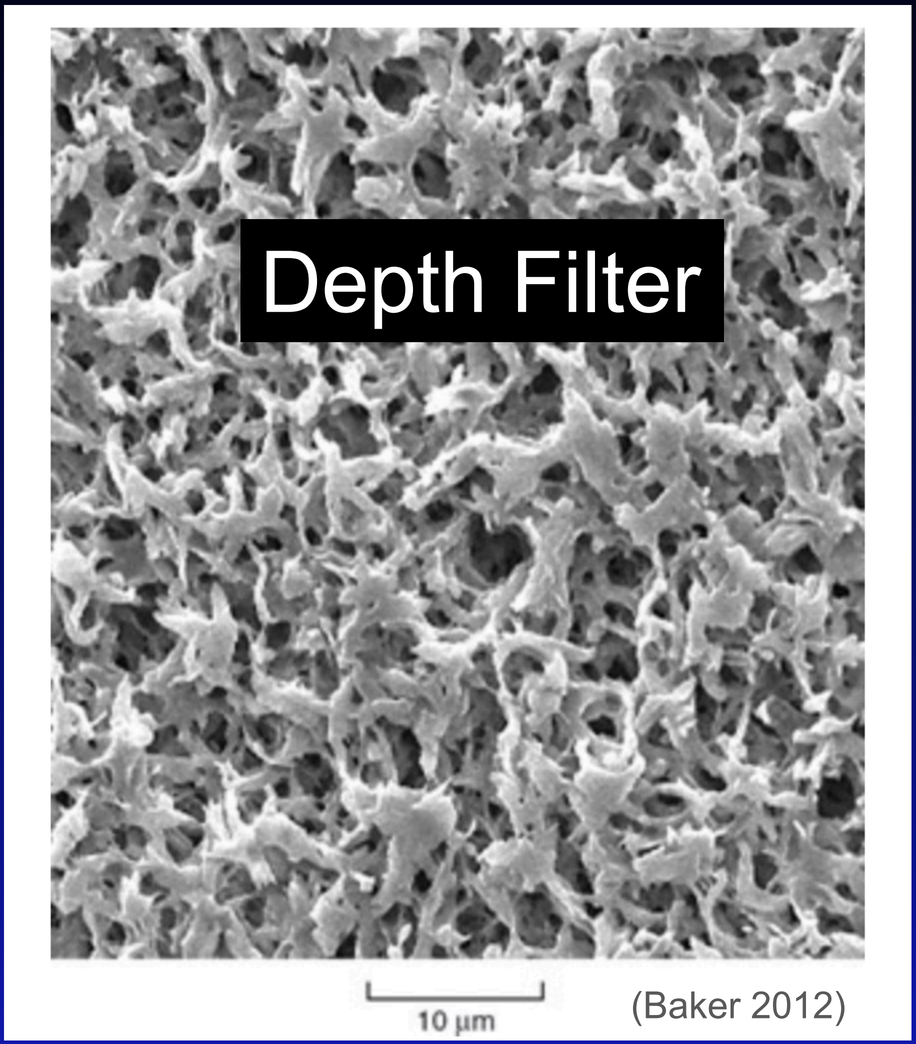


Screen Filtration



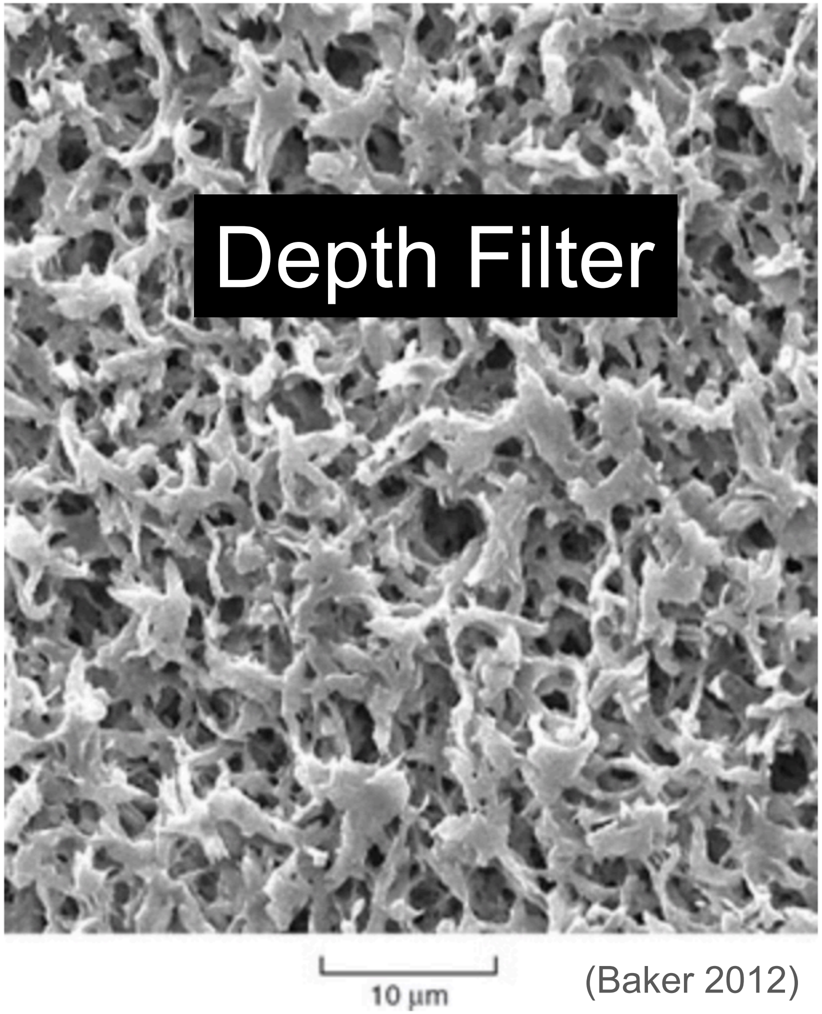
Depth Filtration

Depth Filter vs. Nanoporous Media

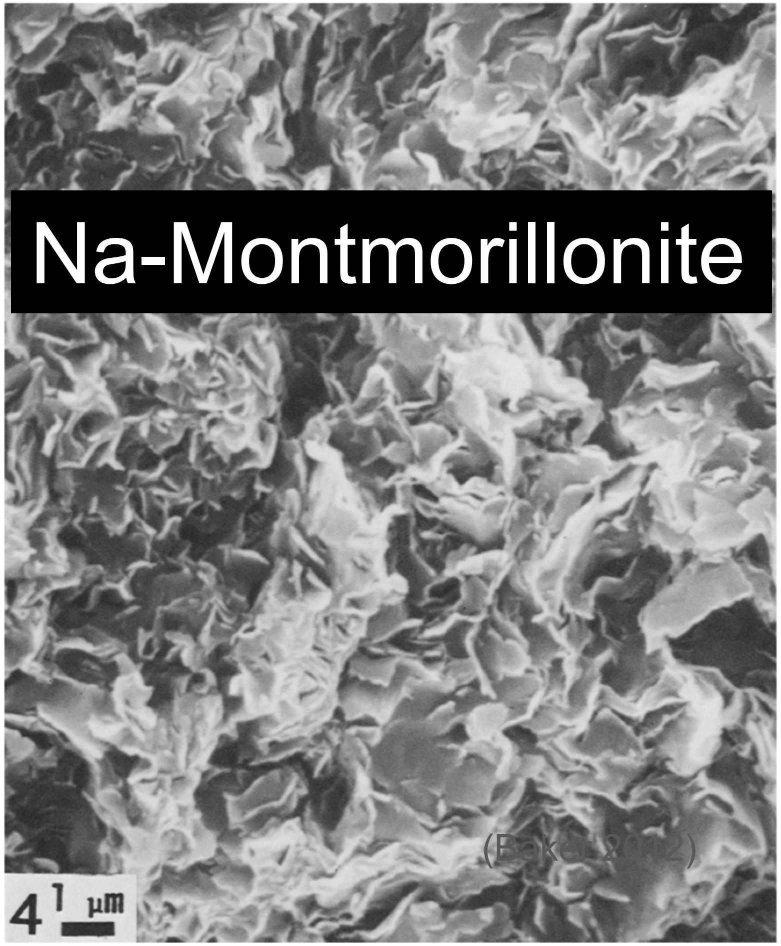


(Baker 2012)

Depth Filter vs. Nanoporous Media

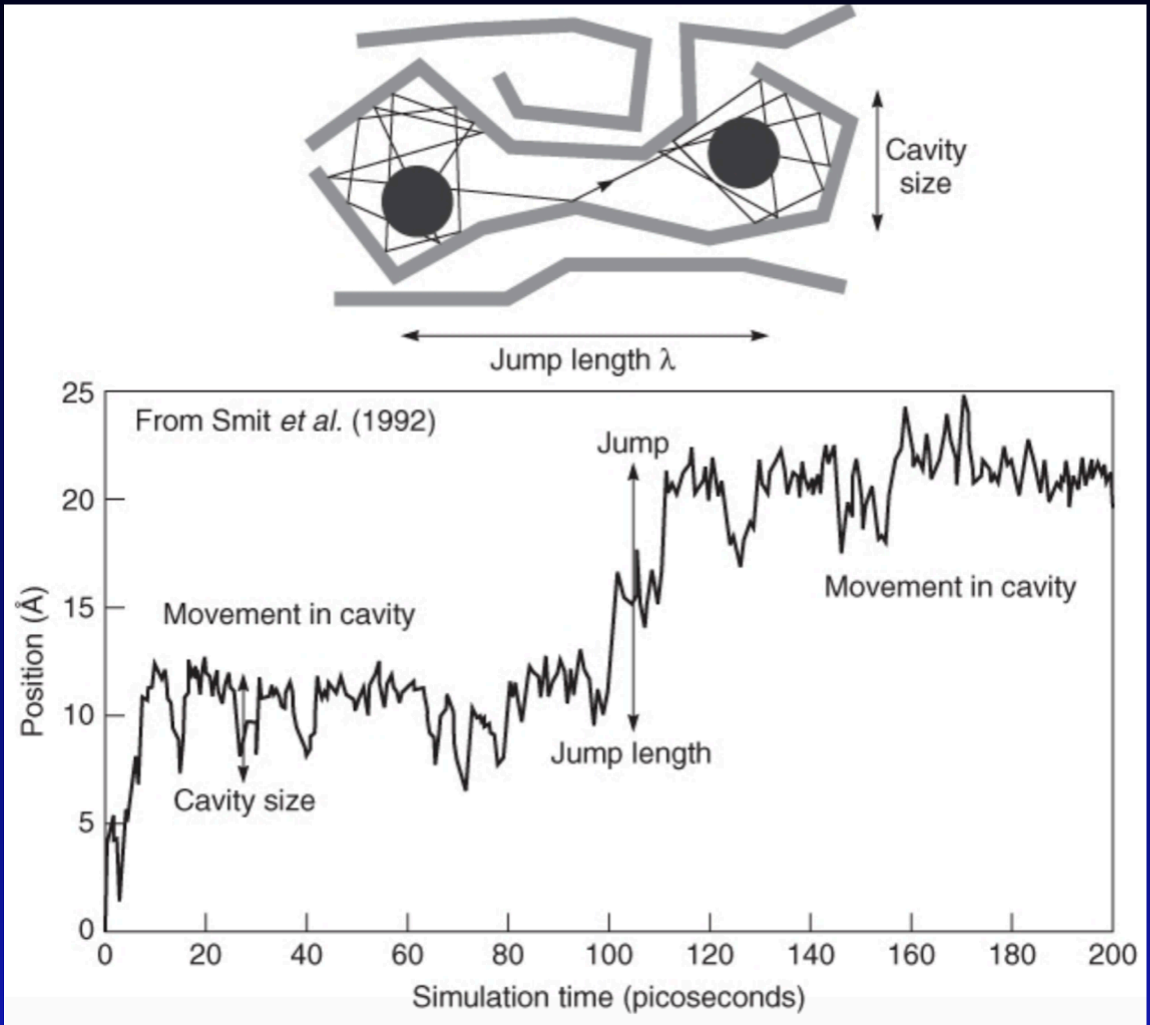


(Baker 2012)



(Keller et al. 1986)

Solution-Diffusion Model of Filtration



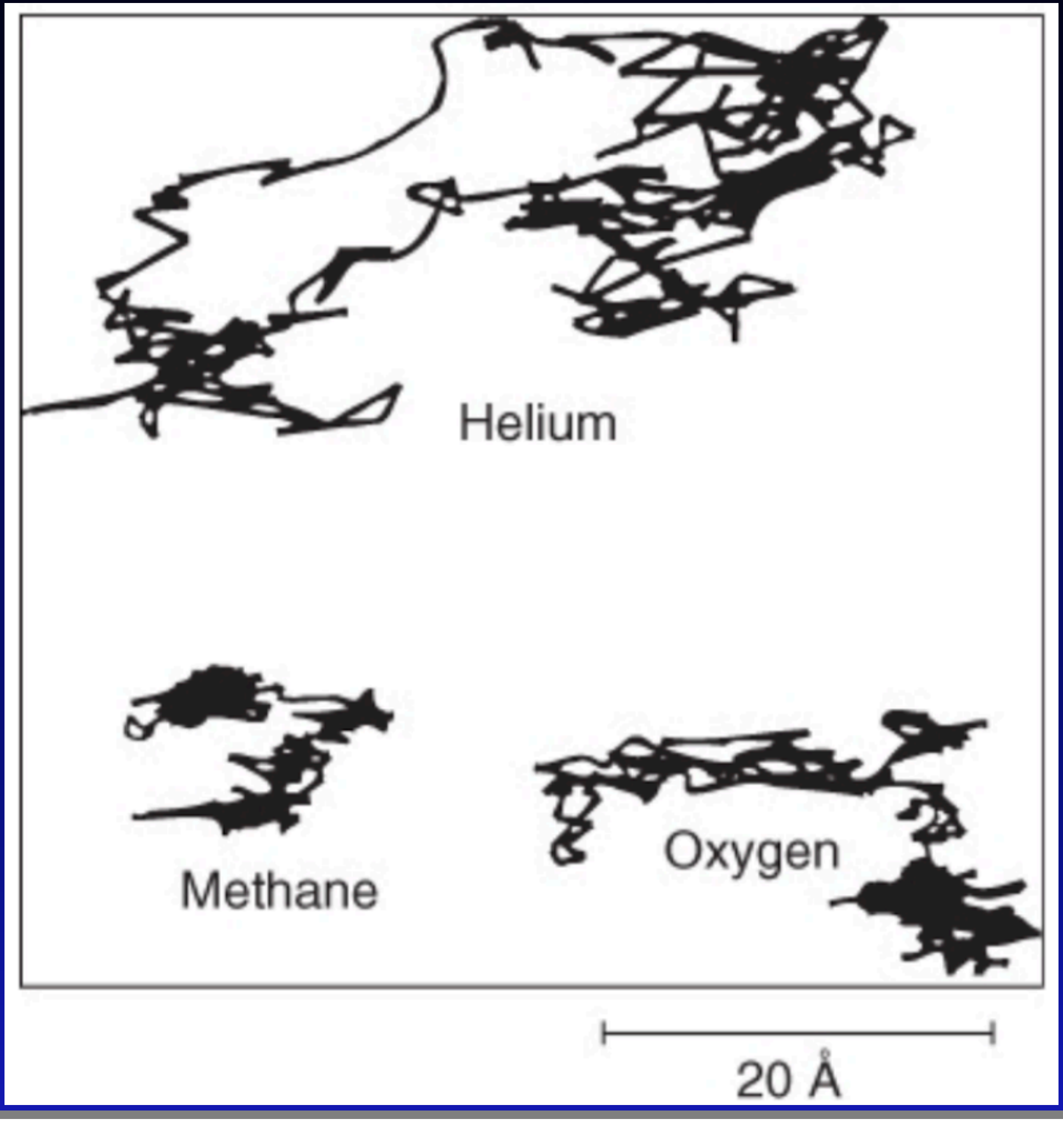
Dense Solution- Diffusion Membranes

Molecular Dynamics simulation of the motion of a CO_2 molecule in a 6FDA-4PDA polymer matrix

Transport occurs by molecular diffusion

(Baker 2012)

Solution-Diffusion Model



Dense Solution- Diffusion Membranes

Movement of molecules in over a period of 200 ps in a silicone rubber polymer matrix
polymer matrix

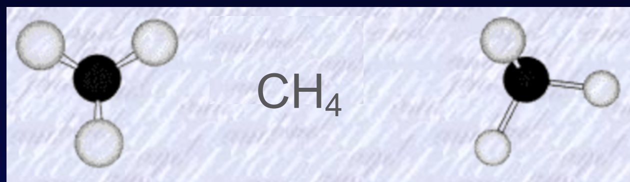
Smaller molecules can move more frequently (have more opportunities to jump from one position to another) and make larger jumps

(Charati and Stern 1998)

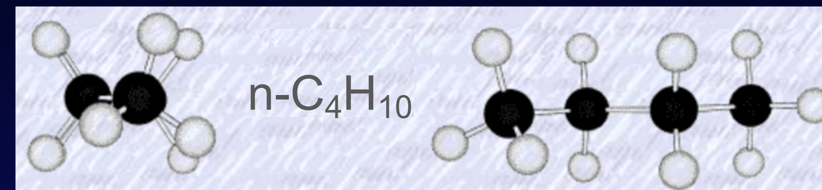
Size and Shape Matter

Effective HC Molecular Sizes

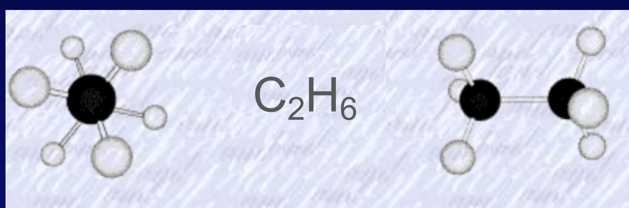
3.988 Å 3.988 Å



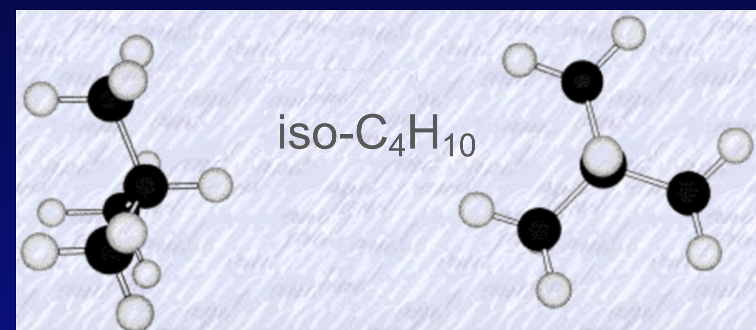
4.150 Å 8.240 Å



3.988 Å 4.755 Å



4.150 Å 8.240 Å



Molecular Type	***d (Å)***	***f (Å)***	***f/d***
CH_4 (methane)	3.988	3.988	1.000
C_2H_6 ((ethane)	3.988	4.755	1.20
$n\text{-}C_4H_{10}$ ((n-butane)	4.150	8.240	1.99
$iso\text{-}C_4H_{10}$ ((iso-butane)	4.150	8.240	1.99

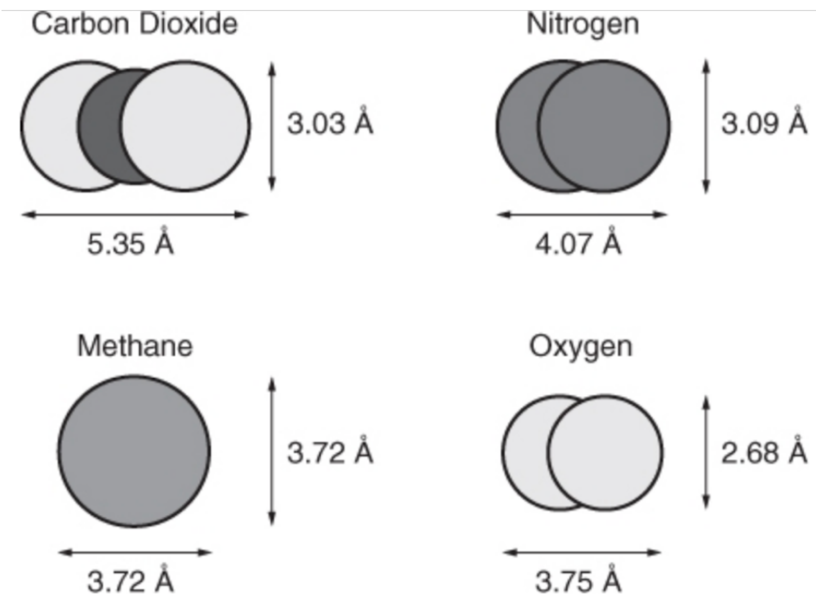
d - ***effective diameter of the molecule***
f - ***effective length of the molecule***

* As either d or f increases, the size of the molecule increases.
* As the ratio *f* / *d* increases, the linearity of the molecules increases.

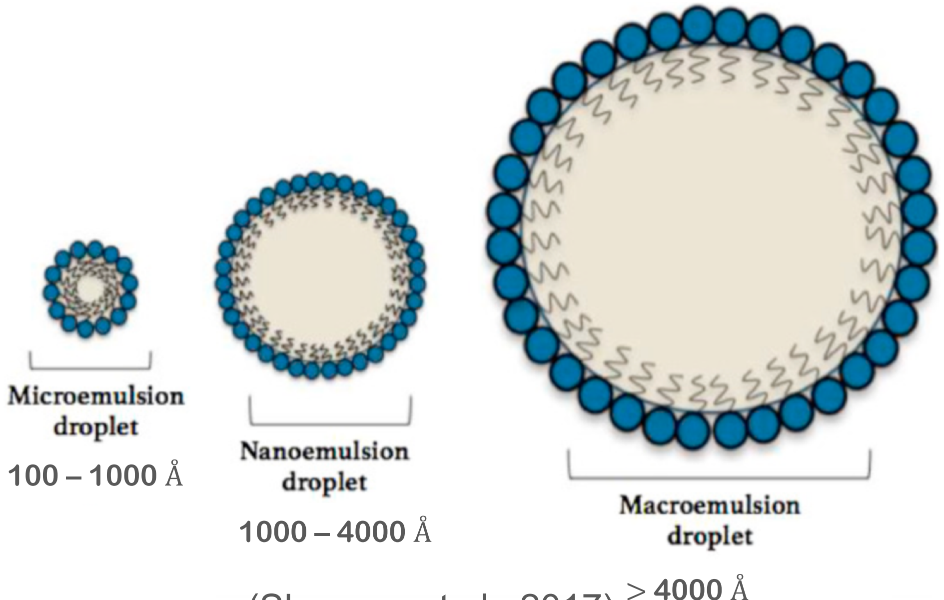
(Mao and Sinnott 2001)

Implications on EOR

Size Comparisons of Gas Molecules vs. Surfactant Microemulsions



(Baker 2012)



(Shannon et al. 2017)

What Do We Know?

Is it only size exclusion (steric hinderance)? No

- The higher the concentration of heavier HCs, the higher their production
- Molecular sizes do not have to be larger than pore sizes for exclusion
- Selective adsorption is an important factor

Is it possible to decrease filtration efficiency? Yes

- Pressure, temperature, activation energy, chemical composition, …

If heavier HCs are permitted to flow, does the flux increase? Yes

- We have experimental evidence

How does CO_2 work

- Diffusion activation energy?

Transport in Nanoporous Media

Empirical Darcy or Fix 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

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

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