EU funded Project

Innovation and Networks Executive Agency
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Modelling Solubility and Diffusivity in Facilitated Transport Membranes: Microscale and Macroscale Approaches

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UNIBO

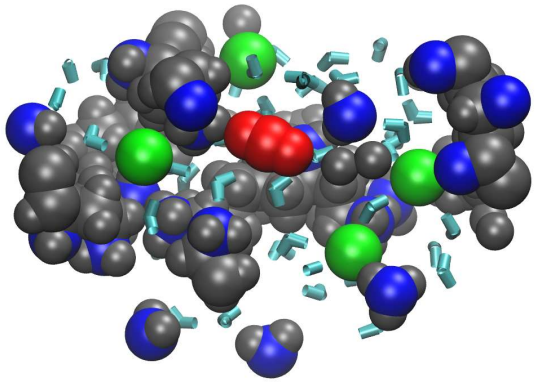
Paris, 03/07/2019

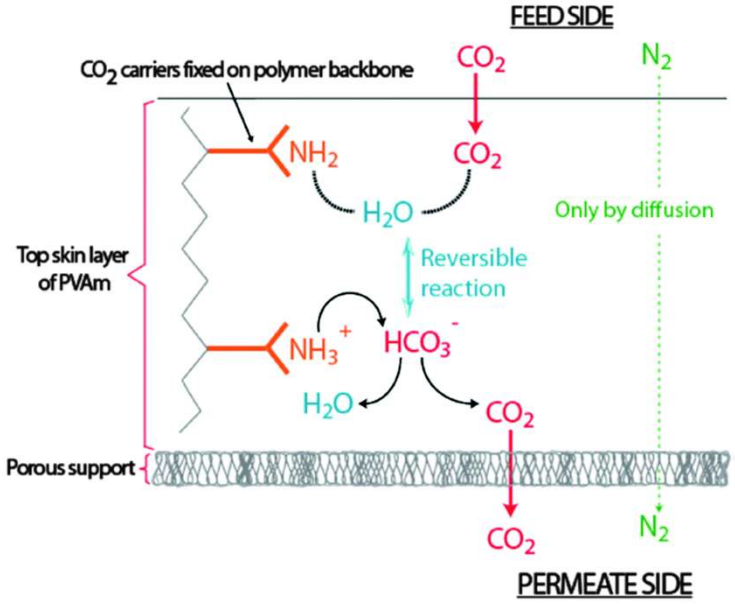
THE UNIVERSITY of EDINBURGH

Multiscale Models

Molecular Models

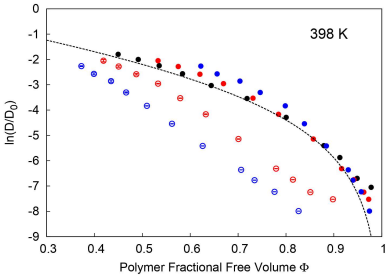
- Transport properties
- Explicit ionic species
- Polymer chain conformation





Empirical Models

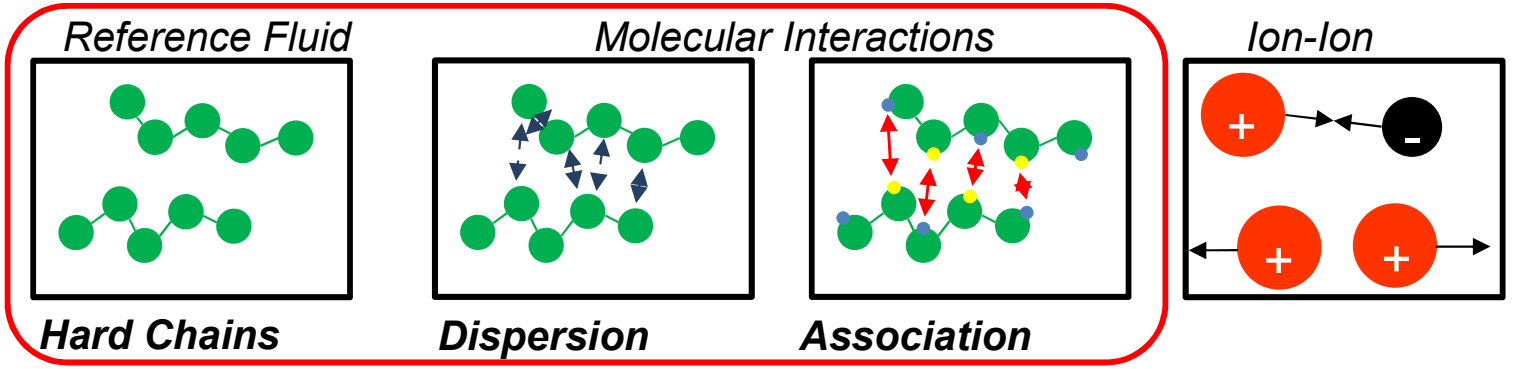
- Diffusivity correlation
- Hydration/Permeability relationship
- Macroscopic behavior



$$\frac{D}{D_0} = \left(\frac{1-\Phi}{1+\Phi}\right)^2$$

SAFT Equation of State

- Water absorption
- "Reaction" equilibrium
- Speciation



Kim, T. J., Li, B., & Hägg, M. B., J. Pol. Sci. B: Pol. Phys., 42 (23), 4326-4336, 2004

Facilitated Transport for Gas Separation

Transport Mechanism

Dense
Solution Diffusion

$$J_i = P_i \frac{\Delta p_i}{L}$$

$i = 1\ldots,n_c$

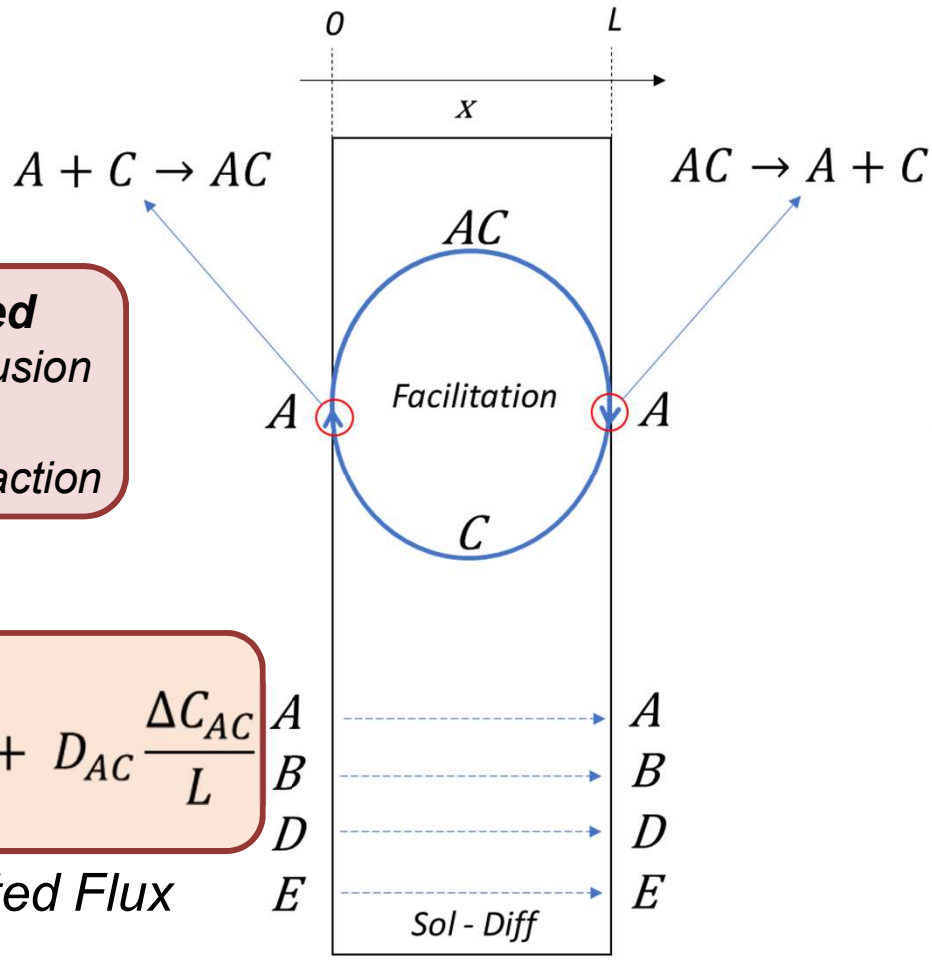
Sol-Diff Flux

Facilitated
Solution Diffusion
&
Chemical Reaction

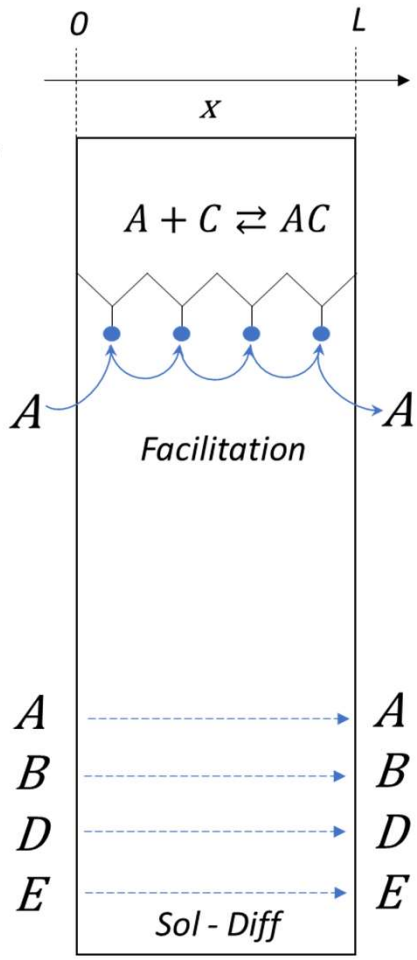
$$J_A = P_A \frac{\Delta p_A}{L} + D_{AC} \frac{\Delta C_{AC}}{L}$$

Facilitated Flux

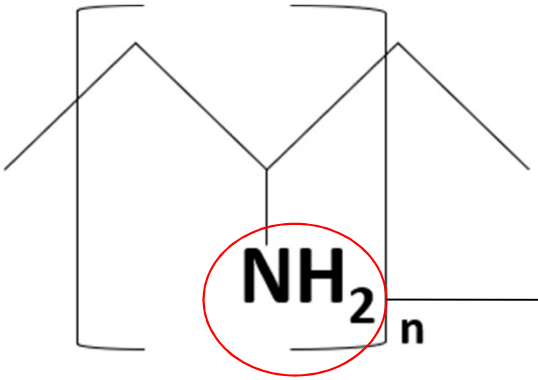
Improved Performance



Mobile Carrier

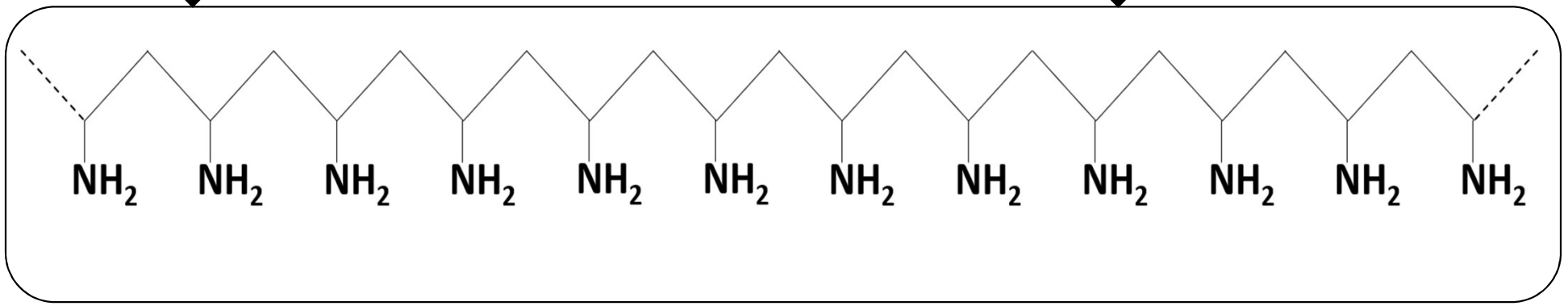


Fixed Carrier



Poly-(vinylamine)

Highest Density of Amino Group on Chain

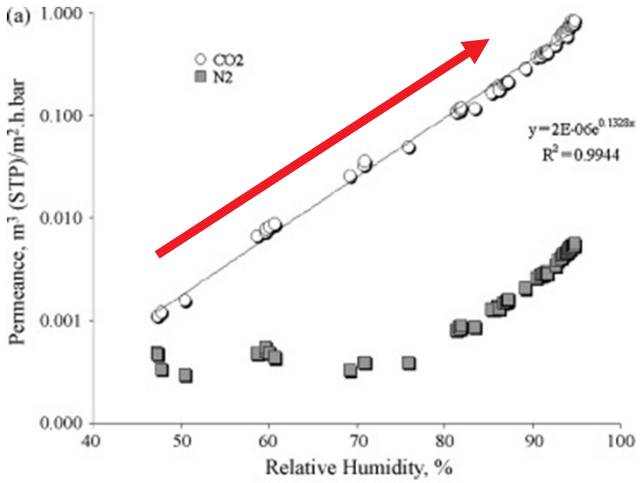


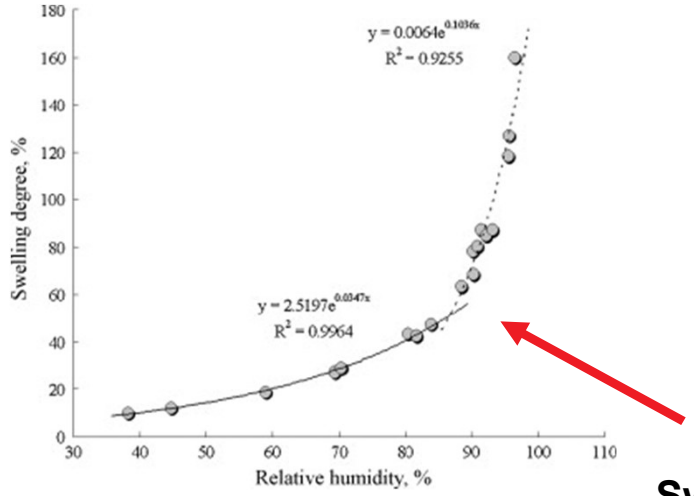
POLYBASE PROPERTIES → **Suitable for CO_2 separation**

Multiscale Models

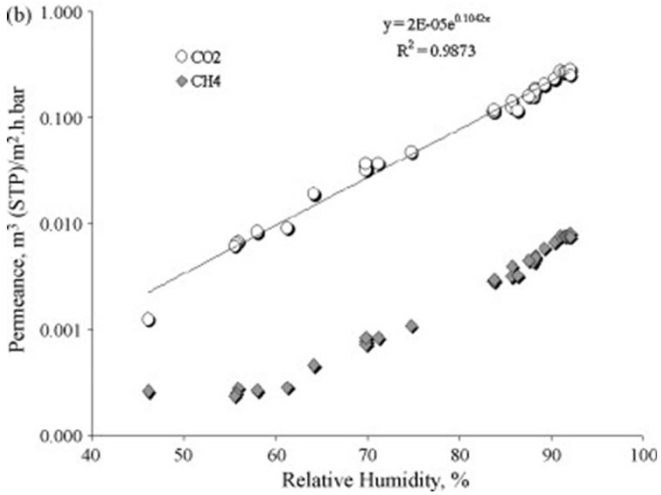
R. H. vs. Permeance

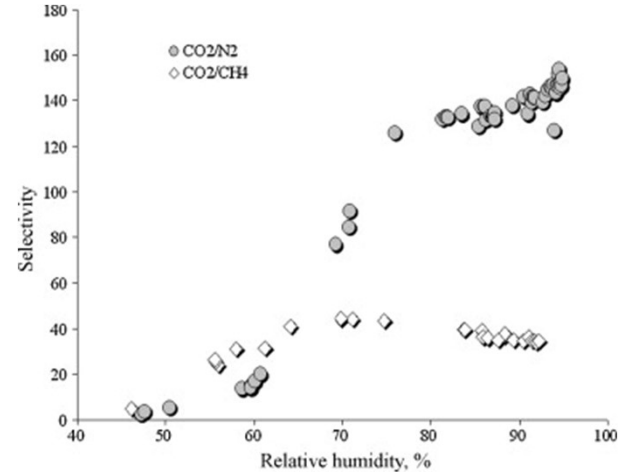
+ CO_2 absorption
+ Reaction products
+ Permeant mobility





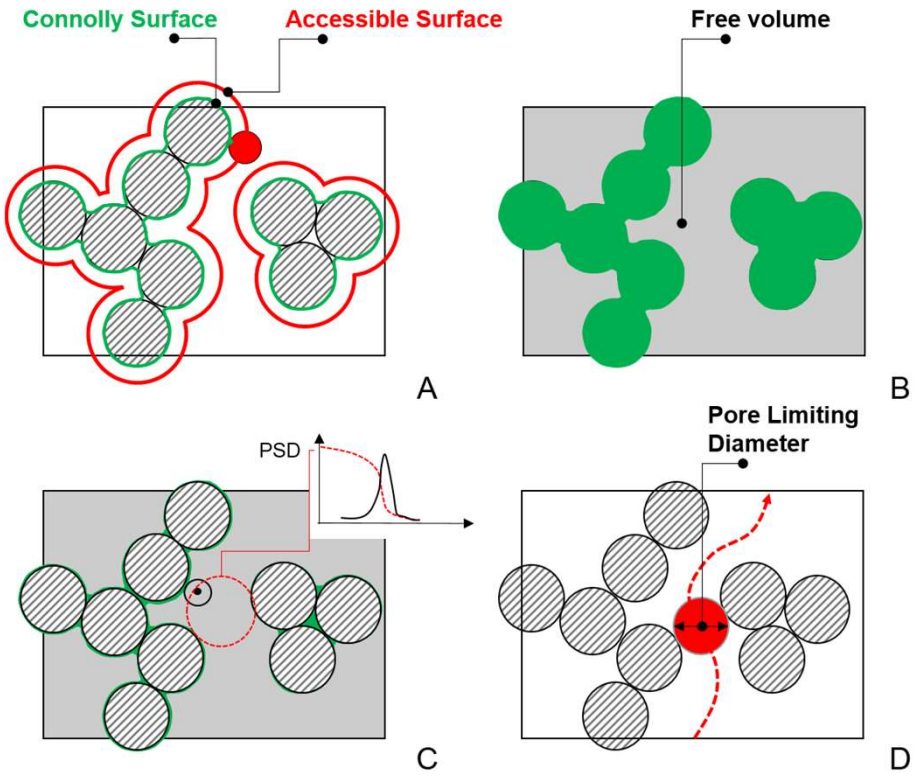
Swelling Regimes



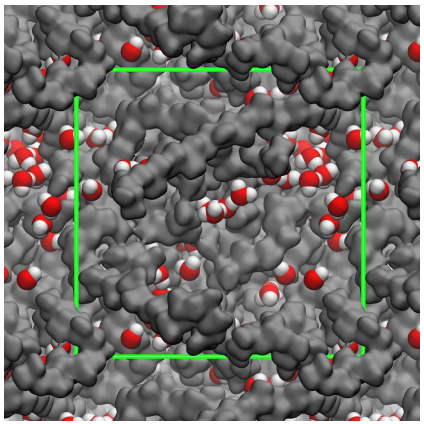


L. Deng and M. B. Hägg, J. Mem. Sci. 363, 295-301 (2010)

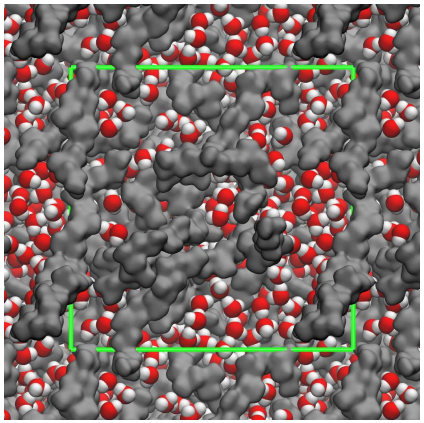
Volume Effects – Hydrated PVAm



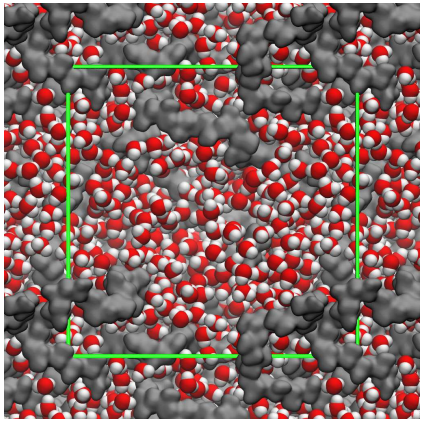
0.1
gH2O
gPVAm



0.5
gH2O
gPVAm



0.9
gH2O
gPVAm

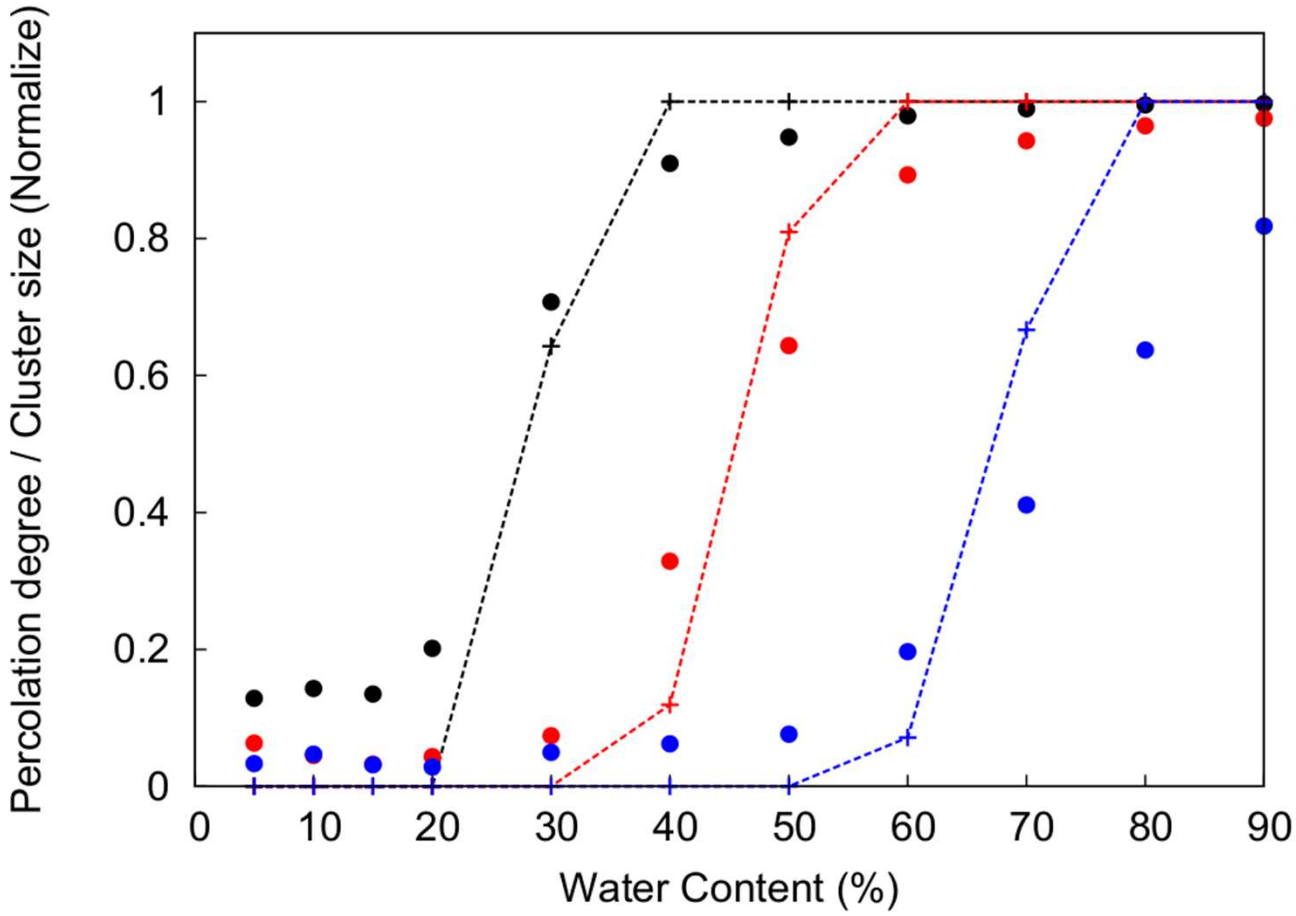


Water clusters as effective free volume

- Pore limiting diameter
- Pore size distribution
- Percolation degree

What is the effect of (poly) electrolytes?

Percolation Degree – Hydrated PVAm



Black: Neutral PVAm

Red: 20% Protonated PVAm

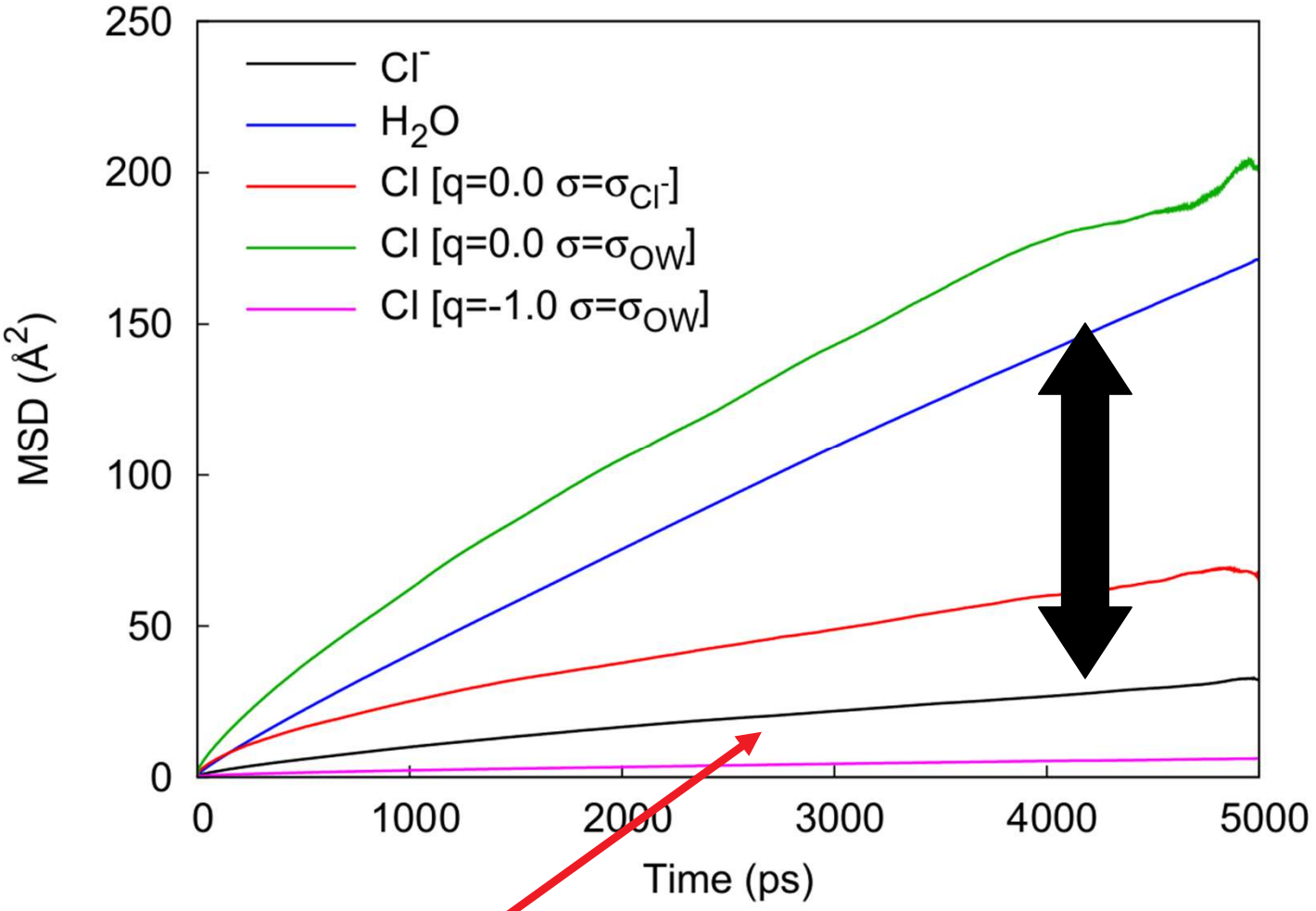
Blue: 50% Protonated PVAm

Percolation Degree – Hydrated PVAm

Simulated displacement as function of time

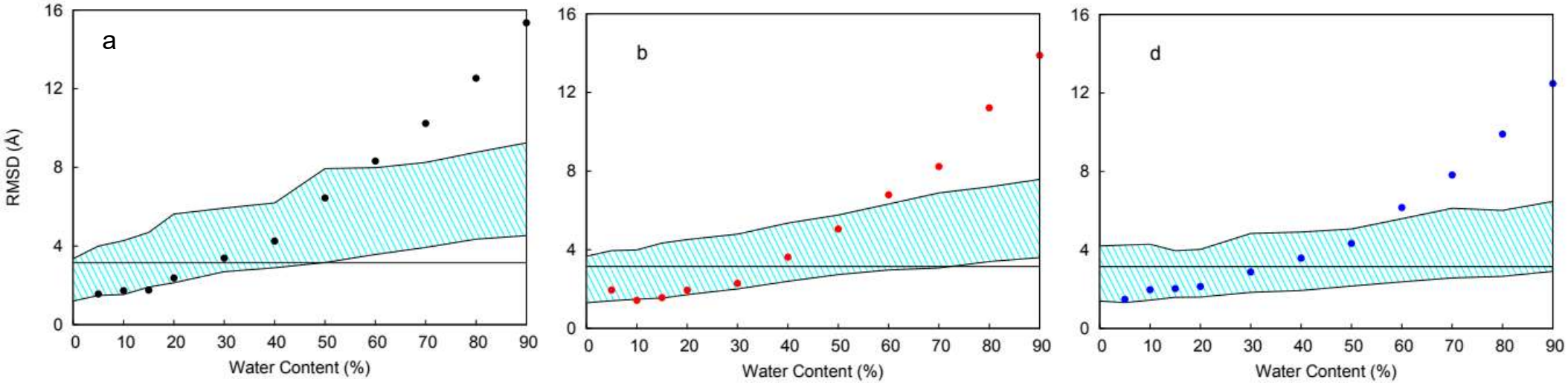
Diffusive dynamics dominated by H_2O

- Pore limiting diameter
- Pore size distribution
- Percolation degree



Charged particles strongly couple to polymer motion

Volume Effects – Hydrated PVAm



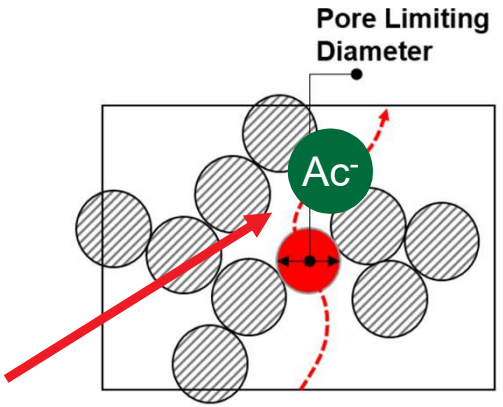
Black: Neutral PVAm

Red: 20% Protonated PVAm

Blue: 50% Protonated PVAm

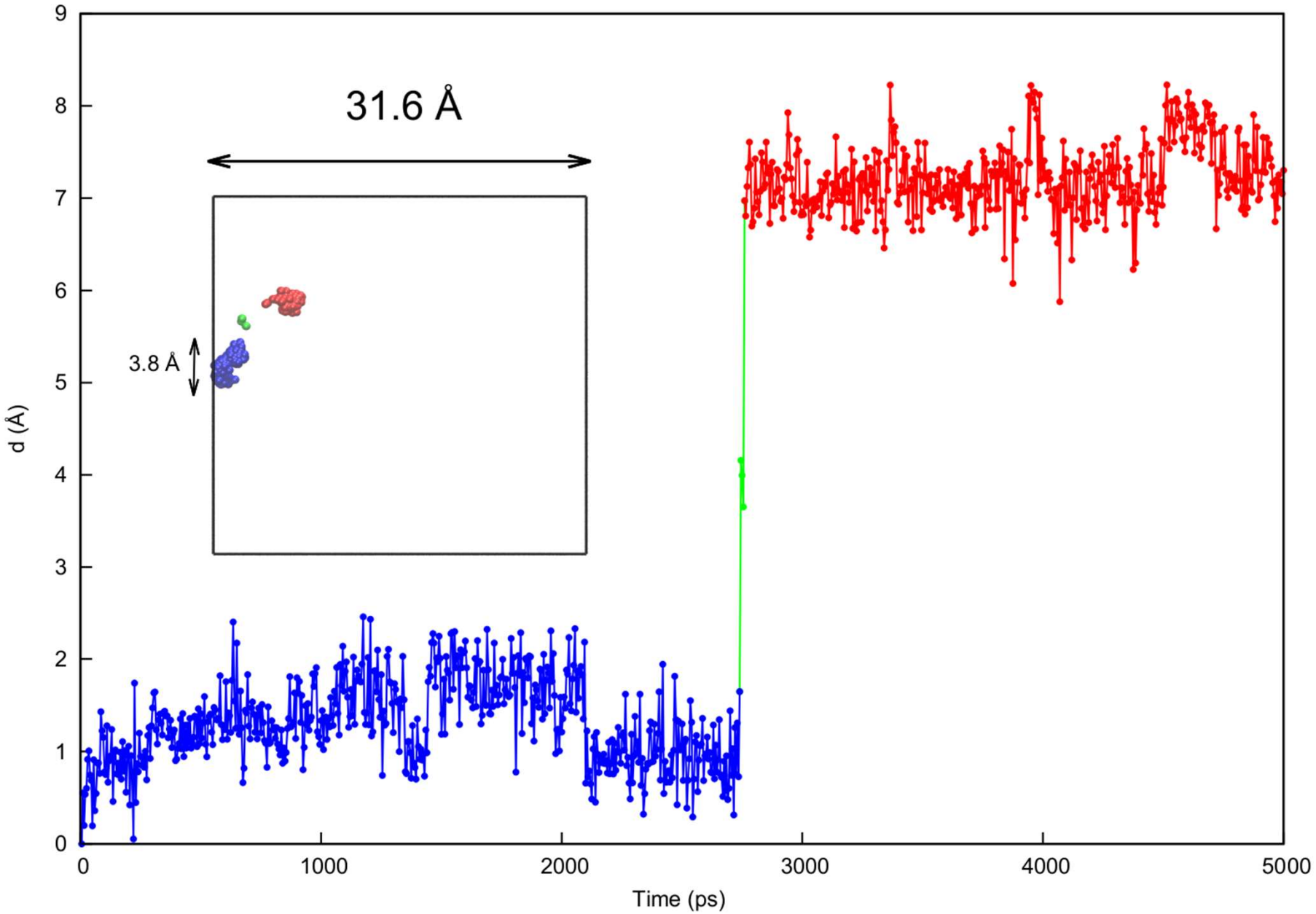
Upper shaded area: maximum pore volume

Lower shaded area: limiting pore diameter



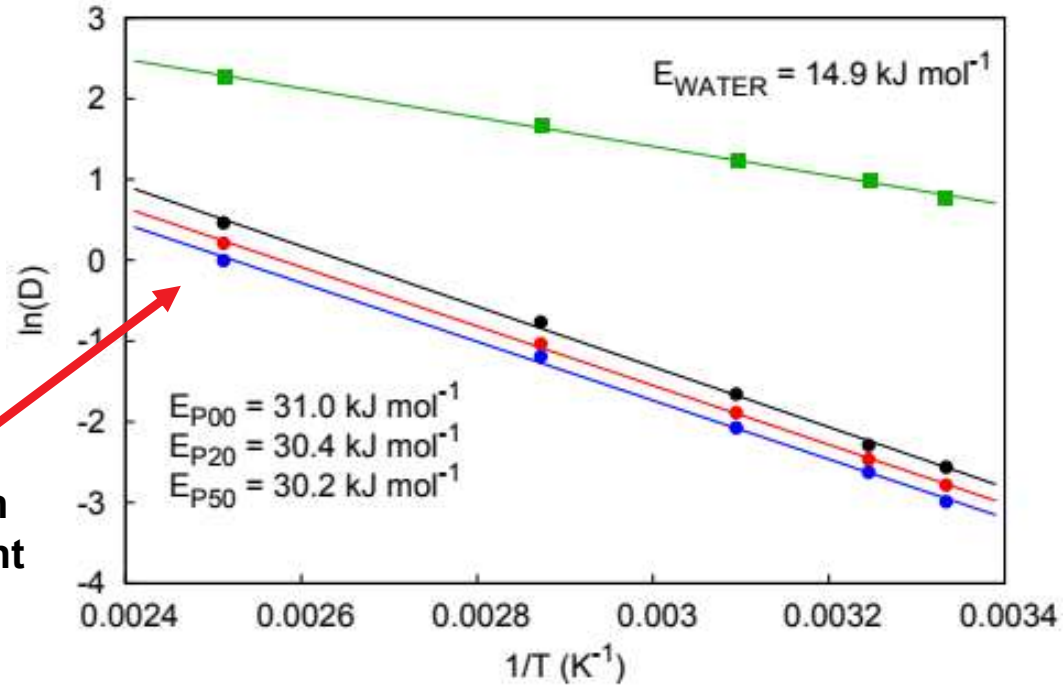
Slow-moving ionic species obstruct water channel formation

Low R.H.: 'Rare-event' diffusion



Arrhenius Behavior

$$D = D_0 \cdot \exp\left(-\frac{E_A}{RT}\right)$$

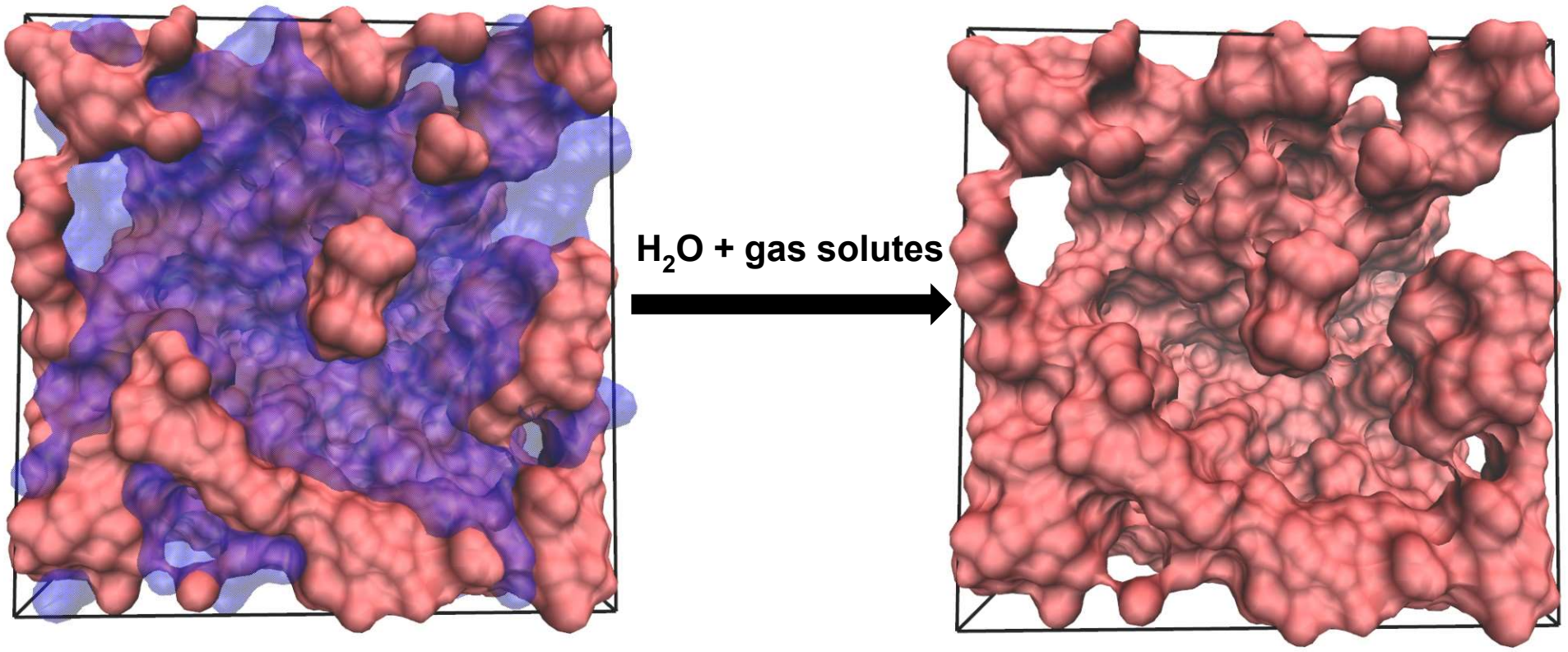


Similar activation energies, different volume effects

For highly hydrated systems, diffusion follows Arrhenius power law behavior. Tortuosity-controlled environment as function of protonation.

Black: Neutral PVAm
Red: 20% Protonated PVAm
Blue: 50% Protonated PVAm
Green: Bulk water

Effective Free Volume



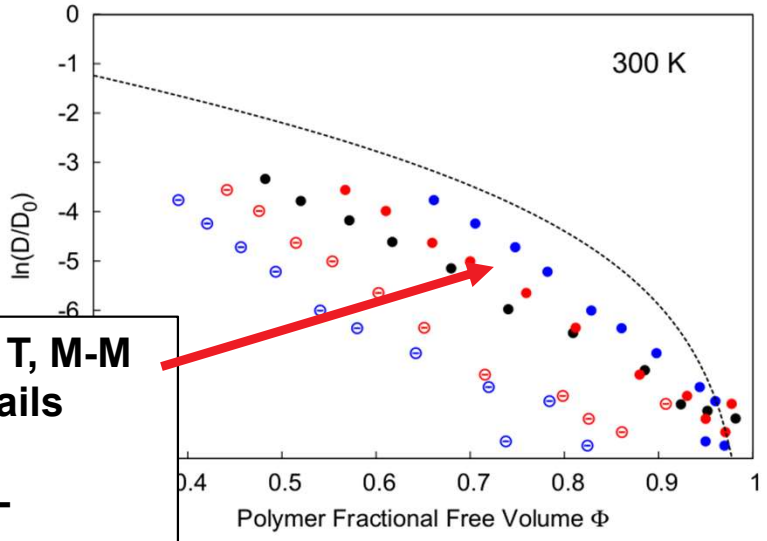
Numerous polymer + solvent theories, e.g. Mackie-Meares equation

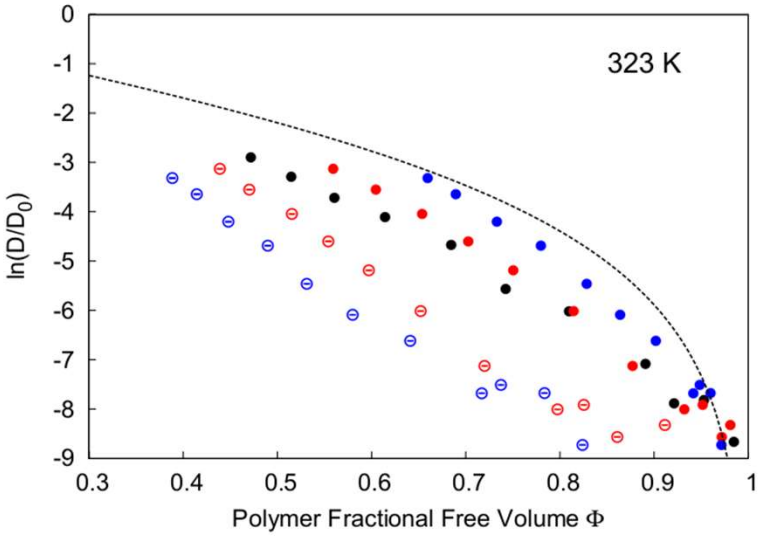
$$\frac{D}{D_0} = \left(\frac{1-\Phi}{1+\Phi}\right)^2$$

D : diffusion coefficient
D_0 : bulk solvent diffusion coefficient
Φ : effective free volume

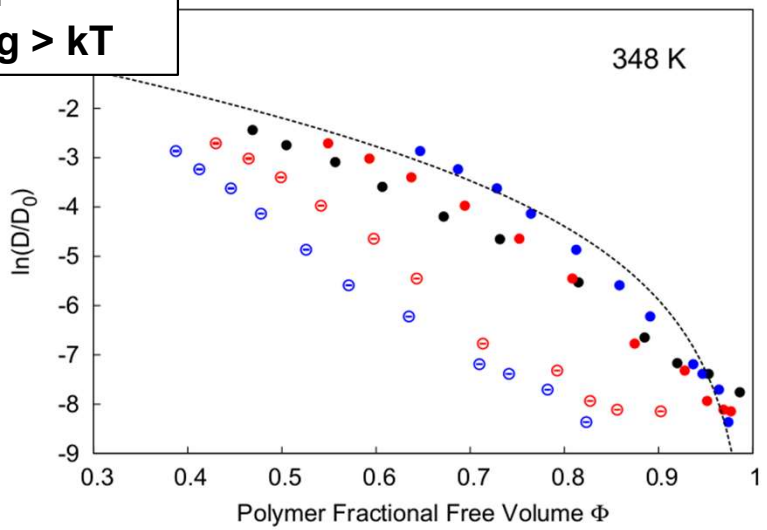
J.S. Mackie, P. Meares, Proc. R. Soc. London A232, 1955

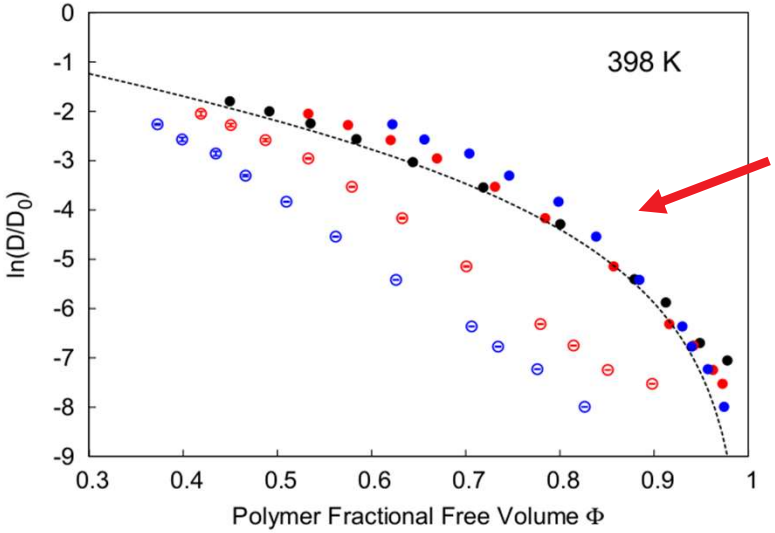
Effective Free Volume





For low T, M-M model fails
=
Solvent-polymer coupling > kT





For high T M-M model reasonable
=
Free volume effect

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$$\frac{D}{D_0} = \left(\frac{1-\Phi}{1+\Phi}\right)^2$$

Summary

Protonation-dependent Percolation threshold

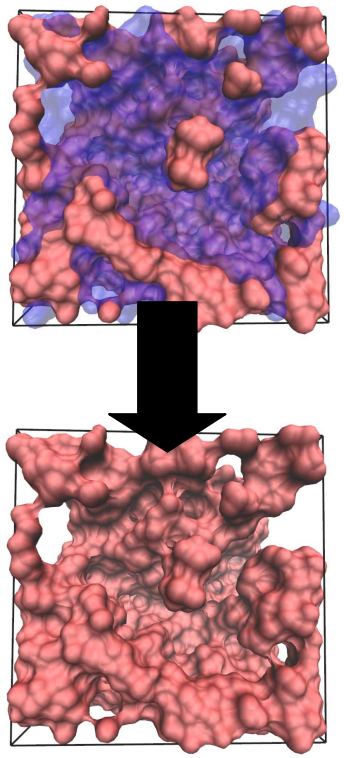
- Charge groups acting as gatekeepers
- H_2O and gas transport modulated by H_2O channels

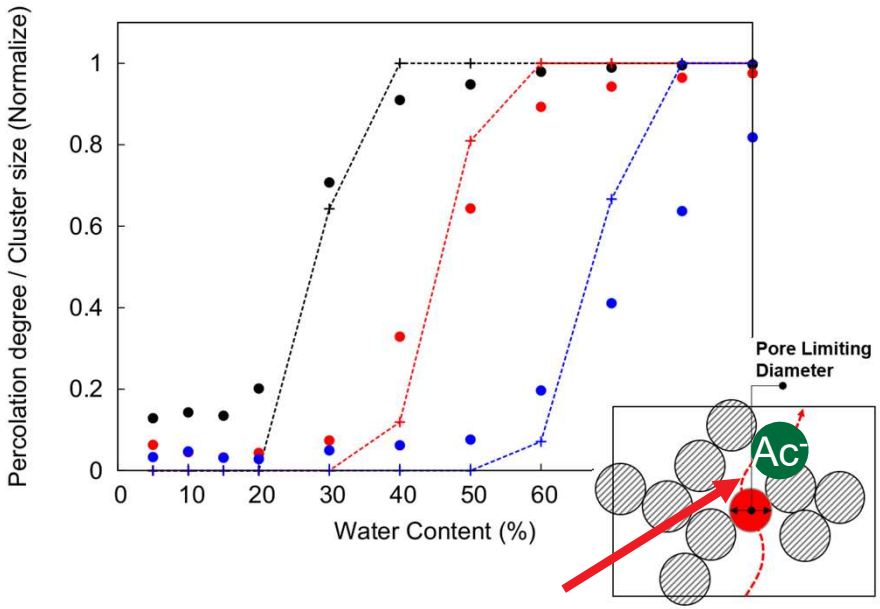
Effective Free Volume

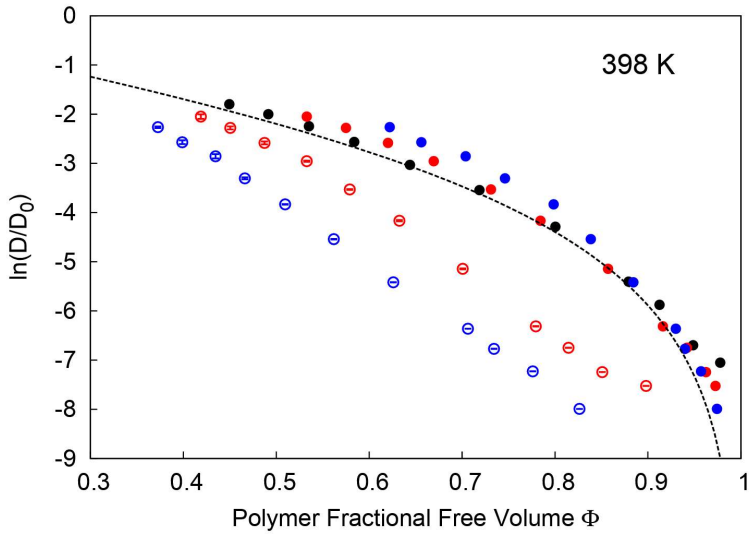
- Ions strongly couple to amine groups

Free-volume effects dominate for high-T

- Decoupling of solvent-polymer interactions
- H_2O and gas diffusion modulated by H_2O







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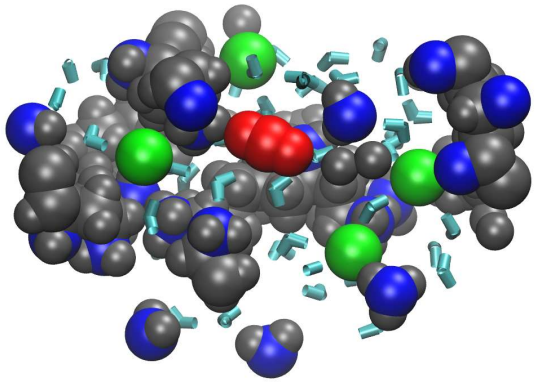

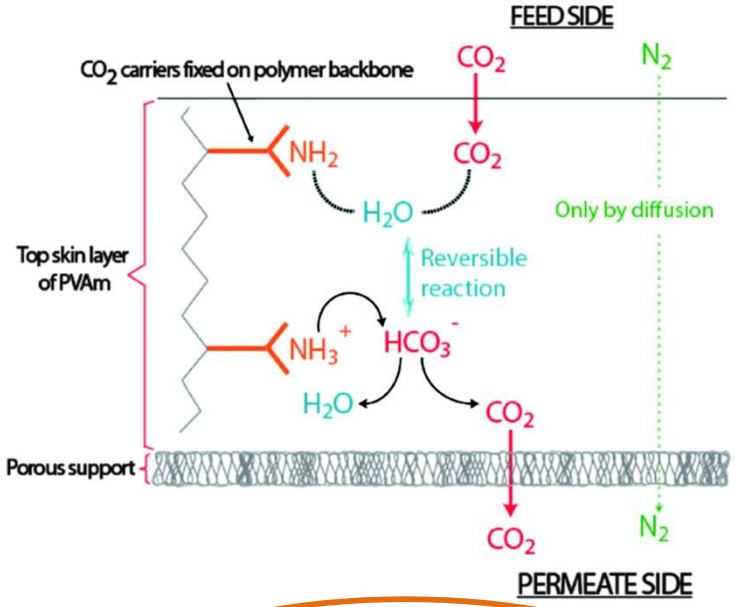

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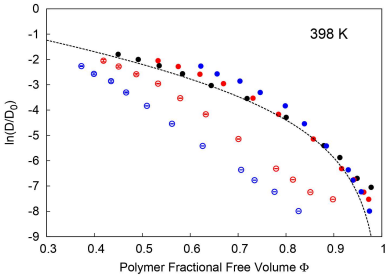

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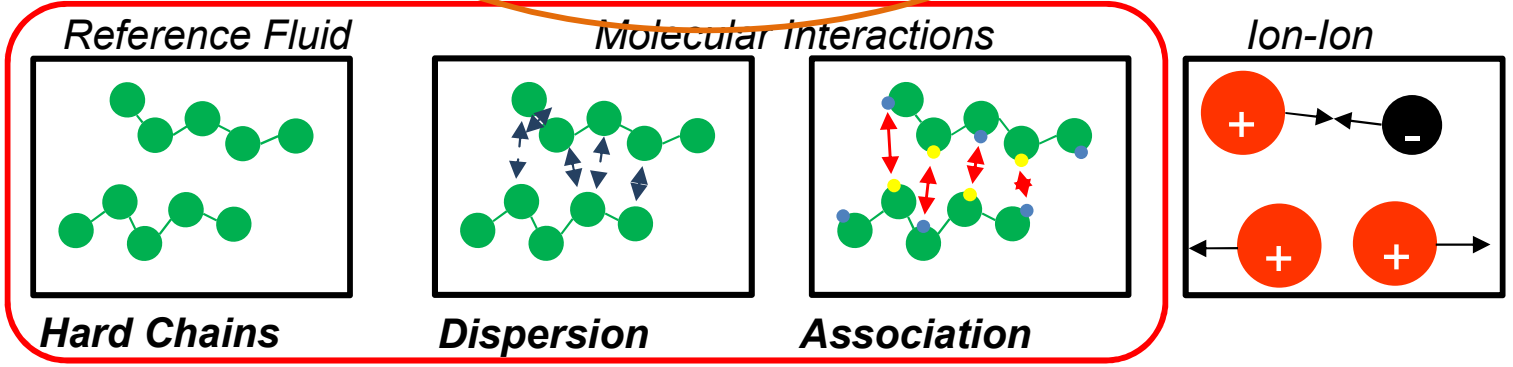
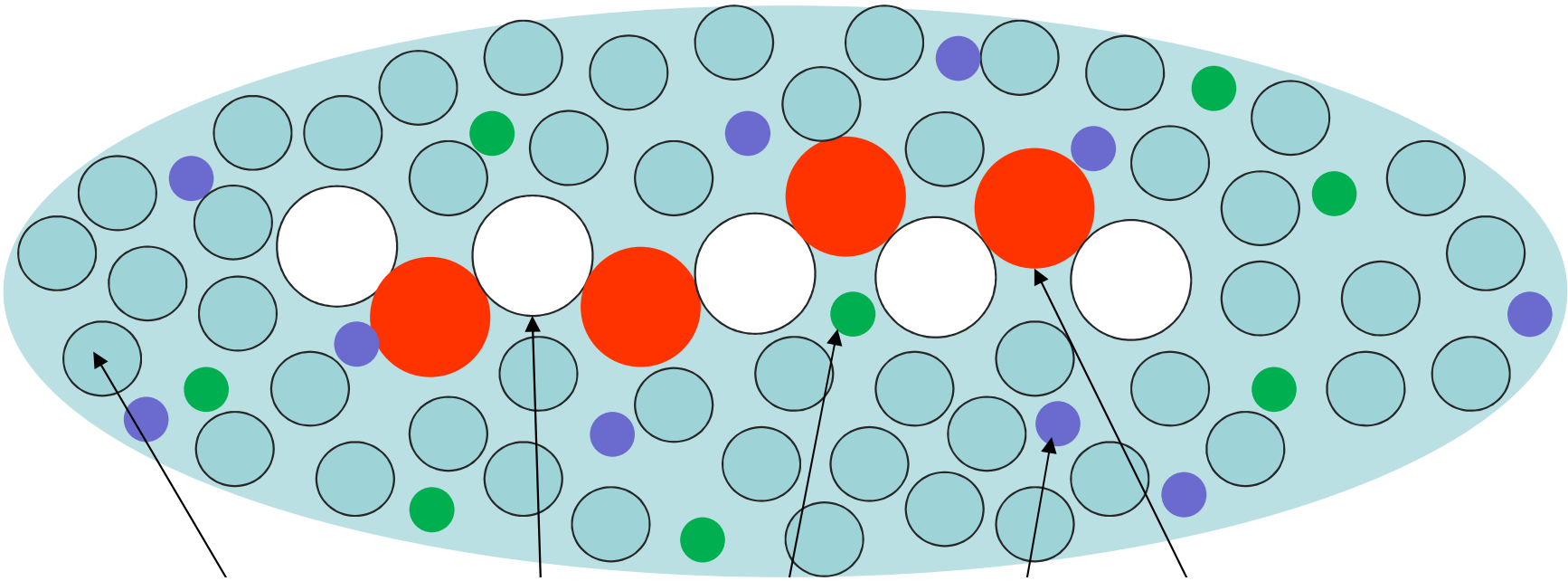


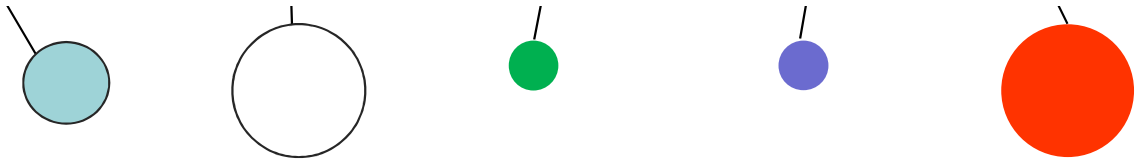
Kim, T. J., Li, B., & Hägg, M. B., J. Pol. Sci. B: Pol. Phys., 42 (23), 4326-4336, 2004

Reacting Water Swollen Polymer System

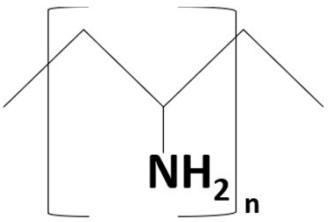
Adsorbed Water Molecules Enhance the Reaction



$$H_2O + \text{-}[RNH_2]\text{-} + CO_2 \rightleftarrows HCO_3^- + \text{-}[RNH_3^+]\text{-}$$

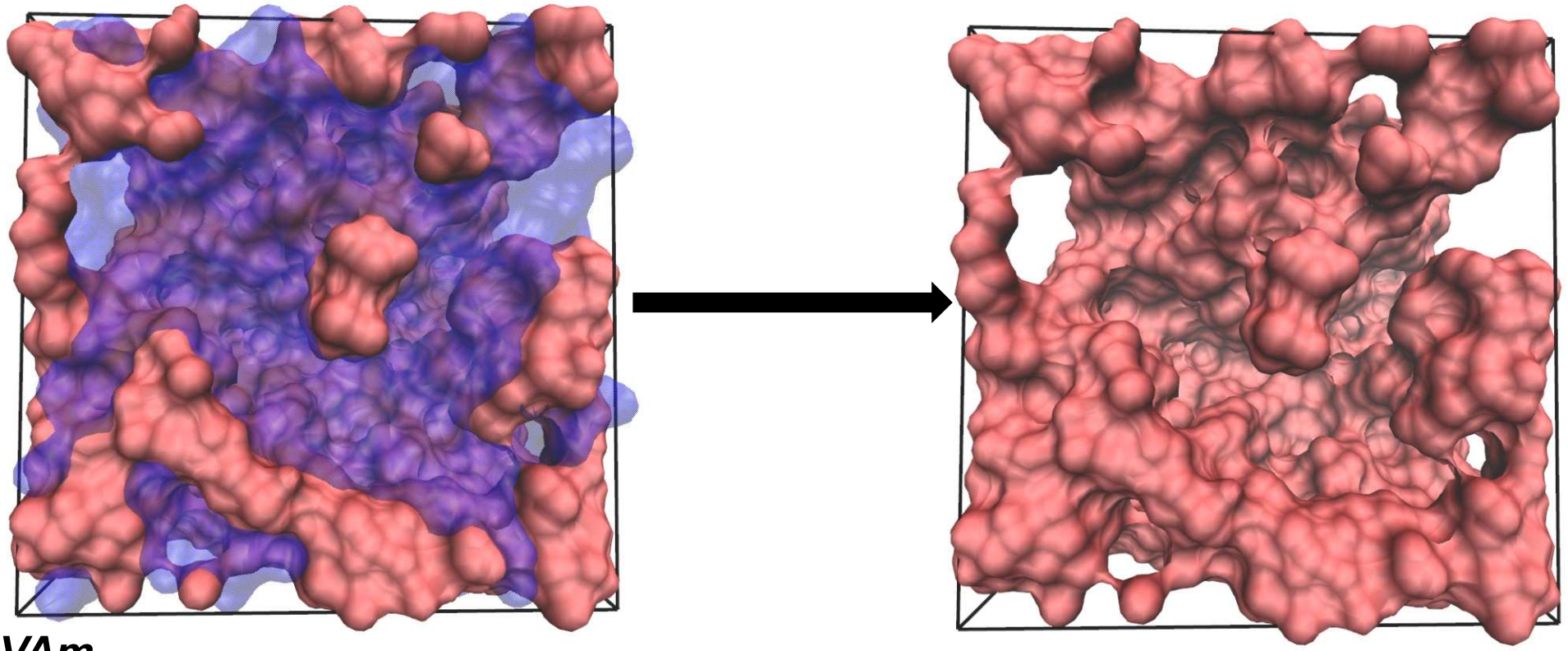


PVAm

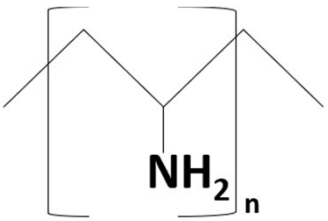


Reacting Water Swollen Polymer System

Adsorbed Water Molecules Swell the Polymer Matrix

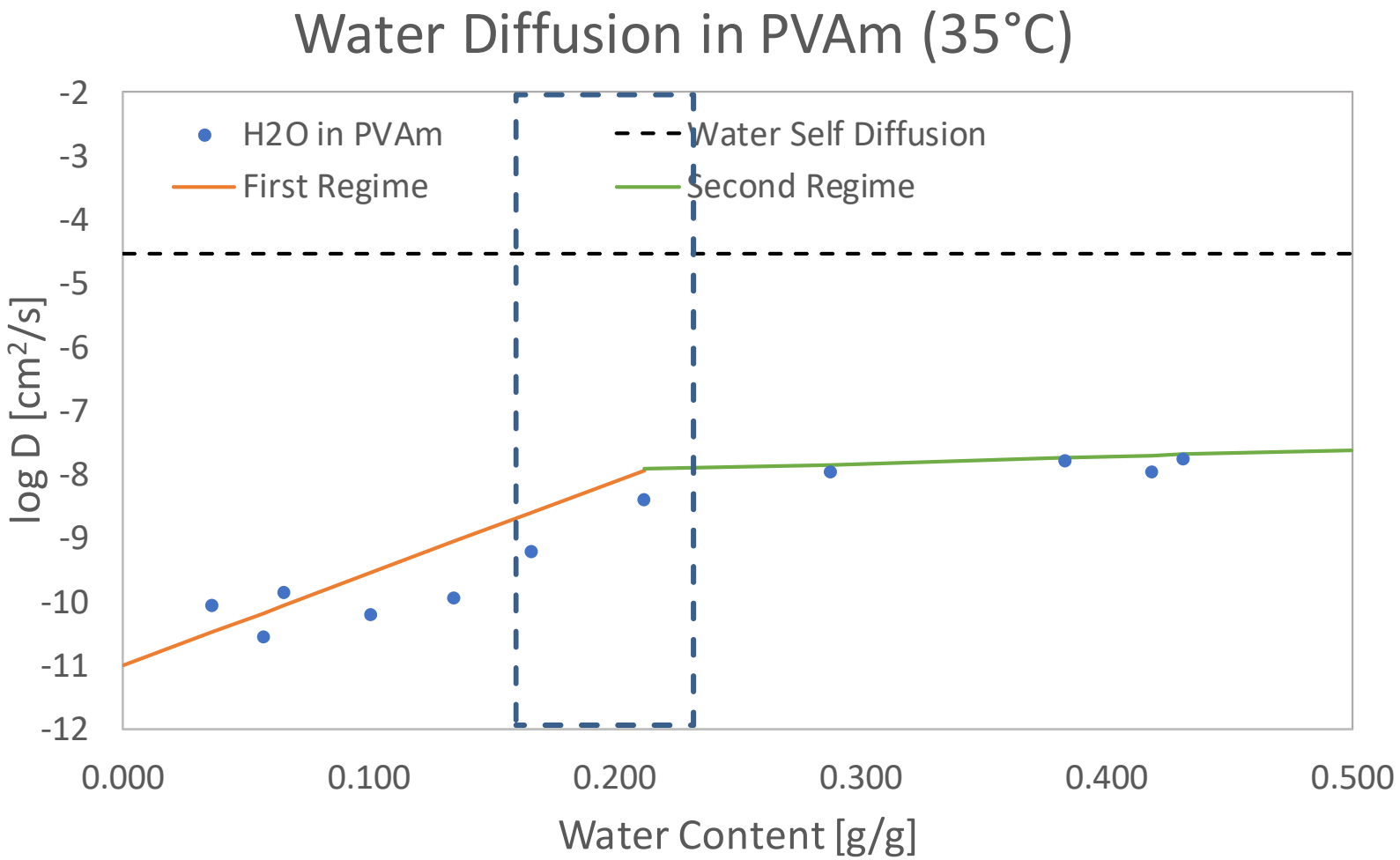


PVAm



Adsorbed Water Molecules Open New ‘Windows’

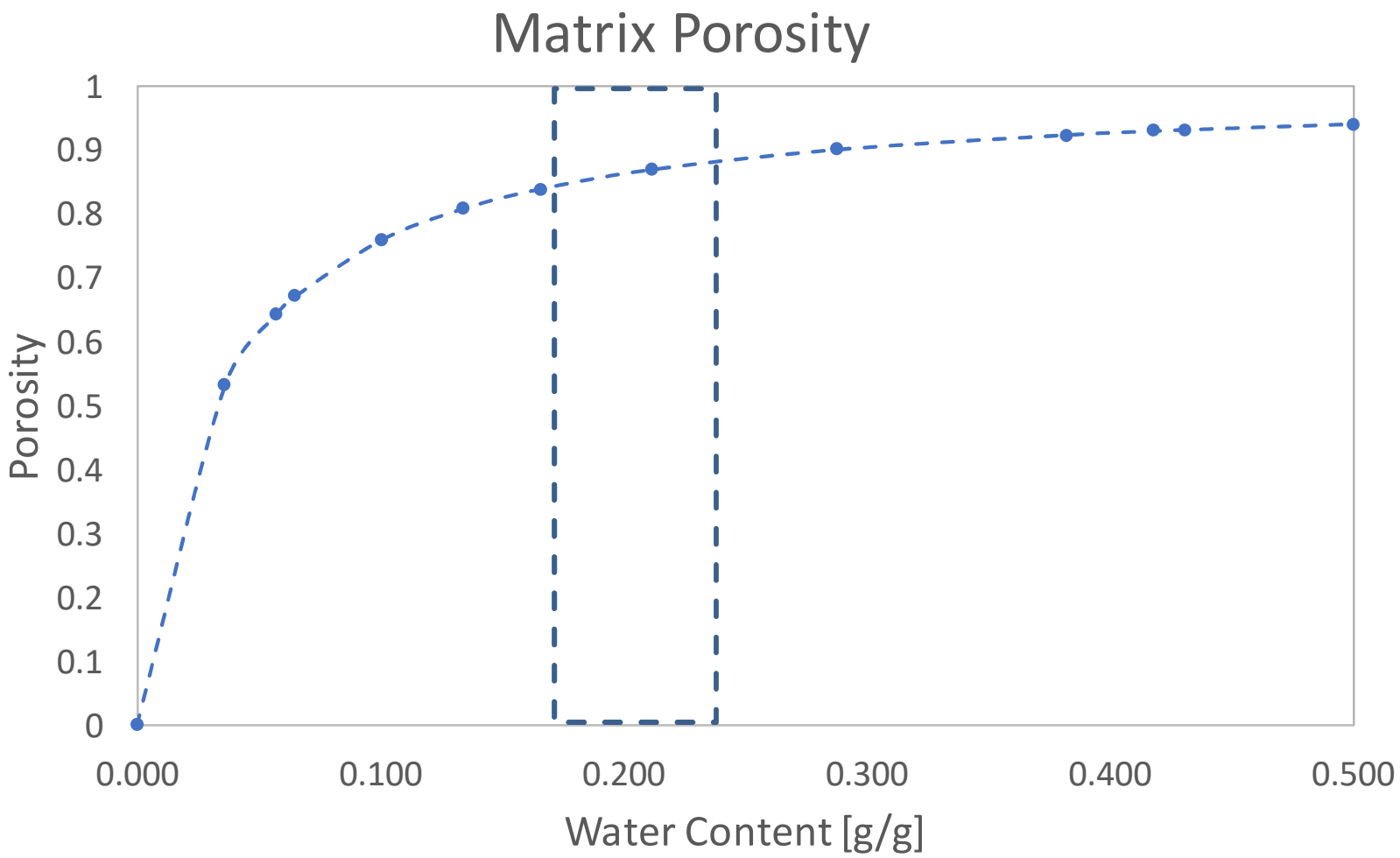
Diffusivity: experimental



Two Regimes Identified:

- Water Sorption ***Around Amino Groups***
- Water Sorption in a ***Water Medium Environment***

Diffusivity: Porosity



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S. Prager, *J. Chem. Phys.*, **1960**
Choi P. et al., *J. Electrochem Soc.*, **2005**

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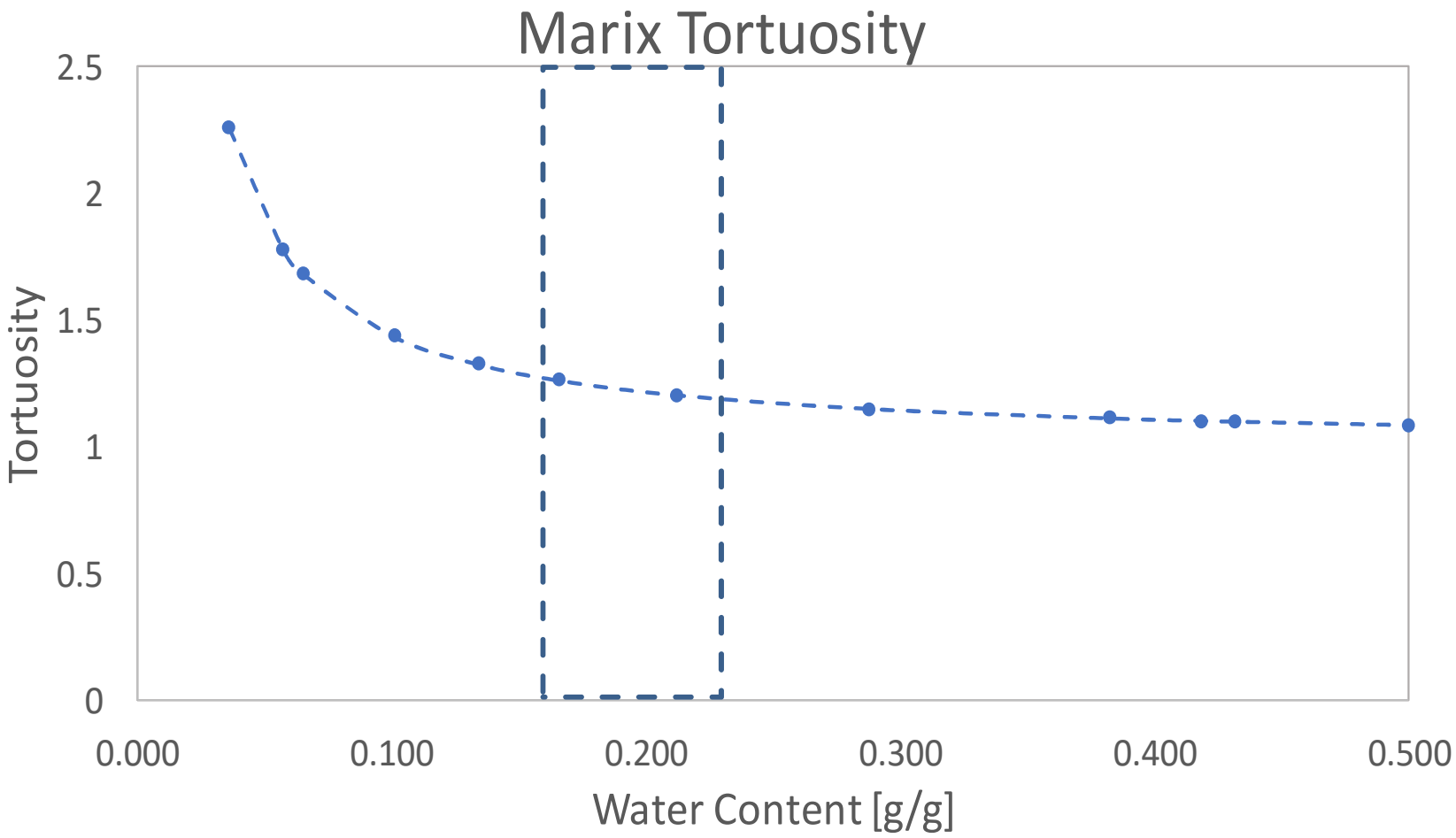

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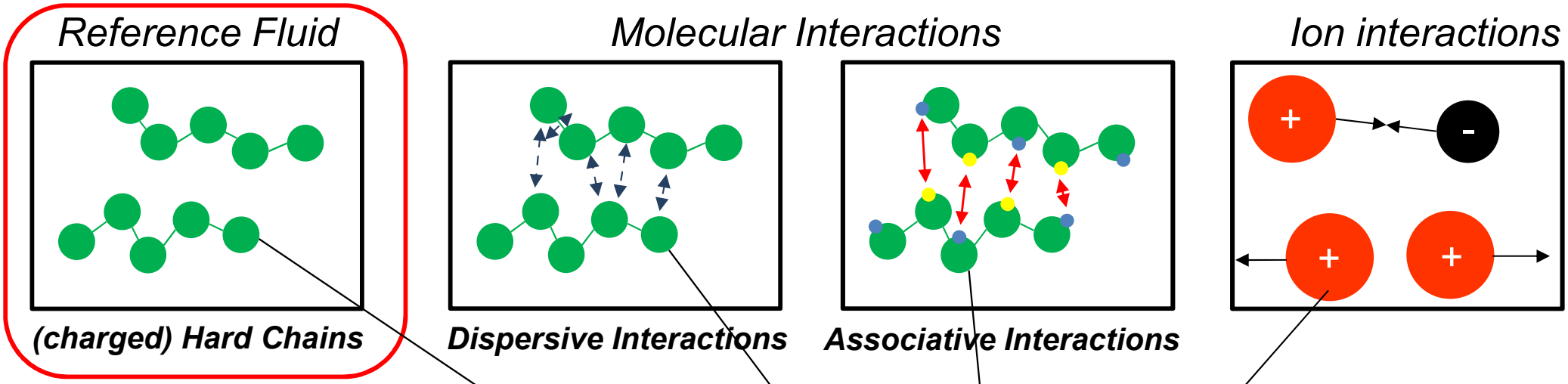
PC-SAFT EoS

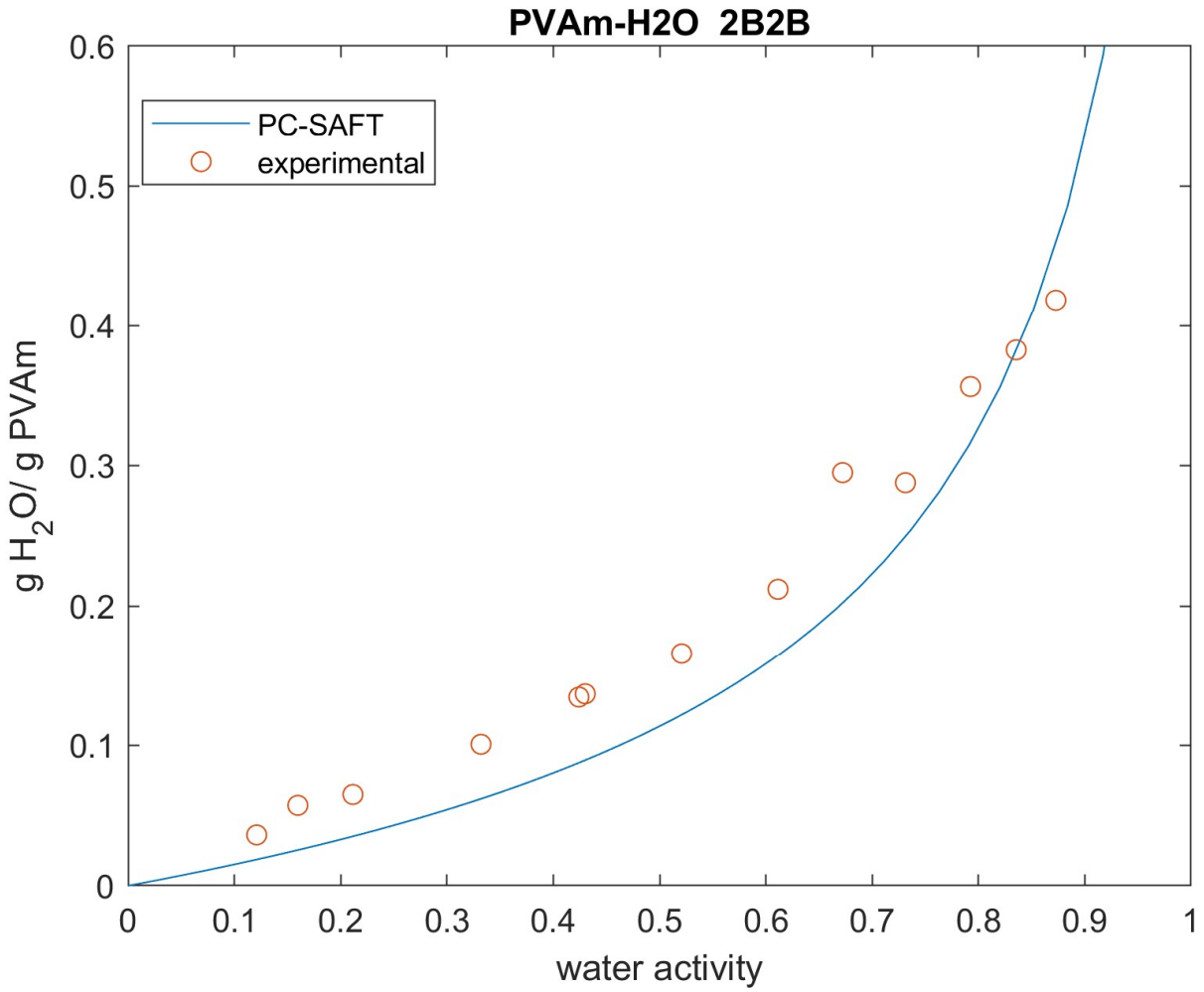
***P**erturbed **C**hain **S**tatistical **A**ssociating **F**luid **T**heory Equation of State*



$$a^{res} = a^{ref} + a^{disp} + a^{hb} + a^{ion}$$

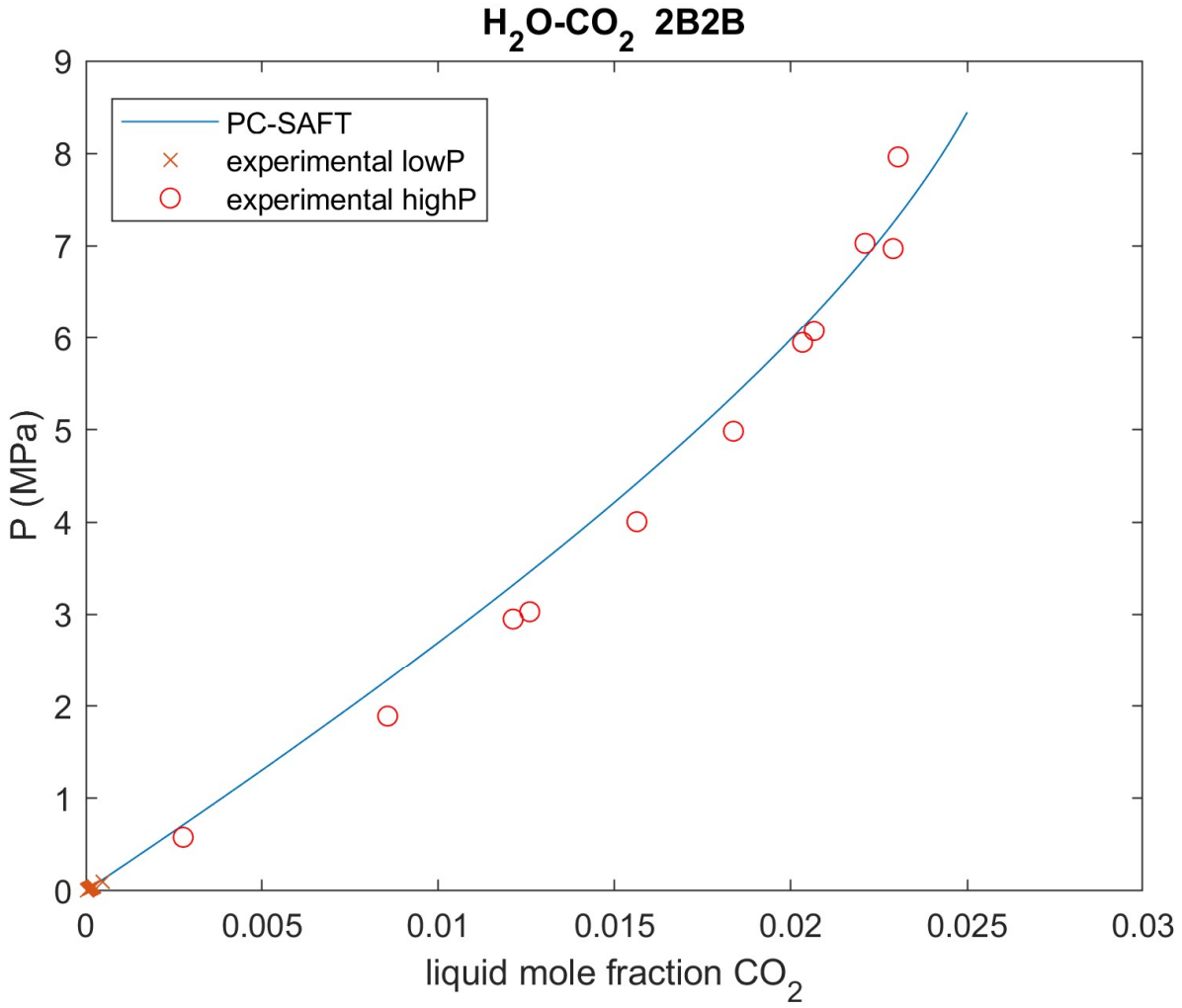
Huang, Radosz, *Ind. Eng. Chem. Res.*, **1990**
Gross, Sadowski, *Ind. Eng. Chem. Res.*, **2001**
Naeem, Sadowski, *Fluid Phase Equilib*, **2010**

PVAm / Water



Water **2B**: 2sites for H Bond (+/-)
PVAm **2B**: 2sites for H Bond (+/-)

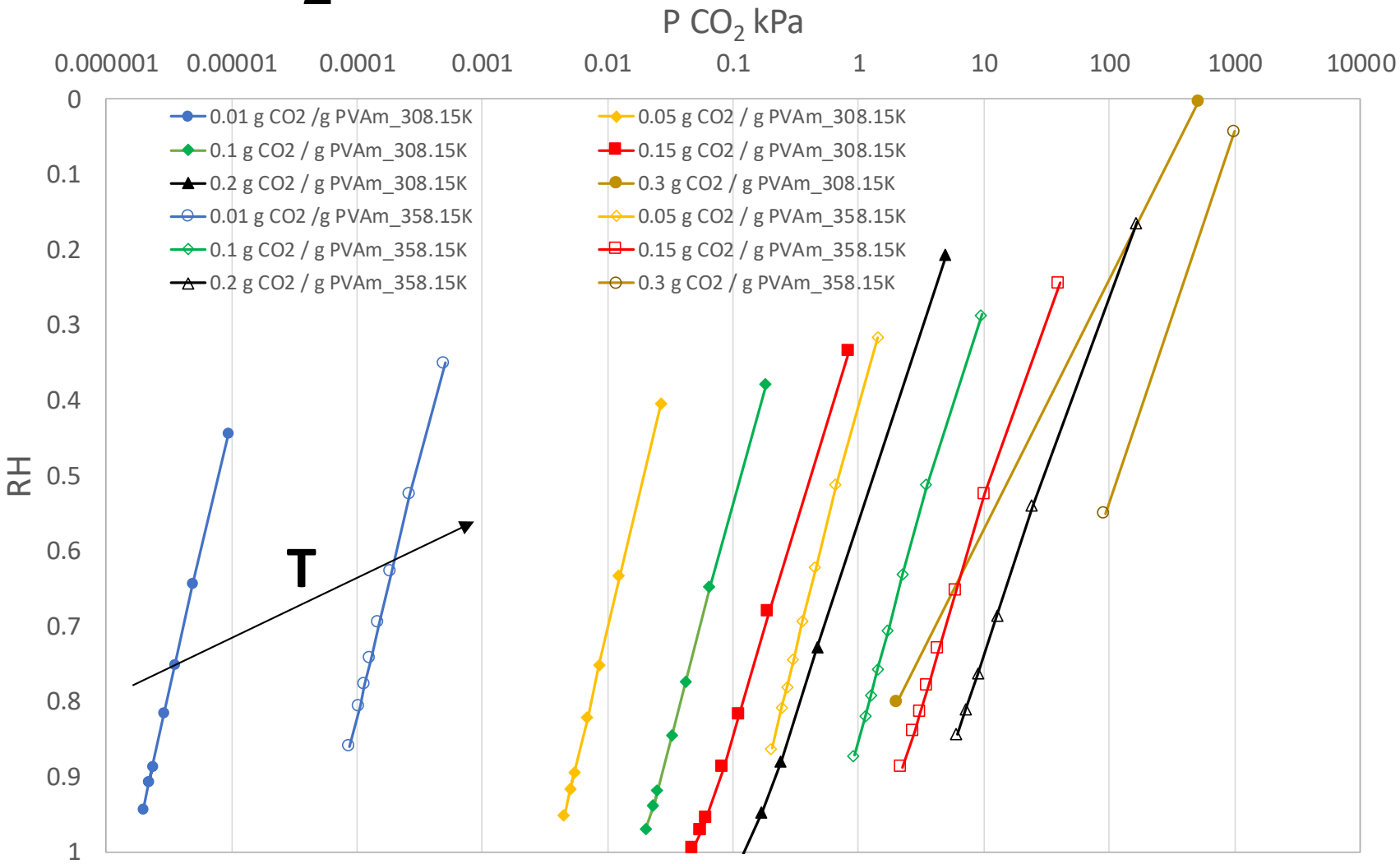
CO_2 / Water



Water **2B**: 2sites for H Bond (+/-)

CO_2 **2B**: 2sites for H Bond (+/-)

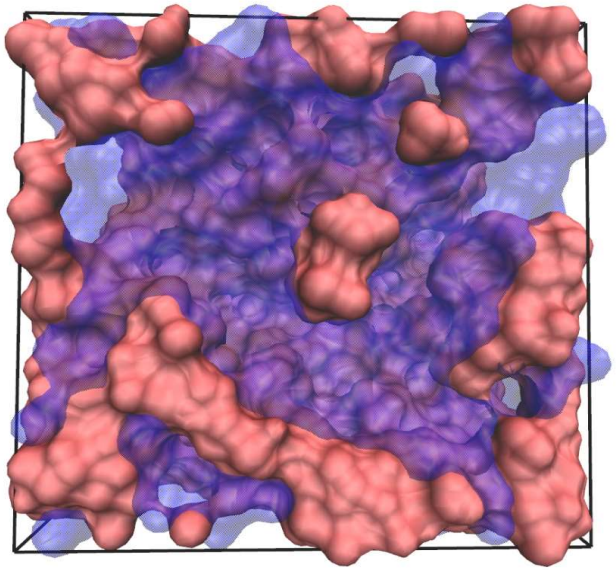
PVAm / CO_2 / Water

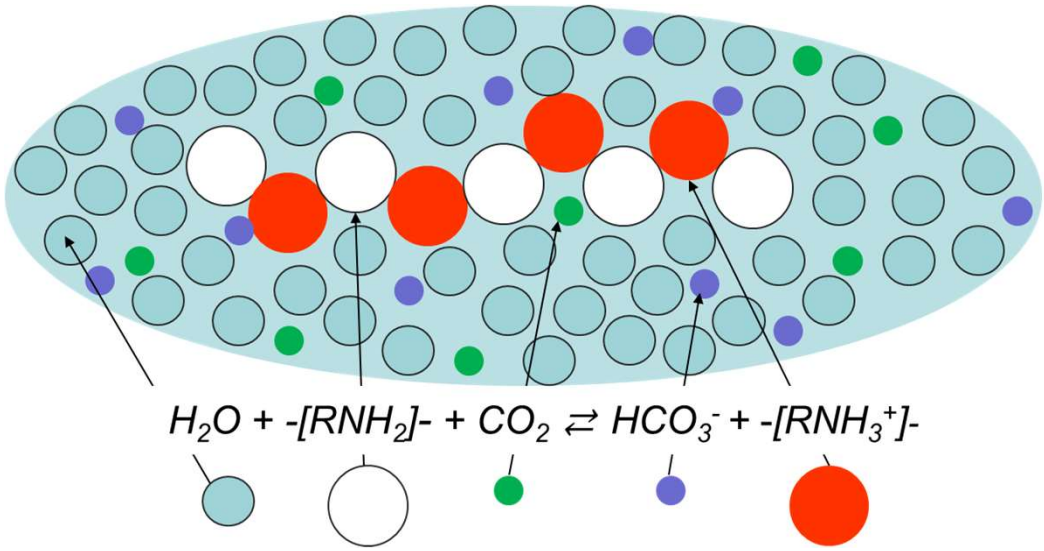


Water **2B**: 2sites for H Bond (+/-) CO_2 **2B**: 2sites for H Bond (+/-)

PVAm **2B**: 2sites for H Bond (+/-)

Summary





Understanding Diffusivity

- The increase in water content open new windows in the internal structure
- At higher water content the species flow towards the water channels
- This causes the higher mobility / diffusivity values

Understanding Solubility

- The PC-SAFT it is able to describe the water uptake in PVAm
- The chemical reaction used can explain the water role in the ion formation
- The pePC-SAFT can predict the total CO_2 uptake as function of process parameters: **T**emperature **R**elative **H**umidity Partial **Pressure**

Thank you!

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