SFU SIMON FRASER UNIVERSITY
ENGAGING THE WORLD

Ionomer bundles: a fundamental approach

P.-É. A. Melchy and M. E. Eikerling

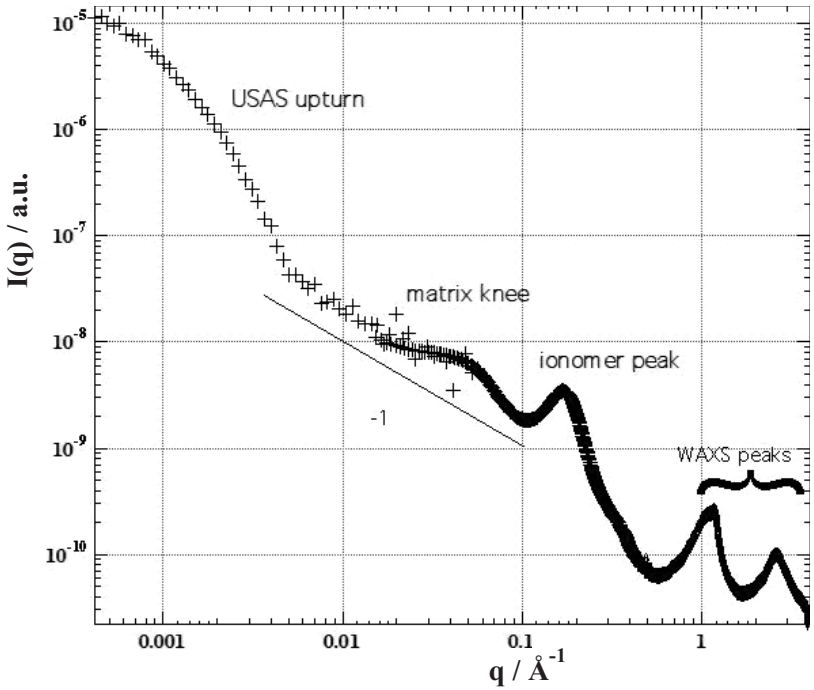
SFU — Eikerling Group
Burnaby, BC, Canada

Carisma Conference, September 5th, 2012

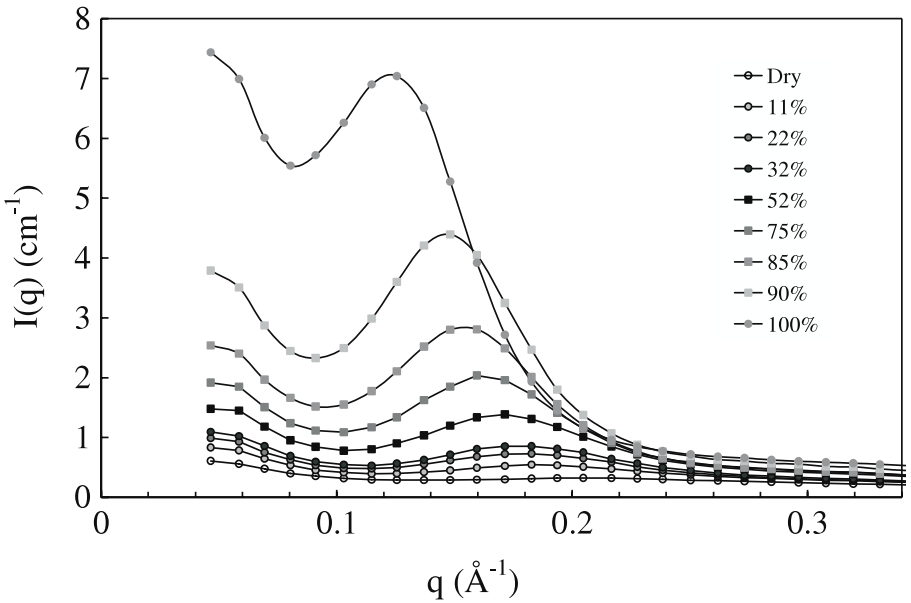
Structure

Outline

Context



Gebel *et al.*, (2005, 2011)



Outline

Motivation (polymer physics)

- Aggregation mostly studied with strong electrostatic effects
- Electrostatic attraction due to the fluctuations of multivalent counterions

Motivation (polymer physics)

- Aggregation mostly studied with strong electrostatic effects
- Electrostatic attraction due to the fluctuations of multivalent counterions
- With no multivalent counterions, another attractive mechanism is required such as
  - Sticker groups (able to form strong bonds, e.g. disulfide bonds)
  - Hydrophobicity

Motivation (polymer physics)

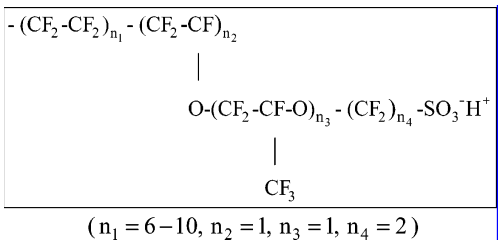
- Aggregation mostly studied with strong electrostatic effects
- Electrostatic attraction due to the fluctuations of multivalent counterions
- With no multivalent counterions, another attractive mechanism is required such as
  - Sticker groups (able to form strong bonds, e.g. disulfide bonds)
  - Hydrophobicity
- The case of a solution without any salt has not been treated to our knowledge

Motivation (fuel cells)

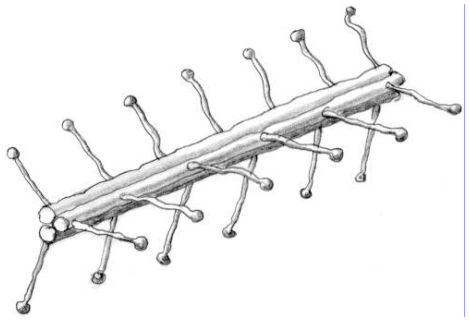
- Polymer electrolyte membrane (PEM) appears to be a critical component for the durability of PEFC
- The degradation of PEM involves the coupling of chemical and mechanical mechanisms
- Understanding the structure formation of PEM is a prerequisite to rationalise its degradation

Structure of a PEM

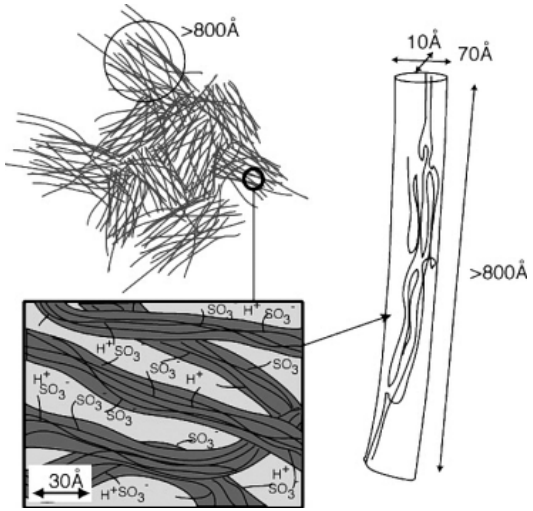
The hierarchical structure should be described at different length scales:



Short: chemical structure of the ionomer



Intermediate: bundle of ionomers



Long: porous structure due to the assembly of bundles

Ioselevitch, Kornyshev, Steinke, J. Phys. Chem. B **108**, 11953 (2004).

Gebel, Diat, Fuel Cells **5**, 261 (2005).

Outline

Basic framework

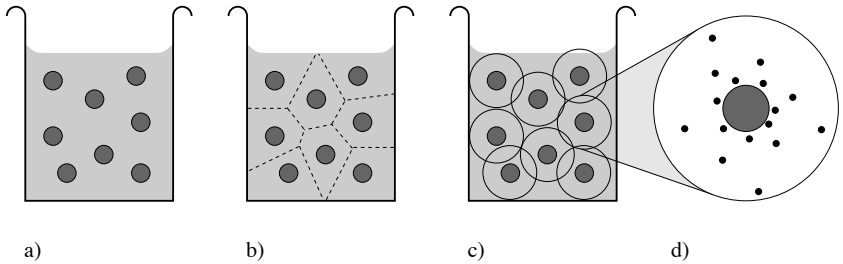
- Structural simplification:
  - No side chains
  - Ionomers considered stiff rods (persistence length of Teflon®-based materials: 10Å to 50Å— average sum of the projection of bonds $j \geqslant i$ onto bond i)
  - Continuous surface charge on the polymer instead of discrete charges

Basic framework

- Full dissociation (strong acidity of sulfonic acid)

Basic framework

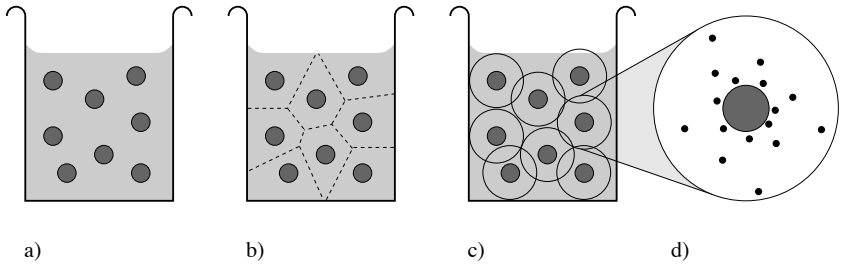
- Full dissociation (strong acidity of sulfonic acid)
- Cell model (mean-field approximation)



Deserno, Holm, 2001

Basic framework

- Full dissociation (strong acidity of sulfonic acid)
- Cell model (mean-field approximation)



Deserno, Holm, 2001

- Poisson-Boltzmann formalism:

$$\nabla^2\varphi - \kappa^2\varphi = -\frac{qn_H^0}{\varepsilon}$$

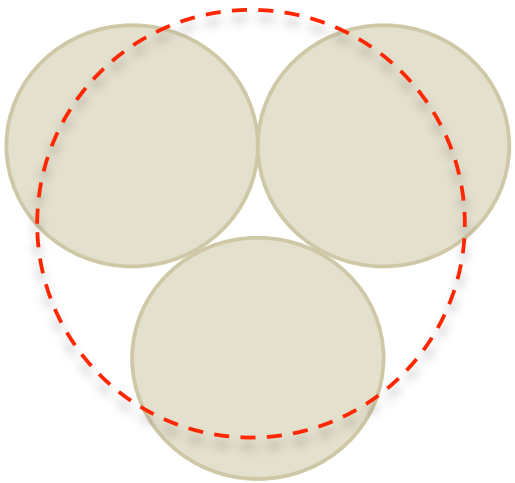
Boundary conditions:

$$\hat{e}_r \cdot (\varepsilon_{ext}\vec{\nabla}\varphi_{ext}|_{r=r_e} - \varepsilon_{int}\vec{\nabla}\varphi_{int}|_{r=r_e}) = -4\pi\sigma$$

$$\vec{\nabla}\varphi(r = R_c) = 0$$

Outline

A first model: dry core



- The core of the bundle is solvent-free; all charge at the surface of the bundle
- Homogeneous surface charge density σ
- A single dielectric constant in the whole cell for the solvent around the bundle
- Hydrophobicity is accounted for by surface tension
- Hexagonal packing of rods

Outline

Free energy

$$\beta f_k = \gamma S + \ell_B \int_{r_e}^{R_c} dr\, \varphi(r) n_H(r) + \int_0^{\sigma} d\sigma' \varphi_{r_e}(\sigma')$$

With

- γ the surface tension
- n_H the proton distribution in the cell
- φ the electrostatic potential created by the surface charge on the bundle
- σ surface charge density at the surface of the bundle

Electrostatic potential

Poisson-Boltzmann equation:

$$\nabla^2\varphi - \kappa^2\varphi = -\frac{4\pi q n_H^0}{\varepsilon}$$

Boundary conditions:

$$\hat{e}_r \cdot (\varepsilon_{ext}\vec{\nabla}\varphi_{ext}|_{r=r_e} - \varepsilon_{int}\vec{\nabla}\varphi_{int}|_{r=r_e}) = -4\pi\sigma$$

$$\vec{\nabla}\varphi(r = R_c) = 0$$

Electrostatic potential

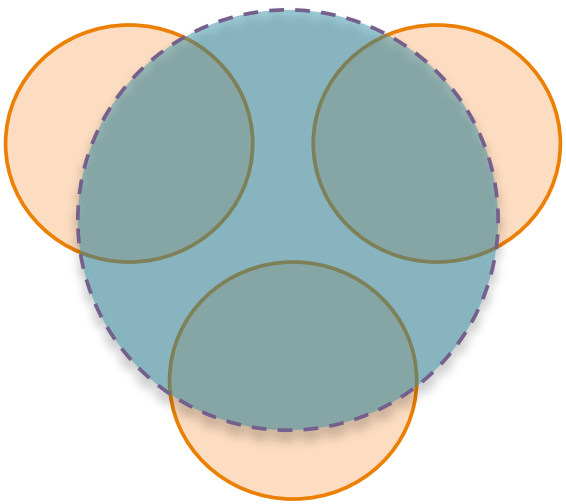
$$\varphi(r) = \frac{4\pi\sigma}{\varepsilon\kappa\Delta}\Big(K_1(\kappa R_c)I_0(\kappa r) - I_1(\kappa R_c)K_0(\kappa r)\Big) + \frac{4\pi n_H^0 q}{\varepsilon\kappa^2}$$

where

$$\Delta = I_1(\kappa R_c)K_1(\kappa r_e) - I_1(\kappa r_e)K_1(\kappa R_c)$$

Outline

A second model: wet bundle



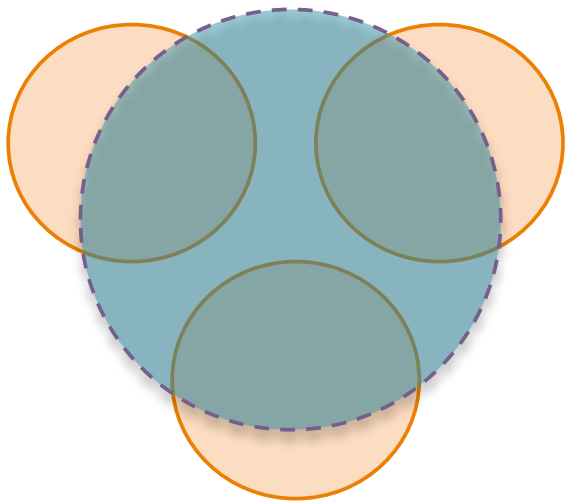
- Each rod is completely immersed in the solvent
- Two cases are considered:
  - Uniform dielectric constant and homogeneous surface charge density
  - Low-dielectric constant core and condensation of the protons on the surface of the rods that is inward-oriented

Outline

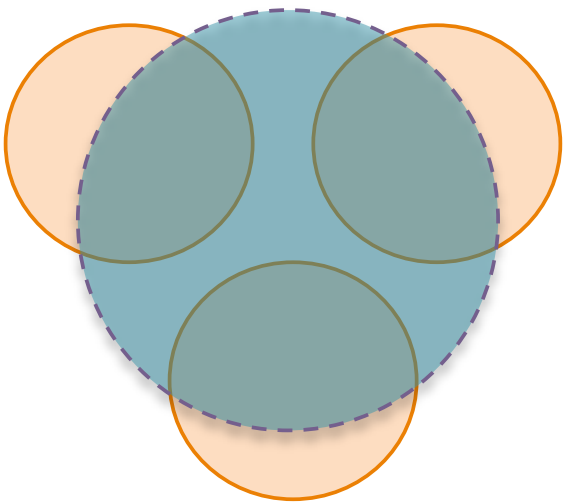
Free energy

$$\beta f_k = -c \int d\vec{r}\, \frac{\rho(\vec{r})^2}{r^6} + \ell_B \int d\vec{r}\, \varphi(\vec{r}) n_H(\vec{r})$$
$$+ \sum_{i \neq j} \int_0^{2\pi} \int_0^{2\pi} \frac{d\theta_i\, d\theta_j}{(2r^2 + d^2 + 2dr \sin(\theta_i + \theta_j) - 2r^2 \cos(\theta_i + \theta_j))^{1/2}}$$

In the first case of a constant surface charge (uniform dielectric constant)



Free energy



In the second case we consider, a two-zone surface charge appears corresponding to the inner region (high dielectric constant) and the outer region (low dielectric constant)

- A crude approximation: full condensation in the low-ε core, hence zero surface charge
- Altered electrostatic potential
- Rods are divided into two zones, each of homogeneous surface charge density ($\sigma_{inner} = 0$)

Outlook

- Stability of the equilibrium structures for different number of rods per bundle

Outlook

- Stability of the equilibrium structures for different number of rods per bundle
- Phase diagram: lowest free energy bundles (size)

Outlook

- Stability of the equilibrium structures for different number of rods per bundle
- Phase diagram: lowest free energy bundles (size)
- Transitions between dispersed, three-rod bundle phase, six-rod bundle phase, etc.

Outlook

- Stability of the equilibrium structures for different number of rods per bundle
- Phase diagram: lowest free energy bundles (size)
- Transitions between dispersed, three-rod bundle phase, six-rod bundle phase, etc.

Beside the density of ionisable groups and the concentration of rods, key parameters to determine the equilibrium structure are:

Outlook

- Stability of the equilibrium structures for different number of rods per bundle
- Phase diagram: lowest free energy bundles (size)
- Transitions between dispersed, three-rod bundle phase, six-rod bundle phase, etc.

Beside the density of ionisable groups and the concentration of rods, key parameters to determine the equilibrium structure are:

- Dry core model:
  - surface tension γ
  - effective radius of the rods

Outlook

- Stability of the equilibrium structures for different number of rods per bundle
- Phase diagram: lowest free energy bundles (size)
- Transitions between dispersed, three-rod bundle phase, six-rod bundle phase, etc.

Beside the density of ionisable groups and the concentration of rods, key parameters to determine the equilibrium structure are:

- Dry core model:
  - surface tension γ
  - effective radius of the rods
- Wet bundle model:
  - Hamaker parameter
  - inter-rod distance d
  - condensation of protons

Acknowledgements

Automotive Partnership Canada

BALLARD®