Investigating lamellar structures in hydrated Nafion thin films

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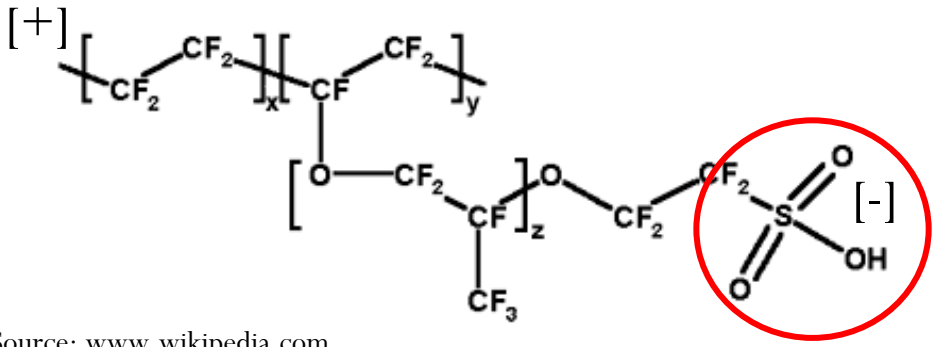
Overview

- Motivation: Why are we interested in thin polymer films?
- Theory: What do we expect to see in thin polymer films?
- Sample Preparation: How do we make these films?
- Sample Characterization: How do we characterize these films?
  - Neutron reflectivity
- Results and Conclusions: What did we observe and learn from our data?

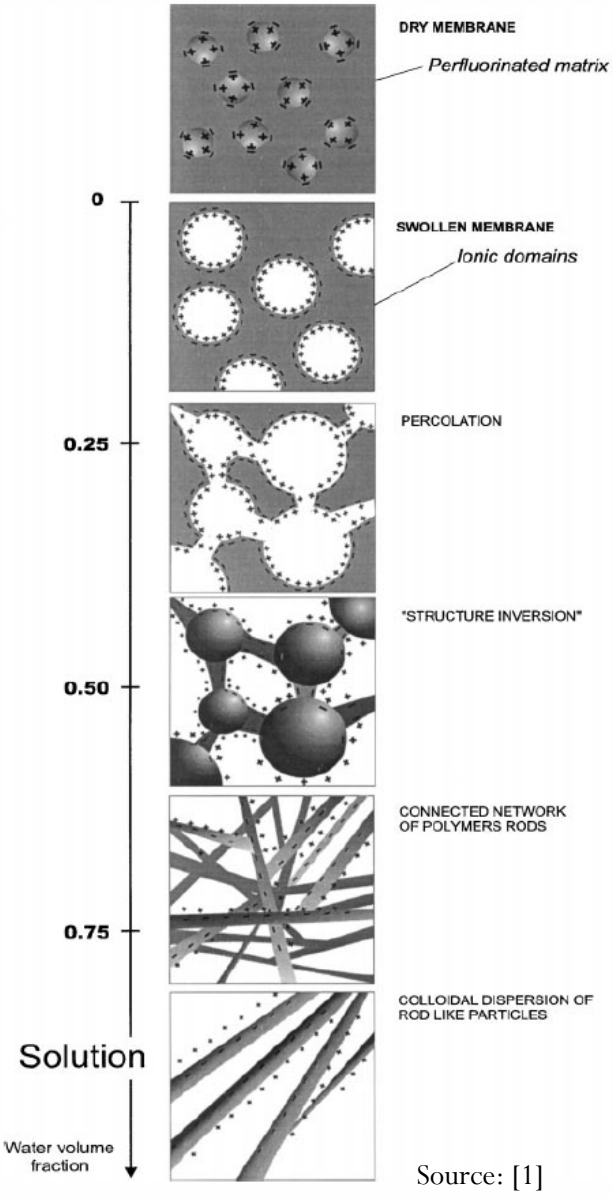
Introduction

- Nafion is a polymer consisting of sulfonic acid groups attached to a Teflon backbone
  - Sulfonic acid groups conduct H^+ ions
  - Does not conduct electrons



Source: www.wikipedia.com

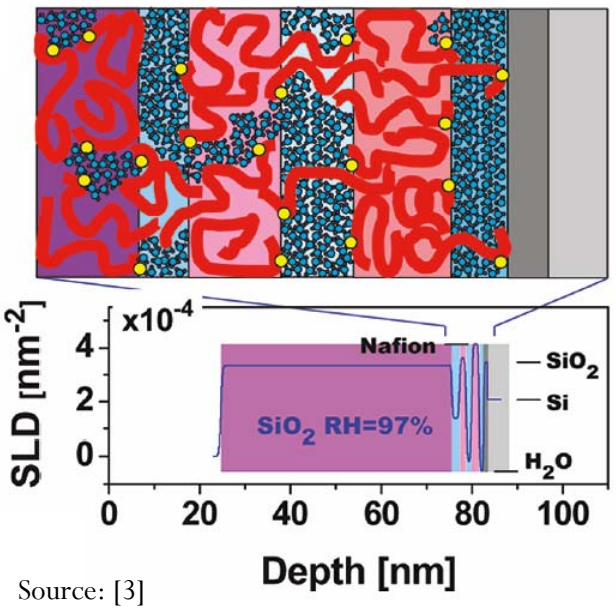
- Ideally suited for fuel cell membranes
- Difficult to characterize bulk structure [1]
  - Phase segregation into water and Nafion rich regions



Source: [1]

Background work

- Dura et al. showed that 5 lamellae exist at the interface between thick Nafion films (~500Å) and SiO_2 layers on a Si substrate [3]
  - Lamellae consist of alternating, phase segregated water and Nafion-rich layers measuring ~15Å



Source: [3]

- It is proposed that depositing films as thick as these 5 lamellae could yield a film composed **entirely of lamellae**
- Learning more about interfacial structure can improve fuel cells
  - Identify potential inefficiency in conduction
  - Learn how structures affect degradation

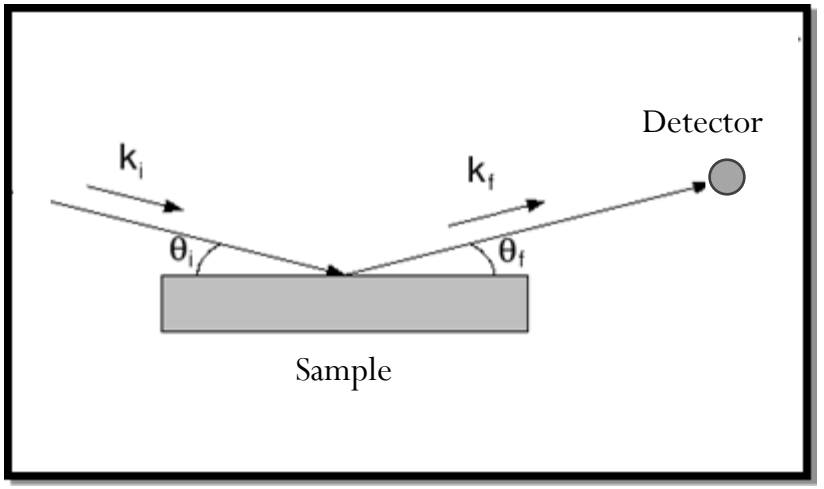
Objective

By studying the structure and thickness of lamellae as a function of film thickness we can gain insight into their causes and effects

Neutron Reflectivity

- Technique used to characterize thin film samples
  - Neutron beam (k_i) hits sample at varying incidence angles (θ_i)
  - Detector measures intensity of reflected neutrons (k_f)
  - Feature resolution $2\pi/Q_{max} \approx 15$Å

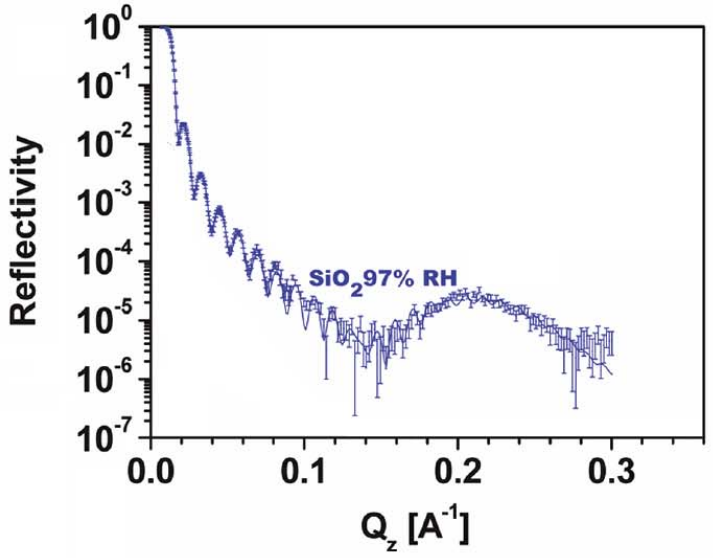
- Scattering Length Density (SLD)
  - Scattering potential
  - Property of each material which depends on atomic composition and isotope
- Isotopic contrast variation
  - Isotopes (i.e. H_2O and D_2O) with different SLDs are used in conjunction to verify structures in films
  - Act similarly chemically

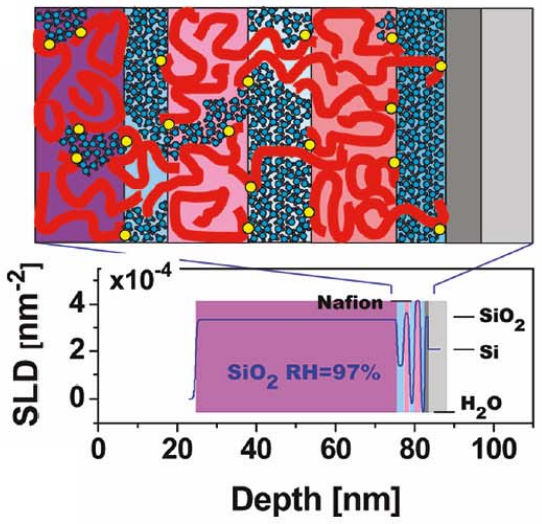


Source:
www.ncnr.nist.gov

Interpreting Reflectivity Data

- Reflectivity can be analyzed to reveal make-up, thickness and roughness of film





r.nist.gov

- Reflectivity of films with multiple layers constructively and destructively interferes; can be analyzed with software

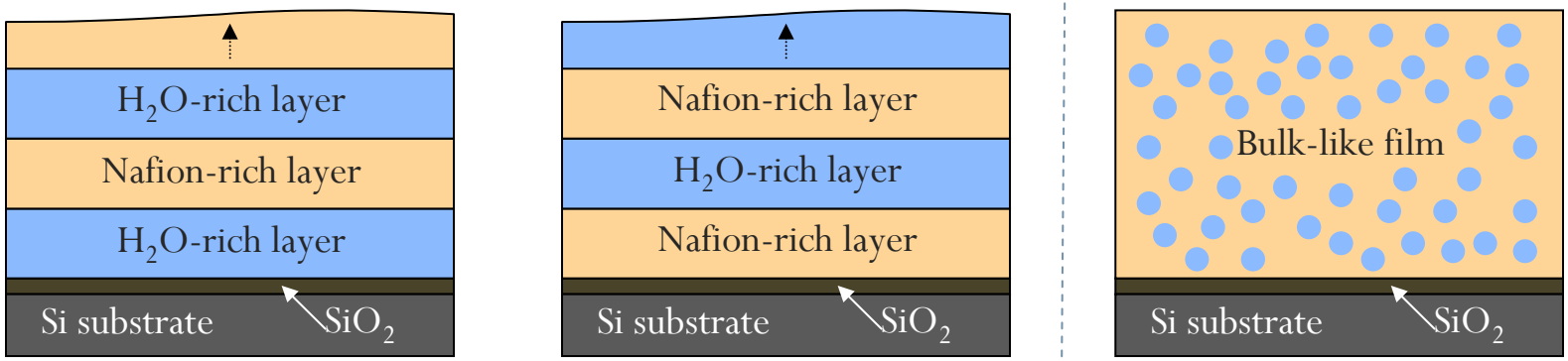
- Neutron reflectivity is optimal for analyzing 1-400 nm thick layered structures

Theory

- It is proposed that depositing films **as thick as the 5 lamellae** could yield:

Lamellae

No lamellae

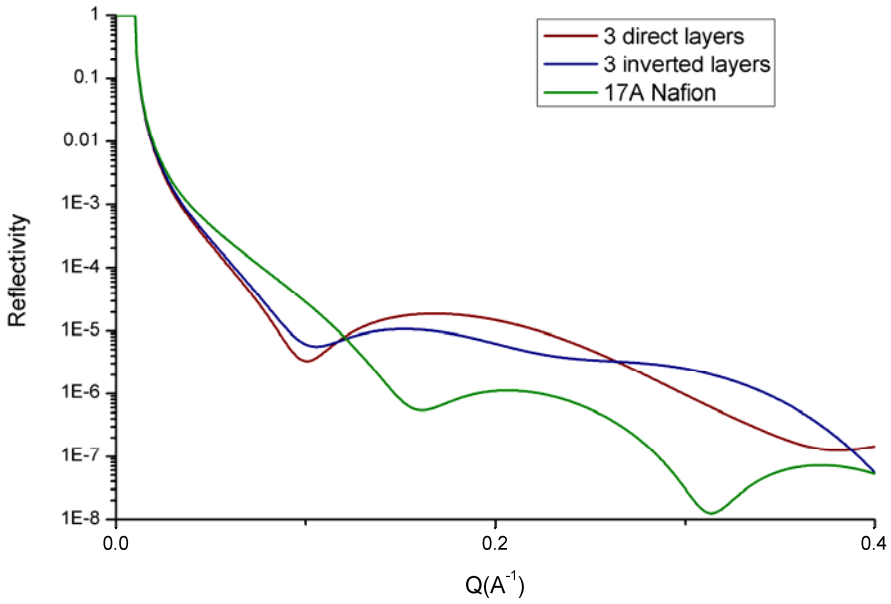


- Direct layers
- Inverted layers
- Bulk-like film
- Lamellae with outer bulk layer

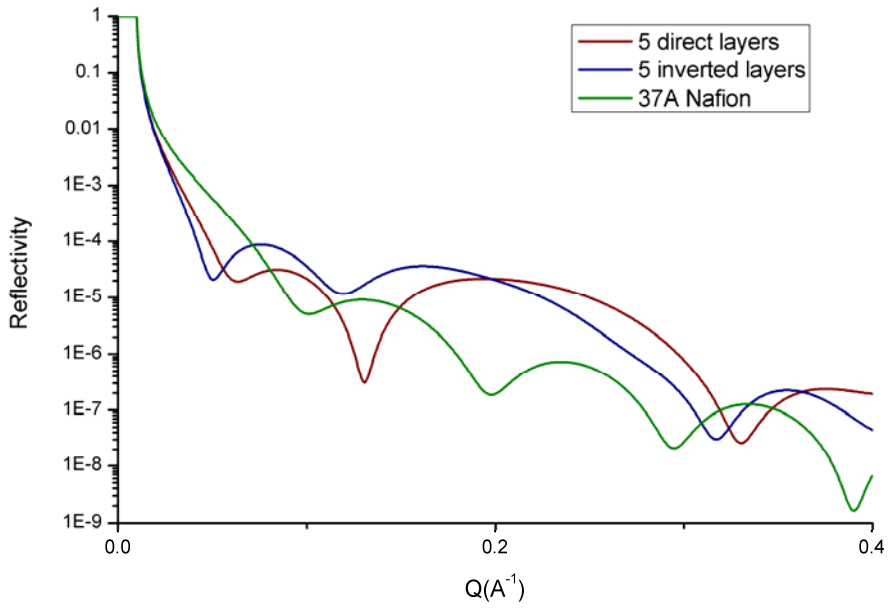
Preliminary Modeling

- Possible structures were modeled using fitting software [5]
  - Parameters were taken from lamallae at interface of thick films [3]
  - Reflectivity of direct layers, inverted layers and bulk-like films were compared

Reflpak neutron reflectivity of structures of 17A film on 20A NO with H2O



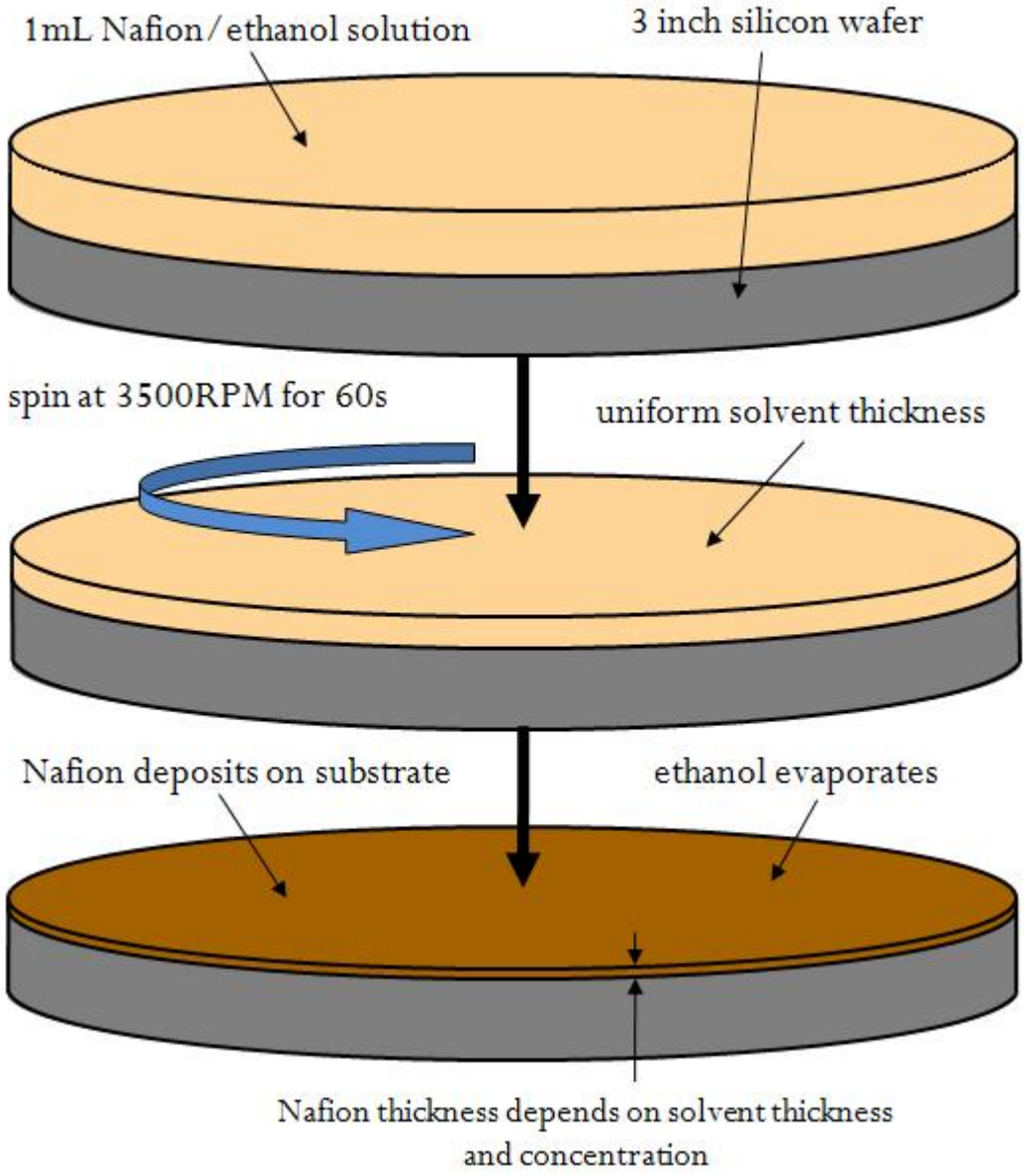
Reflpak neutron reflectivity of structures of 37A film on 20A NO with H2O



- Shows sensitivity to different possible layer structures

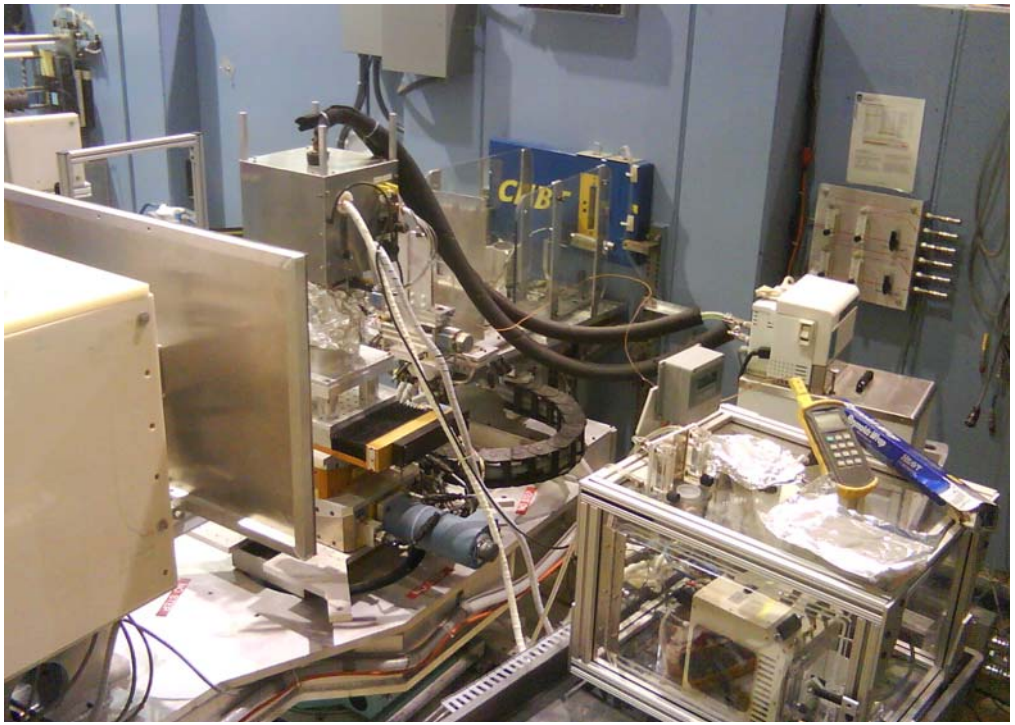
Sample Preparation

- Spincoating (right) used to deposit films
- Expected thicknesses ranged from **20-300Å**
- Samples annealed for 1 hour at 60°C in vacuum to ensure adhesion to the substrate

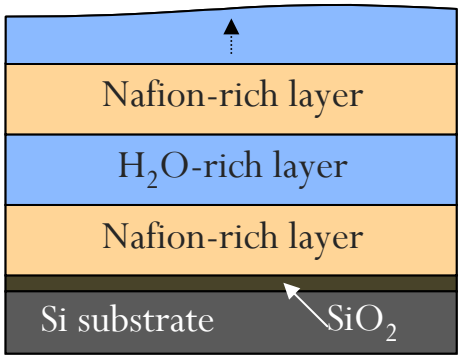


Experimental

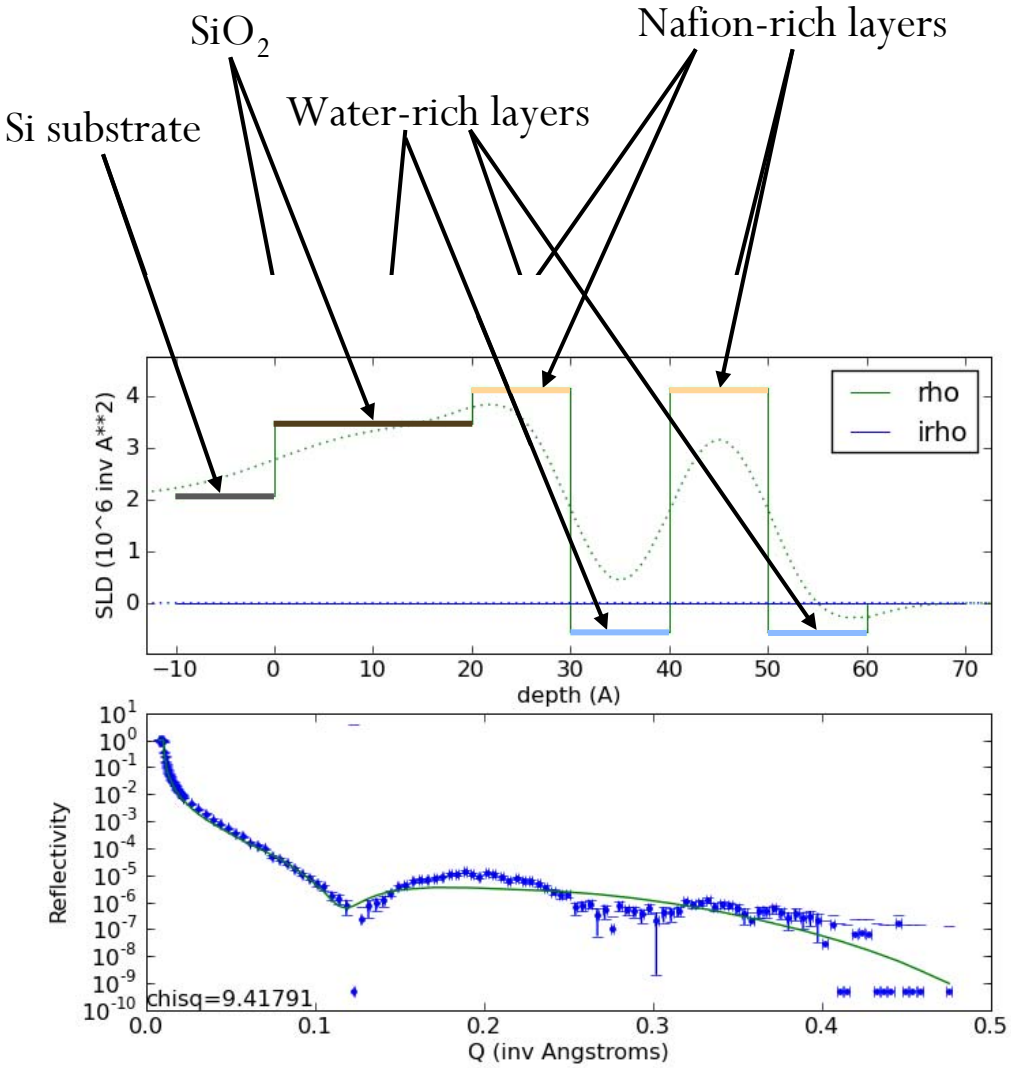
- Neutron reflectivity experiments performed on AND/R at the NCNR
- Constant temperature = 30°C
- Constant relative humidity = 90%
- Tested films in both H_2O and D_2O vapor (isotopic contrast variation)



Analysis: 60Å Film

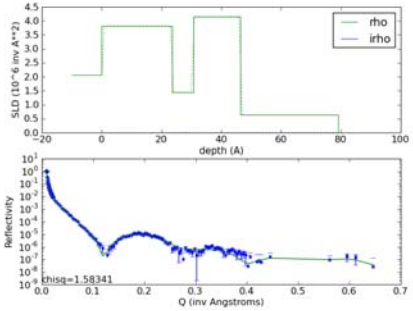


Started with a model containing 4 inverted layers

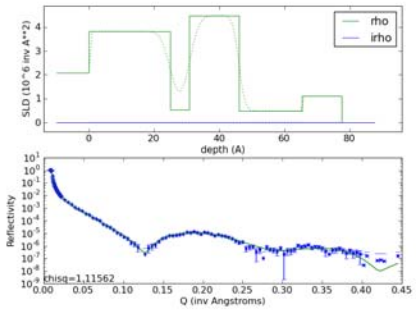


Analysis: 60Å Film

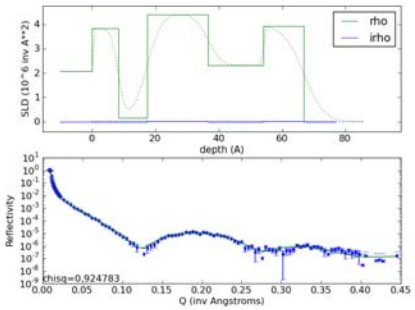
- Additional fits revealed other possible structures:



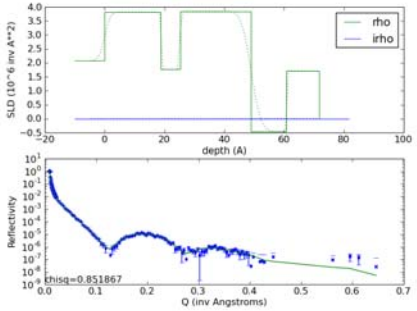
$\chi^2 = 1.58$



$\chi^2 = 1.11$



$\chi^2 = 0.925$



$\chi^2 = 0.852$

- 3 direct layers
- 4 direct layers – differing layer thicknesses and water contents
- No unique solution for a single data set

Analysis: 60Å Film

- Look at reflectivity of sample in D_2O to find most accurate model
  - Assuming Nafion absorbs D_2O the same as it does H_2O
  - Assuming film is composed only of Nafion and water
  - Use SLDs of H_2O model to **solve for layer water volume fractions** (1)
  - Solve for SLD of each layer using SLD of D_2O, creates "converted" D_2O model (2)

Knowing:

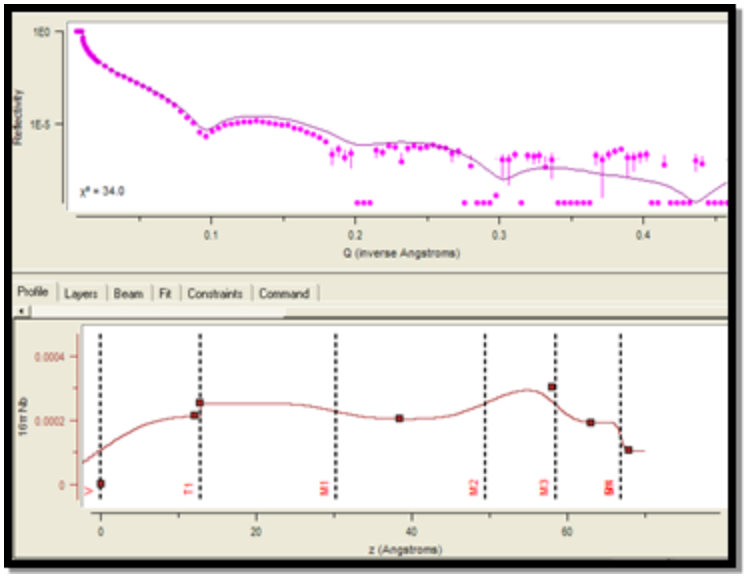
$$SLD_{overall,H_2O} = SLD_{H_2O}V_{water} + SLD_{Nafion}V_{Nafion}$$

and $V_{water} + V_{Nafion} = 1$

$$V_{water} = \frac{SLD_{overall,H_2O} - SLD_{Nafion}}{SLD_{H_2O} - SLD_{Nafion}} \quad (1)$$

Similarly:

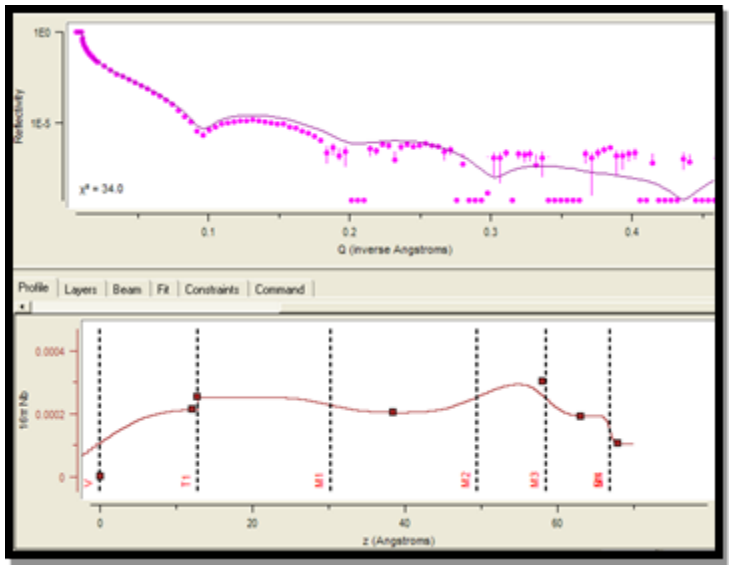
$$SLD_{overall,D_2O} = SLD_{D_2O}V_{water} + SLD_{Nafion}V_{Nafion} \quad (2)$$

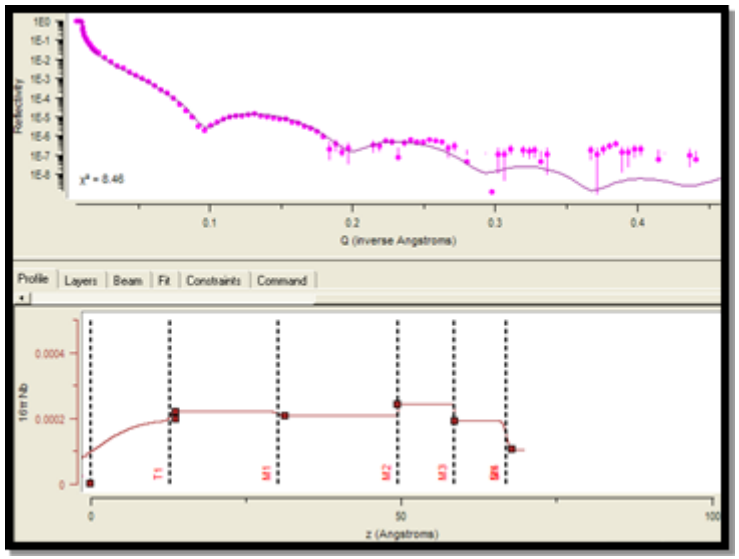


- Converted model

Analysis: 60Å Film

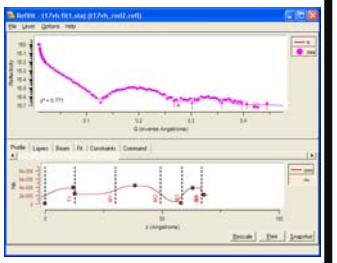
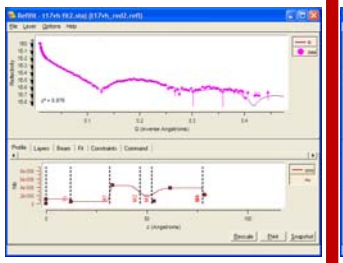
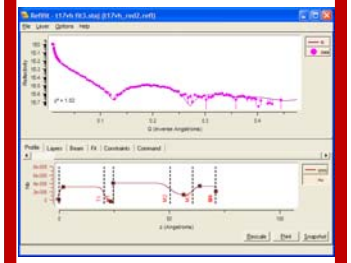
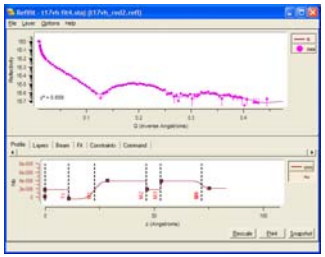
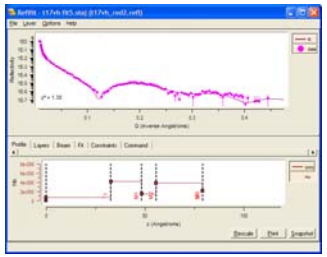
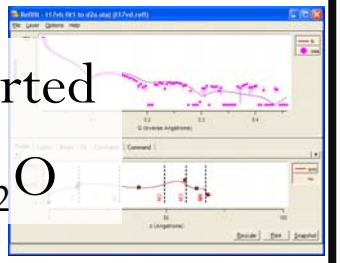
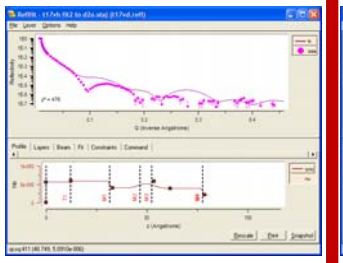
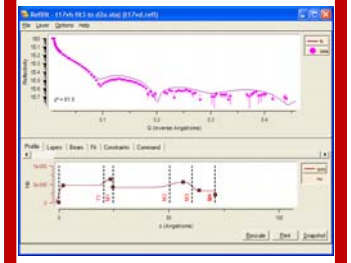
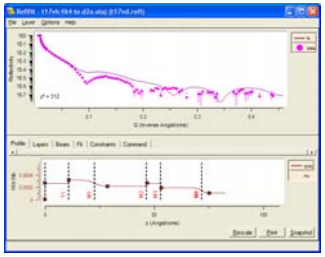
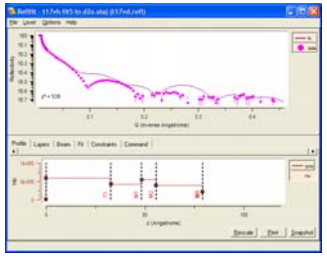
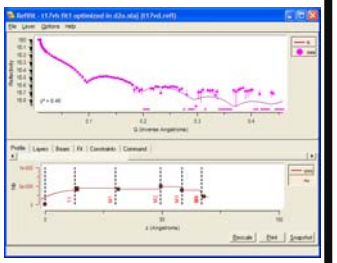
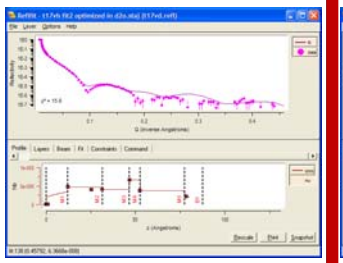
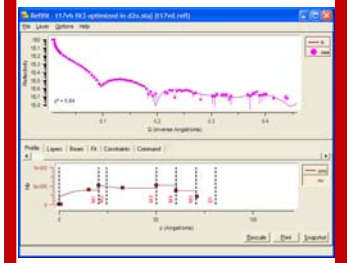
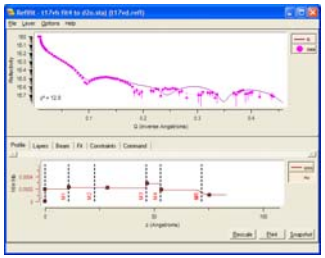
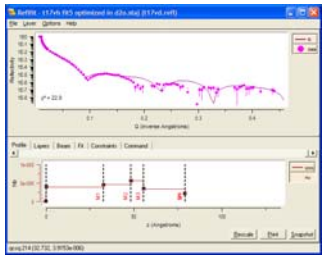
- Converted fits do not fit D_2O data perfectly: a third component, such as porosity, may exist
  - Re-fit SLD and roughness of each layer of D_2O model to D_2O data
  - Compare results to determine most accurate model
  - Determine volume fractions of Nafion, water and porosity from best H_2O and D_2O fits



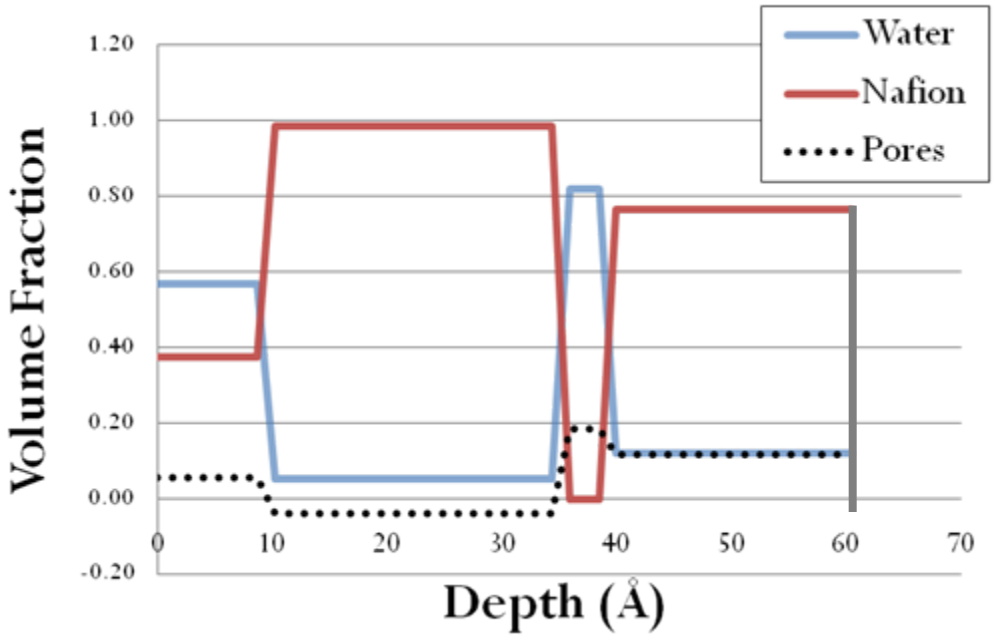


- Converted model
- Refined fit

Analysis: 60Å Film

H_2O fit					
	$\chi^2 = 0.771$	0.976	1.02	0.689	1.38
Converted to D_2O					
	$\chi^2 = 34.0$	476	81.5	312	539
D_2O fit					
	$\chi^2 = 8.46$	15.6	5.64	12.8	22.9

60Å Film Composition

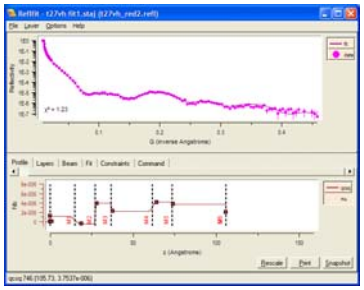


- It is possible to calculate volume fractions of film components
  - Water
  - Nafion
  - Pores

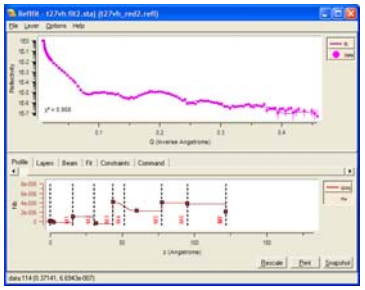
Layer	1	2	3	4
Thickness(Å)	10.208	25.662	4.075	20.510
SLD (H2O model)	1.245E-06	4.067E-06	-4.664E-07	3.107E-06
SLD (D2O model)	5.182E-06	4.437E-06	5.195E-06	3.939E-06
Water vol frac	0.569	0.053	0.818	0.120
Pore vol frac	0.055	-0.039	0.184	0.116
Nafion vol frac	0.376	0.986	-0.002	0.764

Analysis: 100Å Film

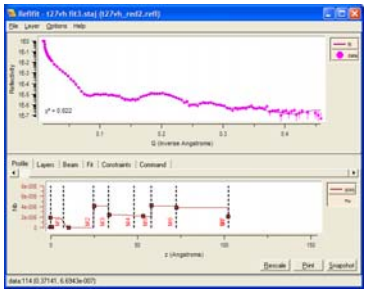
H_2O fit



$\chi^2 = 1.23$

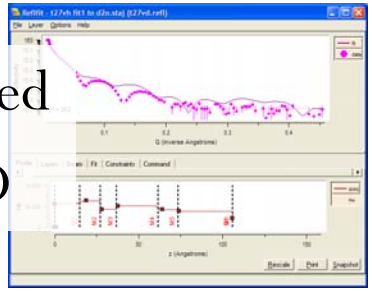


0.906

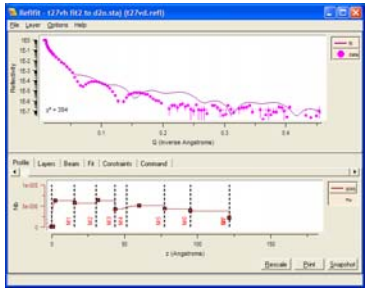


0.822

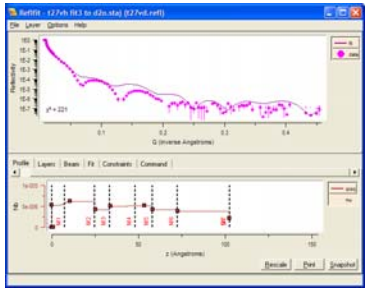
Converted to D_2O



$\chi^2 = 262$



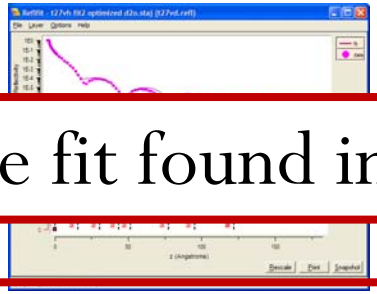
384



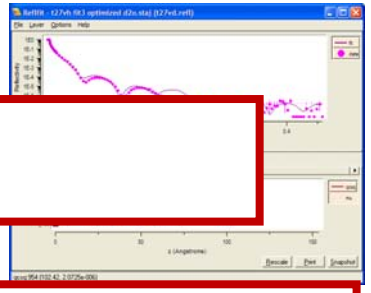
221

D_2O fit

$\chi^2 = 19.3$



17.4



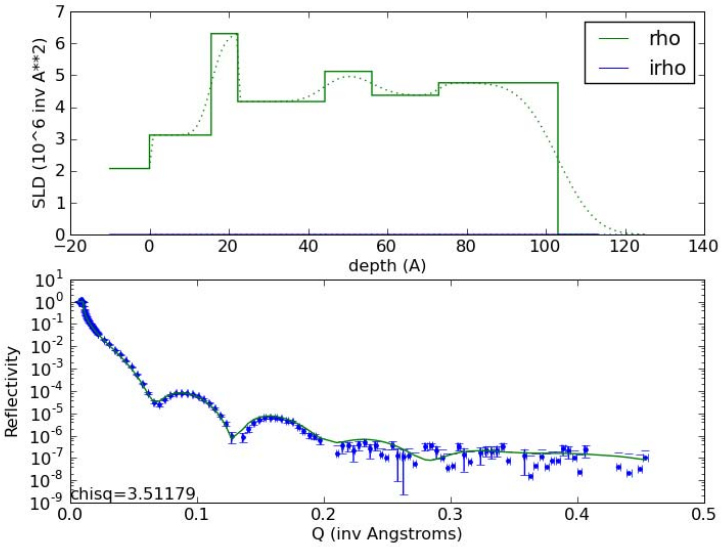
36.0

No acceptable fit found in comparison

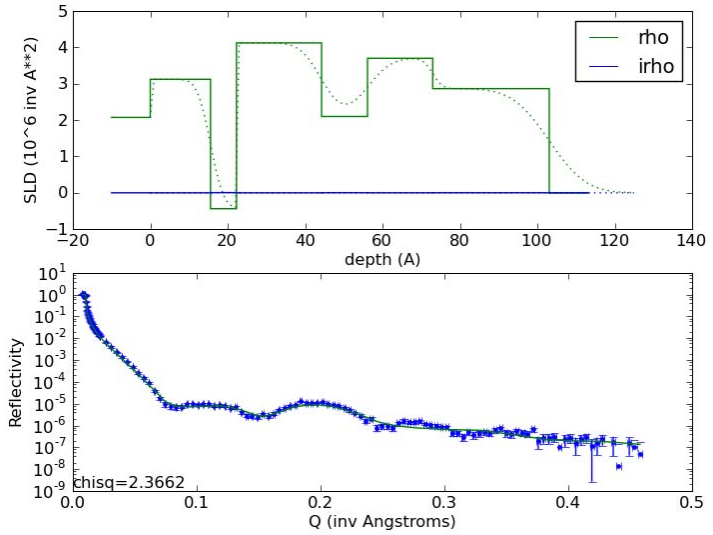
Analysis: 100Å Film

- Simultaneous fit H_2O and D_2O data sets with a model having common:
  - Layer thickness
  - Roughness
  - Nafion volume fraction
  - Water volume fraction
    - Using H_2O SLD or D_2O SLD
- Refine common parameters to minimize combined χ^2

H_2O:



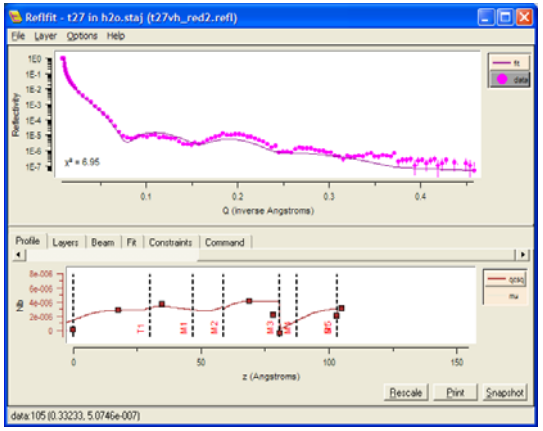
D_2O:



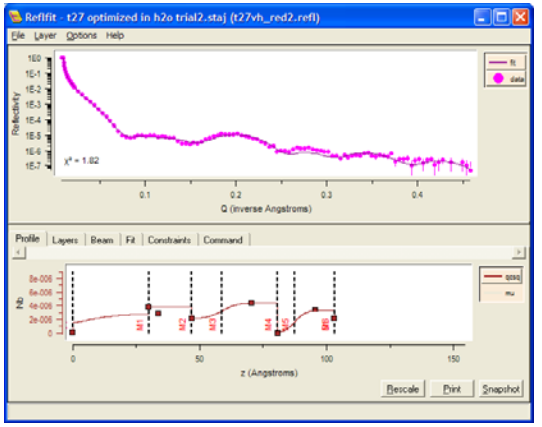
Analysis: 100Å Film

- Simultaneous Fit
- Independent Fits

H_2O:

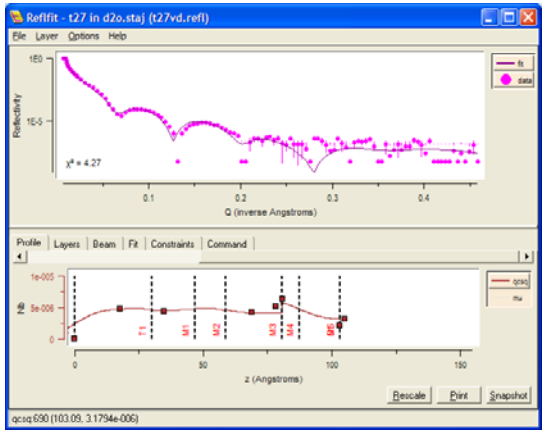


$\chi^2 = 6.95$

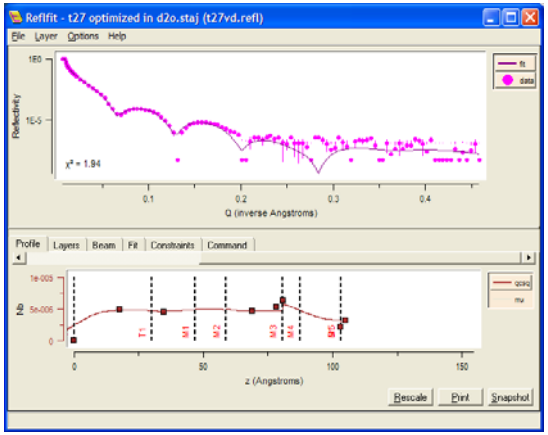


$\chi^2 = 1.82$

D_2O:

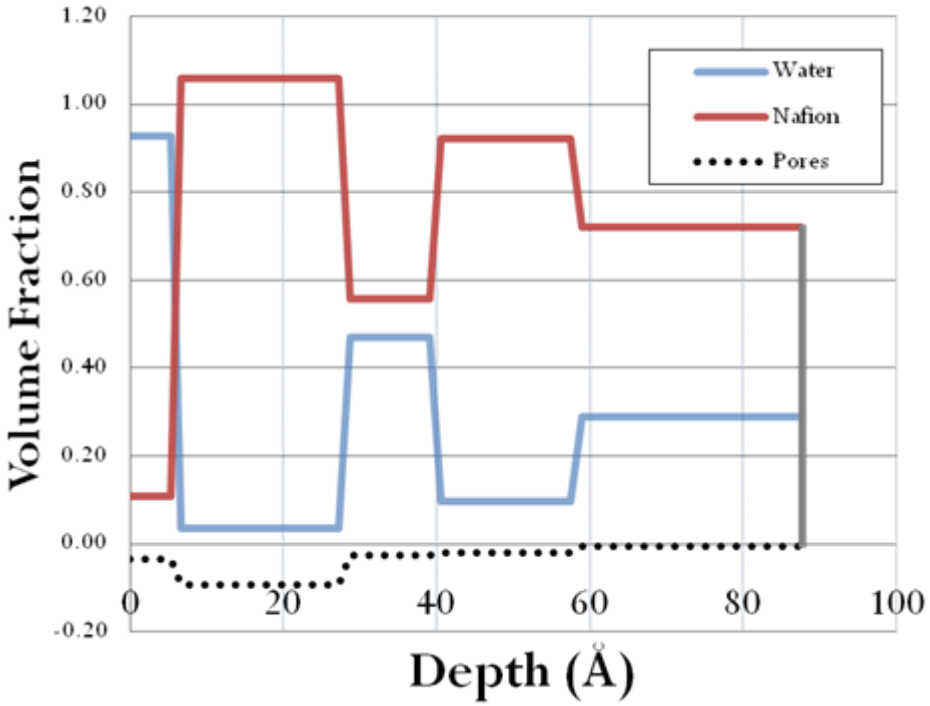


$\chi^2 = 4.27$



$\chi^2 = 1.94$

100Å Film Composition

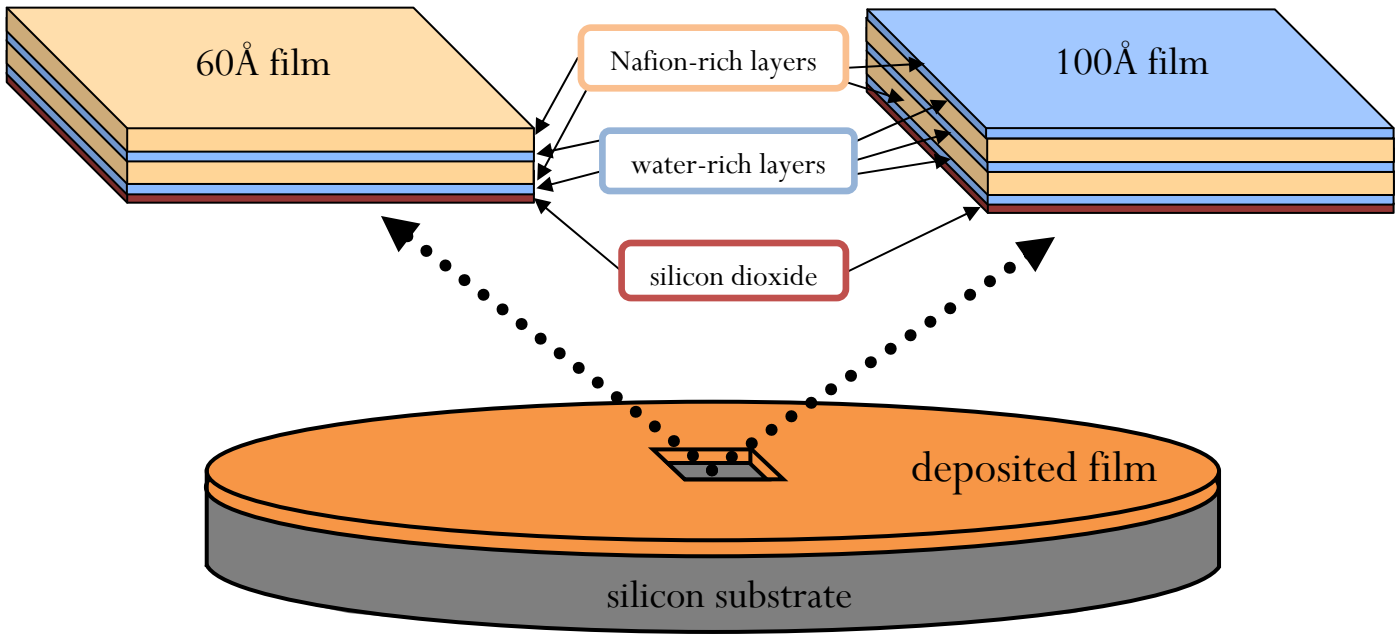


- Given independent fits, calculate component volume fractions, including porosity
- Negative porosity proportional to Nafion volume fraction

Layer	1	2	3	4	5
Thickness(Å)	6.707	21.981	11.870	16.856	30.102
SLD (H2O model)	-6.779E-08	4.377E-06	2.054E-06	3.777E-06	2.828E-06
SLD (D2O model)	6.340E-06	4.619E-06	5.294E-06	4.451E-06	4.818E-06
Water vol frac	0.926	0.035	0.468	0.098	0.288
Pore vol frac	-0.034	-0.093	-0.025	-0.019	-0.006
Nafion vol frac	0.108	1.057	0.557	0.922	0.719

Conclusions

- 60Å film composed of **4 direct layers**
- 100Å film composed of **5 direct layers**
- Both films terminate with Nafion-rich layers on the free surface
- Water layers are generally thinner than Nafion layers
- Negative porosity values correspond to Nafion-rich layers and indicate lamellar Nafion is denser than bulk Nafion



Future Work

- Continue to refine simultaneous fits for 100Å film
- Fit reflectivity data for thicker films
  - Determine relationship between number of layers and lamellar thickness
  - Find thickness where film is not entirely composed of lamellae
- Investigate the dependence of the structure on relative humidity

Works Cited and Acknowledgements

[1] Gebel, G., Structural evolution of water swollen perfluorosulfonated ionomers from dry membrane to solution, Polymer, 41, 2000, 5829-5838.

[2] Heinrich, F., Neutron Reflectometry for Studying Membrane Proteins, NIST Summer School 2008, http://www.ncnr.nist.gov/summerschool/ss08/pdf/Heinrich_BiologyWithRefl.pdf.

[3] Dura, J.A., et. al, Multilamellar Interface Structures in Nafion, Macromolecules 2009, 42, 4769–4774.

[4] Bhargava, P., Creating a Nafion Thin Film with a Surface Water Layer in order to Improve the Accuracy of Neutron Reflectometry Studies on Lipid Bilayers, 2009.

[5] Keinzle, P.A., Reflpak and GArefl

Thank you:

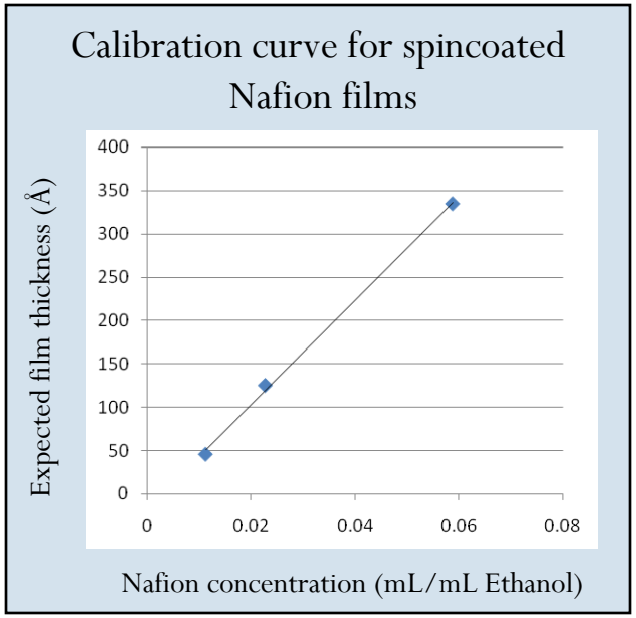
Steven DeCaluwe – SURF Co-advisor

Pavan Bhargava– SHIP student

Joe Dura – SURF advisor

Sample Preparation

- Calibration curve used to predict sample thickness [3]
  - Nafion resin diluted with ethanol
  - Expected thicknesses ranged from 20-300Å
- Spincoating used to deposit films
  - Solution evenly applied over substrate
  - Substrate is spun at 3500 RPM for 1 minute
  - Centrifugal force spreads dilution over substrate as ethanol evaporates, creating even film
- Samples annealed for 1 hour at 60C in vacuum to ensure adhesion to the substrate

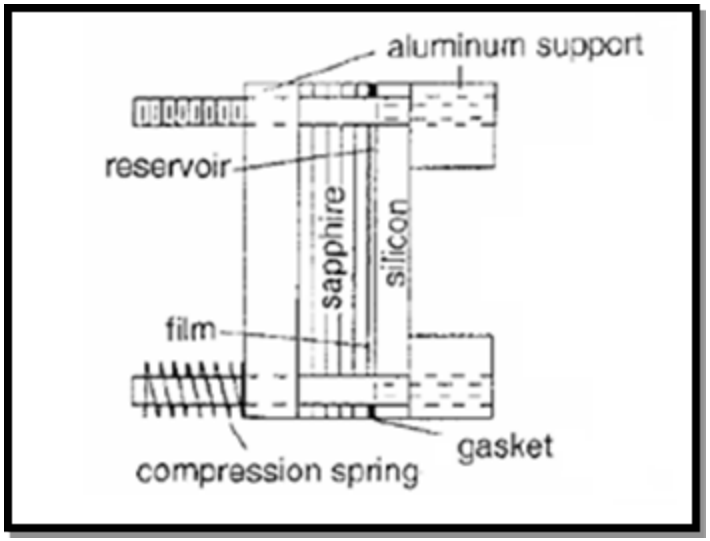


Source: [3]

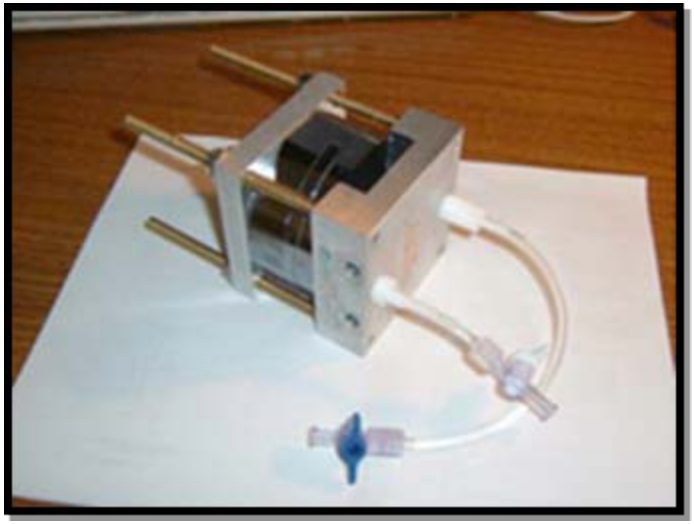
Source: www.ncnr.nist.gov

Motivation

- Neutron reflectivity can be used to study biological samples [2]
- Water reservoirs are used to hydrate and contain these samples
  - Water causes an excessive amount of background scattering (poor signal to noise)
- A Nafion film which terminates in water can be very useful
  - Reduce amount of water in reservoir
  - Increase scan accuracy and range
  - Reveal more information about structure of membranes

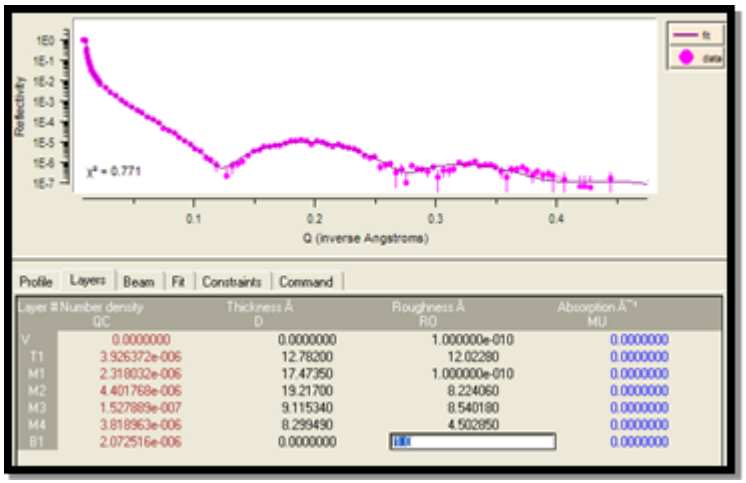


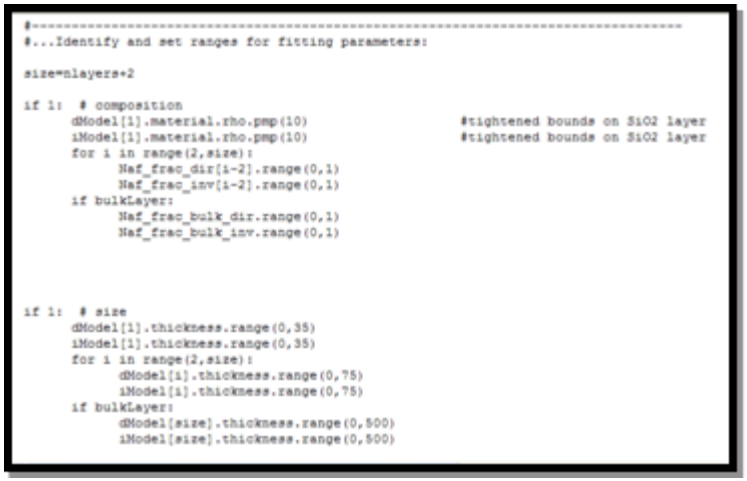
Source: [2]



Source: [2]

Reflpak and GArefl

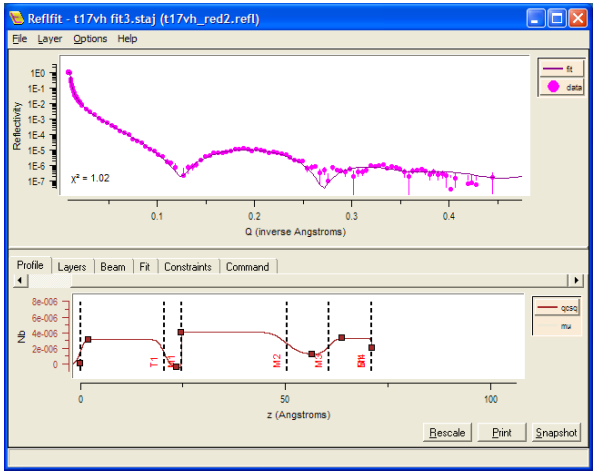




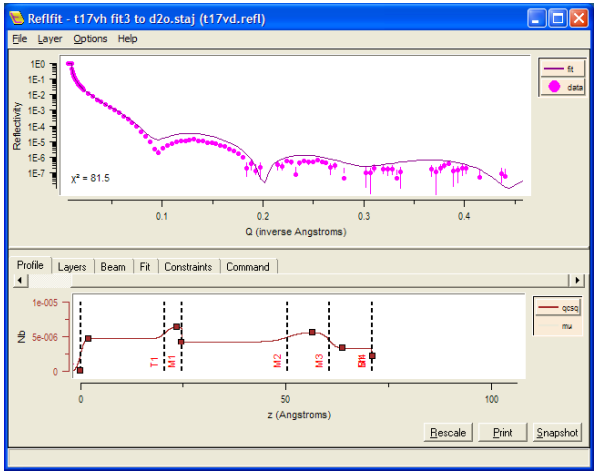
```
#...Identify and set ranges for fitting parameters:

size=nlayers+2

if 1:  # composition
      dModel[1].material.rho.pmp(10)                  #tightened bounds on SiO2 layer
      iModel[1].material.rho.pmp(10)                  #tightened bounds on SiO2 layer
      for i in range(2,size):
            Naf_frac_dir[i-2].range(0,1)
            Naf_frac_inv[i-2].range(0,1)
      if bulkLayer:
            Naf_frac_bulk_dir.range(0,1)
            Naf_frac_bulk_inv.range(0,1)



if 1:  # size
      dModel[1].thickness.range(0,35)
      iModel[1].thickness.range(0,35)
      for i in range(2,size):
            dModel[i].thickness.range(0,75)
            iModel[i].thickness.range(0,75)
      if bulkLayer:
            dModel[size].thickness.range(0,500)
            iModel[size].thickness.range(0,500)
```

- Fitting software [5] used to provide possible physical interpretation of reflectivity data:
  - Reflpak – input layer "models" and solve for local minima
  - GArefl – input layer parameter ranges, solve for global minima
- Fitting parameters
  - SLD, roughness, absorption, thickness

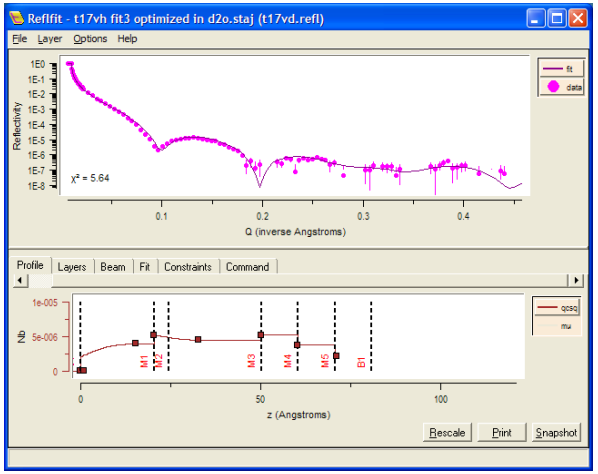
60Å Best Fit



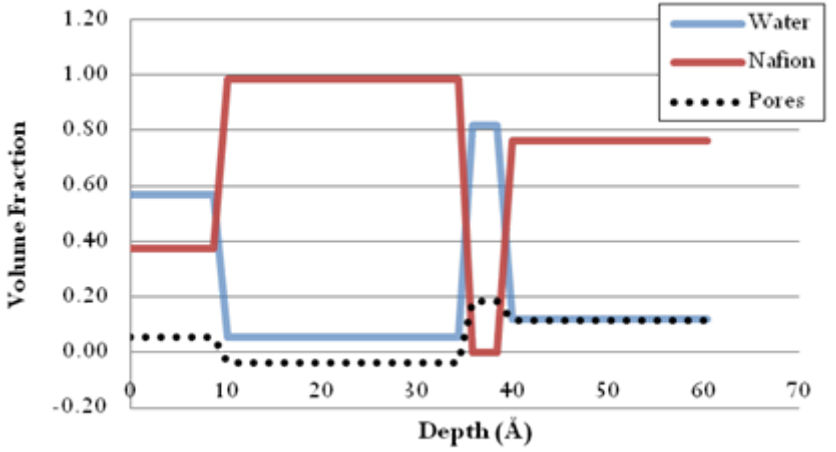
1. H_2O best fit



2. H_2O model converted to D_2O



3. D_2O fit optimized



4. Calculated Volume Fractions