Small Angle X-ray Scattering (SAXS) Laboratory

Learning Experiences

- Use of small angle X-ray scattering instrumentation
- Programs that you will use
  - SAXS (BRUKER AXS)
  - PRIMUS (Konarev, Volkov, Koch and Svergun)

"PRIMUS: Program PRIMUS performs the manipulations with experimental small-angle scattering data files such as: averaging, subtraction, merging, extrapolation to zero concentration and curve fitting and evaluates the integral parameters from Guinier and Porod plots such as radius of gyration (for globular, flat and rod-type particles), Porod's volume, zero intensity and molecular weight"


In this lab you analyze a small angle x-ray scatter pattern powder from a known sample. You will need to use the computers in the X-ray Laboratory. Bring a calculator, your notebook and a pencil.
Introduction

In the diffraction experiment the minimum size that can be measured is equivalent to \( \lambda/2 \), however Bragg’s law does not predict a maximum size. Bragg's Law predicts that information pertaining to nano-scale structures will be seen below 6° 2\( \theta \) in the diffractometer trace (\( \lambda \sim 1.0 \text{Å} \)). By examining x-ray scattering between 0 and 6° 2\( \theta \), we can measure information that is directly proportional to the size and shape of nanometer sized objects. The characteristics of materials at these larger size scales are fundamentally different than at atomic scales. Atomic scale structures are characterized by high degrees of order, i.e. crystals, and relatively simple and uniform building blocks, i.e. atoms. On the nano-scale, the building blocks of matter are rarely well organized and are composed of rather complex and non-uniform building blocks. The resulting features in x-ray scattering from diffraction are sharp peaks in the XRD range and comparatively nondescript diffuse patterns in the SAXS range.

In XRD the atomic scattering factor, \( f^2 \), is equal to the square of the number of electrons in an atom at low angles, \( n_e^2 \). Additionally, the intensity of scattering is known to be proportional to the number of scattering elements in the irradiated volume, \( N_p \).

\[
I \propto N_p n_e^2
\]

In small-angle scattering we can consider a generalized rule that describes the behavior of scattered intensity as a function of Bragg size "r" that is observed at a given scattering angle 2\( \theta \), where \( r = 1/q \) and where \( q = 4\pi \sin(\theta)/\lambda \). All scattering patterns in the small-angle regime reflect a decay of intensity in q and can be described by considering that the decreasing size reduces the number of electrons in a particle in a given volume, while the number of particles increases with 1/volume. The scattered intensity (equation 1) is proportional to the decay of the particle volume with size. This analysis implies that the definition of a particle( r) does not necessarily reflect a real domain, but reflects the size, r, of a scattering element that could be a component of a physical domain.

Guinier's Law for mono-dispersed particles.

The scattering event for a single particle involves interference from waves emanating from two points in that particle separated by a distance \( r = 1/q \). For an isotropic system one must consider first averaging any starting point in a particle and secondly averaging any direction for the vector r. This leads to a double summation that is identical to the determination of the moment of inertia for a particle. When the electron density is used as the weighting rather than the mass density, this moment of inertia is called the radius of gyration (\( R_g \)) of the particle. The radius of gyration reflects a second moment of the distribution of the shape and size of a particle (domain) about the mean.

The process of obtaining \( R_g \) involves two steps, first averaging all possible positions in the particle from which a vector "r" can start and be within the particle. Second, determining the probability that a randomly directed vector "r" from an arbitrary
starting point in the particle will fall in the particle. The meaning of this probability \( p(r) \), in the vicinity of \( r \) (the particle size), can be graphically represented by a Gaussian probability cloud created by the summation of all possible positions of the particle where the center of the probability cloud is in the particle phase.

At very low \( q \) this corresponds to the volume fraction particles squared. At sizes, \( r = 1/q \), close to the average particle size or radius or gyration, this probability is reflected by a decaying exponential function. The decaying exponential function can be written in terms of \( r \) or in terms of \( q \) (Fourier transform of a Gaussian distribution is a Gaussian distribution). Such an analysis leads to Guinier's Law, where the average size is reflected in the radius of gyration, \( R_g \). \( R_g \) is the moment of inertia for the particle using the electron density rather than the mass as a weighting factor.

\[
I(q) = N_p n_e^2 \exp \left( -q^2 \frac{R_g^2}{3} \right)
\]

**Sphere:** radius \( R = \sqrt[3]{5} R_g \)

To perform the experiment, the particles to be measured should be dispersed in such a way that the diameter of the particle is much smaller than the distance between the particles (mono-dispersed). The problem is that the sample must be dispersed on or in some sort of median and the median itself will scatter X-rays. We therefore need to subtract the scattered intensity of the sample mount from the mounted sample to obtain the scattered intensity from only the sample.

One method to disperse the particles is to dust the sample on MYLAR tape. Unfortunately the MYLAR tape will also scatter X-rays and so the sample scattering must be determined by subtraction of the X-rays scattered from a blank slice of MYLAR tape. To subtract the sample from the blank you need to adjust for absorption of the X-rays. The sample on the tape will always absorb more radiation as compared to tape alone. The difference must be compensated for by scaling the intensity of the X-rays scattered by the tape and then subtracting that intensity from the sample + tape measurement. This can be accomplished by multiplication of the tape sample by a transmission factor (TS) that is calculated from the comparison of the X-ray intensities obtained from a calibrated glass carbon (GC) reference.
Procedure

In this experiment you will build a dust chamber and prepare the sample. You will need to run six measurements.

(1) Sample on TAPE  
(2) TAPE only  
(3) AIR (no sample no tape) only  
(4) Sample on TAPE + Glassy carbon reference  
(5) TAPE + Glassy carbon reference  
(6) AIR + Glassy carbon reference

From these measurements you will calculate the scale factor TS. You will then re-load (1) and subtract TS*(2) to obtain the SAMPLE ONLY measurement. From the SAMPLE ONLY measurement you can obtain an ASCII file of I(q) and q. This file can then be input to the program PRIMUS to obtain Rg for the sample.

Experiment

Place a few “grains” of the NANO-DUR powder into a 400ml beaker. Measure and cut a section of PARAFILM that will completely cover and wrap over the top of the beaker. Punch (use the punch or hole cutter) a small (about 1cm in diameter) hole in the PARAFILM near it center. Secure the PARAFILM to the beaker with a rubber band. Place a small piece of very clean MYLAR tape over the hole. With the plastic straw from a CANNED AIR bottle punch a second hole in the PARAFILM near the beaker side. Attach a can of CANNED AIR to the straw and insert the straw in the hole you just created. When complete depress the trigger on the CANNED AIR and allow an air-stream to flow into and out of the beaker for about 2 secs. The grains of NANO-DUR should now disperse and a few grains should adhere to the tape over the hole. Carefully remove the tape and attach it to the sample holder. The sample should be placed over the large hole in the sample mount. Take a strip of clean tape and attach it to the sample holder below the sample tape.

Move the sample holder to the SAXS instrument. Place the holder in its positioner and close the SAXS chamber. Evacuate the chamber.

1. Start the SAXS program, create a new project and start the radiograph subprogram.
2. Input the coordinates and begin the radiograph.
3. When complete you will see a radiograph like the one shown.

4. Move the cursor over the darker portion of the radiograph and record the coordinates

5. Return to the main program and point to collect/scan/edit targets. Type in the coordinates from 4 and the coordinates of the blank tape and the coordinates where there is no sample or tape (this is called air). For the time use 600 secs

6. Lower the Glassy Carbon and start a short data collection. Be sure to add the _GC in the file names
7. This will take about 30 mins. The instrument will automatically change sample positions. If you placed your sample on the top and the blank tape below it then you should record the frames information in your notebook as shown below.

<table>
<thead>
<tr>
<th>name</th>
<th>description</th>
</tr>
</thead>
<tbody>
<tr>
<td>nanodur_gc_1_001,gfrm</td>
<td>sample and tape + glassy carbon</td>
</tr>
<tr>
<td>nanodur_gc_2_002,gfrm</td>
<td>tape + glassy carbon</td>
</tr>
<tr>
<td>nanodur_gc_3_003,gfrm</td>
<td>air + glassy carbon</td>
</tr>
</tbody>
</table>

8. After completion lift the glassy carbon. Change the time from 600 to 21600 secs (collect/scan/edit targets) and collect the long data sets (6 hours each). This collection will run over night.

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<tr>
<td>nanodur_1_001,gfrm</td>
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</tr>
<tr>
<td>nanodur_3_003,gfrm</td>
<td>air</td>
</tr>
</tbody>
</table>

9. Record the information in your notebook.

10. When you return to the lab you will need to reduce the data (if all goes well). First calculate TS (transmission) for the sample/tape and the blank tape. Go to analyze/transmission.
11. Input the files

for the standard only input the air + glassy carbon file
for the std + sample input the sample and tape + glassy carbon file
for the sample only input the sample and tape file
for the air only input the air file

point to OK you will see ...

Note the Ts number (here it is 0.958) as TS1. Write this in your notebook.

12. Repeat this for the blank tape.

for the standard only input the air + glassy carbon file
for the std + sample input the tape + glassy carbon file
for the sample only input the tape file
for the air only input the air file

point to OK and record the Ts number (in this case it will be 0.959) as TS2. This number should be greater than the number calculated in step 11.

13. Divide TS1/TS2 and set that to T. If T > 1 then let T=1.0

14. Now open the sample and tape file and subtract the tape file employing the scale factor T (input minus T).
15. The frame you see will be the sample only x-ray scattering pattern.

16. Reduce the 2D data to a 1D trace
17. Save the frame (file/save) and exit the program
18. Open the text file you just created and delete all lines beginning with !@

```
!@!GA DDS PLOTSQ FILE: Chi integration type
!@!Title: nano dur 36nm
!@!Comment: ?
!@!Wavelengths 1.54184 1.54056 1.54439
!@!Integration range: 2Theta: 0.000 to 4.500 Gamma: -219.100 to 36.000
!@!Integration method: bin normalized
!@!N
!@!S5
!@!M
!@!L 0.0 0.0 0.0 0.0
!@!XDegrees
!@!YCounts
0.005 7.090389 0.000000 0.000356
0.010 16.183947 11.528491 0.000711
0.015 23.43815 9.198822 0.001067
0.020 24.516391 7.512139 0.001422
0.025 25.851786 6.723185 0.001778
0.030 25.111153 6.097002 0.002134
0.035 23.428503 5.363479 0.002489
```

19. Save the file as `your_file.txt` (where your file is a name you will remember)
20. Open a command window and navigate to your directory. At the prompt type `plotso2q your_file.txt`. You should see a confirmation that the program has completed successfully. You have now created a file named `your_file.dat`.
21. Start the program PRIMUS

22. Point to TOOLS and input the *your_file.dat* that you created in step 20.

23. Plot your file to check for errors.
24. Point to Guinier and create a Guinier plot

Adjust nBeg and nEnd until you see a linear slope defined by the line. Record \( R_g \) (in this case it is 163 Å).

25. Finally calculate the particle size \( (R_g \times 2.581988) \). Record the size.

26. Prepare a report to be turned in. Follow the example report given below. Report the \( R_g \) and particle size of your sample.
Data Collection

A BRUKER NANOSTAR SAXS (small angle x-ray scattering) instrument was employed for data collection. The X-ray radiation employed was generated from a Cu sealed tube fine-focus X-ray source (K\(\alpha\) = 1.54184Å with a potential of 40 kV and a current of 35 mA). The X-rays were filtered through cross-coupled Gobel mirrors and collimated (collimator distance = 20mm) by two 0.2mm pin-holes. The detector [MWPC hi-star area detector] was set at 62mm from the sample and the sample chamber and x-ray paths were evacuated. The detector distance and beam intersection was calibrated employing a silver behenate standard. The instrument was controlled with the SAXS software suite (Microsoft Win 2000 operating system) and the data was collected in the still (add) mode. Mylar tape was employed to mount the sample and placed in the sample chamber at room temperature. The sample chamber and x-ray beam paths were evacuated and a 21600sec scan was performed. The glassy carbon standard was then inserted between the sample and the detector and a 600 sec standard scan was collected. The sample was then replaced with a blank tape and a blank scan of 21600 sec was completed, which was followed by insertion of the glassy carbon and a 600sec standard scan. Finally a 21600sec background scan (air only) which was followed by insertion of the glassy carbon and a 600 sec standard scan were preformed. Transmission factors were then calculated for the sample and the blank. The blank was then subtracted from the sample employing the scale factor calculated by dividing the sample transmission factor by the blank transmission factor. An area integration (GADDS NT software reference manual pp 1-11 to 1-15) was employed to reduced the data to a one-dimensional \(q = (4\pi \sin \theta / \lambda)\) versus ln(Intensity) trace.

The Guiner analysis [ \(I(q) = C exp(q^2 R_g^2/3)\) ] was preformed with the program PRIMUS (SAXS interpretation program is written by P.V. Konarev, V.V. Volkov, M.H.J. Koch and D.I. Svergun. Version 2.2 12.03.03) and the results are shown below. To confirm \(R_g\) the program GNOM (Small-Angle Scattering Data Processing by Means of the Regularization Technique, an indirect transform program for small-angle scattering data processing. Version E4.5a 11/03/03 by D.Svergun & A.Semenyuk) was employed.