X-Ray Reflectivity—Substrate

General Notes

- This experiment was performed to get a general sense of the thicknesses and surface roughnesses of each layer in the substrate.
- Sample was composed of the substrate only with no additional Nafion on top. Layers:
  - Silicon
  - Silicon oxide
  - Permalloy
  - Platinum
  - Air

Active/Best Fit

- LOCATION: `.\Desktop\XRay_Second\Correct_Fit\`
- STATUS: Currently being fitted.
- NOTES:
  - This fit is the UpdatedSLD fit from below, but the fit parameters were adjusted to conform with the others. Namely: Burn-in = 100,000. Population = 20. Initializer = LHS. Steps = 2,000.
  - The fit is good in the sense that it has converged, the variances are normally distributed, and any correlations are minor.
  - The XRSLD of the silicon oxide layer is nowhere near the nominal value, indicating that the silicon and permalloy layers had created an unknown alloy of sorts.
- NEXT-STEPS:
  - Take this file and reconcile it with the "UpdatedSLD" fit from below.
  - Upload the files and figures to GitHub.

Other Fits

- Base Fit
  - `~\Fits\X-Ray\Base`
  - The initial fit of the data using what we knew about the substrate on our first pass.
  - The goodness of fit is 25.945(44).
  - The fit was poor because it had not fully converged, the traces in the parameter trace and log-likelihood travel all over the place.
  - The errors were range limited for the ρ_i of the oxide and platinum layers, which is also reflected in the correlations plot.
  - We came up with two alternative fitting possibilities:
    - The SLDs were incorrect and needed to be updated, this is the "UpdatedSLD" below.
    - There could be an interfacial layer between two of the layers listed above, these are the "Interfacial Layers" below.
- UpdatedSLD
  - `~\Fits\X-Ray\UpdatedSLD\`
  - This folder will be reconciled with the best fit above.
- Interfacial Layers
  - `~\Fits\X-Ray\Interfaces\~`
  - This folder contains four fits, each represents the base fit with an additional interfacial layer located between pairs of layers.
  - In all four fits, these layers were dubbed "interfacial" and had a large range of thickness and scattering length densities of the adjoining layers.
  - The four fits were numbered, and their numbers and adjacent layers were:
    1. Silicon-SiOx
    2. SiOx-Permalloy
    3. Permalloy-Platinum
    4. Platinum-Air
  - In general, the fits improved on the base fit, but some of the parameters in each fit were range limited.

- It may be worthwhile to apply the same interfacial layers to the 'UpdatedSLD' above, but that may not be useful as the neutron data sets are converging.

- NEXT STEPS:
  - Write down specifics of each of the interfacial layer.
  - Consolidate the UpdatedSLD and Active fits.
  - Update these notes to reflect the joining of those two folders.
  - Calculate the BICs and chi-squared values for each fit.

Argon Gas

General Notes

- This experiment was the second neutron reflectivity measurement, performed after the H2O vapor test.
- The sample was composed of the substrate measured with x-rays plus an additional Nafion layer.
- The main goal of this project is to determine the interfacial structure of Nafion at the platinum interface, so I attempted to fit the data with various models to find the one that most accurately describes the data.
- Because there were so many candidate fits, I will quickly summarize the early fits and focus on the relevant ones.

Early Attempts to Fit the Data:

- Box Models
  - `~\Fits\Ar Gas (Dry)\Box Models\~`
  - This folder contains five different fits, each of which is composed of a simple box model plus some slight modifications.
  - Base Model–simple box representation of the water layer that shows no interfacial behaviors.
  - Lamellae–As the base model with an additional lamellae layer, but the SLD of the interfacial area has many different spikes that are non-physical.
  - Lamellae2– As the lamellae model, but with slight tweaking that gives even more non-physical spikes in the SLD of the water interface.
  - Magnetic SiOx–I took the box model and allowed the oxide layer to be magnetic, however the thickness of that layer approached zero while the magnetic SLD was very small with large error. I concluded that it was not necessary to treat the oxide layer as magnetic, but it was a useful test.
  - Substrate informed–This was the box model, but I attempted to restrain the thicknesses and surface roughnesses of the substrate layers to the best-fit values I measured in the x-ray reflectivity measurement but the fit did not converge and the fit parameters were range-limited.
  - z4 dependence–I added a single z^{-4} layer to represent the interfacial water layer, but the parameters were all over the place and nonphysical.
- Spline models
  - In addition to the simple box models above, I also attempted to fit the Nafion layer with an amorphous spline that had between 5 and 7 control points.
  - While an amorphous spline would reduce the χ^2 of the fit, we decided to focus on the z^{-4} dependance because that is more physical.
- Take away messages:
  - Box models are insufficient for describing the layers of the interfacial Nafion.
  - There is no evidence that there are magnetic layers besides the permalloy layer.

Active/Best Fits

- `~\Nafion\Active\Argon\~`
- There are actually four different lamellae models that I am attempting to decide between as the "best fit" they are:
  - Base–Lamellae fit that had four lamellae layers: water-rich layer, nafion-rich, water-rich, nafion-rich, gradient, and bulk.
    - While this fit was quite good, the errors for the thickness of a couple of parameters (NRL2 rho, NRL2 thickness, and gradient rho) were bimodal, having two peaks.

- Based on the above information I refitted the data but expanded the range of the NRL2 rho and then split the thicknesses into two ranges: {4 Å, 25 Å} and {25 Å, 50 Å}.
  - The thought behind this split was that I would then fit each layer to see which of the two distributions was the better fit and then that would be the correct one.
  - As we will see below, these fits were all roughly equivalent (χ^2 = 1.995 to 2.044, BIC = 1528 to 1547) and I still haven't picked the "best" of the four fits.
- NRL2_4_25: the fit above where the thickness was limited to {4 Å, 25 Å}
  - This is the best of the four fits mathematically, χ^2 = 1.995, BIC = 1528, however I am unsure of it because NRL2 had a very high spike.
  - The uncertainties presented in the model uncertainty plot also overlaps significantly with the plot of the best-fit value, casting doubt on the model.
- NRL2_25_50: this is the companion of NRL2_4_25 but the thickness was limited to {25 Å, 50 Å}.
  - The variance of the different fit parameters was more normally distributed and not ranged limited as was the case in the base model.
  - The SLD of NRL2 was a step below the gradient layer, which was in turn a step below the bulk layer.
  - The bulk layer was significantly thinner than the gradient layer.
- No_NRL2: As above, but I removed the NRL2 layer, where I assumed that the layer was not there.
  - Ironically, this layer is the "worst" of the four, χ^2 = 2.044 and BIC = 1547, but the model uncertainties are the smallest and the individual lamellae stand out the most clearly.

D_2O Vapor

General Notes

- This was the third neutron measurement, performed during the same setup as the argon gas experiment.
- This is the data set that I have spent the second greatest amount of time on after the argon data and there are many different early attempts to fit the data.

Early Attempts to Fit the Data:

- Box Models:
  - Base–Simple model that treats every single layer as a box, this was the first fit that indicated that the SLD of the oxide layer would not be significantly lower than we initially expected.
  - Lamellae–This is the first "good" fit that shows clear interfacial structure in the data. The problem is that the lamellae was ordered as Nafion-rich, water-rich, Nafion-rich, water-rich, which is opposite of what we expected. It should be noted that the SLD of the form a gradient step up towards the bulk layer, which was approximated by a large surface roughness in the base fit. Note: this fit does not have a gradient layer between the lamellae and bulk Nafion.
  - Magnetic Oxide–I attempted to fit the data using the same model as the base box model but an additional magnetic SLD in the oxide layer. The fit did not converge, and the oxide layer has a vanishingly small thickness.
  - Z4 Dependance–This is the same issue as the z4 dependance in the argon data. The surface roughnesses between individual layers became so large that they would then pour over into other layers. Another issue was that the SLD of the water layer was so large that it almost matched that of platinum.
- Fixed Substrate
  - I set the thicknesses and surface roughnesses of the substrate layers to the values determined in the base fit of the x-ray model, and treated the interface with lamellae (WNWNG).
  - This is a terrible fit, with a χ^2 = 100.822.
- Lamellae test
  - This is actually three different fits where I attempted to understand how the lamellae work. I attempted different attempts, but found that directly fitting the SLD (as opposed to the volume factions) was the easiest to understand, which ultimately led me to my other fits.
- Splines
  - Like in the argon vapor fit, I attempted to directly fit Nafion using an amorphous spline using between 5 and 7 control points.

- It also does not really work because the surface roughnesses overlap into adjacent layers, and then there are weird jumps in the SLD in the Nafion layer.

Active/Best Fit

- `~\Nafion\Active\D2OVapor\~`
- Surprisingly, I have three fits under this folder.
- Base Fit
  - I called it the "base fit" because I have no idea what I should actually call it…
  - Exhibits the characteristic stepping up/gradient of SLD in the lamellae layers again.
  - Yet again, there are two distributions in the errors for the platinum thickness, WRL1 rho, grad thickness and bulk Nafion thickness.
- No gradient
  - I removed the gradient layer, so that there is a nafion-rich layer that immediately goes into the bulk phase, this is equivalent to leaving the "gradient" layer in and removing the NRL2 layer.
  - This one fits better.
- October 26
  - This is a longer run of the base fit to allow it to converge, which the original did not.

H_2O Vapor

General Notes

- This experiment was the first neutron experiment, performed about a month prior to the argon data.
- I have not spent as much time on this dataset as I did on the other two neutron experiments.

Early Attempts to Fit the Data

- Base
  - I fitted the data to the same box model that I did the argon and D_2O vapor datasets.
  - A weird feature of the fit, that returns in other fits of the data, is that the SLD of the oxide layer is greater than Silicon.
  - The surface roughnesses of the permalloy and platinum layers are both so wide that they overlap with the adjacent layers.
  - The water interface is a very thin layer, but it is obscured by the surface roughness of the platinum layer adjacent to it.
- Fixed Substrate
  - This is actually a really bad fit where I kept the fit parameters of the substrate fixed while treating the Nafion layer as a series of lamellae.
  - The fit is terrible, with a chi-squared about 45.
- Lamellae
  - I fitted the data using a lamellae model, however the SLD would spike at the Nafion-rich layer to near 5.0, which is non physical.

Active/Best Fit

- `~\Nafion\Active\H2OVapor\~`
- There is a single fit, which uses the same lamellae model that I fitted the other datasets with.
- The SLD of the NRL are a little higher than the bulk Nafion SLD.
- The model uncertainties were very large, with significant overlap between adjacent layers.
- The oxide layer has an SLD that matches the silicon substrate.
- The following fit parameters have two peaks in their errors:
  - Platinum thickness
  - WRL1 rho
  - NRL1 rho
  - WRL2 rho
  - NRL2 rho
  - gradient rho

- gradient thickness

- I need to go through the fit, and refine the thickness of the platinum layer to the ~50 Å thickness that I see in the other layers and refit to see if that resolves the multiple peaks.

Next Steps

1. Select fits to run while doing the following tasks.
2. Export figures into a PowerPoint including the *key* messages from the notes above.
3. Meet with Joe to discuss the fits from above.