

Network Formation and Ion Conduction in Ionomer Membranes

Renewable Fuels for the Future

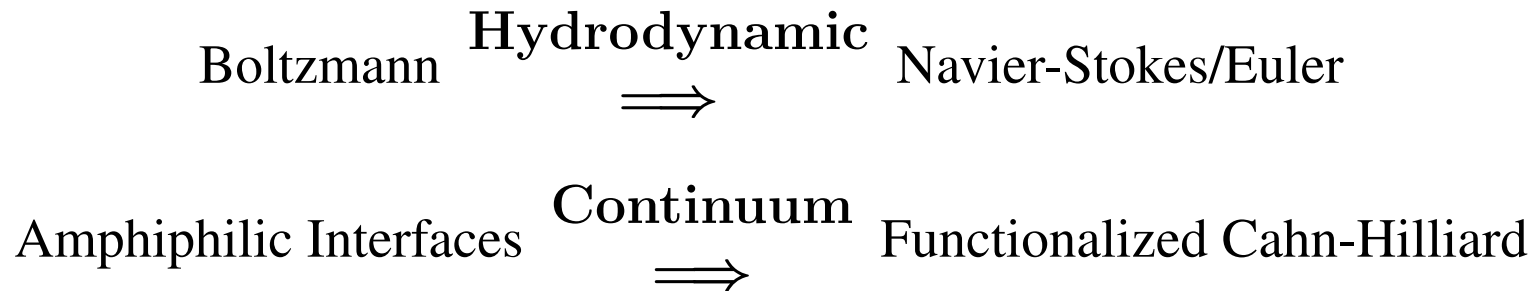
Jan 19, 2013

K. Promislow, G. Baker, A. Christlieb, and N. Gavish

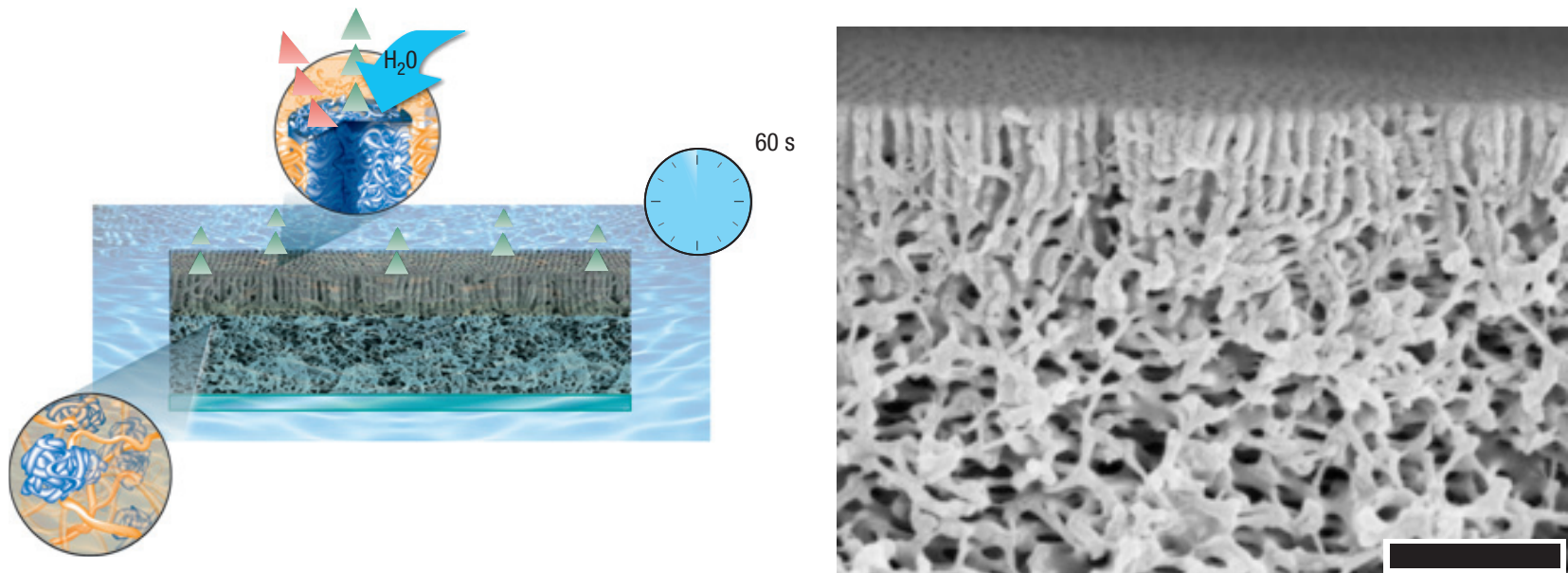


Goals

- Develop a novel **continuum framework** for the network formation in amphiphilic mixtures
- Incorporate the role of solvent quality, functional groups, counter-ions
- Propose connections between charge transport and network morphology
- All within the context of a “minimal system” which respects a governing energy.



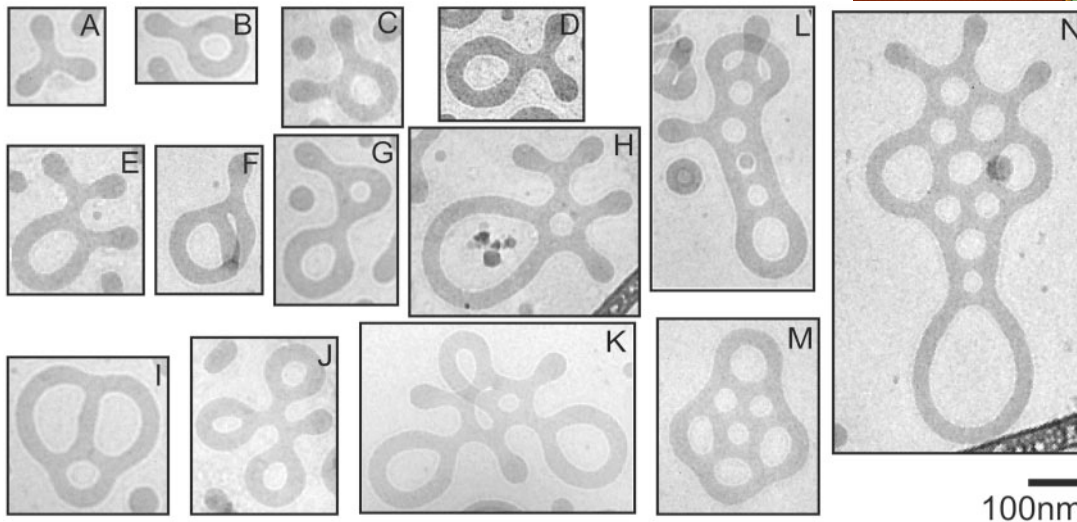
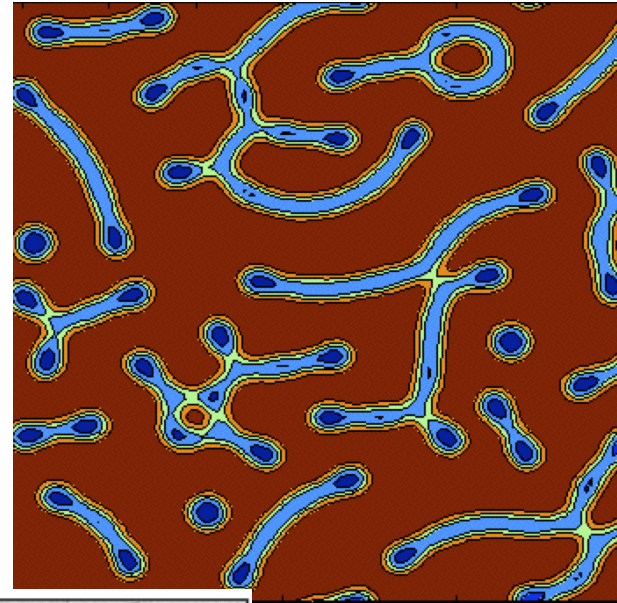
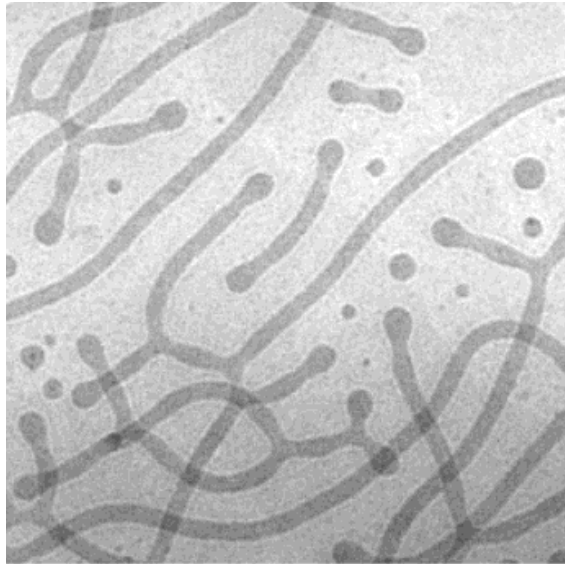
Role of Solvent in Cast-Driven Morphology



Mix two miscible solvents (DMF and THF) with an amphiphilic diblock co-polymer (PEO-poly vinyl pyridine) one of whose components is soluble only in DMF. Evaporating off the THF changes the "goodness" of the solvent. Then immerse in water.

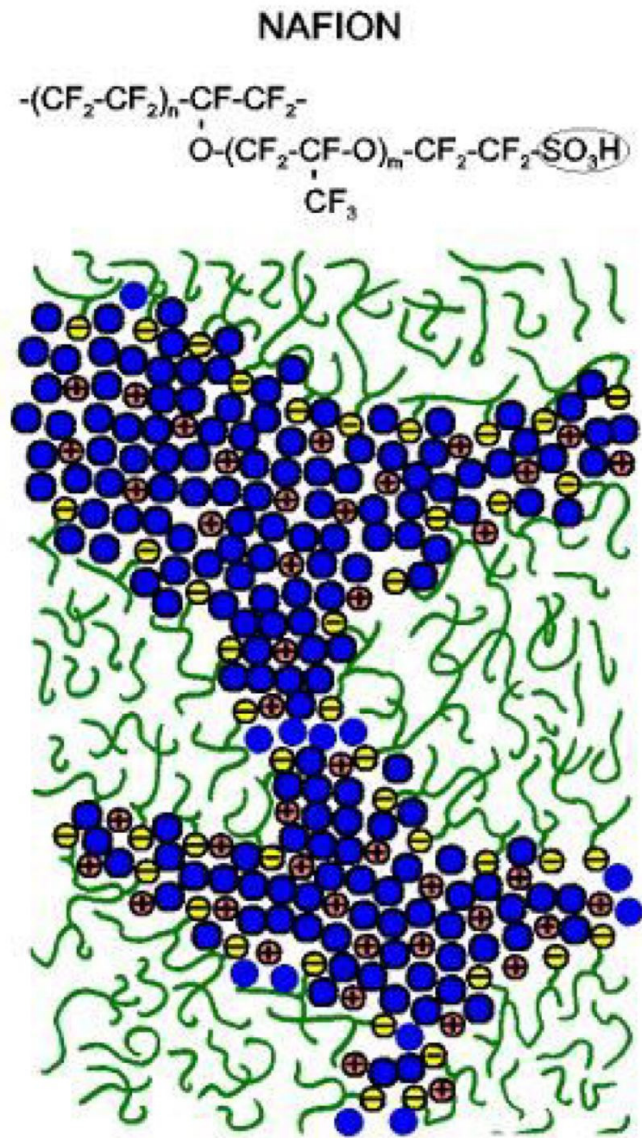
K.-V. Peinemann, V. Abetz, P. F. Simon, *Nature Materials* (2007)

Amphiphilic diblocks – The role of charge density

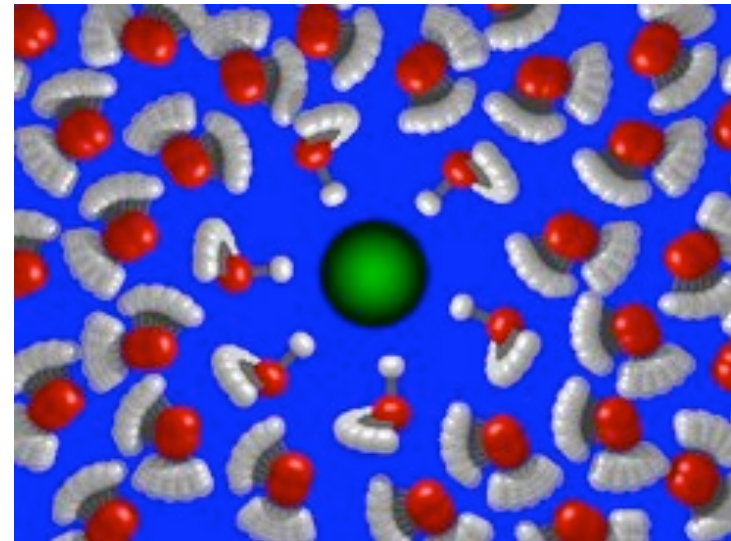
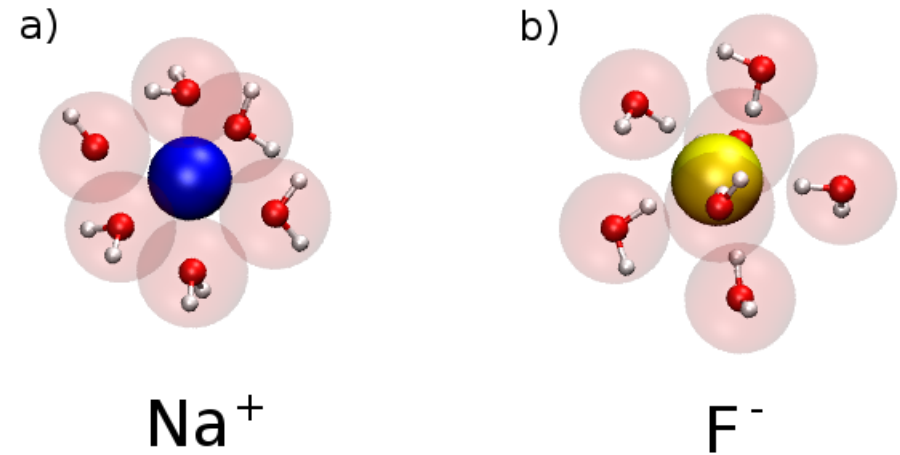
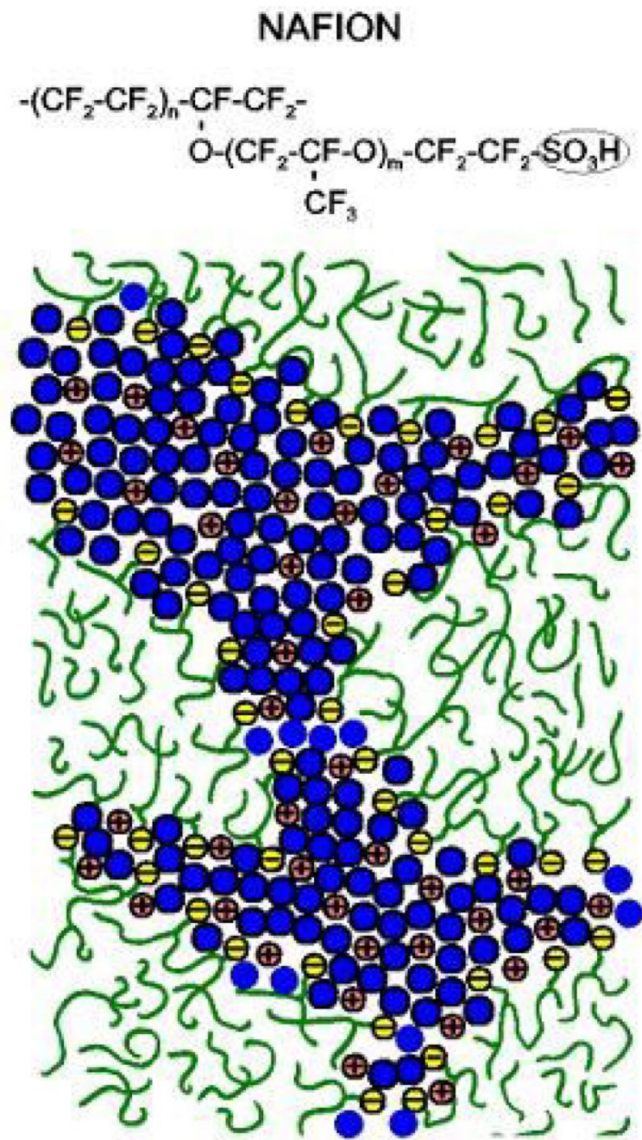


Amphiphilic PEO-Polybutadiene block co-polymers (F. Bates 2004)

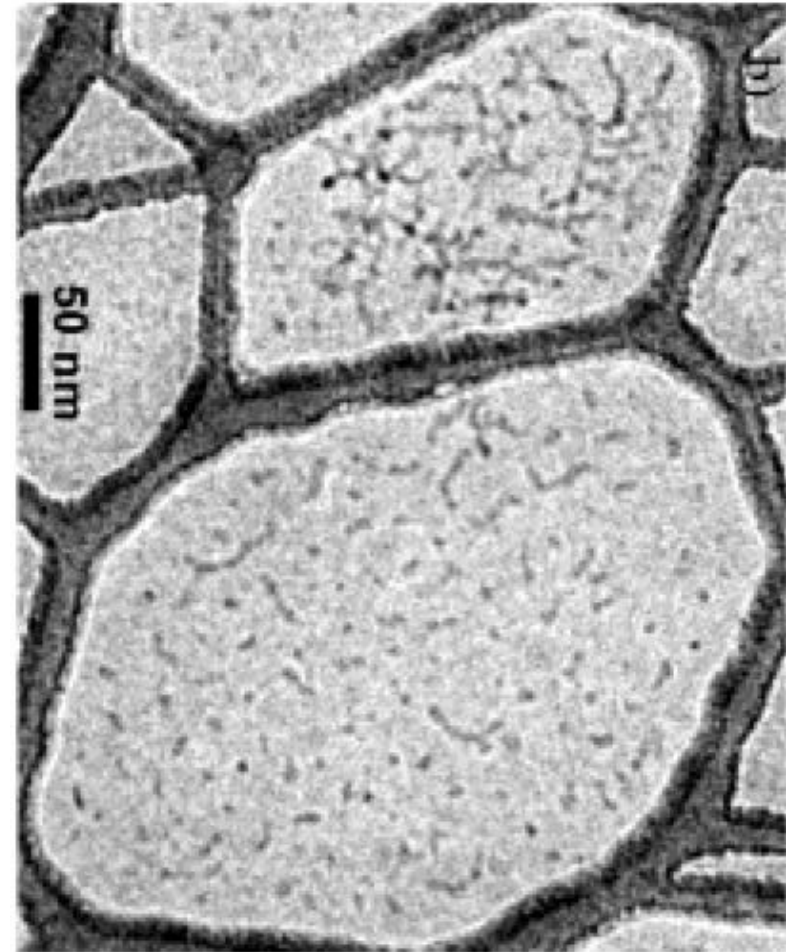
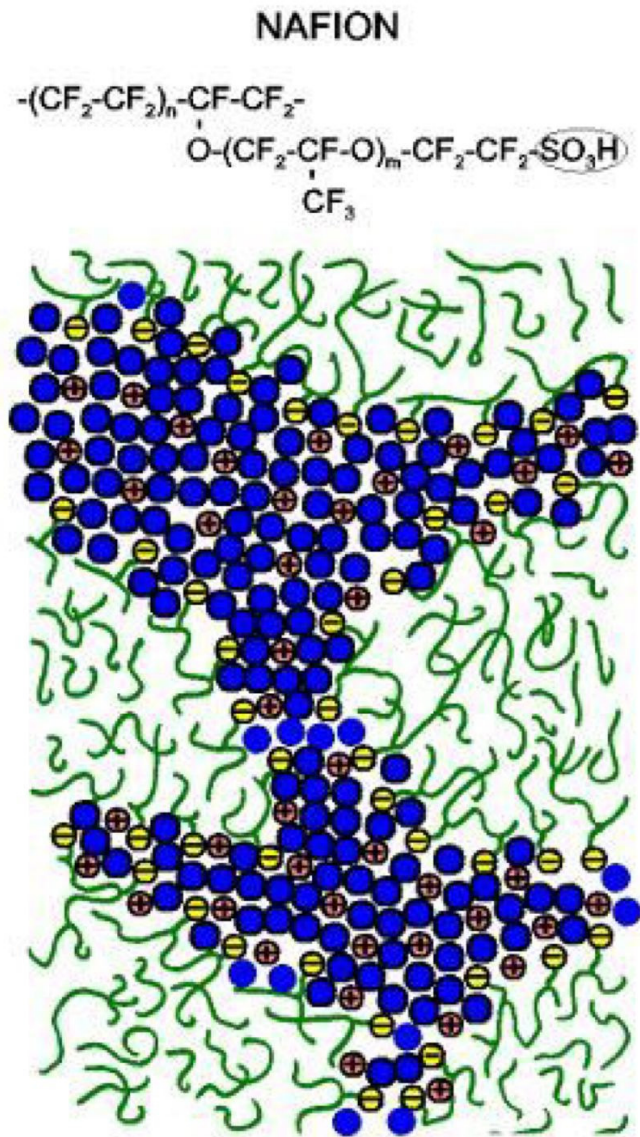
Ionomer Membranes: Selective charge transport



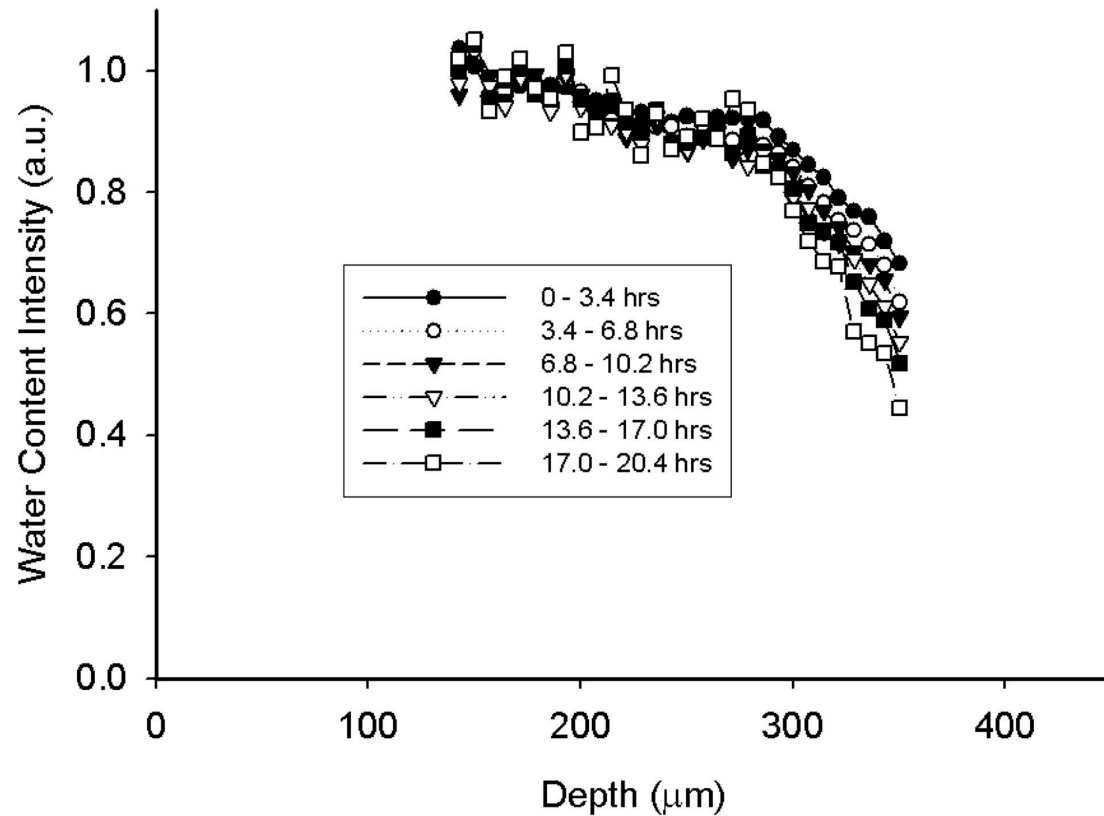
Ionomer Membranes: Incorporation of Solvation Energy



Ionomer Membranes: Incorporation of Solvation Energy



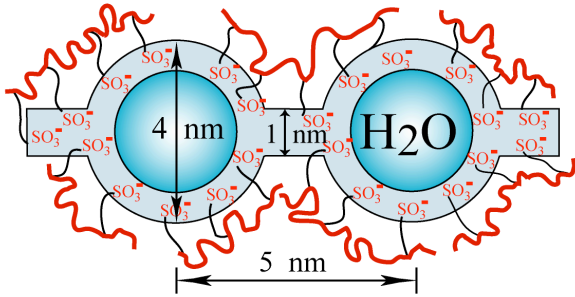
Hysteresis in Nafion



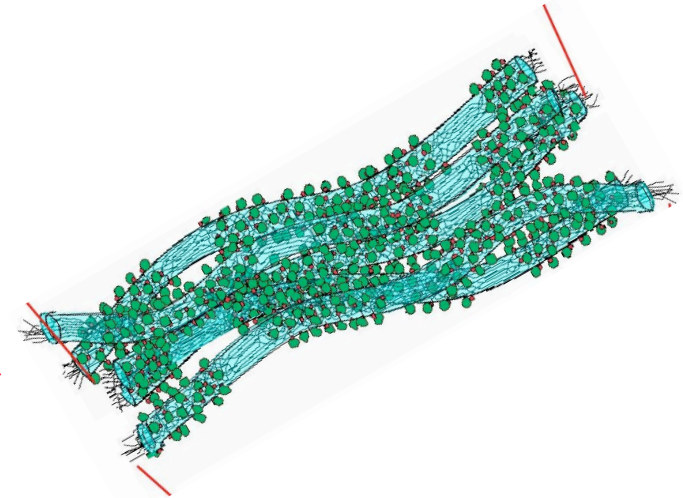
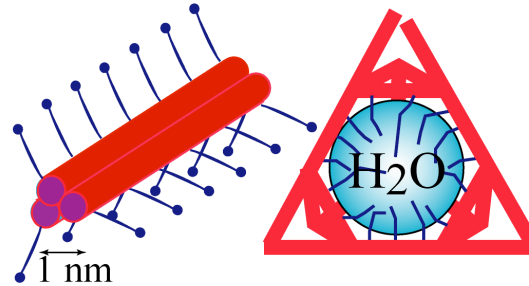
In-situ MRI data of Nafion membrane exposed on one side to liquid water and on the other air at constant RH, (Z. Zhang, B. Balcom, K. Promislow, et al J. Magnetic Resonance 2008, J. Power Sources, 2011).

Schematics of Nafion Morphology

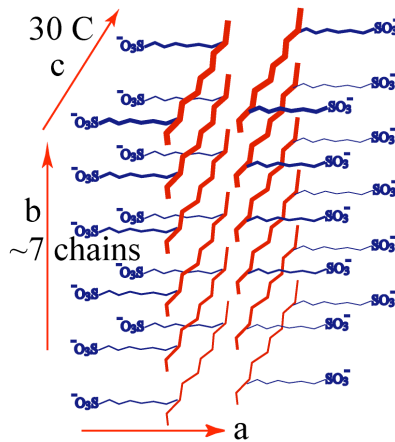
Gierke et al., 1981
Kumar, Pineri, 1986



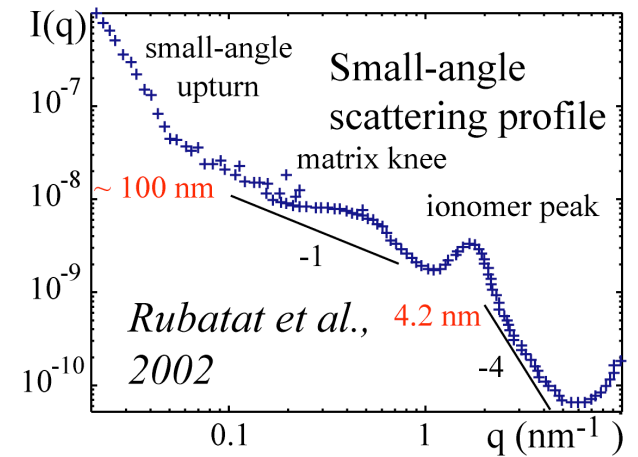
Ioselevich et al., 2004



Starkweather, 1982
Krivanlin et al., 2003

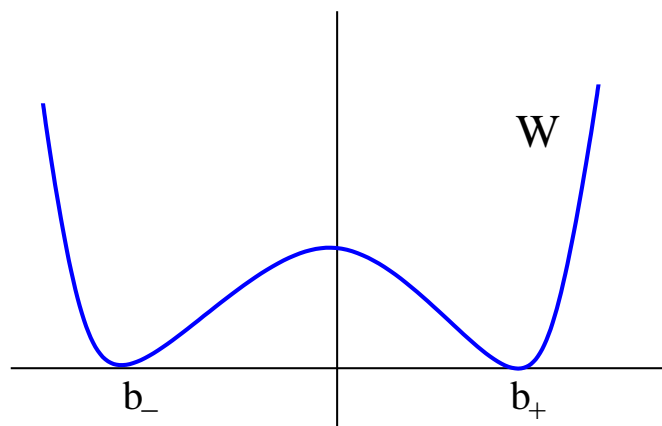


Rubatat, Rollet, Gebel, Diat, 2002
Heijden, Rubatat, Diat, 2004
Rubatat, Gebel, Diat, 2004



Hsu and Gierke postulated that a **balance of elastic deformation and hydrophilic surface interactions** lead the water phase to pearl.

An Unlikely Starting Point: The Phase Field Approach



Let $u(x)$ denote the density of one component of a binary mixture. The Cahn-Hilliard free energy is

$$\mathcal{E}_{\text{CH}}(u) = \int_{\Omega} \frac{\epsilon^2}{2} |\nabla u|^2 + W_b(u) \, dx.$$

Parameter $\epsilon \ll 1$ is ratio of interfacial thickness to domain size. The Γ -limit of \mathcal{E}_{CH} is the area functional (Modica and Mortola/ Sternberg).

$$\lim_{\epsilon \rightarrow 0} \mathcal{E}_{\text{CH}}(\phi) = \int_{\Gamma} a_1 \, dS.$$

The Canham-Helfrich energy is a general sharp-interface energy for $\Gamma \subset \mathbb{R}^3$ in terms of mean $H = (k_1 + k_2)/2$ and Gaussian $K = k_1 k_2$ curvatures,

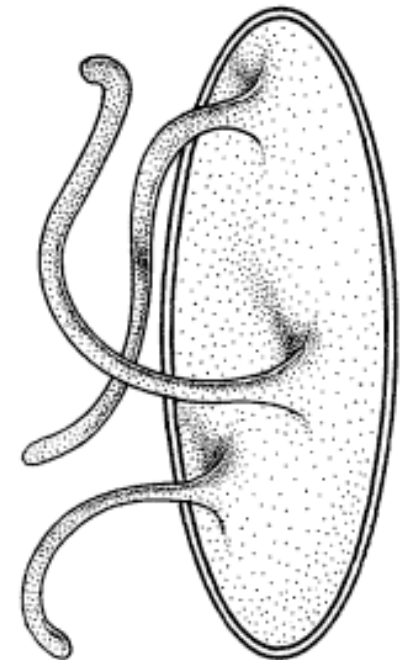
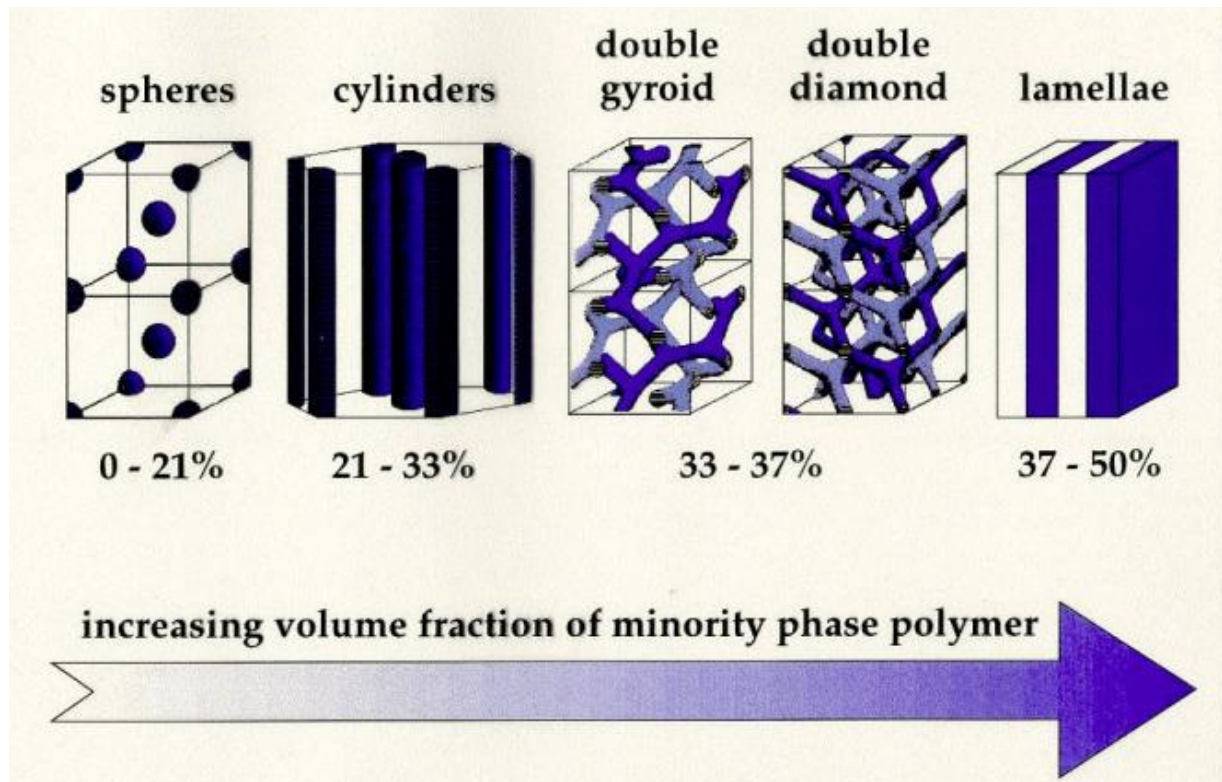
$$\mathcal{E}_{\text{Hel}}(\Gamma) = \int_{\Gamma} a_1 + a_2 (H - a_3)^2 + a_4 K \, dS.$$

Critical Points of the Cahn-Hilliard Energy

Minimizers of the Cahn-Hilliard Energy subject to a mass constraint satisfy the critical point equation

$$\epsilon^2 \Delta u = W'_b(u) + \lambda.$$

Minimizers are constructed of one “inner” structure (heteroclinic/single-layer) which arrange into various “outer” morphologies. (Morgan: Geometric Measure Theory).



Embedding Cahn-Hilliard in a Larger Structure

Under the Cahn-Hilliard gradient flow

$$u_t = \Delta(\epsilon^2 \Delta u - W'_b(u)) \implies \frac{d}{dt} \mathcal{E}_{\text{CH}}(u) \leq 0,$$

most of the zoo of critical points is unstable.

De Giorgi proposed the following energy

$$\mathcal{F}_0(u) = \int_{\Omega} \frac{1}{2} (\epsilon^2 \Delta u - W'_b(u))^2 dx,$$

for which *all critical points* of Cahn-Hilliard are global minimizers.

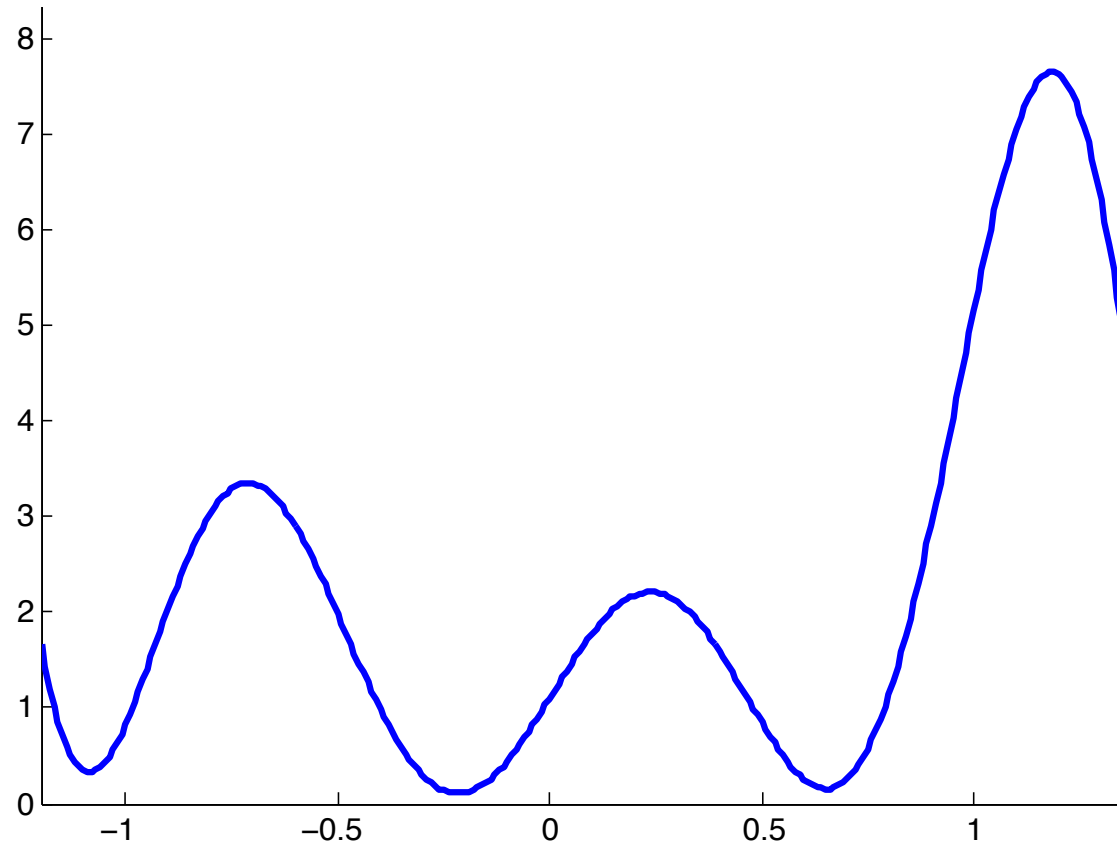
Functionalized Cahn-Hilliard: “Orwellian” unfolding of the De Giorgi energy:

$$\mathcal{F}_{\text{CH}}(u) = \int_{\Omega} \frac{E_b}{2} (\epsilon^2 \Delta u - W'_b(u; \tau))^2 - \left(\frac{\epsilon^2 \eta_{\text{solv}}}{2} |\nabla u|^2 + \eta_{\text{ent}} W_s(u; \tau) \right) dx.$$

Small parameters: $\epsilon, \eta_{\text{solv}}, \eta_{\text{ent}} \ll 1$. Order of 1: E_b, τ .

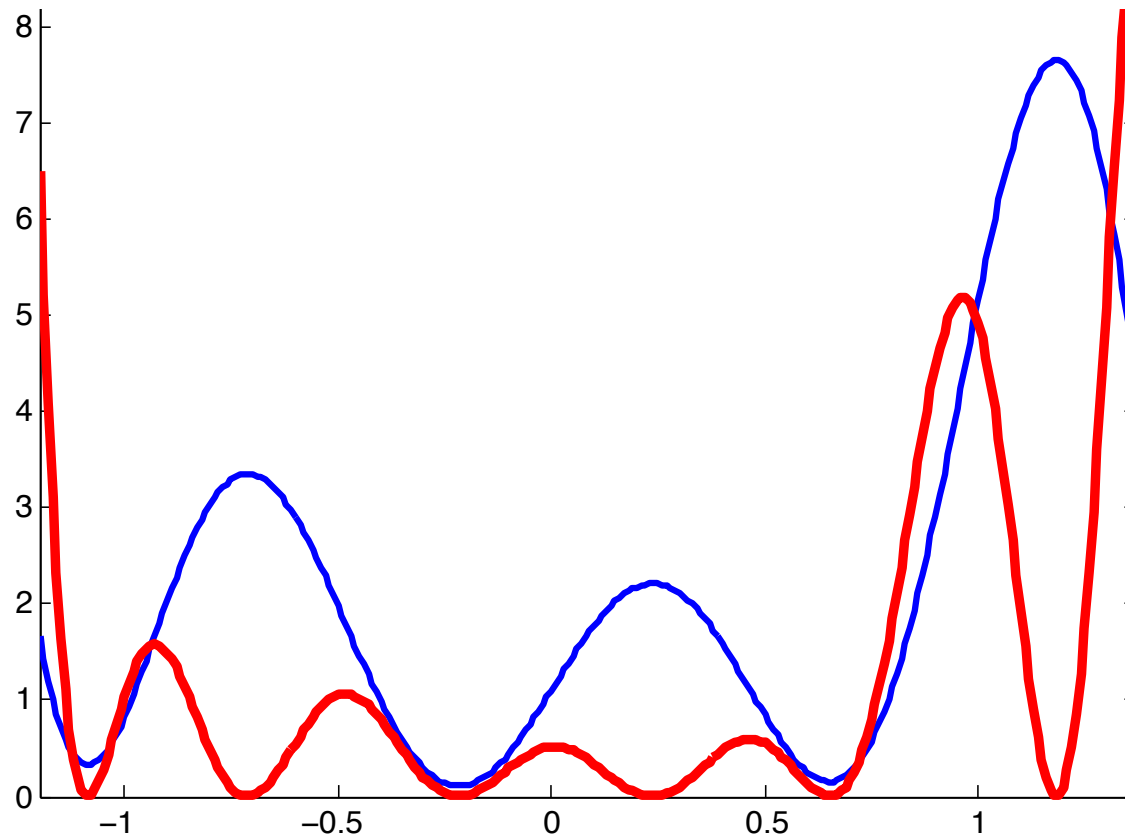
Reformulation of Cahn-Hilliard changes which critical points are minimizers.

Gradient Flow



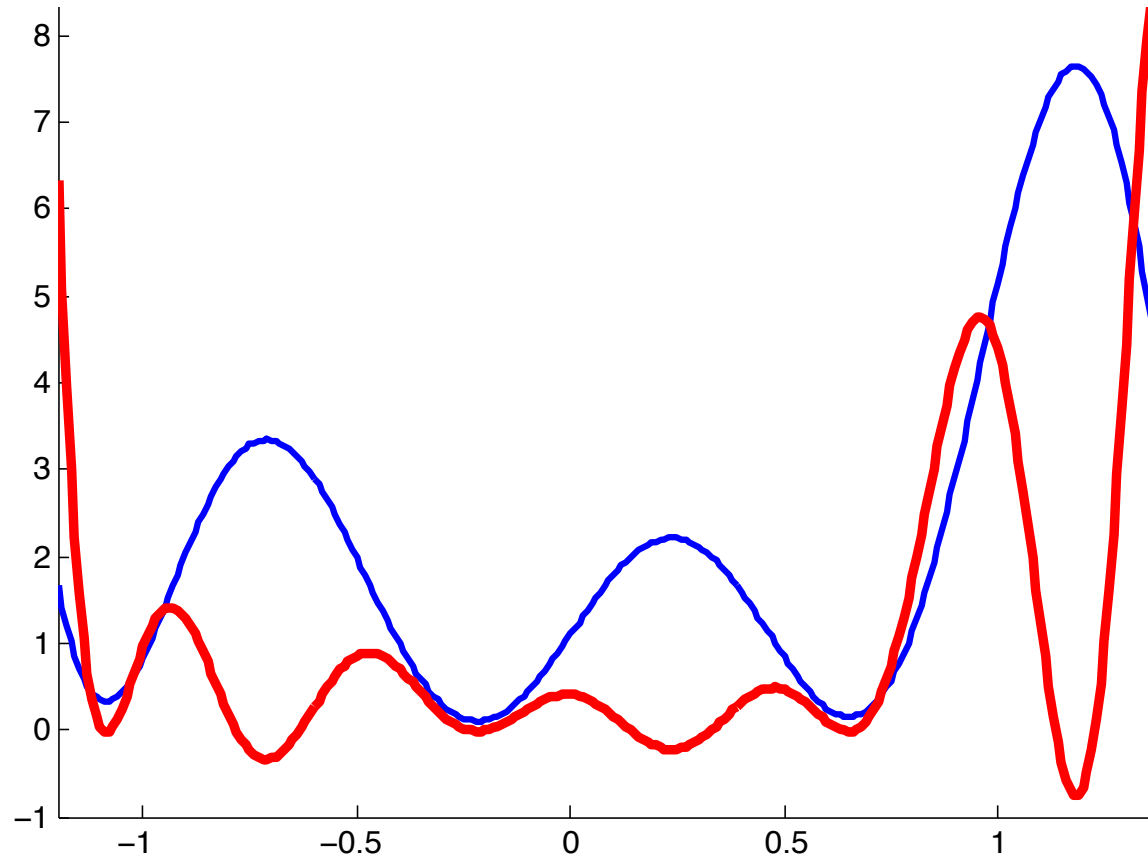
Consider a gradient flow in a complex energy landscape $F(x)$.

Remapping



To find all critical points, flow on $\mathcal{F}_0 := (F')^2$.

Functionalization

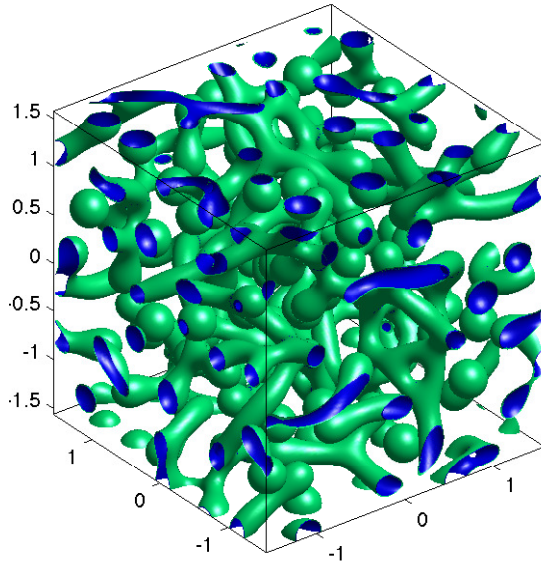


The Gradient flow on
 $\mathcal{F} := (F')^2 - \epsilon G(x)$

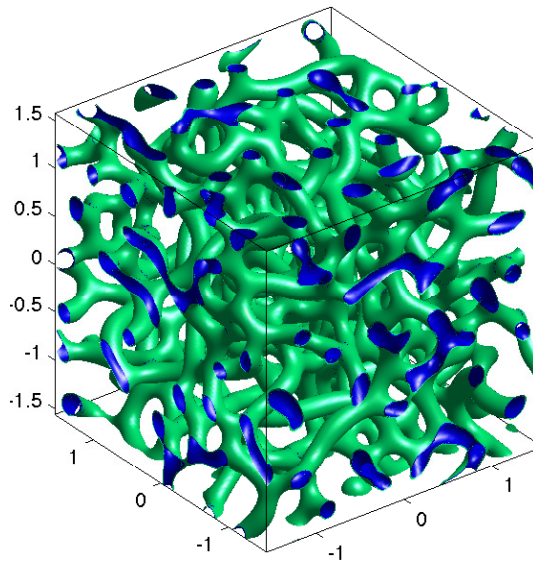
allows an exploration of critical points of F which are "good" for G .

Sample of Parameter Space $\tau = -0.4, \epsilon = 0.03$

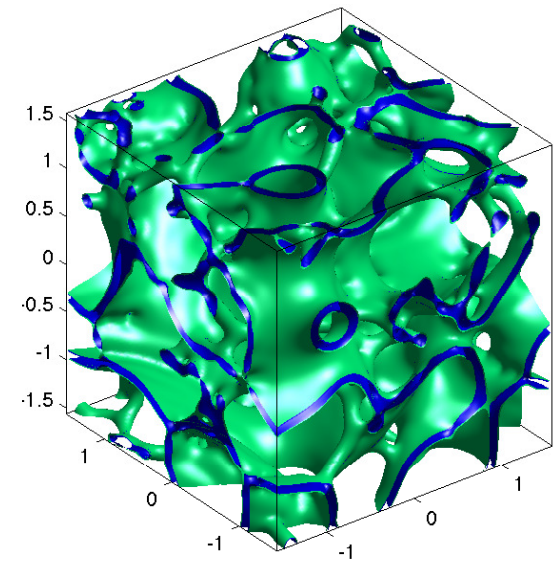
$$u_t = \Delta \frac{\delta \mathcal{F}_{\text{CH}}}{\delta u} \implies \frac{d}{dt} \mathcal{F}_{\text{CH}}(u) \leq 0$$



$\eta_{\text{ent}} = -2\epsilon$
 Micelles - Pores
 Co-dim 2 & 3



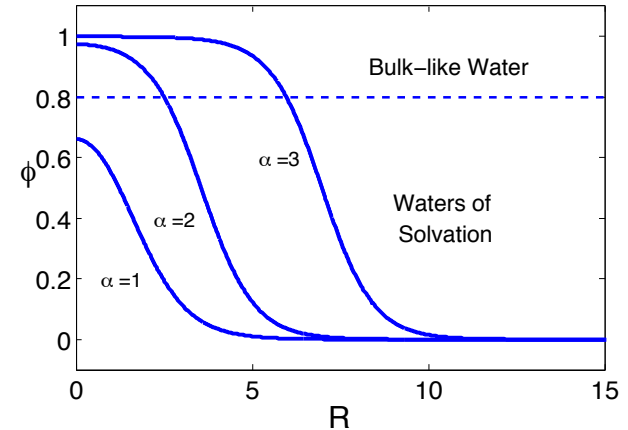
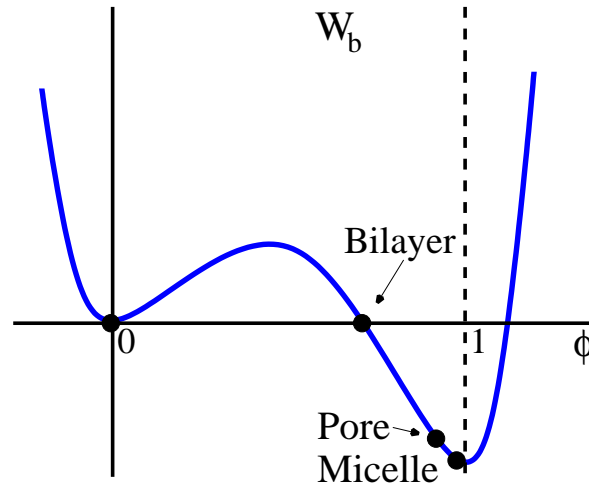
$\eta_{\text{ent}} = \epsilon$
 Pore Network
 Co-dim 2



$\eta_{\text{ent}} = 5\epsilon$
 Bilayers
 Co-dim 1

Identical, randomly ± 1 initial data. Co-dimension = choice of inner structure.

The Well Tilt Parameter τ



Well tilt, τ differentiates the self-energy of the solvent and polymer phases.

$$\partial_R^2 \phi_\alpha + \frac{\alpha}{R} \partial_R \phi_\alpha = W'(\phi_\alpha; \tau).$$

The liquid-phase self energy is reflected by its pressure

$$P = P_l + P_{\text{osm}}, \quad P_{\text{osm}} = RT \rho_+ \approx 80 - 100 \frac{\text{J}}{\text{cm}^3}.$$

The balance between the liquid pressure and bulk modulus of polymer phase tunes the pore radius. This is encoded in a [constitutive relation](#) for the well-tilt:

$$\tau = \tau(P).$$

Solvation Energy

$$\mathcal{F}_{\text{CH}}(u) = \int_{\Omega} \frac{1}{2} (\epsilon^2 \Delta u - W'_b(u))^2 - \left(\frac{\eta_{\text{solv}}}{2} \epsilon^2 |\nabla u|^2 + \eta_{\text{ent}} W_s(u) \right) dx.$$

$\eta_{\text{solv}} > 0$ drives the creation of interface.

The values of Gibbs free energy of solvation shells depends upon the nature of the solvent and the density of ionic groups, n , within the polymer

$$\eta_{\text{solv}} = \eta_{\text{solv}}(n).$$

For ionic group densities typical of Nafion literature values range

$$\eta_{\text{solv}} \approx 3 - 4 \frac{\text{kJ}}{\text{cm}^3},$$

roughly 30 times higher than energy associated to backbone stiffness:

$$\frac{\eta_{\text{solv}}}{\epsilon^2 E_b} \approx 30.$$

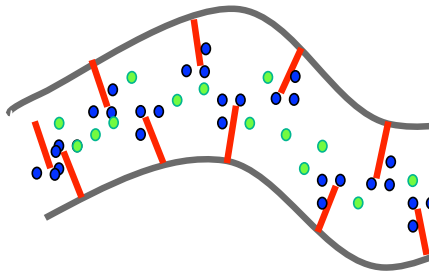
In our simulations we choose:

$$E_b = 1, \epsilon = 0.03, \eta_{\text{solv}} = O(\epsilon) > 0.$$

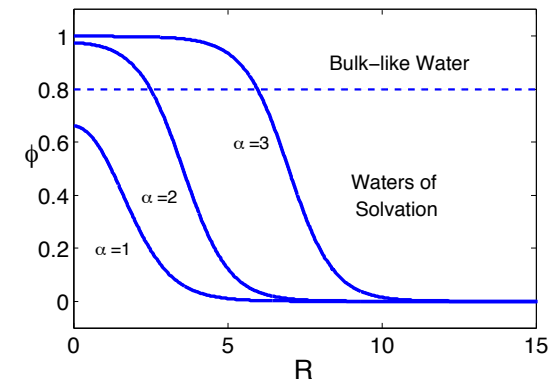
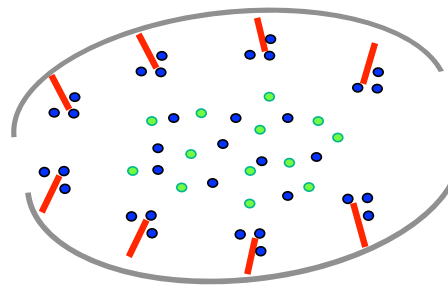
Impact of Counter-ion Mixture Entropy

$$\mathcal{F}_{\text{CH}}(u) = \int_{\Omega} \frac{1}{2} (\epsilon^2 \Delta u - W'_b(u))^2 - \left(\frac{\eta_{\text{solv}}}{2} \epsilon^2 |\nabla u|^2 + \eta_{\text{ent}} W_s(u) \right) dx.$$

Low mixing energy



High mixing energy

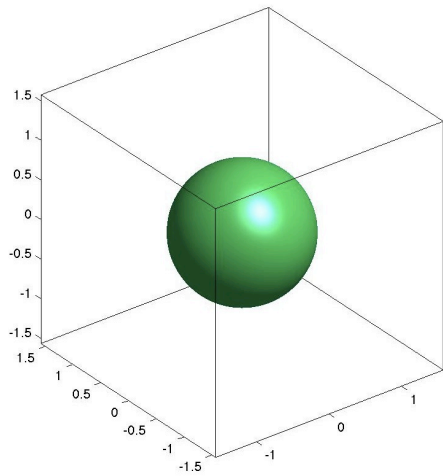


For simplicity take $W_s = W_b$.

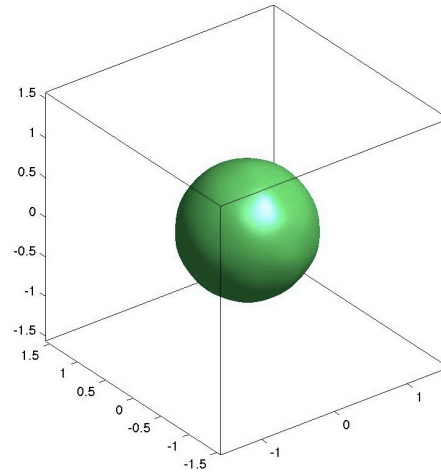
The parameter η_{ent} expresses the entropic preference for counter-ions (protons) for bulk-like water versus waters of solvation.

Key Prediction: A preference for bulk-like water selects pores over bilayers and selects micelles over pores.

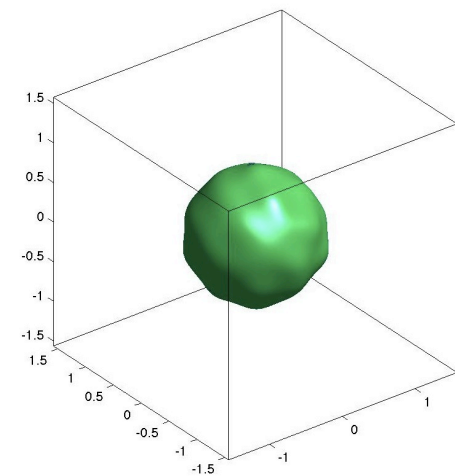
Time Evolution from Spherical Initial Data



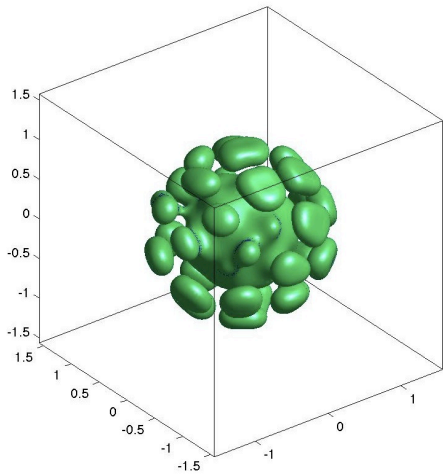
time = 0



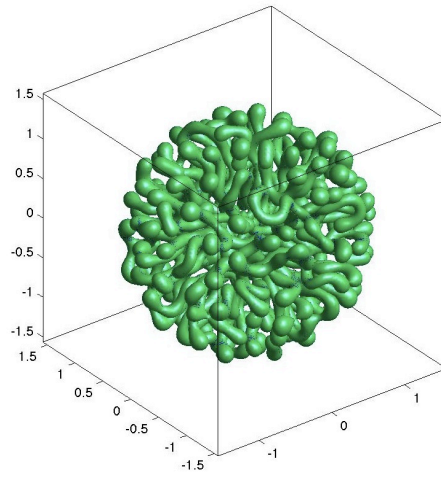
600



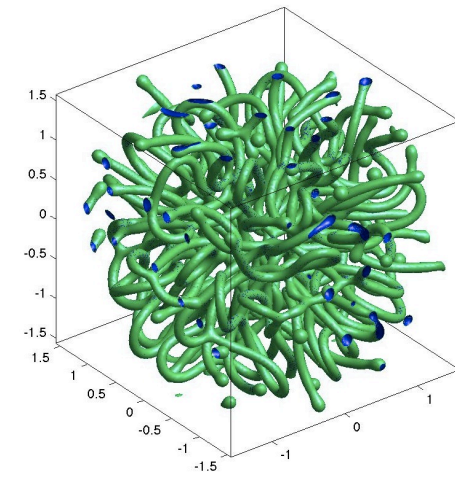
630



time = 640

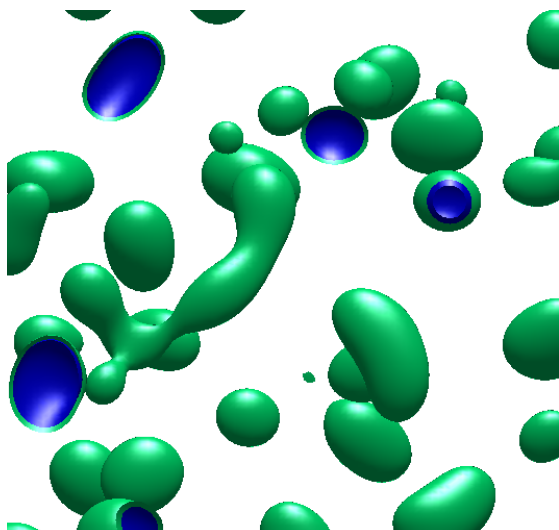


650

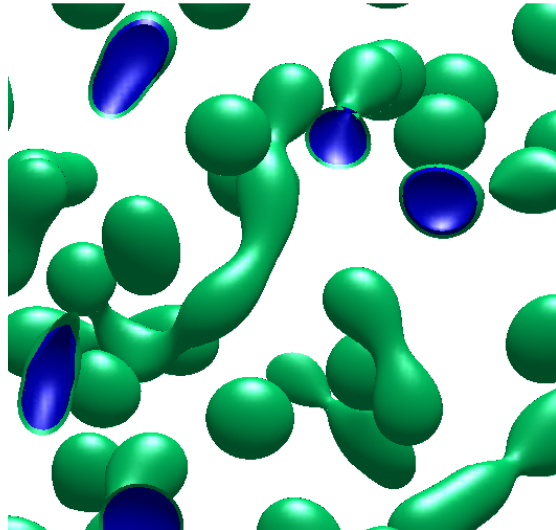


10,000

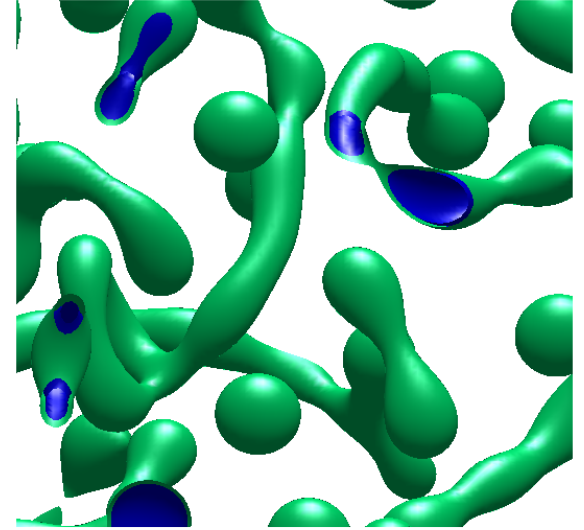
Merging of Dumb-bell Structures into Pore Network



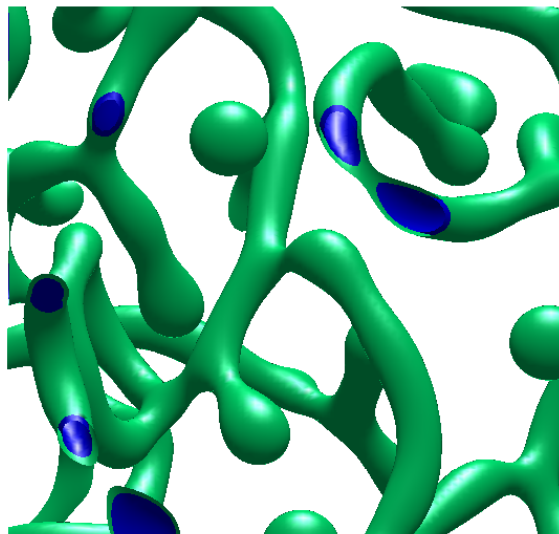
(a)



(b)



(c)



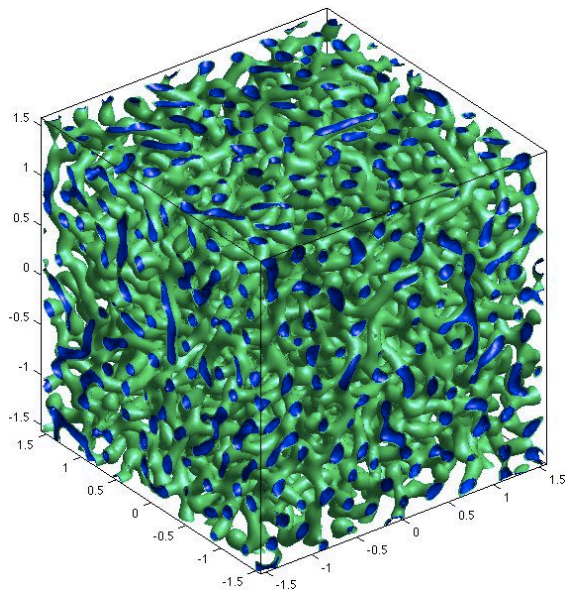
(a) Random initial data coarsens into micelles,
(b) over-sized micelles are unstable and grow into dumb-bells,
(c-d) dumb-bells elongate, merge and form a pore network.

Hysteretic Behavior

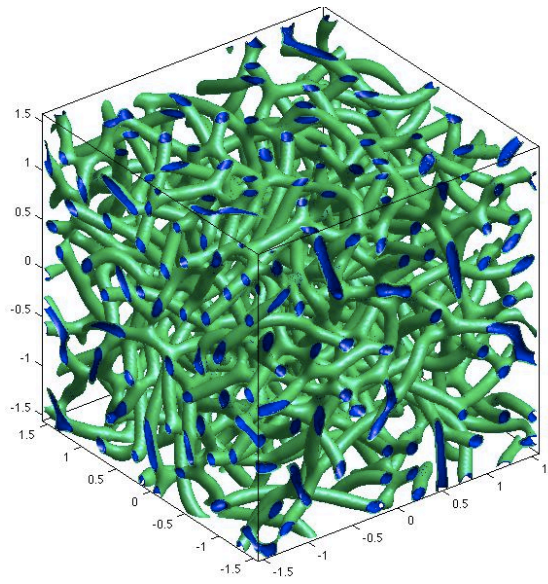
Gradient flow from random initial data with slow evaporation.

This yields sparse network not attainable from random initial data

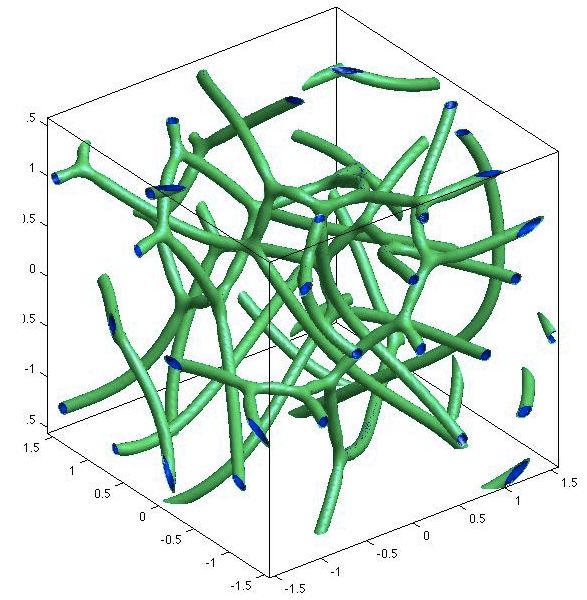
$$\tau = -0.4, \epsilon = 0.03, \eta_{\text{solv}} = 5\epsilon, \eta_{\text{ent}} = -4\epsilon.$$



30.2% Solvent
 $t = 1$

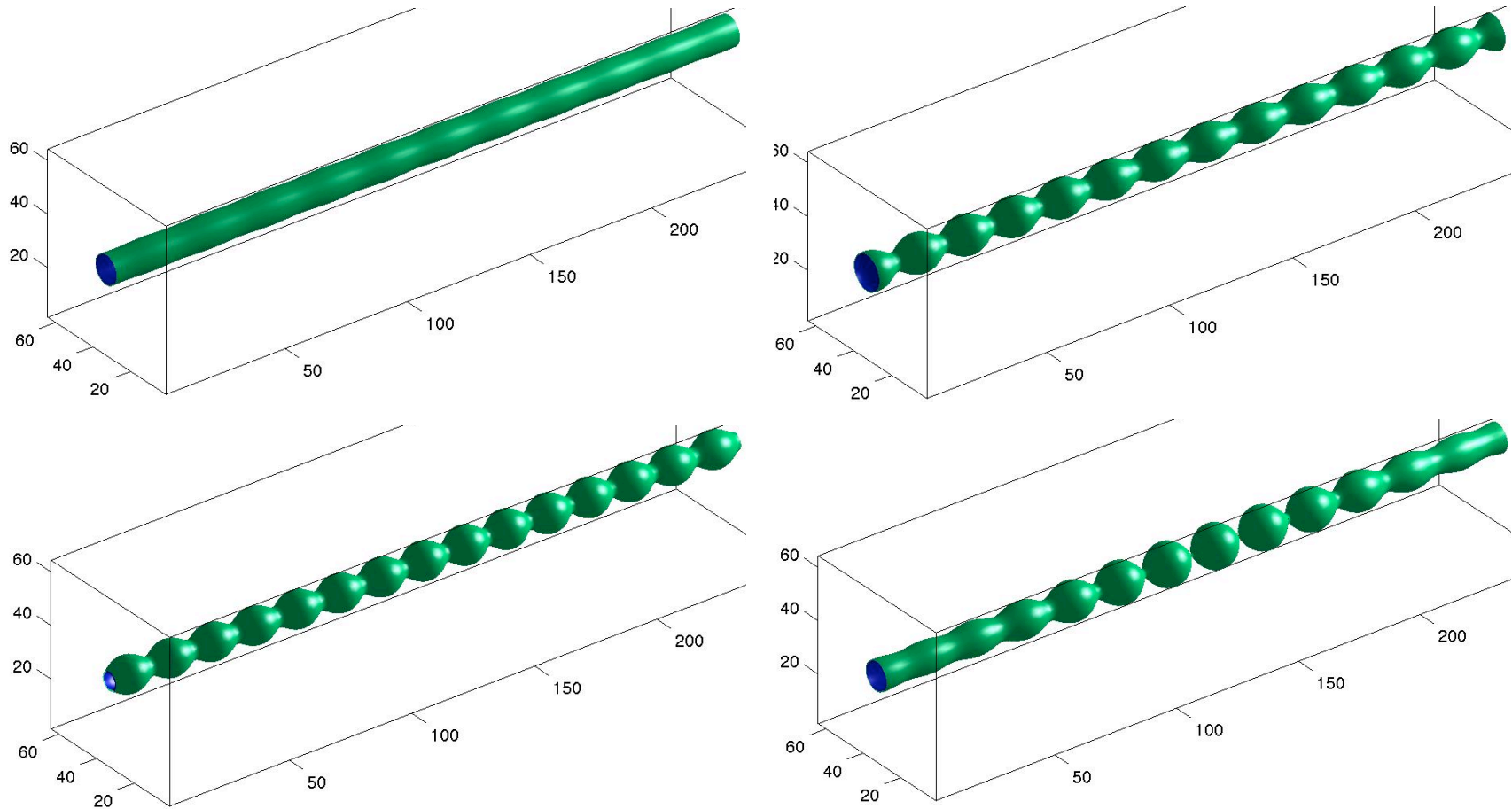


19.7%
 $t = 200$



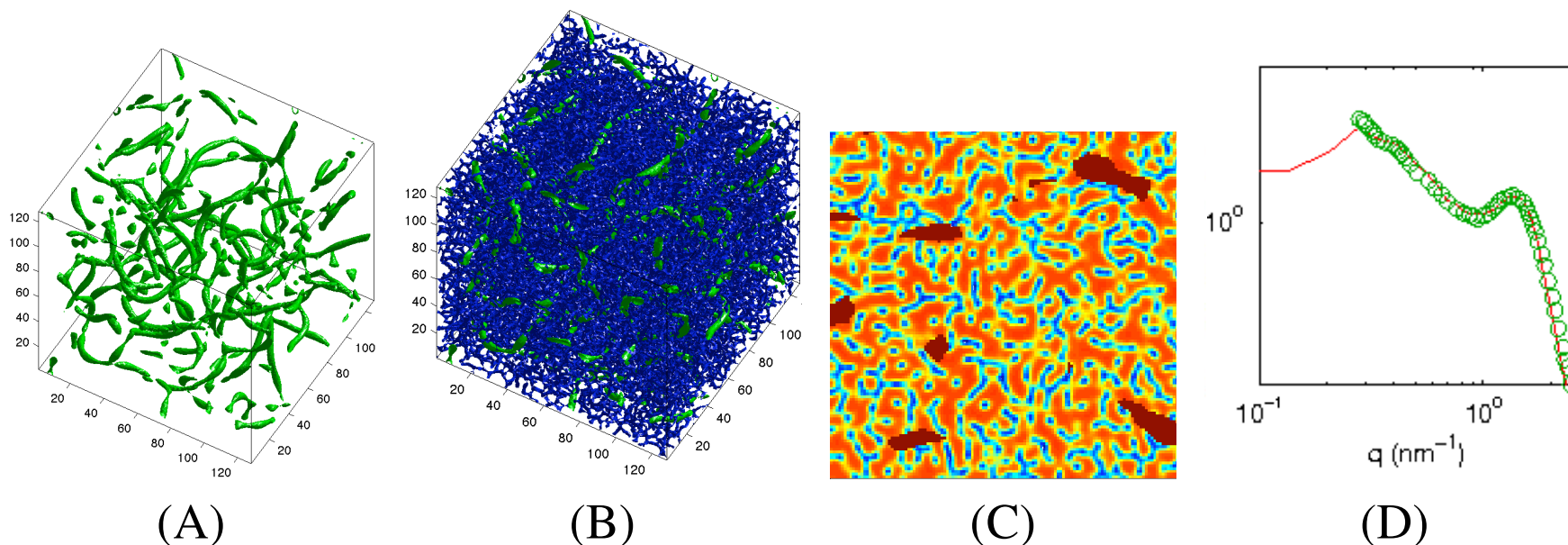
8.24%
 $t = 1000$

Pearling Bifurcation in 3D



Equilibria after evolution from a cylindrically symmetric, perturbed pore for $\eta_{\text{solv}} = 5\epsilon$ and $\eta_{\text{ent}} = -4, -6, -8, -10\epsilon$ respectively.

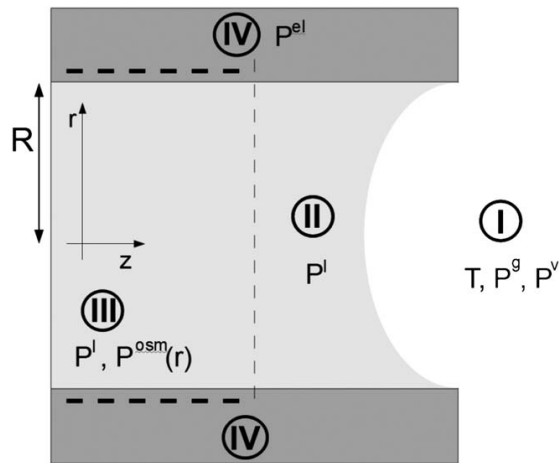
Applications: Nafion and SAXS Data



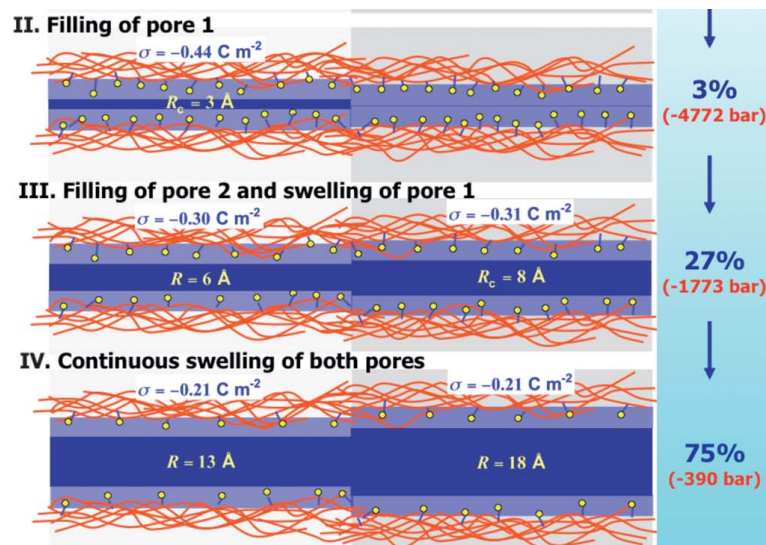
- (A) Crystalline network calculated has smaller (negative) η_i .
- (B) The solvent network (blue) has larger (positive) values of η_i and non-zero tilt τ .
- (C) Cross-section of solvent-crystalline matrix, enlarged for detail.
- (D) SAXS data: Log of scattering intensity versus Log of scattering parameter q , in nm^{-1} , for the composite network (red line) and experimental data of hydrated Nafion, Rubidat-2002 (circles).

Gavish, Jones, Xu, Christlieb, Promislow *Polymers* (2012).

Part II: Connections to “Reality”



A continuum resolution of the pressure and elastic forces. The local pressure in the liquid phase is an intrinsic component of the self-energy of the liquid and should couple to the value of the well tilt parameter $\tau = \tau(P)$.



Eikerling, 2010

A mechanism to track the local density of tethered ionic groups as the pores swell and shrink.

A description of the counter-ion distribution, their coupling to the interface energy, and to the transport of solvent within the pore network.

Incorporate Electrostatics into Gradient Flow

Statistical mechanics: obtain a continuum description from the mean-field approximation of the partition function. Consider an action

$$\mathcal{A} = \int_{\Omega} \overbrace{k_B T \left(p \ln p + h(p, n(u)) \right)}^{\text{entropy \& finite volume}} + \overbrace{q_0(p - n)\phi - \frac{1}{2}\bar{\epsilon}(I, p, n)}^{\text{electrostatic}} dx,$$

where h denotes the form of the short-range or finite-volume interactions, q_0 is the elemental charge, $I = |\nabla\phi|$ is electrostatic field intensity, and $\bar{\epsilon}$ is related to the polarization or displacement field induced by the electric field.

Derive a [Poisson equation](#) by requiring ϕ to be a critical point of action

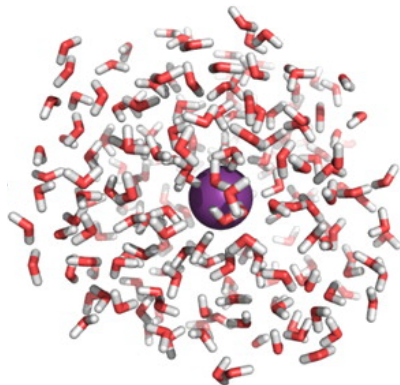
$$\frac{\delta \mathcal{A}}{\delta \phi} := \nabla \cdot \left(\frac{\partial \bar{\epsilon}}{\partial I} \nabla \phi \right) + q_0(p - n) = 0,$$

in particular the classic orientational permittivity (dielectric) takes the form

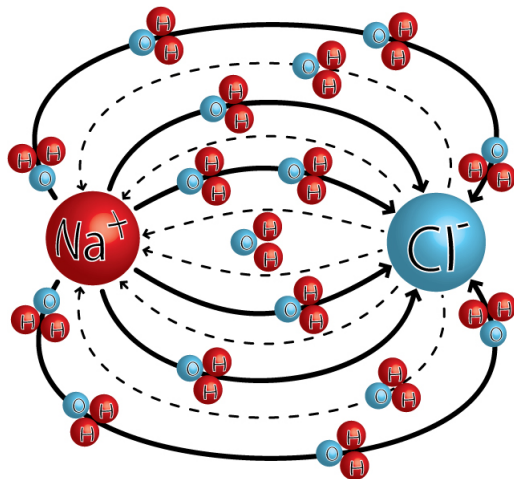
$$\epsilon := \frac{\partial \bar{\epsilon}}{\partial I} = -2 \frac{\delta \mathcal{A}}{\delta I}.$$

Equivalent the standard derivation of statistical mechanics.

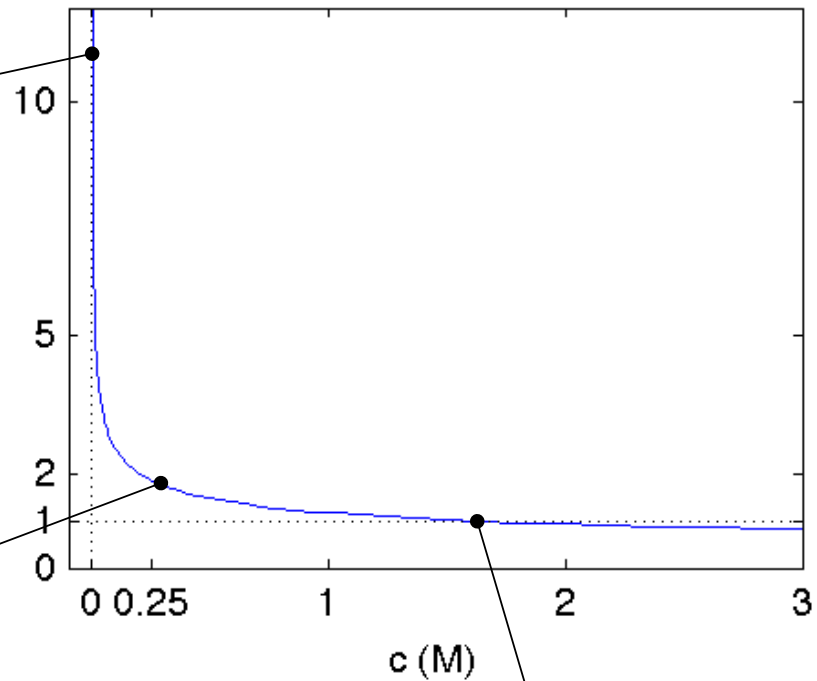
Solution structure at high concentrations



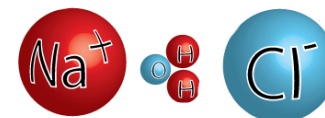
Field due to neighboring ions negligible



Field due to neighboring ions not negligible
Water screening important



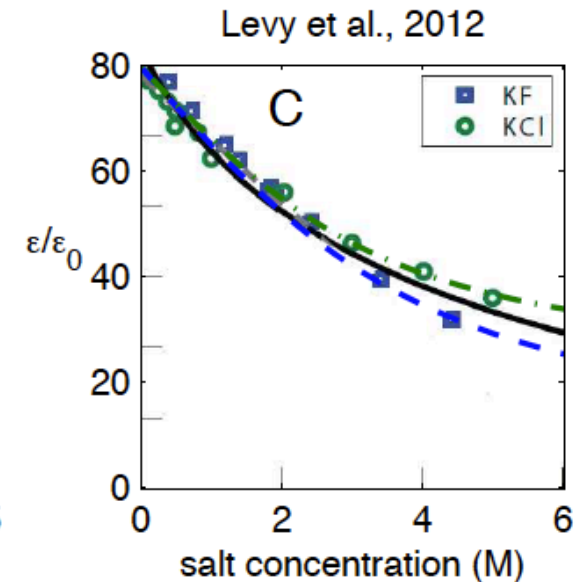
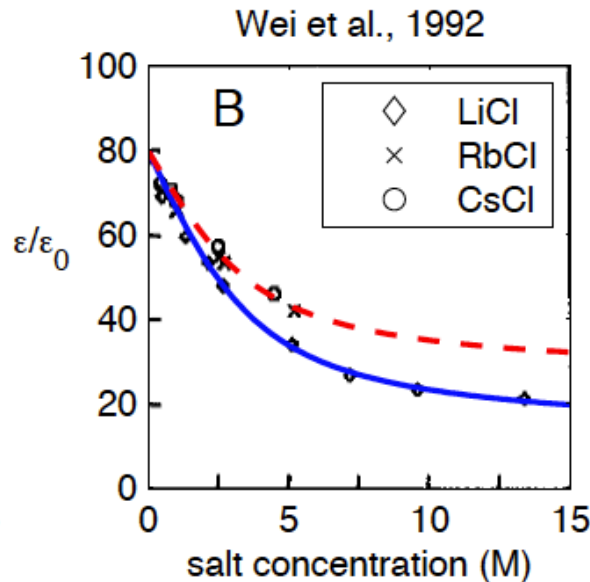
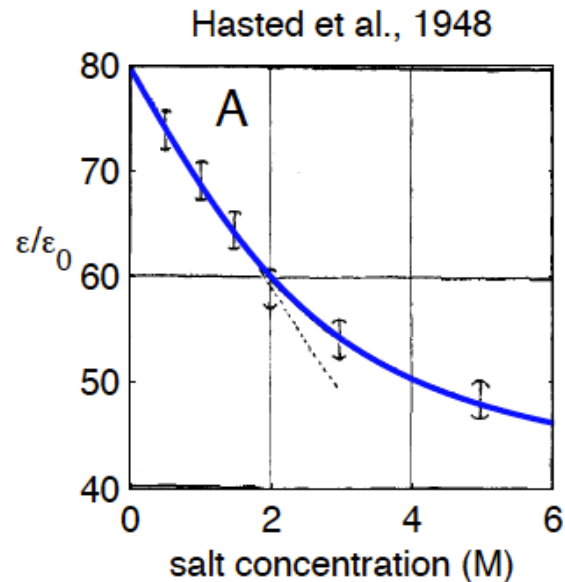
1 nm between ions
Fitting 1-2 water molecules



Ionic field dominant
Water screening negligible

Theory validation

$$\varepsilon(c) = \varepsilon_{water} - \beta L\left(\frac{3\alpha}{\beta} c\right),$$



- Agreement at 13M!
- Solid black curve – field theory (Levy et al., 2012)
- KCl has higher tendency to form ion pairs
- Very good accuracy for 6 different salts

Comparison with the FCH energy

It is tempting to make the associations,

Solvation energy:

$$\eta_{\text{solv}} \frac{\epsilon^2}{2} |\nabla u|^2 \approx \left(q_0 \phi + \frac{1}{2} \frac{\partial \bar{\epsilon}}{\partial n} \right) \frac{\partial n}{\partial u},$$

Mixing Entropy

$$\eta_{\text{ent}} W_s(u) \approx -k_B T \frac{\partial h}{\partial n} \frac{\partial n}{\partial u}.$$

A careful study of the two models to better understand the functional dependence of the hydration and mixing energies within the FCH is a particularly rich vein for future investigation.

Summary

- Network Morphology can be described, at a phenomenological level, by a continuum system with few (4-5) key parameters
- Numerical simulations corresponding to minutes and hours of real-time evolution are possible
- More sophisticated gradient flows can be developed which couple electrostatics, momentum balance, and interfacial morphology into a gradient flow
- Numerical limitations are still very significant – validation of the models, beyond very rough 'eye-ball' test, will be a significant undertaking.

Acknowledgments



NSF-DMS 0707792
NSF-DMS 0934568 (Solar)
NSF-DMS 0929189 (IGMS)
NSF-DMS 1109127

