Paradoxes of Nafion:
Hydration, Nanostructure and Relaxation

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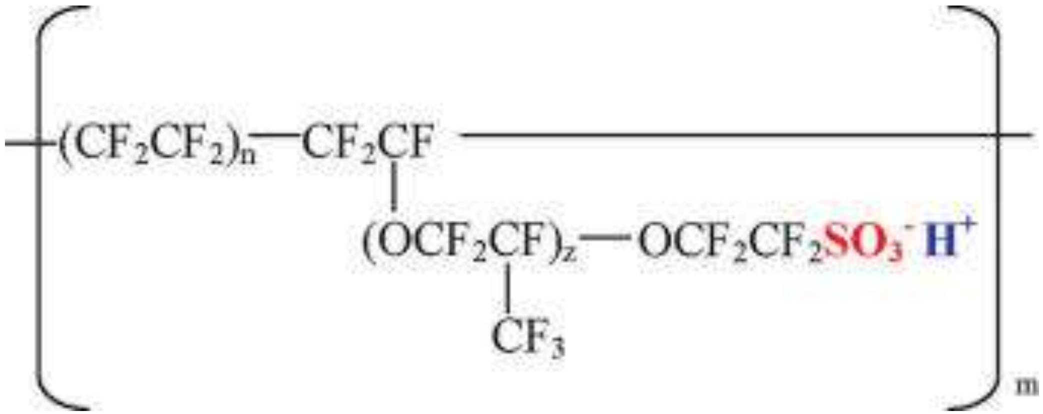
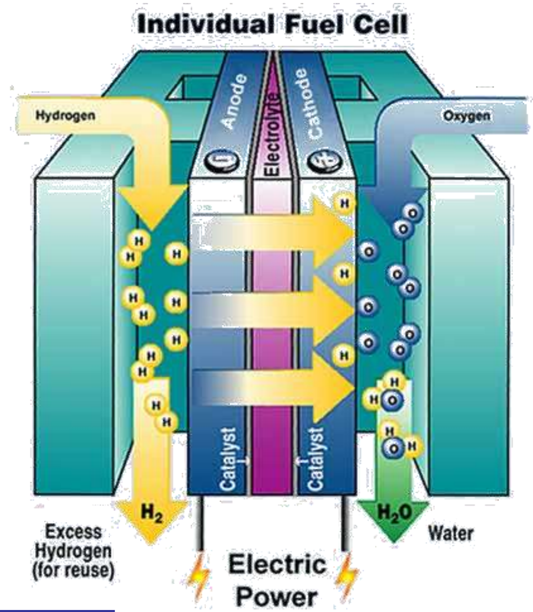
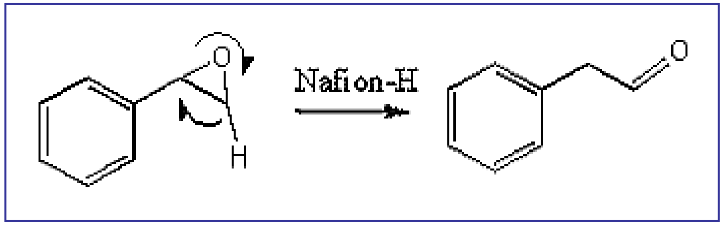
Nafion and Its Uses

An ionomer developed by DuPont in 70s

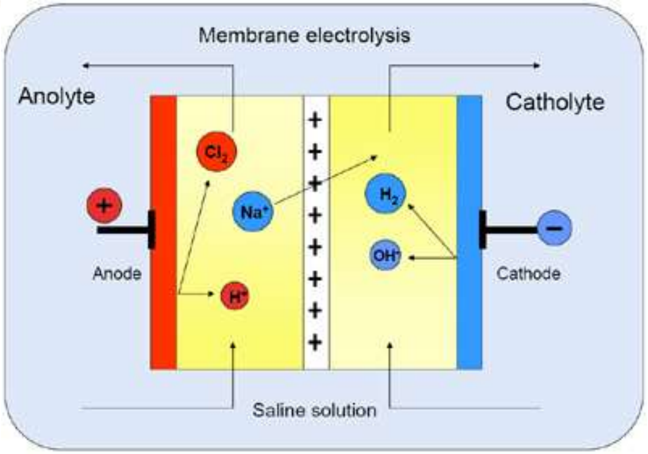


Fuel Cells



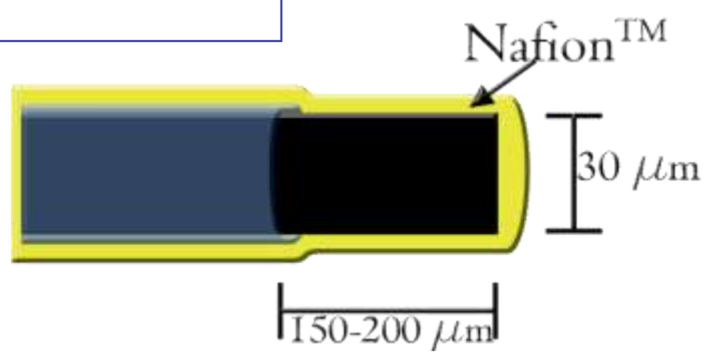


Catalysis



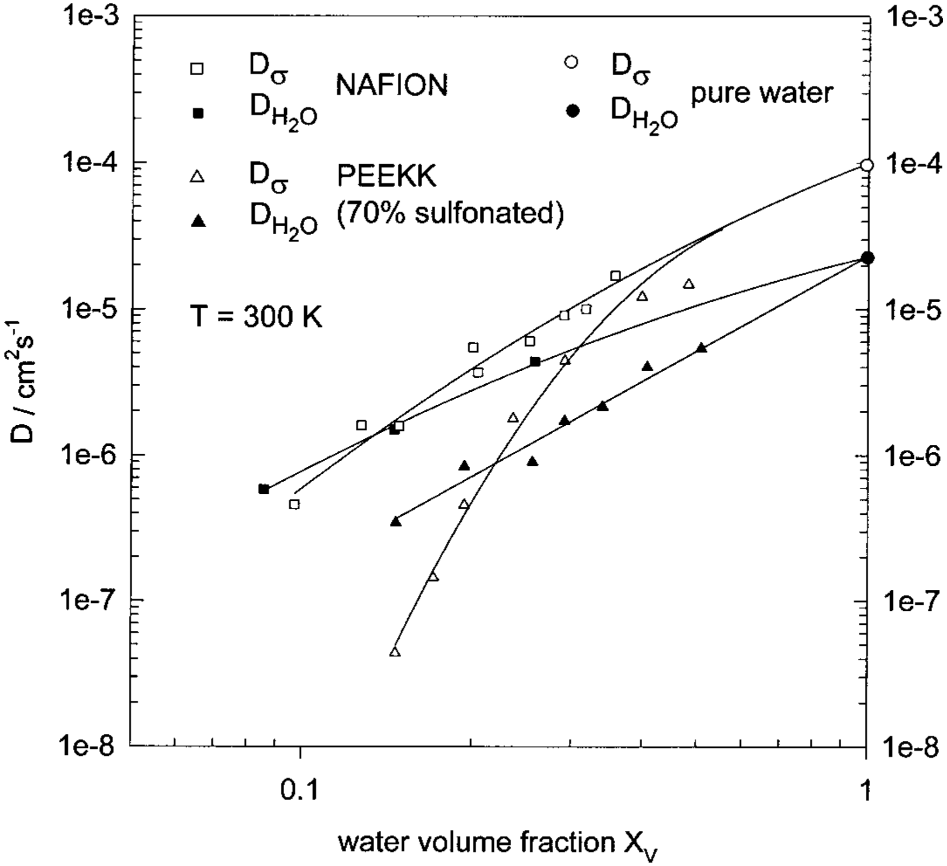
Membrane electrolysis

Sensors



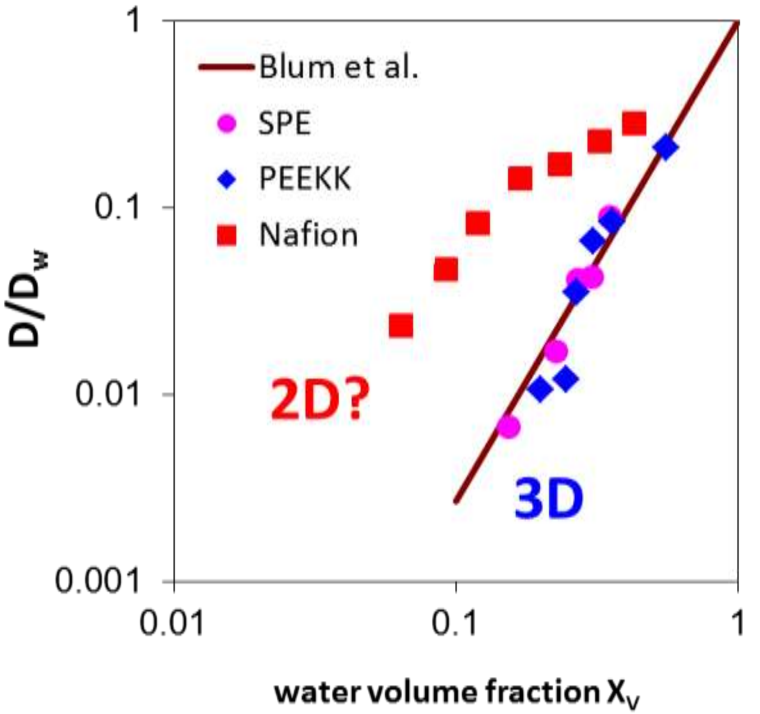
Transport vs. Hydration

Conductivity



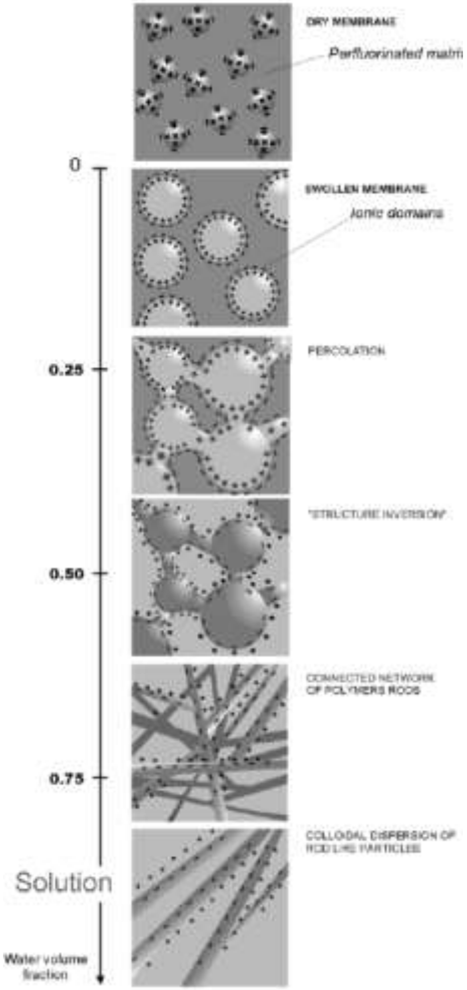
Kreuer, *JMS*, 2001

Water self-diffusion (NMR)

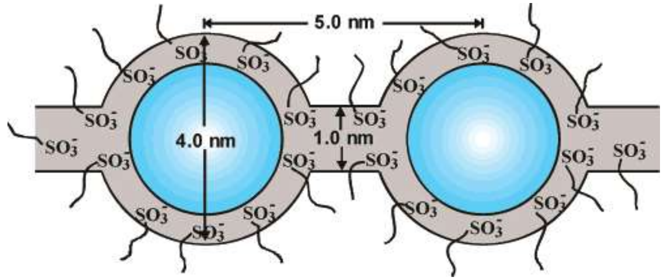


VF et al., *JMS*, 1999, 2000

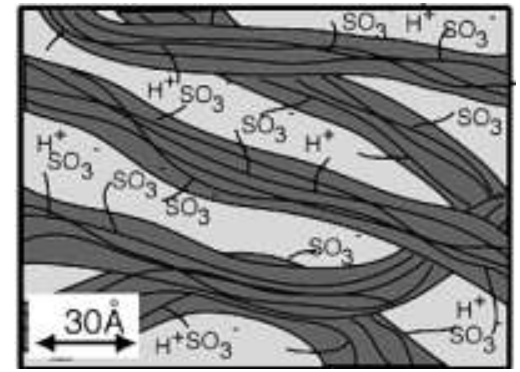
Microphase Separation and Micro-Morphology



Gebel, *Polymer*, 2000

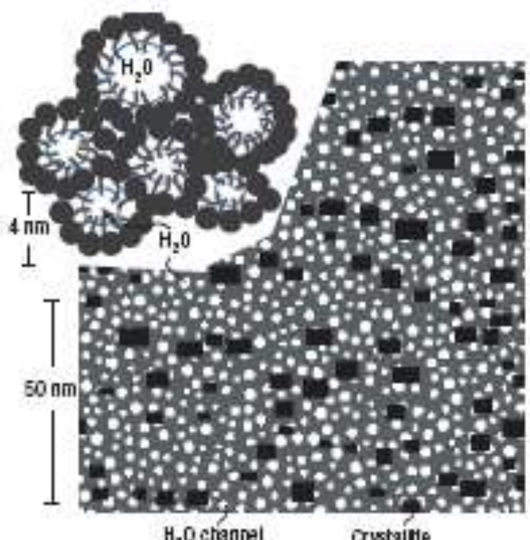


Hsu & Gierke, 1983



Rubatat et al, 2002, 2004

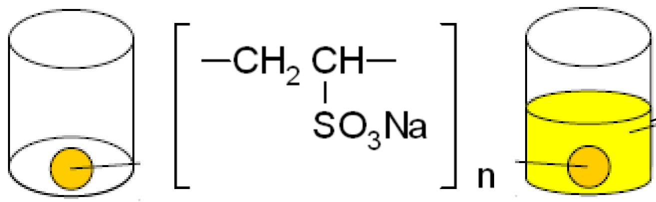
Schmidt-Rohr & Chen, 2008

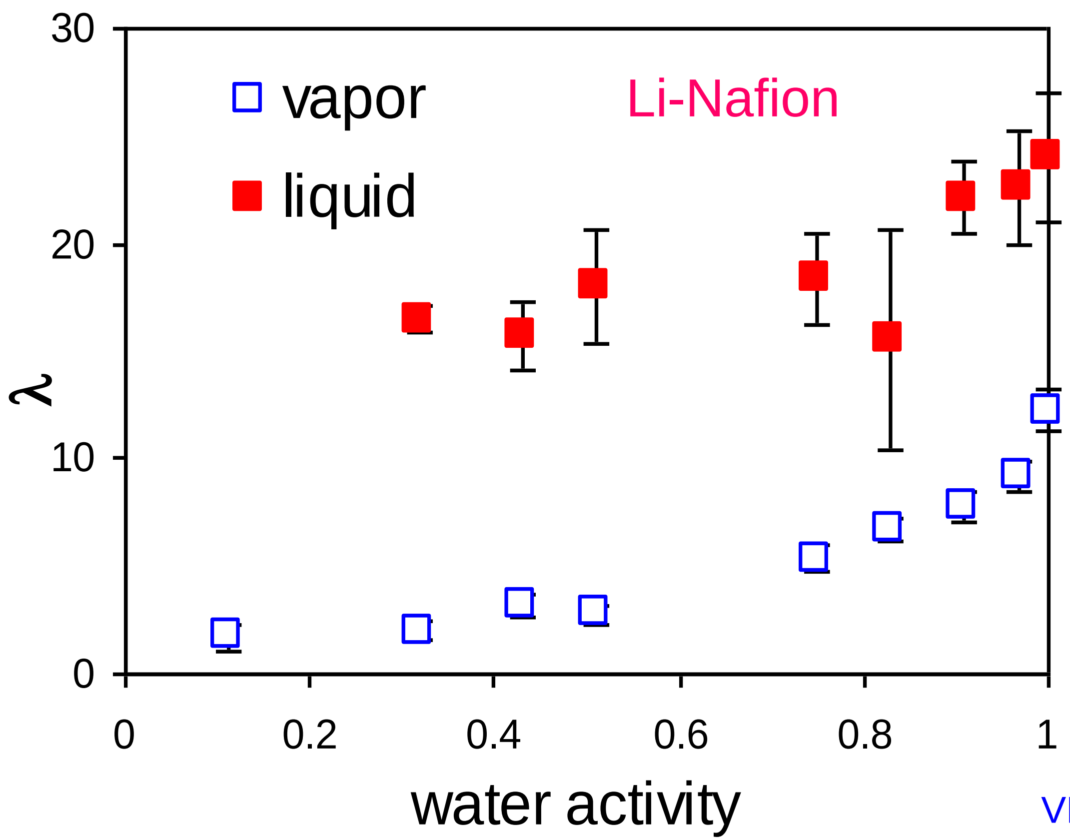


Litt, 1997

Kreuer & Portale, 2013

Schroeder's Paradox:
Non-Thermodynamic Hydration

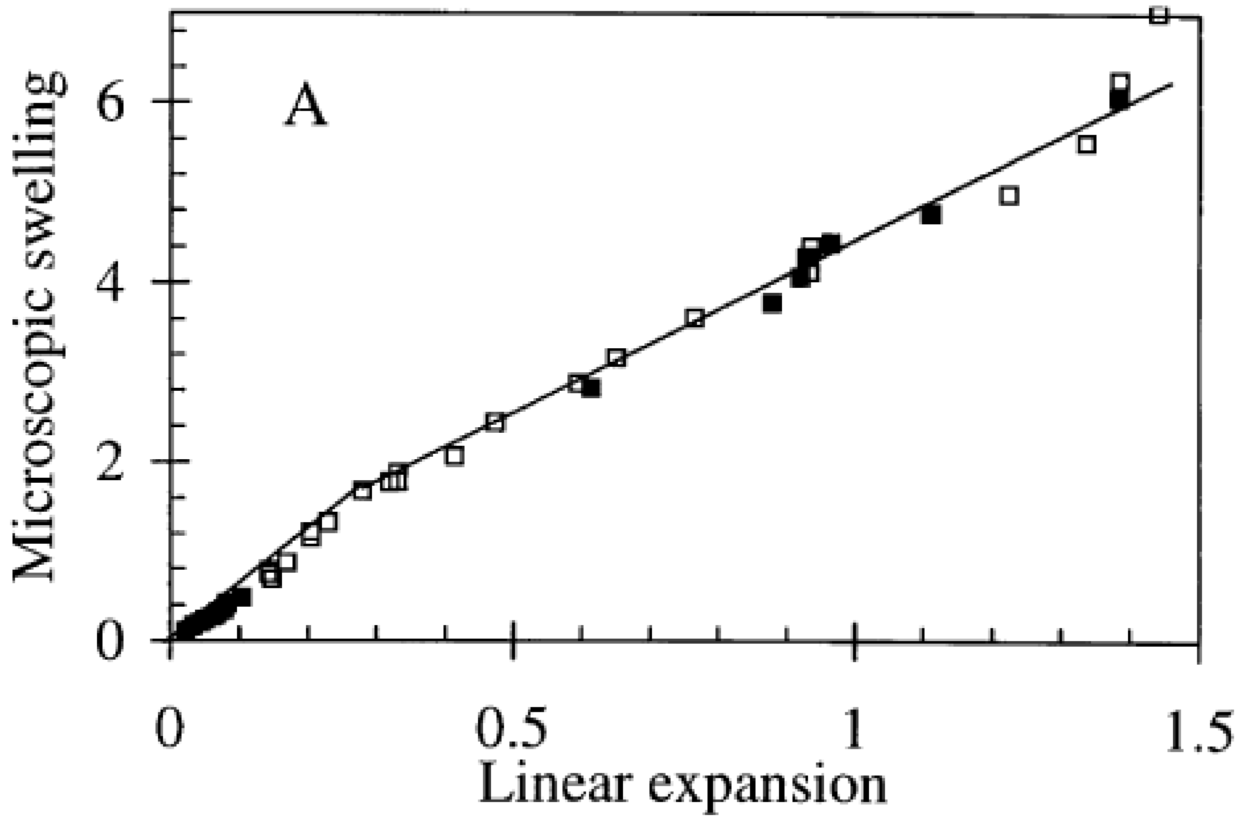




VF et al., JMS, 2000

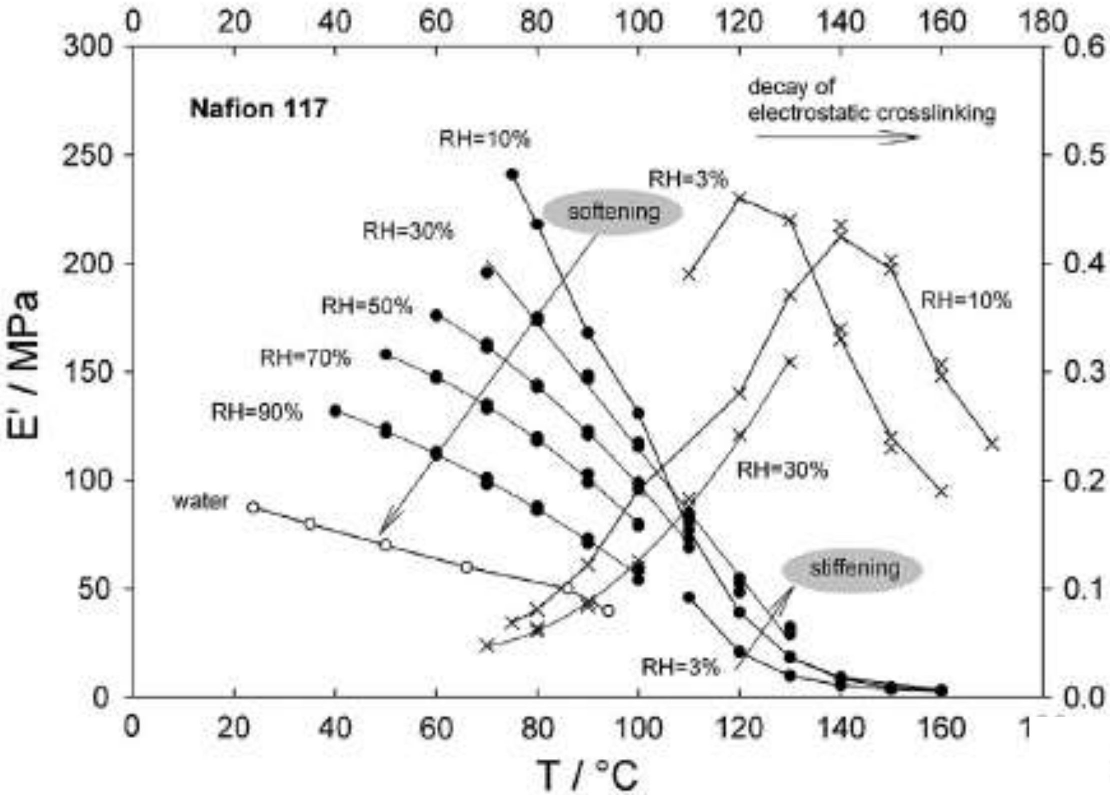
Bass and Freger, 2008

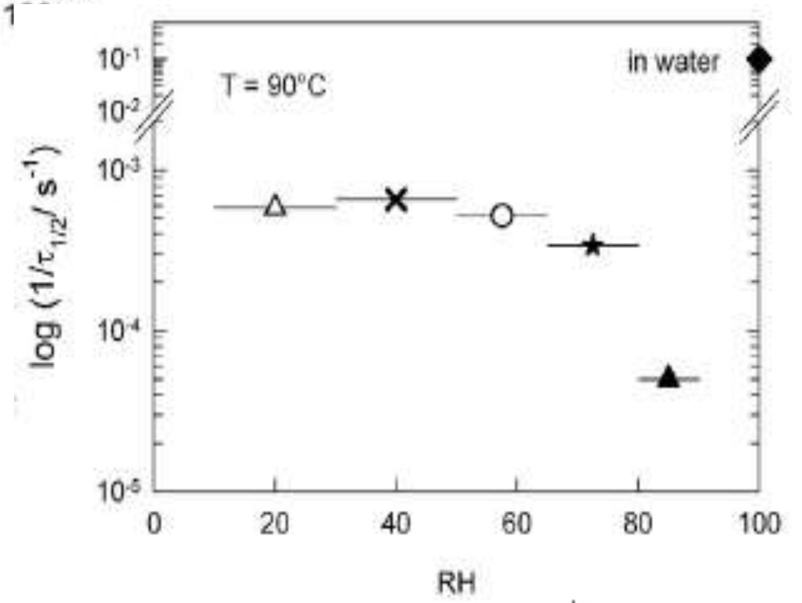
Microscopic vs. Microscopic Swelling



Gebel, 2000;
Fujimura et al., 1981, 1982

Mechanical Properties and Swelling Kinetics





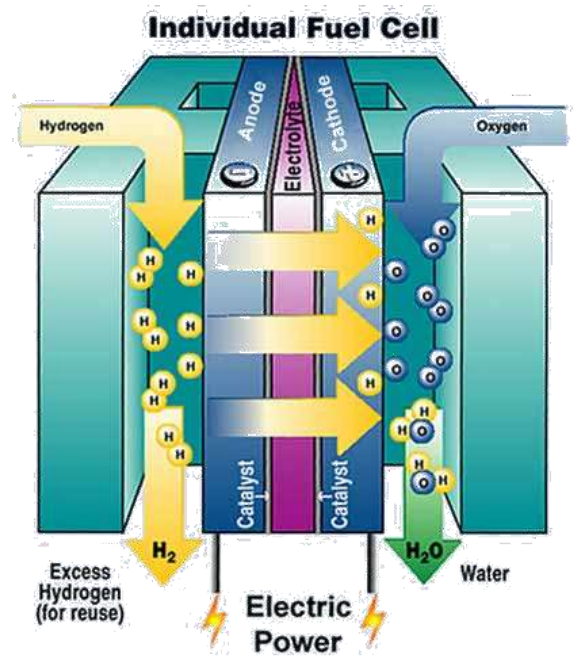
Kreuer, Solid State Ionics, 2013

Benziger et al, 2009-2013

Schroeder's Paradox and Water Transport

$$J_w = -\frac{D_w C_w}{RT}\nabla\mu_w + \chi J_{H^+}$$

$$\chi \sim 1 \div 5$$



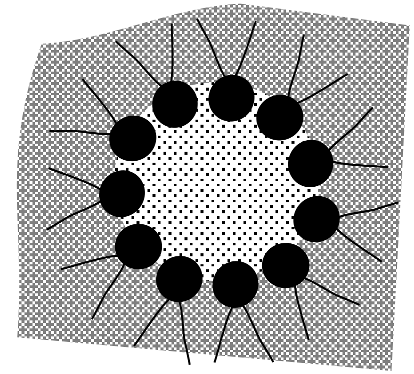
- If the thermodynamic potential of water is ill-defined, how does one model water transport, "water management" etc?
- How can one explain Schroeder's paradox?

Model: Connecting Structure and Hydration

- Four terms are the minimal set

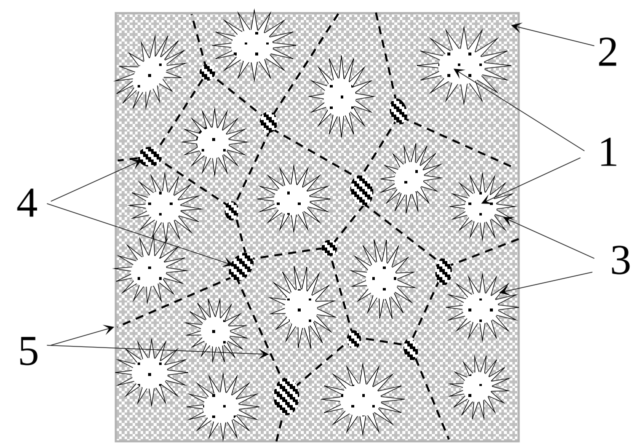
$$f = g_o(\phi) + G_{ef}(\phi - \phi_0)^2 + \gamma\sigma + B\nu_e\phi\sigma^2$$

osmotic "inflation" interface "corona"



$$R \cong \frac{\nu_e\phi}{\sigma} \text{ (3D, 2D) or } R \cong \frac{\nu_e}{\sigma} (1D)$$

- Minimize last 2 terms to find $\sigma(\phi)$
- Minimize $g = f - \mu\lambda$ to get $\mu(\phi)$

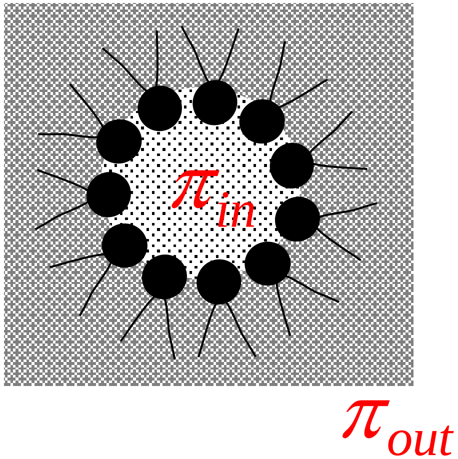


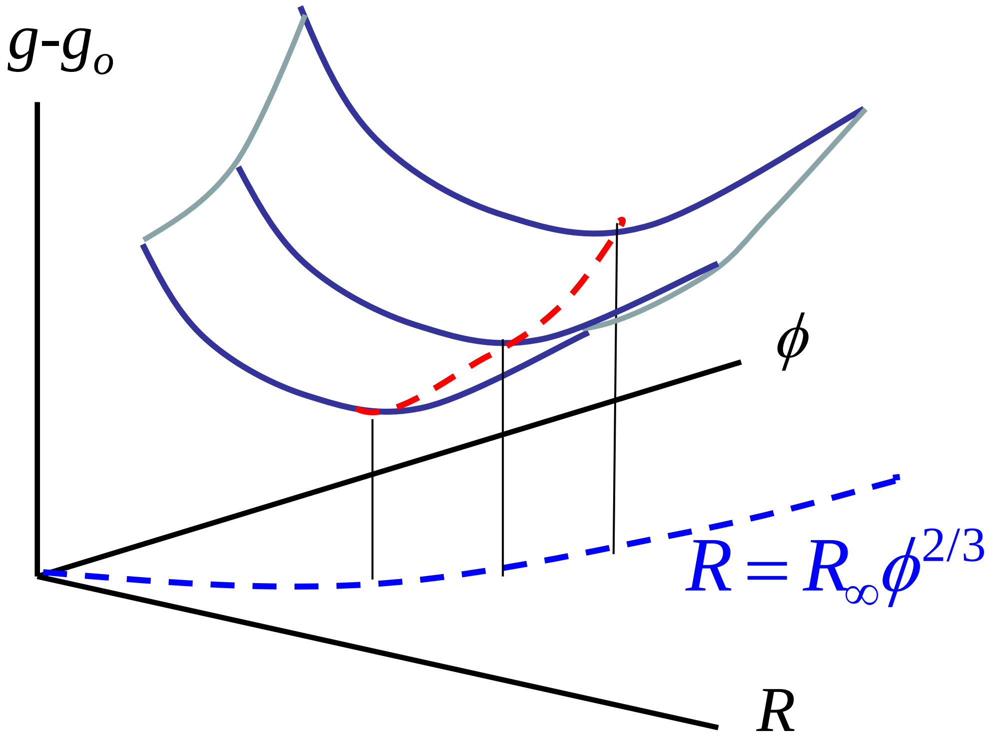
VF, *Polymer*, 2003; *JPC B*, 2009

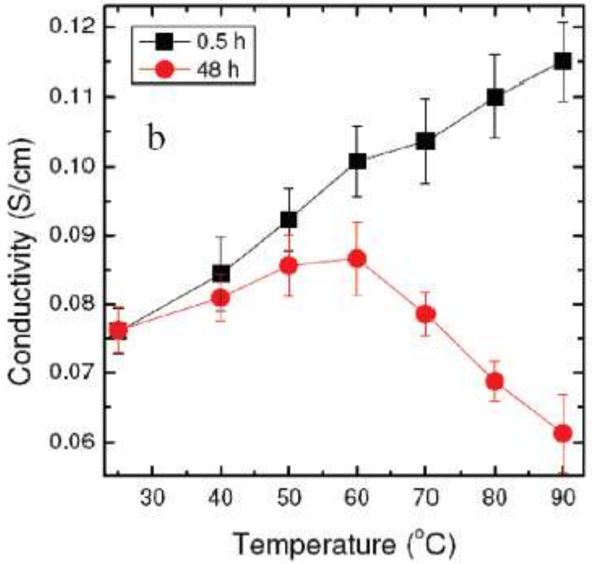
Microstructure: Interface, "Corona" and Inflation

$$R = R_\infty \phi^{2/3}; \quad \sigma = \sigma_\infty \phi^{1/3}$$

$$\pi_{in} - \pi_{out} = \pi_s + \pi_d$$







Park et al, *NanoLett*, 2007

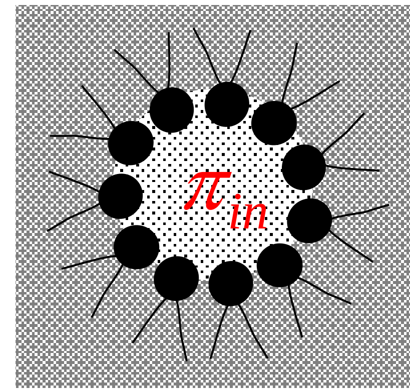
VF, *JPC B*, 2009

"Laplace" Pressure and Schroeder's Paradox

$$\pi_{in} - \pi_{out} = \pi_s + \pi_d$$

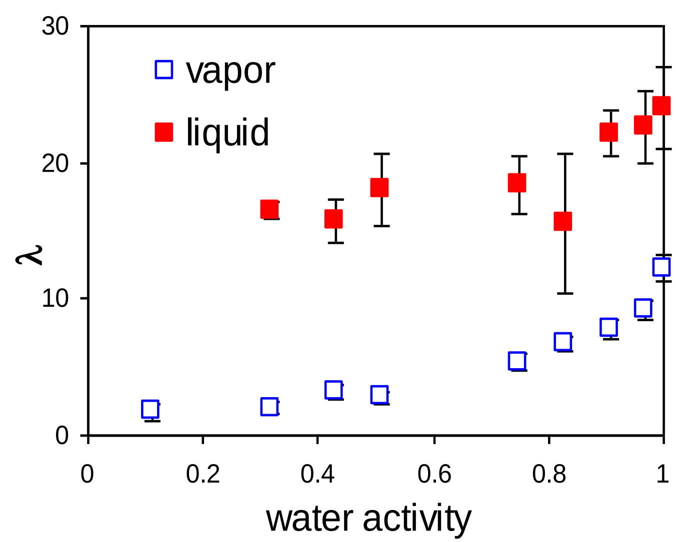
$$\pi_d \cong G(\phi - \phi_0)$$

$$\pi_s \cong \left(\frac{G\gamma^2}{v_e^{2/3}} \right)^{1/3} \phi^{-2/3}(1-\phi)^2$$



$$\gamma v_e^{-1/3} \sim 10^7\,\mathrm{Pa} \ \text{ vs } \ G \sim (0.1 \div 60) \times 10^7\,\mathrm{Pa}$$

- The "Laplace" pressure must vanish in liquid – resulting in a larger uptake of water
- For the same level of hydration the chemical potential of water is not equivalent in liquid and vapor

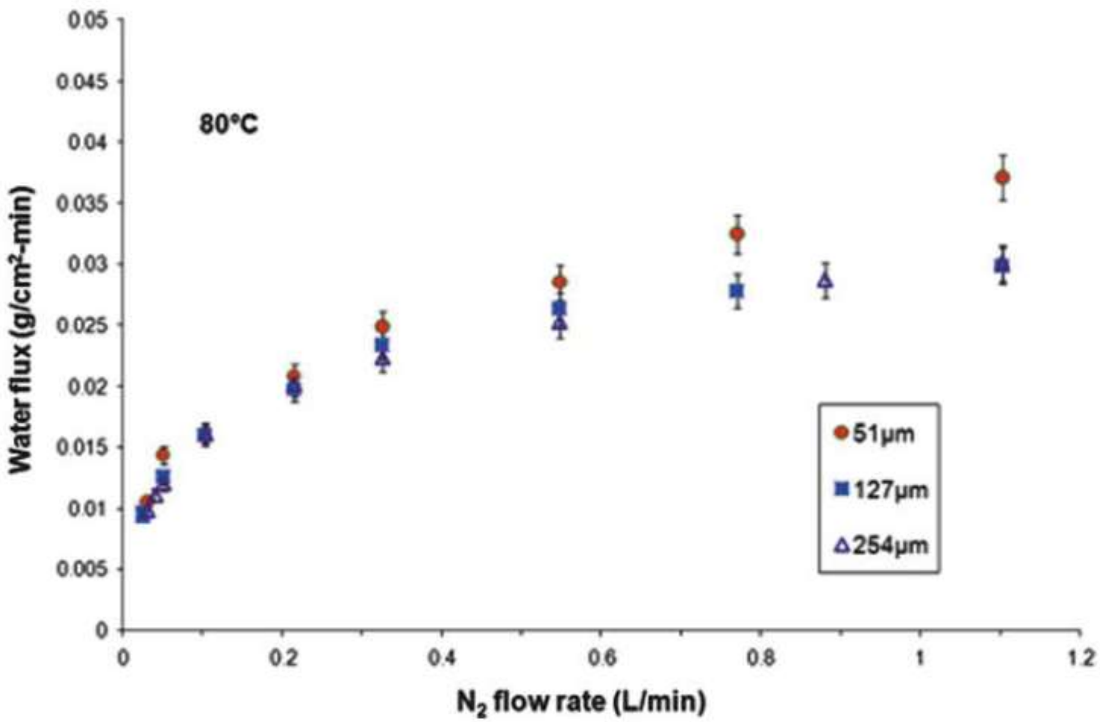


Interfacial ("Apple-to-Oranges") Resistance

- To have an "apples-to-apples" situation, the extra pressure at v-interface may need to be accounted for in transport modeling.

$$J_w = \Delta\mu_{cor} / R$$

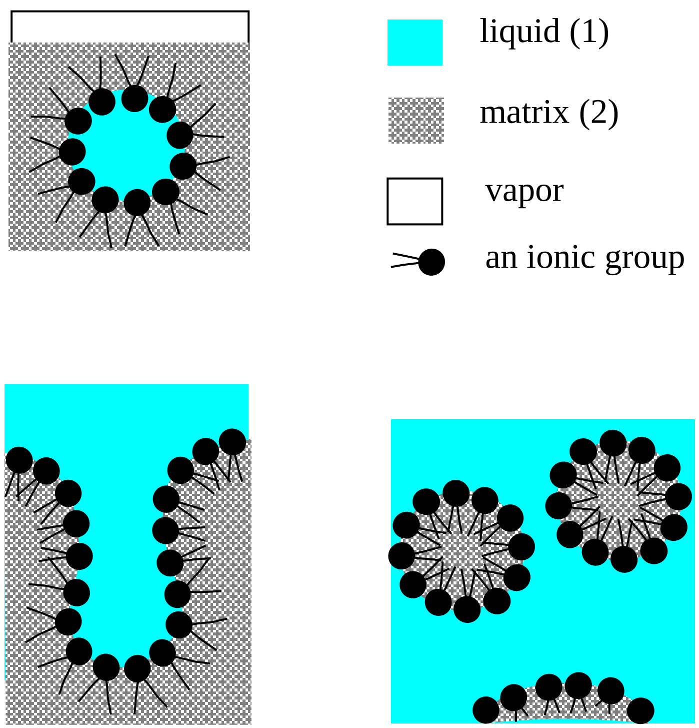
$$R_{app} = \Delta\mu / J_w = R_{cor} + \pi_s / J_w$$



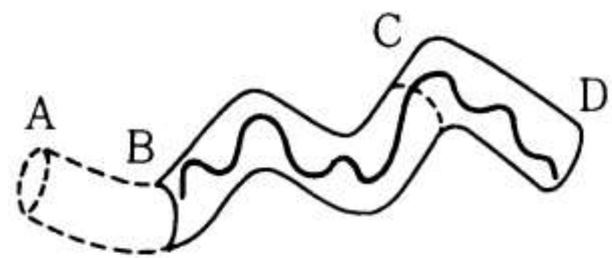
Benziger et al, 2009

Bulk Equilibrium vs. Surface Equilibrium

- Thermodynamic theory predicts that Nafion will dissolve in water; this does not happen due to very long relaxation ($\geq 10^5$ -10^6 s). *Solid Nafion membrane is a quasi-equilibrium system.*
- However, equilibrium may be approached more closely and “dissolution” may occur at the surface

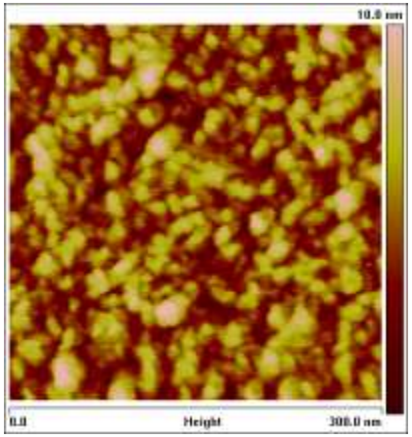


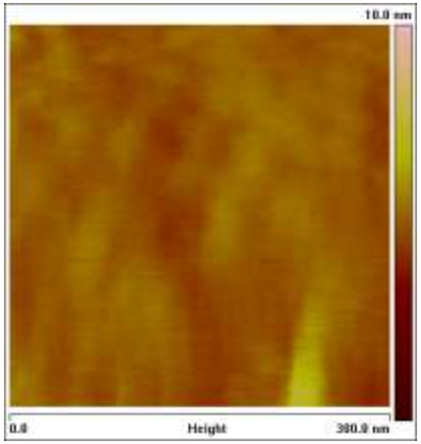
VF, *JPC B*, 2009

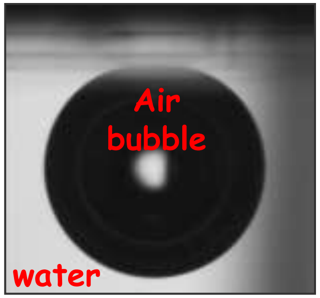


$$\tau = \frac{L_{tube}^2}{D_{tube}} \sim M^3$$ (de Gennes, 1978)

Surface Morphology and Alignment

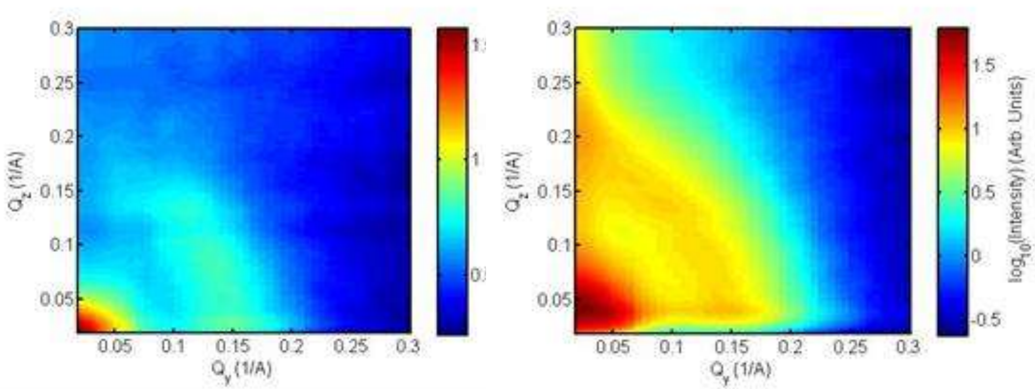


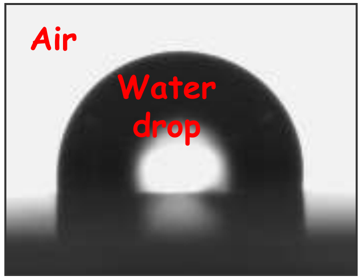




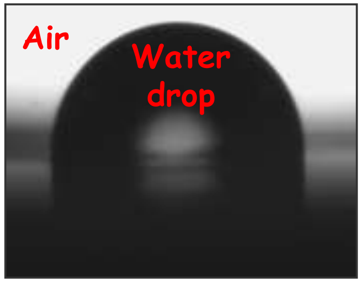
25.4 ± 0.25°

Water vs. Vapor

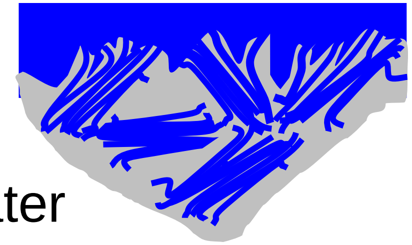




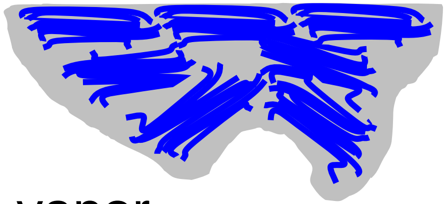
96.4 ± 1.2°



94.5 ± 1.1°



water



vapor

Bass et al., JPC B, 2010
Bass et al., Macromolecules, 2011

Summary

- Solid Nafion is a non-equilibrium structure.

- Non-relaxed pressures in Nafion result in a non-thermodynamic behavior (Schroeder's paradox, T and RH-dependent mechanical and swelling relaxation); this needs to be accounted for in transport modeling.

- Interfaces affect the morphology and orientation of micelles in thin Nafion films; this could be attractive for developing barriers with enhanced and stable transport characteristics.

$$\pi_s \cong \frac{\gamma}{R}(1-\phi)^2$$

Thanks

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